



Preparation and characterization of polybenzimidazole/diethylamine hydrogen sulphate for medium temperature proton exchange membrane fuel cells



M. Mamlouk^{a,*}, P. Ocon^b, K. Scott^a

^a School of Chemical Engineering and Advanced Materials, Merz Court, University of Newcastle, Newcastle upon Tyne NE1 7RU, United Kingdom

^b Department of Physical Chemistry, University of Autonoma of Madrid, C/Tomás y Valiente n° 7, 28049 Madrid, Spain

HIGHLIGHTS

- Diethylamine bisulphate/sulfate was synthesised and characterised for HT-PEMFCs.
- FTIR spectra showed that ionic liquid did not change the PBI structure.
- PBI/xDES membranes conditions with conductivity $>0.01 \text{ S cm}^{-1}$ at 150°C .
- The measured proton conductivity is ca. 4 times lower than ionic conductivity.
- The ionic liquid drag will limit the life of the cell due to the IL migration.

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ABSTRACT

Diethylamine bisulphate/sulphate, an ionic liquid, was synthesised and characterised for high temperature fuel cell applications. Composite hybrid membranes of PBI and the ionic liquid diethylamine bisulphate/sulfate were fabricated at different composition ratios PBI/xDES. FTIR spectra showed that the IL did not change the PBI structure. The ionic liquid only weakly interacts with PBI and remains free inside the structure allowing for the observed ionic conduction.

PBI/xDES membranes could operate under a higher temperature values/low humidity conditions with conductivity $>0.01 \text{ S cm}^{-1}$.

The measured proton conductivity, from symmetrical H_2 cell, however, is ca. 4 times lower than that of the measured ionic conductivity. This could be estimated roughly by considering proton conduction where the proton is associated with two anions A^- resulting in ionic agglomerate HA^{2-} with more than double the ionic radius of A^- and consequently less than half of its diffusivity. Additionally, considering the solvation number of that agglomerate to be 1.0 will result not only in a slower proton diffusion and lower conductivity but will also cause serious flooding and mass transport limitation at the cathode. This cumulative effect will limit the life of the cell due to the IL migration from anode and membrane to the cathode.

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1. Introduction

Polymer electrolyte membrane fuel cell, PEMFC, using hydrogen and oxygen, directly convert their chemical energy into electrical energy with only water as the by-product. Current fuel cells most often contain polymer electrolyte membranes carrying sulfonic acid groups [1–3]. The main obstacles to the commercial use of per-fluorinated polymers for fuel cell applications are cost, efficiency,

durability, thermal and mechanical stability and water management [4,5]. Water is essential for the mobility of their protonic charges carriers as it solvates the proton and promotes its mobility by structure diffusion and by vehicle-type transport [6–8]. The conductivities of these membranes rely on maintaining a sufficient hydration level, and thus constant humidification is required and their operating temperature is usually limited to $<90^\circ\text{C}$. A factor allowing further progress in polymer electrolyte membranes fuel cell is an increase in operational temperature above 100°C [9], in an ideal case above 150°C . PEMFCs operating at higher temperatures have a number of benefits: the reaction rate at both electrodes, anode and cathode, is increased, a better CO tolerance allows a

* Corresponding author. Tel.: +44 191 222 5207; fax: +44 191 222 5292.

E-mail address: mohamed.mamlouk@ncl.ac.uk (M. Mamlouk).

simplified fuel pre-treatment [10–13], a higher operating ionic conductivity can be obtained and cogeneration of heat and power production becomes possible [14].

Research on membrane development for sustainable high temperature PEMFCs operating under dry conditions is frequently directed towards dense polybenzimidazole (PBI, Poly(2,2'-m-(phenylene)-5,5'-bibenzimidazole)) membranes. PBI is a promising candidate for use in a high temperature environment. It has excellent chemical and thermal stability and it is often used in thermal protective clothing and fire blocking applications. Depending on its grade, PBI has an upper working temperature between 260 °C and 400 °C. Ideally, the electrolyte within these fuel cells would allow operation without humidification with a strong drive to increase the available operating temperatures to at least 120 °C. As with most polymers, PBI is an electrical insulator and many attempts have been made in recent years to improve its proton conductivity. Often PBI is doped with phosphoric acid to provide proton conductivity [12,15,16], but the chemical stability of the PBI membranes rapidly degrades at temperature above 150 °C due to dehydration of phosphoric acid and other environmental issues [17]. It has been reported that oxygen reduction activities of platinum electrodes, in 85% H₃PO₄, was much higher when the oxide layer was removed (by pre-treatment at cathodic potentials) compared to oxidized platinum electrodes. In addition, there would be deactivation with phosphate anion adsorption at positive potentials [16,18]. Besides, acid leaching is another factor that needs addressing. Sulphuric acid [15] and other organic molecules as imidazole and pyrazoles [19] were used in order to improve the ionic conductivity of PBI.

Different authors [19,20] propose the use of ionic liquids (IL) as a conductive electrolyte to replace phosphoric acid with the intention to overcome the disadvantages resulting from the acid. IL, i.e. molten salts at low temperatures <100 °C, have very interesting properties as high temperature electrolytes due to their low volatility, chemical and thermal stability, non-flammability and high ionic conductivity.

The use of IL based membranes as anhydrous electrolyte is well documented in the literature [21–24]. Most of the materials are evaluated in terms of ionic conductivity. With values in the range of 10^{−3}–10^{−2} S cm^{−1}, ILs are claimed to be an alternative for anhydrous fuel cell operation. However, data on their use in fuel cell is very limited. Relying only on ionic conductivity values can be misleading, for a start: there is confusion between the measured ionic conductivity σ_{imp} of IL based composite membranes and their proton conductivity. σ_{imp} is related to the ionicity (dissociation) of the IL. Proton conductivity might be only a fraction of the observed ionic conductivity.

The transport of the charge is mainly ionic rather than protonic in several IL [21], because the ratio of equivalent conductivity to fluidity (Walden Plot) is below the ideal KCl plot, unlike aqueous mineral acids (above KCl) where the transport is assisted by the independent jumping of protons [21].

The molar conductivity ratio $\Lambda_{\text{imp}}/\Lambda_{\text{est}}$ is a precise physico-chemical parameter for representing the self-dissociation of ILs, Λ_{imp} is calculated from the ionic conductivity from impedance measurement and Λ_{est} is the estimated value from the self-diffusion coefficient of cation D⁺ and anion D[−] given by Nernst–Einstein equation [22]:

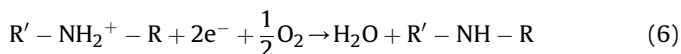
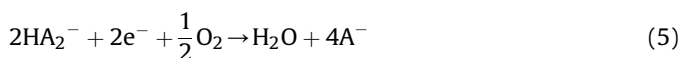
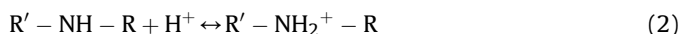
$$\Lambda_{\text{est}} = \frac{F^2}{RT} (D^+ + D^-) \quad (1)$$

where F is Faraday constant, R is gas constant, and T is the absolute temperature.

Equation (1) assumes that every diffusing species contributes to the molar conductivity. In contrast, Λ_{imp} relies on the migration of

charged species in an electric field. The ratio $\Lambda_{\text{imp}}/\Lambda_{\text{est}}$, therefore, indicates the proportion of ions that contribute to ionic conduction from all the diffusing species and can be used as a quantitative measure of ionicity [22]. When the association of anions and cations is predominant, in which charges are completely neutralized $\Lambda_{\text{imp}}/\Lambda_{\text{est}}$ will show very low value. Although ideal ILs consists of non-associated ions, in reality they form aggregates or clusters to some extent. There is experimental evidence of ionic association in ILs [22]. The increase in the cohesive energy and consequently the extremely low vapour pressure of ILs is a result of predominant coulombic interactions, short distance interaction, between the anion and cations leading to $\Lambda_{\text{imp}}/\Lambda_{\text{est}}$ values below 1.

In amine based protic ILs, the acceptor of the proton generated by the HOR is either amine [23,24] (Reaction (2)) or the anion as shown in Reaction (3), or if the used anion is relatively a strong acid that can further ionize to release another proton such as HSO₄[−] ($pK_a = 1.99$ at 25 °C) as of Reaction (4). The protonated product of Reactions (2), (3) or (4) will diffuse to the cathode and react with O₂ to produce water (Reaction (5)) for the case of Reaction (3) or Reaction (6) for the case of Reaction (2):



In anhydrous systems, Reaction (3) is the most likely to occur as the degree of dissociation in Reaction (2) is very small ($pK_a = 10.68$ at 25 °C) and Reaction (4) become negligible without water. However diffusion of HA₂[−] is much slower than that of A[−] (less than half by simply using the Stokes–Einstein equation). Moreover, interactions between the solute (H⁺) and the dipolar solvent (IL), result in a number of solvent molecules orientating themselves around each solute molecule, forming a complex aquo-ion (hydration shell) equal to 4 for H⁺ in H₂O [25]. This increase in ion radius due to solvation will result in decrease in conductivity accordingly allowing for the calculation of the solvation number even in nonaqueous solution, for example: Li⁺/Methanol equal to 7 [26]. Li⁺/N-methylacetamide and H⁺/N-methylacetamide equal to 5 and 3, respectively [27].

While most of the attention in current research is focussing on the ionic conductivity, the suitability of the electrolyte for fuel cell application is of paramount importance, this includes: proton transport number (conductivity), thermal stability, dimensional stability with changes in temperature and hydration, electrochemical stability on Pt (under reducing and oxidizing potentials in the presence of O₂ and H₂). The compatibility with the electrocatalyst in the fuel cell is also critical (its performance can be significantly impacted by loss of contact or adsorption of the IL material [28]). The conducting salt significantly affects the reversibility and kinetics of oxygen reduction in non-aqueous electrolytes [29]. Viscosity also strongly influences mass transport of electroactive species hence determining kinetics of the reaction [29].

The low open circuit voltage could arise from the IL anion adsorption on the noble catalyst or its electrochemical activity as an intermediate in Reactions (2) and (5) above or due to a mixed potential arising from electrochemical instability of the IL ions

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