



Effect of anion functional groups on the conductivity and performance of anion exchange polymer membrane fuel cells

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ABSTRACT

A study of the effect of anion functional group on the conductivity and performance of alkaline anion exchange membrane fuel cells (AAEMFCs) is reported.

Membranes and ionomer were characterised in terms of ionic conductivity and separate anode, cathode and cell performances. TMA functionalised (LDPE-co-VBC) or PVBC offered the highest conductivity amongst the various selections of amine/sulphide-based functional groups with conductivities values up to 0.25 (in plane) and 0.043 S cm⁻¹ (through plane). Sulphide-based groups showed lower stability with temperature in comparison to amine-based groups. The increase in length of the chain in the aryl group attached to the nitrogen or sulphur led to lower conductivity. The high OH⁻ conductivity in membranes functionalised with TMA is reflected by its low activation energy of 12 kJ mol⁻¹; close to the reported value for H⁺ conductivity in Nafion.

The ionomer functional groups affected oxygen permeability, the activation energy and the exchange current density for oxygen reduction. TMA functionalised ionomer provided an improved medium for the oxygen reduction reaction with exchange current density some 300 times higher than that with DMS. Anode flooding appeared to severely restrict cell performance and was determined by the type of functional group used for the ionomer. TMA functionalized electrodes showed superior cell performance with a current density of 0.722 A cm⁻² at 0.6 V and a peak power density of 478 mW cm⁻².

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1. Introduction

Solid (cation-free) OH⁻ ion conducting polymer AEMs could hold the key answer to many of the limitations of Proton Electrolyte Membrane Fuel Cell (PEMFC). AEMs exhibit several advantages over PEMFCs including: the oxygen reduction reaction (ORR) is faster under alkaline conditions than in acidic conditions therefore providing lower activation losses [1], non-precious metal catalysts (NPMCs) can be used quite effectively [2,3], increased number of inexpensive materials for cell components due to less corrosive environment [4]. Other major issues with PEMFCs, of water management, crossover and cathode flooding are potentially addressed in Alkaline Electrolyte Membrane Fuel Cells (AEMFCs) by water and ion transport away from the cathode to the anode, mitigating crossover and flooding problems [5].

A large number of electro-active polymers have been studied to prepare modified electrodes such as chloromethylstyrene [6,7], 2,4,5-trichlorophenyl acrylate [8], polyacrylamides [9], quaternized

poly(ether sulfone) PES [10–12], quaternized poly(2,6-dimethyl-1,4-phenylene oxide) PPO [13], quaternized poly(phthalazinone ether sulfone ketone) PPEK [14], and quaternized poly(phenylene) [15,16]. Poly(Chloromethyl Styrene) or Poly(Vinylbenzyl Chloride) PVBC is one of the widely used as base polymer for anion exchange membranes [17–19].

Alkaline electrolyte ionomers are solid polymer electrolyte membranes that contain positive ionic functional groups (e.g. quaternary ammonium (QA) functional groups such as poly – N⁺CH₃) and mobile negatively charged anions (e.g., usually OH⁻). While quaternary ammonium based functional groups are the most commonly used for anion exchange ionomers, other functional groups include tertiary and mixed amine, organic sulfides [20], phosphonic, secondary phosphate, and carboxylic groups.

Ammonium groups were thought to have a higher thermal and chemical stability compared to phosphonium or sulfonium groups [21]. However, it was proved that phosphonium groups have demonstrated their potential and seem to be more stable towards attack by the hydroxide ion than the more conventional quaternary ammonium [22].

Park et al. [23] investigated the effect of the length of alkyl chain of the diamines on membrane properties such as ion conductivity and

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thermal characteristics. Poly(sulfone) and MEAs were aminated by mixing amine agents of trimethylamine (TMA) as a monoamine and various diamines such as *N,N,N,N'*-tetramethylmethanediamine (TMMDA), *N,N,N,N'*-tetramethylethylenediamine (TMEDA), *N,N,N,N'*-tetramethyl-1,3-propanediamine (TMPDA), *N,N,N,N'*-tetramethyl-1,4-butanediamine (TMBDA) and *N,N,N,N'*-tetramethyl-1,6-hexanediamine (TMHDA). They concluded that mixing TMA and TMHDA (with longer alkyl chain) showed better hydroxyl ion conductivity and thermal stability than those aminated by a diamine with peak power densities of 30 mW cm^{-2} with air using 0.5 mg cm^{-2} Pt/C at the anode and the cathode, respectively.

Comparative analysis of the alkaline stability of AAEM prepared with trimethyl, triethyl, tri-*n*-propyl- and tri-*n*-butyl ammonium groups showed that as the chain length of alkyl groups bonded to ammonium groups increased the loss of ion-exchange capacity was significant [24].

Komkova et al. [25] prepared a series of anion exchange membranes from chloromethylated polysulfone and aliphatic diamine compounds. They showed that the quaternization with diamines with long aliphatic chain of the alkyl groups bonded to amine nitrogen require lower excess of diamine to produce membrane with low electrical resistance and high perm-selectivity. It was generally shown that bi-quaternization with diamine was more preferable than mono-quaternization. However, an exception was found for the di-amine with bulky substitute at the amine nitrogen.

We have reported [7] an increase of around 60% of the power density at 0.4 V when TMA was used instead of TMHDA at 60 °C.

In this work, the effect of functional groups has been studied in terms of OH⁻ conductivity and ionomer suitability for fuel cell electrodes.

2. Experimental

2.1. Membrane preparation

The functionalized poly (LDPE-co-VBC) membranes (DOG 26%) were produced by the mutual radiation grafting technique as described in previous papers [4,19,26]. Pieces of the required polymer were initially weighed and then interleaved with a non-woven material and rolled up into a “Swiss roll” configuration. The roll was placed in a glass grafting tube and filled with monomer solution until the complete roll was saturated and covered. The oxygen in the vessel was then removed by purging with nitrogen. The irradiation was carried out at 23 ± 1 °C using a Cobalt 60 gamma radiation source for a pre-determined time at a known dose rate. Once grafted, the films were washed in toluene to remove any homo-polymer, prior to drying to constant weight in an oven at 70 °C. The degree of grafting (DOG) of the membrane, which represents the proportion of the grafted polymer in the membrane was calculated using the following formula:

$$\text{DOG}\% = \frac{W_g - W_0}{W_g} \times 100 \quad (1)$$

where W_g is the weight of grafted copolymer and W_0 is the weight of polymer film before grafting. Therefore, a polymer with a DOG = 26%, consists of 26% of the grafted monomer and 74% original polymer.

The reaction conditions have to be altered for different groups to achieve full functionalization of the VBC (Table 1). This was checked by immersing the membranes in the solution of a given function group at room temperature at different periods of 4, 8, 24, 48 and 72 h after which the films were washed to neutrality using demineralised water. The conductivity of the functionalized membranes

Table 1

A selection of various studied amine and sulfide functional groups.

Name	Conditions	Functional group
TMA	8 h/20 °C/50% in water	Trimethyl amine
DABCO	48 h/50 °C/saturated solution in water	1,4-Diazabicyclo[2.2.2]octane
DMS	72 h/20 °C/100%	Dimethyl sulfide
DES	48 h/50 °C/100%	Diethyl sulfide
TEA	72 h/20 °C/100%	Triethyl amine
TMHDA	48 h/20 °C/100%	<i>N,N,N,N'</i> -tetramethyl-1,6-hexanediamine

then was measured and when the conductivity did not increase with reaction time it was considered that full functionalization was achieved. However, in the case of DES and DABCO the experiment was repeated at 50 °C as no noticeable difference in the conductivity was observed at 20 °C between the pristine and the doped membranes.

2.2. Ionomer testing and fuel cell testing

Fuel cell electrodes were made from catalyst inks to which PVBC was added to facilitate ionic conductivity. The catalyst ink was prepared by sonicating the catalyst 30% Pt/C (E TEK, USA) with 30% wt PVBC in THF. The ink was then airbrushed 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 was $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$.

The PVBC in the electrodes was then functionalized with the different studied groups as mentioned in Table 1. The resulting electrodes were washed thoroughly several times with DI-water and converted to OH⁻ conducting groups by immersing them in 1.0 M KOH for 1 h and changing the solution every 20 min. Finally, they were washed thoroughly several times with DI-water.

For the experimental single cell, titanium was used with 1 cm² serpentine flow fields surrounded by O-ring seal. 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 temperature of 10 °C higher than the cell operating temperature prior to entering the cell, this provided humidification conditions close to 100% RH. The flow rates were controlled manually by means of appropriate flow metres for each gas (Platon (RMandC), U.K). The cell was tested under ambient pressure unless otherwise specified and all gases used were CO₂ free grade.

Trimethylamine functionalized radiation grafting poly (LDPE-co-VBC) CEAM-2 was used as membrane to test the various electrodes; the membrane exhibits DOG of 32%, with initial film thickness of 50 (LDPE). The final membrane thickness obtained in OH⁻ form and fully hydrated conditions were 90 μm. The membrane conductivity when fully hydrated was in the range of $0.04\text{--}0.076 \text{ S cm}^{-1}$ at 20–60 °C, further membrane characterization is reported elsewhere [3,27].

Anode and cathode data were collected separately against an in-situ RHE located next to the anode electrode similar to one reported elsewhere [28]. The IR losses contribution from the membrane was therefore included in the cathode data.

Frequency response analysis and polarization curves using a cathodic sweep at a scan rate of 5 mV s^{-1} were recorded by employing Autolab PGSTAT 30 (Eco Chemie, The Netherlands). The electrodes were subjected to several cycles until a steady performance was reached. Previous tests confirmed that this sweep rate was slow enough to approximate to steady state operation [4,7]. The relative humidity was obtained from an intrinsically safe humidity sensor (Vaisala HUMICAP®, Finland).

3. Results and discussion

3.1. Conductivity results

The membrane conductivities were measured using the four-point probe technique (in plane) and two-point technique (through plane). The four-point technique used four equally spaced probes in contact with the measured material; two of the probes were used to source current while the other two were used to measure the voltage drop. The membranes were cut into 10 mm × 20 mm strips and placed across four platinum foils with equal spacing of 5 mm. AC impedance measurements were carried out between frequencies of 1 and 20 kHz.

The membrane conductivity was measured at 100% RH, with values in the temperature range of 20–80 °C. The samples were held at 30 min for each condition and for further 40 min at 80 °C.

Fig. 1 shows the in plane conductivity of poly (LDPE-co-VBC) membrane with various function groups in OH⁻ form at 100%RH. Membranes functionalized with TMA, DES, DABCO and TMHDA exhibited increase of conductivity with temperature up to 70 °C beyond which conductivity decreased. At 80 °C when the conductivity measurement was repeated after 40 min (second data point at 80 °C, Fig. 1) a large fall in conductivity occurred for all studied functional groups membranes.

The highest measured in plane conductivity, in the range of 0.1–0.25 S cm⁻¹, was obtained for membranes functionalized with TMA. While membranes functionalized with TMHDA showed the lowest in plane conductivity in the range of 0.007–0.02 S cm⁻¹. The studied functional groups can be classified in the following order in terms of OH⁻ conductivity: TMA > DMS > DES > TEA > DABCO > TMHDA.

Fig. 2 shows the through plane conductivity of poly (LDPE-co-VBC) membrane with various function groups in OH⁻ form at 100%RH. The conductivity behaviour with temperature was the same as that of the in plane conductivity. Similarly, the conductivity of the functional group followed the same order above. However, the values of the measured through plane conductivity was much lower than that (around 3–5 times lower) of the in plane conductivity for a given group (also known as degree of anisotropy). For example the highest obtained value was for TMA functionalized membrane in the range of 0.02–0.04 S cm⁻¹. Similarly, the through plane conductivity of TMHDA functionalized membrane was in the range of 0.002–0.006 S cm⁻¹. Larger amounts of the VBC monomer will be grafted on the surface on the LDPE film rather than in its core leading to this observed phenomenon [7]. Values of 2.4 and 5.4 were reported

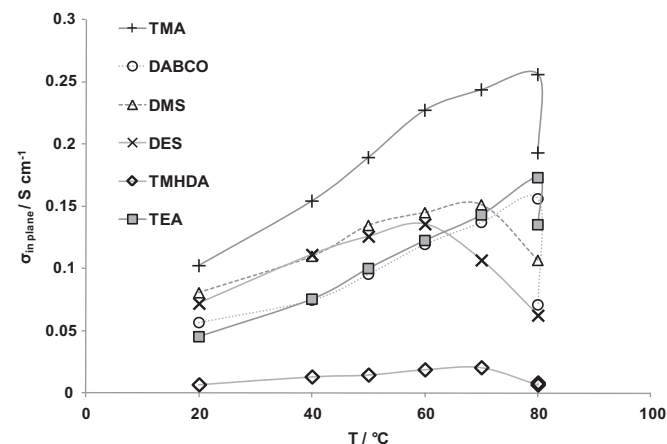


Fig. 1. The in plane conductivity of poly (LDPE-co-VBC) membrane with various function groups in OH⁻ form at 100%RH.

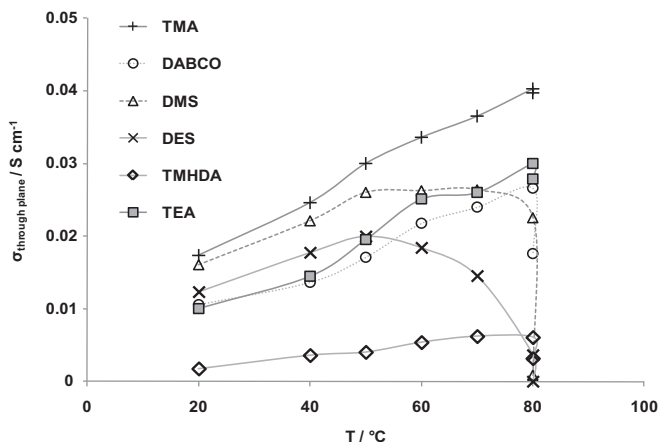


Fig. 2. The through plane conductivity of poly (LDPE-co-VBC) membrane with various function groups in OH⁻ form at 100%RH.

for degree of anisotropy in the literature for co-polymers with perforated lamellae and lamellae morphology, respectively [29].

The increase in length of the chain in the aryl group (for example from methyl to ethyl) attached to the nitrogen (amine) or sulphur (sulphide) led to lower conductivity. Sulphide-based groups showed lower stability with temperature in comparison to amine-based groups. In plane and through plane conductivities of DMS and DES functionalized membranes decreased sharply after 60 °C. Sulphide-based anion exchange groups are thought to have lower thermal and chemical stability in comparison to amine-based groups [21]. The stability of DMS and TMA was reported in ethanol at 4 °C [30]. Fifty percent of DMS was decomposed over a period of just over 6 days while, less than 7% of TMA was decomposed over period exceeding 9 days. The instability of DMS is believed to be caused by its oxidation by hydroxyl radicals [31].

The OH⁻ conductivity variation with temperature followed an exponential temperature dependency. The Arrhenius plot of the conductivity at fully hydrated conditions in the range of 20–80 °C for the studied functional group (except sulphide compounds, 20–40 or 50 °C) is shown in Fig. 3. All studied membranes exhibited positive temperature–conductivity relationship indicating thermally activated process. We can write:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

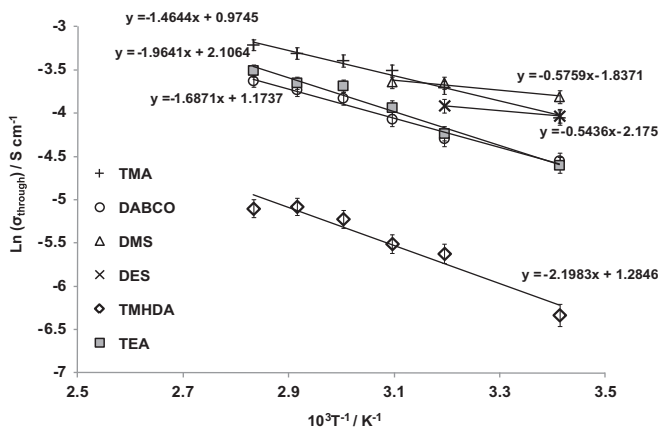


Fig. 3. The Arrhenius plot of the OH⁻ conductivity at fully hydrated conditions in the range of 20–80 °C for poly (LDPE-co-VBC) membranes with the studied functional groups.

where σ is the OH^- conductivity, σ_0 is the pre-exponential factor, E_a is the activation energy of OH^- conduction (kJ mol^{-1}), R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$) and T is the absolute temperature (K).

Sulphide-based anion exchange membranes showed much lower activation energy in comparison to that of amine-based compounds with values in the range of 4.5 (DES) to 4.8 (DMS) kJ mol^{-1} . This explains their high OH^- conductivity at low temperature (20 °C), however, their discussed limited thermal stability hinder their use at elevated temperatures. On the other hand, amine-based compounds had similar activation energy values with TMA showing the lowest value of ca 12, followed by DABCO 14, TEA 16.3 and TMHDA 18.3 kJ mol^{-1} . The high OH^- conductivity in membranes functionalised with TMA is reflected by its low activation energy close to the reported value 8.5 kJ mol^{-1} for H^+ in Nafion [32].

Conductivity of ions is a function of both the ion mobility and the concentration of charge carriers. The PEMs and AEMs have similar water uptake as a function of IEC (ca 1.66) which leads to similar bulk concentrations of potential charge carriers in each case [33]. The average measured value of OH^- conduction activation energy using amine-based groups is around 15 kJ mol^{-1} . The ratio of the ion mobility in dilute solution of that of H^+ (4.76) and OH^- (2.69) (relative to K^+) is around 1.77. This agrees to a great extent with the obtained around 1.77 inverse ratio of the average measured value of OH^- conduction activation energy using amine-based groups to that of Nafion.

3.2. Ionomer evaluation

3.2.1. Anode ionomer

Figs. 4 and 5 show anode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 40 and 50 °C, respectively. The ionomer functional group had a great impact on anode performance. No clear activation region is observed (<30 mV) on all anode polarization curves. The anode showed approximately linear behaviour at low current densities followed by curving towards limiting current (except TMA) indicating mass transport limitation behaviour at high current densities. The mass transport limitation could be caused by low hydrogen permeability or water flooding. The low hydrogen permeability is unlikely as the system operated using pure hydrogen and utilized the same base

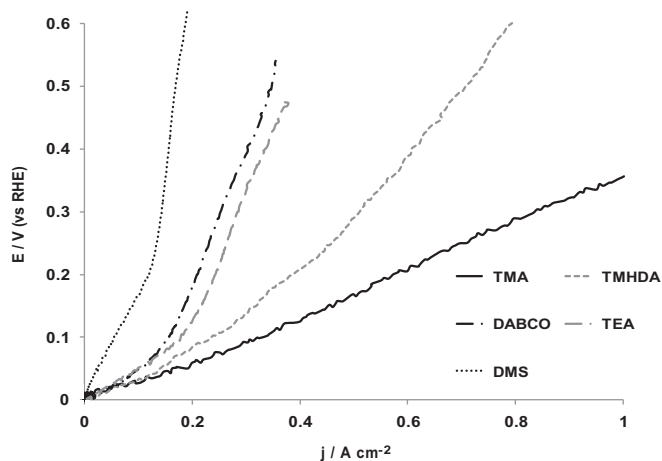


Fig. 4. Anode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 40 °C under hydrogen (atm).

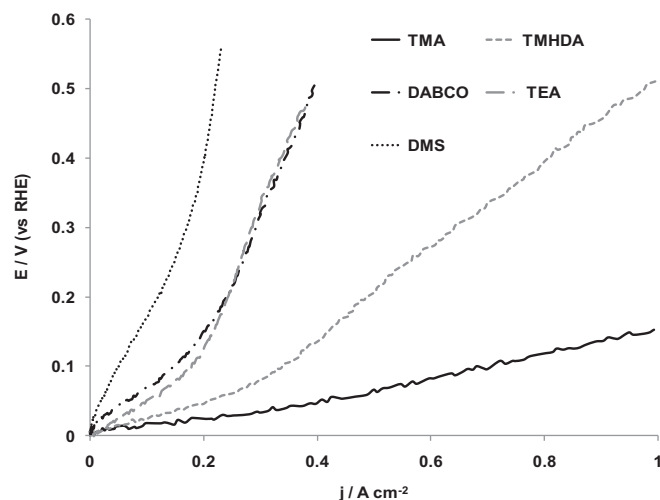


Fig. 5. Anode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 50 °C under hydrogen (atm).

polymer (PVBC) with variation of the functional groups, and electrodes with the same functional groups did not show any mass transport limitation when operated as cathode under air or oxygen (Figs. 6 and 7).

The highly humidified anode stream along with large amount of water produced at the anode at high current densities could lead to flooding if water was not removed quickly to the cathode via the membrane (back diffusion) where it is consumed. The ionomer's water uptake, interaction (hydrophilic/hydrophobic) and permeability are likely to change with the different functional group used.

The observed limiting current (none for TMA) and anode performance can be classified in the following increasing sequence: DMS < DABCO < TEA < TMHDA < TMA.

The direct link between the observed low limiting current and low anode performance confirm the important role of ionomer in the water flooding and water management phenomena in AAEMFCs electrodes.

On the other hand, ionomer OH^- conductivity did not seem to play major role in anode's performance. TMHDA functionalized

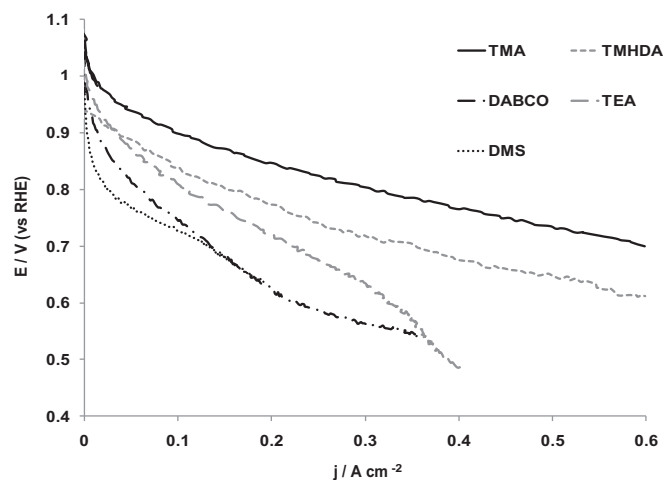


Fig. 6. Cathode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 40 °C under oxygen (atm).

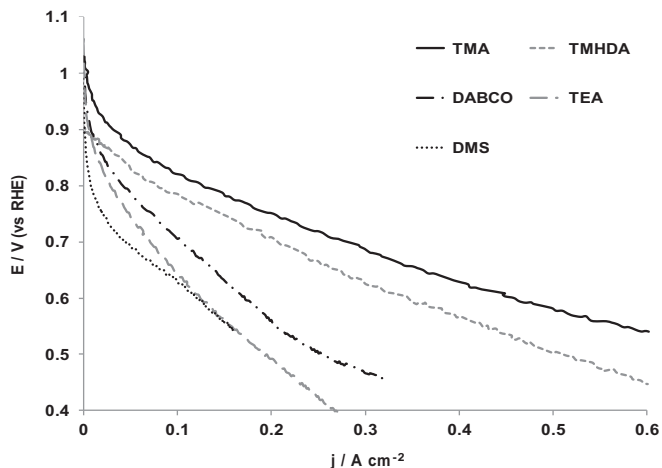


Fig. 7. Cathode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 40 °C under air (atm).

ionomers, for example, exhibited the lowest conductivity (ca $10^{-2} \text{ S cm}^{-1}$) but displayed second best anode's performance. This is due to electrode flooding imposing severe mass transport limitation and restricting the electrode's performance to low current densities where any significant IR loss is hardly observed. Additionally, anode's ionomer IR losses were measured using the impedance high frequency intercept (HFI) of the anode data vs. reference (RHE). Values of 22.5, 30 and 45 mohm cm^{-2} were obtained for TMA, DABCO and TEA functionalized anodes at 50 °C, respectively. These values are relatively small to create the observed large difference in anodes' performances in the obtained current range.

However, by analysing the gradient of the slope of the $I-V$ curve for TMA anode data two linear regions were observed. The slopes obtained for TMA anode data at 40 °C (in Fig. 4) were 231 and 424 mohm cm^{-2} at low and high current densities, respectively. At 50 °C (Fig. 5) the values decreased to 135 and 171 mohm cm^{-2} , respectively.

Considering Tafel slope of 105 mV dec^{-1} for hydrogen oxidation reaction at the anode [34] will translate to losses of 105 mV in the studied current range of 100 mA cm^{-2} to 1000 mA cm^{-2} or 116 mohm cm^{-2} . The expected potential loss at the anode is equal to kinetic loss (Tafel) of 116 mohm cm^{-2} and IR loss (ionomer) of 22.5 mohm cm^{-2} with total of ca 138 mohm cm^{-2} . This value is significantly lower than the fitted value of 231 mohm cm^{-2} at 40 °C and very close to the fitted value at 50 °C of 135 mohm cm^{-2} .

This difference along with the appearance of a second slope (anode) at higher current densities ($>180 \text{ mA cm}^{-2}$) can be explained by mass transport losses caused by electrode gradual flooding and losses of ESA. The effect of this flooding – as expected – becomes less severe as the temperature increased from 40 to 50 °C. This can be seen from the decrease in the difference between the two anode slopes with temperature from 193 to 36 mohm cm^{-2} at 40 and 50 °C, respectively.

Table 2

Current density in mA cm^{-2} for anodes utilizing ionomer functionalized with a selection of amine and sulfide groups at potential of 100 mV (vs. RHE).

Condition	DMS	TEA	DABCO	TMHDA	TMA
40 °C	56.4	179	157	238	339
50 °C	48.2	179	153	340	682

Table 3

Current density in mA cm^{-2} for cathodes utilizing ionomer functionalized with a selection of amine and sulphide groups at potential of 800 mV (vs. RHE).

Condition	DMS	TEA	DABCO	TMHDA	TMA
40 °C – O ₂	26.7	113	63.5	167	320
40 °C – air	9	26.4	41.8	80.4	129
50 °C – O ₂	17.3	49.3	104	207	374

The severely limited anode performance of DMS, TEA and DABCO did not change significantly or decreased slightly with temperature increase from 40 to 50 °C (Table 2). Measured current density at anode over potential of 100 mV was 56, 179 and 157 mA cm^{-2} , respectively. On the other hand, the decrease of flooding of TMA and TMHDA anodes at high current densities (second slope) at 50 °C led to significant increase of anode's performance with temperature. Measured current density at anode over potential of 100 mV increased from 339 to 682 (TMA) and 238 to 340 mA cm^{-2} (TMHDA), when temperature increased from 40 and 50 °C, respectively.

3.2.2. Cathode's ionomer

Figs. 6 and 7 show cathode polarization data vs. RHE (incl. membrane IR) for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulphide groups at 40 °C using oxygen and air, respectively. The ionomer functional group has great impact on cathode performance. Clear activation region is observed for all studied cathodes. The activation losses increased in the following order under oxygen: TMA < TMHDA < TEA < DABCO < DMS.

A difference of 150 mV, recorded between the best (TMA) and the worst (DMS) performing cathodes at a given current density (kinetic region), corresponds to a decrease in the exchange current of oxygen reduction reaction by a factor of around 300 (considering Tafel slope of 60 mV dec^{-1} [35]). This highlights the importance of the used functional group on determining the catalyst–ionomer interaction and the effective accessible catalyst electrochemical surface area and consequently the exchange current density. Measured current density at cathode potential of 800 mV (vs. RHE) under oxygen were 26.7, 63.5, 167 and 320 mA cm^{-2} at 40 °C for DMS, DABCO, TEA, TMHDA and TMA, respectively. Looking at the ratio of these current densities to those under air at the same temperature (Table 3) we obtain, 3, 1.5, 4.3, 2.1 and 2.5, respectively. This suggests that the oxygen permeability through the ionomer is also affected by the used functional group. The high oxygen permeability when using DABCO caused its performance under air to surpass that of TEA (the lowest) on contrary to oxygen results. Oxygen permeability through the studied ionomers does not seem to be a limitation as no apparent limiting current was observed for cathode data even under air operation, this partially due to the limitation of anode (flooding) restricting the cell from reaching high enough current densities where such oxygen mass transport effects might be observed. Increasing the temperature from 40 to 50 °C caused cathode performance to decrease in the case of DMS and TEA, this could be caused by the poor thermal stability of these two specific functional groups. On the contrary, the current density at 800 mV (Table 3) increased by factor of 1.6, 1.2 and 1.2 for DABCO, TMHDA and TMA, respectively. This confirms the functional group impact on the activation energy of oxygen reduction reaction at the ionomer interface.

Unlike the anode data, cathode polarizations showed only one slope. The gradient of the fitted slopes for cathode data under oxygen at 40 °C (in Fig. 6) and 50 °C (Fig. 8) were 303 and

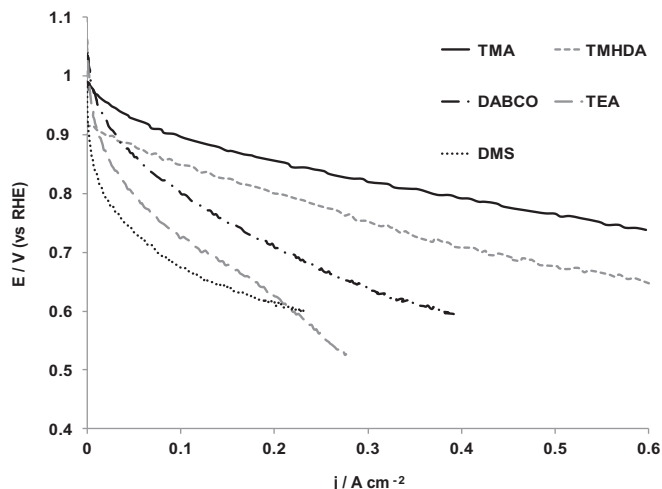


Fig. 8. Cathode polarization data vs. RHE for electrodes utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 50 °C under oxygen (atm).

202 mohm cm^{-2} , respectively. This corresponds to cells I – V slope of ca 720 and 370 mohm cm^{-2} at 40 °C and 50 °C, respectively. These values are much higher than the value obtained for the whole MEA resistance from the impedance high frequency intercept (HFI) of 178 and 150 mohm cm^{-2} at 40 and 50 °C, respectively. We have reported similar observation previously [7]. This translates into membrane resistances of 133 and 105 mohm cm^{-2} at 40 and 50 °C, respectively, assuming that IR losses from cathode and anode's ionomer are the same since both electrodes were identical.

Considering Tafel slope of 60 mV dec^{-1} for oxygen reduction reaction at the cathode [35], will translate to losses of 60 mV in the studied current range of 100 mA cm^{-2} to 1000 mA cm^{-2} or 67 mohm cm^{-2} . The total estimated potential losses due to cathode and membrane are membrane IR loss, cathode ionomer IR loss and kinetic contribution (Tafel) is therefore around 222 and 194 mohm cm^{-2} at 40 and 50 °C, respectively. The value at 40 °C is lower than the fitted value of 303 mohm cm^{-2} , while at 50 °C the estimated value is in good agreement with the fitted value of 202 mohm cm^{-2} .

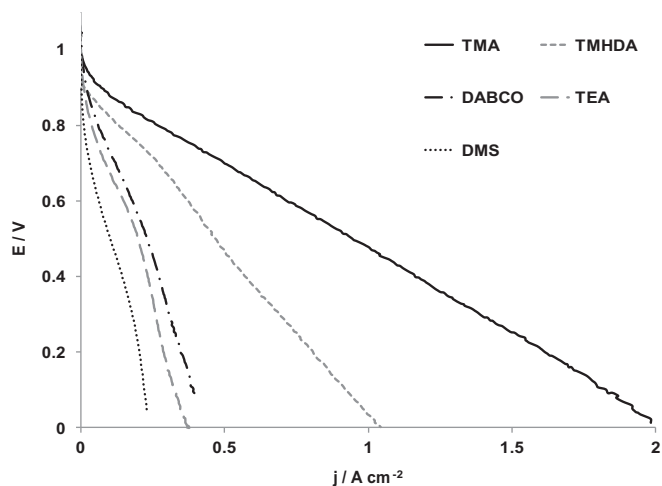


Fig. 9. Performance comparison between MEAs utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 50 °C under hydrogen–oxygen (atm).

Table 4

Current density in mA cm^{-2} at cell potential of 0.6 V and peak power density in mW cm^{-2} for AAEMFCs utilizing ionomer functionalized with a selection of amine and sulfide groups:

	DMS	TEA	DABCO	TMHDA	TMA
j (A cm^{-2})	62	150	176	379	722
P_d (mW cm^{-2})	58	100	116	236	478

3.2.3. Cell performance and power density

Fig. 9 shows polarization curves of AAEMFCs using poly (LDPE-co-VBC) membrane with electrodes utilizing ionomers with various functional groups in OH^- form at 50 °C under O_2 (atm). TMA functionalized electrodes showed superior cell performance by far in comparison to the other studied functional groups with current density of 0.72 A cm^{-2} at 0.6 V with a very high peak power density of 478 mW cm^{-2} (Table 4). No limiting current was observed for TMA functionalized cell even at high current densities up to 2 A cm^{-2} .

TMHDA electrodes showed the second best performance after TMA electrodes in contrary to its lower conductivity results. Measured current density was 0.379 A cm^{-2} at 0.6 V and a considerable peak power density of 236 mW cm^{-2} . Anode mass transport (flooding) showed clear impact on cell performance at current densities above 0.4 cm^{-2} (Figs. 5 and 9) with gradual performance decline approaching limiting current of just over 1 A cm^{-2} at cell potential of 0 V. This confirms that while ionomer's conductivity is an important factor in electrode's performance, other properties such as the interaction and possible adsorption of catalyst/positive ionic functional groups, thermal stability and water permeability should be equally considered when selecting suitable ionomers for AAEMFCs. (Fig. 10)

TEA and DABCO performed similarly with current density of 0.15 and 0.176 A cm^{-2} , respectively, at 0.6 V and a peak power density of 100 and 116 mW cm^{-2} , respectively. Both cell performances were limited by anode flooding with limiting current ca. 360 mA cm^{-2} (Figs. 5 and 9).

DMS functionalized electrodes showed worst performance with current density of 0.062 A cm^{-2} at 0.6 V with a peak power density of 58 mW cm^{-2} . This not a surprise due to its lack of stability especially at elevated temperatures as both anode's and cathode's performance declined with temperature increase from 40 to 50 °C (Tables 2 and 3).

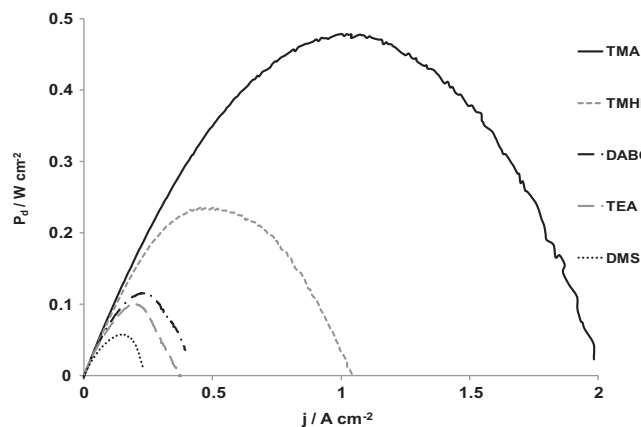


Fig. 10. Peak power density comparison between MEAs utilizing PVBC as ionomer functionalized with a selection of amine and sulfide groups at 50 °C under hydrogen–oxygen (atm).

4. Conclusions

TMA functionalised (LDPE-co-VBC) or PVBC offered highest conductivity among various selections of amine/sulphide-based functional groups with conductivities values up to 0.25 (in plane) and 0.043 S cm⁻¹ (through plane). Sulphide-based groups showed lower stability with temperature in comparison to amine-based groups.

The increase in length of the chain in the aryl group (for example from methyl to ethyl) attached to the nitrogen (amine) or sulphur (sulphide) led to lower conductivity.

Measured activation energy for OH⁻ conductivity for TMA functionalized membrane was ca. 12, followed by DABCO 14, TEA 16.3 and TMHDA 18.3 kJ mol⁻¹.

Anode flooding seems to severely restrict cell performance and is determined to a great extent by the type of functional group used for the ionomer. The observed limiting current (none for TMA) and anode performance can be classified in the following increasing sequence: DMS < DABCO < TEA < TMHDA < TMA.

The ionomer functional group has also great impact on cathode performance affecting oxygen permeability, activation energy and exchange current density for oxygen reduction. TMA functionalized electrodes showed superior cell performance by far in comparison to the other studied functional groups with current density of 0.722 A cm⁻² at 0.6 V and a remarkable peak power density of 478 mW cm⁻². No limiting current was observed for TMA functionalized cell even at high current densities up to 2 A cm⁻².

While ionomer conductivity is an important factor in electrode's performance, other properties such as the interaction and possible adsorption of catalyst/positive ionic functional groups, thermal stability and water permeability/flooding should be equally considered when selecting suitable ionomers for AAEMFCs.

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