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In situ magnetic resonance imaging of electrically-induced water diffusion in a Nafion ionic polymer film†

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By deploying a functioning electrochemical cell inside a Magnetic Resonance Imaging (MRI) instrument, images of the electrically-induced diffusion of water through a Li$^+$ ion-exchanged Nafion‡ ionic polymer film in the form of two-dimensional maps of proton density and transverse relaxation time, T_2, were generated and changes in these images over time and with respect to changes made to the applied potential were followed.

The Nafion group of materials are perfluorinated ionic polymers prepared as the copolymer of tetrafluoroethene and perfluorinated monomers containing sulfonic acid groups. Nafion is able to absorb large amounts of water and other protic liquids. The poly-tetrafluoroethene backbone gives rise to hydrophobic regions in the polymer and the sulfonic acid groups are thought to cluster together forming hydrophilic regions.[1] The hydrogens on the sulfonic acid groups can be exchanged for cations in protic media. Nafions are used in catalysis, fuel cells and ion exchange membranes.[2]

A potential application of cation-exchanged Nafion is in Electro-Active Polymer (EAP) actuator devices. Such devices bend dramatically and reversibly when a moderate electrical potential is applied across their thickness.[3] EAP devices are prepared by exchanging the protons for cations, usually Li$^+$ or Na$^+$, which are highly solvated in aqueous media and generate relatively high forces in working EAP devices.[4] In the absence of an applied potential, the –SO_3^- groups, attached to the polymer, and the cations are associated. When a potential is applied, the anionic groups are unable to move far towards the (positively charged) anode, since they are attached to the polymer backbone, whereas the cations are able to break away from the anionic groups and move towards the (negative) cathode, taking their solvation shell of water molecules with them. This causes a net movement of water towards the cathode and away from the anode. The result is the swelling of one side of the polymer film and the contraction of the opposite side causing a reversible bending motion of the polymer film as a whole.

Squares of Nafion 117 film (Aldrich) were converted completely to the acid form, carefully washed and the H$^+$ groups exchanged for Li$^+$ ions before storage in distilled, deionised water§. In the MRI experiments¶ the sample holder was arranged so that electrical contact was made to each face of the polymer square at opposite edges, such that the electrical current would pass through the width of the polymer square rather than merely through its thickness. This arrangement was chosen in order to better spacially resolve changes in the density and relaxation time of the protons within the polymer caused by the imposition of the electrical potential. The assembly was mounted in a 25 mm OD NMR tube and connected to the power supply. A constant saturated water vapour pressure was maintained inside the tube by enclosing a water-soaked paper plug within it.

T_2 and proton density maps extracted from MRI images recorded during an extended experimental run on a single Nafion sample are presented in Figure 1. Four regimes were imposed on the sample. In chronological order these were: no applied potential (Figure 1(a)); application of a 5V d.c. potential (Figure 1(b)); application of a 5V d.c. potential of reversed polarity (Figure 1(c)) and application of a 5V d.c potential after a second reversal of polarity (Figure 1(d)). The potential was applied continuously. However, because of the high Ag/polymer contact resistance, currents flowing through the Nafion film were very small (~ 10μA). The raw MRI data were treated to yield maps of proton density and of transverse relaxation time, T_2. The magnitude of T_2 for protons in water is largely dependent on the freedom of rotation of the H_2O molecules, being long for ‘free’ or ‘liquid’ water and short for ‘bound’ water, where there is strong interaction between the H_2O molecules and a solid surface or large molecules. Since the Nafion polymer itself contains no protons, being perfluorinated, the two sets of images in Figure 1 can be considered to relate uniquely to the ^{1}H atoms of the water molecules contained in the polymer sample. The polarity of the applied potential is indicated in the figure.

Considering first the distribution of the long T_2 protons (bright areas), it is clear that with no applied potential, none is observed except in small, localised areas of the polymer sample. However, within the 30 min. period after application of the potential required to acquire the next image (Figure 1(b)(i)), the T_2 is dramatically increased over the whole sample and particularly in the vicinity of the cathode. Over time, the region of high T_2s becomes further concentrated here. On reversal of the polarity, the distribution of long-T_2 protons is reversed over time with an increase in T_2 near the new cathode. The effect of the second reversal of polarity is less dramatic, possibly because of loss of water from the sample by forced evaporation. Nevertheless, a further partial switch is observed in which the region of longer T_2 on the left side of the image becomes more localised to the cathode. A thin high T_2 strip also becomes trapped between the anode and the extreme right edge of the polymer sample. Values of average apparent T_2 were extracted from small regions of these images. Before application of the potential (Fig. 1(a)(i)), the T_2 over the dark part of the image was 40 ms. After application of the potential (Fig. 1(b)(i)), there was a dramatic change. The apparent T_2 was 218 ms at the anode, 247 ms at the centre of the sample and 364 ms at the cathode. In Fig. 1(c)(ii), this trend was reversed with T_2 = 209 ms at the new anode, 219 ms at the sample centre and 357 ms at the new cathode. Therefore, the water molecules at the cathode are consistently those which are expected to be least strongly bound and most mobile. Furthermore, apparent T_2 is significantly higher over the whole sample when a potential is applied than at zero potential.

The set of images showing the evolution of total proton density are presented in Figure 1(a)′(i) to 1(d)′(iii). The changes in these images are less obvious than in the T_2 maps. However, increases in proton density near the cathode, and decreases in the rest of the sample, can be discerned against a high background intensity. Analysis of this data indicates that the proportion of water molecules that move over large distances is

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† Electronic supplementary information (ESI) available: structure of Na-exchanged Nafion and schematic description of actuation mechanism of an electro-active polymer actuator device. See http://www.rsc.org/suppdata/cc/b3/b301039b/

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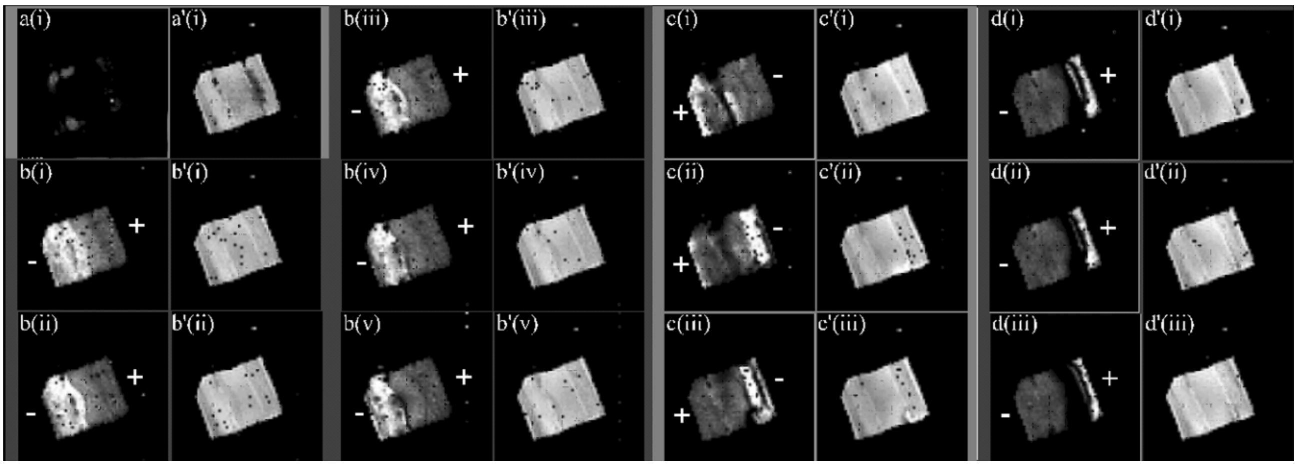

Fig. 1 T_2 maps (top images) and proton density maps (bottom images, primed labels) (a, a′) with no potential applied; (b, b′)(i) 0; (ii) 29; (iii) 60 (iv) 89 and (v) 122 min. after application of a 5Vd.c. potential in the sense indicated; (c, c′) (i) 0; (ii) 36 and (iii) 96 min. after reversal of the polarity of the 5V d.c. potential; (d, d′) (i) 0; (ii) 30 and (iii) 91 min. after the second reversal of the polarity of the 5V d.c. potential. In each case, the T_2 map and proton density map were extracted from the same raw data set. Field of view, 18 mm; slice thickness, 2.0 mm; T_R = 3.0 s; acquisition time, 30 min.

about 10% of the total. However, the T_2 data suggest that there is widespread displacement of water from bound to less bound environments, even though these displacements may be below the resolution of this experiment on the timescale used.

This behaviour is consistent with the mechanism of detachment and electrically-driven diffusion of solvated $[Li(H_2O)_x]^+$ species towards the cathode as described in the actuation mechanism of EAP devices. The initial application of the potential supplies sufficient energy to remove them from close association with the most hydrophillic regions of the polymer structure, causing a general increase in T_2. These species diffuse towards the cathode under the influence of the potential gradient and up to 10% are sufficiently mobile to reach the region of the cathode within the timescale of this experiment. The direction of this diffusion is reversed by reversal of the polarity of the potential.

In an early model,[5] Nafion was thought to contain clusters of hydrophillic ionic groups. Cluster diameters were estimated to be about 3–6 nm, depending on the water content of the polymer, to contain up to 100 ion pairs with up to 20 water molecules associated with each site and to occur at a periodicity of 6–10 nm.[6] To explain the fast diffusion of water through Nafion, channels between clusters were suggested. In recent studies employing ^1H NMR[7] and ^{19}F and ^{129}Xe NMR,[8] a modified structural model was proposed for unexchanged Nafion when swollen with H_2O which consisted of two domains. Water diffusion was proposed to occur through a minor, continuous, hydrophilic domain made up of water, ionic sulfonate groups and the pendant side-chains to which they are attached. A major, hydrophobic domain containing the perfluorinated polymer backbone into which water was not able to diffuse was also proposed. Combining this model and that of Yeager,[9] we suggest a more disordered model than that of Gierke *et al.*[5] in which highly ionic regions exist within a highly hydrophobic major domain but which are connected to each other by regions of a range of thicknesses and a range of intermediate hydrophilicities. In this model, self-diffusion of water in the absence of an applied potential would be expected to take place via low activation energy routes through hydrophilic regions of the polymer. On application of a potential, however, forced diffusion of $[Li(H_2O)_x]^+$ ions (and any water molecules sterically entrained with them) would be expected, and higher activation energy routes would become accessible. More water would be present for longer in the less hydrophilic environments of the polymer. This would result in a decrease in the efficiency of spin–spin relaxation processes and explain the observed increase in T_2 values. Changes in T_2 values of protons within the highly ionic regions alone are unlikely to explain our results since there is evidence that the T_2 values in this environment are short and uniform due to rapid exchange with a small fraction of protons on the $–SO_3^-$ acid site.[6] Finally, water neither associated with mobile solvated Li^+ ions nor entrained with these ions is expected to be less affected by the application of the potential and to remain in the highly hydrophilic, ionic regions of the polymer, contributing to the high background observed in the total ^1H density images.

Notes and references

‡ Nafion is a registered trademark of the DuPont Company.

§ Nafion squares of side 8 mm and 0.2 mm thickness were heated at 80 °C in 2M $HNO_3(aq)$ for 2 h to convert the polymer completely to the acid form and washed by repeated boiling in fresh deionised distilled water. To remove any paramagnetic species, the samples were soaked for 24 h in 0.01 M EDTA solution and again repeatedly boiled in deionised distilled water to wash. To remove oligomer and organic precursor fragments remaining from the preparation of the Nafion, the samples were immersed in a 50 vol% ethanol–50 vol% water solution, sonicated for 2 h and washed as described above. To effect the ion exchange, the Nafion squares were soaked in saturated LiOH(aq) at 60 °C for 1 h. The samples were boiled in deionised distilled water to remove residual LiOH and were stored in fresh deionised distilled water until use.

¶ The Nafion squares were held under moderate pressure between two 8 mm square glass plates. Narrow silver paint electrical contacts were painted onto the inner surfaces of these. Data for images were accumulated on a Bruker 300 FT NMR spectrometer with a wide bore 7.1 T magnet fitted with a Bruker Microimaging accessory. The NMR tube was fitted into a 25 mm birdcage resonator and electrical connection to the electrochemical cell made. The standard Bruker pulse sequence msme, which is designed to collect a train of echos after a 90° pulse, was used to accumulate the data which were converted into T_2 and proton density maps using Paravision© software supplied with the spectrometer. A minimum T_E of 3 ms with 64 echos was used with a T_R of 3 s.

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