

Novel Proton Conductive Composite Membranes for High Temperature Proton Exchange Membrane Fuel Cells

Mayur Mistry, Surya Subianto, Namita Roy Choudhury, and Naba Dutta*

Ian Wark Research Institute, ARC Special Research Centre for Particle and Material Interfaces
University of South Australia, Mawson Lakes, South Australia 5095, Australia.
naba.dutta@unisa.edu.au

ABSTRACT

Composite proton conducting membranes have been prepared from NafionTM using functionalized molecular silica and ionic liquids. These membranes show increased thermal stability and glass transition temperature compared to NafionTM, as well as superior proton conductivity at low humidity. This shows that both the functionalized molecular silica and the ionic liquids are able to enhance proton conductivity below the percolation threshold in Nafion.

Keywords: Proton Exchange Membrane, Functionalized Molecular Silica, Organic-Inorganic Composite, Ionic Liquid

1 INTRODUCTION

Today most of our energy supply comes from non-renewable energy resources such as fossil fuels, but there is an increasing drive towards the use of more environmentally friendly, renewable energy source. Of these alternative energies, hydrogen fuel cells are attracting significant attention due to their potential as a “clean” fuel, and in particular the polymer electrolyte membrane fuel cells (PEMFC) represent a credible alternative to fossil fuels especially in portable applications such as the automotive industry.

Currently, there are significant research interest in raising the operating temperature of these PEMFCs to 120-140°C that will increase the catalyst’s CO tolerance and improves electrode kinetics and cell efficiency¹. However, perfluorosulfonic acid membranes, such as NafionTM that is traditionally used as membrane, are unsuitable for this application as they show a marked decrease in conductivity and mechanical integrity at those temperatures². The incorporation of hydrophilic inorganic particles such as silica have been shown to significantly improve the high temperature performance of such membranes^{3,4}. However, incorporation of such particles results in a reduction in free volume, which lowers the proton conductivity of the membrane.

It is realized that the use of smaller particles and silica functionalised with acid groups can improve the

performance of such composite^{5,6}, resulting in equal or greater conductivity than NafionTM. However, studies in this area have been carried out mainly with silica particles, and few studies have been focused regarding the use of molecular silica⁷.

Molecular silica such as Polyhedral Oligomeric Silsesquioxane (POSS) have shown great potential for use in composite materials⁸. Their molecular nature and functionalizability means that they would be able to maximise the interaction between the filler and the matrix with little reduction in free volume. Thus have the potential to achieve better dispersion and conductivity with the addition of smaller inorganic content. But although these inorganic particles may aid water retention at high temperatures, they themselves are often insufficient to impart conductivity under very low humidity or anhydrous conditions. In order to achieve protonic conductivity under these conditions, an alternative charge carrier is required, and a possible solution is the use of Ionic Liquids (ILs).

Ionic liquids have a high ionic conductivity, low vapour pressure, wide electrochemical window and show good chemical and thermal stability^{9,10}. Incorporating ionic liquids within NafionTM can improve conductivity as proton conduction in NafionTM is not limited to the water content¹¹. Ionic liquids can act as charge carriers for proton conduction within NafionTM, eliminating the need for water, which would allow good conductivity at lower humidity¹².

In this study we present the synthesis and incorporation of functionalised molecular silica into NafionTM membranes. Studies have also been done in the use of ionic liquids, with the penultimate goal of achieving conductivity in the absence of water.

2 EXPERIMENTAL

Polyhedral Oligomeric Silsesquioxanes (POSS) bearing aromatic functionalities was sulfonated by direct sulfonation. The sulfonated molecular silica was then dissolved in aqueous alkaline solution and NafionTM 117 membrane was soaked in the solution for 5 days. The membrane was then washed, annealed at 120°C and reprotonated by soaking in dilute HCl.

Ionic liquid composite membranes were prepared by infiltration of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide within Nafion™ 117 membranes. The composite membrane contained 15% ionic liquid by weight.

Thermogravimetric Analysis (TGA) were carried out using a TA Instruments 2950 Thermal Analyser under nitrogen atmosphere. Dynamic Mechanical Analysis (DMA) was performed on a TA Instruments DMA 2980 in tension mode. In-plane proton conductivity values were obtained by AC impedance using a Solartron 1260A electrochemical analyser in a 2-electrode setup¹³. The conductivity of the film were then calculated as per equation 1

$$\sigma = \frac{l}{R * h * w} \quad (1)$$

where l is the distance (cm) between the two Pt electrodes, h and w are the thickness (cm) and width (cm) of the membrane respectively, and R (Ω) is the resistance of the membrane obtained from the complex impedance plot. All measurements were done inside an Espec SH-241 humidity and temperature controlled chamber.

3 RESULTS AND DISCUSSION

In this study, molecular silica bearing aromatic groups was functionalised with sulfonic acid functionalities by direct sulfonation. The resultant material shows high ion exchange capacity and solubility in alkaline aqueous solutions. The yield of the reaction was directly affected by the degree of sulfonation, as very highly sulfonated species was water soluble and thus unsuitable for use in a PEM composite.

When incorporated into proton conducting membranes such as Nafion™, the resultant composite membrane remains transparent, indicating a small particle size and good dispersion. TEM images shows that there was aggregation of the molecular silica, which may have form during annealing, resulting in clusters of silica between 20-50 nm in size. These clusters are found throughout the material showing good penetration of the silica into the Nafion™ membrane.

TGA shows that the composite has an inorganic content of 1-2%, and there was a 20°C increase in the onset of thermal degradation compared to Nafion™. This indicates greater thermal stability of the composite, and is consistent with what has been observed in the literature using sol-gel synthesised silica particles¹⁴. Although Dynamic Mechanical Analysis (DMA) shows a reduction in the storage modulus of the material compared to Nafion™, there was a 10°C increase in its glass transition temperature, which indicates good interaction between the functionalised molecular silica and Nafion™ through ionic

crosslinking. This increase in glass transition temperature is also found to be greater when the material is in its sodium salt form due to greater ionic interaction.

The composite membrane showed a 10% increase in its maximum proton conductivity at 80°C and 100% relative humidity. This result was achieved with a very small loading of POSS (1-2%), and it is believed the molecular nature of the POSS enables it to achieve better dispersion within the polymer matrix, while its multiple acidic functionalities are able to provide greater proton conductivity.

Investigation of the conductivity of the material at varying temperature and relative humidity shows that the conductivity of the hybrid material increases with temperature and relative humidity. Figure 1 shows the plot of conductivity against relative humidity at 80°, and it shows that the conductivity of Nafion™ drops significantly below 40% relative humidity, whereas the drop is significantly less in the hybrid material. At 20% relative humidity, the conductivity of the hybrid material was an order of magnitude greater than Nafion™.

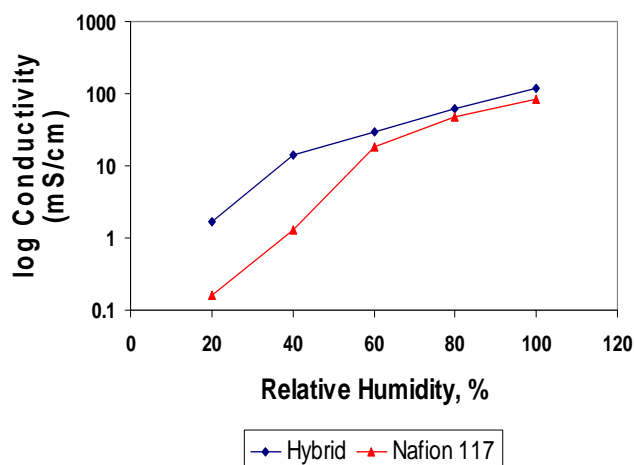


Figure 1. Conductivity versus relative humidity for Nafion™ and the hybrid material

This temperature dependence and conductivity at low hydration indicates that the functionalised molecular silica may have some mobility, and as such may possess limited function as a charge carrier in place of water below the percolation threshold of Nafion™ especially at higher temperatures.

When ionic liquids instead of molecular silica were incorporated into Nafion 117, the composite membranes appeared transparent but were much softer after infiltration of ionic liquid. Similarly to when molecular silica was used, the Nafion-ionic liquid composite membrane has a low storage modulus compared to unmodified Nafion membrane. The unmodified Nafion membrane has a storage

modulus value of 305 MPa in comparison to the composite membrane which has a storage modulus of 136 MPa as shown in Figure 2¹¹. However, similarly to the previous observation with molecular silica, the ionic liquid has increased the glass transition temperature of the composite. Unmodified NafionTM membrane showed a glass transition temperature of 101°C which increased to 135°C in the case of the composite membrane.

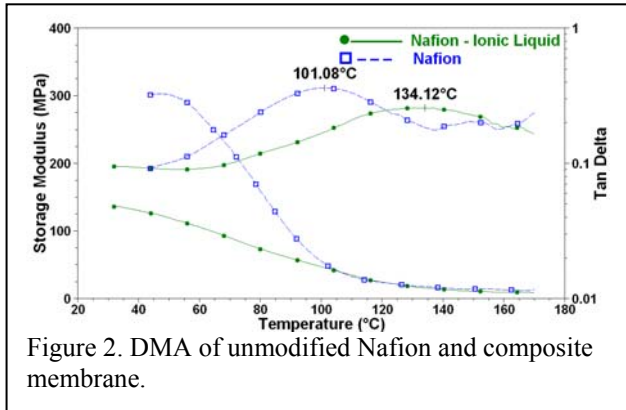


Figure 2. DMA of unmodified Nafion and composite membrane.

TGA in Figure 3 shows that the presence of the ionic liquid has increased the onset of thermal decomposition. In the case of the unmodified membrane onset of thermal decomposition did not occur until 290°C which is related to the loss of sulfonic acid groups in the polymer. In contrast, the composite membrane did not show any weight loss until 375°C. This shows that the presence of the ionic liquid within the Nafion membrane has significantly increased the thermal stability of the material by 85°C. This indicates that in the composite the sulfonic acid groups are deprotonated by the ionic liquid as the TGA curve observed is similar to the sodium salt form of Nafion. This would support the increase in glass transition temperature that was previously observed as it indicates greater ionic interaction within the material.

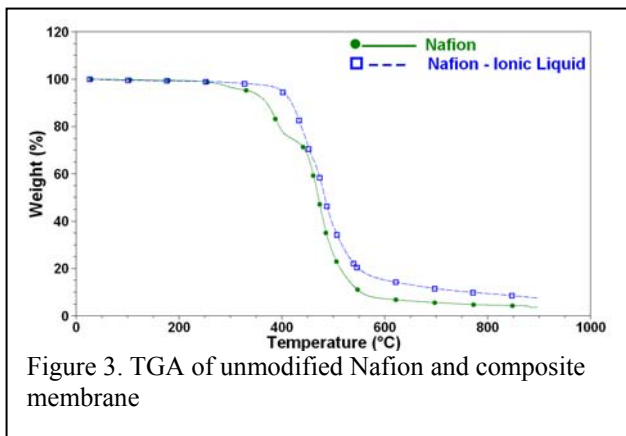


Figure 3. TGA of unmodified Nafion and composite membrane

TGA was also used to determine the status of water in swollen membranes to see how these membranes can retain

water as a function of temperature. The unmodified Nafion membrane lost most of the water contained within the membrane by 100°C. This indicates that Nafion contains mostly interfacial water which is only weakly bound to the polymer. A small amount of water was lost between 100 and 200°C which can be related to bound water which interacts with the polymer through strong hydrogen bonding.

On the other hand, the composite membrane did not show the presence of bound water, as all the water loss occurred at 90°C, indicating that the composite membrane only contains free water and small amounts of interfacial water. This is supported by the water uptake measurements which show unmodified Nafion having a water uptake of 11% and the composite membrane only 2%. These results were consistent with TGA results of swollen membranes. Uptake of the ionic liquid into Nafion has reduced the free volume within the polymer, which restricts the uptake of further water.

Proton conductivity measurements clearly show that the ionic liquid composite membrane is much less dependent on humidity and water content in comparison to unmodified Nafion. At 80°C and 100% RH Nafion shows its highest conductivity which is 75% higher than the composite membrane at the same condition. However at lower humidity the composite membrane shows much higher conductivity values than the unmodified membrane. At 80°C and 30% RH the composite membrane showed a 43% increase in conductivity over unmodified Nafion at the same conditions. These results show that the composite membrane is not dependent on water content for conductivity as the ionic liquid is the charge carrier.

4 CONCLUSION

Functionalized molecular silica and ionic liquids have been incorporated into NafionTM 117. In both cases, the composite membrane show an increase in glass transition temperature and thermal stability especially when ionic liquids are used. Both composite membranes also show greater proton conductivity than NafionTM under low humidity. However, although the incorporation of functionalized molecular silica increased the conductivity of NafionTM, the use of ionic liquid resulted in lower conductivity under hydrated conditions.

5 ACKNOWLEDGEMENTS

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REFERENCES

- (1) J. Zhang; Z. Xie; J. Zhang; Y. Tang; C. Song; T. Navessin; Z. Shi; D. Song; H. Wang; D.P. Wilkinson; Z. Liu; and S. Holdcroft. *Journal of Power Sources* 2006, 160, 872-891.
- (2) Y. Shao; G. Yin; Z. Wang and Y. Gao *Journal of Power Sources* 2007, 167, 235-242.
- (3) I. Honma; H. Nakajima; O. Nishikawa; T. Sugimoto and S. Nomura *Solid State Ionics* 2003, 162-163, 237-245.
- (4) H. Tang; Z. Wan; M. Pan and S.P. Jiang. *Electrochemistry Communications* 2007, 9, 2003-2008.
- (5) D. Gomes; I. Buder and S.P. Nunes. *Desalination* 2006, 199, 274-276.
- (6) Y. Su; T.H. Wei; C.H. Hsu; Y.L. Liu; Y.M. Sun and J.Y. Lai. *Desalination* 2006, 200, 656-657.
- (7) K. Miyatake; T. Tombe; Y. Chikashige; H. Uchida and M. Watanabe. *Angewandte Chemie, International Edition* 2007, 46, 6646-6649.
- (8) G. Li; L. Wang; H. Ni and C.U. Pittman. *Journal of Inorganic and Organometallic Polymers* 2001, 11, 123-154.
- (9) S.S. Sekhon; B.S. Lalia; C.S. Kim and W.Y. Lee. *Macromolecular Symposia* 2007, 249/250, 216-220.
- (10) A. Fericola; S. Panero; B. Scrosati; M. Tamada and H. Ohno. *ChemPhysChem* 2007, 8, 1103-1107.
- (11) C. Schmidt; T. Glueck and G. Schmidt-Naake. *Chemical Engineering & Technology* 2008, 31, 13-22.
- (12) R. Fortunato; C. A. M. Afonso; M.A.M. Reis and J. G. Crespo. *Journal of Membrane Science* 2004, 242, 197-209.
- (13) Z. Xie; C. Song; B. Andreaus; T. Navessin; Z. Shi; J. Zhang and S. Holdcroft. *Journal of The Electrochemical Society* 2006, 153, E173-E178.
- (14) B.P. Ladewig; R.B. Knott; A.J. Hill; J.D. Riches; J. W. White; D.J. Martin; J.C. DinizdaCosta and G.Q. Lu. *Chem. Mater.* 2007, 19, 2372-2381.