New Polymer Electrolyte Membranes for Low Temperature Fuel Cells

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SUMMARY: Partially fluorinated proton exchange materials were synthesised by pre-irradiation grafting of styrene into poly(vinylidene fluoride) films with subsequent sulfonation. The grafted and sulfonated membranes, PVDF-g-PSSA membranes, have been studied with respect to water uptake, ion and water clustering, ion conductivity and water diffusion coefficients. Water associates with the membranes in three different ways: bound non-freezable water, freezable bound water and feeezable free water. The proton conductivity of the membrane is strongly dependent on the hydration, it decreases more rapidly than the water self diffusion with decreasing water content. Ion clusters with a Bragg distance of 25 Å form the conducting channels in the membranes.

Solid materials with high protonic conductivity are candidates for electrolytes in sensors, batteries, fuel cells, electrolysers, etc. By most measures the leading solid proton conductors are the polymer based ones. Partly fluorinated or perfluorinated ionomers have found applications due to good chemical stability and mechanical strength as well as high electrical conductivity when hydrated[1]. These hydrated polyelectrolytes used as thin membranes have liquid-like regions of water which transport the protonic species. Numerous studies have focused on the water balance and ion transport in the hydrated membrane, issues that are critical in optimising the performance of the membranes in *e. g.* low temperature fuel cells.[2,3,4] Modelling has been developed to understand the mechanisms of water and ion transport in ionomers.[5,6] In this paper we describe results of studies on the structure, hydration, ion cluster formation and conductivity in styrene grafted and sulfonated partially fluorinated membranes intended for use in low temperature fuel cells.

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Materials and methods

Proton conducting membranes, PVDF-*g*-PSSA membranes, were prepared from PVDF films (Goodfellow 80 μm) in a three-step procedure.[7] The degree of grafting, d.o.g., was determined gravimetrically. X-ray diffraction measurements, (WAXS and SAXS), were done at ambient temperature as described in ref. 7. The electrochemical characterisation was done separately.[8] Atomic force microscopy was done with a Topometrix Explorer 2000 AFM microscope used in contact mode under ambient conditions. The water diffusion experiments were done with a Varian ^{UNITY}INOVA spectrometer operating at 300 Mhz for protons, equipped with a pulsed field gradient, PFG, probe by Varian Inc. Atomistic modelling of the proton conducting membranes was done with the MSI Insight II and Polymer[9] modules with modified CVFF force fields.[10]

Results and discussion

The bulk properties of proton conducting membranes will depend on the hydrophilic-hydrophobic interactions, and thus, on the distribution of of water and grafts in the membrane. For proton transport to occur, the water uptake of the material has to exceed a treshold value. We have recently reported[11] that the minimum water content for ion conductivity in the PVDF-g-PSSA membranes is around 10 molecules of water per sulfonic acid group, which are considered to form the primary hydration shell around the sulfonic acid groups, but do not alone form the aqueous domains necessary for efficient ion and water transport. This is the primary solvation shell of the sulfonic acid groups, the non-freezing water, the phase transition of which could not be detected down to -50 °C. The proton conductivity of the membranes is related to the water content and reaches practically useful values (around 100 mS cm^{-1}) only in membranes with a water uptake considerably over 10 molecules per sulfonic acid group. The less closely associated water in the membranes is present as freezing water weakly bound to the polymer matrix, and freezing free water in pores or sites of a broad distribution of sizes. Thus it is concluded that the PVDF-g-PSSA membranes contain water of three different types associated with the polymer: non-freezing water bound to the ionic sites, freezing water bound to the polymer backbone, and freezing free water. Similar results have been reported for other proton conducting membranes

based on results from impedance spectroscopic studies and calorimetric measurements.[12,13,14]

As water is taking part in the charge transport it is important to know how the diffusion coefficient of water in the membrane, D_{H2O}, depends on the water content in the membrane. In the case of polymer electrolyte membranes it is possible to measure the self diffusion of mobile protons in the membrane by PFG-NMR.[2] As the ratio of water protons to acid protons is typically over six in the membranes, the NMR signal arises mostly from the water and the diffusion coefficient is a close approximation of D_{H2O}. This value can then be compared to the proton diffusion coefficient from conductivity data, and thus gives information about the conduction mechanism at various water concentrations. The Nernst-Einstein equation for strong electrolytes was used to estimate the proton diffusion coefficient from conductivity data. At high water concentrations the proton diffusion coefficient is higher than D_{H2O}. As the water content decreases, the proton diffusion coefficient decreases rapidly compared with D_{H2O}.[15] This is in contrast to what has been reported for Nafion®.[2] Thus we conclude that the morphology of the PVDF-g-PSSA membranes is different from the clustered structure of Nafion, because the acid groups in these membranes are not free to rearrange into clusters. Drying of the membrane makes some of the acidic groups become isolated from the conduction paths.

We have further studied the PVDF-g-PSSA membranes with X-ray diffraction measurements. The SAXS intensity curves of the hydrated PVDF-g-PSSA membranes show a weak maximum at around 0.24 $Å^{-1}$ corresponding to a Bragg distance of 25 Å. Such a SAXS peak is typical for ionomers although in most cases larger Bragg distances are observed.[16] We believe that this difference is due to the degree of sulfonation which in our case is higher than in most previous studies. To enhance the electron density of the ion aggregates the membranes were ion exchanged with zinc or caesium. In the dry membranes the peak was thus shifted to 0.37 $Å^{-1}$ for all membranes corresponding to a Bragg distance of 17 Å. In all the samples the intensity of the ionic peak increases with temperature which indicates an increase of order at increasing temperatures.

Conclusion

The state of water, the diffusion of water and the ion clustering in proton conducting membranes of PVDF-g-PSSA have been studied. Water associates with the membranes in three different ways: bound non-freezable water, freezable bound water and feeezable free water. The proton conductivity of the membrane is strongly dependent on the hydration, it decreases more rapidly than the water self diffusion with decreasing water content. Ion clusters with a Bragg distance of 25 Å form the conducting channels in the membranes.

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