Synthesis of Ion Exchange Membranes for Reverse Electrodialysis via Radiation Induced Graft Co-polymerisation

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“Love many things, for therein lies the true strength, and whosoever loves much performs much, and can accomplish much, and what is done in love is done well.”

— Vincent Van Gogh
Abstract

A major disadvantage of fossil fuels being the primary source of global energy is the negative effect that the burning of such fuels has on the planet. This is evident in factors including climate change. Reverse electrodialysis (RED) is an emerging membrane-based process for clean energy conversion. The technique works by utilising the transport of cations and anions through ion-exchange membranes (IEMs) to create an electrical current, via differences in chemical potential, when mixing salt solutions of different concentrations. The core components of a RED cell, and the largest factor affecting the performance and economic viability, are the IEMs.

Recently, increased efforts have been made with regard to the preparation of IEMs and understanding the relationships between membrane properties and RED cell power performance. The work in this thesis has focused on the development of RED-focused IEMs by radiation induced grafting polymerisation (RIG). The RIG technique has been used to chemically modify commercially available polymer films to produce a large sample of IEMs targeted for application in RED. The IEM properties were experimentally determined and used as part of a literature recognised mathematical model to estimate the gross power densities that can theoretically be obtained by each IEM in a working RED cell.

The results obtained for RIG IEMs contradicts the earlier notion that IEM permselectivity is of less significance than area resistance and indicate that a minimum permselectivity (≈ 90%) is required for RED IEMs. A trade-off relationship between the two properties is observed, rationalised by Donnan exclusion factors surrounding IEM water content. Chemical crosslinking was implemented into RIG methods to control excessive gravimetric water uptake (WU%). Linear tertiary diamine head-groups were used to produce crosslinked anion-exchange membranes (AEMs), with tetramethylhexanedianime (TMHDA) head-group yielding theoretical gross power densities of 3.42 W m⁻² for single IEM RED model calculations and 1.89 W m⁻² for AEM/CEM pair calculations (paired with literature SPEEK 65 CEM). Crosslinked CEMs were produced via chemical crosslinking by divinylbenzene (DVB) and bis(vinylphenyl)ethane (BVPE) was implemented into the RIG method, which resulted in cation-exchange membranes (CEMs) yielding theoretical gross power densities of 5.55 and 5.99 W m⁻² respectively, for single IEM RED model calculations and 2.81 and 2.71 W m⁻² for AEM/CEM pair calculations (paired with commercial Neospeta® AFN AEM).
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1. Introduction

1.1 Concerns About Climate Change and the Use of Fossil Fuels

The greenhouse effect is a critical component of the Earth’s ability to promote the growth and development of all flora and fauna on the planet, without which the global temperature would be too low to support life [1]. The ability of the Earth’s atmosphere to contain greenhouse gasses such as CO$_2$ and H$_2$O vapour is therefore essential to the stability of the planet’s ecosystems. However, exponential rises in human technologies, such as industrialisation in the mid nineteenth century, have contributed to an anthropogenic increase in certain greenhouse gasses, particularly CO$_2$.

Reconstructions of trends in the Earth’s climate demonstrate that it is ever-changing, with irregular oscillations at different time intervals. However, observations made in recent years indicate a hastening in adverse climate effects over the last few decades [2]. The Intergovernmental Panel on Climate Change (IPCC) report an unequivocal change in the Earth’s climate since the 1950s, resulting in the warming of the atmosphere and oceans, diminishing snow and ice, rising sea levels and an increase in greenhouse gas concentration [3]. The report goes on to state that, in all likelihood, more than half of the observed increase in the global average surface temperature from 1951 to 2010 can be attributed to the anthropogenic increase in greenhouse gas concentration.

Figure 1 - Map of the observed change in surface temperature from 1901 to 2012 [3].
1.2 Climate Change and Fossil Fuels

The ICPP 2013 reports that atmospheric concentrations of greenhouse gasses CO₂, CH₄ and N₂O have increased to levels unparalleled in the last 800,000 years. The most important anthropogenic greenhouse gas with respect to climate change is CO₂, of which atmospheric concentrations are measured at a 40% increase since pre-industrialisation. Global atmospheric concentrations of CO₂ have increased dramatically from a pre-industrialisation value of around 280 ppm to 379 ppm in 2005 [4], increasing further to 391 ppm in 2011 [3].

![Figure 2 - Atmospheric concentrations of CO₂ in ppm from Mauna Loa, Hawaii (red) and South Pole (black) since 1958 [4].]

The increase in atmospheric CO₂ since 1750 is attributed therein to human activity, predominantly due to emissions from fossil fuel usage, with CO₂ emission from fossil fuels and cement production accumulating to between 345–405 Gigatonnes of carbon (GtC) from 1750–2011 [3]. The average annual CO₂ emissions for the 1980s was 5.44 GtC per year [5] and emission increased further throughout the 1990s with average values reaching 6.4 GtC per year [4]. CO₂ emissions continue to increase, with the average for the period 2002–2011 reaching 8.3 GtC per year peaking at 9.5 GtC per year in 2011 [3].

Recognising the importance of fossil fuel emissions on global temperature, in 2008 the G8 nations agreed to limit the increase in global temperature to 2°C indefinitely by reducing global CO₂ emissions by 50% before 2050. This translates to an 80% cut in CO₂ emissions from the nations involved in order to offset increasing fossil fuel use in the developing world [6], a concept reinforced by the United Nations in 2015 [7]. Reaching these goals will require
a vast effort from G20 nations, including the UK, with extensive research and funding into the development and optimisation of new and existing sources of renewable energy generation and storage.

1.3 Renewable Energy in the United Kingdom

As an example, the United Kingdom currently utilises a number of renewable sources of energy and the Department for Business, Energy and Industrial Strategy report that the contribution of renewable energy sources to the UK’s energy requirements was 64.7 TWh for the period 2014–2015. [8] This value includes the use of renewables to generate electricity, burning of renewable fuels to generate heat and the use of liquid biofuels for transport. The percentage uses of renewable by type can be seen in Figure 3. The largest source of renewable energy in the UK is the accumulated Bioenergy at 70.7%. However, other sources include wind, solar, geothermal, hydro and shoreline.

![Figure 3. Renewable energy fuel use by type 2015](image)

As of 2015 3.2% of renewable energy sources employed by the UK included well known water-based technologies such as hydro and shoreline power. These technologies function by harnessing the kinetic energy of large bodies of water in the form of tides and waves, and expending this kinetic energy to power machinery such as turbines which in turn generate electricity. One source of water-based renewable energy not currently employed in the UK however is salinity-gradient power (SGP). Unlike more traditional methods which exploit
the force of ocean currents or flow of river water to generate electricity, salinity gradient technologies produce an electrical current via the chemical potential difference that occurs during the controlled mixing of solutions containing differing concentrations of salt (e.g. NaCl). The mixing of salt solutions of different concentrations is a natural process that occurs every second in estuaries all over the world when low salinity fresh or river water flows into high salinity sea water.

The concept for the production of electric power by mixing fresh and salt waters was first discovered by Pattle in 1953, who reported that free energy equal to that obtainable from a 680 foot high waterfall is lost when a river mixes with the sea. [9] The concept was further expanded in the 1970s and the global energy potential of salinity-gradient energy (SGE) was estimated to be between 1.4 and 2.6 TW [10] [11], a value which as of 2006 represented approximately 20% of the worldwide energy demand [12]. It is unfortunate however that these values are based on a certain degree of assumption and simplification, such as averaging of salt concentrations and temperatures, and assuming every river mouth is exploitable for SGE production regardless of the actual salinity gradient or environmental impact. A recent study by Silva et al. provides an estimation of the practical extractable global SGE resources and reports a value of 625 TWh year⁻¹, equivalent to 3% of global energy consumption [13]. The authors also indicate the positions of all river mouths potentially suitable as SGE resources, several of which are located around the North and Mediterranean Seas (Figure 4).

Figure 4 - Global map of extractable SGE resources, Extractable energy (TWh year⁻¹) [13].
1.4 Salinity Gradient Energy

Of the possible technologies that can be put into place to harness this energy, two membrane based energy conversion techniques are at the forefront of current research. These are pressure retarded osmosis (PRO) and reverse electrodialysis (RED). PRO is able to extract SGE from the mixing of two solutions of different salinity by controlling the diffusion of water across a semi-permeable membrane. The potential energy difference between the two solutions permits the transport of water from the dilute solution to the concentrated solution via osmosis, if the concentrated solution is held at a higher pressure than the dilute solution. The volume of water being transported will undergo a pressurisation which can then be used to generate electricity by powering a turbine. Energy is derived from a RED system when aqueous ions undergo diffusion through an ion-selective membrane, facilitated by the difference in free energy between the two saline solutions. By alternating ion-selective membranes of opposing charge, it is possible to transport the ions to electrodes where they are converted to an electrical current [14].

Several evaluations and comparisons have been undertaken in the literature as to the suitability of each technique to best harvest SGE. Both Ramon et al. and Yin Yip and Elimelech report that PRO is capable of producing considerably higher energy efficiencies and power densities than RED [15] [16]. However, Post et al. state that each technique is best suited to its own field of application, with PRO reserved for energy generation through utilisation of concentrated brines, whereas RED is better suited to power generation using seawater and river water resembling the natural process that occurs where the mouth of a river meets the sea [12]. Logan and Elimelech recognise that an advantage of RED is its ability to capture energy directly from salinity gradients without necessarily requiring any pre-treatment or optimisation of the saline solutions [17].

1.5 Energy Production Using RED

The principle of RED was first demonstrated in the 1950s [9] with further investigation and development in the following decades [18] [11] [19]. In a RED cell, often referred to as a ‘stack’, a series of alternating anion- and cation-exchange membranes (AEMs and CEMs respectively), are stacked in pairs between an anode and cathode (Figure 5). The membrane compartments are then filled in an alternating fashion with concentrated saline solution, i.e.
seawater, and a dilute saline solution, *i.e.* river water. The more concentrated of the two saline solutions can be considered as the source of energy and a greater amount of energy is extracted from the process the more dilute the solution becomes [15]. The RED process is driven by the diffusion of aqueous ions through ion-selective membranes which arises due to the concentration difference between the feed solutions. The cationic species in the saline solutions diffuse from the concentrated to the dilute solution compartments through the CEMs, whilst the anionic species permeate through the AEMs in the opposite direction. The salinity gradient present between compartments induces a potential difference across each membrane (*ca.* 80 mV for sea vs. river water) [12], where the total electronic potential of the stack is the sum of the potential differences over each individual membrane. The ionic current in the RED stack is then converted into an electric current by means of a reversible redox reaction with a ferrocyanide solution that is circulated around the two electrodes.

![Figure 5 - Schematic representation of energy conversion in a reverse electrodialysis stack; where AEM is an anion-exchange membrane and CEM is a cation-exchange membrane.](image)

Theoretically, RED appears to be a feasible method of energy production. However, does it have the potential to become a commercially viable source of renewable energy? Several studies have investigated the practicality and feasibility of RED as a potential source of renewable energy on a laboratory scale. Reported power densities (power per square meter of membrane) obtained from experimental RED stacks are between 0.05 and 0.41 W m$^{-2}$ [9] [18] [20]. Turek and Bandura produced the highest reported peak power of 0.46 W m$^{-2}$ from
RED stack consisting of 4 AEM-CEM cell pairs [20]. Two further studies conducted by Veerman et al. investigate much larger stacks consisting of 50 cells with functional membrane areas of 10x10 cm and 25x75 cm, reporting values for net power density of 0.71–0.93 and 0.4 W m\(^{-2}\) respectively [21] [22]. The authors conclude that power density and efficiency are counteracting and, although efficiency is important, the first goal should be to maximise power density [21]. By optimising stack hydrodynamics with regard to spacer properties, Post et al. achieved an energy recovery of around 80%, equivalent to an energy yield of >1.2 MJ per cubic meter of dilute salt water [23], whereas Długolęcki et al. increased the direct power output of their RED stack yielding power densities of 1.25 W m\(^{-2}\) [24]. Veerman et al. reported that it was possible to improve power densities by a further 15%, under realistic operating conditions, through segmentation of the electrodes [25]. Vermaas et al. further advanced the viability of RED, calculating theoretical net power densities for RED to be as high as 20 W m\(^{-2}\) and stating that higher net power densities are obtainable by further improving stack design and membrane properties, including ion-selectivity and resistance [26].

1.6 The Role of Ion-Exchange Membranes in RED

The most fundamental components in a RED stack are the ion-exchange membranes (IEMs), without which it would not be possible to facilitate the controlled mixing of the saline feed solutions. In the 1970s Weinstein and Leitz stated that large-scale application of RED would only be feasible after improvement to IEM manufacturing [18]. Then, in the early 1980s, Lacey concluded that RED membranes would need to be low cost with low ionic resistance and high permselectivity [19]. These conclusions are shared by Ramon et al. and Logan and Elimech, who stress that the development of cost-effective IEMs provides a promising avenue for the economic viability of RED and predict the cost of IEMs to fall with system advances [15] [17]. Therefore, for RED to achieve its potential as a viable source of renewable energy, it is first necessary to further develop cost-effective IEMs, with specific chemistries best suited to maximise performance, in terms of power density. Veerman et al. investigated the power density and thermodynamic efficiency of six different commercially available IEM pairs and the product of these two parameters was then used as a response parameter to rank the membrane pairs. The authors obtained power densities of 1.2 W m\(^{-2}\) for Fumasep\textsuperscript{®} (FAD and FKD) and Selmion\textsuperscript{®} (AMV and CMV) combinations, but were
unable to relate power densities to specific membrane properties [27]. Before a process specific membrane can be developed, it is necessary to determine the contributing factors of membrane properties. Długołęcki et al. conducted a systematic study into the bulk chemistry of commercially available IEMs [28]. The bulk properties, including ion-exchange capacity (IEC), permselectivity (ion-selectivity), resistance (area resistance, Ω m²) and gravimetric water uptake, were experimentally determined for 13 commercially available IEMs (Table 1).

Table 1 - Experimentally determined bulk membrane properties of 13 commercial IEMs [28]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC[a]</th>
<th>α[b]</th>
<th>R[c]</th>
<th>SD[d]</th>
<th>δ[e]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CEMs</strong></td>
<td></td>
<td></td>
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<tr>
<td>Fumasep*</td>
<td></td>
<td></td>
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<tr>
<td>FKE</td>
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<td>2.46</td>
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</tr>
<tr>
<td>CM-1</td>
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<td>1.67</td>
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<td>2.91</td>
<td>18</td>
<td>164</td>
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<tr>
<td>CMH-PES</td>
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<td>94.7</td>
<td>11.33</td>
<td>31</td>
<td>764</td>
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<td>CMV</td>
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<tr>
<td>Fumasep*</td>
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<td></td>
</tr>
<tr>
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<td>0.89</td>
<td>34</td>
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<td>1.84</td>
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<tr>
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<td>90.7</td>
<td>2.35</td>
<td>16</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>AMH-PES</td>
<td>1.97</td>
<td>89.3</td>
<td>7.66</td>
<td>56</td>
<td>714</td>
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<td></td>
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<tr>
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<td>89.9</td>
<td>1.03</td>
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<td>88.4</td>
<td>0.68</td>
<td>147</td>
<td>138</td>
</tr>
</tbody>
</table>

[a] Ion-exchange capacity (mmol g⁻¹). [b] Permselectivity (%). [c] Area resistance (Ω cm²). [d] Swelling degree (%). [e] Thickness (µm).

The experimentally determined values were then input into a mathematical model, derived previously [18], to calculate the theoretical gross power densities obtainable by the IEMs in a RED stack (Eqn. 1).
\[
P_{d_{aem/cem}} = 0.5 \times \left( \frac{[\alpha_{av}RT/F \ln(a_c/a_d)]^2}{R_{aem} + R_{cem} + (d_c/\kappa_c) + (d_d/\kappa_d)} \right) \quad \text{(Eqn. 1)}
\]

where \(\alpha_{av}\) is the average membrane pair permselectivity, \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(T\) is the absolute temperature (K), \(F\) is the Faraday constant (96,485 C mol\(^{-1}\)), \(a_c\) is the concentrated solution activity (mol dm\(^{-3}\)), \(a_d\) is the diluted solution activity (mol dm\(^{-3}\)), \(R_{aem}\) is the AEM resistance (Ω m\(^2\)), \(R_{cem}\) is the CEM resistance (Ω m\(^2\)), \(d_c\) is the thickness of the concentrated compartment (m), \(d_d\) is the thickness of the diluted compartment (m), \(\kappa_c\) is the concentrated compartment conductivity (4.648 S m\(^{-1}\)) and \(\kappa_d\) is the diluted compartment conductivity (0.551 S m\(^{-1}\)). If the model is used to predict the power output of only a single IEM type (i.e. AEM or CEM) it is expressed in the following form:

\[
P_{d_{iem}} = 0.5 \times \left( \frac{\alpha_{RT/F \ln(a_c/a_d)]^2}{R_{iem} + (d_e/\kappa_e) + (d_d/\kappa_d)} \right) \quad \text{(Eqn. 2)}
\]

where the average membrane pair permselectivity term is replaced by the individual membrane permselectivity (\(\alpha\)), the sum of membrane resistance is replaced with the single IEM resistance (\(R_{iem}\)) and the terms relating to compartment thickness are divided by 2.

Theoretical power densities obtained from the mathematical model support the previous accounts that call for the development of low resistance membranes, concluding that the area resistance is the single most critical property for RED and ideally should not exceed a value of 2 Ω cm\(^2\). In relation, the permselectivity is said to be of minor importance; however, the highest ranked membranes in this study were all thin films (120 – 200 μm) and possess permselectivity in excess of 90%.

### 1.7 RED Focused IEMs in the Literature

Güler et al. were the first to report on the use of ‘tailor-made’ AEMs in a RED stack. The AEMs developed were solution-cast films based on poly(epichlorohydrin) (PECH) functionalised by co-polymerisation with 1,4-diazobicyclo[2,2,2]octane (DABCO) to
introduce positively charged head groups; the mechanical properties of the AEMs were improved by the addition (blending) of inert poly(acrylonitrile) (PAN, Figure 6) [29].

\[
\begin{align*}
\text{O} \quad \text{Cl} & \quad + \quad \text{N} \quad \text{N} \\
\text{O} & \quad \text{N} \quad \text{N}
\end{align*}
\]

Figure 6 – Amination / crosslinking of PECH with DABCO with inert PAN to produce AEMs for RED [29]

These bespoke AEMs were synthesised at different blend ratios (i.e. functionality) and their properties experimentally determined (Table 2). The highest performing membrane, PECH B1, had an area resistance of 0.82 Ω cm\(^2\), 87% permselectivity and produced a gross power density of 1.27 W m\(^{-2}\), exceeding the power output obtained with commercially available AEMs. The same authors later developed tailor-made CEMs by solution casting a series of sulfonated poly(ether ether ketone) (PEEK) membranes (Figure 7). Extensive research has been carried out with regard to sulfonated poly(ether etherketone) (S-PEEK) membranes for use in polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [30] [31] [32], however this is the first example of being used for RED application.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{SO}_3^-
\end{align*}
\]

Figure 7 – Sulfonated poly(ether etherketone) (SPEEK) ‘tailor-made’ CEM for RED [33]

As before with the PECH based AEMs, the CEM properties were experimentally determined (Table 2) and RED performance tested. The highest performing CEM was SPEEK 65 which had a thickness of 72 μm, area resistance of 1.22 Ω cm\(^2\) and 89% permselectivity. When
combined in an experimental RED stack with the previously synthesised literature AEM PECH B1 the gross power density was determined to be 1.3 W m$^{-2}$ [33].

Table 2 - Experimentally determined bulk properties of tailor made PECH AEMs and SPEEK CEMs

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC$^{[a]}$</th>
<th>$\alpha^{[b]}$</th>
<th>R$^{[c]}$</th>
<th>SD$^{[d]}$</th>
<th>$\delta^{[e]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEMs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPEEK 65</td>
<td>1.76</td>
<td>89</td>
<td>1.22</td>
<td>36</td>
<td>72</td>
</tr>
<tr>
<td>SPEEK 40</td>
<td>1.23</td>
<td>95</td>
<td>2.05</td>
<td>23</td>
<td>53</td>
</tr>
<tr>
<td>AEMs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PECH A</td>
<td>1.31</td>
<td>90</td>
<td>2.05</td>
<td>32</td>
<td>77</td>
</tr>
<tr>
<td>PECH B1</td>
<td>1.68</td>
<td>87</td>
<td>0.82</td>
<td>49</td>
<td>33</td>
</tr>
<tr>
<td>PECH B2</td>
<td>1.68</td>
<td>87</td>
<td>0.94</td>
<td>49</td>
<td>77</td>
</tr>
<tr>
<td>PECH B3</td>
<td>1.68</td>
<td>87</td>
<td>1.32</td>
<td>49</td>
<td>130</td>
</tr>
<tr>
<td>PECH C</td>
<td>1.68</td>
<td>79</td>
<td>1.14</td>
<td>54</td>
<td>77</td>
</tr>
</tbody>
</table>

[a] Ion-exchange capacity (mmol g$^{-1}$); [b] Permselectivity (%); [c] Area resistance (Ω cm$^2$); [d] Swelling degree (%); [e] Thickness (µm).

Geise et al. produced a series of AEMs intended for the application of SGP [34]. The AEMs (see Figure 8) were prepared by solution-casting commercially available polymers, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and Radel poly(phenylsulfone), that had undergone prior functionalisation (quaternisation) by treatment with tertiary amines. Three different membranes were produced, each of multiple analogues with varying levels of functionality.

![aRadel-IEC](image)

![aPPO-x](image)

![aPPO-CxDy](image)

Figure 8 - Quaternary ammonium functionalised AEMs produced for SGP techniques [34]
The study aimed to deduce a relationship between AEM water content and transport properties. Results generally demonstrated that water content is inversely proportional to permselectivity and resistance, whereby membranes with higher water content tend to have lower ionic resistance and lower permselectivity. Results unfortunately are not presented specifically for RED with regard to power density. However, AEM aRadel-2.66 had the lowest resistivity ($1.6 \, \Omega \, m$), and a permselectivity of around 85% with several other membranes possessing comparable properties.

A series of nanoporous polycarbonate track-etched CEMs with varying pore sizes for specific application in RED were produced by Kwon et al. [35]. The membranes in this study varied from typical IEMs as they contained charged nanofluidic channels rather than fixed charge functionalised head groups within the polymer matrix. Ion transport occurs when counter-ions, in this case cations, concentrate at the surface of the charged pores forming an electric double layer (EDL). The EDL allows preferential transport of counter-ions while co-ions are excluded due to electrostatic repulsion (Figure 9). The authors state this is a viable cost-effective method for producing IEMs because of the ease at which the nanopores can be modified to give high ion selectivity. Unfortunately, the authors provide very limited information regarding the final membranes, and no information regarding materials or methodology. The highest performing CEMs, in terms of total power output, were those with pore sizes of 15 nm and increasing pore size led to a significant drop in power.

Figure 9 - Schematic of electrochemical energy conversion in negatively charged nanopores between two reservoirs of different salinity [35].
Hong and Chen, like Güler before them, investigated the wider field of membrane-based energy technologies when considering membranes for the RED process [36]. They focused on the development of organic–inorganic nanocomposite IEMs based on sulfonated poly(2,6-dimethyl-1,4-phenyleneoxide) (sPPO, Figure 10) and sulfonated iron(III)oxide (Fe$_2$O$_3$-SO$_4^{2-}$). The CEMs were cast into thin films from a solution of pre-sulfonated PPO and 0-0.7 wt% Fe$_2$O$_3$-SO$_4^{2-}$. Incorporating Fe$_2$O$_3$-SO$_4^{2-}$ into IEMs has been considered previously for application in fuel cells, however this is the first example of such membranes being applied to RED. Of the membranes produced, the highest performing example contained 0.7 wt% Fe$_2$O$_3$-SO$_4^{2-}$, a thickness of 30 μm, an area resistance of 0.82 Ω cm$^2$, and a permselectivity of 86%, with bulk properties resulting in a gross power density of 1.4 W m$^{-2}$ [37]. The membranes with the highest permselectivity possessed a water uptake in the region of 30%; these findings are consistent with an early paper [36].

![Figure 10 - Sulfonation of poly(2,6-dimethyl-1,4-phenylene oxide)](image)

### 1.8 Radiation-Induced Grafting Co-polymerisation

To date IEMs developed specifically for application RED, where specified, have all been produced on a laboratory scale via the solution-casting method [29][33][34]. In the solution-casting method, polymers and functional/functionisable monomers are dissolved in a solvent which is then typically heated and stirred. On cooling, the solution is cast onto a glass or metal plate and the excess solution is allowed to evaporate leaving behind a thin polymer film. Although solution casting is one of the oldest technologies in plastic film manufacture and widely used in industry [38], on a laboratory scale in can be more difficult to produce highly homogenous films with uniform thickness. Production volumes of materials are also limited by typical small-scale laboratory set-ups. Radiation-induced grafting co-polymerisation (RIG), is a versatile method used to chemically modify commercially
available polymer films to incorporate desired functionality, such as ion exchange groups, into the existing polymer matrix.

1) Simultaneous radiation grafting:

2) Pre-irradiation grafting in inert atmosphere:

3) Pre-irradiation grafting in air:

Figure 11 - Methods of radiation-induced grafting co-polymerisation. M is the monomer being grafted and (n) is an integer representing chain length, adapted from source [40].

The first example of using RIG to produce IEMs was published in the mid-1950s [39]. Radical or ‘active’ sites are implemented into the polymer matrix by irradiating the film with a radiation source such as a $^{60}$Co γ-ray. The radical sites then initiate free radical polymerisation reactions with the grafting monomer, resulting in functionalised polymer membranes. The technique was studied in depth by Chapiró [40] in the early 1960s who identified three methods to produce radiation grafted co-polymers: 1) Simultaneous radiation grafting, where the base polymer and grafting monomer are exposed in situ to a radiation source; 2) Pre-irradiation grafting in inert atmosphere where polymer films are sealed in a vessel which is then purged with an inert gas (to remove air) before being subjected to a radiation source, with a subsequent exposure to the grafting monomer; 3) Pre-irradiation grafting in air, which is performed as above but without first evacuating the air. The physical
chemistry of each method varies and opting for one method over another typically involves a trade-off between chemical properties and the practicality of the methodology (see Figure 11). The extent of grafting achieved varies between each method and the amount and speed of radiation applied to the polymer film.

Simultaneous radiation grafting is perhaps the most efficient use of radicals generated as they initiate an instantaneous polymerisation, whereas pre-irradiation grafting methods risk the degradation of radicals over time (e.g. via crosslinking of the base polymer film). Significant radical decay will occur if pre-irradiation is carried out above the glass transition temperature (TG) of the polymer or a temperature high enough to cause decomposition of peroxides [41]. A comprehensive review of the experimental parameters of RIG was carried out in 2004 by Nasef and Hegazy, who reported that factors including total absorbed radiation dose, radiation dose rate, type of base polymer film and the type and concentration of monomer solution all have a significant effect on the bulk membrane properties of the IEM produced [42].

1.8.1 Radiation source, irradiation dose and dose rate

Ionising radiation or high energy radiation is broadly grouped into two general forms: photon radiation, which involves the emission of x-rays or γ-rays, and corpuscular radiation, which includes fluxes of charged particles (i.e. electrons and protons) [43]. With regard to the radiation processing of polymers, γ-rays (typically from a 60Co source) or an electron beam (from an electron accelerator) are the two major kinds of ionising radiation. Both sources produce essentially the same radical events within the irradiated polymer, relative to absorbed dose, and the results of subsequent graft modification are independent of the type of radiation used [41]. The type of radiation used, however, does have an effect depending on the thickness of the polymer to be modified. With thicker polymers, γ-rays are more advantageous as they can penetrate much further into the bulk compared to electrons; as electrons continuously lose energy on passage through the material [42]. As the level of penetration of electrons is less than γ-rays, it is often limited to the purpose of surface modification; however, bulk penetration extends to the region of 200 µm [44] and hence it is therefore a viable option for the bulk modification of thin films. Energy transfer of the source to a substrate is the linear energy transfer (LET). Both γ-rays and electrons possess low LET resulting in a homogenous deposition of radicals in the irradiated polymer [41].
their 2004 review Nasef and Hegazy devise that irradiation dose and dose rate have a substantial effect on the levels of grafting achieved. Generally, higher irradiation absorbed doses lead to higher degrees of grafting due to enhanced free radical formation during irradiation and chain-growth propagation. In contrast, higher dose rates in simultaneous grafting methods result in lower degrees of grafting due to radical recombination events and termination of chain growth [42].

1.8.2 Requirements of polymer base films

To date, efforts to synthesise IEMs from RIG have all incorporated high-grade, commercially available polymer films that have been commonly produced for use within the fields of civil engineering or architecture. For suitability as a base film for RIG membranes there are several necessary requirements. For the initial grafting reaction to be successful, the base polymer must be able to yield and retain radical sites in order to initiate radical graft co-polymerisation. Secondly, the diffusion of the grafting monomer into the polymer matrix must also be allowed for the grafting reaction to occur throughout the bulk material. For the purposes of application base films should be mechanically robust, especially after radiation exposure, chemical stability is another key factor and films must be stable both to the solvents used during synthesis and also the intended environment of the final application.

Polymer films are exposed to ionising radiation to produce radical sites for either the initiation of immediate grafting in the case of in-situ grafting, or subsequent grafting reactions via trapped radicals or peroxide groups with pre-irradiation methods (Figure 11). The key irradiation event of interest is the overall ability of a polymer substrate to form radicals (G(R•)), the more radicals formed the more graft chains formed leading to higher degrees of grafting. As well as radical formation, ionising radiation, through homolytic bond cleavage, initiates several other radiation events such as chain scission, crosslinking, and gas evolution [45]. The radiation-induced events that have the greatest effect on the structural backbone of a polymer film and therefore mechanical structure are chain scission or crosslinking. A polymer’s tendency to crosslink or undergo chain scission during exposure to radiation is therefore a critical parameter for its suitability as a base film in RIG. Excessive chain scission will ultimately lead to degradation of the polymer chain and mechanically
weak membranes. Crosslinking, via recombination of radicals, is sometimes desirable although highly crosslinked polymers can become brittle and tear easily [46].

In a recent comprehensive review of RIG membranes for fuel cells, Gubler tabulates literature findings for the irradiation responses of various polymers to ionising radiation (Table 3) [41]. From the data presented in Table 3 it can be concluded that the polymers most susceptible to radical formation are poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF) and poly(ethylene) (PE), all of which have purely aliphatic structures, whereas poly(amides) and aromatic structures, poly(styrene) (PS) and poly(ethylene terephthalate) (PET), are orders of magnitude lower in their ability to form radicals.

**Table 3** - Irradiation response of polymer films to ionising radiation expressed as radical chemical yield G, which signifies the number of radiation events of a given type per 100 eV of absorbed dose.

<table>
<thead>
<tr>
<th>Polymer film</th>
<th>G(R•)(^{[a]})</th>
<th>G(X)(^{[b]})</th>
<th>G(S)(^{[c]})</th>
<th>G(g)(^{[d]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(tetrafluoroethylene)</td>
<td>0.14 – 0.40</td>
<td>0.1 – 0.3</td>
<td>1.0 – 4.0</td>
<td>0.02 - 0.03</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>3.3</td>
<td>0.65 – 1.0</td>
<td>0.3 – 0.64</td>
<td>1.7</td>
</tr>
<tr>
<td>Poly(ethylene)</td>
<td>2.8 – 3.3</td>
<td>1.0 – 3.0</td>
<td>0.2 – 0.9</td>
<td>2.8 – 3.9</td>
</tr>
<tr>
<td>Poly(styrene)</td>
<td>0.1</td>
<td>0.02 – 0.05</td>
<td>0.01 -0.02</td>
<td>0.02 – 0.07</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>0.02 – 0.03</td>
<td>0.08 – 0.14</td>
<td>0.07 – 0.17</td>
<td>0.016</td>
</tr>
<tr>
<td>Poly(amide 6)</td>
<td>0.05</td>
<td>0.4 – 0.7</td>
<td>0.6 – 0.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Formation of radicals. \(^{[b]}\) Crosslinking events. \(^{[c]}\) Chain scission events. \(^{[d]}\) Gas evolution.

Fluoropolymers are considered chemically inert materials able to resist high temperatures and are often chosen as materials for harsh chemical environments. These properties are attributed to the presence of the strong carbon–fluorine bond, and the ability of the larger fluorine atoms to sterically protect the carbon backbone of fluoropolymers from chemical attack [47]. More relevant for RIG perhaps is the ability of a polymer to produce radical sites. The data compiled in Table 3 demonstrates that G(R•) values for radical formation in fluoropolymers are roughly comparable to those of their protonated analogues. The data compiled for PVDF with regard to its suitability as a base polymer for RIG is of interest. The partially fluorinated polymer is equivalent to non-fluorinated PE in radical formation and chain scission, yet is similar to fluorinated PTFE with respect to the extent of crosslinking. The author comments that from a radiation chemistry point of view PVDF shows similarities to PE, yet from a chemical stability point of view, it behaves more like
PTFE [41]. To understand the radiation chemistry of fluoropolymers one can look towards the varying bond dissociation enthalpies. In the simplest terms, PTFE, PVDF and PE all have the same primary structure (Figure 12), however the fluorine content of each polymer varies significantly. PTFE has a perfluorinated structure containing only C-C and C-F bonds, PVDF is partially fluorinated so also contains C-H bonds, while PE is a fully saturated hydrocarbon and contains no C-F bonds within its structure. In PTFE, the C-F bond (dissociation energy 480–520 kJ mol\(^{-1}\)) is stronger than the C-C bond (370–420 kJ mol\(^{-1}\)), therefore when subjected to a source of high energy the C-C bonds would break before the C-F bonds making scission of the main chain more likely to occur. In PVDF and PE although the C-H bond at 430–450 kJ mol\(^{-1}\) is stronger than the C-C bond, large amounts of cleaved C-C bonds recombine due to the restricted mobility of the main carbon chain leading to a net cleavage of the C-H bond [43].

![Structural formulae and bond dissociation enthalpies of ideally structured aliphatic polymers PTFE, PVDF and PE illustrating the effect of fluorine content on structure.](image)

A relationship is observed between the effect of high energy irradiation on a fluoropolymer and the amount of hydrogen atoms in the fluoropolymer. The trend is approximated for a particular sample of polymers and expressed as follows: For crosslinking, PVF > PVDF > ETFE > FEP > PFA > PTFE and for chain scission, PTFE > PFA > FEP > ETFE > PVDF >
PVF [48]. In general terms, a high hydrogen/low fluorine content polymer has a higher tendency for crosslinking, whereas a low hydrogen/high fluorine content polymer will favour chain scission. As PVDF is a partially fluorinated polymer it is found around the centre of this sequence, which explains the relationship observed between its crosslinking and scission events. Another polymer located at the centre of this radiation ‘hierarchy’ is ETFE (poly(ethylene tetrafluoroethylene)). ETFE is a fluoro-co-polymer with a synonymous structure to PVDF. The ideal ETFE backbone consists of alternating units of ethylene, C₂H₄ and tetrafluoroethylene, C₂F₄ (Figure 13). The radiation chemistry, physical and chemical properties and the commercial availability of these two materials make them ideal candidates for use as base polymers to produce RIG IEMs. A multitude of examples for various membrane based technologies are readily found in the literature [49; 50; 51].

Figure 13 – Ideal repeat units of partially fluorinated polymers PVDF and ETFE illustrating structural similarities of the two materials.

1.8.3 Grafting monomer

During the progression of RIG as a technique to produce IEMs for membrane-based energy technologies, successful grafting has been achieved with a large array of various vinyl monomers. The most common grafting monomer used in the vast amount of experiments is styrene. The effectiveness of styrene-based IEMs for fuel cells has been questioned due to their limited durability in strongly acidic or alkali conditions with several degradation mechanisms being put forward [52]. However, the stability of styrene-based IEMs in harsh fuel cell conditions will be of little to no concern for RED specific IEMs as RED involves conditions where IEMs will be under neutral pH and low ambient temperatures. The popularity of styrene and styrene derivatives for RIG is largely due to their low cost and high availability, and these factors fit the essential criteria for RED membrane development,
making styrenic monomers of key interest to this work [53]. Another major appeal of styrenic monomers is the ease at which they are incorporated into bulk films via RIG reactions. A survey of the literature for styrene-based RIG membranes produces many examples, over the past decade or so, of styrene grafting onto a wide range of polymer films, including but not limited to PTFE [54], PEEK [55], PVDF [56], and ETFE [57]. Once grafted, styrene requires a simple sulfonation reaction to yield sulfonic acid functionalised CEMs (Figure 14-A). Furthermore, styrene has a lower tendency for homopolymerization during the RIG process, relative to more radiation-sensitive monomers such as acrylic acid [42].

![Figure 14 – Grafting of styrenic monomers to polymer films and subsequent modification: A. Sulfonation of styrene with chlorosulfonic acid; B. amination of 3/4-vinylbenzyl chloride with trimethylamine.](image)

Of the styrene derivatives to be investigated to date, vinylbenzyl chloride (VBC) is of interest as a RIG monomer as it contains a synthetically versatile methylene chloride ring substituent. Herman et al. used RIG of 3/4-VBC to poly(hexafluoropropylene-co-tetrafluoroethylene) (FEP) film to produce highly functionalised AEMs intended for use in alkaline fuel cells. Varcoe and Slade later employed this method to graft VBC onto ETFE film, producing physically stronger AEMs [58]. Once incorporated into a bulk polymer, VBC can readily facilitate a simple substitution reaction with trimethylamine (TMA) to yield a quaternary ammonium functionalised AEM (Figure 14-B) [59]. The CH₂Cl chloride can be theoretically substituted with any tertiary amine to yield AEM in just two steps. This then has the potential to facilitate the fine tuning of AEM properties by incorporating different ammonium pendant...
head-groups into the membrane design. Furthermore, the implementation of such a versatile synthetic group provides a starting point to carry out an entire series of complex synthetic reactions should they be required. The cost and commercial availability of styrenic monomers together with the relative ease at which they are incorporated into polymer films, previously identified as suitable for RIG base films, makes them most suitable for RED membrane production and they are therefore of considerable interest in the progression of this project.

1.8.4 Plant-scale production of radiation-grafted IEMs

To date RIG is predominately a laboratory scale method for producing experimental IEMs. The quantities of membrane required for a full scale RED plant would be of the order of thousands of m². If producing IEMs via RIG is to be considered commercially viable, the synthetic methods employed in the laboratory would need to be able to translate to a plant scale. The literature indicates several good examples of RIG as a large-scale roll-to-roll process. Fujiwara in 2007 reports on a continuous, plant scale, pre-irradiation process to produce various functional woven fabrics producing rolls of materials under strict reaction parameters in as little as 2 h [60]. Later in 2011, the author’s company report a 3.8 times increase in production, producing 130,000 m² of material in a six-month period [61].

![Figure 15 - Schematic illustration of Fujiwara continuous RIG apparatus (left), and a photograph of the actual plant process machinery (right).](image)

Tamada et al. use a pre-irradiation grafting method for the production of adsorbant materials for water treatment. Although not a continuous process, the authors report large-scale RIG
processes involving grafting solutions of up to 30 L in volume, producing functional membranes 0.3 m wide and 18 m in length [62]. In a 2012 review, The Japan Atomic Energy Agency report a large-scale synthesis producing RIG materials by the roll for Cs adsorption from the fallout waters of the Fukushima disaster [63]. Hoshina et al. use RIG to incorporate functionality into poly(ethylene) fabric for water treatment where this is again a large-scale synthesis producing rolls of materials 0.3 m in width [64]. Considering that RIG materials are already in production via both large-scale, batch and continuous processes it is realistic to assume that existing film companies would be able to incorporate alternative RIG IEM production into their pre-existing plants. The examples serve to demonstrate RIG as versatile, cost effective and feasible method for plant scale IEM production.

1.9 Chapter Summary

With the effects of climate change and the complex geopolitics of traditional fossil fuels, the requirement for the development of clean renewable energy sources is constantly increasing. Salinity gradient technology is a clean energy technology able to generate power from the chemical potential difference between salt solutions of different concentrations. Reverse electrodialysis (RED) is a salinity gradient technique that generates power when a low concentration salt solution (river water) mixes with a high concentration salt solution (seawater), a process that occurs naturally in estuaries the world over. RED is a membrane-based technique and the fundamental component of a RED cell is the ion-exchange membrane (IEM). A major requirement for commercial viability of RED is the development of process specific, cost-effective membranes. One low cost method of producing IEMs is through radiation induced grafting (RIG) of polymer films, a process where otherwise inert thin films are functionalised by the addition of ionic head groups. With radiation grafting it is possible to ‘fine tune’ IEMs to exhibit certain levels of bulk properties by modifying various reaction parameters including the source, dose and dose rate of radiation, polymer base film, grafting monomer and the nature of head group functionalisation. Radiation grafting has been extensively utilised in the development of IEMs for fuel cells but as yet has not been used to develop RED specific membranes. Despite the IEMs developed for fuel cell purposes having good bulk properties, they have often fallen short of commercial benchmarks due to poor stability in harsh conditions, e.g. high pH or high temperatures. The RED process takes place around neutral pH and in ambient temperature and it is therefore
possible that IEMs found unfit for fuel cell application could be re-assessed and further developed for RED.

1.10 Aims and Objectives

The general aim of this research is to incorporate the technique of (RIG) as a versatile method to produce IEMs targeted specifically for RED application. IEMs will be synthesised from co-polymerisation of partially fluorinated 50 µm ETFE and PVDF polymer films. For ease of transport and handling, polymer films will be irradiated using electron beam radiation in air. Aromatic vinyl monomers, specifically styrene and 3/4-vinylbenzylchloride, will then be subsequently grafted to the base films via the pre-irradiation method. A multitude of IEMs will be produced by varying reaction parameters such as grafting methods (i.e. single-step and conventional multi-step routes), total radiation absorbed dose, type of polymer base film used, and changing the chemistry of the pendant head-group. This work aims to produce a number of experimental IEMs and to evaluate their bulk properties, including area resistance, permselectivity, ion-exchange capacity and gravimetric water uptake. The bulk properties will be used to estimate the gross power density of a single membrane or membrane pair (cation/anion-exchange membranes) by employing a literature-recognised mathematical model (Eqn. 1 & 2) [28] [33]. A future ambition would be to perform an up-scaled synthesis of any IEMs that demonstrate high theoretical power density for actual RED cell testing.

Previous publications regarding radiation-grafted IEMs have focused on fuel cell and electrolyser applications and therefore the measurements of bulk properties have all been performed with the membrane in H⁺ form for CEMs (for hydrogen fuel cells) or OH⁻ form for AEMs (for use in solid alkaline fuel cells), rather than the Na⁺ or Cl⁻ form that is more relevant to RED. Some of the radiation-grafted AEMs in the literature intended for uses in solid alkaline fuel cells have been unfit for application due to alkaline stabilities or degradation at elevated temperature, and therefore should be re-evaluated for milder RED operating conditions.
2. Experimental

2.1 Synthetic methods

2.1.1 Materials

The following section details the materials used throughout the entirety of the project in order of supplier. The 50 µm thick polymer films, poly(vinylidene fluoride) (PVDF) and ethylene tetrafluoroethylene (ETFE) were supplied by Nowofol Germany. Reagents 4-vinylbenzene sodium sulfonate (technical, ≥ 90%), styrene (ReagentPlus®, contains 4-tert-butylcatechol as stabiliser, ≥99%), chlorosulfonic acid (99%), 4-vinylbenzylchloride (technical, ≥90%), pyridine (anhydrous, 99.8%), 2,6-dimethylpyridine (≥99%), N,N,N′,N′-tetramethyl-1,4-butanediamine (98%), 1,4-diazabicyclo[2.2.2]octane (≥90%) and H2O2 (30% in H2O, w/w, contains stabiliser) were all purchased from Sigma-Aldrich and used without any further purification. NaCl solutions were prepared using sodium chloride (BioXtra, ≥99.5%), supplied by Sigma-Aldrich. Vinylbenzylchloride (97%, Mixture of 3- and 4-isomers, contains stabilisers, 1-octyl-2-pyrrolidone (98%), trimethylamine solution (~45 wt. % in H2O), 1-methylimidazole (ReagentPlus®, 99%), 1,2-dimethylimidazole (98%), N,N,N′,N′-tetramethyl-1,3-propanediamine (≥99%), N,N,N′,N′-tetramethyl-1,6-hexanediame (99%) and divinylbenzene (technical grade, 80%) were purchased from Aldrich and used as supplied without any further purification. N,N,N′,N′-tetramethylethylenediamine (bioreagent, suitable for electrophoresis, ~99%) was supplied by Sigma life sciences and used as supplied. Thiourea (99%, extra pure) was purchased from Acros Organics and used as supplied. Acetic acid (glacial, reagent grade) and lithium hydroxide (reagent grade) were supplied by Fisher Scientific and used as supplied. H2SO4 solutions were prepared using sulphuric acid (Certified ACS Plus, 98%) supplied by Fisher scientific and diluted with ultra-pure deionised water.

The solvents N,N-dimethylformamide (≥ 98%) and dichloromethane ≥99.9% were supplied by Sigma-Aldrich and used as received. Toluene (low in sulphur) and 2-propanol (extra pure) were purchased from Fisher Scientific and also used as received. Tetrahydrofuran (HPLC grade) was supplied by Fisher Scientific and distilled to remove excess H2O. Analytical standards potassium hydroxide solution (volumetric, 0.1 M KOH), Silver nitrate solution (volumetric, 0.02 M AgNO3) and nitric acid solution (volumetric, 2 M HNO3) were purchased from Fluka Analytical.
2.1.2 Pre-irradiation of thin polymer films

PVDF and ETFE thin polymer films were cut to an area of 120×120 mm, and up to 10 films were then placed into sealable polythene bags. Films were then subjected to total radiation doses up to 90 kGy (±10%) via 10 kGy increments from a 5 MeV electron-beam (Synergy Health Sterilisation UK Ltd, Swindon). Actual total doses used are indicated later in the revilement sections. Immediately after irradiation the polymer films were stored under dry ice for approximately 1.5 h during transportation before being transferred to a -40°C cold storage immediately on arrival at the laboratory.

2.1.3 Graft co-polymerisation (and subsequent sulfonation) of styrene onto thin polymer films

Grafting of styrene onto PVDF and ETFE films was carried out using a solution of styrene in toluene in accordance with the available literature [53] [65]. A grafting solution of styrene:toluene (2:3) was prepared in a large glass reaction vessel. Pre-irradiated PVDF and/or ETFE films with an area of 120×120 mm were rolled between sheets of single-ply tissue paper and submerged in the grafting solution, the reaction vessel was then sealed and purged with low pressure N\textsubscript{2} for 1 h. After 1 h the vessel was heated to 70°C and the reaction was allowed to continue for 72 h. On completion styrene grafted films were removed from the reaction vessel and washed with toluene before drying in a vacuum oven at 70°C for 5 h.

Styrene graft co-polymers were sulfonated to functional CEMs following the sulfonation procedure described in Horsfall 2002 [65]. Dry styrene grafted PVDF and/or ETFE films were placed into a 5% (v/v) chlorosulfonic acid in DCM solution, at ambient temperature, for 2 h. After 2 h the sulfonation reaction was quenched by immersing the polymer films into a large volume of deionised water. The sulfonated membranes were then washed several times and boiled in ultra-pure deionised water for 1 h to assume a fully hydrated form of the CEM. CEMs were then stored under ultra-pure deionised water until required (Mechanism 1).
Mechanism 1 – Graft co-polymerisation (and subsequent sulfonation) of styrene onto thin polymer films, polymer is either ETFE or PVDF.

2.1.4 Grafting of 4-vinylbenzene sodium sulfonate to PVDF films

Graft co-polymerisation of VBS into PVDF film was carried out as in Nasef 2009 [66]. A grafting solution consisting of VBS monomer, 1 mol dm$^{-3}$, in DMF / H$_2$SO$_4$, 0.2 mol dm$^{-3}$ (DMF: H$_2$SO$_4$ = 9:1) was prepared and decanted into a glass reaction vessel. The vessel was modified to allow for better solution kinetics, by fitting a perforated platform at the base.
VBS was prevented from falling out of the solution improving the homogeneity of the grafting solution. Several pre-irradiated PVDF films of area 120×120 mm were rolled between sheets of single-ply tissue paper and submerged into the grafting solution. The vessel was then sealed and purged with N₂ for 1 h before being heated to 60°C for a period of 48 h. After 48 h the grafted films were washed several times in deionised water and placed in an ultra-sonic bath overnight to remove any excess or homopolymerised VBS monomer. Grafted cation exchange membranes (CEMs) were stored under ultra-pure deionised water until needed (Mechanism 2).

Mechanism 2 – Radiation-induced grafting of 4-vinylbenzene sodium sulfonate to PVDF films.
2.1.5 Graft co-polymerisation (and subsequent sulfonation) of 3/4-VBC onto ETFE thin polymer films

Mechanism 3 – Graft co-polymerisation (and subsequent sulfonation) of 3/4-VBC onto ETFE thin polymer films. Oxidation of thiol to sulfonic acid (in red), does not currently have an established mechanism [67].
ETFE-g-poly(3/4-VBC) graft co-polymers were prepared via pre-irradiation grafting of 3/4-VBC onto ETFE film (Mechanism 3). Several ETFE films, pre-irradiated to total dose of 70 kGy, were rolled between sheets of single-ply tissue paper and placed into a large glass vessel. The ETFE films were then covered with a grafting solution consisting of 79% 2-Propanol, 20% VBC and 1% 1-Octyl-2-pyrrolidone (v/v/v). The vessel was then sealed and purged with low pressure nitrogen for 1 h before heating to 60°C for 72 h. On completion, the resulting ETFE-g-poly(3/4-VBC) graft co-polymers were washed with and then soaked in toluene at 60°C for 24 h to remove any excess starting materials and homopolymer. Finally, the films were dried in a vacuum oven at 70°C for 4–5 h.

ETFE-g-poly(3/4-VBC) co-polymers were sulfonated to ETFE-g-benzylsulfonate, as opposed to ETFE-g-styrene sulfonate reported previously, in a three-step synthetic reaction. Firstly, the prepared ETFE-g-poly(3/4-VBC) graft co-polymers were immersed in a Thiourea solution, 1 mol dm\(^{-3}\) in H\(_2\)O, and heated at 80°C for 48 h, substituting the benzyl chloride moiety to the benzyl thiouronium salt. The resulting polymer films were washed in deionised water and dried under vacuum at 50°C for 5 h. The thiouronium salt co-polymers were then submerged in LiOH solution, 1 mol dm\(^{-3}\) in H\(_2\)O, at room temperature for 48 h to undergo base hydrolysis to the thiol. On completion, the resulting polymer films were again washed in deionised water and dried under vacuum at 50°C for 5 h. Finally, the film (in thiol form) was oxidised to sulfonate by treatment with a solution of H\(_2\)O\(_2\) and acetic acid (30:70, v/v) at room temperature for 48 h. The resulting CEM was washed and then boiled in deionised water for 1 h to assume a fully hydrated form of the CEM. CEMs were stored under ultra-pure deionised water until needed.

2.1.6 Grignard coupling of 4-VBC to yield bis(vinyl phenyl)ethane

Bis(vinylphenyl)ethane (BVPE) was prepared via Grignard coupling of 4-VBC as in Li 1994 (Mechanism 4) [68]. Magnesium turnings (1 g, 0.04 moles) were placed into a three-necked round-bottom flask along with 2–3 crystals of iodine, the flask was then sealed and stirred for 1 h. After 1 h dry THF (100 cm\(^3\)) was added and the flask was purged and evacuated three times with low pressure N\(_2\). 4-VBC (13 cm\(^3\), 0.08 moles) was added dropwise to the flask via pressure equalised dropping funnel and temperature was maintained between 0 and -10°C. After addition, the reaction was allowed to slowly come to room temperature. After
16 h the reaction mixture was filtered to remove unreacted magnesium and the solvent was removed under reduced pressure. The resulting residue was dissolved in DCM and washed several times with HCl (6%), water and brine. The organic phase was then dried over MgSO₄ before filtering and removing any remaining solvent under reduced pressure. The resulting residue was recrystallised from hot MeOH producing 60% yield of solid BVPE. Confirmation of synthesis was obtained using NMR spectroscopy.

Mechanism 4 – Grignard coupling of 4-VBC to yield bis(vinyl phenyl)ethane crosslinking agent.

### 2.1.7 Graft co-polymerisation of both styrene and crosslinking agents onto thin ETFE films

Grafting of styrene onto 50 µm ETFE films was carried out using a solution of styrene in toluene as previously reported. Crosslinking agents, DVB and BVPE, were added in accordance with Lehtinen et al. 1998. Grafting solutions containing styrene:toluene, (2:3, v/v) and either 0, 2.5, 5 or 10 mol% crosslinking agent, was prepared in 80 cm³ ground-glass boiling tubes. ETFE film, pre-irradiated to a total dose of 30 kGy with an area of 120×120 mm was rolled in single-ply tissue paper and submerged into each grafting solution. The reaction boiling tubes were then sealed and purged with N₂ for 1 h. After 1 h the boiling tubes were heated to 70°C and the reactions were allowed to continue for 8 h. On completion, the grafted films were removed from the boiling tubes and washed with toluene before drying in a vacuum oven at 70°C for 5 h.

Crosslinked ETFE-g-styrene co-polymers are sulfonated to functional CEMs following the sulfonation procedure reported previously. The dry grafted ETFE films were placed into a 5% chlorosulfonic acid solution in DCM (v/v) at ambient temperature for 2 h. After 2 h, the
reaction was quenched by immersing the polymer films into a large volume of deionised water. The sulfonated CEMs were washed several times and then boiled in ultra-pure deionised water for 1 h to assume a fully hydrated form (Mechanism 5).

Mechanism 5 – Graft copolymerisation of both styrene and crosslinking agents onto thin ETFE films. Crosslinking agent is either DVB (shown) or BVPE.
2.1.8 Amination of ETFE-g-poly(3/4-VBC) to yield various quaternary ammonium functionalised AEMs

ETFE-g-poly(3/4-VBC) graft co-polymers were prepared via pre-irradiation grafting of 3/4-VBC onto ETFE film using the same method reported on earlier in this chapter. A general amination procedure was developed to convert the ETFE-g-poly(3/4-VBC) grafted intermediate films to the quaternary ammonium functionalised AEMs. ETFE-g-poly(3/4-VBC) films were rolled and placed into boiling tubes, the boiling tubes were then filled with solutions containing a large molar excess of each tertiary amine (see Table 4), each with a different targeted anion-exchange head-group. The boiling tube was then fitted with a reflux condenser and heated to a set temperature for the duration of the reaction. The concentration of amine solutions varied from 50% in aqueous solutions (v/v) (TMA) to pure undiluted reagents (pyridine). The temperature was typically 80°C with the exception of trimethylamine (TMA) where amination was carried out at room temperature due to the vapour pressure of aqueous TMA solution. The reaction time generally ranged from 16 to 48 h, although some of the larger amines were allowed 7 d for amination to occur. On completion, the AEMs were washed several times in deionised water to remove any excess amine. The AEMs were then boiled in deionised water for 1 h for AEM to adopt a fully hydrated form and stored under ultra-pure deionised water. The optimised reaction conditions for specific membranes are detailed in Table 4.

Mechanism 6 – Amination of ETFE-g-poly(3/4-VBC) to yield various quaternary ammonium functionalised AEMs.
Table 4 - Reaction conditions for the amination of ETFE-g-VBC

<table>
<thead>
<tr>
<th>Tertiary amine</th>
<th>Conc. (Vol%)</th>
<th>T (°C)</th>
<th>Amination (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylamine</td>
<td>50% (v/v) in H₂O</td>
<td>25</td>
<td>16 h</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>100%, as supplied</td>
<td>80</td>
<td>7 d</td>
</tr>
<tr>
<td>Pyridine</td>
<td>100%, as supplied</td>
<td>80</td>
<td>48 h</td>
</tr>
<tr>
<td>2,6-dimethylpyridine</td>
<td>100%, as supplied</td>
<td>80</td>
<td>7 d</td>
</tr>
<tr>
<td>1-methylimidazole</td>
<td>100%, as supplied</td>
<td>80</td>
<td>48 h</td>
</tr>
<tr>
<td>1,2-dimethylimidazole</td>
<td>100%, as supplied</td>
<td>80</td>
<td>48 h</td>
</tr>
</tbody>
</table>

2.1.9 Amination of ETFE-g-poly(3/4-VBC) with diamine crosslinking agents

A general amination procedure was used to convert ETFE-g-poly(3/4-VBC) grafted co-polymers to quaternary ammonium functionalised AEMs. Grafted ETFE-g-poly(3/4-VBC) films were placed in a boiling tube and covered with an aqueous diamine solution. Linear diamine solutions consisted of 50% aqueous solutions (v/v) of one of either N,N,N′,N′-tetramethylethylenediamine (TMEDA), N,N,N′,N′-tetramethylpropanediamine (TMPDA), N,N,N′,N′-tetramethylbutanediame (TMBDA) or N,N,N′,N′-tetramethylhexanediamine (TMHDA) diamines. Amination with bicyclic diamine 1,4-diazabicyclo[2.2.2]octane (DABCO), was carried out with 1 mol dm⁻³ aqueous solution. The boiling tube was then fitted with a reflux condenser and heated to 80°C for 48 h. On completion, the AEMs were washed several times in deionised water to remove any excess amine. The AEMs were then boiled in deionised water for 1 h for AEM to adopt a fully hydrated form and stored under ultra-pure deionised water.

![Mechanism 7 – Amination of ETFE-g-poly(3/4-VBC) with diamine crosslinking agents, ETFE-g-poly(3/4-VBC) intermediate prepared as previously demonstrated.](image-url)
2.2 Experimental Characterisation

2.2.1 Ion exchange

Before performing membrane characteristic experiments, it is first necessary to convert AEMs and CEMs to the appropriate form, Cl\(^-\) for AEMs and Na\(^+\) for CEMs respectively. An ion exchange was performed by soaking the membranes in aqueous NaCl solution, 1 mol dm\(^{-3}\), for three 30 min intervals. After each interval, the NaCl solution was discarded and replaced. After ion exchange to Cl\(^-\)/Na\(^+\) is complete any excess ions were removed by thoroughly washing three times in ultra-pure deionised water.

2.2.2 Ion-exchange capacity

Ion-exchange capacity (IEC) is a quantification of the ionic sites that are able to undergo ion-exchange with a counter-ion per gram of dehydrated membrane, which is expressed in units of mmol g\(^{-1}\) for IEMs with singly charged ion-exchange sites. IEC was determined using a Metrohm 848 Titrino plus autotitrator with Ag-Titrodes. Three repeat measurements were recorded on different samples for each IEM. Titration standards were purchased from Fluka Analytical and used as supplied.

2.2.3 Cation-exchange capacity

The IEC of CEMs was determined with the CEM in H\(^+\) form via an acid/base titration. CEM samples were cut to an approximate area of 25×25 mm and ion exchanged, as described previously, with aqueous HCl, mol dm\(^{-3}\) to yield the protonated form. The CEM samples were dried under vacuum at 50°C overnight (ca. 16 h). The dry mass of each CEM sample was recorded and the samples were placed in a poly(propylene) bottle containing 25 cm\(^3\) aqueous NaCl solution, 1 mol dm\(^{-3}\), and were left overnight (ca. 16 h) undergoing continuous stirring. The free H\(^+\) in solution were titrated against aqueous KOH titration standard, 0.1 mol dm\(^{-3}\) until an end point of neutral pH was obtained and the titration endpoint was determined from the point of steepest gradient of the pH plot. The IEC in mmol g\(^{-1}\) was calculated using Equation 4.
\[ IEC = \frac{EP \times [\text{titrant}]}{m_d} \quad \text{(Eqn. 3)} \]

where EP (cm\(^3\)) was the determined endpoint, [titrant] is the concentration (mol dm\(^{-3}\)) of titrant used and \(m_d\) (g) is the dehydrated mass of each membrane sample.

2.2.4 Anion-exchange capacity - Quaternary

Determination of the IEC of AEMs was carried out with AEMs in the Cl\(^-\) form. IEC is measured \textit{via} chloride precipitation titration with AgNO\(_3\) titrant. AEM samples in Cl\(^-\) form were dried under vacuum at 50°C overnight (\textit{ca.} 16 h) and the dry mass of each AEM sample was recorded. The samples were then placed in a poly(propylene) bottle containing 25 cm\(^3\) aqueous NaNO\(_3\) (2.4 mol dm\(^{-3}\)) and left overnight (\textit{ca.} 16 h) undergoing continuous stirring. The free Cl\(^-\) ions in solution were titrated with AgCl solution until the electrochemical endpoint was reached, determined \textit{via} the maximum in the differential curve \((\text{d(Voltage)}/\text{d(titrant)})\). Equation 4 was then used to calculate the IEC in mmol g\(^{-1}\).

2.2.5 Anion exchange capacity – Total

In instances where non-quaternary ion exchange groups, \textit{i.e.} NR\(_3\), are present it is necessary to perform a secondary ‘total’ IEC titration. This is carried out as above for AEMs although the initial ion exchange is performed with aqueous HCl (1.0 mol dm\(^{-3}\)) as opposed to NaCl. The addition of acid protonates any tertiary or secondary amines within the AEM bulk structure to a quaternary state, therefore making them detectable by this chloride titration method. Total IEC is calculated using Equation 4.

2.2.6 Gravimetric water uptakes

Gravimetric water uptake (WU\%) is a measurement of an ion-exchange membranes (IEMs) ability to absorb water and is expressed as a percentage with respect to the water content of
a hydrated membrane. It is calculated by determining the mass of a membrane in its dry and fully hydrated states.

Fully hydrated IEMs (after boiling in deionised water), in appropriate counter-ion form, were blotted dry with filter paper to remove any surface water and the mass of each sample was recorded to 0.1 mg on an analytical balance. Samples were then dried in a vacuum oven overnight (ca. 16 h) at 50°C. On removal from the oven, the mass of the IEMs was recorded a second time and the WU% is determined by Equation 5.

\[ WU(\%) = 100 \times \frac{m_h - m_d}{m_d} \]  
(Eqn. 4)

where \( m_h/g \) is the hydrated mass and \( m_d/g \) is the dehydrated mass of each membrane sample.

### 2.2.7 Electrochemical impedance spectroscopy

Electronic impedance spectroscopy (EIS) is an alternating current (AC) technique that measures the current response of a circuit when a sinusoidal voltage is applied. The technique operates over a range of frequencies, typically in the range of mHz, and is therefore capable of measuring ohmic resistances around an order of magnitude lower than typical voltmeters. This is useful to determine the ionic resistance of IEMs. In an AC circuit the electrical impedance is a measure of a circuit’s ability to resist the flow of electrical current, which is analogous to resistance in a direct current (DC) circuit, the latter expressed by Ohm’s law:

\[ R = \frac{V}{I} \]  
(Eqn. 5)

where R (Ω) is resistance, V (V) is potential and I (A) is current.

Impedance extends the notion of DC resistance to an AC circuit, whereas DC circuits possess only magnitude an AC circuit possesses both magnitude and phase which is considered using vectors. The addition of phase is introduced by the electronic mechanisms of inductance and capacitance, referred to collectively as reactance. The electrochemical impedance of a circuit is measured using an excitation signal provoking a quasi-linear response. In a quasi-linear
system, the response to an excitation potential is a sinusoid of the same frequency that has experienced a shift in phase and magnitude. The excitation signal in terms of a function of time is expressed as:

\[ V_t = V_0 \sin(\omega t) \]  

(Eqn. 6)

where \( V_t \) is the potential (V) at time (s), \( V_0 \) is the amplitude of the signal, and \( \omega \) is the radial frequency (rad s\(^{-1}\)).

The relationship between radial frequency, \( \omega \), and frequency, \( f \) (Hz) is:

\[ \omega = 2\pi f \]  

(Eqn. 7)

In a linear / quasi-linear system, the current response to an excitation potential \( (I_t) \) is shifted in phase \( (\phi) \) and has a different amplitude than initial signal \( (I_0) \):

\[ I_t = I_0 \sin(\omega t + \phi) \]  

(Eqn. 8)

Resistances, capacitances and inductances within an AC circuit disrupt the flow of electrical current by means of differing mechanisms with varying effects on the phase angle \( (\phi) \). In a purely resistive circuit the current and potential are in phase and \( \phi = 0 \). In purely capacitive circuit the current leads the potential and \( \phi = \pi/2 \), whereas in an inductive circuit the current trails the potential and \( \phi = -\pi/2 \).

Impedance spectra are represented on a complex plane in the form of an Argand diagram by means of complex algebra (Figure 16). The polar form consists of factors of magnitude and phase with each point representative of a vector at different frequency, this is expressed as:
\[ \hat{Z}(\omega) = |\hat{Z}(\omega)| \cos \phi + j \sin \phi \]  
(Eqn. 9)

where \( |\hat{Z}(\omega)| \) is the magnitude of the impedance, \( \phi \) is the phase angle and \( j \) is the imaginary component (also denoted by \( i \)).

In Cartesian form the relationship is expressed as:

\[ \hat{Z}(\omega) = R + j \chi \]  
(Eqn. 10)

where real component, \( R \), is the resistance and imaginary component, \( j \chi \), is the reactance.

Figure 16 – Argand diagram of an impedance represented in the complex plane.

The impedance response of a system can be used to determine the resistance of an electrochemical system, a typical impedance plot and its associated circuit is represented in Figure 17. As the reactive impedance of ideal inductors and capacitors is purely imaginary, the inductive impedance will increase as the sinusoidal frequency increases whereas the capacitative impedance will decrease as frequency increases. The purely real behaviour of an ideal resistor means that \( V \) and \( i \) are in phase and of the same magnitude so \( \phi = 0 \): Therefore, at certain frequencies reactance is zero \( (\chi = 0) \) and only resistive impedance is in effect.
Impedance spectra were recorded using a Solartron 1260 frequency response analyser/1287 electrochemical interface combination controlled by ZPlot v.2 software (Scribner Associates), with subsequent data analysis performed by ZView v.2 software (Scribner Associates). Resistance was taken as the x intercept at high frequencies, where reactive impedances = 0.

2.2.8 Through-plane ionic conductivity

The through-plane resistance of IEMs is determined by impedance spectroscopy. IEMs are hot pressed at 80°C at 150 ± 50 kg cm\(^{-2}\) between two pieces of single-sided carbon powder coated carbon cloth (A = 1 cm\(^2\)). The mini membrane electrode assemblies (MEAs) were fixed between two graphite electrodes and impedance spectra was recorded in ultra-pure deionised water. Resistance was taken as the x intercept and corrected for electronic resistance of the circuit and electrodes. The IEM conductivity (Sm\(^{-1}\)) could then be calculated using Equation 13.

\[
C = \frac{T}{R \times A} \quad \text{(Eqn. 11)}
\]

where T (cm) is the membrane thickness, A (cm\(^2\)) is the electrode area (A=1 cm\(^2\)) and R (Ω) is the resistance.
2.2.9 Membrane permselectivity

The permselectivity of an IEM is a fundamental parameter for the membrane performance in electrochemical techniques such as RED. It is a quantification of an IEM’s ability to pass an ion of one charge whilst repelling or retaining one of opposite charge. The permselectivity of IEMs is defined by the following equations for CEMs and AEMs respectively:

\[ \psi_{cem} = \frac{\hat{\iota}_{cem} - \hat{\iota}_{+}}{\hat{\iota}_{-}} \]  
(Eqn. 12a)

and

\[ \psi_{aem} = \frac{\hat{\iota}_{aem} - \hat{\iota}_{-}}{\hat{\iota}_{+}} \]  
(Eqn. 12b)

where \( \psi_{cem} \) and \( \psi_{aem} \) is the specific membrane permselectivity, \( \hat{\iota}_{cem} \) or \( \hat{\iota}_{aem} \) represents the transport number of counter ions in the membrane phase for CEMs and AEMs respectively, and \( \hat{\iota}_{+} \) and \( \hat{\iota}_{-} \) refer to the transport numbers of the cations and anions in solution.

For an ideal permselective CEM, \( i.e. \) one that transports only cations \( \hat{\iota}_{cem} = 1 \) and the membrane permselectivity is one, \( \psi_{cem} = 1 \). The permselectivity approaches zero as the transport number of cations within the membrane approaches the transport number of the solution, \( i.e. \) if \( \hat{\iota}_{cem} \equiv \hat{\iota}_{+} \) then permselectivity is zero, \( \psi_{cem} = 0 \). The transport number of an IEM can be determined indirectly by considering the membrane potential. When two different electrolyte solutions are separated by an IEM a potential difference is created across the membrane, this is known as the diffusion potential. If the IEM separates solutions comprising of different concentrations of the same counter-ion (\( e.g. \) dilute and concentrated NaCl solutions) this potential is known as the membrane potential. The Nernst equation for the membrane potential when an IEM separates two different solutions of the same electrolyte is:
\[ E = \frac{RT}{F} \ln \frac{a_d}{a_c} \]  
(Eqn. 13)

where \( E \) is the membrane potential, \( R \) is the ideal gas constant, \( T \) is absolute temperature (K), \( F \) is the Faraday constant, \( a_d \) is the activity of the dilute solution and \( a_c \) is the activity of the concentrated solution.

For a CEM the membrane potential arises because CEMs facilitate transport of cations while restricting transport of anions through the bulk material. This results in a difference of electrochemical potential as the concentrated solution now contains a higher percentage of anions and is negative whilst, conversely, the dilute solution contains a higher percentage of cations and is positive. The membrane potential can be measured directly by measuring the decrease in diffusion potential between the two solution compartments. For a completely selective membrane the decrease in diffusion potential is zero.

Permselectivity was determined using the static membrane potential method with an effective membrane area of 50×50 mm. Prior to measurement, each membrane was equilibrated in aqueous NaCl solution, 1 mol dm\(^{-3}\), for 24 h. The experimental cell consists of two compartments separated by the membrane under investigation. One compartment is filled with aqueous NaCl solution, 0.1 mol dm\(^{-3}\) and the other an aqueous NaCl solution, 0.5 mol dm\(^{-3}\). Both solutions were kept mobile by magnetic stirring at 600 rpm and fresh solution is circulated into the cell at a rate of 5 cm\(^3\) min\(^{-1}\) using a peristaltic pump. After 40 min, and when the system has reached a steady state, the potential difference between the two compartments was measured using Ag/AgCl reference electrodes (BASi, RE-5B). Three replicate measurements were performed for each membrane, and the membrane permselectivity is calculated from the mean as:

\[ \alpha(\%) = \frac{E_{measured} - E_{offset}}{E_{theoretical}} \]  
(Eqn. 14)

where \( \alpha \) is the membrane permselectivity (%), \( E_{measured} \) is the measured membrane potential, \( E_{offset} \) is the potential difference between electrodes when both are immersed in 0.5 M NaCl, and \( E_{theoretical} = 44.1 \) mV (calculated from Eqn. 13).
2.2.10 Summary of IEM bulk properties

A comprehensive list of experimentally determined properties; IEC, WU%, conductivity, permselectivity, area resistance and $C_{\text{fix}}$ for all of the IEMs synthesised throughout this thesis can be found below in Table 5.

Table 5 – Summary of experimentally determined properties for the RIG IEMs synthesised in this study

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC$^{(a)}$</th>
<th>WU%$^{(b)}$</th>
<th>$C^{(c)}$</th>
<th>$\alpha^{(d)}$</th>
<th>AR$^{(e)}$</th>
<th>$C_{\text{fix}}^{(f)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chapter 3</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-STY-30</td>
<td>2.46</td>
<td>51</td>
<td>24.4</td>
<td>65</td>
<td>0.40</td>
<td>2.4</td>
</tr>
<tr>
<td>P-STY-30</td>
<td>2.60</td>
<td>50</td>
<td>26.7</td>
<td>65</td>
<td>0.38</td>
<td>2.6</td>
</tr>
<tr>
<td>P-VBS-70</td>
<td>2.31</td>
<td>50</td>
<td>23.3</td>
<td>53</td>
<td>0.32</td>
<td>2.3</td>
</tr>
<tr>
<td>E-VBC-70</td>
<td>1.29</td>
<td>26</td>
<td>9.8</td>
<td>62</td>
<td>0.42</td>
<td>3.7</td>
</tr>
<tr>
<td><strong>Chapter 4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMA</td>
<td>1.86</td>
<td>49</td>
<td>27.2</td>
<td>59</td>
<td>0.37</td>
<td>2.0</td>
</tr>
<tr>
<td>TEA</td>
<td>1.58</td>
<td>41</td>
<td>14.1</td>
<td>66</td>
<td>0.69</td>
<td>2.3</td>
</tr>
<tr>
<td>Mim</td>
<td>1.84</td>
<td>32</td>
<td>26.3</td>
<td>53</td>
<td>0.54</td>
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<tr>
<td>DMIm</td>
<td>1.75</td>
<td>31</td>
<td>35.1</td>
<td>42</td>
<td>0.31</td>
<td>3.8</td>
</tr>
<tr>
<td>PYR</td>
<td>1.82</td>
<td>35</td>
<td>27.3</td>
<td>61</td>
<td>0.39</td>
<td>3.5</td>
</tr>
<tr>
<td>DMP</td>
<td>1.13</td>
<td>20</td>
<td>2.7</td>
<td>72</td>
<td>2.75</td>
<td>4.4</td>
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<td><strong>Chapter 5</strong></td>
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</tr>
<tr>
<td>DABCO</td>
<td>1.63</td>
<td>28</td>
<td>19.1</td>
<td>61</td>
<td>0.57</td>
<td>4.3</td>
</tr>
<tr>
<td>TMEDA</td>
<td>1.20</td>
<td>23</td>
<td>6.1</td>
<td>76</td>
<td>1.53</td>
<td>4.0</td>
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<tr>
<td>TMPDA</td>
<td>1.06</td>
<td>26</td>
<td>10.0</td>
<td>74</td>
<td>0.90</td>
<td>3.1</td>
</tr>
<tr>
<td>TMBDA</td>
<td>1.46</td>
<td>15</td>
<td>2.3</td>
<td>-</td>
<td>2.97</td>
<td>7.6</td>
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<tr>
<td>TMHDA</td>
<td>1.51</td>
<td>12</td>
<td>3.4</td>
<td>95</td>
<td>2.39</td>
<td>11.5</td>
</tr>
<tr>
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<tr>
<td>0% Crosslinker</td>
<td>1.88</td>
<td>42</td>
<td>15.0</td>
<td>80</td>
<td>0.65</td>
<td>2.6</td>
</tr>
<tr>
<td>2.5% DVB</td>
<td>2.57</td>
<td>31</td>
<td>16.1</td>
<td>89</td>
<td>0.60</td>
<td>5.5</td>
</tr>
<tr>
<td>5% DVB</td>
<td>2.37</td>
<td>21</td>
<td>6.4</td>
<td>74</td>
<td>1.32</td>
<td>9.3</td>
</tr>
<tr>
<td>10% DVB</td>
<td>1.92</td>
<td>15</td>
<td>4.1</td>
<td>97</td>
<td>2.16</td>
<td>10.4</td>
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<tr>
<td>2.5% BVPE</td>
<td>2.3</td>
<td>45</td>
<td>17.0</td>
<td>85</td>
<td>0.49</td>
<td>2.1</td>
</tr>
<tr>
<td>5% BVPE</td>
<td>2.86</td>
<td>51</td>
<td>26.9</td>
<td>83</td>
<td>0.37</td>
<td>2.8</td>
</tr>
<tr>
<td>10% BVPE</td>
<td>3.07</td>
<td>41</td>
<td>15.7</td>
<td>92</td>
<td>0.58</td>
<td>4.3</td>
</tr>
</tbody>
</table>

[a] Ion-exchange capacity (mmol g$^{-1}$). [b] Water uptake (%). [c] Conductivity (mS cm$^{-1}$). [d] Permselectivity (%). [e] Area resistance (Ω cm$^2$). [f] Fixed charge density (mmol g$^{-1}$ H$_2$O).
2.2.11 Raman spectroscopy

Raman spectroscopy is a vibrational spectroscopic technique used to observe the characteristic vibrational and rotational modes of a molecular system. Unlike IR, which is fundamentally an absorption spectroscopy, Raman produces emission spectra due to inelastic scattering of monochromatic light.

In Raman spectroscopy, a sample is irradiated with a high intensity light source, typically a laser in the visible, near infrared or near ultraviolet region of the electromagnetic spectrum. The Raman scattering derives from the transfer of energies between the incident radiation and the system under observation. When the system is irradiated, it is able to make a transition from a ground state to an excited state by absorbing and then reverting by emitting photons of incident radiation. The emitted radiation can be either elastic scattering (Rayleigh scattering), where energy is equal to incident radiation or inelastic scattering where the emitted radiation is not equal to the incident radiation (Stokes, anti-Stokes scattering, Figure 18) [69].

![Energy level diagram of elastic and inelastic scattering in Raman spectroscopy](image)

Figure 18 – Energy level diagram of elastic and inelastic scattering in Raman spectroscopy [69].

Inelastic scattering is very weak relative to Rayleigh scattering and to produce Raman spectra the high intensity Rayleigh scattering is filtered out by holographic gratings before the emitted radiation passes to the detector. Not all vibrational modes are Raman active, to be Raman active the vibrational mode must provoke a change in the molecular electric-
dipole polarisability of the system. The intensity of Raman scattering is directly proportional to the change in polarisability.

Raman spectra were obtained using a Thermo Scientific - DXR Raman Microscope equipped with a 780 nm IR laser and an Olympus model LMPLFLN 50x / 0.50 objective. Raman spectra for each IEM was recorded as an average of 8 - 16 scans over the range 3200–200 cm\(^{-1}\) with a spot size of ca. 1 µm. Data was collected and analysed using Omnic for dispersive Raman software.

2.2.12 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy exploits the magnetic properties of atomic nuclei to determine key physical and chemical information. It is an effective tool and widely used in determining the structure of organic molecules.

Atomic nuclei with an odd number of protons or neutrons, such as \(^1\)H or \(^{13}\)C, possess the magnetic moment required for NMR to occur. In the absence of a strong magnetic field, the nuclear magnetic moment of a sample of nuclei will be of random orientation. If a magnetic field is then applied to the system the nuclei spins will align either parallel or anti-parallel to the field, with a slight excess in the parallel configuration. In Fourier transform NMR spectroscopy (FT-NMR) a sample in the presence of a magnetic field is irradiated with a short radio frequency pulse consisting of multiple frequencies in a broad band. The multiple frequencies excite the resonance of all spins within a sample at once. When excited the nuclei spins arranged parallel to the field will ‘spin-flip’ and align against the field. After the excitation pulse the excited spins relax, emitting an aggregate of the total absorbed radiation which is recorded as a function of time. The collected data (time domain) is then converted to the frequency domain using Fourier transform mathematics.

The NMR spectra represents a plot of absorption as a function of applied frequency, with frequency increasing from right to left, low-field to high-field, expressed in terms of chemical shifts in parts per million (ppm) vs. the shift reference used. The chemical shift refers to the resonant frequency of nuclei in a magnetic field relative to a standard, commonly tetramethylsilane (TMS). The effective force of the magnetic field is affected by the physical arrangement of nuclei within a molecule. Nuclei of different environments possess different
chemical shifts. The chemical shift is characteristic to particular functional groups and nuclei adjacent to more electronegative groups appear further down-field (at higher frequencies), whereas nuclei not adjacent to electronegative groups appear further up-field (lower frequency). Chemical shift patterns of common organic functional groups can be seen in Figure 19.

![Figure 19 – Typical chemical shift ranges of common organic functional groups in $^{13}$C-NMR spectroscopy.](image)

$^1$H-NMR in particular is a quantitative technique as the integration ratios of the peaks are directly proportional to the number of $^1$H nuclei that absorb at that given frequency; by performing integration it is possible to determine the relative number of $^1$H nuclei in each environment per molecule. Structural information can also be obtained through peak splitting patterns where peaks are split into doublets, triplets and multiplets due to interaction with the magnetic fields of $^1$H nuclei on adjacent carbon atoms.

The spectra gathered in high resolution NMR of species in solution appear as a series of sharp peaks, this is due to the averaging of anisotropic interactions by random tumbling of said species. In the solid state where particles are considerably more constrained the full spectrum of anisotropic interactions is observed and the spectral peaks appear broad, with potentially identical nuclei in different arrangements and orientations appearing at different
chemical shifts. Fortunately, there are three available techniques that can refine the complex peaks of solid state NMR (SS NMR) producing resolved spectra.

Strong heteronuclear dipolar interactions between protons and nuclei such as $^{13}$C and $^{15}$N lead to excessive line broadening in SS NMR spectra. High-powered proton decoupling (HPPD) eliminates dipolar coupling in hydrogen rich samples by applying a constant wave decoupling pulse throughout spectral collection. Magic angle spinning (MAS) is used to deconvolute SS NMR spectra. By rapid spinning of a sample about an angle of $54.44^\circ$ anisotropic interactions are overcome and the spectra is resolved to several sharp peaks.

Another problem with SS NMR is the signal intensities of dilute spins ($^{13}$C, $^{15}$N), the relaxation times for dilute spin solids can be up to hours long making the typical methods for spectral acquisition inefficient. Cross polarisation exploits the natural polarisation of an abundant spin ($^1$H) to increase the polarisation of a dilute spin by irradiation of the sample with radio waves at a frequency that corresponds to the difference in the rotational frequency between the two spins.

Liquid phase $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 500 mHz NMR spectrometer with data analysis and manipulation performed on Topspin version 3.0 software. Solid state NMR; $^{19}$F NMR spectra were recorded on Bruker Avance III HD spectrometer, while $^{13}$C and $^{15}$N NMR spectra were recorded on Varian VNMRS. All SS-NMR measurements were performed by staff at EPSRC National Solid-state NMR Service at Durham University.
3. Radiation-Induced Grafted Poly(styrene sulfonate) based Cation-Exchange Membranes for RED

3.1 Introduction

Cation exchange membranes (CEMs) are typically thin (µm), hydrophilic, ion selective polymer films, and in reverse electrodialysis (RED) comprise one half of the most fundamental components, with the other half being the anion exchange membrane (AEM). One of the largest challenges facing the implementation of RED as a global energy source is the high costs associated with current commercially available CEMs. Another is that with the relative novelty of RED as a source of green energy generation, compared with older more established techniques, RED-specific components are rare and most CEMs used in RED laboratory studies are produced for other intended applications such as desalination and electrodialysis; they are therefore not tailored to specific RED requirements. The key properties required for a membrane to function suitably in a RED stack are permselectivity (the ability of a membrane to repel co-ions while facilitating the transport of counter-ions), and area resistance (a measure of the resistance to counter-ion motion through the membrane bulk).

CEMs include a fixed anionic component or ‘head-group’ that acts to facilitate ion exchange of cations through the membrane bulk. For both commercial and experimental membranes, the typical head group is a sulfonate group(R-SO$_3^-$). Nafion® by DuPont is the current benchmark CEM for fuel cell technologies, and its structure consists of equally spaced side chain perfluoro-sulfonate groups extending from a poly(tetrafluoroethylene) backbone [70]. Neosepta® CMX is a CEM developed and manufactured by Tokuyama Corp. for electrodialysis, and its structure is based on crosslinked poly(styrene sulfonate) [71]. Radiation-induced grafting (RIG) is a method that can incorporate functional side chains or head groups into otherwise inert polymer films. This potential route to produce cost-effective CEMs from readily available commercial polymer films is one that has been explored a good deal in literature, with a focus on the addition of sulfonated styrene to a range of polymer matrices for application in technologies such as fuel cells [42].

Styrene can be readily added to polyvinylidene fluoride (PVDF) and poly(ethylene-co-tetrafluoroethylene) (ETFE) films in a RIG co-polymerisation reaction to prepare a precursor
membrane that can be subsequently sulfonated to yield CEMs. The extent of grafting is dependent on reaction variables, including radiation dose, dose rate, styrene concentration, grafting time and temperature. Horsfall and Lovell determined in 2001 that for the pre-irradiation grafting, using $^{60}\text{Co} \gamma$-radiation, of 50 µm thick PVDF and ETFE films, the degree of grafting (DOG) generally increases with the above parameters [65]. The exception is the reaction temperature, where DOG was found to increase steadily up to 60°C before falling at 70°C. An increased DOG gives rise to an amplification of bulk membrane properties, where CEMs with higher DOGs have increased ion-exchange capacity (IEC), water uptake (WU%), and lower area resistance (therefore higher conductivity) [65]. Similar findings were reported by Nasef et al. in 2000 via the simultaneous RIG of styrene onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [72] and also Gürsel et al., who in a 2007 study modified 25 µm thick ETFE films via an electron beam pre-irradiation method [73]. Interestingly, the graft solution used in the latter study consisted of a styrene/isopropanol/water mix as opposed to more conventional organic solvents (Toluene) in the two former studies.

In the examples given above, the introduction of sulfonated poly(styrene) groups into the bulk polymer via RIG is typically carried out in a two-step synthetic reaction. Firstly, styrene is introduced via a radiation-induced radical initiated polymerisation reaction. Secondly, after the poly(styrene) is introduced into the bulk polymer the grafted styrene rings are then sulfonated with chlorosulfonic acid (HSO$_3$Cl) resulting in functional poly(styrene sulfonate) side chains. Nasef et al. has also reported a single-step method for the preparation of proton exchange membranes (PEMs) via the RIG of sodium styrene sulfonate (SSS) onto electron-beamed pre-irradiated PVDF [66]. The single-step method is proposed as advantageous as it negates the use of highly corrosive HSO$_3$Cl. The authors carried out a comparison between the two methods, and demonstrated that for similar DOG comparable values for bulk properties were obtained, including IEC, WU% and conductivity [74].

Vinylbenzyl chloride (VBC), another styrene derivative, can be used for yet another alternate CEM synthesis [75]. Hwang et al. were able to produce a poly(ether ether ketone) (PEEK) based precursor membranes via the simultaneous RIG reaction of VBC followed by a subsequent 3-step reaction, involving thiourea, hydroxide and peroxide, yielding a sulfonate functionalised CEM. The authors have also previously carried out similar graft reactions onto FEP and perfluoroalkoxy alkanes (PFA) fluoropolymers [76]. Although analogous, the
resultant head group differs to that produced via the previous chlorosulfonic acid and single-step synthetic routes. The head group obtained via the chlorosulfonic acid and single-step methods is a styrene sulfonate where a sulfonate group is directly bonded to an aromatic ring, whereas the head group from the VBC route contains a methylene (-CH₂-) linkage between the sulfonate and the aromatic ring components (Scheme 1).

The focus of the experiments in these previous studies was the production of CEMs for fuel cell application; as such, information vital for their RED suitability, such as permselectivity and area resistance, is lacking. Furthermore, when such properties are reported they are done so with the CEM in the protonated form (PEM) used in fuel cells and not the sodium ion form more relevant for RED. The use of RIG is novel with regard to synthesis of CEMs for RED, and in order to identify its potential to produce RED-specific CEMs, a range of synthetic approaches were assessed. Confirmation of synthesis is obtained using Raman and NMR spectroscopies. Bulk membrane properties were experimentally determined and these parameters were then used to estimate RED performance via a mathematical RED model (Chapter 1, Eqn. 1, Eqn. 2).

3.2 Experimental

A full and detailed account of the experimental synthesis of the CEMs discussed in this chapter can be found in Chapter 2. To recap, CEMs were synthesised via pre-irradiation grafting of styrene and styrene derivatives onto 50 µm thick PVDF and ETFE films. Polymer films, cut to an area of 130×130 mm, were irradiated up to a total absorbed dose of 70 kGy using a 5 MeV electron accelerator. Irradiated films were initially stored under solid CO₂ (for transport to the laboratory) before being transferred to a -20°C freezer for longer-term storage. Prior to graft reaction, the pre-irradiated films were rolled between single-ply tissue paper and submerged in a solution containing the desired styrenic monomer and the solution was purged with N₂ for 1 h, then heated at 60°C for 48 h. On completion, the RIG films were soaked in a suitable solvent to remove any excess monomer or homopolymer. If required, sulfonation was carried out via an appropriate method. Finally, the CEMs were placed into boiling water for 1 h to ensure a fully hydrated form and stored under ultra-pure 18.2 MΩ cm water. The CEM synthesis protocols used are summarised in Scheme 1.
Scheme 1 – Synthesis of RIG CEMs: blue is E-STY-30, orange is P-STY-30, red is P-VBS-70 and green is E-VBC-70.
3.3 Results and Discussion

The focus of this chapter is the development of sulfonate (R-SO$_3^-$) functionalised RIG CEMs for application in RED Cells. Three types of CEMs were synthesised via the pre-irradiation method grafting in air, and all contained pendant styrene sulfonate as the functional cation-exchange head-group. Different chemistries were investigated by altering the polymer base film or the synthetic grafting reaction used (conventional two-step method or the more recent single-step synthesis). For all three variants a series of CEMs was developed by varying total radiation dose to a maximum of 70 kGy. CEM nomenclature is in the form X-YYY-00, where X represents the base polymer (“P” for PVDF or “E” for ETFE), YYY represents the grafting monomer (“STY”, “VBS” or “VBC” for styrene, vinylbenzenesulfonate or 3/4-vinylbenzyl chloride, respectively), and 00 indicates the total radiation dose in kGy absorbed by the base polymer during pre-irradiation. For example, styrene grafted onto PVDF film at 30 kGy is P-STY-30. The CEMs were produced in such a manner that they all share at least one common variable, making it more simple to compare the effects of different base films and synthetic methods.

To evaluate the potential of each CEM for RED application, a series of experiments were performed to determine membrane bulk properties. Initially all CEMs were characterised by evaluation of their IEC and water uptake WU%. Once these two properties were determined, the fixed charge density ($C_{fix}$), which is a ratio of ionic groups per g of H$_2$O, was calculated using Equation 18.

$$C_{fix} = \frac{\text{IEC}}{\text{WU}}$$  \hspace{1cm} (Eqn. 18)

where $C_{fix}$ is the charge density (mmol g$^{-1}$ H$_2$O), IEC is the ion-exchange capacity (mmol g$^{-1}$) and WU is the water uptake (g H$_2$O / g CEM).

After a general comparison of IEC, WU% and $C_{fix}$ the specific RED properties area resistance and permselectivity were measured for select membranes. The RED membrane properties were then factored into the RED model equation (Chapter 1, Eqn. 1, Eqn. 2), to estimate the gross power density obtainable by each membrane in a RED cell. Except for IEC, which is determined via acid/base titration with the CEM under investigation in a H$^+$
form, all CEM characterisation techniques were performed with the CEMs in the Na\(^+\) counter-ion form most relevant to RED.

As part of the broader investigation into RIG CEMs for RED, a supplementary study was carried out in conjunction with the main body of this work. The accompanying study produced an additional CEM whose head-group chemistry varied relative to the other three CEMs as it contained a -CH\(_2\)- spacer group between the aromatic ring and sulfonate group (Ar-CH\(_2\)SO\(_3\)). The additional CEM was produced via pre-irradiation grafting of 3/4-VBC (mixed isomers) and a subsequent three-step synthetic reaction. RIG of 3/4-VBC was carried out at a single radiation dose of 70 kGy (Scheme 1).

### 3.3.1 IEC, WU\% and C\(_{\text{fix}}\) of RIG CEMs

The IEC of an ion-exchange membrane (IEM) is representative of the number of fixed charge groups per mass unit, most typically grams, of dehydrated membrane. It is an intrinsic property of the IEM and is related to the majority of other bulk membrane properties.

![Image of data graph showing IEC vs. radiation total absorbed dose.](image-url)

Figure 20 – IECs of SO\(_3\) functionalised radiation grafted CEMs with varying total radiation dose. Error bars represent standard deviation for \(n \geq 3\) samples of each CEM.
Figure 20 shows the relationship between total absorbed radiation dose and IEC. The expected general trend of increased IEC at higher radiation dose is observed. This is because an increase in radiation dose leads to an increase in the bulk radical propagation owing to more initiating sites for graft co-polymerisation to occur [42]. Therefore resulting in a higher degree of grafting and an increased, post work-up, IEC and overall functionality. For all synthetic routes, IEC consistently increases with E-STY and P-VBS CEMs, indicating a possible plateau at higher radiation doses over the experimental range tested. Prolonged exposure to ionising radiation has a detrimental effect on polymer strength as higher doses ultimately lead to an increase in C-C chain scission events [41]. Identifying a minimum and maximum effective dose would therefore be useful for future synthesis. Observed standard deviations for IECs, (n ≥ 3 samples of each CEM) are minor and therefore indicate homogeneous graft co-polymerisation as samples were taken from various points across the CEMs. If graft distribution was uneven one would expect to see a fluctuation in IECs across the membrane and between the experimental samples.

The overall IEC, and therefore level of grafting, is higher for styrene than for substituted styrene monomers for the same total dose and base film. Comparison of CEMs at 70 kGy demonstrates P-VBS-70 and E-VBC-70 CEMs to have considerably lower IECs than styrene analogues. 0.7 mmol g\(^{-1}\) lower in the case of P-VBS-70 compared to P-STY-70 and 1.46 mmol g\(^{-1}\) lower between E-VBC-70 and E-STY-70. Monomer concentrations are higher for the styrene graft reactions than for the substituted analogues; however, in all routes, the monomers are present in large excess so the deficient grafting levels are therefore likely caused by the effect of the substituent on radical polymerisation kinetics. Free radicals are stabilised by the presence of both electron withdrawing and electron donating functional groups, as either group initiates a net lowering in energy of the molecules electronic configuration [77]. For the graft co-polymerisations carried out here the styrene ring’s ability to form stable radicals via resonance stabilisation is enhanced by the presence of ring-deactivating substituents. Increased radical stability leads to a lowering in the rate of reaction and radical propagation, resulting in decreased IECs in the final CEM [78].

Water uptake is an important parameter for RED IEMs as the RED process takes place in a constantly hydrated state. The amount of water absorbed by an IEM has a fundamental effect on the positioning of fixed ionic groups within the IEM bulk. Figure 21 illustrates the relationship between percentage water uptake by mass (g H\(_2\)O / g CEM) (WU%) and
radiation total absorbed dose. The same trends can be observed for WU% as for IEC, as both are dependent on the total amount of charged ionic head-groups present. Values obtained for P-VBS and E-VBC CEMs are again lower than those of the CEMs synthesised from unsubstituted styrene monomers.

The IEC and WU% can be used to determine a membranes $C_{fix}$. The $C_{fix}$ is representative of the number of ionic head groups per gram of water sorbed into the membrane bulk and higher $C_{fix}$ is obtained for IEMs with high IECs and low water uptakes. In general terms, IEMs with higher $C_{fix}$ are expected to possess stronger co-ion exclusion, and a high charge density is a potential indicator of high permselectivity [28]. Figure 22 shows $C_{fix}$ for the RIG CEMs with varying radiation total absorbed dose. As expected, the highest charge densities are obtained for the RIG CEMs with the lowest water uptakes. The $C_{fix}$ of E-VBC-70 CEM is higher than its styrene grafted counterpart (3.7 mmol g$^{-1}$ H$_2$O), showing it possessed the highest IEC relative to water uptake. The $C_{fix}$ of the remaining three CEMs at 70 kGy are considerably lower (around 2.3 mmol g$^{-1}$ H$_2$O). The relationship between charge density and total dose is perhaps less simple than that of IEC or WU% as it is a ratio of these two parameters. This

Figure 21 – WU% of SO$_3^-$ functionalised radiation grafted CEMs with varying radiation total absorbed dose. Error bars represent standard deviation for $n \geq 3$ samples of each CEM.
can be observed by the fact that charge densities for P-STY and E-STY CEMs plateau at total doses of 50 kGy, whereas the $C_{\text{fix}}$ of P-VBS appears to continue to decrease steadily up to a total dose of 70 kGy. The effect of charge density on permselectivity is assessed later for select CEMs.

![Figure 22](image)

Figure 22 – Fixed charge density of SO$_3^-$ functionalised radiation grafted CEMs with varying total radiation dose, error bars represent standard deviation for $n \geq 3$ samples of each CEM.

### 3.3.2 Membrane benchmarking

Owing to constraints of time and resources, it was not possible to evaluate every CEM for RED application. The initial bulk CEM properties reported thus far were therefore used as a screening tool to identify select membranes with which to pursue further. CEMs determined to have the most similar bulk properties were selected, which included one membrane from each synthetic pathway. Preferably CEMs would be selected on the basis of highest charge densities with minimal total dose; however, to keep individual properties between CEMs as synonymous as possible, a trade-off was necessary. Bulk membrane properties IEC, WU% and $C_{\text{fix}}$ were comparable at low radiation doses for CEMs produced via styrene grafting and at higher dose rates for CEMs produced via grafting of substituted styrene monomers. CEMs selected for further experimentation were therefore P-STY-30, E-STY-30, P-VBS-70 and
E-VBC-70. A relative comparison of bulk properties for the select membranes is summarised in Figure 23 (values for WU% are log_{10} for illustrative purposes).

![Bar chart showing relative comparison of bulk membrane properties for select RIG CEMs.](image)

Figure 23 – A relative comparison of bulk membrane properties for select RIG CEMs. IEC = ion exchange capacity (mmol g^{-1}), WU% = percentage water uptake (plotted as log_{10} for visual clarity), C_{fix} = fixed charge density (mmol g^{-1} H_2O).

### 3.3.3 Structural characterisation by Raman spectroscopy of RIG CEMs

Raman spectra were recorded with a 780 nm laser on a DXR Raman Microscope under a 50× objective producing an estimated spot size of 1 μm. Raman spectra for each membrane were recorded as an average of 8 scans over the range 3200–250 cm^{-1}. For each CEM Raman spectra were recorded at every synthetic stage. The following figures display superimposed Raman spectra for the base films, CEMs and where relevant, any intermediate synthetic stages (see figure captions for details). The depicted range is 1750–250 cm^{-1} as only lower priority structural information (CHs) can be gleaned at wavenumbers above 1750 cm^{-1}, the full and complete spectra can be found in the appendices. For illustrative purposes, all spectra are normalised to base film peak at 797 and 835 cm^{-1} for PVDF and ETFE based membranes respectively.
Figure 24 – Raman spectra of P-STY-30 CEM, PVDF base film, and styrene grafted intermediate films. Spectra normalised to peak at 797 cm$^{-1}$ for illustrative purposes.

Figure 24 displays Raman spectra for P-STY-30 CEM at various synthetic stages (normalised to base film peak at 797 cm$^{-1}$). The addition of styrene groups in the grafted intermediate (P-STY-int) is confirmed by the introduction of several new peaks relative to the PVDF base film. Peaks indicative of aromatic structure are present throughout the spectra; 1605 cm$^{-1}$ is an aromatic C=C stretching band, 1034 cm$^{-1}$ is caused by C-H in-plane bending of the aromatic ring and a very strong diagnostic peak at 1001 cm$^{-1}$ is typical of aromatic ring breathing (seen in the spectra of poly(styrene)) [79]. Notable in the spectra of P-STY-30 CEM is the absence of the strong peak at 1001 cm$^{-1}$. This peak attributed to the aromatic ring breathing is not present in 1,2 and 1,4 di-substituted benzene rings; the absence of this peak and the introduction of a new peak at 1130 cm$^{-1}$, characteristic of the S=O stretching band in a sulfonic acid group [80], indicates that sulfonation of the styrene ring has taken place, and therefore confirms the success of the synthetic route.

The Raman spectra for E-STY-30 CEM, ETFE base polymer, and styrene grafted intermediate film (normalised to base film peak at 835 cm$^{-1}$) are presented in Figure 25. Just as before with the P-STY-30 CEM, RIG of styrene grafting has introduced several key aromatic peaks into the spectra of the base film at; 1605, 1034 and 1001 cm$^{-1}$. Also, as before with P-STY-30, sulfonation sees the disappearance of the strong ring breathing peak at 1001 cm$^{-1}$ and the introduction of an S=O sulfonic acid peak at 1130 cm$^{-1}$; this again indicates successful sulfonation of the styrene ring.
Figure 25 – Raman spectra of E-STY-30 CEM, ETFE base film, and styrene grafted intermediate film. Spectra normalised to the peak at 835 cm\(^{-1}\) for illustrative purposes.

The Raman spectra of P-VBS-70 CEM and PVDF base polymer can be seen in Figure 26 below. Unlike previous CEMs, where aromatic groups and sulfonation are introduced into the polymer in subsequent steps, this single-step reaction sees characteristic aromatic and sulfonate peaks at 1603 and 1133 cm\(^{-1}\) introduced simultaneously. As with two-step styrene grafted CEMs the presence of both bands in the final CEM confirms synthesis has been successful. The lack of a peak at 1001 cm\(^{-1}\) is expected as the VBS grafting monomer is the 1,4-isomer.

Figure 26 – Raman spectra of P-VBS-70 CEM and PVDF base film. Spectra normalised to the peak 797 cm\(^{-1}\) for illustrative purposes.
As Raman spectroscopy is both qualitative and quantitative it is possible to derive crucial information concerning the extent of grafting from the spectra. Direct comparison of P-VBS-70 with the styrene grafted analogue P-STY-30 demonstrates an obvious difference in the peak heights of the sulfonate peaks relative to the peak heights of the PVDF base film peaks. The lower degree of functionality and therefore grafting for P-VBS-70 (assuming 100% sulfonation for P-STY-30) would explain the lower IEC and WU% for P-VBS-70 as less sulfonate groups have a direct effect on the IEC and water uptake.

Figure 27 – Raman spectra of E-VBC-70 CEM, ETFE base film and intermediate films (E-VBC, E-VBC-TS and E-VBC-SH). Spectra normalised to peak at 835 cm\(^{-1}\) for illustrative purposes

The amassed Raman spectra for the E-VBC-70 CEM, ETFE base film and three intermediate films is presented in Figure 27. The introduction of VBC into the base film is evidenced by the presence of several new peaks. Peaks indicative of styrenic structures appear at wavenumbers 1610, 1034, and a strong band at 1001 cm\(^{-1}\), corresponding to aromatic C=C stretching, aromatic C-H in-plane bending and aromatic breathing modes respectively. The presence of the CH\(_2\)Cl is confirmed by a key diagnostic peak at 1268 cm\(^{-1}\) (CH\(_2\)-Cl deformation) [81], as well as four somewhat convoluted peaks between 748–676 cm\(^{-1}\) that are characteristic of CH\(_2\)-Cl stretching modes [79]. The introduction of thiourea to the VBC grafted intermediate film (ETFE-VBC-TS) can be observed by the addition of three characteristic thiourea peaks. Peaks at wavenumbers 737, 481 and 403 cm\(^{-1}\) correspond to
C-S stretching, N-C-N bending and NH₂ torsion vibrational modes [82]. The diagnostic CH₂-Cl deformation peak is no longer present at 1268 cm⁻¹ and instead a lower intensity peak is observed at 1251 cm⁻¹. The diagnostic thiourea peaks at wavenumbers 737, 481 and 403 cm⁻¹ are no longer present in the Raman spectra of the thiol-intermediate (ETFE-VBC-SH). No further new peaks are present, but the peak observed in the previous spectra at 1251 cm⁻¹ appears to have shifted back to a more familiar 1267 cm⁻¹, indicating that the thiourea nucleophile may be unable to carry out the complete substitution of CH₂Cl chloride. The Raman spectra of the final E-VBC-70 CEM displays characteristic sulfonate peaks at 1044 and 775 cm⁻¹ corresponding to S-O and C-S vibrational modes [83]. These assignments vary to the previous three sulfonate functionalised CEMs as the sulfonate group of E-VBC-70 is located in an aliphatic benzyl position and not as an aromatic substituent group. The peak corresponding to CH₂Cl appears to have shifted again to 1277 cm⁻¹.

3.3.4 Structural characterisation by Solid state NMR spectroscopy (SS-NMR) of RIG CEMs

¹⁹F and ¹³C SS-NMR was used for structural characterisation of the RIG CEMs. Spectra were recorded for each of the synthetic stages. ¹⁹F NMR provides little structural information other than that base film F environments remain unchanged throughout the modification of each film (¹⁹F spectra can be found in the appendices). ¹³C NMR was used to differentiate between the carbon environments at each synthetic stage. The SS-NMR spectra for each RIG CEM at each synthetic stage are presented below.

![Figure 28 - ¹³C SS-NMR spectra of P-STY-30 CEM, PVDF base film and styrene grafted intermediate film. Spectra normalised to signal at 43 ppm for illustrative purposes.](image-url)
The $^{13}$C SS-NMR spectra of the P-STY-30 CEM, PVDF base film and the styrene grafted intermediate film used to synthesise it, are presented in Figure 28. The PVDF spectra has only two signals of note, $\delta_C = 43$ (CH$_2$) and $\delta_C = 120$ (CF$_2$). The introduction of styrene to the base film is evident by the addition of several signals in the aromatic spectral region; $\delta_C = 121.8$ corresponds to the para- aromatic CH, $\delta_C = 128.4$ shows a broad signal corresponding to other aromatic CH$_2$s and $\delta_C = 146.3$ is indicative of the quaternary aromatic CR$_n$. The broadening of signal $\delta_C = 43$ also indicates additional aliphatic carbon environments originating from the aliphatic poly(styrene) CH$_2$. The spectra of P-STY-30 features a new signal that can is clearly observed at $\delta_C = 139.5$ corresponding to a new quaternary C-SO$_3^-$. The position of C-SO$_3^-$ signal confirms sulfonation of the styrene ring at the para- position to yield predominantly 1,4-isomers. Small molecule NMR modelling performed on acd i-lab software for di-substituted methylenesulphonate isomers calculates C-SO$_3^-$ signal at $\delta_C = 144.1$, $\delta_C = 133.6$ and $\delta_C = 140.0$ for 1,2, 1,3 and 1,4 isomers, respectively.

![Figure 29 - $^{13}$C SS-NMR spectra of E-STY-30 CEM, ETFE base film and styrene grafted intermediate film. Spectra normalised to signal at 22 ppm for illustrative purposes.](image)

Figure 29 shows the $^{13}$C SS-NMR spectra of the E-STY-30 CEM, precursor ETFE base film and styrene grafted intermediate film. The ETFE spectra shows two signals at $\delta_C = 22$ (CH$_2$) and $\delta_C = 119$ (CF$_2$). The $^{13}$C spectra of styrene grafting intermediate demonstrates several new signals. $\delta_C = 40.6$ is indicative of additional aliphatic carbons attributed to the aliphatic poly(styrene) backbone chain CH$_2$. Three new signals can be observed downfield, these are all indicative of aromatic carbons; $\delta_C = 118.9$ corresponds to the aromatic CH in position 4,
\[ \delta_C = 128.1 \] corresponds to 4 aromatic \( \text{CH} \), and \[ \delta_C = 146.4 \] corresponds to the quaternary \( \text{CR}_n \).

The spectra of E-STY-30 features a level of noise due to the probe being unable to properly tune. However, a new signal at \[ \delta_C = 141.0 \] is indicative of \( \text{C-SO}_3^- \). Resolution of this signal is not as clear as the previous example and given the broadening of signal it is perhaps possible to speculate that sulfonation has taken place in various positions around the ring. However, the lack of diagnostic Raman peak at 1001 cm\(^{-1}\) again supports sulfonation at position 4 only.

Figure 30 – \(^{13}\)C SS-NMR spectra of P-VBS-70 CEM and PVDF base film. Spectra normalised to signal at 43 ppm for illustrative purposes.

Figure 30 displays \(^{13}\)C SS-NMR spectra recorded for the P-VBS-70 CEM and PVDF base polymer. The addition of three new signals can be observed in the aromatic spectral region. \[ \delta_C = 127.0 \] is a broad signal corresponding to four aromatic \( \text{CH} \), \[ \delta_C = 141.0 \] corresponds to a \textit{para}- quaternary carbon (\( \text{C-SO}_3^- \)) and \[ \delta_C = 146.0 \] corresponds to quaternary aromatic \( \text{CR}_n \).

Figure 31 shows the \(^{13}\)C SS-NMR spectra for E-VBC-70 CEM, the ETFE base film and the three intermediate membranes involved in the 5-step reaction (see Scheme 1 earlier in this chapter). Grafting of VBC into the ETFE is evidenced by several new signals in the NMR spectra; \[ \delta_C = 40.5 \] corresponds to aliphatic \( \text{CH}_2 \) on the backbone poly(styrene) chain, while \[ \delta_C = 46.6 \] corresponds to the more deshielded \( \text{CH}_2\text{-Cl} \). The aromatic spectral region is more complicated: \[ \delta_C = 119.0 \], \[ \delta_C = 128.7 \], \[ \delta_C = 135.6 \], \[ \delta_C = 145.5 \] all correspond to aromatic carbon, but due to the presence of \textit{meta-} and \textit{para-} isomers in the VBC reagent it is not possible to definitively assign each signal to a particular \( \text{CH} \) due to the broad signal profiles. NMR spectra for membrane E-VBC-TS features a small signal far downfield at \[ \delta_C = 172.2 \] which
corresponds to the thiocarbonyl in the thiourea nucleophile (C=S). The strong signal at \( \delta_C = 46.6 \) (corresponding to \( \text{CH}_2\text{-Cl} \)), although significantly reduced, is still present indicating that substitution at Cl is not 100%. No new signals are observed in the spectra for E-VBC-SH however, the small signal indicative of C=S at \( \delta_C = 172.2 \) is no longer present. Finally, the spectrum of E-VBC-70 CEM shows a new signal at \( \delta_C = 65.0 \) corresponding to \( \text{CH}_2\text{-SO}_3^- \).

Figure 31 – \( ^{13}\text{C} \) SS-NMR spectra E-VBC-70 CEM, ETFE base film and intermediate films (E-VBC, E-VBC-TS and E-VBC-SH). Spectra normalised to signal at 22 ppm for illustrative purposes.

### 3.3.5 The effect of IEC and conductivity on RIG CEM bulk properties

The IEC, reported on earlier as a function of the total absorbed radiation dose, is the determining factor to all other CEM bulk properties. As such the effect of IEC on bulk CEM properties is analysed further for select RIG CEMs. Figure 32 shows the effect of IEC on conductivity, WU\%, permselectivity, and area resistance. A good correlation is observed between IEC and conductivity where, as expected, conductivity of select RIG CEMs appears to increase proportionally with increasing IEC. This relationship is due to the fact that a higher degree of fixed charged groups dispersed throughout the bulk polymer better facilitates counter-ion transport reducing resistivity, therefore increasing conductivity [84]. The conductivity measured for E-VBC-70 CEM is substantially lower than those recorded for the remaining three RIG CEMs which are otherwise comparable within the experimental error.
This is due to its possessing a significantly lower IEC originating from the initial grafting reaction. As demonstrated in the NMR spectra, the thiourea nucleophile used to introduce the initial S atom into the graft chains failed to completely substitute the CH$_2$Cl chloride. The resultant CEM therefore contains a degree of ‘un-spent’ non-functional VBC units and a true determination of the amount of grafting cannot be obtained from the IEC data. Speculatively E-VBC-70 CEM could yield IECs and conductivity comparable to the other RIG CEMs if this stage of the five-step synthesis can be improved upon in future. The relationship observed for IEC and WU% is similar to that observed for IEC and conductivity, where E-VBC-70 is significantly lower than the remaining three. Higher concentrations of fixed charge groups present throughout the polymer bulk give rise to increased hydrophilicity of the CEM and generally higher WU%.

Figure 32 – The effect of IEC on bulk CEM properties for select RIG CEMs: A. Conductivity, B. WU%, C. Permselectivity and D. Area Resistance. Error bars represent standard deviation $n \geq 3$ samples for each CEM.
The relationship between IEC and area resistance of select RIG CEMs (Figure 32-D) resembles the inverse to the relationship demonstrated between IEC and conductivity. The substantial degree of error for E-VBC-70 most likely originates from the inhomogeneous sulfonation of the poly(3/4-VBC) graft chains and means it is not possible to derive a firm conclusion. The observed trend is expected as conductivity is the inverse of resistivity, a significant contributing factor to resistance, and therefore area resistance. The permselectivity of the select RIG CEMs does not demonstrate a simple correlation with IEC. The permselectivity of the E-VBC-70 CEM appears somewhat anomalous with respect to other bulk properties and sits not as an outlier but somewhere in the middle of the other RIG CEMs. The permselectivity recorded for the P-VBS-70 CEM is also surprising, considering that all other bulk properties are comparable with E-STY-30 and P-STY-30 CEMs one might also expect its permselectivity to follow the trend. This observation is an early indication that CEM permselectivity may be the product of other variables not considered in detail here, such as structure, and not simply electronic properties.

Figure 33 – The effect of conductivity on bulk CEM properties for select RIG CEMs: A. Area Resistance and B. Permselectivity. Error bars represent standard deviation n ≥ 3 samples for each CEM.

Literature studies regarding RED IEMs tend to focus exclusively on the specific RED application properties area resistance and permselectivity. For IEMs synthesised via RIG, where variables affecting these two properties are hard to control, the ionic conductivity of an IEM is useful to assess such properties with regard to counter-ion transport through the bulk CEM (Figure 33). For the RIG CEMs the trends in the relationships between
conductivity with area resistance and permselectivity are comparable to that of relationships between IEC and the same two properties, with E-VBC-70 falling well outside the rest with regard to area resistance and P-VBS-70 lacking in permselectivity. The similarity between these trends is expected considering the correlation between IEC and conductivity.

3.3.6 Effects of Cfix on permselectivity and area resistance of RIG CEMs

Figure 34 shows the effect of charge density on permselectivity for the four select RIG CEMs. From the graph, it is apparent that the relationship is not as simple as previously hypothesised and a correlation between the two parameters is not observed. Although it possesses higher charge density, E-VBC-70 CEM presented a lower permselectivity than both E-STY-30 and P-STY-30 CEMs. In terms of their RED application E-STY-30 and P-STY-30 membranes possess the highest permselectivities (each at 65%). Although this value is considerably lower than the permselectivities of commercially available CEMs or those produced in other literature studies (>90%) [33]. The relationship observed between charge density and area resistance is also lacking any firm correlation (Figure 35). Again, the graph shows a clustering of points for the styrene sulfonic acid functionalised CEMs as opposed to the positive correlation one might expect if the relationship between charge density and area resistance was a simple one. The E-VBC-70 CEM again goes against the apparent trend as despite possessing the highest charge density, has an area resistance more than double the rest of the RIG CEMs (1.18 Ω cm²). Although a direct comparison with literature CEMs is not possible due to different experimental methods being used, the area resistances of all four RIG CEMs are considerably lower than those reported for both the literature benchmark and commercially available membranes [28]. The most resistive RIG CEM, E-VBC-70, has an area resistance equal to that of literature benchmark SPEEK 65 [33], with the remaining RIG CEMs yielding significantly lower area resistances of 0.40, 0.37 and 0.32 Ω cm² for E-STY-30, P-STY-30 and P-VBS-70, respectively. Evaluation of the relationship between permselectivity and area resistance (Figure 36) further demonstrates a lack of a correlation between the two parameters. E-STY-30 and P-STY-30 CEMs with comparable area resistances both have a permselectivities of 65% whereas P-VBS-70, despite possessing comparable area resistance, has considerably lower permselectivity than the two previously mentioned CEMs. This further indicates that it cannot be only electronic properties that play a role in ion transport, but other factors are also playing a part (e.g. structural factors).
Figure 34 – Effect of charge density on permselectivity for select RIG CEMs. Error bars represent standard deviation $n \geq 3$ samples for each CEM.

Figure 35 – Effect of charge density on area resistance for select RIG CEMs. Error bars represent standard deviation $n \geq 3$ samples for each CEM.
Figure 36 – Effect of area resistance on permselectivity for select RIG CEMs. Error bars represent standard deviation \( n \geq 3 \) samples for each CEM.

The results demonstrate that relationships between charge density, permselectivity and area resistances of RIG CEMs are not simple. Similar observations have been made with tailor-made RED membranes [33] [34] which suggest that the homogeneity of membrane composition, and therefore distribution of ionic groups or the degree of crosslinking within the bulk film, may be contributing factors. The extent of crosslinking alters the distribution of the fixed charge groups and the localised environment of the CEMs in their hydrated states [85]. CEMs with a higher degree of crosslinking form a tighter more rigid chain structure and are physically less able to take on as much water as a CEM with a less dense polymer structure (i.e. one with less crosslinking). An increased water content means that the distance between charged groups is therefore greater and the IEM’s ability to repel like charges is affected. Excessive WU\% and therefore spacing of fixed charge groups, could inadvertently lead to formation of an electric double layer where aggregated counter-ions could actually facilitate rather than exclude co-ion transport through the membrane bulk as observed with certain nano porous IEMs in the literature [35].
3.3.7 Effect of membrane thickness on RIG CEM bulk properties

The thickness of an IEM is an important factor with respect to electrochemical properties such as permselectivity and area resistance. Data published on bulk membrane properties for a series of commercial and tailor made CEMs demonstrates a general trend of higher area resistance for thicker membranes that are structurally analogous [86]. Membranes tailor-made for RED should therefore be thin enough in their water swollen states for ease of ion transport whilst not so thin as to compromise their physical integrity or permselectivity. For the RIG CEMs considered here, the thickness is not a directly controlled parameter but a pre-determined quality that is a result of variables such as the base film, degree of grafting (and sulfonation) and WU%. The effect of thickness on IEC, conductivity, permselectivity and area resistance are considered with the CEMs in a fully hydrated state (Figure 37).

Figure 37 – The effect of thickness on CEM bulk properties for select RIG CEMs: A. IEC, B. conductivity, C. Permselectivity and D. Area Resistance. Error bars represent standard deviation n ≥ 3 samples for each CEM.
For IEC and conductivity no correlation with CEM thickness is observed, however, once again trends observed for IEC closely resemble that of conductivity. Permselectivity of RIG CEMs is shown generally to increase with increasing thickness suggesting that a thicker polymer matrix improves co-ion exclusion. This is important for RED IEM design although does not demonstrate a true trend as the RIG CEMs presented here are not structurally analogous. With the exception of E-VBC-70 CEM, a general trend is observed for CEM area resistance where thinner membranes possess lower area resistances (as expected). The position of E-VBC-70 with respect to other RIG CEMs is again indicative that bulk membrane properties are not necessarily dependent on a single parameter but a complex trade-off between many. As before the associated errors make it difficult to draw firm conclusions regarding the area resistance of E-VBC-70 CEM.

3.3.8 Theoretical RED gross power density of RIG CEMs

The empirical RED model, presented in Chapter 1 (Eqn. 1), is a simple mathematical model that incorporates the experimentally determined bulk membrane properties of an IEM pair (AEM/CEM) to estimate the gross power density (W m\(^{-2}\)) obtainable of said IEMs in an ideal RED stack. It can also be adapted to determine the maximum power output of a single IEM (AEM or CEM) in an ideal RED stack (Eqn. 2). The theoretical gross power density of RIG CEMs, relative to the fundamental RED properties area resistance (Figure 38) and permselectivity (Figure 39) is considered.

Despite possessing a marginally lower area resistance, P-VBS-70 CEM has a theoretical gross power density lower than that of the styrene grafted analogues (P-STY-30 and E-STY-30), the lower theoretical power density must therefore be attributed to the CEM’s lower permselectivity. This is somewhat contrary to literature findings, which generally state that for highest possible power densities the area resistance should be as low as possible, whilst membrane permselectivity is of less importance [28]. This study from which this conclusion was drawn did however feature commercial IEMs with significantly higher permselectivity (>90%) than the RIG CEMs discussed here. These findings suggest that although increasing the permselectivity when it is already high (≥90%) has only a minor effect on power density, permselectivity is of higher priority if it is below a certain threshold (<90%).
Figure 38 – Effect of area resistance on the theoretical gross power density of the select RIG CEMs calculated using Eqn. 2 (single IEM model). Error bars represent standard deviation $n \geq 3$ samples for each CEM.

Figure 39 – Effect of permselectivity on the theoretical gross power density of the select RIG CEMs calculated using Eqn. 2 (single IEM model). Error bars represent standard deviation $n \geq 3$ measurements for each CEM sample.
The theoretical gross power densities of P-STY-30 and E-STY-30 CEMs are comparable with several of the commercial CEMs mentioned in literature [28] [33] [37], including Neosepta® CMX and Fumasep® FKD, whereas the theoretical gross power density for P-VBS-70 and E-VBC-70 are significantly lower. As previously stated the permselectivity of both commercial CEMs is considerably higher than for the RIG CEMs tested; however, the area resistances recorded for RIG CEMs are for the most part substantially lower than the commercial CEMs. Neosepta® CMX and Fumasep® FKD are reported to have area resistances of 2.91 and 2.14 Ω cm² respectively compared to P-STY-30 and E-STY-30 with area resistances ca. 0.4 Ω cm². Three out of the four RIG CEMs tested have the lowest reported area resistances for RED membranes to date, although as previously stated direct comparison is difficult as measurements were obtained via different experimental methods. Considering the area resistances of the RIG CEMs and the results of the calculations presented here, it is evident that the main contributing factor to the lower theoretical power densities of certain RIG CEMs is their permselectivity.

The mechanism for IEM permselectivity, in terms of co-ion exclusion, is attributed to Donnan exclusion. Donnan potential repels co-ions from the IEM and prevents the membrane phase co-ion concentration from increasing beyond an equilibrium value [87]. Spacing of the fixed charge groups in sulfonated polymers has been shown to increase as the volume fraction of water in the IEM increases and polymers with lower water sorption tended to follow ideal Donnan exclusion to a greater extent [85]. As water sorption increases the ionic conductivity increases; however, the effective Donnan exclusion is reduced resulting in lower permselectivity. As high WU% ultimately leads to decreased permselectivity it is important to consider controlling WU% in future IEM design.

The empirical RED model is implemented to evaluate the maximum power output of an AEM/CEM pair as in an ideal RED stack (Chapter 1. Eqn. 1). This method allows for a comparison with the available literature as well as providing a more complete evaluation of RED conditions, as it includes, within the calculation, the key effects attributed to the paired AEM. The RIG CEMs developed in this chapter and a commercial benchmark (Neosepta® CMX) were modelled alongside both a commercial and literature benchmark AEM (Neosepta AFN and PECH B2). The AEMs were selected as high performing commercially available and tailor-made RED AEMs [29]. The theoretical RED stack considered at 25°C consists of a concentrated, or seawater, compartment (0.5 mol dm⁻³ NaCl) and a dilute, or
freshwater, compartment (0.05 mol dm$^{-3}$ NaCl) separated by spacers with a thickness of 150 µm. The experimental input parameters values for the CMX, AFN and PECH B2 membranes were taken from literature [33]. The effects of area resistance and permselectivity on the theoretical gross power density theoretical RED stack are presented in Figure 40 and Figure 41 respectively.

![Figure 40 – Effect of CEM area resistance on the estimated gross power density of RIG CEMs and Neosepta CMX in conjunction with AEMs; Neosepta AFN and tailor-made PECH B2. Calculated using Eqn. 1 (RED model).](image)

The effects of area resistance and permselectivity on the theoretical gross power density of the theoretical RED stack agree with the single CEM calculations reported previously. Where RIG CEMs P-STY-30 and E-STY-30 yield higher theoretical power densities, a similar pattern is also observed for the effect of permselectivity. The commercial CEM (Neosepta® CMX) is modelled alongside the RIG CEMs to allow a more complete evaluation of RED potential. It is clearly demonstrated that the theoretical gross power densities of E-STY-30 and P-STY-30 are higher than CMX when paired with both AFN and PECH B2 AEMs, and the values estimated for P-VBS-70 are lower. When modelled in conjunction with AFN, theoretical gross power densities of 2.12, 2.14 and 1.97 W m$^{-2}$ were obtained for P-STY-30, E-STY-30 and CMX respectively. When modelled in conjunction with PECH B2 power densities of 1.96, 1.98 and 1.87 W m$^{-2}$ were obtained.
Figure 41 – Effect of CEM permselectivity on the estimated gross power density of RIG CEMs and Neosepta CMX in conjunction with AEMs (Neosepta AFN and PECH B2).

This agrees with theoretical power densities modelled for single RIG CEMs and supports the hypothesis that it is the substantially lower area resistance that results in the increased power density relative to the commercial CMX CEM. Increasing the permselectivity of RIG CEMs, whilst maintaining lowest possible area resistances, would result in CEMs with improved estimated gross power densities relative to the top performing commercial CEMs.

3.4 Chapter Summary

The research in this chapter builds on the prior literature regarding the importance of the bulk properties of ion-exchange membranes (IEMs) in relation to their application in reverse electrodialysis (RED). In response to the need to develop minimum resistance IEMs for RED specific application, radiation induced grafting (RIG) has been employed to develop four RED focused cation-exchange membranes (CEMs). Three of the RIG CEMs possess the lowest area resistances reported to date in Na\(^+\) form (0.37–0.40 \(\Omega\) cm\(^2\)). Using a mathematical model to evaluate theoretical gross power densities, the modelled RED power
densities of styrene grafted, sulfonated CEMs (E-STY-30 and P-STY-30) were calculated to exceed that of any prior reported commercially available CEMs (2.12 and 2.14 W m$^{-2}$, respectively) despite possessing significantly decreased permselectivity relative to commercially available CEMs. Overall this research demonstrates the RIG method to be a viable method to produce IEMs for RED application. However actual RED cell testing needs to be considered after further improvement of CEMs.

There is scope to further improve CEMs by fine tuning bulk membrane properties such as permselectivity and area resistance. Increased permselectivity of the final RIG CEMs with minimal concomitant increase to area resistance would result in a CEM highly tailored to RED application. Although a simple relationship is not demonstrated here, the literature suggests that a high \( C_{\text{fix}} \) is desirable for RED IEMs [37]. Structure-property relationships between the transport properties, and both the water content and fixed charge concentration \( (C_{\text{fix}}) \) of IEMs have been demonstrated elsewhere [34]. IEM permselectivity and area resistance were shown to be sensitive to the water content of the IEM and generally IEMs that contained a higher water content possessed lower permselectivity and area resistance. The priority for the further development of these CEMs should be to investigate ways of decreasing the water content of the hydrated CEMs to improve CEM permselectivity with a limited reduction in area resistance. Providing good ion-exchange capacities (IECs) of the CEMs are maintained, reduced water content would also result in higher \( C_{\text{fix}} \).
4. Quaternary Ammonium Functionalised Radiation Grafted Anion-Exchange Membranes for RED

4.1 Introduction

The previous chapter focused on the radiation-induced grafting (RIG) of styrene and styrene derivatives onto poly(ethylene-tetrafluoroethylene) (ETFE) and poly(vinylidene fluoride) (PVDF) thin polymer films to yield functional cation-exchange membranes (CEMs) for use in reverse electrodialysis (RED). The focus of the works discussed in this chapter was to investigate the suitability of RIG to produce highly selective AEMs with low area resistance. Perhaps the most successful RED specific AEM to date is PECH B2 with determined permselectivity of 87% and area resistance of 0.94 Ω cm² [29]. PECH B2 is a poly(epichlorohydrin) based polymer, with 1,4-diazabicyclo[2.2.2]octane (DABCO) to incorporate functional quaternary ammonium groups and to provide a degree of crosslinking to the bulk polymer structure (Figure 6, Ch 1). Conversely, the commercially available benchmark AEM regarding RED specific application is Neosepta® AFN by Tokoyama (Japan), which consists of a divinylbenzene (DVB) structure with quaternary ammonium (Ar-N(CH₃)₃) functionality [88] possessing 89% permselectivity and an area resistance of 0.7 Ω cm².

Radiation-induced grafting (RIG) is a co-polymerisation technique that has long been used to produce AEMs for energy production, including AEMs for alkaline fuel cells (AFCs) [51] [89]. However, its potential to produce IEMs specifically for application in RED was until recently untested. After a study of the available literature, one method for producing RIG AEMs stands out due to its apparent synthetic simplicity. Varcoe and Slade, in 2006, reported the production of quaternary ammonium functionalised AEMs via RIG of 3/4-vinylbenzylchloride (3/4-VBC) onto thin films of ETFE polymer followed by subsequent quaternisation of chloride moiety with trimethylamine (TMA) [58]. The versatility of this synthesis is also demonstrated in later works where AEM analogues are produced by substituting TMA with one of two imidazole compounds [81] [90]. Despite each AEM demonstrating good electrochemical properties, they were deemed inadequate with respect to their intended application due to limited alkaline stability. As RED takes place under neutral pH it can potentially make use of the AEM’s good electrochemical properties without
alkali stability ever being a concern. Furthermore, the apparent ease at which various anion-exchange groups can be introduced into the bulk polymer implies that it would be relatively simple to investigate alternate fixed cationic head-groups that have demonstrated good electrochemical properties in other fields. This includes various pyridinium compounds used in AEM production for redox flow batteries (RFBs) and AFCs [91] [92].

With the focus of prior studies being the production of RIG AEMs for application in AFCs the evaluation of these AEMs did not stretch to include information regarding fundamental RED properties, such as permselectivity. Furthermore, ion transport properties are typically expressed in terms of conductivity rather than area resistance required for input into RED model calculations. In the previous chapter (Chapter 3), the effectiveness of RIG as a method to produce CEMs for RED was assessed, and it was concluded that, although some properties may require fine tuning, the method did demonstrate potential as an effective technique for large lab-scale synthesis of CEMs. These RIG CEMs yielded significantly reduced area resistance relative to pre-existing literature or commercial RED CEMs although the permselectivity values obtained were too low to be efficient (≤65%). The key contributing factor to permselectivity was originally considered to be the fixed charge density (C_{fix}), which reflects the effect of the ‘packing’ of fixed charge ion-exchange groups within the ion-exchange membrane (IEM) bulk polymer [28]. This is based on the mechanism of Donnan exclusion and repulsion of like charges, where closer packed charged groups are a more effective ‘barrier’ to repel co-ions [87]. However, a more recent study demonstrates that ion-transport is affected by other Donnan variable factors such as the water content of hydrated IEMs and IEMs with higher water content tend towards low permselectivity and area resistance (high conductivity) [34]. Controlling the water uptake (WU%) is therefore a potential means to increase the permselectivities of RIG IEMs.

Providing a versatile method to alter head-group chemistry can be employed, there is the potential to control the WU% of IEMs by varying the head-group. Taking the literature example from above of BTMA functionalised AEMs [58]; if the TMA head-group was to be substituted for a more hydrophobic analogue, such as triethylamine (TEA) yielding TEA based quaternary ammonium head-groups, the resultant AEM would presumably reflect the increased degree of hydrophobicity and possess lower WU%, thereby restricting the amount of water sorbed into the AEM polymer matrix thus increasing permselectivity.
4.2 Experimental

Scheme 2 - General reaction scheme for pre-irradiation grafting and subsequent amination to form RIG AEMs. Tertiary amines used are: 1. Trimethylamine (TMA), 2. Trimethylamine (TEA), 3. 1-methylimidazole (MIm), 4. 1,2-dimethylimidazole (DMIm), 5. pyridine (PYR) and 6. 2,6-dimethylpyridine (DMP).

A full and detailed account of the experimental methods used to produce the AEMs in this chapter can be found in Chapter 2. To recap on synthesis: AEMs were synthesised via pre-irradiation grafting of 3/4-VBC onto 50 µm thick ETFE. Polymer films cut to an area of 130×130 mm were irradiated at 10 kGy passes to a total dose of 70 kGy using a 5 MeV electron accelerator. Irradiated films were immediately stored under solid CO₂ before being
transferred to the laboratory and a -40°C freezer. Prior to the grafting reaction, the pre-irradiated films were rolled between single-ply tissue paper and submerged in a solution consisting of 79% 2-propanol, 20% VBC and 1% surfactant (v/v/v). The solution was then purged with N₂ for 1 h before being heated to 60°C for 72 h. On completion, the ETFE-g-poly(3/4-VBC) grafted films were washed and then soaked in toluene at 60°C for 24 h to remove excess starting materials and homopolymer. The graft co-polymer films were then dried in a vacuum oven at 70°C for 4–5 h.

The general amination procedure used to convert the ETFE-g-poly(3/4-VBC) intermediate films to the quaternary ammonium functionalised AEMs is as follows. The ETFE-g-poly(3/4-VBC) films were submerged in solutions containing a large excess of a particular tertiary amine, that was dependent on the desired anion-exchange head-group. Except for the TMA which was used at room temperature, the solutions were heated to 80°C for a period between 16 h and 7 d, depending on the amine used. On completion, the AEMs were washed several times, boiled in ultra-pure water for 1 h and then stored under ultra-pure water.

4.3 Results and Discussion

The primary focus of this chapter is the production of quaternary ammonium functionalised, RED specific AEMs by RIG co-polymerisation. To further evaluate the potential of RIG to produce RED specific AEMs, a versatile synthetic route is employed to produce a series of ETFE-g-poly(3/4-VBC) based, RIG AEMs with varying head-group chemistry. Head-groups were selected firstly for their electronic properties, while keeping cost effectiveness in mind. Head groups were selected in paired analogues with varying degrees of aliphatic chain length or alkyl substituent groups to evaluate their effects on properties such as WU%. For example, TMA was selected alongside TEA, as well as pairs of analogous imidazole compounds and pyridine rings. The work carried out is largely based on the versatile method of VBC grafting reported on in previous literature [81] [90]. By incorporating this method, a total of six analogous AEMs were produced: a benchmark TMA functionalised AEM and five other quaternary ammonium analogues. Because all RIG AEMs share the same base polymer, the AEM nomenclature is an acronym abbreviated from the amine used in the synthesis of each AEM. TMA is trimethylamonium, TEA is triethylamonium, MIm is 1-
methyylimidazolium, DMIm is 1,2-dimethyylimidazolium, PYR is pyridinium and DMP is 2,6-dimethylpyridinium (Scheme 2).

As in the previous chapter, structural characterisation of each RIG AEM was carried out using Raman and solid state nuclear magnetic resonance spectroscopies (SS-NMR). SS-NMR was used to obtain $^{19}$F, $^{13}$C and $^{15}$N spectra for qualitative analysis. The bulk properties determined for each membrane include ion-exchange capacity (IEC), water uptake (WU%), $C_{\text{fix}}$, area resistance and permselectivity. The RED model (Chapter 1, Eqn. 1 and Eqn. 2) was then used to estimate the theoretical gross power density obtainable by each membrane as per a functioning RED stack. The results generated by the model were used to provide a general comparison analysis with current commercially available and literature AEMs (where values for area resistance and permselectivity are available). All AEM characterisation techniques were performed with the AEMs in the Cl$^-$ counter-ion form most relevant to RED.

### 4.3.1 Structural characterisation by Raman spectroscopy of RIG AEMs

Raman spectra were recorded with a 780 nm laser on a DXR Raman Microscope using a 50× objective producing an estimated laser spot size of 1 µm. Raman spectra for each AEM was recorded as an average of 8 scans over the range 3200–250 cm$^{-1}$. For each AEM Raman spectra were recorded at each synthetic stage. The following figures display superimposed Raman spectra for ETFE base films, ETFE-g-poly(3/4-VBC) grafted intermediate films and the final AEM. The depicted range is 1750–250 cm$^{-1}$ as little structural information is present outside this range. Full and complete spectra can be found in the appendices. For illustrative purposes, all spectra are normalised to -CF$_2$ peak present in ETFE base film at 835 cm$^{-1}$.

Figure 42 demonstrates the Raman spectra for the TMA functionalised RIG AEM, and precursor membranes. Structurally TMA$^+$ is the simplest quaternary ammonium available and therefore serves as a useful benchmark for later, more complex ammonium head-groups. The ETFE base film possesses only one prominent peak at 835 cm$^{-1}$. The addition of VBC into the base film introduces several new peaks. Peaks indicative of styrenic structures appear at wavenumbers 1610, 1034, and a strong peak at 1001 cm$^{-1}$, corresponding to aromatic C=C stretching, aromatic C-H in-plane bending and aromatic breathing modes respectively. The presence of the CH$_2$Cl moiety is confirmed by a key peak at 1268 cm$^{-1}$.
which is indicative of $\text{CH}_2\text{-Cl}$ deformation [81], as well as four somewhat convoluted peaks between 748–676 cm$^{-1}$ characteristic of various $\text{CH}_2\text{-Cl}$ stretching modes [79]. The spectrum obtained for the aminated TMA AEM demonstrates two clear transformations. Firstly, peaks relating to $\text{CH}_2\text{Cl}$ chloride at 1268 cm$^{-1}$ and 748–676 cm$^{-1}$ are no longer present and, secondly, the introduction of a new peak at 759 cm$^{-1}$ consistent with symmetric stretching in quaternary ammonium groups [93] [94]. The disappearance of key $\text{CH}_2\text{-Cl}$ alongside the introduction of N-C confirms successful amination of grafted intermediate.

Figure 42 – Raman spectra of the TMA AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra normalised to base film peak at 835 cm$^{-1}$ for illustrative purposes.

TEA is the second of the aliphatic tertiary amines in this study to be incorporated into a RIG AEM. The superimposed Raman spectra for the membranes related to this synthesis are presented in Figure 43. As with the TMA functionalised analogue, the Raman spectra for TEA AEM demonstrate key transformations between the intermediate poly(3/4-VBC) grafted film and the final AEM. The spectrum recorded for TEA AEM lacks the distinctive $\text{CH}_2\text{-Cl}$ peaks at 1268 cm$^{-1}$ and 748–676 cm$^{-1}$ that are present in the intermediate film and includes a new peak of medium intensity at 691 cm$^{-1}$. The new peak is consistent with symmetric stretching in the tetraethylammonium ion, which falls in the range of 672–666 cm$^{-1}$ [93].
The Raman spectra of both imidazole functionalised AEMs, MIm and DMIm, including base film and intermediate films are presented in Figure 44 and Figure 45, respectively. The spectra for both the aminated AEMs are indicative of successful amination having taken place as they both lack any of the characteristic CH$_2$-Cl peaks associated with the poly(3/4-VBC) grafted intermediate. The spectrum recorded for MIm AEM also lacks any decisive quaternary ammonium peaks such as those observed for TMA and TEA AEMs, although a new peak can be observed at wavenumbers around 620 cm$^{-1}$. A strong, sharp peak is observed at 1020 cm$^{-1}$, this peak is characteristic of a ring deformation mode of C-N=C occupying positions 2-3=4 of the imidazolium ring [95]. Raman spectra obtained for DMIm AEM possesses a peak of high intensity at 1515 cm$^{-1}$, this is consistent with ring stretching deformation of the methyl substituent found in position 2 of the imidazolium ring. The presence of substituent methyl group at position 2 also disrupts C-N=C ring deformation mode and hence no band is observed around 1020 cm$^{-1}$. Contrary to the MIm analogue, DMIm does show a skeletal N-C symmetric stretching mode at 725 cm$^{-1}$.
Figure 44 – Raman spectra of MIm AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.

Figure 45 – Raman spectra of DMIm AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.
Although imidazole compounds contain two N atoms, only one is basic and therefore a suitable nucleophile. Both N atoms within the imidazole ring structure are in an sp\(^2\) conformation with bond angles around 120°. However, the lone pair of electrons on N\(_1\) are located in the remaining p-orbital perpendicular to the plane of the ring, whereas the lone pair on N\(_3\) are located in an p-orbital level with the plane of the ring. The N\(_1\) is synonymous with N-methylpyrrole, with a pKa around -0.3 (calculated by acd ilab software) and is a poor nucleophile. The N\(_3\), however, is synonymous to pyridine which has a pKa of 5.25 and is a good nucleophile [96]. The strong peak at 725 cm\(^{-1}\) present in the spectrum of DMIIm is consistent with the skeletal NC\(_3\) stretches of a tertiary amine such as N\(_1\). The presence of this peak therefore confirms that quaternization has taken place at N\(_3\) as the peak would have been disrupted if quaternization had occurred at N\(_1\). Unfortunately the spectrum of MIIm appears to be lacking any definitive N-C skeletal peaks.

Figure 46 and Figure 47 display the superimposed Raman spectra for the pair of pyridinium functionalised AEMs. Successful amination is again evidenced by the loss of the CH\(_2\)-Cl band at 1268 cm\(^{-1}\) and the peaks between 748–676 cm\(^{-1}\). The spectrum for PYR AEM exhibits one new peak at 1030 cm\(^{-1}\) due to C-H in-plane bending on the pyridinium aromatic rings. The spectrum for DMP has just one new peak at 1035 cm\(^{-1}\) due to aromatic C-H in-plane bending, although this is not as intense as PYR analogue as it contains fewer ring H’s than simple pyridinium analogue.

Figure 46 – Raman spectra of PYR AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.
4.3.2 Structural characterisation by SS-NMR spectroscopy of RIG AEMs

$^{19}$F, $^{13}$C and $^{15}$N SS-NMR were used to confirm successful grafting and amination via structural characterisation at each synthetic stage for each RIG AEM. $^{19}$F NMR provides little structural information other than confirming that the ETFE base film CF$_2$ environment remains unchanged throughout modification of each film with the $^{19}$F spectra remaining identical for each AEM. For this reason, $^{19}$F spectra are not presented here or discussed in detail and can be found in the appendices.

The $^{13}$C SS-NMR spectra of each RIG AEM is presented below (Figure 48–Figure 53). Each spectrum is superimposed with that of ETFE base polymer and ETFE-g-poly(3/4-VBC) intermediate graft co-polymer. The ETFE spectrum shows only two signals of note corresponding to backbone C: $\delta_C = 22.0$ (CH$_2$) and $\delta_C = 119.0$ (CF$_2$). Confirmation of VBC grafting is made evident by the introduction of several new aromatic signals in the NMR spectra for ETFE-g-poly(3/4-VBC): $\delta_C = 40.5$ corresponds to CH$_2$ on the ‘poly(styrene) chain’ and $\delta_C = 46.6$ corresponds to the de-shielded C3 (CH$_2$-Cl). The aromatic spectral region is more complicated and displays four signals, $\delta_C = 119.0$, $\delta_C = 128.7$, $\delta_C = 135.6$, and...
δC = 145.5 all corresponding to aromatic carbons. As the VBC reagent used contains a mixture of meta- and para- isomers it is not possible to conclusively assign each individual signal in the grafted poly(3/4-VBC) chains. Spinning sidebands are also visible at δC = 70.0 and δC = 189.0. The NMR spectra of the final TMA AEM (Figure 48) shows a new signal at δC = 53.3 belonging to the three methyl- substituents of the TMA head-group (-N(CH3)3) and another at δC = 69.2 corresponding to the Ar-CH2-N methylene linkage. Amination at CH2Cl is confirmed further by the loss of the diagnostic VBC signal at δC = 46.6. Spinning sidebands are again present in the spectra of the TMA AEM.

The NMR spectra of the TEA functionalised AEM is presented in Figure 49. As with the TMA AEM, successful amination of the grafted VBC is evidenced by the loss of signal correlating to CH2-Cl between the intermediate film and the final AEM. A new signal in the spectra is observed at δC = 9.3 corresponding to methyl- substituents (-N(CH2CH3)3) on the more alkyl substituted TEA head-group and a second signal at δC = 53.4 corresponding to the more deshielded CH2 groups of the ammonium head-group (-N(CH2CH3)3). A final new signal present at δC = 63.5 corresponds to the Ar-CH2-N methylene linkage. Generally, signals present in the NMR spectra for the TEA AEM that correspond to the ammonium fragment of the head-group (N'R4+) are less intense than in the TMA analogue, this could be an indication that a lesser extent of amination has been achieved for TEA relative to TMA.

Figure 50 and Figure 51 display NMR spectra for the pair of imidazole functionalised RIG AEMs. The aromatic/unsaturated regions of each of the AEMs is significantly more complex than that of the intermediate VBC-grafted polymer, as would be expected with successful amination. Broad signals consisting of multiple peaks can be observed between δC = 123.0–139.0, with a single more resolved signal at δC = 147.0 and δC = 145.0 for MIm and DMIm respectively. The CH2-Cl signal present at δC = 46.6 is absent in both imidazolium AEMs. MIm has two new signals in the aliphatic region relative to VBC-grafted intermediate; δC = 53.1 corresponding to CH2-N, which is now shifted downfield as it is adjacent to an electronegative N; and δC = 37.5, which corresponds to substituent CH3 on the second ring N. The aliphatic spectral region of DMIm displays three new signals, visible at δC = 51.9 representing CH2-N and δC = 36.4 representing the CH3 substituent on ring N as well as a signal at δC = 11.3 characteristic of CH3 on the ring C situated between two N atoms.
Figure 48 – $^{13}$C SS-NMR spectra of the TMA AEM, ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to ETFE base film signal $\delta_C = 22$ for presentation purposes.

Figure 49 – $^{13}$C SS-NMR spectra of TEA AEM, ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to ETFE base film signal $\delta_C = 22$ for presentation purposes.
Figure 50 – $^{13}$C SS-NMR spectra of MIm AEM, ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to ETFE base film signal $\delta_C = 22$ for presentation purposes.

Figure 51 – $^{13}$C SS-NMR spectra of DMIm AEM, ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to ETFE base film signal $\delta_C = 22$ for presentation purposes.
The $^{13}$C NMR spectra for the two pyridinium functionalised AEMs, PYR and DMP, are presented in Figure 52 and Figure 53 respectively. The addition of heteroaromatic pyridinium is apparent in the aromatic region of the PYR spectra with signals at $\delta_C = 146.0$, $\delta_C = 130.0$ and $\delta_C = 119.0$. Aromatic signals for PYR AEM are of far greater intensity and significantly more defined than the aromatic signals of the grafted intermediate that are attributed to only a single aromatic ring system. Increased intensity of the aromatic signals leads to an increase in the intensity of spinning sidebands which are plainly visible at $\delta_C = 189.0$ and $\delta_C = 70.0$. Loss of $\text{CH}_2\text{Cl}$ signal located at $\delta_C = 46.6$ in the VBC intermediate and the presence of a new signal in a downfield position at $\delta_C = 64.5$ in the final AEM is indicative of a successful amination with pyridine taking place via substitution of Cl at the benzylic position. The NMR spectra for DMP AEM has some similarities to that of the PYR, as would be expected for a homologue. Although not as intense as in PYR the aromatic spectral region remains comparable to the grafted intermediate with notable signals between $\delta_C = 145.0$ and $\delta_C = 119.0$. Again, spinning sidebands are observed at $\delta_C = 189.0$ and $\delta_C = 170.0$. The typical downfield shift from $\delta_C = 46.6$ ($\text{CH}_2\text{Cl}$) to $\delta_C = 63.5$ ($\text{CH}_2\text{N}$) is again evidence of successful amination having occurred. The reduction in intensity of the signals for DMP relative to PYR analogue coupled with the substantially lower IEC suggest that less quaternisation has been achieved with the more substituted DMP head-group than with the PYR head-group, despite the extended reaction times (see Table 4, page 33).

![Figure 52 - $^{13}$C SS-NMR spectra of PYR AEM, ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to ETFE base film signal $\delta_C = 22$ for presentation purposes.](image)
In this investigation, $^{15}$N is employed as a qualitative method for structural characterisation and conformation of synthesis. As limited quantities of N are present within the grafted membrane structures (1–2 atoms per head-group) only a small amount of structural information can be ascertained. The $^{15}$N SS-NMR spectra for all six RIG AEMs are presented collectively in Figure 54 below. Although reasonably high levels of noise are present, signals can be discerned for the majority of RIG AEMs. The pyridine head-group functionalised AEMs each show a single signal indicative of a single N within their structures, whereas imidazole functionalised AEMs display two signals illustrative of their structures containing two N environments (one quaternary and one tertiary signal). The TMA AEM also displays a strong N signal; however, the aliphatic analogue TEA does not. This is inconsistent with the structural data obtained via Raman and $^{13}$C NMR which both indicate that successful amination has taken place at $-\text{CH}_2\text{Cl}$ by the presence of strong ammonium signals ($\text{NR}_4^+$). Whether the synthesis of TEA functionalised AEM has been successful remains somewhat inconclusive due to this degree of uncertainty between the spectral techniques. The $^{13}$C NMR spectra does demonstrate a lesser degree of amination for the TEA AEM relative to its TMA functionalised counterpart AEM. A possible outcome for the lack of a definitive $^{15}$N NMR signal is simply that the AEM sample submitted for $^{15}$N NMR analysis was not aminated and, as SS-NMR is recorded externally, it was not possible to acquire another spectra in time. Determination of bulk AEM properties of the TEA AEM will doubtless provide further evidence concerning the success of TEA amination.
4.3.3 The effect of IEC and conductivity on RIG AEM bulk properties

The IEC represents a quantitative measure of a membrane’s overall functionality and for RIG polymers also provides an indication of the level of grafting achieved. For the AEMs presented here, IEC relates to quaternary ammonium groups only. The IEC goes on to influence other AEM properties, including WU% and ionic conductivity. WU% represents the percentage increase (by mass) of a membrane between hydrated and non-hydrated states. It is an important value as it affects the thickness and area of an IEM and appears to influence factors effecting ion transport [34]. The ionic conductivity represents an AEM’s ability to transport counter-ion throughout its matrix. As with the select RIG CEMs in Chapter 3, the effect of IEC on specific RED AEM bulk properties, permselectivity and area resistance, are also investigated.

The IECs of all six RIG AEMs (in Cl– form) are presented in Figure 55. The bar graph demonstrates comparable IEC values for the majority of AEMs with TMA, MIIm, DMIm and PYR membranes all with IECs between 1.75–1.86 mmol g⁻¹, whereas TEA and DMP AEMs possess lower IECs at 1.58 and 1.13 mmol g⁻¹ respectively.
Given that AEMs are synthesised via an established synthetic route and all stem from a common intermediate, one would expect the IECs to be comparable if not identical. As IEC is dependent on mass, minor variances between AEMs are acceptable with heavier head-groups, however, for TEA and DMP AEMs the reduced IEC is significant of incomplete quaternisation as suggested by the spectroscopic data. Structural analysis carried out for all six RIG AEMs by Raman spectroscopy appears to indicate that near complete amination has occurred via substitution of Cl at the benzylic position. The SS-NMR spectra recorded for RIG AEMs agree with Raman findings for most AEMs but are conflicting with respect to TEA and DMP. The signals belonging to head-group Cs in these two AEMs are significantly weaker than signals arising from base-film Cs in other RIG AEM analogues. Minimal standard deviations across all AEMs with respect to IEC, although not absolutely definitive, are indicative of a high level of graft homogeneity as prior to IEC determination membrane samples were taken from various points across the AEM. This suggests that head-group dispersion is also homogenous and the reduction in IEC for TEA and DMP is due to decreased amination averaged across the AEMs and not simply due to one area that has undergone less reaction. The lesser degree of amination for TEA and DMP head-groups can be explained considering the physical chemistry of the head-groups relative to TMA and PYR, respectively. The degree of steric hindrance around the basic N is higher in TEA and
DMP than in their less substituted analogues making them poorer nucleophiles and therefore less likely to displace Cl in the VBC-grafted intermediate film. Pyridines with alkyl substituents not in positions adjacent to functional N+ could be considered for future experiments: 3,5 or 4,5-dimethyl pyridine analogues may reduce WU%, relative to PYR, without the reduced IECs observed with the 2,6-isomer.

![Figure 56](image)

Figure 56 – The effect of IEC on bulk AEM properties for select RIG AEMs: A. Conductivity, B. WU%, C. Permselectivity and D. Area Resistance. Error bars represent standard deviation n ≥ 3 samples for each AEM.

The influence of IEC on the bulk properties conductivity, WU%, permselectivity and area resistance for the RIG AEMs is presented in Figure 56. A strong correlation is observed between IEC and ionic conductivity for RIG AEMs where, as with previously reported RIG CEMs, conductivity tends to increase with IEC. A higher amount of fixed charge groups dispersed throughout the bulk polymer evidently results in increased ion transport. TMA,
PYR, and MIm AEMs whose IEC fall within a range of ±0.04 mmol g⁻¹ have similar conductivities (ca. 27.0 mS cm⁻¹). The exception is DMIm which possesses the highest ionic conductivity of all RIG AEMs despite possessing an IEC lower than three of the others. As expected, considering their lesser degree of amination and resultant lower IECs, conductivities of TEA and DMP fall behind the rest by some margin.

The relationship between IEC and WU% for RIG AEMs is not as straightforward as that observed for the RIG CEMs reported previously where CEMs with higher IEC generally possessed higher WU%. For the RIG AEMs investigated here IEC is evidently not the only factor effecting WU%, clearly the nature of the head-group itself has an effect. This is apparent when considering TEA which, despite possessing lower IEC and a decreased degree of amination, still has WU% notably higher than several of the other RIG AEMs. The degree of substitution is not easily quantified across the whole range of RIG AEMs, although comparison between analogous head-group pairs is simple enough. With regard to the varying degree of alkyl-substitution between head-group pairs the WU% is seen to decrease with increased substitution as expected. The observed trend was generally expected as a higher percentage of organic substituents would increase the degree of hydrophobicity, therefore decreasing WU%.

Water uptake measurements are susceptible to errors due to reduced experimental precision, which occurs due to incomplete removal of surface water in (hydrated states) and rapid absorption of atmospheric water (in the dehydrated state) whilst the masses are recorded, and the results do present some uncertainty. Another difficulty in stating a firm conclusion regarding the head-group and WU% is that certain AEMs have undergone less amination compared to their paired analogues, reducing their IECs, and therefore not possessing the potential maximum WU% obtainable. However, these results do indicate that WU% can be fine-tuned for RIG AEMs by varying the type of organic substituents present in the AEMs.

Interestingly, imidazolium functionalised AEMs exhibit a decrease in WU% with almost no reduction in IEC between substituted analogues. Imidazole head-groups with further degrees of alkyl substitution should therefore be considered for future experimentation (perhaps containing propyl or even isopropyl substituents in position 2). The highest performing commercial and non-commercial AEMs reported on to date, with high degree of co-ion exclusion, all possess WU% below 50% (the majority around 30%) [86]. This is supported by the results obtained for the RIG CEMs featured in Chapter 3, where the majority of CEMs
had WU% towards the high end of this range and possessed only average permselectivity. As demonstrated above, all the RIG AEMs possess WU% below 50% although pyridine head-groups are the lowest, with PYR at 34% and DMP at 22%. The PYR AEM combines low WU% with a high IEC and conductivity, and although these are not the only influences on membrane performance, both factors are of high significance when designing IEMs for RED.

There appears to be no firm correlation between IEC and permselectivity (Figure 56-C) however RIG AEMs with the lowest IECs, DMP and TEA, have the highest permselectivity, and generally RIG AEMs with higher IEC tend towards possessing lower permselectivities. This is contrary to previously synthesised RIG CEMs and literature IEMs [28] [37] where IEC appeared to have little influence on permselectivity. As was also the case for the RIG CEMs featured in the previous chapter (Chapter 3) the effect of IEC on area resistance shows an inverse relationship to that between IEC and conductivity. With the exception of DMP all RIG AEMs possess low area resistances, ca.0.5 Ω cm², which is comparable to area resistances recorded for RIG CEMs previously.

Typically, with RED literature, it is more common to consider counter-ion transport in terms of area resistance and permselectivity as these are the two fundamental properties for power generation as stated by the RED model equation. However, with RIG IEMs where factors affecting these two properties are not as simple to control it is useful to consider an IEM’s conductivity.

Figure 57 – The effect of conductivity on bulk AEM properties for select RIG CEMs: A. Permselectivity and B. Area resistance. Error bars represent standard deviation n ≥ 3 samples for each AEM.
Figure 57 demonstrates the relationships between conductivity and RED application properties permselectivity and area resistance for the RIG AEMs. Permselectivity of IEMs is generally shown to decrease with increasing conductivity [97] and for RIG AEMs, the most permselective AEMs, PYR and TEA, yield the lowest conductivities. This relationship is counter-productive with respect to designing RED IEMs, as to operate at high power densities RED IEMs require highly permselective, low resistance (highly conductive) IEMs [17]. Therefore, for RIG to be able to produce effective RED IEMs it is vital that a means to improve permselectivity with minimal reduction to conductivity is found.

A compromise could potentially be reached by reducing the WU% of RIG AEMs, most of which are significantly higher than commercial AEMs. The concentration of ionic head-groups in the AEM is inversely related to the concentration of free co-ions present in the membrane bulk due to the Donnan exclusion of co-ions through repulsion of like-charges [98]. When the water content of an IEM in a hydrated state is taken into consideration, the IEC is lower than the measured value (on dried IEMs). This is because as the IEM takes on water there are effectively less fixed charge groups per gram of IEM. Donnan exclusion implies that this will result in a larger concentration of co-ions being able to pass through the IEM matrix and consequently a lower permselectivity. This is supported by examples in the literature where both IEM permselectivity and WU% data is presented. RED specific examples including PECH based AEMs [29] and sulfonated poly(ether etherketone) CEMs [33] both demonstrate increasing permselectivity and \( C_{\text{fix}} \) at lower WU%. This trend is also generally demonstrated on a wider range of commercial and literature IEMs featured in a comprehensive review of RED IEMs [86] and a specific study demonstrating ion transport property trade-offs in AEMs [34]. There are however exceptions and a series of crosslinked 2-(dimethylamino)ethylmethacrylate-based AEMs go against the trend, yielding higher permselectivity with increased water content [99] [100].

Typically, reducing the WU% of an IEM whilst maintaining high IECs would result in a larger number of ionic head-groups per gram of AEM in the hydrated state (\( C_{\text{fix}} \)) resulting in increased permselectivity. Increased \( C_{\text{fix}} \) through decreased WU% would also effect the conductivity as the conductivity of an IEM depends on the concentration of fixed charged groups in the membrane phase [84]. Increasing \( C_{\text{fix}} \) whilst maintaining high IEC results in the IEM having a more efficient IEC in the hydrated state and higher conductivity. However, achieving lower WU% at the expense of IEC would likely result in IEMs with lower
conductivity. To avoid this WU% can perhaps be reduced by the implementation of head-groups with increased alkyl substituents, as discussed previously, or even by increasing the degree of crosslinking present in the bulk polymer to physical restrict the WU% [97].

The relationship between conductivity and area resistance is as one would expect, considering the physical relationship between the two parameters, and area resistance decreases with increasing conductivity. The effect of conductivity on permselectivity and area resistance for RIG AEMs varies when compared to the same relationships observed for that of previously synthesised RIG CEMs. For RIG CEMs these relationships mirrored that of IEC whereas this is not observed for the RIG AEMs here. This is evidenced by the position of the DMIm AEM with respect to the other RIG AEMs and the DMIm AEM is more conductive than its MIm analogue, despite possessing lower IEC.

4.3.4 \( C_{\text{fix}} \), permselectivity and area resistance property relationships of RIG AEMs

Although IEC is a fundamental property of IEMs in general, the charge density is perhaps more relevant when considering RED focused membranes [28]. This is because the RED process occurs in an aqueous environment and membranes are in a permanently hydrated state. \( C_{\text{fix}} \) therefore better represents the electrochemical properties of an AEM intended for RED. The \( C_{\text{fix}} \) of an IEM can be a general indication of its permselectivity where IEMs that possess higher \( C_{\text{fix}} \) typically have higher permselectivity [86] as \( C_{\text{fix}} \) has a direct effect on the fundamental ion-transport properties. The amount and distribution of ionic groups within the AEM bulk affects the ion permselectivity through repulsion of like charges. The area resistance is also effected by the amount and positioning of ionic groups throughout the AEM and will determine the rate at which counter-ions can permeate through the polymer bulk.

Figure 58 demonstrates a surprising lack of correlation between \( C_{\text{fix}} \) and permselectivity, which is in agreement with results obtained for RIG CEMs previously. TEA AEM is a strong example of the lack of trend and is in possession of one of the lowest charge densities despite having the second highest permselectivity at 66%. The AEM with the highest charge density, DMP, is the most permselective of the RIG AEMs at 72%, although this value is still substantially less than \( ca. \) 90% permselectivity obtained by commercially available and non-commercial bespoke RED AEMs in the literature [33].
The area resistance of RIG AEMs as a function of $C_{\text{fix}}$ are presented in Figure 59. The graph demonstrates that for the RIG AEMs the relationship between $C_{\text{fix}}$ and area resistance is more complex than the relationship between area resistance and IEC (AEMs with highest IEC have lowest area resistances) with no apparent correlation between the two parameters. In contrast to permselectivity values, which fell short of values obtained for literature AEMs, the resistance of RIG AEMs is comparable to or better than values reported in the literature. The most resistive, therefore least conductive, of all RIG AEMs is DMP at 2.7 Ω cm$^2$, although high relative to other RIG AEMs this is still comparable to, or even lower than, several AEMs from literature including Neosepta® ACS, Neosepta® AMX, and Selemion® ASV [37]. The area resistances for the remaining five RIG AEMs are substantially lower than those reported in literature, falling in the range of 0.3–0.7 Ω cm$^2$. Area resistances for RIG AEMs have not been collected via the same methodology so a direct comparison is not possible. Considering the RIG AEMs in the relevant hydrated state emphasises the importance of controlling the WU% when designing IEMs for RED.
Finally, the relationship between area resistance and permselectivity is shown in Figure 60, which depicts a general trend for RIG AEMs with lower resistance to be less permselective (inverse to conductivity). These results reflect those found previously for RIG CEMs and those in literature [37]. For RIG AEMs the membrane with lowest resistance is DMIm which is the least selective, whereas the most resistive AEM, DMP, is the most selective. The remaining 4 RIG AEMs with area resistance in the range of 0.3–0.68 cm$^2$ cluster together. The clustering pattern observed with RIG AEMs is somewhat in contrast to the more widespread distribution found with the RIG CEMs. As the RIG AEMs are all derived from a common VBC-grafted intermediate it is only the cationic head-group and IEC that varies and not the bulk polymer structure and therefore one might expect similar bulk properties across the series. It is again worth noting that DMP has the lowest IEC amongst RIG AEMs, attributed to the difficulties of reacting the bulky 2,6-dimethylpyridine amine, which will certainly account for the large differences between this and the other RIG AEMs.
The results obtained for the RIG AEMs in this chapter demonstrate that the relationships between the bulk properties of IEMs are complex and their effect on each other can vary by some extent between different IEMs. Some of the general trends observed here were therefore not noted for the RIG CEMs previously and *vice-versa*. This is because with RIG IEMs the bulk properties are all associated and, in most examples, influenced by one another. For example, the ionic conductivity is highly dependent on the IEC but is also dependent on the WU% (as this affects ion mobility). However, WU% is itself dependant on IEC while also influencing permselectivity. Considering this simple example, it is apparent just how complex the relationships between bulk IEM properties are and how changing one can potentially lead to a domino effect affecting several others. It is also worth noting that in this work only bulk IEM properties are considered, factoring in detailed structural information such as localised phase segregation of the polymer structure introduces a much greater degree of variables for consideration. This highlights the complexity of designing IEMs *via* RIG and why increasing one fundamental property often results in a trade-off with one or more others.
4.3.5 The relationship of thickness on RED properties of RIG AEMs

The thickness of the AEMs is an important factor with respect to properties such as permselectivity and area resistance. The non-commercial literature PECH AEMs that have been made specifically for the RED process demonstrate a trend of higher area resistance in thicker AEMs that were structurally analogous to thinner AEMs [33].

![Figure 61](image-url) – The effect of AEM thickness on permselectivity for RIG AEMs. AEMs are fully hydrated and in Cl⁻ counter-ion form. A. IEC, B. Conductivity, C. Permselectivity, and D. Area resistance. Error bars represent standard deviation n ≥ 3 samples for each AEM.

In thinner IEMs, providing they are structurally analogous, the area resistance will be lower as less material is needed to be penetrated by the counter-ions (area resistance \( \propto \) thickness). Thinner AEMs were also found to produce higher power output in experimental RED cells [29], therefore RED AEMs should be thin enough in their water swollen states for ease of
ion transport, providing physical integrity or permselectivity is not compromised. Recall that for the RIG AEMs considered here, the thickness is not a controlled pre-determined quality but is instead a function of the introduction of varying head-group chemistries to the base film. It is possible however in future synthesis to produce thinner and structurally analogous IEMs by changing the thickness of the starting polymer base film used prior to the grafting reaction. Figure 61 demonstrates the effect of AEM thickness on the properties of the RIG AEMs. The IEC generally increases with increasing thickness, DMIm AEM is again the obvious exception. AEM thickness is presented in the relevant hydrated form and, for most of the RIG AEMs, WU% increases with IEC and therefore a higher water content contributes to thicker AEMs. Similarly to observations made earlier regarding several properties, DMIm is thicker despite possessing a lower IEC and comparable WU% to the other RIG AEMs. For the RIG AEMs presented here there is a general trend between membrane thickness and permselectivity whereby thicker membranes tend towards being less selective than their thinner analogues with PYR AEM appearing to be an exception (a firm conclusion cannot be made due to the experimental errors).

These results are surprising as they suggest the opposite to the previous RIG CEMs, literature PECH AEMs also demonstrate little or no effect to permselectivity with varying thicknesses and the same chemistry [29]. Except for TMA, a trend is observed where thicker membranes yield lower area resistances and not thinner as would be expected. As previously stated bulk AEM properties are largely affected by each other in varied and complex relationships, the apparent correlations between thickness and permselectivity/area resistance are likely due to another contributing factor, i.e. WU%. A direct comparison with relationships observed for literature PECH AEMs is not possible as the RIG AEMs possess differing structures relative to each other whereas PECH B2 AEMs varied in thickness only.

4.3.6 Theoretical RED gross power density of RIG AEMs

The theoretical gross power densities (W m$^{-2}$) for the RIG AEMs were calculated based on a theoretical RED stack at 25°C consisting of a concentrated compartment (0.5 mol dm$^{-3}$ NaCl) and a dilute compartment (0.05 mol dm$^{-3}$ NaCl) separated by spacers with a thickness of 150 µm using the single IEM RED model (Eqn. 2) presented in Chapter 1. The
relationship between bulk AEM properties and theoretical gross power density of RIG AEMs is presented below in Figure 62.

Figure 62-A demonstrates that there is no simple relationship exhibited between the IEC and theoretical gross power density for RIG AEMs. This is evidenced by the fact that TEA, with significantly lower IEC, is estimated to outperform the higher IECs of both imidazolium head-groups. Furthermore, DMP with the lowest IEC of all RIG AEMs (1.13 mmol g\(^{-1}\)) is estimated to outperform DMIm AEM (1.75 mmol g\(^{-1}\)). Interestingly, both TEA and DMP AEMs possess higher area resistances compared to the other RIG AEMs. The effect of conductivity on theoretical gross power density (Figure 62-B) is almost the inverse of the effect of permselectivity (Figure 62-C). Power density appears to increase consistently with conductivity to a critical point at PYR where it then begins to decrease, there is however some uncertainty due to experimental errors relating to TMA and TEA head-groups. Again, for the effect of permselectivity of RIG AEMs, a similar trend is demonstrated where permselectivity correlates with power density to a certain point. The exceptions here are the more resistive TEA and DMP AEMs. The graph shows that the theoretical power densities increase consistently up to PYR (60% permselectivity) before falling for TEA (66% permselectivity) and again for DMP (72% permselectivity). This is because, as previously stated, the permselectivity and ionic conductivity of RIG AEMs demonstrate a trade-off relationship. It appears that for the RIG AEMs featured here, a peak optimum is reached at permselectivities of around 60%. This is substantially lower than the apparent minimum threshold relative to RED (ca. 90%). The effect of area resistance on theoretical gross power density does not show a correlation. PYR and TMA produce the highest theoretical power density and have similar area resistances (0.39 and 0.37 \(\Omega\) cm\(^2\), respectively). TEA and MIm AEMs are also similar in power density and their area resistances are 0.68 and 0.53 \(\Omega\) cm\(^2\) respectively. Although it is generally accepted that area resistance is the most fundamental RED property affecting power density [26] [33], DMIm, with the lowest area resistance, surprisingly has the lowest theoretical power density of all the RIG AEMs, although it is worth noting that DMIm does also possess the lowest permselectivity of all RIG AEMs. The results obtained here for RIG AEMs reflect those of the RIG CEMS previously and again contradicts prior literature reports which state that permselectivity is of minor importance compared to area resistance [28]. It is important to note, however, that literature conclusions were derived from IEMs with all permselectivities >90%.
The results obtained here (and for RIG CEMs reported previously) suggest that permselectivity is perhaps only of minor importance above a certain threshold. For example, and to reiterate, above 90%, increasing the permselectivity may have minor effect on power density; however, this is clearly not the case for the much less selective membranes evaluated here. This is further evidenced by the DMP AEM which, despite comparatively very high resistances of 2.75 Ω cm², is still able to produce theoretical gross power densities higher than those for DMIm (0.31 Ω cm²), due to its higher permselectivity.

Figure 62 – Effect of bulk AEM properties on theoretical gross power density of the RIG AEMs calculated using Eqn. 2 (single IEM model). A. IEC, B. Conductivity, C. Permselectivity, and D. Area resistance. Error bars represent standard deviation n ≥ 3 samples for each AEM.
As discussed in Chapter 3, to obtain the theoretical power densities for a single membrane type *i.e.* CEM or AEM (as above) the modified RED model (Eqn. 2) is used. However, conventionally the RED model is implemented to evaluate the maximum power output of CEM/AEM pairs as in a functional RED stack (Eqn. 1). This method provides a more complete evaluation of RED conditions and allows for a better comparison to available literature. The RIG AEMs and a commercial benchmark, Neospeta® AFN, were modelled alongside commercial and literature benchmark CEMs (Neosepta® CMX and SPEEK 65 respectively), as well as RIG CEM E-STY-30 from Chapter 3, for consideration of their RED potential. The CEMs selected were the current highest performing commercially available and non-commercial RED membranes and the best performing, most structurally analogous from the previous chapter. The experimental values for AFN, CMX and SPEEK 65 membranes were taken from literature [33]. The theoretical gross power density for IEM pairs are presented as a function of the two key variables, permselectivity and area resistance, presented in Figure 63 and Figure 64, respectively.

![Figure 63 – Effect of AEM permselectivity on the estimated gross power density of RIG AEMs and Neospeta AFN in conjunction with the CEMs; Neosepta CMX and non-commercial SPEEK 65. Calculated using Eqn. 1 (RED model).](image-url)
Figure 64 – Effect of AEM area resistance on the estimated gross power density of RIG AEMs and Neosepta AFN in conjunction with the CEMs; Neosepta CMX and non-commercial SPEEK 65. Calculated using Eqn. 1 (RED model).

As expected, the effects of AEM permselectivity and area resistance on gross power density in the theoretical RED stack agree with the single membrane calculations discussed previously. Generally, membranes possessing higher permselectivity and lower area resistances have higher estimated power density, with DMIm and DMP AEMs being notable exceptions. The data demonstrates that theoretical gross power density for commercial AEM Neospeta® AFN is considerably higher than even the highest performing RIG AEM. The highest theoretical power densities are obtained when all AEMs are paired with the non-commercial SPEEK 65 CEM. Commercial AFN produces a theoretical power density of 2.37 W m⁻², although PYR, the highest performing RIG AEM, is only able to produce a theoretical power density of 1.80 W m⁻². The theoretical gross power density of TMA AEM is very close to that of PYR at 1.76 W m⁻². Both TMA and PYR possess similar area resistances, around half that of Neosepta® AFN, however permselectivity for both AEMs is substantially lower than the 90% possessed by the commercial AEM. This further demonstrates that minimising area resistance only becomes effective after a minimum permselectivity threshold is achieved. Speculatively, increasing the permselectivity of RIG
AEMs whilst maintaining low resistances would result in AEMs with theoretical gross power densities closer to or higher than the top performing commercial AEMs.

4.4 Chapter Summary

The research in this chapter set out to build upon the results obtained in the previous chapter for radiation-induced grafted cation-exchange membranes (RIG CEMs), and on pre-existing literature regarding the importance of the bulk properties of ion-exchange membranes (IEMs) in relation to their application in reverse electrodialysis (RED). For the development of cost-effective and highly selective IEMs with minimum resistance for RED specific application, RIG has been employed to develop a series of RED focused anion exchange membranes (AEMs) from a common, 3/4-vinylbenzyl chloride (VBC) grafted, intermediate. The six RIG AEMs produced in this chapter differ principally in terms of head-group chemistry and all share the same basic polymer structure. Five of the six AEMs possess the lowest area resistance reported to date for RED AEMs in Cl⁻ counter-ion form, (0.31–0.68 Ω cm²) although a direct literature comparison is not possible due to the different measuring techniques used in this study compared to in the literature (Literature values for IEM area resistance were determined in aqueous saline solutions). However, when analysing theoretical gross power densities through implementation of a mathematical model, the RED power densities of all six RIG AEMs were calculated as being less than that of commercially available AEM Neospeta® AFN. The reduced performance, despite low area resistances, was due to the poor permselectivity of the RIG AEMs with the most permselective AEM at ca. 70% permselectivity. This research demonstrates the potential of RIG as a useful method to produce AEMs for RED application, although fine tuning of the method through further development is required.

Despite poor theoretical gross power densities due to low permselectivities, the RIG AEMs do possess very low area resistances and there is therefore scope for further improvement by fine tuning the AEM chemistries. Increasing the permselectivity of the RIG AEMs with minimal impact on area resistance would result in AEMs highly tailored to the specific RED performance criterion. The main issue regarding this is the trade-off relationship that exists between IEM permselectivity and ionic conductivity. One potential compromise is to reduce the water uptake (WU%) of AEMs, as this effects both permselectivity and conductivity.
The theoretical relationship between fixed charge density \((C_{\text{fix}})\) and permselectivity has been shown not to be a simple one and methods to control \(H_2O\) content whilst maintaining high ion-exchange capacities (IEC) and low area resistances should be investigated. Areas for consideration are the implementation of more hydrophobic head-groups (such as longer alkyl substituted imidazoles) or increasing the degree of crosslinking in the graft co-polymer chains to physically reduce WU% and increase the \(C_{\text{fix}}\).
5. Crosslinked Radiation Grafted Ammonium-based Anion-Exchange Membranes for RED

5.1 Introduction

Previous work has demonstrated radiation-induced grafting (RIG) as a potential method to produce highly functionalised ion-exchange membranes (IEMs) from low cost commercially available precursor polymer films. The RIG method has previously been utilised to produce IEMs for various polymer membrane electrolyte cells, the accumulated details of which are reported on in recent review articles [101] [102]. To date, efforts to utilise RIG methods to produce anion-exchange membranes (AEMs) specifically for reverse electrodialysis (RED) have been successful only to a limited extent. In the previous chapter, the versatile RIG method was employed to produce an analogous series of pendant quaternary ammonium functionalised AEMs from RIG of poly(ethylene tetrafluoroethylene) (ETFE) films grafted with 3/4-vinylbenzylchloride (VBC) followed by subsequent amination steps.

Early studies concerning RED IEM properties hypothesised permselectivity to be dependent on charge density ($C_{\text{fix}}$), which represents the number of fixed ionic groups within the bulk polymer per gram of sorbed H$_2$O [28]. Results attained in the previous chapters of this thesis however, demonstrate that a straightforward relationship between $C_{\text{fix}}$ and permselectivity does not exist and highlight the importance of other bulk properties such as water uptake (WU%). RIG IEMs presented in the previous two chapters yielded area resistances substantially lower than literature examples, although the permselectivities obtained fell short of that required for RED (≥90%). An inverse relationship between these two properties was observed by Geise et al. who rationalised this trade-off on the water content of the AEM where AEMs possessing a higher water content tended to produce a lower resistance but a decreased permselectivity [34]. This is fitting with the observed trends of the previous RIG IEMs, the majority of which possessed high WU% (ca. 50%). A key contributor to both WU% and area resistance is the IEC and generally RIG IEMs with higher IECs yield higher WU%. Decreasing IEC would reduce WU%, although it would also increase the area resistance. The challenge therefore is to control the WU% of IEMs to improve area resistance and permselectivity without decreasing the IEC.
Previously synthesised AEMs saw a decrease in WU% with an increased percentage of alkyl substituents; trimethylammonium (TMA) functionalised AEMs contained 49% H₂O when fully hydrated whereas ‘greaser’ triethylammonium (TEA) head-group contained only 41% H₂O. TEA AEM also had a higher charge density and permselectivity, although the theoretical RED cell power density was less than its TMA analogue due to it possessing a lower IEC (and therefore being more resistive). A potential avenue to restricting WU% with minimum impact on functionalisation is by implementing a degree of crosslinking to the grafted co-polymer chains. A further degree of crosslinking within RIG AEMs would inhibit the graft chains from moving apart, reducing WU% by physically restricting the amount of H₂O sorbed into the bulk, and therefore increasing the permselectivity. Polymer crosslinking is typically achieved during the polymerisation or polycondensation phase by incorporating a reagent blend of process monomer and a small percentage of a crosslinking agent [103]. Polymer crosslinking agents already under experimentation for the production of IEMs in general include divinylbenzene (DVB), N,N-methylenebisacrylamide (MBAA) and 2,2’-diallylbisphenol-A (ABFA); all contain two functional vinyl groups that can take part in a free-radical polymerisation reaction prior to any later functionalisation [102] [104].

Alternatively, with regard to crosslinked AEMs, it is possible to incorporate crosslinking and functionalisation in a single step using tertiary diamines as crosslinking agents that have the potential to substitute multiple alkyl halide groups present on the polymer chains. There are several examples in the literature where tertiary diamines were used in substitution reactions simultaneously implementing both crosslinking and ion-exchange groups (quaternary ammonium). Komokova et al. prepared AEMs from chloromethylated poly(sulfone) and various aliphatic tertiary diamines with an increase in permselectivity and electronic resistance for IEMs produced with higher diamine percentage (although in each case IECs were relatively low) [105]. Liu et al. incorporated N,N,N’,N’-tetramethylethlenediamine (TMEDA) as a bifunctional crosslinking agent in poly(phthalazinone ether ketone) (PPEK) based AEMs producing an AEM with relatively low WU% with respect to a high IEC of 2.63 mmol g⁻¹ using only 4% of the crosslinking agent [106]. Zhang et al. used N,N,N’,N’-tetramethylpropanediamine (TMPDA) and N,N-dimethylethlenediamine (EDA) to crosslink brominated poly(2,5-bis(perfluorophenyl)-1,3,4-oxadiazole-co-allyl bisphenol) based AEMs to yield low WU% and high IECs [107]. The cyclic diamine 1,4-diazabicyclo[2.2.2]octane (DABCO) was used as a crosslinking agent in the synthesis of poly(epichlorohydrin) (PECH) based AEMs, currently the literature
benchmark for bespoke RED membranes [29]. In all these examples, the AEMs were synthesised using the solution casting method with crosslinking being implemented at the same stage as polymerisation. It has not yet been established if crosslinking of bulk polymers can occur after the initial polymerisation reaction has taken place such as between the graft copolymer chains in a RIG material.

5.2 Experimental

Scheme 3 - General reaction scheme for pre-irradiation grafting and subsequent amination for RIG AEMs. Tertiary diamines used are: 1. N,N,N',N'-tetramethylethylenediamine (TMEDA) 2. N,N,N',N'-tetramethylpropanediamine (TMPDA) 3. N,N,N',N'-tetramethylbutanediadmine (TMBDA) 4. N,N,N',N'-tetramethylhexanediadmine (TMHDA) and 5. 1,4-diazabicyclo[2.2.2]octane (DABCO). The AEMs are depicted in the target fully crosslinked form.
A comprehensive description of the experimental procedures used for the synthesis and characterisation of diamine functionalised RIG AEMs, including the initial step of pre-irradiation grafting of 3/4-VBC onto ETFE films, can be found in Chapter 2 of this work. In summary, a general amination procedure was used to convert pre-grafted ETFE-g-poly(3/4-VBC) co-polymers to quaternary ammonium functionalised AEMs (Scheme 3). The VBC grafted intermediate films were submerged in diamine solutions consisting of 50% (v/v) H₂O and either TMEDA, N,N,N',N'-tetramethylpropanediamine (TMPDA), N,N,N',N'-tetramethylbutanediamine (TMBDA) or N,N,N',N'-tetramethylhexanediamine (TMHDA). In the case of DABCO, amination was carried out using a 1 mol dm⁻³ aqueous solution. The specific aminations were then conducted under reflux at 80°C for 48 h. The resultant AEMs were then washed several times in deionised water to remove any excess amine and boiled in deionised water for 1 h to fully hydrate the AEMs before storage in de-ionised water. The amination and characterisation of the TMHDA AEM were carried out by a final-year undergraduate research project student under my daily supervision.

AEM nomenclature for the RIG AEMs in this chapter is taken as the five-letter acronym of the diamine head-group present (TMEDA, TMPDA, TMBDA, TMHDA or DABCO) and collectively as “diamine AEMs”. The AEMs from previous chapter will be collectively referred to as monoamine AEMs. Structural confirmation for diamine AEMs was obtained using Raman and solid state nuclear magnetic (SS-NMR) spectroscopies. As with the RIG IEMs previously synthesised in Chapters 3 & 4, the bulk membrane properties were experimentally determined (see Chapter 2) and the experimental values were then used to calculate the theoretical gross power density obtainable in an experimental RED cell.

5.3 Results and Discussion

The prime objective of this work was to determine whether tertiary diamines can be incorporated into the previously established method of the production of RIG AEMs, as bi-functional crosslinking agent/fixed cationic head-groups. A series of tertiary diamines were incorporated into ETFE-g-poly(3/4-VBC) films that had been previously synthesised via the RIG of 3/4-VBC into commercially available 50 µm ETFE films. Structural characterisation of diamine RIG AEMs was performed using Raman and solid state nuclear magnetic
resonance spectroscopies (SS-NMR). SS-NMR was used to obtain $^{19}$F, $^{13}$C and $^{15}$N spectra for qualitative analysis. The experimentally determined bulk properties for each AEM include ion exchange capacity (IEC), water uptake (WU%), fixed charge density ($C_{fix}$), area resistance and permselectivity. AEM characterisation techniques for diamine based RIG AEMs were performed with the AEM in the Cl$^{-}$ counter-ion form most relevant to RED. The theoretical gross power density obtainable by each membrane as per a functioning RED stack was estimated via the RED model. The results generated by the model were then used to provide a general comparison analysis with current commercially available and literature AEMs (where values for area resistance and permselectivity are available).

5.3.1 Structural characterisation by Raman spectroscopy of diamine RIG AEMs

The Raman spectra of diamine RIG AEMs were recorded using a 780 nm laser on a DXR Raman Microscope using a 50× objective producing an estimated laser spot size of 1 μm. Raman spectra for each diamine AEM was recorded as an average of 8 scans over the range 3200 cm$^{-1}$–250 cm$^{-1}$ and Raman spectra were recorded for each stage of AEM synthesis. The following figures display superimposed Raman spectra for the ETFE base films, ETFE-g-poly(3/4-VBC) intermediate films and the final diamine AEM. For presentation purposes the depicted range is 1750–250 cm$^{-1}$ as lower priority (e.g. C-H stretch) structural information is present outside this range. The full and complete spectra can be found in the appendices. For illustrative purposes, all spectra are normalised to -CF$_2$ peak present in ETFE base film at ca. 835 cm$^{-1}$.

Figure 65–Figure 68 present the Raman spectra for the aliphatic diamine RIG AEMs along with the Raman spectra of the ETFE and VBC grafted precursor films. The most prominent peak present in the ETFE base film is that already mentioned, at 835 cm$^{-1}$ due to the CF$_2$ group present in the base polymer. The addition of VBC into the base film introduces the customary peaks indicative of styrenic structures appearing at wavenumbers 1610, 1034, and 1001 cm$^{-1}$, which correspond to aromatic C=C stretching, aromatic C-H in-plane bending and aromatic breathing modes respectively. The peak present at 1268 cm$^{-1}$ is indicative of CH$_2$-Cl deformation [81], as well as four somewhat convoluted peaks between 748–676 cm$^{-1}$ that are characteristic of CH$_2$-Cl stretching modes [79]. The linear aliphatic diamines are essentially a homologous series, varying structurally by only the length of the
carbon chain that connects the two terminal tertiary Ns and, as expected, the spectra obtained for all of the aliphatic diamine AEMs are similar. As with the RIG AEMs in Chapter 4, peaks relating to the CH₂-Cl group at 1268 cm⁻¹ and 748–676 cm⁻¹ are no longer present in the spectra of the final diamine AEMs. New peaks are also present at wavenumbers around 750 cm⁻¹ consistent with C-N symmetric stretching and 1147 cm⁻¹ indicative of C-N asymmetric stretching in quaternary ammonium groups [93] [94]. Interestingly for the TMEDA AEM, the antisymmetric stretching peak is more intense than that of the symmetric stretch, whereas for the remaining linear diamine AEMs the opposite is observed. The disappearance of CH₂-Cl peaks and introduction of N-C backbone stretching peaks confirm that amination of the grafted intermediate has been successful.

The Raman spectra for the DABCO AEM and precursor films is presented in Figure 69. Loss of the diagnostic CH₂-Cl peaks at 1268 cm⁻¹ and 748–676 cm⁻¹ are indicative that substitution of the Cl has occurred. New peaks appear in the spectra at 691 and 797 cm⁻¹, the latter of which is consistent with C-N symmetric stretching and a doublet type peak at 1060 and 1074 cm⁻¹ consistent with C-N asymmetric stretching. A new peak is also visible at 1460 cm⁻¹ attributed to -CH₂ deformation of the DABCO chain.

![Figure 65 – Raman spectra of TMEDA AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra are normalised to base film peak at 835 cm⁻¹ for illustrative purposes.](image)
Figure 66 – Raman spectra of TMPDA AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.

Figure 67 – Raman spectra of TMBDA AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.
Figure 68 – Raman spectra of TMHDA AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra are normalised to base film peak at 835 cm$^{-1}$ for illustrative purposes.

Figure 69 – Raman spectra of DABCO AEM, ETFE base film and the ETFE-g-VBC intermediate film. All spectra are normalised to base film peak at 835 cm$^{-1}$ for illustrative purposes.
5.3.2 Structural characterisation by SS-NMR spectroscopy of RIG diamine AEMs

$^{13}$C and $^{15}$N SS-NMR were used to confirm both grafting and amination via structural characterisation at each synthetic stage for each RIG diamine AEM. The $^{13}$C SS-NMR spectra of each of the five RIG diamine AEMs are presented in Figure 70–Figure 74. Each figure displays three superimposed spectra including the final AEM, ETFE base polymer and ETFE-g-poly(3/4-VBC) intermediate graft co-polymer. The familiar ETFE spectrum shows only two signals of note corresponding to backbone C: $\delta_C = 22$ (CH$_2$) and $\delta_C = 119$ (CF$_2$). Confirmation of VBC grafting is made evident by the introduction of multiple new signals, including four in the aromatic region, in the NMR spectra for ETFE-g-poly(3/4-VBC). The signal found at $\delta_C = 40.5$ corresponds to the aliphatic backbone of the graft ‘poly(styrene) chain’ and $\delta_C = 46.8$ corresponds to the de-shielded (CH$_2$Cl). The aromatic spectral region is to some extent convoluted, as the VBC reagent used contains a mixture of meta- and para- isomers. There are however four signals, $\delta_C = 119$, $\delta_C = 128.7$, $\delta_C = 135.6$, $\delta_C = 145.5$, that all correspond to aromatic carbons. Spinning sidebands are also visible in the spectrum of DABCO AEM at $\delta_C = 70$ and 189. The $^{13}$C SS-NMR spectra of the linear diamine functionalised AEMs are similar to each other and that of the grafted poly(3/4-VCB) intermediate film.

![Spectra](image.png)

Figure 70 – $^{13}$C SS-NMR spectra of the TMEDA diamine AEM, the ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to the height of the ETFE base film peak $\delta_C = 22$ for presentation purposes.
Figure 71 – $^{13}$C SS-NMR spectra of the TMPDA diamine AEM, the ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to the height of the ETFE base film peak $\delta_C = 22$ for presentation purposes.

Figure 72 – $^{13}$C SS-NMR spectra of the TMBDA diamine AEM, the ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to the height of the ETFE base film peak $\delta_C = 22$ for presentation purposes.
Initially the signal corresponding to CH$_2$-Cl ($\delta_C = 46.8$) appears to remain in the spectra of the TMEDA aminated AEM; however, subtle differences in chemical shift determine that a new signal is present at $\delta_C = 46.0$ corresponding to N-($\text{CH}_3$)$_2$. This implies that not all amine groups have undergone quaternisation and have therefore failed to crosslink, interestingly the signal appears less intense for diamine head-groups with longer alkyl chains. Weak signals at $\delta_C = 52.7$ and $\delta_C = 64.5$ correspond to N$^+$-$\text{CH}_3$ and N-($\text{CH}_2$)$_R$-$\text{N}$ of the diamine head-groups alkyl chain, and $\delta_C = 70.5$ corresponding to Ar-$\text{CH}_2$-$\text{N}$ formally (Ar-$\text{CH}_2$-Cl). These characteristic changes in signal are also observed in the spectra of TMPDA, TMBDA and TMHDA indicating successful amination.

Unlike the spectra of the linear diamine AEMs, the $^{13}$C NMR spectrum of DABCO shows more obvious changes and three new signals are observed. A signal at $\delta_C = 45.8$ lies next to a second signal of similar intensity at $\delta_C = 53.1$. These two signals offer a wealth of information with regard to the amination of the chloride moiety with DABCO. The signal at $\delta_C = 45.8$ corresponds to three CH$_2$-$\text{N}$ of the bicyclic structure whereas the downshifted signal at $\delta_C = 53.1$ corresponds to three CH$_2$-$\text{N}^+$. This indicates that the DABCO head-group has not undergone complete crosslinking and at least some tertiary amine groups have failed to initiate nucleophilic attack on CH$_2$-Cl. The spectrum of DABCO shows one more signal further downfield at $\delta_C = 67.8$ ppm corresponding to Ar-$\text{CH}_2$-$\text{N}$. 

Figure 73 – $^{13}$C SS-NMR spectra of the TMHDA diamine AEM, the ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to the height of the ETFE base film peak $\delta_C = 22$ for presentation purposes.
Figure 74 – $^{13}$C SS-NMR spectra of the DABCO diamine AEM, the ETFE base polymer and the ETFE-g-poly(3/4-VBC) intermediate film. Spectra normalised to the height of the ETFE base film peak $\delta_C = 22$ for presentation purposes.

Figure 75 – $^{14}$N SS-NMR of the RIG diamine AEMs. Spectra are normalised for presentation purposes where the most intense signal of each of the amassed spectra = 1.
$^{15}$N NMR is a useful tool in confirming that amine/ammonium groups are present in the graft co-polymers. The $^{15}$NMR spectra of all diamine AEMs and the TMA benchmark are presented in Figure 75. Successful amination is confirmed with all diamine AEMs displaying the presence of at least one N environment (assuming no trapped unreacted diamine is present). DABCO, as expected from $^{13}$C NMR, clearly shows two N environments as does TMEDA through a splitting of the dominant signal. The $^{15}$N spectra for the remaining three diamine AEMs appear to show a single discernible signal that is consistent with complete crosslinking. It should be kept in mind that, for the linear diamine spectra, there is a degree of noise especially for TMPDA, TMBDA and TMHDA, which could potentially conceal a second signal (especially given the relative lower intensity of the second signal for DABCO AEM).

5.3.3 IEC, conductivity and WU% property relationships for diamine RIG AEMs

As with all previous RIG IEMs, the IEC of the diamine AEMs is regarded as the fundamental property due to its influence over all other bulk properties. Furthermore, IEC measurements of the diamine AEMs can provide clues regarding the degree of crosslinking that has been achieved. During amination, the CH$_2$Cl chloride of the poly(3/4-VBC) graft co-polymer is displaced by one of the head-group’s tertiary diamines, resulting in a quaternary ammonium functionalised AEM (Mechanism 7, Chapter 2). The second tertiary amine group, located at the opposite end of the molecule to the N that has reacted, is then able to facilitate the same reaction on a second CH$_2$Cl chloride resulting in the desired crosslinked chains and a second functional ammonium site. The experimentally determined IEC (described previously) is a direct measurement of the number of quaternary ammonium sites however, it is also possible to determine the number of remaining tertiary amines (total IEC) by first treating the AEMs with HCl$_{(aq)}$. On treatment with HCl, 1 mol dm$^{-3}$, any remaining tertiary amines become quaternised to NR$_3$H$^+$ groups and the IEC then measured is indicative of all N atoms within the bulk matrix and therefore designated as the ‘total IEC’ (Figure 76). Once obtained, the total IEC is divided by the quaternary IEC to determine the potential of each diamine to crosslink the poly(3/4-VBC) graft copolymer chains, where a ratio equal to 1 indicates 100% crosslinking and a ratio equal to 2 indicates 0% crosslinking.
The total and quaternary IECs for the diamine AEMs, and TMA reference, are presented in Figure 77 below. It is apparent that the three shorter chained linear diamines, TMEDA, TMPDA and TMBDA have a higher ratio of total IEC relative to quaternary IEC and therefore have undergone minimal crosslinking. Of these three AEMs, TMPDA shows a small degree of crosslinking with a ratio of 1.82 while TMEDA and TMBDA demonstrate zero crosslinking with IEC ratios equal to 1.99 and 2.00 respectively. This is somewhat unexpected as TMEDA and TMPDA have both previously demonstrated their use as bifunctional crosslinking agents, although, in both these prior cases, crosslinking was performed prior to polymerisation and not afterwards as was attempted here [106] [107].
Despite appearing to possess a high total IEC, and therefore low level of crosslinking, the physical appearance of TMBDA AEM is more like a crystalline plastic than an amorphous film. This AEM is more brittle than any of the others, a common observation with crosslinked polymers, and easily breaks when attempting to cut the material for experimental measurements. The $^{13}$C SS-NMR data recorded for TMBDA suggests good levels of crosslinking with corresponding N-(CH$_3$)$_2$ signal intensity lower than TMEDA or TMPDA AEMs. The $^{15}$N SS-NMR also supports crosslinking with only one definitive signal present in its spectrum. The value for the total IEC of TMBDA AEM does present a larger experimental error than for the other AEMs and, at the lower end of this error margin, the AEM would in fact exhibit a degree of crosslinking higher than TMPDA. The degree of crosslinking is substantially higher for TMHDA and DABCO AEMs with IEC ratios of 1.09 and 1.04 respectively, indicating close to 100% crosslinking for both head-groups.

The first consideration of the inefficiencies of crosslinking in TMEDA, TMPDA and TMBDA is the aliphatic chain length; for linear diamines, only the longest chain exhibits significant crosslinking. Initially it appears that the shorter ethyl- propyl- and butyl-homologues are too short to extend between separate poly(3/4-VBC) graft chains, but this is contradicted by the DABCO head-group which exhibits a high degree of crosslinking despite being a similar length to TMEDA. A possible explanation then for non-crosslinking with the shorter linear diamines may be that the initial quaternisation reaction (N$_1^+$) moves to disrupt the electron density at the opposite end of the molecule with the second lone pair moving to stabilise the positively charged quaternary ammonium and reduce the nucleophilicity of the second amine group (N$_2$). A base’s pKa can give a good insight into its nucleophilicity. Bryantsev et al. demonstrated a drop between the initial and second pKa values for aliphatic diamines (specifically TMEDA, TMPDA and TMBDA), see Table 6 [108].

<table>
<thead>
<tr>
<th>Diamine</th>
<th>pKa$^1$</th>
<th>pKa$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,N,N',N'$-tetramethylethylenediamine</td>
<td>9.0 – 9.2</td>
<td>5.6 – 5.9</td>
</tr>
<tr>
<td>$N,N,N',N'$-tetramethy-1,3-propanediamine</td>
<td>9.7 – 9.8</td>
<td>7.5 – 7.7</td>
</tr>
<tr>
<td>$N,N,N',N'$-tetramethy-1,4-butanediamine</td>
<td>10.66</td>
<td>9.04</td>
</tr>
</tbody>
</table>

Table 6 – Calculated* and experimental first and second pKa values of aliphatic diamines [108]
For TMEDA the second pKa is significantly lower than the first, meaning that the grafted poly(3/4-VBC) chains would be more likely to undergo nucleophilic attack from N₁ of a second diamine molecule than N₂ of the first. The difference between pKa¹ and pKa² values decreases with increasing chain length, while the nucleophilicity (pKa²) of N₂ increases with increasing alkyl chain length. Assuming the trend continues, the pKa¹ and pKa² of TMHDA would be comparable which would explain the near 100% degree of crosslinking observed. The pKa argument however cannot explain the high degree crosslinking observed when using DABCO because of the significant decrease between its two pKa values (pKa¹ = 8.8 and pKa² = 3.0) [77]. Another major contributor to nucleophilicity in amines is the steric hindrance around the nucleophilic N. In all cases the tertiary N atoms are sp³ with their lone pair in the remaining sp³ orbital. However, because of the bicyclic conformation of DABCO its lone pair is held away from the other alkyl- groups in a ‘cage’ system in a quasi-pyridine arrangement [109]. The effect of this is that almost no steric hindrance is present around the nucleophilic lone pairs of N₁ and N₂ (relative to linear diamines) leaving it available to readily initiate a nucleophilic attack on the CH₂Cl of the poly(3/4-VBC) chains.

As with the RIG IEMs presented in Chapters 3 and 4, the effect of IEC on the bulk properties of the diamine AEMs is considered in Figure 78 alongside the TMA benchmark AEM. For the RIG IEMs synthesised in the previous chapters, a general trend was observed between the IEC and the WU% and conductivity, and both increase with increasing IEC. In contrast the WU% for the diamine AEMs demonstrates a more complicated relationship with IEC where WU% initially decreases with increasing IEC before increasing again for the DABCO and TMA AEMs. Overall the WU% values are some of the lowest achieved for the RIG IEMs produced so far. Of the two highly crosslinked diamine AEMs, TMHDA demonstrates the ability to maintain respectable IECs with a significantly reduced WU%, whereas the IEC and WU% of the DABCO AEM are closer to that of the monoamine RIG AEMs synthesised previously. A similar trend is observed for the effect of IEC on conductivity with the exception of the TMHDA AEM which has a lower WU% than TMBDA while its conductivity is marginally higher. The general trend in decreased conductivity of the linear diamine AEMs is surprising as IEM conductivity is dependent on counter-ion concentration. As observed previously for RIG IEMs in this study, increasing IEC typically results in increased concentration of counter-ions in the membrane phase and ultimately increased conductivity. The linear diamine AEMs would be expected to behave the in the same manner, but this is not the case.
The ionic conductivity of an IEM represents the relationship between the activity and the concentration of the counter-ion being transported. As previously stated, the counter-ion concentration is dependent on the IEC, but the activity is dependent on the solvation of the ion and depends on water content which, in turn, is largely effected by IEC. The somewhat circular nature of the observed relationships is very complex and a definitive conclusion is not possible considering the available data. However, one factor for consideration is the WU%. The results here suggest for RED focused IEMs there may be an optimal minimum value for WU%. As an example, the WU% recorded for TMHDA AEM (ca. 12%) is lower than for any other RIG IEM in this study thus far and, despite possessing a relatively high IEC (ca. 1.5 mmol dm$^{-3}$), yields a very low ionic conductivity (ca. 10 mS cm$^{-1}$). It appears

Figure 78 – The effect of IEC on bulk AEM properties for select diamine AEMs and TMA benchmark: A. WU%, B. Conductivity, C. Permselectivity and D. Area Resistance. Error bars represent standard deviation n $\geq$ 3 samples for each AEM.
then that finding a trade-off point in the relationship between permselectivity and conductivity cannot be achieved by simply minimising the IEMs WU%, as a certain degree of water content is necessary for optimal ion conductivity.

Despite the high degree of crosslinking determined it appears that the DABCO head-group can facilitate an unexpectedly large WU% and conductivity. Hypothetically DABCO is able to crosslink the grafted poly(3/4-VBC) chains in one of two ways; firstly, DABCO is able to crosslink VBC groups on different graft chains forming ‘inter-chain’ crosslinks as targeted in this study, and secondly, given its high nucleophilicity and short chain length, is also able to crosslink neighbouring VBC groups on the same chain, resulting in ‘intra-chain’ crosslinks (see Figure 79). A higher degree of ‘intra-chain’ crosslinking could explain the apparent anomalous properties of the DABCO AEM. Intra-chain crosslinking would affect the total vs. quaternary IEC in the same way as inter-chain crosslinking although, as crosslinking is occurring intra-chain, the morphology of the grafted chains, and therefore the WU% and conductivity, would be relatively unaffected, resulting in AEMs comparable in structure to the TMA benchmark AEM.

![Figure 79 – Examples of ‘inter’ and ‘intra’ chain crosslinking for DABCO head-group and comparative non-crosslinked TMA benchmark AEMs.](image)

Except for the DABCO AEM the conductivity of the diamine AEMs are generally lower than the previous monoamine RIG AEMs; this is expected given that the IEC of the linear diamine AEMs is significantly lower than the DABCO and TMA benchmark AEMs (ca. 0.5 mmol g\(^{-1}\)). The one advantage to the decreased conductivity values, regarding the previous RIG AEMs, is the increased permselectivity. As already discussed in some detail, RIG IEMs synthesised in previous chapters and several literature examples have demonstrated a trade-off relationship between conductivity (or area resistance) and permselectivity. The diamine
functionalised AEMs here also demonstrate this trade-off relationship and those with low conductivity tend to yield higher permselectivity.

The highly crosslinked TMHDA AEM possesses a very high permselectivity of around 95%, the highest yet achieved by any of the RIG IEMs produced in this thesis. The relationship between IEC and area resistance for diamine AEMs typically resembles the inverse of the relationship between IEC and conductivity. As the literature opinion is that permselectivity is a less fundamental parameter than area resistance [28] and the results from previous chapters indicate that a certain level of RIG AEM permselectivity (≥90%) is required for RED performance, it is therefore initially unclear how the TMHDA AEM (with relatively high area resistance and high permselectivity) will perform. Due to the brittle nature of TMBDA it was not possible to measure its permselectivity as the AEM tended to crack and tear when cutting, TMBDA AEM is therefore absent from Figure 78-C.

![Figure 80](image)

**Figure 80** – The effect of conductivity on: A. Permselectivity and B. Area resistance for the diamine AEMs and the TMA benchmark. Error bars represent standard deviation n ≥ 3 samples for each AEM.

The effect of conductivity on key RED application properties permselectivity and area resistance for diamine AEMs and TMA benchmark is presented in Figure 80. A general reduction in both properties is observed with increasing conductivity, where area resistance is affected in an exponential type curve. The correlation between RED specific properties and conductivity highlights the importance of evaluating conductivity and not simply area resistance when considering IEM potential for RED. With respect to the effects of
crosslinking and the trade-off between conductivity and permselectivity, the conductivity of the crosslinked DABCO AEM is \( \text{ca. } 10 \, \text{mS cm}^{-1} \) less than the benchmark TMA AEM although it is only marginally more selective. The linear diamine head-groups demonstrate a significant increase in permselectivity although at conductivities less than \( 10 \, \text{mS cm}^{-1} \) and area resistances above \( 1.0 \, \Omega \, \text{cm}^2 \). Although area resistance is higher than for the previous monoamine RIG AEMs, these values are comparable with several commercially available AEMs, including Neosepta® ACS (2.0 – 2.5 \( \Omega \, \text{cm}^2 \)) and AMX (2.0 – 3.5 \( \Omega \, \text{cm}^2 \)) [86].

![Figure 81](image-url)  
**Figure 81** - The effect of WU% on: A. Permselectivity and B. Area resistance for the diamine AEMs and the TMA benchmark. Error bars represent standard deviation \( n \geq 3 \) samples for each AEM.

It was hypothesised previously that an ideal trade-off between conductivity and permselectivity may be found by implementing diamine head-groups as bi-functional crosslinking agents, reducing WU% and therefore increasing Donnan exclusion whilst maintaining high IECs and ionic conductivities. The effect of WU% on permselectivity and area resistance is presented in Figure 81. The relationship demonstrated is generally as expected with AEMs containing the lowest percentage of water being more permselective. The 95% permselectivity possessed by TMHDA AEM occurs with a WU% of only 12%; in contrast DABCO AEM has a WU% that is over double this value at 28% and therefore less selective, as expected. The area resistance of diamine AEMs generally decreases with increasing WU% with the least resistive, DABCO AEM, holding the highest percentage of water. The exception is the TMBDA AEM, the most resistive of the diamine AEMs, which does not possess the lowest WU%. Considering the trends observed for area resistance, a
fair assumption could be made that this would also be the case for permselectivity of the TMBDA AEM. Recall that TMBDA AEM was too brittle to be cut and sealed into the experimental cell and it was therefore not possible to determine its permselectivity.

5.3.4 $C_{\text{fix}}$, permselectivity and area resistance property relationships for the linear diamine RIG AEMs

The $C_{\text{fix}}$ of an IEM is largely considered as a pivotal factor for ion transport as it is dependent on the amount of ion exchange groups per gram of water (rather than per gram of IEM), present in the membrane phase [28] [110] [111]. Although the previous chapters have demonstrated that simple relationships are not observed between $C_{\text{fix}}$ and RED related IEM properties, it is still a useful parameter as it considers the IEC of IEMs in the hydrated state that is more relevant to RED application.

The relationship between $C_{\text{fix}}$ and area resistance and permselectivity of the diamine AEMs as well as TMA benchmark AEM are presented in Figure 82. In agreement with the results collected for the RIG IEMs in previous chapters, a simple correlation between $C_{\text{fix}}$ and these

![Figure 82](image-url)
key RED parameters is not apparent. Theoretically, AEMs with higher $C_{fix}$ are said to be more likely to possess higher permselectivities and lower area resistances, although this is not found here. The diamine AEMs generally tend to possess a relatively high $C_{fix}$ (compared to monoamine RIG AEMs synthesised in the previous chapter) and consequently have higher permselectivity however, as expected, they also yield higher area resistance. The exception in both cases is the DABCO AEM which, despite a reasonably high $C_{fix}$, has a reduced area resistance and permselectivity (relative to its simple linear structured counterparts). The DABCO AEM has the highest IEC and WU% of all the diamine AEMs (1.63 mmol g$^{-1}$ and 28% respectively) and its $C_{fix}$ is 4.3 mmol g$^{-1}$ H$_2$O. With respect to these bulk properties the DABCO AEM is more comparable to previous monoamine RIG AEMs.

The relationship between area resistance and permselectivity is presented in Figure 83. In contrast to the monoamine RIG IEMs synthesised previously, the area resistances of the diamine AEMs cover a much wider range and as such a clearer trend is visible. The TMHDA head-group has the highest area resistance and permselectivity (2.4 $\Omega$ cm$^2$ and 95% respectively). In terms of area resistance and the WU% TMHDA AEM is comparable with the DMP monoamine AEM (2.8 $\Omega$ cm$^2$ and 20%) the latter being predicted to be ineffective as a RED AEM by the RED model. However, the TMHDA AEM also possesses significantly higher permselectivity (95% for TMHDA vs. 72% for DMP) therefore one can expect a higher theoretical power density than that obtained for DMP previously (discussed later).

The implementation of diamine head-groups capable of crosslinking was intended to find an optimal trade-off position between conductivity and permselectivity, sacrificing some of the extremely low area resistances achieved by previous monoamine RIG AEMs to improve AEM permselectivity. In the case of TMHDA, this has been successful in obtaining a very high permselectivity but perhaps by sacrificing more area resistance than is ideal. The bulk properties of TMHDA are however closely comparable to commercially available AEM Neosepta® AMX which demonstrated a theoretical RED cell gross power density of 3.0 W m$^{-2}$ [28]. Although the TMHDA AEM has the highest permselectivity, the TMEDA and TMPDA AEMs also demonstrate improved permselectivities relative to the previous monoamine RIG AEMs without conceding as much area resistance. The permselectivities of 76% and 74%, however, fall short of the targeted 90% by a large margin. Because of the contradictory relationship, a trade-off between these two properties will always involve a compromise; the question then is whether a viable compromise is achievable. Relative to the
TMA monoamine benchmark AEM, the area resistance of TMEDA has increased by 1.0 Ω cm\(^2\) and the permselectivity by 15% (the area resistance of the TMHDA AEM has increased by approx. 2.0 Ω cm\(^2\) and the permselectivity by approx. 35%). Based on these values, it is unlikely that a compromise AEM with ≥90% permselectivity and an area resistance under ≤1.0 Ω cm\(^2\) can be achieved by these particular RIG AEMs without any further modification.

![Figure 83](image.png)

Figure 83 – The relationship between area resistance and permselectivity for the diamine AEMs and the TMA benchmark. Error bars represent standard deviation n = 3 samples for each AEM for area resistance and n = 3 measurements for each AEM for permselectivity.

5.3.5 Theoretical RED gross power density of diamine functionalised RIG AEMs

As for all the monoamine RIG IEMs synthesised before, the experimental values for permselectivity and area resistance were used to evaluate the diamine AEMs by calculating the theoretical power density (W m\(^{-2}\)) obtainable in a RED stack. As a reminder, the theoretical gross power densities for the diamine RIG AEMs were calculated using the single
IEM RED model (Eqn. 2). The results of the RED model calculations are considered against the various properties in Figure 84 below.

Figure 84 - Effect of AEM properties on the theoretical gross power density for the diamine AEMs calculated using Eqn. 2 (single IEM model). A. IEC B. Conductivity, C. WU%, D. Cfix, E. Permselectivity, and F. Area resistance. Error bars represent standard deviation n ≥ 3 samples (n = 3 measurements for permselectivity).
Overall the highest theoretical power densities belong to the TMPDA and TMHDA AEMs at 3.36 and 3.45 W m\(^{-2}\) respectively, both of which demonstrate some level of crosslinking. The TMPDA and TMHDA AEMs both exceed the theoretical power density of the highest performing monoamine RIG AEM (PYR, 2.89 W m\(^{-2}\)). However, these values fall short of the 5.29 W m\(^{-2}\) estimated for the commercial Neosepta® AFN or the 4.59 W m\(^{-2}\) reported in the literature with the PECH B2 AEMs (calculated from literature values [29]). Despite a high degree of crosslinking (calculated from total vs. quaternary IEC measurements) the bulk properties of the DABCO AEM were more comparable to the previous monoamine RIG AEMs and not its linear diamine counterparts. Therefore, it is not surprising that the theoretical power density of the DABCO AEM is comparable to that of the earlier monoamine RIG AEMs. The theoretical power density calculated for the DABCO AEM is the lowest of all the diamine AEMs at 2.65 W m\(^{-2}\), which is even lower than that of the benchmark TMA head-group (2.74 W m\(^{-2}\)).

Figure 84-A demonstrates the effect of IEC on the theoretical power density and, in agreement with all previous results, shows that there is not a simple relationship between IEC and power density. The TMPDA and TMHDA AEMs, with highest theoretical power densities, do not possess the highest IECs (in fact they have IECs lower than all but one of the earlier monoamine RIG AEMs). As both these AEMs contain linear diamine head-groups and exhibit a degree of crosslinking, this implies that it is not simply the amount of charged groups present in the polymer matrix but how they are dispersed throughout the bulk polymer and the local environment that effect AEM functionality. For example, the simple TMA head-group yields an AEM with IEC of 1.86 mmol g\(^{-1}\), is not able to crosslink the poly(3/4-VBC) graft chains, and has theoretical power density of 2.74 W m\(^{-2}\). In contrast the TMPDA head-group produces an AEM with an IEC of only 1.06 mmol g\(^{-1}\), demonstrates low levels of crosslinking and yields a theoretical power density of 3.36 W m\(^{-2}\). The IEC is a good measure of how much the original ETFE base film has been modified through RIG but not for evaluating the RED cell theoretical power output of an IEM. The overall plot of the effect of WU% on theoretical power density resembles that of conductivity; this was expected given that both properties previously displayed a similar general trend with regard to their effects on permselectivity and area resistance.

Similarly, the effect of C\(_{\text{fix}}\) on theoretical power density does not demonstrate a simple relationship. The TMHDA AEM, yielding the highest theoretical power density, does
however possess the highest $C_{\text{fix}}$. In contrast the TMPDA AEM, with the second highest calculated power density, has the lowest $C_{\text{fix}}$ of all diamine AEMs (that falls just above the TMA benchmark). The graphs depicting the effects of permselectivity and area resistance on theoretical power density resemble each other to a degree and neither shows a straightforward relationship. The effect of permselectivity and area resistance on theoretical power density demonstrated by the TMHDA AEM further contradicts the prior stated notion that permselectivity is less important than area resistance [28] (as it possess the highest theoretical power density and permselectivity yet also has the highest area resistance). In contrast, the DABCO AEM has an area resistance 2.0 $\Omega$ cm$^2$ lower than TMHDA AEM and a significantly lower permselectivity but possesses the lowest theoretical power density of all the diamine AEMs. In fact, despite having the highest area resistance, the TMHDA AEM is estimated to out-perform all other diamine RIG AEMs, and this observation lends further support to the hypothesis that permselectivity is only of secondary importance to RED cell power output once it is above a threshold ca. $\geq$90%.

Calculations to estimate the theoretical power density (W m$^{-2}$) were also carried out for AEM/CEM pairs to evaluate their potential in a RED stack (Eq. 1). The diamine AEMs, TMA benchmark and commercial Neosepta® AFN were modelled alongside literature standard SPEEK 65, commercial Neosepta® CMX and RIG E-STY-30 CEMs synthesised in Chapter 3. The values for the theoretical RED stack are the same as those used previously, consisting of a concentrated compartment (0.5 mol dm$^{-3}$ NaCl) and a dilute compartment (0.05 mol dm$^{-3}$ NaCl) at 25°C with 150 $\mu$m spacers. The experimental values for AFN, CMX and SPEEK membranes were taken from the literature [33]. The theoretical gross power densities of each AEM/CEM pair are considered vs. permselectivity and area resistance, in Figure 85 and Figure 86 respectively.

As found with the results obtained with the simple (monoamine) RIG AEMs, the commercially available Neosepta® AFN AEM is predicted to yield higher power densities than for all the diamine RIG AEMs. As is typical, the theoretical gross power densities for the AEM/CEM pairs are substantially lower than those calculated for the single AEMs. The commercial Neosepta® AFN yielded significantly higher theoretical power densities than all RIG diamine AEMs irrespective of which CEM it is paired with (with SPEEK 65 providing the highest theoretical gross power density).
Figure 85 – Effect of AEM permselectivity on the estimated gross power density of the diamine RIG AEMs, the benchmark TMA AEM, and the commercial Neosepta AFN modelled when in conjunction with the CEMs: Neosepta CMX, non-commercial SPEEK 65 and RIG CEM E-STY-30. Gross power density is calculated using Eqn. 1 (RED model). Error bars represent $n = 3$ measurements.

Figure 86 – Effect of AEM area resistance on the estimated gross power density of the diamine RIG AEMs, the benchmark TMA AEM, and the commercial Neosepta AFN modelled when in conjunction with the CEMs: Neosepta CMX, non-commercial SPEEK 65 and RIG CEM E-STY-30. Gross power density is calculated using Eqn. 1 (RED model). Error bars represent $n = 3$ AEM samples.
The TMHDA and TMPDA diamine AEMs are estimated to yield improved power densities relative to the simple monoamine RIG AEMs previously. However, improvements in power density are marginal and the diamine AEMs appear to be no more fit for RED application than the simple monoamine RIG AEMs. The results calculated for AEM/CEM pairs do not completely reflect those of the single AEM RED model (without CEM) with the TMPDA AEM being the most notable exception. When paired with SPEEK 65 or E-STY-30, the power density of the TMPDA AEM is calculated to be higher than for the TMHDA AEM, contrary to the single AEM calculations where the power density of the TMHDA AEM was estimated to be the highest. These findings demonstrate the importance of modelling AEM/CEM pairs, as single AEM calculations do not factor into the effects of the paired CEM on the overall power density.

5.4 Chapter Summary

The primary aim of the work carried out in this chapter was to evaluate if tertiary diamine reagents could be used along with the pre-existing radiation induced grafting (RIG) method as bi-functional crosslinking/aminating agents. Previous monoamine RIG AEMs were found to possess low area resistance but too low permselectivities. It was hypothesised that by reducing water uptake (WU%) through crosslinking of the bulk polymer structure, a trade-off could be achieved with improved permselectivities and marginally lower conductivities. A series of linear tertiary diamines consisting of ethyl-, propyl-, butyl- and hexyl- analogues and the bicyclic 1,4-diazabicyclo[2.2.2]octane (DABCO) were used in the successful amination of RIG ETFE-g-poly(3/4-VBC). Of the diamines used, the hexyl- analogue (TMHDA) and DABCO AEMs demonstrated a near 100% degree of crosslinking, whereas the propyl- analogue (TMPDA) AEM demonstrated a lower level of crosslinking and the ethyl- analogue (TMEDA) did not crosslink. However, due the margin of error for the experimentally determined (titration) degree of crosslinking, and the seemingly conflicting physical properties of the butyl- analogue (TMBDA) AEM it was not possible to draw a firm conclusion as to the actual degree of crosslinking. Of the five diamine AEMs, all but the DABCO AEM had significantly reduced WU% and three had significantly improved permselectivities compared to the previously synthesised monoamine RIG AEMs. However, improved permselectivity was achieved at a high cost; the conductivity of the most selective diamine AEM (TMHDA, 94% permselectivity) was eight times lower than the best
performing pyridine functionalised monoamine AEM (Chapter 4). Calculations of theoretical gross power density of diamine AEMs paired with various commercial and literature CEMs estimated their RED performance to be only marginally improved from that of previous monoamine RIG AEMs. The highest performing diamine AEM predicted an average power density of 1.8 W m⁻².

Whereas the prior monoamine RIG AEMs were predicted to produce relatively poor theoretical power densities due to high conductivities but low permselectivities, the crosslinked diamine AEMs appear to have the opposite problem. The aim of finding a trade-off compromise between the two parameters through crosslinking was therefore not met and it appeared that where crosslinking did take place, the balance between conductivity and permselectivity moved too far in favour of the latter. Future work may be to ‘fine-tune’ the degree of crosslinking in the RIG AEMs. Perhaps by simultaneously incorporating TMHDA head-groups into PYR or trimethylamine (TMA) functionalised AEMs, there is potential to produce a 75% or 80% crosslinked AEM as opposed to 100% crosslinked analogue. This could be achieved by simply adding a percentage of TMHDA to a TMA aminating solution or by short pre-treatment of TMHDA followed by a more extensive reaction with TMA. If proven successful, it could potentially be possible to progressively decrease permselectivity and increase conductivity until an ideal trade-off position is found.
6. Crosslinked Cation-Exchange Membranes via Radiation Induced Grafting; Evaluation for Application in Reverse Electrodialysis

6.1 Introduction

Initial attempts to produce cation-exchange membranes (CEMs) for reverse electrodialysis (RED) by radiation induced graft co-polymerisation (RIG) were detailed in Chapter 3. This involved the grafting of styrene or styrenic monomers to either poly(ethene-co-tetrafluoroethene) (ETFE) or (poly)vinylidene fluoride (PVDF) with subsequent functionalisation where necessary. With regard to RED application, several RIG CEMs were estimated to yield theoretical gross power densities, calculated via the RED model equations (Eqn. 1, Eqn. 2), that were higher than for commercially available Neosepta® CMX. The experimentally determined permselectivities recorded for the RIG CEMs were, however, substantially lower than required for RED (≥90%). In contrast, the RIG CEMs possessed some of the lowest area resistances reported to date for RED specific CEMs (although there is some variance with literature values due to the different experimental methods used to obtain the area resistance).

Subsequent to the research into RIG CEMs in Chapter 3, two key observations regarding the properties of RIG ion-exchange membranes (IEMs) have been made. Firstly, when considering the properties for the mechanism of ion transport within the membrane phase, conductivity should also be considered alongside area resistance [29] [33] [86]. Previous chapters have demonstrated a good correlation between permselectivity and conductivity but such a relationship between permselectivity, and area resistance, is not always present. This is because conductivity is an intrinsic property and unlike area resistance is not effected by the thickness or size of an IEM sample. Secondly, an inverse relationship is observed between permselectivity and conductivity where increasing one reduces the other. This is attributed to conflicting effects of conductivity and Donnan exclusion, both of which appear to be dependent on water content in the membrane phase [34].
Previous attempts to find a trade-off between conductivity and permselectivity properties in RIG AEMs by implementing crosslinking were of limited success. Bi-functional tertiary diamines were incorporated as anion-exchange head-groups that could crosslink the grafted poly(3/4-vinylbenzyl chloride) chains, resulting in the simultaneous induction of two ammonium anion-exchange sites per head-group and a degree of crosslinking. Although permselectivities up to 95% were achieved for the highly crosslinked diamine AEMs, the ionic conductivity penalty was too high (conductivities as low as 3.4 mS cm\(^{-1}\) were recorded). For RIG to be successful in producing IEMs for RED a better compromise between ion transport properties is required.

With respect to CEMs, a recent review paper on RIG reports wide utilisation of simultaneous crosslinking and RIG of styrene to produce crosslinked CEMs (for proton-exchange membranes) for fuel cells [102]. The two most common crosslinking agents used were divinyl benzene (DVB) and bis(vinyl phenyl)ethane (BVPE) which, along with styrene, are grafted onto a number of fluorinated and partially fluorinated precursor polymer films. A subsequent sulfonation step, typically carried out with HSO\(_3\)Cl, results in crosslinked CEMs. Holmberg et al. produced PVDF based CEMs from RIG of styrene and varying amounts of either DVB or BVPE crosslinking agent [112]. It was observed that the hydrated swelling degrees decreased with increasing amounts of crosslinking agent: BVPE at 10 mol% produced the smallest swelling degree. Unfortunately, no other RED specific values were reported, although the authors noted that the DVB crosslinked CEMs were more brittle than those crosslinked with BVPE. Gubler et al. produced very thin crosslinked CEMs by grafting styrene and 10 mol% DVB into 25 \(\mu\)m fluorinated ethylene propylene (FEP) films [113]. The resultant CEMs possessed IECs of around 1.3 mmol g\(^{-1}\) and proton conductivities of more than 40 mS cm\(^{-1}\). DVB and BVPE crosslinking agents have also been incorporated into ETFE based poly(styrene) graft co-polymers [114]. 0–23 vol% DVB and 0–67 vol% BVPE were grafted into 50 \(\mu\)m ETFE films along with styrene. Proton conductivities for the 9 vol% BVPE CEM were reported to be as high 200 mS cm\(^{-1}\), although the water uptake by mass (WU%) was high at around 80%. The proton conductivities when using DVB crosslinking agent were considerably lower. RIG CEMs based on poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) and DVB crosslinking agent yielded IECs up to 2.0 mmol g\(^{-1}\), WU% values below 40% and proton conductivities over 100 mS cm\(^{-1}\) by incorporating 10% (v/v) DVB into the styrene grafting solution.
Although no permselectivity data is reported, the above literature has demonstrated that WU% can be reduced by crosslinking RIG IEMs with DVB and BVPE; the previous chapter also showed that crosslinked IEMs with lower WU% tend towards higher permselectivities. By incorporating crosslinking agents in the grafting step of the synthesis rather than in the final functionalisation step, it is more simple to modify the extent of crosslinking by varying the percentage of crosslinking agent used. Given the conductivity data obtained from the literature, and previous observations regarding permselectivity and crosslinking, this additional level of control may lead to an ideal compromise between conductivity and permselectivity.

As is often the case with RIG CEMs, the focus of the prior literature studies has been the production of RIG CEMs for application in fuel cells (PEMs). Therefore, the evaluation of CEMs produced in these studies has not included data that is more relevant to RED (permselectivity and Na⁺ conductivity). The aims and objectives of this chapter are therefore to develop a series of RIG CEMs with varying degrees of crosslinking, using either DVB or BVPE crosslinking agents, and to determine their suitability for RED application. Crosslinked RIG CEM characterisation was performed using Raman and NMR spectroscopies and the mathematical RED model was used to estimate the theoretical gross power density obtainable in a RED stack from the experimentally determined properties of the bulk CEMs.

6.2 Experimental

For the CEMs synthesised in this chapter, full and detailed descriptions of synthetic methods are presented in Chapter 2. To summarise, styrene and divinyl styrenic crosslinking agents (DVB, BVPE) were co-grafted onto 50 µm thick ETFE films with an area of 130×130 mm and irradiated to a total absorbed dose of 30 kGy using a 5 MeV electron accelerator. Irradiated ETFE films were initially stored under solid CO₂ (for transport to the laboratory) before being transferred to a -40°C freezer for longer-term storage. Prior to grafting reactions, the pre-irradiated films were rolled between single-ply tissue paper and submerged in monomer grafting solutions. The solutions contained styrene:toluene (2:3) and 0, 2.5, 5 or 10 mol% of either DVB or BVPE crosslinker. The solutions were purged with N₂ for 1 h and then heated at 70°C for 8 h. On completion, the grafted films were washed with toluene.
before drying in a vacuum oven at 70°C for 5 h. The styrenic monomer grafted ETFE films were then sulfonated by placing them into a 5% chlorosulfonic acid solution in DCM (v/v) at ambient temperature for 2 h. The sulfonated CEMs were washed several times and then boiled in ultra-pure deionised water for 1 h to assume a fully hydrated form.

Scheme 4 - General reaction scheme for pre-irradiation grafting and subsequent sulfonation for non-crosslinked CEM (blue) and DVB (orange) or BVPE (green) crosslinked RIG CEMs.
The BVPE crosslinking agent was synthesised via a Grignard self-coupling of 4-VBC. 4-VBC was added dropwise to an evacuated round bottom flask containing Mg turnings and dry THF at -10°C. The reaction was kept at 0°C and allowed to continue overnight. On completion, excess Mg was removed by filtration and the THF solvent removed under vacuum. The resulting residue was dissolved in DCM and washed with HCl (6%), deionised water and brine. The organic phase was then dried over MgSO₄ and recrystallised from hot MeOH to yield solid crystalline BVPE.

6.3 Results and Discussion

The focus of the work in this final experimental chapter is to synthesise crosslinked CEMs and evaluate them for their suitability for RED. Two series of crosslinked CEMs were synthesised by incorporating varying concentrations of either DVB or BVPE into styrene grafted ETFE thin films followed by a subsequent sulfonation step. As all crosslinked RIG CEMs share a common synthetic route, CEM designation nomenclature refers simply to the type and concentration of crosslinking agent present, e.g. BVPE 5% is therefore ETFE-g-poly(styrene sulfonate) with 5 mol% BVPE crosslinking agent present in the graft solution (although not necessarily present in the final CEM). Using the previous methodology, a styrene sulfonate based RIG CEM containing 0 mol% was produced and used as a standard for comparison with both crosslinked CEMs. Structural data for the crosslinked CEMs was obtained using Raman and solid state nuclear magnetic (SS-NMR) spectroscopies. The RED mathematical model (Ch 1) was used to determine theoretical gross power densities in a RED cell. With the exception of IEC which is determined via acid/base titration with the CEM under investigation in a H⁺ form, all CEM characterisation techniques were performed with the CEMs in the Na⁺ counter-ion form most relevant to RED.

6.3.1 Characterisation of the synthesis of BVPE via ¹H and ¹³C NMR spectroscopy

¹H and ¹³C solvent phase NMR was used to determine the successful synthesis of BVPE crosslinking agent (Figure 87).

¹H NMR (CDCl₃ with 1.0% v/v TMS, 500.13 MHz): δ_H 7.38 (2H, d, J = 7.8 Hz, HA’), δ_H 7.18 (2H, d, J = 7.9 Hz, HB’), δ_H 6.75 (1H, dd, J = 17.6, 10.9 Hz, HC’), δ_H 5.76 (1H, d, J =
17.6 Hz, HD’), $\delta_H$ 5.25 (1H, d, J = 10.9 Hz, HE’), $\delta_H$ 2.95 (2H, s, HF’). $^{13}$C NMR (CDCl$_3$, 125.76 MHz): $\delta_C$ 141.3 (Ca’), $\delta_C$ 136.6 (Dept – CH, Cb’), $\delta_C$ 135.3 (Cc’), $\delta_C$ 128.6 (Dept – CH, Cd’), $\delta_C$ 126.1 (Dept – CH, Ce’), $\delta_C$ 113.0 (Dept – CH$_2$, Cf’), $\delta_C$ 37.5 (Dept – CH$_2$, Cg’).

Figure 87 – $^1$H and $^{13}$C NMR spectrum of the BVPE crosslinking agent (from Grignard coupling of 4-VBC).
6.3.2 Structural characterisation by Raman spectroscopy of crosslinked RIG CEMs

Raman spectra were recorded with a 532 nm (green) laser on a DXR Raman Microscope using a 50× objective using a 50× objective producing an estimated laser spot size of 1 µm. Raman spectra for each CEM was each CEM was recorded as an average of 16 scans over the range 3200–250 cm⁻¹. Due to excessively high excessively high levels of interferent fluorescence when attempting to obtain the Raman spectra of the final spectra of the final sulfonated CEMs

Figure 88 and

Figure 89 present the Raman spectra for the grafted intermediate films only. Each figure displays superimposed spectra for the 0% standard and the 2.5, 5 and 10 mol% crosslinked analogues. The ETFE base film used is the same as that reported in the previous chapters and therefore the Raman spectra of ETFE base film is omitted from these figures for clarity. The depicted range is 1750–500 cm⁻¹ as little structural information is present outside this range. However, the full and complete spectra can be found in the appendices. For illustrative purposes, all spectra are normalised to the intensity of the -CF₂ peak of the ETFE base film (835 cm⁻¹). Raman spectra of DVB and BVPE reagents are presented to help clarify the presence of crosslinking agent peaks in the spectra of the final RIG CEMs.

As is expected considering the structures of both crosslinking agents, the Raman spectra for all crosslinked RIG CEMs are similar to that of the 0% non-crosslinked standard. For each individual spectrum, the only significant base film peak(-CF₂) is present at 835 cm⁻¹. The addition of styrene in the grafted intermediate materials is confirmed by the introduction of several new peaks, relative to the ETFE base film. As observed with earlier RIG CEMs, peaks indicative of the styrene aromatic ring structure are present throughout the spectra: 1602 cm⁻¹ is an aromatic C=C stretching peak and the peak at 1032 cm⁻¹ caused by C-H in-plane bending of the aromatic ring. A prominent diagnostic peak at 1001 cm⁻¹ is typical of aromatic ring breathing, though recall that this peak is not present in 1,2 and 1,4 di-substituted benzene rings [79]. Interestingly the height of this peak changes significantly dependant on the percentage crosslinking agent present in the grafting solution.

In the amassed spectra for the series of DVB crosslinked CEMs the height of the peak at 1001 cm⁻¹ decreases with increasing concentration of DVB crosslinking agent and the peak height for 0% DVB is closer to that of DVB 10% (and not DVB 2.5% as one might expect). This can be explained by a new peak at 1629 cm⁻¹ present in the spectra of DVB reagent
(Figure 90) and the spectra of all DVB crosslinked CEMs but not in the spectra of the 0% DVB CEM.

Figure 88 – Raman spectra of graft intermediate ETFE-poly(styrene) based co-polymer films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% DVB. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.

Figure 89 – Raman spectra of graft intermediate ETFE-poly(styrene) based co-polymer films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% BVPE. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.
The trend observed for the height of this peak is the opposite to the peak at 1001 cm\(^{-1}\) and it increases with increasing DVB concentration. The technical grade DVB supplied by Aldrich contains a mixture of meta- and para- isomers which are typically present in a 2:1 ratio [115]. This new peak is characteristic of para- di-substituted aromatic compounds [116], and is therefore present in the spectrum of the DVB reagent and not styrene (as styrene is only mono-substituted). For CEMs containing DVB, the diagnostic para- aromatic peak (1629 cm\(^{-1}\)) increases in height with increasing percentage of DVB crosslinking agent, demonstrating an increased amount of DVB present in the grafted material. The decrease in peak height at 1001 cm\(^{-1}\) with increasing DVB concentration suggests that increasing DVB grafting results in less styrene grafting overall; however, at lower concentrations DVB reagent appears to improve styrene grafting relative to the 0% crosslinked standard. Due to their structural similarities, differentiation between the two grafting reagents in the spectra of the grafted materials can be difficult. DVB meta- isomers present in the grafted material also contribute towards peak intensity at 1001 cm\(^{-1}\) hence the comparable peak height at 1001 cm\(^{-1}\) in both 0% and 10% grafted analogues.

Figure 90 – Raman spectra of liquid DVB crosslinking reagent (mixture of 1,3- and 1,4-isomers).

Consistent with the DVB intermediate materials, the spectra of the BVPE reagent (Figure 91) and grafted intermediate materials also demonstrate a para- aromatic peak at 1629 cm\(^{-1}\) (magnified in Figure 89). As before with DVB this peak increases in height consistently with increasing BVPE concentration. The height of the diagnostic styrene peak at 1001 cm\(^{-1}\) also increases with increasing BVPE concentration. Unlike DVB, the BVPE reagent doesn’t contribute any
intensity to the peak at 1001 cm$^{-1}$, because the BVPE crosslinking agent is synthesised from isomerically pure 4-VBC and is therefore only present in the \textit{para}- isomer. The entirety of the 1001 cm$^{-1}$ can therefore be attributed to the grafted styrene present in the intermediate material and not the BVPE crosslinking agent. The increase in peak intensity therefore indicates more styrene present in the grafted intermediate material, suggesting that the BVPE reagent is somehow ‘boosting’ the overall grafting reaction.

Figure 91 – Raman spectra of crystalline BVPE crosslinking reagent (from Grignard coupling of 4-VBC).

6.3.3 Structural characterisation by SS-NMR spectroscopy of crosslinked RIG CEMs

$^{13}$C SS-NMR was used to confirm graft co-polymerisation and sulfonation, because the ETFE base film used is identical to that in several of the previous chapters, its spectrum has been omitted for clarity.

Figure 92 and Figure 93 show the $^{13}$C SS-NMR spectra for DVB, BVPE and the 0% standard pre-sulfonated films. As one would expect, the spectra closely resemble each other and that of the ETFE-g-poly(styrene) intermediate material presented in Chapter 3. Signals in the aliphatic spectral region at $\delta_C = 21.0$ and $\delta_C = 40.7$ arise from the -CH$_2$CF$_2$- of the ETFE backbone and the aliphatic backbone chains of the grafted poly(styrene) respectively. Three aromatic carbon signals are present downfield: $\delta_C = 119.0$ corresponds to CHs in position 4
on the styrene ring, $\delta_C = 128.0$ corresponds to CHs in aromatic positions 2,3,5,6, and $\delta_C = 146.0$ corresponds to the quaternary $\text{C}_R_4$. On comparison of the signal intensity for the DVB crosslinked materials, it appears that the total degree of grafting decreases with increasing DVB concentration. The highest degree of grafting appears to occur in DVB 2.5% and the lowest in DVB 10%. The opposite trend is observed for the BVPE crosslinked material and comparison of the signal intensities for the aromatic peaks appears to demonstrate an increase in overall grafting with increasing BVPE concentration. The BVPE 10% intermediate appears to exhibit the highest degree of grafting whereas BVPE 2.5% intermediate is comparable, if not marginally lower, than the 0% standard non-crosslinked intermediate material.

Figure 92 – $^{13}$C SS-NMR spectra of graft intermediate ETFE-poly(styrene) based films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% DVB. All spectra are normalised to base film signal $\delta_C = 22$ for presentation purposes.

Figure 93 – $^{13}$C SS-NMR spectra of graft intermediate ETFE-poly(styrene) based films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% BVPE. All spectra are normalised to base film signal $\delta_C = 22$ for presentation purposes.
$^{13}$C SS-NMR spectra for the final, sulfonated, CEMs are presented in Figure 94 and Figure 95 respectively. Successful sulfonation is evidenced by the appearance of a new aromatic signal at $\delta_C = 141.0$ indicative of $\text{CR}_3\text{S}$ in both DVB and BVPE CEMs. The intensity of the sulfonate signal follows the trends observed for grafting in their respective intermediate films. Where, for DVB crosslinked CEMs the signal intensity decreases with increasing DVB concentration, the opposite is observed for the BVPE crosslinked CEMs.

![Figure 94 - $^{13}$C SS-NMR spectra of DVB crosslinked RIG CEMs E synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% DVB. All spectra are normalised to base film signal $\delta_C = 22$ for presentation purposes.](image1)

![Figure 95 - $^{13}$C SS-NMR spectra of DVB crosslinked RIG CEMs E synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% BVPE. All spectra are normalised to base film signal $\delta_C = 22$ for presentation purposes.](image2)
6.3.4 Effect of crosslinking agent concentration on bulk properties of crosslinked RIG CEMs

The key variable under investigation for the synthesis of the crosslinked RIG CEMs in this chapter is the concentration of crosslinking agent, either DVB or BVPE, present in the grafting solution. The amount of crosslinking agent present during graft co-polymerisation is expected to directly affect the degree of crosslinking, and therefore the bulk chemistry, of the resultant CEMs. Due to the varying kinetics of the multiple free radical polymerisation reactions taking place during the grafting reactions, the degree of crosslinking in the grafted intermediate co-polymer is not necessarily consistent with the composition of the grafting solutions. Although Raman spectra for DVB and BVPE crosslinked intermediate films do demonstrate one key peak unique to the crosslinking agent, the ratio of isomers in the stock DVB and VBC reagents means a firm conclusion is not possible. Hence the assumption was made that the degree of crosslinking increases with increasing concentration of crosslinking agent present in the grafting solution.

Recall that the IEC is the most fundamental bulk property of any RIG IEM as it is a direct measurement of the amount of functionality. Assuming 100% sulfonation of the grafted intermediate films, the IEC is also a firm indication of the degree of grafting overall. Figure 96 demonstrates the effect of concentration of crosslinking agent on the IEC of RIG CEMs. Firstly, to note, the IEC of the non-crosslinked standard (0%) is considerably lower than that achieved for RIG CEMs synthesised using similar grafting solution composition in Chapter 3. This is because of the reduced grafting times needed to control the homopolymerisation (non-ETFE bound polymers) side reactions observed with the addition of crosslinking agents; 0% crosslinked CEM grafting reaction was therefore limited to the same reaction times to enable a proper comparison. For the BVPE CEMs, IEC shows an increase with increasing percentage of crosslinking agent between 0–5% and plateauing between 5–10%. A different trend is observed for the DVB crosslinked CEMs: the initial inclusion of 2.5% DVB to the grafting solution results in an increase in IEC >0.5 mmol g⁻¹ (relative to 0% analogue). But further addition of crosslinking agent in the grafting solution led to the IEC decreasing. Assuming 100% sulfonation, this is consistent with the structural analysis carried out via Raman and SS-NMR. The available literature concerning RIG of styrene and crosslinking agents into ETFE films demonstrates similar trends with IECs for DVB CEMs consistently decreasing and BVPE CEMs increasing to a point before falling at higher BVPE
concentrations [114]. The highest IECs determined for the CEMs in each series are 2.57 and 3.07 mmol g\(^{-1}\) for DVB and BVPE crosslinked CEMs respectively. These values are comparable to earlier RIG CEMs, where the non-crosslinked E-STY-30 CEM produced in Chapter 3 yielded an IEC of 2.46 mmol g\(^{-1}\). However, E-STY-30 was ultimately found unfit for purpose as a RED CEM due to a high WU\% (>50%). As the IECs of the crosslinked CEMs are comparable to the previous non-crosslinked RIG CEMs, any improvement in performance will surely be dependent on their ability to restrict WU%.

![Graph showing the effect of crosslinking agent concentration on the IEC of crosslinked RIG CEMs.](image)

**Figure 96** – The effect of crosslinking agent concentration (in the grafting solution) on the IEC of crosslinked RIG CEMs. Error bars represent standard deviation \(n \geq 3\) samples of each CEM.

The gravimetric WU\% of the crosslinked CEMs is presented in Figure 97. As expected, the DVB crosslinked RIG CEMs demonstrate a reduction in WU\% with increasing percentage of DVB. The WU\% for 0% crosslinking agent (42%) falls to as low as 15% when 10 mol\% DVB is present in the grafting solution. Although firm quantitative analysis regarding the degree of crosslinking was not possible for DVB CEMs, the Raman spectra did demonstrate an increase of crosslinking with increasing DVB concentration. The apparently higher degree of CEM crosslinking results in a physical restriction of water from the CEM bulk and ultimately lower WU%. The trend observed for BVPE CEMs is more complex, initially WU\% increased with increasing BVPE concentration (0–5%) before falling again when
10 mol% BVPE is present in the grafting solution. For the previous non-crosslinked RIG CEMs, WU% was found to be indicative of IEC (generally higher IECs resulted in higher WU%). The crosslinked BVPE CEMs for the most part follow the same trend except at high BVPE concentration, which may indicate a critical point where crosslinking effect becomes a more significant factor over the general degree of grafting. With the exception of BVPE 5% all crosslinked CEMs demonstrate a reduction in WU% compared to earlier non-crosslinked RIG CEMs.

The conductivities of the crosslinked CEMs are presented in Figure 98. A comparison with WU% (Figure 97) demonstrates similar trends. The conductivities of DVB 5% and DVB 10% CEMs fall below 10.0 mS cm\(^{-1}\) and, as discussed for the TMHDA AEM in the previous chapter, are unlikely to be conductive enough for RED application. At the opposite end of the scale, BVPE 5% has a conductivity of 26.9 mS cm\(^{-1}\) which is comparable to the non-crosslinked CEMs synthesised previously. DVB 2.5%, BVPE 2.5%, BVPE 10% and even the 0% standard CEM possess values that show potential as RED CEMs (or at the very least some improvement on earlier attempts to produce RED specific CEMs via the RIG method).
6.3.5 IEC, conductivity and WU% property relationships for crosslinked RIG CEMs

The effect of IEC on WU%, conductivity, permselectivity and area resistance, for the crosslinked CEMs and 0% crosslinked standard are presented in Figure 99. The effect of IEC on WU% and ionic conductivity (Figure 99 A and B) is consistent with the effect of percentage crosslinking agent previously. For DVB CEMs the WU% and conductivity increase with increasing IEC whereas BVPE 10% again goes against the trend and has lower WU% and conductivity than both the BVPE 2.5% and BVPE 5% CEMs despite possessing a higher IEC.

No simple relationship is observed between IEC and permselectivity for the crosslinked CEMs (Figure 99-C). This is because permselectivity is related to Donnan factors which are dependent on the fixed charge concentration of ionic groups in an IEM bulk and the concentration of electrolytes in the membrane phase (affected by both IEC and WU%) [98]. For both groups of crosslinked CEMs, the mid-range 5% analogues are considerably less selective when compared to their counterparts. Although it has been established in the previous chapters that permselectivity and conductivity (not area resistance as suggested by
the relevant literature [28] [34]) are the fundamental properties regarding ion transport through the membrane phase in the RED process, area resistance still needs to be considered as it is a key factor in the RED model equation. Figure 99-D demonstrates the familiar trend for the relationship between IEC and area resistance, where the area resistance has an inverse relationship with conductivity. The margin of error however, particularly of DVB 10%, is high even for this method, making it difficult to draw firm conclusions. The BVPE CEMs plainly have lower area resistances than the DVB CEMs.

Figure 99 – The effect of IEC on bulk AEM properties for the crosslinked CEMs (and non-crosslinked 0% standard CEM): A. WU%, B. Conductivity, C. Permselectivity and D. Area Resistance. Error bars represent standard deviation n ≥ 3 samples for each CEM (n = 3 measurements for permselectivity).

The effect of conductivity on fundamental RED model parameters is presented in Figure 100. In previous chapters an inverse relationship was observed where IEMs with high ionic conductivity tend to be less permselective. Considering the entire range of crosslinked CEMs (including the 0% crosslinked standard) permselectivity surprisingly does not show any clear
relationship with conductivity for crosslinked CEMs. Previously, when considering the permselectivity of RIG IEMs, good correlation was observed between permselectivity and conductivity. This is not the case for the DVB CEMs where DVB 5% is over 20% less permselective than its 10% DVB analogue despite possessing comparable ionic conductivities (6.4 & 4.1 mS cm$^{-1}$). This further suggests that crosslinking effects become more prominent as higher concentrations of crosslinking agent are present. The effect of conductivity on area resistance is the more familiar inverse relationship for each crosslinked CEM series. It should be noted that experimental values for conductivity and area resistance for certain CEMs possess high levels of imprecision meaning firm conclusions are not possible at this stage.

![Figure 100](image)

Figure 100 – The effect of conductivity on: A. Permselectivity and B. Area resistance for the crosslinked CEMs (and non-crosslinked 0% standard CEM). For illustrative purposes area resistances for BVPE CEMs are plotted on the right y-axis. Error bars represent standard deviation n ≥ 3 samples for each CEM (n = 3 measurements for permselectivity).

The effect of WU% on RED properties of crosslinked CEMs is presented in Figure 101. The purpose of utilising styrenic crosslinking agents was to improve the bulk properties by physically restricting the amount of water exploiting the apparent permselectivity/conductivity trade-off relationship present in IEMs. For both series of crosslinked CEMs, permselectivity increases with decreasing WU%, the exception being DVB 5% which is significantly less permselective despite possessing a low WU%. The permselectivity recorded for DVB 5% is surprisingly low given its low WU% and conductivity values. Considering the property values obtained for the DVB CEMs and the trend observed with
the BVPE series, one would expect a more consistent trend and the positioning of DVB 5% may indicate an anomalous result.

Other than DVB 5%, the observed trend is consistent with the behaviour of the diamine crosslinked RIG AEMs (Chapter 5) and literature examples [114] [117]. Area resistance also demonstrates a strong correlation with WU% where CEMs become less resistive with increased WU%. As previously discussed in detail, both permselectivity and area resistance are dependent on ion transport and are therefore affected by the concentration of ionic species in the polymer bulk. The two properties share an inverse relationship to each other, which is affected by IEM water content [34]. Permselectivity is governed by Donnan exclusion through repulsion of like charges and is dependent on the number of fixed charged groups present in the bulk [98]. Conductivity is dependent on the concentration and mobility of ions present in the membrane phase and directly affects the area resistance [84]. Regarding the trade-off between the two parameters, DVB 2.5% and BVPE 10% CEMs appear promising as both possess low area resistances (<0.6 Ω cm²) and relatively high permselectivities (≥ 89%). These values are comparable to current literature benchmarks for RED focused IEMs [86].

Figure 101 – The effect of WU% on: A. Permselectivity and B. Area resistance for the crosslinked CEMs (and non-crosslinked 0% standard CEM). For illustrative purposes area resistances for BVPE CEMs are plotted on the right y-axis. Error bars represent standard deviation n ≥ 3 samples for each CEM (n = 3 measurements for permselectivity).
6.3.6 $C_{\text{fix}}$, permselectivity and area resistance property relationships of crosslinked RIG CEMs

Excess H$_2$O effectively dilutes the concentration of fixed charged groups in the bulk and increased WU% results in fewer fixed charge groups being present per gram of sorbed H$_2$O (when comparing IEMs with the same IEC). Theoretically for RIG CEMs in an aqueous electrolyte, a lower $C_{\text{fix}}$ means that less co-ions are repelled resulting in lower permselectivities. A high $C_{\text{fix}}$ value is therefore generally considered to be a positive property for RED IEMs. Previously synthesised RIG IEMs with a high $C_{\text{fix}}$ (around 10 mmol g$^{-1}$ H$_2$O) have been highly permselective, as high as 94% co-ion exclusion in some cases, although by consequence have possessed very high area resistance ($\geq 2.0$ Ω cm$^2$). The exact reason for this remains unclear; IEM conductivity is proportional to the concentration of mobile counter-ions in the membrane phase, a higher $C_{\text{fix}}$ correlates to a higher concentration of mobile counter-ions and therefore one would expect the area resistance to be lower for a IEMs with high $C_{\text{fix}}$. A possible explanation is that conductivity is also a factor of counter-ion mobility which is in turn effected by the IEM water content. The previous RIG AEMs with high $C_{\text{fix}}$ and area resistance also possessed low WU% (ca. 12%), it is therefore possible that IEM water content was too low for effective ion-mobility which resulted in the high area resistance values observed.

Figure 102 – The effect of charge density on: A. Permselectivity and B. Area resistance for the crosslinked CEMs (and non-crosslinked 0% standard CEM). For illustrative purposes area resistances for DVB CEMs are plotted on the right y-axis. Error bars represent standard deviation $n \geq 3$ samples for each CEM ($n = 3$ measurements for permselectivity).
The relationship of $C_{\text{fix}}$ and key RED properties for crosslinked CEMs are presented in Figure 102. Except for the DVB 5% CEM, the crosslinked CEMs are generally more permselective at higher $C_{\text{fix}}$. DVB 10% has the highest recorded $C_{\text{fix}}$ and permselectivity at 10.4 mmol g$^{-1}$ H$_2$O and 97%, respectively, although similar to the highly crosslinked TMHDA RIG AEM in Chapter 5, this CEM possesses an area resistance greater than 2.0 Ω cm$^2$. DVB 2.5% and BVPE 10%, despite possessing considerably lower $C_{\text{fix}}$ values at 5.5 and 4.3 mmol g$^{-1}$ H$_2$O, were determined to possess respectable permselectivities of 89 and 92%. As stated above, both RIG CEMs possess area resistances ca. 0.6 Ω cm$^2$. This is higher than for the first generation non-crosslinked ETFE-g-poly(styrene) based CEM by ca. 0.2 Ω cm$^2$ although pin possession of considerably higher permselectivities.

6.3.7 Theoretical RED gross power density of crosslinked RIG CEMs

The theoretical gross power density for crosslinked RIG CEMs and 0% standard RIG CEM is considered against their bulk properties in Figure 103. Theoretical gross power density (W m$^{-2}$) was calculated using the RED model (Eqn. 2). None of the properties demonstrate simple relationships but higher theoretical power densities are obtained for CEMs with high IEC and conductivity, moderate WU% and $C_{\text{fix}}$, high permselectivity and low area resistance. Neither is there a simple relationship between theoretical power density and the degree of crosslinking (concentration of crosslinking agent).

The highest theoretical gross power density belongs to BVPE 10% at 5.99 W m$^{-2}$, closely followed by DVB 2.5% and BVPE 5% at 5.55 and 5.42 W m$^{-2}$ respectively. These theoretical values for power densities are significantly higher than those calculated for the first-generation non-crosslinked RIG CEMs as well as commercially available and research literature CEMs [33]. The literature benchmark CEM, SPEEK 65, yields a theoretical power density of 4.31 W m$^{-2}$, while commercial Neosepta® CMX yields 3.29 W m$^{-2}$. BVPE 5% yields a respectable theoretical power density despite possessing a permselectivity reduction of 9% relative to BVPE 10% homologue; this is due to its area resistance being half that of BVPE 10%. For RIG to yield effective RED IEMs, a target IEM possessing ≥90% permselectivity with area resistance remaining at around ≤ 1.0 Ω cm$^2$ would need to be reached. BVPE 10% achieves this target and as such yields the highest theoretical power density to date, DVB 2.5% falls just outside the target range at 89% permselectivity but even
so has power density close to that of BVPE 10%. One major advantage DVB 2.5% has over BVPE 10% is the low cost and availability of reagents. DVB is not only readily available but 7.5 mol% less reagent is required, compared to BVPE, to yield comparable CEMs.

Figure 103 – Effect of bulk AEM properties on theoretical gross power density of crosslinked CEMs calculated using Eqn. 2 (single IEM model). A. IEC. B. Conductivity, C. WU%, D. Cfix, E. Permeability, and F. Area resistance. Error bars represent standard deviation n ≥ 3 samples for each CEM (n = 3 measurements for permeability).
Theoretical gross power density calculations were also carried out for AEM/CEM pairs as they would be under conditions in an operational RED stack. The crosslinked CEMs and 0% crosslinked CEM standard were modelled alongside the literature AEMs PECH B2, commercial Neosepta® AFN and RIG TMHDA AEM. The parameters of the theoretical RED stack are consistent with those used previously and consist of concentrated (0.5 mol dm$^{-3}$ NaCl) and dilute (0.05 mol dm$^{-3}$ NaCl) solution compartments separated by 150 µm thick spacers at 25°C. Experimental values for bulk properties of AFN and PECH B2 AEMs were obtained from the literature [33]. The theoretical gross power densities of each AEM/CEM pair are considered vs. the RED parameters permselectivity and area resistance (Figure 104).

![Graphs showing theoretical gross power density vs. permselectivity and area resistance](image-url)

Figure 104 – Effect of CEM permselectivity and area resistance on the theoretical gross power density of crosslinked RIG CEMs; DVB, A and B, and BVPE, C and D, modelled in conjunction with AEMs; Neosepta® AFN, literature PECH B2 and RIG AEM TMHDA. Error bars represent n = 3 samples (n = 3 measurements for permselectivity).
As expected based on the single CEM RED model calculations, the highest performing CEM is BVPE 10% closely followed by DVB 2.5%. Both crosslinked CEMs achieve highest theoretical power density when paired with commercial AEM Neosepta® AFN: 2.81 and 2.71 W m$^{-2}$ for BVPE 10% and DVB 2.5% respectively. These values represent the highest theoretical power densities obtained for an AEM/CEM pair in this thesis and represents an improvement over the first-generation non-crosslinked E-STY-30/AFN pairing and the literature benchmark SPEEK65/AFN pairing.

The RED model is useful as a screening tool to assess the suitability of an experimental IEM for RED before time consuming and specialised RED cell testing is undertaken. It is however limited by its simplicity and typically overestimates the RED power density of IEM pairs [33]. The next step for these second-generation, crosslinked RIG CEMs is therefore actual RED testing, carried out alongside commercial AEMs to fully access their RED functionality in an operational RED stack. Given the availability and cost effectiveness of DVB reagent and only a 0.1 W m$^{-2}$ reduction in theoretical output relative to BVPE 10%, DVB 2.5% should be immediately put forward for RED testing.

### 6.4 Chapter Summary

The main aim of the work carried out in this chapter was to evaluate the effectiveness of styrenic crosslinking agents to boost the reverse electrodialysis (RED) relevant properties of cation-exchange membranes (CEMs) synthesised via radiation induced grafting copolymerisation (RIG). Previous non-crosslinked CEMs produced via RIG (Chapter 3) possessed water uptakes (WU%) in the region of 50% resulting in highly conductive CEMs but with poor permselectivity. It was hypothesised that crosslinking the grafted co-polymer chains would physically restrict the WU% enough that an acceptable compromise between conductivity and permselectivity could be achieved. Prior literature examples had provided evidence that incorporating divinyl benzene (DVB) and bis(vinyl phenyl)ethane (BVPE) crosslinking agents into poly(styrene sulfonate) based CEMs reduced water uptake (WU%) and conductivity. Example CEMs in the literature were typically intended for use in fuel cells and therefore focused on proton conductivity rather than RED relevant Na$^+$ conductivity, and neglected RED specific properties such as permselectivity.
Two series of crosslinked CEMs were produced with varying degrees (mol%) of crosslinking agents (DVB or BVPE) present during the graft reaction. Almost all crosslinked CEMs demonstrated lower WU% relative to earlier first generation non-crosslinked RIG CEMs with a select few achieving this with a minimal negative impact on ionic conductivity. Amongst such CEMs, the BVPE 10% and DVB 2.5% examples were the most promising. Conductivity for both CEMs was ca. 16.0 mS cm$^{-1}$ translating to area resistance values as low as 0.6 Ω cm$^2$. The theoretical gross power densities were 5.99 and 5.55 W m$^{-2}$ for single IEM RED model calculations and 2.81 and 2.71 W m$^{-2}$ for AEM/CEM pair calculations (paired with commercial Neospeta® AFN AEM). These are the highest theoretical values produced by any CEM, both in this thesis and in the literature (although techniques to determine bulk properties such as conductivity in literature vary in methodology).

This leads to the recommendation that BVPE 10% and DVB 2.5% be submitted for actual RED analysis to glean quantitative data on their actual RED functionality. Future works should also examine whether similar results can be obtained for AEMs by incorporating styrenic cross-linking agents into RIG AEM synthesis. If a highly functionalised, RED specific IEM pair can be produced, this would lead to world leading RED cell performance.
7. Conclusions and Future Work

Throughout this thesis radiation-induced grafting (RIG) has been utilised to produce a range of ion-exchange membranes (IEMs) from commercially available thin polymer films. Initial (non-crosslinked) poly(styrene sulfonate)-based RIG cation-exchange membranes (CEMs) yielded some of the lowest reported area resistances to date. However, they also possessed substantially lower permselectivities relative to literature examples, making them unsuitable for RED application. A conflicting trade-off relationship was observed between fundamental RED application properties, permselectivity and area resistance, where lower area resistance appeared to result in lower permselectivity. This relationship was rationalised by the effect of IEM water content on the dispersion of fixed charge groups; increased water content reduced the fixed charge density ($C_{fix}$), which in turn affects the ion-transport properties due to their complex inter-relationships.

To further study this relationship, a series of anion-exchange membranes (AEMs) were synthesised from a common intermediate but with varying head-group chemistries. Quaternary ammonium head-groups were selected in pairs with varying alkyl substituents to determine if increased hydrophobicity would reduce the AEM gravimetric water uptake (WU%). The results were somewhat inconclusive due to the difficulty of incorporating some of the larger head-groups into the bulk polymer and the resultant variation in ion-exchange capacities (IECs) meaning comparable degrees of quaternisation were not achieved for every head-group pair. However, the imidazolium head-groups did demonstrate a decrease in WU% with an additional methyl- substituent (1-methylimidazolium vs. 1,2-dimethylimidazolium) with almost no reduction in IEC. It is therefore suggested that imidazolium head-groups with increased alkyl substituents in position 2, such as 1-methyl-2-ethylimidazolium, 1-methyl-2-propylimidazolium and 1-methyl-2,3-propylimidazolium (Figure 105) be investigated for use as anion exchange head-groups in RED-focused AEMs. It was generally observed for the RIG AEMs that those with higher permselectivity possessed increased area resistance. Although permselectivity values recorded were a significant improvement on those of the non-crosslinked RIG CEMs, the area resistances were too high. The RIG AEMs failed to achieve theoretical power densities comparable to literature benchmark examples and were therefore deemed unsuitable for RED application.
Crosslinking of the grafted co-polymer chains was considered with the aim of physically restricting WU% to determine if an ideal ‘trade-off’ position between the conflicting ion-transport properties could be achieved for RIG AEMs. Tertiary diamine reagents were used as bifunctional crosslinking agents, with the intended purpose of simultaneous crosslinking the grafted polymer chains and the introduction of functional ammonium groups (to minimise any reduction in IEC). The results demonstrated that not all the diamine reagents led to significant crosslinking, from the range of diamine reagents used the longest linear diamine \( N,N,N',N'\)-tetramethylhexanediameine (TMHDA) and the predominantly unsterically hindered 1,4-diazabicyclo[2.2.2]octane (DABCO) exhibited the highest degrees of crosslinking. The TMHDA AEM demonstrated the highest permselectivity value of any IEM in this thesis (94%), although its high area resistance (2.4 \( \Omega \) cm\(^2\)) resulted in only a marginal improvement in theoretical gross power density compared to the previously synthesised non-crosslinked RIG AEMs.

Finally, crosslinked CEMs were synthesised by adding divinyl aromatic cross-linking agents, divinyl benzene (DVB) and bis(vinyl phenyl)ethane (BVPE), into the styrene grafting solutions, to introduce a degree of crosslinking during the grafting process. The crosslinking agents were then sulfonated, along with the grafted styrene chains, to yield CEMs with no reduction in IEC. The crosslinked RIG CEMs were synthesised from grafting solutions containing 0 – 10 mol% of either DVB or BVPE crosslinking agents. The DVB 2.5% and BVPE 10% CEMs demonstrated good permselectivity (ca. 90%) with only a minimal loss to area resistance relative to first-generation non-crosslinked CEMs (0.6 \( \Omega \) cm\(^2\) vs. 0.4 \( \Omega \) cm\(^2\) respectively). The theoretical RED gross power densities were the highest to date for a single IEM model at 5.6 and 6.0 W m\(^2\) for DVB 2.5% and BVPE 10% respectively, translating to theoretical RED gross power densities of 2.81 and 2.71 W m\(^2\) when paired with commercial Neosepta\textsuperscript{®} AFN (as in an actual RED cell) in the paired IEM model (Eqns. 2 and 1). These RED models are useful tools for the quick evaluation of the potential of IEMs for RED
application. However, these models are known to significantly overestimate the potential RED gross power density. It is therefore recommended that actual RED cell testing must be carried out for the DVB 2.5% and BVPE 10% crosslinked CEMs in a future study.

It should also be established whether DVB and BVPE crosslinking agents can be incorporated into the vinylbenzyl chloride (VBC) grafting method for producing RIG AEMs. The pyridinium head-group AEMs showed reasonable potential as an AEM for use in RED, with a low area resistance (0.4 Ω cm²) and one of the better permselectivities observed with the non-crosslinked RIG AEMs (60%). Incorporating commercially available DVB into the RIG AEMs produced via the VBC grafting method could potentially yield similar effects to the styrene based CEMs resulting in an AEM/CEM pair highly suited to RED (Figure 106). This should be studied in the near future.

![Figure 106](image)

Figure 106 – Proposed reaction scheme for the synthesis of crosslinked pyridinium functionalised AEMs from simultaneous RIG of 34-VBC and DVB monomers.

As well as actual RED cell testing, crosslinked CEMs should be considered for a range of laboratory testing. One particular area of uncertainty in this thesis derives from the difference
in experimental measurements used to gather results relating to the area resistance of the IEMs. The results obtained for the area resistance values in this work were all gathered using a pre-established ‘in-house’ impedance spectroscopy (AC) method with the IEM sample submerged in deionised water (see Chapter 2). The area resistance values obtained for literature IEMs were however recorded using a direct current (DC) method with the IEM under investigation held in contact with an aqueous NaCl solution (0.5 mol dm$^{-3}$). Hence, a direct comparison with literature IEMs is not possible. For an accurate comparison to be made between literature examples and the RIG IEMs synthesised in this study, RIG IEMs should be re-evaluated using the more common type of area resistance measurements.

The IEM characterisation techniques most commonly performed in this thesis utilised ideal solutions of NaCl. Although this is the salt most relevant to the RED process, under realistic operating conditions the IEMs will come into contact with a wide range of ions. IEM property experiments should therefore be carried in NaCl solutions containing ionic interferents such as Li$^+$, K$^+$, Mg$^{2+}$, SO$_3^{2-}$, SO$_4^{2-}$ and NO$_3^-$. Other relevant physical properties of RIG CEMs should also be studied in depth, including: tensile, flexural, shear and compressive properties as well as long term stability chemical testing and weathering.
8. Bibliography


9. Appendices

9.1 Appendix I – Raman and $^{19}$F SS-NMR Spectra of RIG CEMs (Chapter 3)

Appendix i - Raman spectra of E-STY-30 CEM, ETFE base film, and styrene grafted intermediate films. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.

Appendix ii - Raman spectra of P-STY-30 CEM, PVDF base film, and styrene grafted intermediate films. Spectra normalised to peak at 797 cm$^{-1}$ for illustrative purposes.
Appendix iii - Raman spectra of P-VBS-70 CEM and PVDF base film. Spectra normalised to peak at 797 cm\(^{-1}\) for illustrative purposes.

Appendix iv - Raman spectra of E-VBC-70 CEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at 835 cm\(^{-1}\) for illustrative purposes.
Appendix v - $^{19}$F SS-NMR spectra of E-STY-30 CEM, ETFE base film and styrene grafted intermediate film. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix vi - $^{19}$F SS-NMR spectra of E-STY-30 CEM, PVDF base film and styrene grafted intermediate film. Spectra normalised to peak at $\delta=92$ for illustrative purposes.
Appendix vii - $^{19}$F SS-NMR spectra of P-VBS-70 CEM and PVDF base film. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix viii - $^{19}$F SS-NMR Spectra of E-VBC-70 CEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.
9.2 Appendix II – Raman and $^{19}$F SS-NMR Spectra of RIG AEMs (Chapter 4)

Appendix ix – Raman spectra of TMA AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.

Appendix x - Raman spectra of TEA AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.
Appendix xi - Raman spectra of MIm AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.

Appendix xii - Raman spectra of DMIm AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.
Appendix xiii - Raman spectra of PYR AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.

Appendix xiv - Raman spectra of DMP AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.
Appendix xv - $^{19}$F SS-NMR Spectra of TMA AEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix xvi - $^{19}$F SS-NMR Spectra of TEA AEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix xvii - $^{19}$F SS-NMR Spectra of MIm AEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.
Appendix xviii - $^{19}$F SS-NMR Spectra of TMA DMIm, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix xix - $^{19}$F SS-NMR Spectra of PYR AEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.

Appendix xx - $^{19}$F SS-NMR Spectra of DMP AEM, ETFE base film, and grafted intermediate films. Spectra normalised to peak at $\delta=92$ for illustrative purposes.
9.3 Appendix III – Raman Spectra of Diamine RIG AEMs (Chapter 5)

Appendix xxii – Raman spectra of TMPDA diamine AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm\(^{-1}\) for illustrative purposes.
Appendix xxiii – Raman spectra of TMBDA diamine AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.

Appendix xxiv - Raman spectra of TMHDA diamine AEM, ETFE base film and VBC grafted intermediate. Spectra normalised to peak at 835 cm$^{-1}$ for illustrative purposes.
9.4 Appendix IV – Raman Spectra of Crosslinked RIG CEMs (Chapter 6)

Appendix xxv – Raman spectra of graft intermediate ETFE-poly(styrene) based co-polymer films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% DVB. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.

Appendix xxvi – Raman spectrum of DVB crosslinking agent
Appendix xxvii - Raman spectra of graft intermediate ETFE-poly(styrene) based co-polymer films synthesised from grafting solutions containing 0%, 2.5%, 5% and 10% BVPE. All spectra are normalised to base film peak at 835 cm\(^{-1}\) for illustrative purposes.

Appendix xxviii – Raman spectrum of BVPE crosslinking agent