Gupta G, Scott K, Mamlouk M. [Soluble Polystyrene-b-poly \(ethylene/butylene\)-b-polystyrene Based Ionomer for Anion Exchange Membrane Fuel Cells Operating at 70 °C](#). *Fuel Cells* (2018)

DOI link

<https://doi.org/10.1002/fuce.201700176>

ePrints link

<http://eprint.ncl.ac.uk/247354>

Date deposited

12/04/2018

Embargo release date

02/04/2019

Copyright

This is the peer reviewed version of the following article, which has been published in final form at <https://doi.org/10.1002/fuce.201700176>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

**Soluble Polystyrene-*b*-poly (ethylene/butylene)-*b*-
polystyrene Based Ionomer for Anion Exchange Membrane
Fuel Cells Operating at 70 °C**

Journal:	<i>Fuel Cells</i>
Manuscript ID	fuce.201700176.R2
Wiley - Manuscript type:	Original Research Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Gupta, Gaurav; Newcastle University, Chemical Engineering and Advanced Materials Scott, Professor Keith ; Newcastle University, Chemical Engineering and Advanced Materials Mamlouk, Mohamed; Newcastle University, Chemical Engineering and Advanced Materials
Keywords:	Alkaline Anion Exchange Membranes (AAEM), Fuel Cells, Oxygen Reduction Reaction, SEBS Ionomer, Degradation

SCHOLARONE™
Manuscripts

**Soluble Polystyrene-b-poly (ethylene/butylene)-b-polystyrene
Based Ionomer for Anion Exchange Membrane Fuel Cells
Operating at 70 °C**

G. Gupta¹, K. Scott¹, M. Mamlouk^{1,*}

¹Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon
Tyne- NE1 7RU, UK

[*]Corresponding author: mohamed.mamlouk@newcastle.ac.uk

Abstract

A soluble ionomer based on styrene-ethylene/butylene-styrene (SEBS) block polymer was synthesized with an ion exchange capacity (IEC) of 1.91 mmole g⁻¹ and OH⁻ ion conductivity at 100% relative humidity (RH) of 0.14 and 0.18 S cm⁻¹ at 50 and 70 °C, respectively. The performance of the membrane electrode assembly (MEA) with SEBS ionomer was highest compared to polyvinyl benzyl chloride (PVBC) and Acta I2 ionomers at 0.5 V at both 50 °C (239 mW cm⁻²) and 70 °C (285 mW cm⁻²) using air and low-density polyethylene (LDPE) membrane. This was largely due to the lower charge transfer resistance measured for the MEA using SEBS ionomer which is due to higher IEC, better water uptake and water retention properties. Ionomer water permeability is also critical for the back diffusion and the membrane where SEBS ionomer showed large advantage over PVBC ionomer.

The long-term testing of 50 h at 50 and 70 °C also showed better durability of the SEBS compared to the commercial Acta I2 ionomer with an average performance loss of 3 mA h⁻¹ at 50 °C. The MEAs tested at 70 °C failed after 15 h (Acta I2) and 25 h (SEBS) due to pin-hole formation in the membrane.

Keywords: Alkaline Anion Exchange Membranes (AAEM), Fuel Cells, Oxygen Reduction Reaction, SEBS Ionomer, Degradation

1. Introduction

Fuel cells are considered as an important power source due to their high efficiency and low pollution providing an environment friendly solution to the automotive and power industry. Proton exchange membrane fuel cells (PEMFC) based on Nafion® are at the forefront of this technology with the application in automotive, residential and portable power [1-4]. Nafion® and perfluorosulfonic acid (PFSA) membranes exhibit very high proton conductivity along with excellent chemical, mechanical and thermal stability. Cost is a major inhibitor to commercial uptake of fuel cells and PEMFCs and is localized on 3 critical components: (i) Platinum noble metal catalysts (ii) Expensive fluorinated membrane; and (iii) Expensive bipolar plate materials (limited choice of materials compatible with the super-acidic environment of PEM). Recent advances in materials science and chemistry have produced membrane materials which would allow the development of the alkaline-equivalent to PEMs [5-15]. In anion-exchange membranes (AEMs), ion species such as OH^- serve as charge carriers. Such fuel cells offer a number of significant advantages: (i) Catalysis of oxygen reduction at the cathode is faster under alkaline than acidic conditions [16]. (ii) Increased number of cheap, easy fabricated (stamped) thin metal (Ni, stainless steel) bipolar plates [14,17]. (iii) Non-fluorinated membranes such as radiation grafted LDPE [11] or block polymer for example SEBS [18] are feasible and promise significant membrane cost reductions. Therefore, AEMs can be seen as very promising solutions to affordable fuel cells and could consequently facilitate their rapid market uptake.

However, the current state of the art AEM technology still faces several challenges that needs to be addressed before it is considered as a serious candidate for commercial fuel cell systems.

- i. Hydroxide ion mobility is less than half of that of proton meaning that AEM membranes typically should have one and half to double the ion exchange capacity of Nafion of ca. 1 mmole g⁻¹. This results in higher degree of swelling of 48% with an IEC of 2.3 mmole g⁻¹ and weaker mechanical properties (11.2 MPa to 2.4 MPa from dry to fully hydrated membrane) as compared to Nafion 112 which has ultimate tensile strength of 9 MPa (fully hydrated) with a degree of swelling of 39.6% and IEC of 0.91 mmole g⁻¹ [12]. This can be typically addressed by cross-linking the polymer in the membrane which improves the mechanical properties at the cost of conductivity and solubility. Another important aspect of membrane (and ionomer) is fast water permeability to allow water transfer from the anode to the cathode.
- ii. Chemical stability of AEM materials at elevated temperatures and low humidity. We have shown that trimethylamine based AEM membrane had stable OH⁻ conductivity of 0.11 S cm⁻¹ at 80 °C and 100% RH under N₂ for 6 month [12], but conductivity decreased rapidly under oxygen atmosphere due to radicals attacks [19,20] on benzylic ternary carbon [19,20].
- iii. Lack of chemically stable high performance AEM ionomer. Ionomer must have high ion conductivity and stability in the alkaline environment [10,11,13,21-30]. The solubility of ionomer in low boiling point solvents that can easily be removed during the electrode preparation is an important property required for easy usage and to upscale production. While polymer's chemical and mechanical stabilities are improved by cross-linking, the lack of polymer solubility upon cross-linking will restrict its use to the membrane separator only. If non-crosslinked polymer is used as an AEM ionomer, lower IEC is typically used to improve the chemical and

mechanical properties at the cost of the conductivity which is typically in the range of $10^{-2} \text{ S cm}^{-1}$ [11,13,21-23].

Lin et al. [21] synthesized a soluble polyfluorene based ionomer which was soluble in DMSO and DMF where as it was insoluble in water and aqueous methanol. It has hydroxide ion conductivity of $10^{-2} \text{ S cm}^{-1}$ at room temperature. However, there were no electrochemical testing shown based on this ionomer. Cao et al. [13] synthesized a new ionomer based on aminated and cross-linked methylated melamine grafted poly (vinyl benzyl chloride) and reported ion conductivity of $1.7 \times 10^{-2} \text{ S cm}^{-1}$ at 60°C . They also reported a power density of 156 and 76 mW cm^{-2} at 15°C with H_2/O_2 and H_2/air as fuels, respectively. Gao et al. [22] recently reported the use of SEBS ionomer for use in the H_2/O_2 AEMFCs and reported OH^- conductivity of 0.03 S cm^{-1} at 75°C . They also reported a maximum power density of 375 mW at 0.545 V at 50°C and a loss of 0.22 mV h^{-1} over duration of 500 h at a constant current density of 100 mA cm^{-2} . Gu et al. [23] prepared a quaternary phosphonium based soluble ionomer (methanol, ethanol, n-propanol and their aqueous solutions) with hydroxide conductivity of 0.027 S cm^{-1} and an IEC of $1.09 \text{ mmole g}^{-1}$ and good alkaline stability. They reported a peak power density of 138 mW cm^{-2} in a H_2/O_2 AEMFC at 50°C , which was 3.5 times higher for the MEA without ionomers. Sun et al. [24] synthesized quaternary ammonium based ionomers by choosing a novel block copolymer SEBS as the backbone to achieve an IEC of $1.54 \text{ mequiv g}^{-1}$. They obtained a highest peak power density of 210 mW cm^{-2} in a H_2/O_2 AEMFC at 50°C and 2 atm back pressure, which was higher than that of MEA with phosphonium based ionomers but lower than SEBS based ionomers reported by Gao et al. [22]. Although these ionomers exhibited an acceptable ion conductivity and solubility, the performance of the MEA with these ionomers was not comparable to state-of-the art PEMFCs. Previous work in our group [10] based on poly vinyl benzyl chloride with 60% amination based ionomers has shown highest

conductivity of 0.043 S cm^{-1} and a peak power density of 478 mW cm^{-2} at 0.6 V at $50 \text{ }^{\circ}\text{C}$ in H_2/air AEMFC. This was the highest peak power density reported by any research group to date in the AEMFC for H_2 air AEMM system. For the H_2/O_2 AEMFC, the highest peak power density reported in literature was 1.4 W cm^{-2} at 0.55 V at $60 \text{ }^{\circ}\text{C}$ for ETFE-g-VBC ionomers and membranes [31].

The limitation in AEMFC performance comes from two factors: (i) when using non-precious metal catalyst for oxygen reduction reaction (ORR), the AEM environment is reported to exhibit pH equivalent of 10.5 [14,15] which is significantly lower than typical alkaline fuel cell using 5-7 M KOH of $\text{pH} > 14$. Moreover, hydrogen reduction reaction (HOR) in alkaline media is slower than in acidic media with worse Tafel slope therefore resulting in larger over potential loss.

(ii) Water management in AEMFC is very complex particularly at elevated temperatures. Most of the reported high peak power densities in the literature are conducted at 50 or $60 \text{ }^{\circ}\text{C}$ and using oxygen [6,9,10,13,21,27,29-34]. However, AEM should be able to operate at $70 \text{ }^{\circ}\text{C}$ for long term to be able to compete with PEMFCs otherwise the cost and size of heat rejection unit of the fuel cell system might become unpractical and too expensive.

The current low temperature limit of $50\text{-}60 \text{ }^{\circ}\text{C}$ is caused by the optimum humidity level in AEM cathode. RH in the cathode is critical as H_2O and O_2 vapor pressure are both reactants at the cathode and competing. If lower RH is used at the cathode to improve the O_2 mass transport when using air, the ionomer conductivity will then decrease resulting in a lower performance as well as there might be water mass transfer limitation depending how fast is water transport (back diffusion) from the anode. If higher RH is used at the cathode this could cause O_2 mass transport limitation when using air and possible flooding at the anode too. The water balance gets more critical at elevated temperature as higher water vapor pressure is required to maintain the same RH. For example, water saturation pressure at 50

°C is 0.12 atm while at 70 °C is 0.31 atm, if O₂ or air (atm) is fed to the cell cathode then the partial pressure of O₂ before drawing any current from the cell would reduce to 0.88 atm and 0.69 atm under pure O₂ and to 0.18 atm and 0.14 atm under air, respectively. On the other hand, anode operating on pure hydrogen can operate at high relative humidity before experiencing flooding depending on the current density applied and fuel stoichiometry used. Back diffusion through the membrane will also allow water mobility from the higher humidity used at the anode to the cathode. It is therefore critical to find ionomer that provides high ionic conductivity and allow fast water permeability at 70 °C at moderate relative humidity to allow the use of air rather than impractical pure oxygen at the cathode. The current publication focusses on utilizing SEBS based soluble ionomer with the aim of operating the fuel cell at 70 °C. The ionomer has been used previously for DMAFC [35], redox flow battery [36], AEMFC at 50 °C [22], AEM electrolyzers[18] but never been tried for AEMFC at 70 °C. In a follow up publication we will report the system performance under various anode and cathode relative humidity and temperature conditions to give further insight on AEM water management issues.

2. Experimental

2.1 Membrane synthesis

The radiation grafted Anion Exchange Membrane (AEM) was synthesized as previously reported using low-density polyethylene (LDPE) with vinyl benzyl chloride (VBC) as the graft monomer [10,11]. The LDPE-g-VBC copolymer was prepared by immersing the LDPE films (30 µm thick) in nitrogen purged 31/26/45 by volume VBC/toluene/methanol solution placed in a screw-cap vial. Samples were sent to Synergy Health plc (Wiltshire, UK) for mutual gamma radiation grafting. The irradiation was carried out under a dose rate of 2 kGy/h and total radiation dose of 20 kGy. The grafted membranes obtained were washed

thoroughly with acetone to completely remove VBC homopolymers. To produce the anion exchange functionality, Benzyltrimethylammonium groups was obtained by immersing the membrane in trimethylamine (TMA) 45%wt solution in water for 24 h. The counter ion was subsequently exchanged from Cl^- to OH^- by treating the membrane with fresh 1.0 M KOH solution every 20 min, three times (total OH^- exchange time of 1 h) to completely exchange the chloride ions with hydroxide ions. The membrane was then washed with copious amount of deionized water to remove residual hydroxide ions. Removal of excess OH^- ions was confirmed by using pH paper.

2.2 SEBS ionomer synthesis

SEBS ionomer synthesis procedure was the similar as reported in publication on soluble ionomer for electrolyser [18]. 250 mL of chloroform was added to 4.0 g of polystyrene-b-poly (ethylene/butylene)-b-polystyrene SEBS polymer 60%wt styrene (Kuraray, Japan) in nitrogen purged round flask. The flask was attached to a condenser, a thermocouple and a glass tube for the nitrogen flow. The mixture is stirred. Once the polymer was dissolved, 5.4 g of trioxane was added and the flask was then immersed in ice bath until the temperature of the mixture decreased to 1 °C. 22.8 mL of chlorotrimethylsilane and then 3 mL of tin chloride was injected with syringe. The mixture was kept stirring at 2-3 °C for 30 min, and then at room temperature for 17.5 h.

To stop the reaction at the end of the stirring time, the mixture was poured in a beaker filled with 300 mL of methanol/water (50% vol each). The mixture was then poured in a separator funnel to separate the two obtained phases, at the bottom the chloroform with the polymer dissolved, at the top the methanol and water and un-reacted reagents. The process of “washing” the chloroform/polymer solution with methanol/water was repeated for a second time to ensure removal of reagents. The chloromethylated SEBS polymer was then obtained

by evaporating the chloroform. The chloromethylated SEBS polymer was then immersed in 45%wt trimethylamine (TMA) solution for amination of the chloromethyl group. The schematic for ionomer synthesis is shown in Figure 1. The full characterization of the SEBS ionomer has been reported elsewhere[18]. Nuclear magnetic resonance spectroscopy (NMR) and Fourier-transform infrared spectroscopy (FTIR) graphs showing the chloromethylation has been provided in Supplementary information (Figure S1 and S2).

2.3 MEA preparation

Fuel cell electrodes were made from catalyst inks to which SEBS ionomer was added to facilitate ionic conductivity. The catalyst ink was prepared by sonicating the catalyst 20% Pt/C for the anode (ETEK, USA) and 40% Pt/C for the cathode (ETEK, USA) with 37 and 28 wt% SEBS ionomer in THF, respectively [10,11,32]. The higher ionomer content of 37 wt% on the anode side was used to maintain the ionomer to carbon ratio on both sides as the carbon content of the catalyst was different for the catalysts used. Similar samples were prepared by using commercial Acta I2 ionomer and PVBC-60% aminated (Figure S6) and functionalized with TMA [10]. The ink was then sonicated in ultrasonic bath for 30 mins to achieve homogenization and getting rid of any agglomerates. The ink was then sprayed manually using airbrush (Badger, Air-Brush Model 100-LGF) on a gas diffusion electrode, (non-woven carbon cloth) incorporated with wet proofed micro porous layer (Freudenberg FFCCT, Germany) referred to as GDL. The catalyst loading were $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$.

The SEBS based electrodes were then immersed in trimethylamine solution (TMA-45%wt in water- Sigma Aldrich) for 72 h to impart functionality to the ionomer and then washed several times with de-ionized (DI) water. The resulting electrode and the membrane were converted to OH^- conducting group by immersing them in 1 M KOH solution for 1 h and changing the solution every 20 min.

2.4 Electrochemical testing

For the experimental single cell, titanium was used as the building blocks with gold coated active area of 1 cm^2 with serpentine flow field channels surrounded by O-ring seal to prevent leakage. The temperature of the cell was controlled by thermostatically controlled cartridge heaters inserted into the cell body. The anode gas was passed into a home-made humidifier at 100% RH. The cathode humidity was maintained between 15-20% RH [10,11,32]. The flow rates were controlled manually by means of appropriate flow meters for each gas (Platon (RM&C), U.K.). The cell was tested under ambient pressure unless otherwise specified and all gases used were CO_2 free grade. Experimental setup is shown in Figure 2.

Polarization curves were recorded at 50 and 70 °C using a cathodic sweep at a scan rate of 1 mV s^{-1} by employing Autolab PGSTAT 30 (Eco Chemie, The Netherlands). The electrodes were subject to several cycles until a steady performance was reached. Previous tests confirmed that this was slow enough to approximate to steady state operation [10,11,32]. Electrochemical impedance spectroscopy was done at different potentials (0.9 and 0.6 V) in a frequency range of 100 mHz to 400 kHz using an amplitude of 15 mV. Long term durability testing was done by holding the fuel cell at a fixed potential of 0.5 V at 50 and 70 °C for 50 h and 25 h, respectively and recording the polarization curves and EIS before and after the test. The H_2 crossover current can be calculated from the cyclic voltammetry graph from the current density (due to the oxidation of crossed-over hydrogen at the cathode) at 1 V (S8).

In order to study the effect of water uptake and permeability of the studied ionomers and its impact on the fuel cell performance, another set of conductivity tests were carried out by depositing a layer of ionomer material (film) of thickness $25 \text{ }\mu\text{m}$ between two carbon paper GDL and assembling them in a fuel cell configuration. N_2 gas is purged on both sides of the film (GDLs) and impedance spectroscopy measurements were taken at 50 and 70 °C. RH of

the gas was switched from 100% to 0 and back to 100 % on one side of the film while maintaining the other side at 100 % RH. When a different RH is applied across the ionomer film (i.e. 100% and 0%), the water content in the film will reach an equilibrium and consequently the average water content in the film will impact the measured through plane conductivity. The equilibrium water content will be influenced by ionomer water uptake and water permeability of the ionomer film (from 100% RH side to 0% side). By tracking the changes in conductivity, a comparative study between the three ionomers can be made.

3. Characterization of ionomer and membranes

3.1 Measurement of the ion-exchange capacity (IEC)

The OH⁻ exchanged membranes were immersed in a known volume of 1.0 M NaCl solution and were left to stand overnight. The liberated hydroxide ions were titrated with 0.10 M H₂SO₄ solution using a Titrette GMBH bottle-top digital burette and the endpoint was determined visually using methyl red indicator. After titration, the membranes were washed with deionized water to completely remove the salt and dried using a MTI Model DZF-6020-FP vacuum oven. Measurements of the weight were performed until no change in the dry weight was achieved. The IECs were computed using the amount of OH⁻ ions neutralized, expressed in mmole, divided by the dry weight of the membranes, in grams. Degree of grafting (S3) of the membrane based on initial weight (DOG) is 67.5% and IEC (S4) is 2.3 mmole g⁻¹ with final hydrated membrane thickness of 75 μm [12,20]. The ion exchange capacity of the SEBS ionomer was 1.91 mmole g⁻¹ and the degree of chloromethylation (S5) was 49% [18].

3.2 Measurement of the ionic conductivity

The through-plane ionic conductivity of each of the functionalized membranes was measured following the same procedure previously reported [20] using the following formula:

$$\sigma = \frac{L}{RA} \quad (1)$$

where σ is the hydroxide ion conductivity, L is the membrane thickness, R is the resistance derived from the impedance value at zero-phase angle and A is the membrane test area.

Ionic conductivity of the membrane was 0.09 S cm^{-1} at 50°C and 100% RH [12,20]. The ionic conductivity of the SEBS ionomer at 100% RH was 0.14 S cm^{-1} and 0.18 S cm^{-1} at 50°C and 70°C , respectively [18].

4. Results and Discussion

4.1 Ionomer water permeability and conductivity

A study on the effect of relative humidity on the three ionomer resistivity at 50°C and 70°C was carried out and the respective resistivity values are shown in Table 1. All the ionomers follows the same trend of increased area specific resistance (ASR) when the RH was switched from 100 to 0% on one side of the ionomer film (while maintaining the other at 100%) due to reduction in the film average water content. The ASR values reduce back to their original values when the RH was switched back to 100 %. This shows that the change in the ASR is reversible for all the ionomers at both 50°C and 70°C and that the change in conductivity is not due to degradation in this relatively short term test. At 50°C at 100/100 %RH the ionomer with the lowest ASR was SEBS with $0.07 \Omega\text{cm}^2$ then I2 with $0.11 \Omega\text{cm}^2$ and PVBC with $0.14 \Omega\text{cm}^2$ and at 100/0 the ASR of PVBC increased by a factor of 3.5 in comparison to factor of 2 for SEBS and 1.5 for I2. SEBS showed the lowest ASR at 100/0.

At 70 °C, the same trend was followed at 100/100 %RH with SEBS having the lowest ASR value of 0.08 Ωcm^2 followed by I2 at 0.12 Ωcm^2 and PVBC at 0.18 Ωcm^2 . When the relative humidity was changed to 100/0, the ASR for PVBC increased to 0.49 Ωcm^2 which is more than double compared to SEBS (0.23 Ωcm^2) and I2 (0.19 Ωcm^2).

The high rate of ASR change for PVBC was much higher than the other two ionomer and this increased with temperature (for all ionomers). The measured ASR in the 100/0 %RH setup is directly related to the average ionomer film water content which is directly influenced by the ionomer water uptake ability at given RH% (which decrease with increasing the temperature from 50 to 70 °C) and the ionomer film water permeability from the wet 100% side to the dry (0%) side. This suggests that PVBC has lower resilience to dehydration than SEBS/I2. The higher susceptibility of PVBC to dehydration would limit the operating temperature of a PVBC based cathode as cathode drying can be caused by high current densities due to water mass transport and water uptake limitations from the vapor phase in cathode stream of 20% RH (water is reactant at the cathode) and due to low permeability of water from the high humidity anode side (100%) to the cathode side. Whereas the performance of the SEBS and Acta I2 based ionomer showed better tolerance to dehydration.

4.2 Fuel cell tests

Figure 3 (a) shows the polarization curves of the Pt/C catalyst at 50 °C with different ionomers tested in the current study and repeatability of the same is shown in Figure S7. The ionomers PVBC and SEBS (in-house ionomer prepared in the laboratory) and Acta I2 (commercial ionomer) were tested in order to compare the performance of the fuel cells. The power density for the SEBS and PVBC ionomer at 0.5 V was 239 mW cm^{-2} at a current density of 0.475 A cm^{-2} , 240 mW cm^{-2} at a current density of 0.478 A cm^{-2} , respectively.

Whereas with Acta I2, it was 185 mW cm^{-2} at a current density of 0.37 A cm^{-2} . As all the conditions are similar in all the experiments and the ionomer is the only parameter which is varying, this shows that the ionomer interaction with the catalyst is causing the reduced performance. The area specific resistance values as calculated from the impedance testing for the different ionomer at 0.9 V is reported in Table-2 and Nyquist plot for the same is shown in Figure 3 (b). The area specific resistance for Acta I2 was slightly smaller compared to the SEBS and PVBC ionomer at 0.9 V. The value decreased for SEBS and came in line with I2 ionomer when the cell ionic resistance was measured at 0.6 V (Figure 3 (c)) where the current density is higher (For every 1 mole of water produced at the anode, 1 mole is consumed at the cathode). The measured cell ionic resistance includes contribution from mainly the membrane and some contributions from the anode and the cathode ionomers. It is therefore difficult without the addition of in-situ reference electrode (to collect anode and cathode data separately) to know precisely what is the contribution of each of the components. But it can be suggested that the improvement of cell ionic resistance is caused by improved hydration of membrane and possibly cathode ionomer via back diffusion. The higher ionic resistivity of PVBC MEA at both 0.9 and 0.6 V suggests that PVBC at 50°C under the studied conditions has lower ionic conductivity in comparison to SEBS and I2. The charge transfer resistance for the SEBS was lowest around $2.45 \Omega \text{ cm}^2$ compared to around $4.05 \Omega \text{ cm}^2$ for Acta I2 and PVBC at 0.9 V suggesting better ionomer network available for the SEBS for the transfer of ions and water which can be the result of the higher IEC of SEBS ionomer. The lower charge transfer resistance of SEBS is also seen in the kinetic (low current density) region of the I-V curve where SEBS shows lower over potential losses in comparison to Acta I2 ionomer, for example at 0.8 V, the current density was 0.15 A cm^{-2} (SEBS) and 0.10 A cm^{-2} (Acta I2). Even though the charge transfer resistance of all the samples were in the same range as can be seen from the EIS comparison in Figure 3 (c). Once more this charge transfer resistance

includes both contributions of ORR and HOR and in-situ reference electrode is required to separate both contributions.

When the impedance was carried out at 0.6 V, the low frequency resistance (combination of mass transfer and charge transfer resistances) values decreased for all three tested electrodes and showed similar value around $1.7 \Omega \text{ cm}^2$. It can be seen that however in the case of PVBC at higher current density a mass transport limitation is visible in the I-V curve in comparison to SEBS MEA, either due to flooding at the anode or drying at the cathode or combination of both. This can also be seen from Figure 3 (c) where the PVBC based MEA showed an additional impedance semi-circle with mass transfer resistance of $0.67 \Omega \text{ cm}^2$ (from $1.60 - 2.27 \Omega \text{ cm}^2$). This suggests that water permeability (from anode to cathode for example) in PVBC ionomer is slower than that of I2 and SEBS ionomers. This has been shown in the section 4.1 where water permeability of different ionomers was done and PVBC ionomer showed higher tendency to dehydration whereas SEBS/I2 showed better tolerance to dehydration.

Figure 4 (a) shows the polarization curves of the Pt/C catalyst at 70°C with different ionomers and repeatability of the same is shown in Figure S8. The MEA with SEBS performed better compared to other ionomers at 70°C similarly to 50°C . The power density for the SEBS and PVBC ionomer at 0.5 V was 284 mW cm^{-2} at a current density of 0.568 A cm^{-2} , 53 mW cm^{-2} at a current density of 0.106 A cm^{-2} , respectively. Whereas for Acta I2, it was 245 mW cm^{-2} at a current density of 0.490 A cm^{-2} . The main difference observed at 70°C in comparison to 50°C was that the performance of MEA with PVBC dropped considerably compared to the other studied MEAs. The measured area specific resistance at 0.9 V increased slightly for SEBS from 0.15 to $0.20 \Omega \text{ cm}^2$ and increased significantly for Acta I2 from 0.07 to $0.20 \Omega \text{ cm}^2$ and for PVBC from 0.16 to $0.26 \Omega \text{ cm}^2$ when temperature increased from 50 to 70°C (Table 2 and 3). This suggest that I2 and PVBC suffered from

significant dehydration at the cathodes (20% RH at 70 °C) at conditions close to open circuit potential while SEBS showed more resilience.

The reduced performance of PVBC can be caused by the cathode dehydration which will result in high charge transfer resistance as well as possible ionomer instability. This is because ionomer dehydration will: reduce its conductivity and consequently the cathode catalyst layer effectiveness, result in slower water transfer rate from anode to cathode therefore flooding the anode and causing water mass transport limitation at the cathode, and accelerate ionomer degradation. A very high charge transfer resistance value was recorded of around $25 \Omega \text{ cm}^2$ for PVBC at 0.9 V (Figure 4 (b)) which is 5-6 times compared to PVBC at 50 °C of $3.95 \Omega \text{ cm}^2$ and other tested samples at 70 °C ($3.61 \Omega \text{ cm}^2$ and $4.71 \Omega \text{ cm}^2$ for SEBS and Acta I2, respectively).

The lower charge transfer resistance of the SEBS ionomer is reflected by the better performance of the MEA in polarization curve (kinetic region). The lower charge transfer resistance of SEBS based MEA can be explained by the higher IEC of SEBS and consequently higher water uptake and retention at the studied conditions and higher dehydration resilience. This also means better water transport from anode to the cathode as well as better cathode electrode effectiveness from higher water content and ionic conductivity. The testing of water permeability of different ionomers as reported in section 4.1 shows that PVBC is highly prone to dehydration compared to SEBS/I2 which in turn confirm the observation as seen in polarization and EIS testing at 70 °C. Future studies will look into recording the separate contribution of anode and cathode to do more detailed analysis.

When the cell impedance is measured at 0.6 V (Figure 4 (c)), the charge transfer resistance for all the samples decreased but still the charge transfer resistance of PVBC remained very

high $>12 \Omega \text{ cm}^2$ explaining the poor performance at temperature above 50°C . SEBS ($1.92 \Omega \text{ cm}^2$) still showed lower charge transfer resistance than Acta I2 ($2.86 \Omega \text{ cm}^2$). Current density at 0.6 V was 0.402 A cm^{-2} for SEBS and 0.330 A cm^{-2} for I2, respectively.

4.3 Long term testing

Figure 5 (a) shows the chronoamperometry data of MEAs with SEBS and Acta I2 ionomers at 0.5 V and 50°C . The MEAs were held at 0.5 V and then CV and EIS measurements were done to see the change in the performance. One of the observation for both of the samples was that the noise level which is due to the result of liquid water generation at the anode due to a constant hold at 0.5 V . There were large fluctuations (spikes) in current density of both SEBS (3 spikes) and Acta I2 ionomer (8 spikes) sample during the entire tests, a typical characteristic of water accumulation and removal i.e. flooding of the anode catalyst layer. The current density decreased from $0.4\text{-}0.5 \text{ A cm}^{-2}$ to around 0.2 A cm^{-2} after 50 h of testing with an average performance loss of 5 mA h^{-1} for Acta I2 MEA. Whereas for SEBS ionomer sample, the current density decreased slowly and gradually from 0.5 A cm^{-2} to 0.35 A cm^{-2} with an average performance loss of 3 mA h^{-1} . The area specific resistance (Table 4, Figure 5 (c)) slightly increased for SEBS whereas it became almost double that of its initial value for Acta I2 ionomer after 50 h of testing. This suggests that I2 ionomer suffered dehydration in the cathode catalyst layer while the anode catalyst layer flooded.

While the AEM membrane plays an important role in the water back diffusion i.e. its water permeability [10,11,16,31,32] trying to minimize the large water content imbalance between anode and cathode, the ionomer water permeability is also critical in water back diffusion as have been seen in these studied MEAs utilizing the same membrane but different ionomer.

The higher performance loss of the Acta I2 MEA can be clearly seen by comparing the polarization curves of both the samples before and after 50 h of testing as shown in Figure 5

(b). The same conclusion can be drawn from the bigger semi-circle of the sample taken at 50 h (Figure 5 (c) and (d)) showing a higher charge transfer resistance at 0.9 and 0.6 V. The large semi-circle could be caused by anode flooding or cathode dehydration showing large charge transfer resistance. The charge transfer resistance for I2 almost doubled at 0.9 V from 4.05 to 8.31 $\Omega \text{ cm}^2$ after 50 h, while SEBS based MEA measured charge transfer resistance remained almost constant (2.45 and 2.56 $\Omega \text{ cm}^2$). This suggests that the Acta I2 ionomer suffered dehydration at the cathode side.

The measured low frequency resistance at 0.6 V (combination of mass transfer and charge transfer resistances) almost tripled for Acta I2 from 1.59 to 5.87 $\Omega \text{ cm}^2$, while a small increase from 1.72 to 2.57 $\Omega \text{ cm}^2$ was recorded for SEBS MEA. The increase in the low frequency resistance can be caused by anode flooding, cathode dehydration with increased current density or a combination of both.

Figure 6 (a) shows the chronoamperometry curve of MEAs with SEBS and Acta I2 ionomers at 0.5 V, 70 °C. The MEA was held at 0.5 V and then CV and EIS measurements were done to study the change in the performance. Similar noise in the current density seen at 50 °C was also recorded at 70 °C due to the excess liquid water generation at 0.5 V. The magnitude of the fluctuations (spikes) in current density and their frequency decreased sharply when temperature was increased from 50 °C to 70 °C as water saturation pressure increases. The current density of the Acta I2 ionomer sample saw an exponential decay from 0.55 A cm^{-2} to 0.1 A cm^{-2} . The MEA with the Acta I2 ionomer failed after 15 hours with sudden increase in hydrogen crossover current due to membrane failure. The current density of the SEBS MEA remained almost stable after an initial drop from 0.48 A cm^{-2} to 0.3 A cm^{-2} . The area specific resistance ASR at 0.9 V (Table 5, Figure 6 (c)) decreased slightly for the SEBS MEA after the 15 hour testing which can be due to improved membrane/ionomer hydration with higher current densities (water generation at the anode) and also shows that both the membrane and

SEBS ionomer were stable throughout the 15 h testing. However, the ASR values for both SEBS and Acta I2 increased with temperature increase from 50 to 70 °C suggesting some dehydration of the ionomer (decrease in conductivity). The charge transfer resistance at 0.9 V (Figure 6 (c)) of both SEBS and Acta I2 has increased slightly from 2.45 to 3.61 $\Omega \text{ cm}^2$ and 4.05 to 4.71 $\Omega \text{ cm}^2$, respectively, when the temperature increased from 50 to 70 °C. The ionomer dehydration seen from the increase in ASR with temperature, also results in lower catalyst layer utilization (and consequently lower exchange current density) especially at the cathode. The charge transfer resistance for SEBS samples increased slightly after 15 hours of testing from 3.61 to 3.80 $\Omega \text{ cm}^2$. The low frequency impedance measured at 0.6 V of both Acta I2 and SEBS MEAs had similar values at 70 °C to that at 50 °C. The increase in the low frequency resistance after 15 h of testing (for SEBS) combined with the decrease in ASR along with fluctuations in the chronoamperometry measurements can suggest anode flooding. The same conclusion can be drawn by comparing the polarization curves of the sample before and after 15 h of testing as shown in Figure 6 (b). It can be seen that the current density at 0.5 V for SEBS sample has reduced from 0.6 A cm^{-2} to 0.35 A cm^{-2} and mass transport limitation affect the I-V curve.

As the major interest of the current work was the possibility of using SEBS ionomer at 70 °C, longer test beyond 15 h was done for the SEBS based MEA and a detailed hour to hour study was carried out using polarization and EIS. Figure 7 (a) shows the chronoamperometry profile of the MEA at 0.5 V at 70 °C. It can be seen that the current density showed a gradual decrease till around 20 hours of testing and then there was sharp spike in the current density due to membrane failure. The hydrogen crossover can be confirmed from the decrease in the OCP of the polarization curves shown in Figure 7 (b) after 20 h by around 20 mV as well as from the increase in low frequency resistance at 0.6 V (Figure 7 (c)). The crossover current was calculated with each hour and plotted vs time and shown in Figure 7 (d). The crossover

current started increasing after 15 h of testing and reached 15 mA cm^{-2} after 20 hours which is a sign of pinhole formation in the membrane. In order to perform longer term testing for the SEBS based ionomer of 1000 h, membranes with higher mechanical durability at 70°C needs to be synthesized. This is the first time long term testing has been done at 70°C for AEMFC and we have shown that the SEBS based ionomer are stable at least for 15 h operation.

5 Conclusion

A successful demonstration of the SEBS based soluble ionomer in AEMFC at 70°C was shown. The ionomer had an IEC of $1.91 \text{ mmole g}^{-1}$ and OH^- ion conductivity of 0.14 and 0.18 S cm^{-1} at 50 and 70°C (100% RH), respectively. The fuel cell testing of this ionomer at 50°C and comparison with a commercial ionomer Acta I2 was done and the results showed an improved performance with SEBS ionomer compared to the commercial one i.e. a power density of 239 mW cm^{-2} for SEBS compared to only 185 mW cm^{-2} for Acta I2 at 50°C using LDPE grafted membranes. This was largely due to the lower charge transfer resistance for the SEBS ionomer which can be due to higher IEC, better water uptake and water retention properties. SEBS based samples also showed better stability over the course of 50 h testing at 0.5 V . Further testing at 70°C showed better performance for the SEBS ionomers compared to Acta I2 and PVBC i.e. a power density of 285 mW cm^{-2} for SEBS at 0.5 V . While the AEM membrane plays an important role in the water back diffusion trying to minimize the large water content imbalance between the anode and the cathode, the ionomer water permeability is also critical for the back diffusion as have been seen in the three studied MEAs utilizing the same LDPE grafted membrane but three different ionomers.

The 15 h stability test showed SEBS ionomer had better stability compared to the Acta I2. Membrane failure was observed when the SEBS based MEAs were tested for 25 hours which

led to the crossover of gases and thus decrease in the current density and OCP. Further testing needs to be done using in-situ reference electrodes at anode and cathode to find the contribution of the anode flooding and cathode drying on the performance of fuel cells.

Acknowledgements

The authors acknowledge the support of the Engineering and Physical Sciences Research Council (EPSRC) for funding the majority part of this work under Grant Number EP/M005895/1 and the Newcastle Institute for Sustainability grant numbers BH 163940 and BH 141511, EPSRC Impact Acceleration Account grant number BH162217 which supported the work on the SEBS ionomer.

References

- [1] L. Carrette, K. A. Friedrich, U. Stimming, *Fuel Cells* **2001**, 1, 5.
- [2] Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, X. C. Adroher, *Applied Energy* **2011**, 88, 981.
- [3] J. Rozière, D. J. Jones, *Annual Review of Materials Research* **2003**, 33, 503.
- [4] S. J. Peighambaroust, S. Rowshanzamir, M. Amjadi, *International Journal of Hydrogen Energy* **2010**, 35, 9349.
- [5] J. Cheng, G. He, F. Zhang, *International Journal of Hydrogen Energy* **2015**, 40, 7348.
- [6] G. Merle, M. Wessling, K. Nijmeijer, *Journal of Membrane Science* **2011**, 377, 1.
- [7] L. Wang, E. Magliocca, E. L. Cunningham, W. E. Mustain, S. D. Poynton, R. Escudero-Cid, M. M. Nasef, J. Ponce-González, R. Bance-Souahli, R. C. T. Slade, D. K. Whelligan, J. R. Varcoe, *Green Chem.* **2017**, 19, 831.
- [8] T. N. Danks, R. C. T. Slade, J. R. Varcoe, *Journal of Materials Chemistry* **2003**, 13, 712.
- [9] J. Varcoe, R. Slade, *Electrochemistry Communications* **2006**, 8, 839.
- [10] M. Mamlouk, K. Scott, *Journal of Power Sources* **2012**, 211, 140.
- [11] M. Mamlouk, J. A. Horsfall, C. Williams, K. Scott, *International Journal of Hydrogen Energy* **2012**, 37, 11912.
- [12] R. Espiritu, M. Mamlouk, K. Scott, *International Journal of Hydrogen Energy* **2016**, 41, 1120.
- [13] Y.-C. Cao, X. Wang, M. Mamlouk, K. Scott, *Journal of Materials Chemistry* **2011**, 21, 12910.
- [14] J. R. Varcoe, R. C. T. Slade, *Fuel Cells* **2005**, 5, 187.
- [15] J. R. Varcoe, P. Atanassov, D. R. Dekel, A. M. Herring, M. A. Hickner, P. A. Kohl, A. R. Kucernak, W. E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, *Energy Environ. Sci.* **2014**, 7, 3135.
- [16] M. Mamlouk, S. M. S. Kumar, P. Gouerec, K. Scott, *Journal of Power Sources* **2011**, 196, 7594.
- [17] P. Gouérec, L. Poletto, J. Denizot, E. Sanchez-Cortezon, J. H. Miners, *Journal of Power Sources* **2004**, 129.
- [18] G. Gupta, K. Scott, M. Mamlouk, *Journal of Power Sources* **2018**, 375, 387.
- [19] R. Espiritu, B. T. Golding, K. Scott, M. Mamlouk, *Journal of Power Sources* **2018**, 375, 373.
- [20] R. Espiritu, B. T. Golding, K. Scott, M. Mamlouk, *J Mater Chem A* **2017**, 5, 1248.
- [21] B. Lin, L. Qiu, B. Qiu, Y. Peng, F. Yan, *Macromolecules* **2011**, 44, 9642.
- [22] X. Gao, H. Yu, J. Jia, J. Hao, F. Xie, J. Chi, B. Qin, L. Fu, W. Song, Z. Shao, *RSC Adv.* **2017**, 7, 19153.
- [23] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, *Angew Chem Int Ed Engl* **2009**, 48, 6499.
- [24] L. Sun, J. Guo, J. Zhou, Q. Xu, D. Chu, R. Chen, *Journal of Power Sources* **2012**, 202, 70.

- [25] X. Liu, H. Gao, X. Chen, Y. Hu, S. Pei, H. Li, Y. Zhang, *Journal of Membrane Science* **2016**, 515, 268.
- [26] M.-S. Shin, Y.-J. Byun, Y.-W. Choi, M.-S. Kang, J.-S. Park, *International Journal of Hydrogen Energy* **2014**, 39, 16556.
- [27] M. Tanaka, K. Fukasawa, E. Nishino, S. Yamaguchi, K. Yamada, H. Tanaka, B. Bae, K. Miyatake, M. Watanabe, *J Am Chem Soc* **2011**, 133, 10646.
- [28] X. Wu, K. Scott, *Journal of Power Sources* **2012**, 214, 124.
- [29] M. Tanaka, M. Koike, K. Miyatake, M. Watanabe, *Polym. Chem.* **2011**, 2, 99.
- [30] M. Piana, M. Boccia, A. Filpi, E. Flammia, H. A. Miller, M. Orsini, F. Salusti, S. Santuccioli, F. Ciardelli, A. Pucci, *Journal of Power Sources* **2010**, 195, 5875.
- [31] T. J. Omasta, L. Wang, X. Peng, C. A. Lewis, J. R. Varcoe, W. E. Mustain, *Journal of Power Sources* **2017**, 10.1016/j.jpowsour.2017.05.006.
- [32] M. Mamlouk, K. Scott, J. A. Horsfall, C. Williams, *International Journal of Hydrogen Energy* **2011**, 36, 7191.
- [33] J. Pan, S. Lu, Y. Li, A. Huang, L. Zhuang, J. Lu, *Advanced Functional Materials* **2010**, 20, 312.
- [34] Y. Zhao, H. Yu, D. Yang, J. Li, Z. Shao, B. Yi, *Journal of Power Sources* **2013**, 221, 247.
- [35] Q. H. Zeng, Q. L. Liu, I. Broadwell, A. M. Zhu, Y. Xiong, X. P. Tu, *Journal of Membrane Science* **2010**, 349, 237.
- [36] Z. Wang, J. Parrondo, V. Ramani, *Journal of The Electrochemical Society* **2017**, 164, F372.

Figure Captions

Figure 1: Synthesis of SEBS ionomer in Cl⁻ form

Figure 2: Schematic of the experimental setup for fuel cell testing.

Figure 3: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 50 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

Figure 4: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 70 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

Figure 5: Degradation of fuel cell at 50 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

Figure 6: Degradation of fuel cell at 70 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

Figure 7: Degradation of fuel cell at 70 °C with SEBS ionomer (a) Chronoamperometry at 0.5 V, (b) Polarization with time, (c) EIS at 0.6 V and (d) Crossover current density with time. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40 % Pt/C, Loading: 0.4 mg cm⁻², Membrane:

LDPE-VBC-TMA-30 μm , Flow rate: 100 mlpm H_2 , 21% O_2 , 1 bar back pressure. Anode-
100% RH, Cathode- 15% RH.

For Peer Review

Table Captions

Table 1: Area Specific Resistance of ionomers at different temperatures and different humidity values on Anode and Cathode

Anode/Cathode % RH → Ionomer Material ↓	Area Specific Resistance at 50 °C / $\Omega \text{ cm}^2$			Area Specific Resistance at 70 °C / $\Omega \text{ cm}^2$		
	100/100	100/0	100/100	100/100	100/0	100/100
SEBS	0.07	0.14	0.07	0.08	0.23	0.09
Acta I2	0.11	0.17	0.11	0.12	0.19	0.12
PVBC	0.14	0.49	0.15	0.18	0.47	0.15

Table 2: Area Specific Resistance of MEAs with different ionomer at 50 °C

Ionomer Material	Area Specific Resistance	Area Specific Resistance
	at 0.9 V / $\Omega \text{ cm}^2$	at 0.6 V / $\Omega \text{ cm}^2$
SEBS	0.15	0.10
Acta I2	0.07	0.07
PVBC	0.16	0.16

Table 3: Area Specific Resistance of MEAs with different ionomer at 70 °C

Ionomer Material	Area Specific Resistance ² at 0.9 V / Ω cm	Area Specific Resistance ² at 0.6 V / Ω cm
SEBS	0.20	0.20
Acta I2	0.20	0.20
PVBC	0.26	0.26

Table 4: Area Specific Resistance of MEAs with different ionomer during degradation at 50 °C at 0.9 V

Ionomer Material	Area Specific Resistance ² –Initial / Ω cm	Area Specific Resistance ² - 50h / Ω cm
SEBS	0.15	0.12
Acta I2	0.07	0.12

Table 5: Area Specific Resistance of MEAs with different ionomer during degradation at 70 °C at 0.9 V

Ionomer Material	Area Specific Resistance ²	Area Specific Resistance ²
	- Initial / $\Omega \text{ cm}^2$	- 15 h / $\Omega \text{ cm}^2$
SEBS	0.20	0.17
Acta I2	0.20	-

Figure 1: Synthesis of SEBS ionomer in Cl- form

255x164mm (300 x 300 DPI)

Figure 2: Schematic of the experimental setup for fuel cell testing.

237x169mm (150 x 150 DPI)

Figure 3: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 50 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode-20% RH

272x208mm (300 x 300 DPI)

Figure 3: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 50 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode-20% RH

272x208mm (300 x 300 DPI)

Figure 3: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 50 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode-20% RH

272x208mm (300 x 300 DPI)

Figure 4: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 70 °C with different ionomers. Area: 1 cm^2 Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm^{-2} , Membrane: LDPE-VBC-TMA-30 μm , Flow rate: 100 mlpm H_2 , 21% O_2 , 1 bar back pressure. Anode-100% RH, Cathode-15% RH.

272x208mm (300 x 300 DPI)

Figure 4: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 70 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode-15% RH.

272x208mm (300 x 300 DPI)

Figure 4: (a) Polarization, (b) EIS at 0.9 V and (c) EIS at 0.6 V comparison of fuel cell testing at 70 °C with different ionomers. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode-15% RH.

272x208mm (300 x 300 DPI)

Figure 5: Degradation of fuel cell at 50 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

272x208mm (300 x 300 DPI)

Figure 5: Degradation of fuel cell at 50 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

272x208mm (300 x 300 DPI)

Figure 5: Degradation of fuel cell at 50 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

272x208mm (300 x 300 DPI)

Figure 5: Degradation of fuel cell at 50 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH.

272x208mm (300 x 300 DPI)

Figure 6: Degradation of fuel cell at 70 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 6: Degradation of fuel cell at 70 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 6: Degradation of fuel cell at 70 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 6: Degradation of fuel cell at 70 °C with different ionomers (a) Chronoamperometry at 0.5 V, (b) Polarization, (c) EIS at 0.9 V and (d) EIS at 0.6 V. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 7: Degradation of fuel cell at 70 °C with SEBS ionomer (a) Chronoamperometry at 0.5 V, (b) Polarization with time, (c) EIS at 0.6 V and (d) Crossover current density with time. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40 % Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 7: Degradation of fuel cell at 70 °C with SEBS ionomer (a) Chronoamperometry at 0.5 V, (b) Polarization with time, (c) EIS at 0.6 V and (d) Crossover current density with time. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40 % Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 7: Degradation of fuel cell at 70 °C with SEBS ionomer (a) Chronoamperometry at 0.5 V, (b) Polarization with time, (c) EIS at 0.6 V and (d) Crossover current density with time. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40 % Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Figure 7: Degradation of fuel cell at 70 °C with SEBS ionomer (a) Chronoamperometry at 0.5 V, (b) Polarization with time, (c) EIS at 0.6 V and (d) Crossover current density with time. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40 % Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

272x208mm (300 x 300 DPI)

Soluble Polystyrene-b-poly (ethylene/butylene)-b-polystyrene
Based Ionomer for Anion Exchange Membrane Fuel Cells
Operating at 70 °C

G. Gupta¹, K. Scott¹, M. Mamlouk^{1,*}

Figure S1: NMR graph of SEBS and Chloromethylated SEBS with the structure of chloromethylated SEBS.

Figure S2: FTIR spectra of the chloromethylated SEBS. (1265 is the chloromethyl peak)

S3: The degree of grafting (DOG) of the membrane was measured from the weights of the membrane before and after gamma irradiation using the following formula:

$$\text{DOG}(\%) = \frac{W_1 - W_0}{W_1} * 100$$

where W_1 is the weight of the polymer after irradiation and W_0 is the weight of the polymer before irradiation.

S4: Calculation of Ion Exchange Capacity

$$\text{IEC (mmol g}^{-1}\text{)} = \frac{2 * V_1 * M_1 * V_2}{W} * 1000$$

Where, V_1 = Volume of H_2SO_4 titrated, M_1 = Molarity of H_2SO_4 used for titration, V_2 = Total amount of Chloride Solution, W = Dry weight of the membrane

S5: Calculating of degree of chloromethylation from figure S1

$$\text{Degree of chloromethylation} = \frac{\frac{\text{Area}(f)}{2}}{\frac{\text{Area}(a) + \frac{\text{Area}(f)}{2}}{5}}$$

Figure S6: Structure of PVBC-60% (y/x = 60/40)

Figure S7: Polarization comparison of fuel cell testing at 50 °C with SEBS ionomer. Area: 1 cm² Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm⁻², Membrane: LDPE-VBC-TMA-30 μm, Flow rate: 100 mlpm H₂, 21% O₂, 1 bar back pressure. Anode-100% RH, Cathode- 20% RH

Figure S8: Polarization comparison of fuel cell testing at 70 °C with SEBS ionomer. Area: 1 cm^2 Anode: 20% Pt/C, Cathode: 40% Pt/C, Loading: 0.4 mg cm^{-2} , Membrane: LDPE-VBC-TMA-30 μm , Flow rate: 100 mlpm H_2 , 21% O_2 , 1 bar back pressure. Anode-100% RH, Cathode- 15% RH.

S8: Calculation of hydrogen crossover current

Hydrogen crossover current was calculated from the cyclic voltammetry graph at the open circuit potential (1V). This was done by calculating the amount of negative current at OCP which has been caused by the oxidation of crossed-over hydrogen at the cathode.