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COMMUNICATION

Alkaline ionomer with tuneable water uptakes for electrochemical energy technologies†

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A simple aqueous-processable alkaline ionomer (amenable to scale-up) has been developed for enhancing electrode/electrolyte interfaces in clean energy devices (*e.g.* alkaline polymer electrolyte membrane fuel cells). The water uptake of the alkaline ionomer is tuneable allowing its use as a tool for fundamental studies into these interfaces.

1. Introduction

Clean energy generation and energy efficient wastewater treatment technologies such as fuel cells and microbial desalination cells, which typically involve complex interfaces between electrodes and electrolytes, are increasingly important contributors towards the realisation of sustainable and secure energy supplies and mitigation of anthropogenic climate change. These systems require simple and high performance components. A critical need is for ionomers that enhance the ionic contact in electrode/electrolyte interfaces. There are widely available ionomers for systems containing cation(proton)-exchange electrolytes, but this is not the case for systems containing anion-exchange polymer components.

For example, Alkaline Polymer Electrolyte Membrane Fuel Cells (APEMFC) are attracting worldwide interest; this recent class of fuel cell offers the potential to utilise cheaper and abundant non-platinum catalysts.[1] There is also growing evidence that the use of a solid alkaline polymer electrolytes in alkaline fuel cells (instead of the traditionally used aqueous KOH) leads to increased tolerance to CO_2 in the cathode gas supply.[2] Recently developed alkaline anion-exchange membranes (AAEM) show high ionic conductivities (OH^- anion) that are approaching the proton conductivities of proton-exchange membranes (PEM) such as Nafion.[3] This strongly indicates that high performance APEMFCs, with performances comparable to the more widely known proton-exchange membranes fuel cells (PEMFC), are technically feasible. However the performances of H_2-fuelled APEMFCs reported to date have not achieved this parity with the more highly developed PEMFCs. A detailed understanding of the processes occurring in APEMFCs is still being developed and is the subject of significant worldwide research and debate. Previous studies[4,5] highlight the critical importance of the alkaline ionomer (also known as an anionomer) in lowering the contact resistance of the interface between the catalyst layer and the AAEM and provide

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† Electronic supplementary information (ESI) available: The detailed methodology used and further characterisation data for the alkaline ionomers. See DOI: 10.1039/c1ee02349g

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Broader context

A wide range of electrochemical energy systems will be required to help address problems relating to climate change, energy security and the sustainability of energy use (no one technology will solve these problems). These systems include chemical fuel cells (efficient energy generation using alternative energy vectors such as hydrogen), reverse electrodialysis (osmotic energy generation from waters of different salinities, such as river, brackish and sea waters), supercapacitors and redox flow batteries (for energy storage – essential for load balancing and with the widespread implementation of intermittent renewables), microbial fuel cells and microbial desalination cells (energy efficient wastewater treatment and production of freshwater from desalination), and electrochemical devices for carbon dioxide sequestration. Most of these systems involve the interface between electrodes and ionically conducting polymer materials. New and enhanced polymer electrolytes (membranes and ionomers) are urgently required; this is especially true for anion-exchange ionomers/electrolyte-binders (anionomers) that are often required for optimal ionic contact of the electrodes with anion conducting electrolytes (cation/proton-conducting analogues are widely available, such as the Nafion® dispersions produced by Du Pont). For safe scale-up of the manufacture of electrodes containing both ionomers and nanocatalysts, the use of aqueous-based ionomer systems is recommended.

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maximum ion conductivity in the catalyst layer. It has been shown that low APEMFC performance can be due to high overpotentials at the anode (converse to the typical situation found with PEMFCs).[6]

This communication details the latest advances based on a concept first reported in a recent patent application.[7] The concept involves water soluble commercially available poly(vinylbenzyltrimethylammonium chloride), PVBTMACl, that is insolubilised with a simple thermal treatment step. The difficult challenge of developing a high performance but simple alkaline ionomer that is processable in an aqueous form was deliberately targeted. This makes the process of preparing membrane electrode assemblies (MEAs) more environmental friendly and safer on scale-up (if MEA manufacture is to be truly mass production, the use of large quantities of flammable organic solvents alongside the large quantities of high surface area, finely divided, nano-catalysts is ultimately non-viable). Also of importance, this ionomer has a tuneable water-uptake (an indirect indicator of hydrophobicity), which makes it a unique candidate for the facilitation of fundamental studies into the effect of water on the reactions and processes at the electrodes. This is demonstrated below for APEMFC application. The results show the effect of the water content at the electrocatalyst/ionomer interface on performance and that the efficient removal of water from the surface of the catalyst at the anode is critical for high performance.

2. Results and discussion

The ion exchange capacity (IEC) is stable when the water soluble poly (vinylbenzyltrimethylammonium chloride), PVBTMACl, was heated at 160 °C (Fig. 1a) even for 72 h; this is not the case for treatments at 190 °C. The linear expansion, a key property of the polymer that is related to water uptake, of the thermally treated PVBTMACl anionomers (t-PVBTMACl) is tuneable from 300% to 50% by variations in the heat treatment process (inset in Fig. 1a). The conductivity of the thermally treated films when converted to the application relevant hydroxide anion forms is strongly correlated with the linear expansion of the t-PVBTMACl films (Fig. 1b). Detailed spectroscopic analysis, solid state ^{13}C and ^{15}N NMR (Electronic Supplemental Information, ESI, Figure S1†) and Raman spectroscopy (ESI Figure S2†), indicated that there were no significant differences between the samples heated at 190 °C for 20 min to 1 h and the untreated polymer. However, a weak peak at $\delta = 335$ was detected in the ^{15}N NMR spectrum of t-PVBTMACl treated for 1 h at 190 °C. This peak is ascribed to N nuclei in tertiary amine functional groups.

These NMR and Raman experiments only yield information on the polymer's bulk constitution and the results suggest that the chemical properties of the bulk polymer remains unchanged when heated for these short time periods. However, X-ray photoelectron spectroscopy (XPS, Fig. 2 and ESI Table S1,† which compares atomic ratio of N atoms in the polymer and the ratio between the peaks observed at 399.2 eV and 402.0 eV), which probes the surface properties of the polymer films, is more revealing. The N content of the t-PVBTMACl surface was reduced on increased thermal treatment at 190 °C. A N1s peak at 399.2 eV appeared on the thermal treatment of PVBTMACl after only 10 min and the intensity of this peak increased as a function of thermal treatment time, whilst the intensity of the peak at 402.0 eV decreased. After 1 h of thermal treatment at 190 °C, the binding energy of N1s was almost completely changed from 402.0 eV to 399.2 eV. This is strong evidence that the quaternary ammonium groups (402.0 eV peak) in
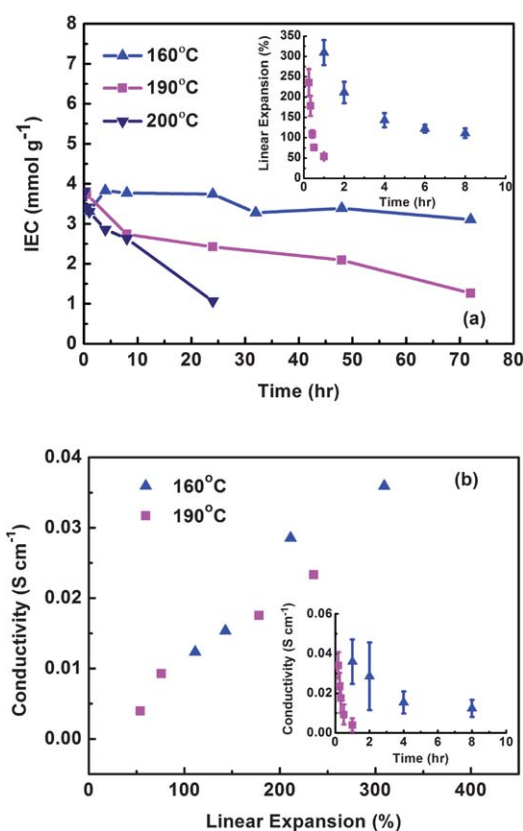

Fig. 1 (a) The changes in ion-exchange capacity (IEC) and linear expansion (inset graph) on increasing PVBTMACl thermal treatment times; (b) The through-plane (2-probe) ionic conductivity of the resulting thermally treated PVBTMACl in hydroxide form. The error bars for the linear expansion are sample standard deviations ($n = 3$) and for conductivity are sample standard deviations ($n = 4$). The relative standard deviations of the IEC for each condition are <5%.

the untreated polymer are being converted to the tertiary amine forms (399.2eV) during the heat treatment process. The ratio of TA/QA (tertiary amine/quaternary ammonium) increased from 0 to 6.67. This is direct evidence that the surface groups of the polymer films are being transformed to the less hydrophilic tertiary amine after such heat-treatment resulting (desirably) in the anionomer becoming insoluble to water (clear evidence of the increase in hydrophobicity).
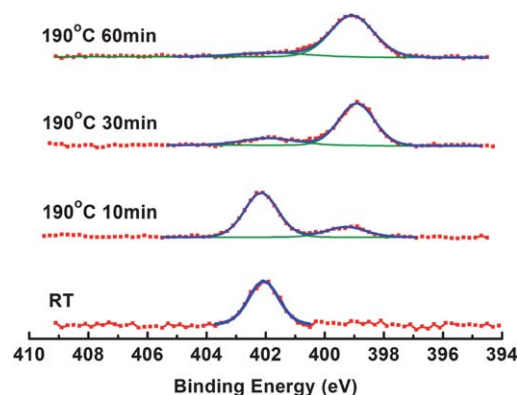

Fig. 2 The X-ray photoelectron spectroscopy (XPS) of t-PVBTMACl on increasing thermal treatment times at 190 °C (from bottom to top).
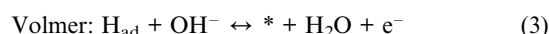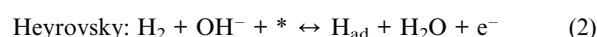
The PVBTMACl polymers that were thermally treated on the electrodes themselves at 190 °C for 10 min, 20 min, 30 min, and 40 min, and after subsequent conversion to the hydroxide forms, were used as the anionomer in fuel cell electrodes. The potentials of the anode (Va) and cathode (Vc) were recorded *vs.* REa (reference electrode located in the anode area) and *vs.* REc (reference electrode located in the cathode area) respectively according to our previous study[8] (refer to ESI Scheme S1†) and presented in Fig. 3. Inset (a) of Fig. 3 shows the polarization (*V vs. i*) and the power density curves, which were recorded simultaneously to the measurement of the anode and cathode potentials and inset (b) shows the internal ohmic resistances of the fabricated membrane electrode assemblies (MEAs).

The internal resistance of the APEMFCs increased as expected with longer thermal treatment times. The resistance of the cell containing t-PVBTMACl(40 min) is 2.6 times larger than the cell containing t-PVBTMACl(10 min). The conductivity of the anionomers in the electrodes (catalyst layers) can affect the performance of anode and cathode *via* numerous different mechanisms. The increased ohmic resistance of the cells with longer anionomer thermal treatments cannot explain the magnitude of the differences of the performances of the MEAs alone. If the ionic conductivity of the anionomer was the primary factor behind the deterioration of the electrodes performance, the changes in the overpotentials of the anode and cathode would be symmetrical (as the same electrodes were used at each). However, the overpotentials of the cathodes increased much less than the overpotentials of the anodes on increased thermal treatment. The overpotential of the cathode only increased by *ca.* 50 mV for t-PVBTMACl(20 min) compared to t-PVBTMACl(10 min) even at a high current density of 600 mA cm⁻². On the other hand, the over potential of the anode changed from 95 mV to 200 mV and 260 mV to 670 mV at current densities of 200 mA cm⁻² and 600 mA cm⁻² respectively.

As shown in Fig. 3, there was a limiting current density plateau at 600 mA cm⁻² for the anode response with an MEA containing t-PVBTMACl treated for only 10 min at 190 °C. This is a typical feature of mass transport derived voltage loss originating from flooding (limits H₂ gas access to the surface of the catalysts). This was confirmed on doubling the volumetric flow rate of the H₂ gas, which

resulted in this mass transfer derived plateau feature being removed within the potential window studied (ESI Figure S3†). Therefore, an appropriate question to pose is "Does the swelling of the anionomer affect the performance of the anode?". The linear expansion of t-PVBTMACl(10 min) is very high >280% but reduces to 160% for t-PVBTMACl(20 min) when in the pristine ex situ cast chloride forms. As the increase in ion conductivity of the hydroxide form anionomer is small on going from 10 to 20 min thermal treatment times (corroborated by the concomitant small increase in the cathode overpotentials for the 20 min anionomer), a superior performance for t-PVBTMACl(20 min) over t-PVBTMACl(10 min) would be observed if limited H₂ mass transport in the anode catalyst layer was the primary cause of the performance limitation (higher swelling of the anionomer on water generation at the anode would block H₂ access). This was not observed and the performance of the MEA containing t-PVBTMACl(20 min) was much lower (despite the apparent lack of this mass transport limited plateau feature at high currents). All of the above suggests that the different anode potentials that were observed at low overpotentials for the different t-PVBTMACl anionomers were not caused by changes of H₂ access to the surface of catalyst under the test conditions used.

Keeping in mind that the anionomer films swell less (uptake less water) on increased thermal treatment (as shown in Fig. 1b) and that water is generated at the anode on the oxidation of hydrogen, it is strongly suspected that the manifest drop in anode performance, even at low overpotentials, originates from the changes in the water contents at the interface between the electrocatalyst and the alkaline ionomer. Consider the hydrogen oxidation reaction/hydrogen evolution reactions (HOR/HER), which proceed through a combination of the following elementary steps[9] in alkaline electrolytes (where * = surface site):

$$\text{Tafel: } H_2 + 2^* \leftrightarrow 2H_{ad} \tag{1}$$

$$\text{Heyrovsky: } H_2 + OH^- + ^* \leftrightarrow H_{ad} + H_2O + e^- \tag{2}$$

$$\text{Volmer: } H_{ad} + OH^- \leftrightarrow ^* + H_2O + e^- \tag{3}$$

If the electro-generated water is not efficiently removed, water coverage of the surface of the electrocatalyst would be increased and lead to a lower concentration of the unoccupied surface sites (= 1 − θ_H, where θ_H is not only the surface coverage of H_{ad} but also the surface coverage of water). This will affect all of the elementary steps above and lower the kinetic performance of the cell. Therefore the common assumption of only a small variation in θ_H (which includes both the surface coverage of H_{ad} and water) at different potentials is not applicable, even if the HOR/HER kinetics are measured in a reasonably narrow potential range,[9] as our results indicate a strong relationship between the water content of the anionomer film and the potential of the anode. We therefore hypothesise that the higher degree of swelling of the least thermally treated anionomer, located at the interface with electrocatalyst, facilitates the removal of water from the surface of the electrocatalyst leading to the improved performance and anode kinetics. The anionomer films with lower water uptakes (longer thermal treatment) introduce a barrier preventing diffusion of the electro-generated water away from the anode catalyst surfaces. The efficient removal of water away from the surface of the electrocatalyst at the anode is therefore a key factor in improving the performance of the APEMFCs.
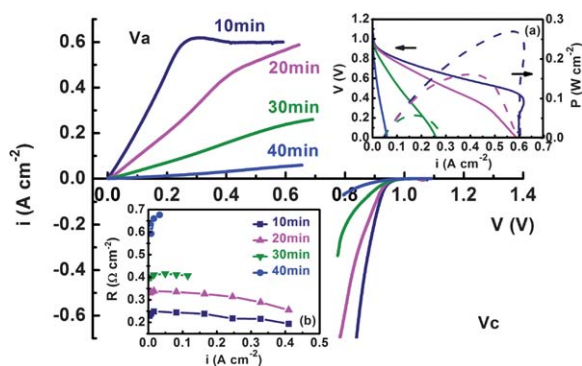

Fig. 3 The main plot presents the potentials of the anodes and cathodes as a function of current density of the MEAs containing PVBTMACl thermally treated at 190 °C for increasing times. Inset (a) gives the *V vs. i* polarization curve and power densities of the APEMFCs. Inset (b) gives the internal ohmic cell resistances of the cells. T_{cell} = 50 °C; H₂/O₂ gases at flow rates of 400 cm³ min⁻¹, delivered with no external pressurization, and RH = 100%; Scan Rate = 2 mV s⁻¹.

A recent study by Fukuta *et al.*[10] presents work on the optimisation of MEA fabrication where it is claimed that an increase in the ion conductivity of the anionomer is not enough on its own to explain differences in power densities. The IEC and ion conductivities (in HCO_3^- counter ion form) of the anionomers used, AS-4 and AS-X (both from Tokuyama, Japan), were 1.5 and 1.8 mmol g^{-1} and 14 and 17 mS cm^{-1} respectively. The surface of AS-X is more hydrophilic due to its higher IEC. The significant increase of the performance reported with the more hydrophilic AS-X is in-line with the observations and hypothesis presented in this study.

The power density obtained with the MEA containing t-PVBTMACl(10 min) anionomer and a 80 μm thick AAEM was 210 mW cm^{-2} at 0.6 V in a H_2/O_2 fuel cell with a cell temperature of 50 °C: This is greatly improved over similar tests with our first generation anionomer (SION1),[4] which yielded 52 mW cm^{-2} at 0.6 V (ESI Figure S4†) under the same test conditions. The study by Fukuta *et al.*[10] yielded a very high performance of 300 mW cm^{-2} at 0.6 V at 50 °C in a H_2/O_2 fuel cell with AS-X, which is a propanol-solvent based anionomer. As stated above, this study is targeted at the challenging ambition of developing an aqueous solution based anionomer system with tailorable water uptakes. Optimisation and lifetime studies of this simple but novel aqueous anionomer concept without the presence of any organic solvent is now a research priority (the development of new fuel cell materials always requires extensive optimisation studies as fuel cell conditions optimised for a particular MEA will not be optimised with the introduction of different MEA components including the ionomers).

3. Conclusions

The results presented highlight the potential of the novel aqueous solution based anionomer system developed. This was demonstrated by the application of the anionomer in an alkaline polymer electrolyte fuel cell (APEMFC) as a tool to probe the source of the performance losses encountered with this new class of fuel cell: The performance was constrained by the overpotential of anode, which is highly correlated to the water uptakes of the anionomer at the interface with the electrocatalyst. The conductivity of the ionomer was not the primary cause of the increase in performance of the APEMFC. The water removal from the surface of the anode catalyst was identified as being fundamental to improving the performance of the APEMFC. The results suggest that a low swelling anionomer film with a highly hydrophilic surface is recommended. Extensive optimisation studies are now on-going, including the realisation of an organic solvent free system, as well as the application of this anionomer for enhanced electrode/electrolyte interfaces relevant to other technologies such as redox flow batteries (for large-scale energy storage), and biological energy systems (such as Microbial Fuel Cells) for energy efficient wastewater treatment and desalination.

Acknowledgements

Notes and references

1 S. Lu, J. Pan, A. Huang, L. Zhuang and J. Lu, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 20611; S. D. Poynton, J. P. Kizewski, R. C. T. Slade and J. R. Varcoe, *Solid State Ionics*, 2010, **181**, 219; X. Li, B. N. Popov, T. Kawahara and H. Yanagi, *J. Power Sources*, 2011, **196**, 1717; K. Matsumoto, T. Fujigaya, H. Yanagi and N. Nakashima, *Adv. Funct. Mater.*, 2011, **21**, 1089; J. Ni, C. Zhao, G. Zhang, Y. Zhang, J. Wang, W. Ma, Z. Liu and H. Na, *Chem. Commun.*, 2011, **47**, 8943; L. An and T. S. Zhao, *Energy Environ. Sci.*, 2011, **4**, 2213.

2 L. A. Adams, S. D. Poynton, C. Tamain, R. C. T. Slade and J. R. Varcoe, *ChemSusChem*, 2008, **1**, 79; J. Zhou, M. Ünlü and P. A. Kohl, *Electrochem. Solid-State Lett.*, 2009, **12**, B27; J. A. Vega, S. Smith, C. Chartierand and W. E. Mustain, *ECS Trans.*, 2010, **28**, 103; Z. Siroma, S. Watanabe, K. Yasuda, K. Fukuta and H. Yanagi, *J. Electrochem. Soc.*, 2011, **158**, B682.

3 N. J. Robertson, H. A. Kostalik IV, T. J. Clark, P. F. Mutolo, H. D. Abruna and G. W. Coates, *J. Am. Chem. Soc.*, 2010, **132**, 3400; J. H. Wang, Z. Zhao, F. X. Gong, S. H. Li and S. B. Zhang, *Macromolecules*, 2009, **42**, 8711; J. Zhou, M. Unlu, J. Vega and P. Kohl, *J. Power Sources*, 2009, **190**, 285; B. P. Tripathi, M. Kumar and V. K. Shahi, *J. Membr. Sci.*, 2010, **360**, 90; M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Macromolecules*, 2010, **43**, 2657; J. H. Wang, S. H. Li and S. B. Zhang, *Macromolecules*, 2010, **43**, 3890.

4 J. R. Varcoe and R. C. T. Slade, *Electrochem. Commun.*, 2006, **8**, 839; J. R. Varcoe, R. C. T. Slade and E. Lam How Yee, *Chem. Commun.*, 2006, 1428.

5 M. Tanaka, M. Koike, K. Miyatake and M. Watanabe, *Polym. Chem.*, 2011, **2**, 99; W. Li, J. Fang, M. Lv, C. Chen, X. Chi, Y. Yang and Yanmei. Zhang, *J. Mater. Chem.*, 2011, **21**, 11340.

6 R. Zeng, S. D. Poynton, J. P. Kizewski, R. C. T. Slade and J. R. Varcoe, *Electrochem. Commun.*, 2010, **12**, 823.

7 WO Pat. 2010/018370 A1.

8 R. Zeng, R. C. T. Slade and J. R. Varcoe, *Electrochim. Acta*, 2010, **56**, 607.

9 W. Sheng, H. A. Gasteiger and Y. Shao-Horn, *J. Electrochem. Soc.*, 2010, **157**, B1529.

10 K. Fukuta, H. Inoue, Y. Chikashige and H. Yanagi, *ECS Trans.*, 2010, **28**, 221.