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^1H and ^{19}F FFC-NMR of Catalyst Layer Materials for Polymer Electrolyte Membrane Fuel Cells

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Abstract

^1H and ^{19}F spin lattice relaxation rates of catalyst layer materials (CLM) of polymer electrolyte membrane fuel cells were measured by the fast field cycling (FFC) method. In contrast to ionomer membranes, ^1H relaxation rates of adsorbed water in both platinum-Ketjen black (Pt-KB) catalyst powder and CLM were strongly dependent on Larmor frequency approximated by a power law due to the strong surface interaction of adsorbed water. The difference in the frequency dependence in the Pt-KB and the CLM was attributed to higher acidity of the CLM.

Keywords

Fast field cycling, spin lattice relaxation, water, diffusion, fuel cells, ionomers, catalyst layer

1. Introduction

Catalyst layers (CL) are one of the essential components in a membrane electrode assembly of polymer electrolyte membrane fuel cells. They work as a cathode for the oxygen reduction reaction and an anode for the hydrogen oxidation reaction in the case of proton exchange membrane fuel cells. Typically they are made of metallic platinum catalyst (~3 nm in diameter) supported on carbon black primary particles (~30 nm in diameter) of mesoporous agglomerates (~55 nm in pore size distribution maxima) which are coated with ionomer thin films (~5 nm thick) [1]. Although both proton conductivity and diffusivity of reactants (H_2 and O_2) should be maximized in the CL for better cell performance, higher ionomer content favourable for proton transport would block mesopores for gas diffusion onto the catalyst surface through mesopores [2]. Thus understanding the internal structure is important to improve transport properties of the CL.

Unfortunately, most of the analytical methods which have been successfully applied for the polymer electrolyte membranes would be of limited use for the CL due to its optically opaque character and complex internal structure on the nanoscale. As for the NMR methods, application of pulsed field gradient NMR which has been successfully applied for the measurement of self-diffusion coefficients of protons (mostly as water molecules) in the membranes would be difficult for the CL as the relaxation rates are too rapid for echo signal detection. Even if the self diffusion coefficients are measured, their interpretation would be difficult as they are averaged values over length scales much larger than those characteristic of the CL. Thus in this study we attempted to apply fast field cycling (FFC) NMR relaxometry to the CL as the method has been successfully applied for studies on molecular motions and interactions in nanoporous materials.

2. Experimental

The CL samples were prepared as described by Iden et al. [3]. Platinum-Ketjen Black (Pt-KB) was dispersed in a water-alcohol mixture as “catalyst ink” and Nafion® aqueous solution was then added with ionomer/catalyst (I/C) weight ratios of 0.6, 0.9 and 1.2 which correspond to ionomer loadings of 24, 32 and 39 wt%, respectively. An ink solution was sprayed onto a polymer film substrate and was dried to form a layer. In this study the layer was not hot-pressed and it was removed from the substrate for NMR measurement which we denote here as catalyst layer materials (CLM). Nafion® membranes (DuPont NR212, 50 μm thick) and metallic platinum powder (Aldrich, 0.15-0.45μm in diameter) were also used as reference materials. Nafion® membranes were immersed in 2M HCl and subsequently in deionized water at 80°C to remove impurities. They were cut into strips (about 7mm in width) and then stored in desiccators with saturated salt solutions to control the relative humidity (RH). Platinum was used as received and either water or acid solution (2M H_2SO_4 or $HClO_4$) was added (about 30 wt%) for proton NMR measurement. Spin-lattice relaxation rates of ^{1}H and ^{19}F at Larmor frequencies between 0.01 and 40 MHz were measured with Spinmaster FFC-2000 (Stelar s.r.l., Italy) at 30°C.

3. Results

Figure 1 shows ^{1}H spin-lattice relaxation rates of NR212 Nafion® membranes at different values of relative humidity. Relaxation rates decrease with increasing RH and all the profiles show weak logarithmic dependence on Larmor frequency. These profiles are similar to those reported by Perrin et al. for the N112 Nafion® membranes at low RH, although they report practically no frequency dependence at higher RH [4].

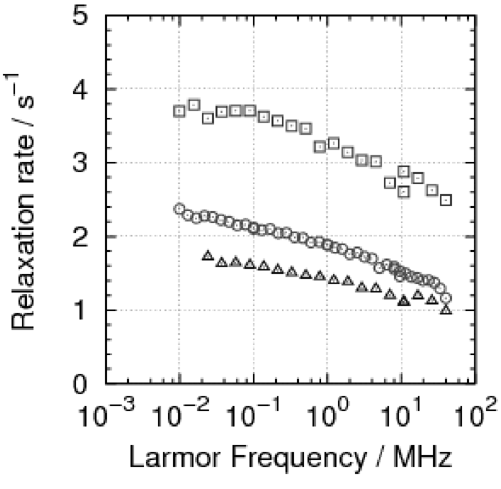

Fig.1 ^{1}H spin-lattice relaxation rates of NR212 Nafion® membranes at different RH: 33%(□), 50%(○), 97%(△).

Figure 2 shows ^{1}H spin-lattice relaxation rates of the Pt-KB at different RH. In contrast to the case of the Nafion® membranes the measured profiles show strong Larmor frequency dependence which are approximated by a power law as typically observed for water in porous glasses [5,6] with exponents approximately -0.75 between 0.1 and 10 MHz The profiles are almost identical in their shape at three RH values and the relaxation rates become slightly smaller at higher RH.

^{1}H spin-lattice relaxation rates of the CLM in Figure 3 also show strong Larmor frequency dependence which can be described by a power law with indices ~ -0.5 below 10 MHz for the samples of I/C=0.6 and 0.9. The profile of the I/C=1.2 sample showed higher relaxation rates than the other two profiles of lower I/C values above 0.5MHz, while below 0.5 MHz the profiles are almost identical. The profiles at 50 and 90% RH of the same sample are almost parallel below 10 MHz as observed in the case of the Pt-KB.

Although both the Pt-KB and the CLM samples show proton spin-lattice relaxation rates which are strongly dependent on Larmor frequency, the relaxation rates of the latter at the same RH are larger and the difference gradually increases towards higher frequencies. One important difference between the two systems is that the ionomer contains acid sites and consequently water in the CLM would become a highly concentrated acid that would affect proton spin-lattice relaxation rates. In fact, sulphuric acid solution added to the Pt-KB showed slightly higher relaxation rates than water in the Pt-KB as shown in Figure 4. This effect was more pronounced in the case of metallic platinum particles and it was attributed to hydronium ions as the same effect was observed in the case of perchloric acid whose anion does not adsorb on metallic platinum surface.

^{19}F spin-lattice relaxation rates of the CLM with different I/C values showed almost identical profiles with that of the Nafion® membrane which are approximated by a power law with indices ~ -0.75 implying almost no difference in the spin-relaxation mechanism of ^{19}F in the CLM and in the membrane.

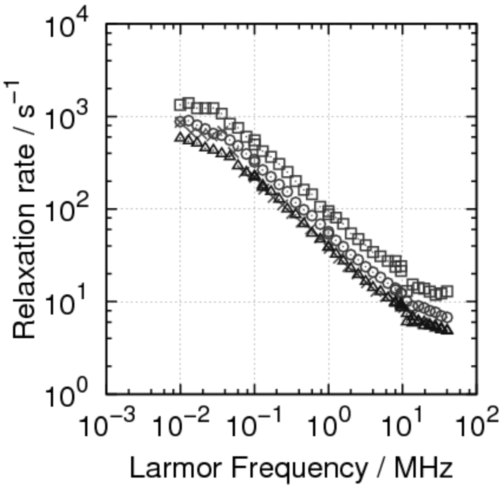

Fig.2 ^{1}H spin-lattice relaxation rates of Pt-KB at different RH: 33%(□), 50%(○), 97%(△).

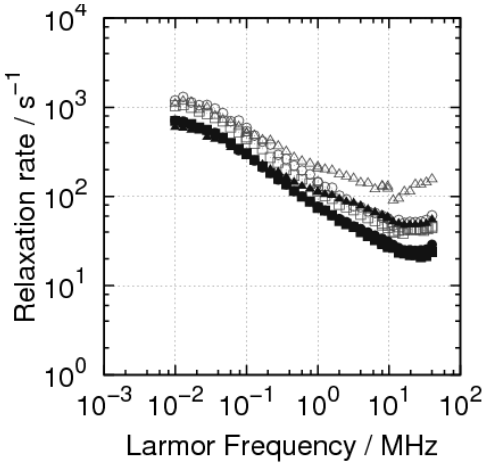

Fig.3 ^{1}H spin-lattice relaxation rates of CLMs of different ionomer/catalyst ratio. I/C=0.6(square), 0.9(circle), 1.2(triangle). open: RH 50%, solid: RH 97%.

4. Discussion

Larmor frequency dependence of the ^{1}H spin-lattice relaxation rates observed either in the Pt-KB or the CLM samples indicate strong surface relaxation as in the case of water adsorbed in nanoporous glasses [5,6]. In these samples water adsorbs on hydrophilic sites such as metallic platinum particles and functional groups containing oxygen at low RH to form localized clusters which eventually coalesce to become continuous liquid water at high RH [2]. Thus the adsorbed water molecules are either in the surface phase or in the bulk-like phase. If fast exchange of adsorbed water molecules between those two phases occurs and the ^{1}H relaxation rates in the bulk-like phase are negligible, the proton relaxation rates of adsorbed water become inversely proportional to the fraction of the surface phase and the profiles of the relaxation rates against Larmor frequencies are vertically shifted downward by increasing RH values as shown in Figure 2. Such a two phase relaxation model has successfully been applied by Perrin et al. for the spin-lattice relaxation rates of sulfonated polyimide membranes [4].

The ^{1}H spin-lattice relaxation rates of the CLM plotted against Larmor frequency also scarcely change and shift downwards by increasing RH values as shown in Figure 3. Although the surface of the carbon particles is coated with Nafion®, its interaction with water would be weaker than the hydrophilic surface sites on the Pt-KB and water diffusion in Nafion® is not severely restricted and the two phase relaxation model can be applied.

Although both the Pt-KB and the CLM showed Larmor frequency dependence approximated by a power law, their differences became gradually larger towards higher Larmor frequency. By referring to the results of the Pt-KB and the metallic platinum particles with acid solutions we attribute the difference in the profiles between the Pt-KB and the CLM to the effect of acidity in the CLM. Anions adsorbed on the metal surface are weakly hydrated and do not affect diffusion of water molecules and therefore have no effect on the spin lattice relaxation due to reorientation mediated by translational displacement. On the other hand, hydronium ions on the metal surface would form hydrogen bonds between water molecules during their surface diffusion and change their orientation that would accelerate spin lattice relaxation. ,

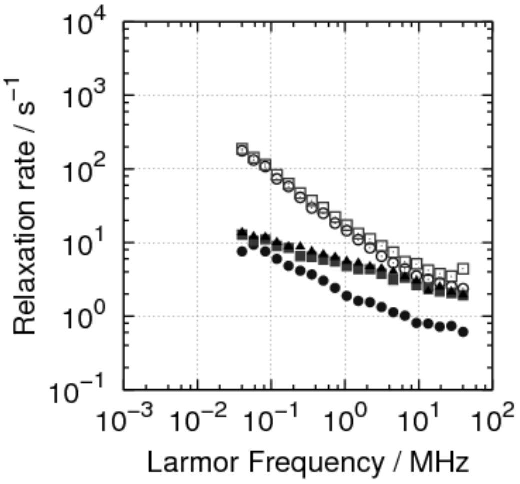

Fig.4 ^{1}H spin-lattice relaxation rates of Pt-KB with water (○) and 2M H_2SO_4 (□) and metallic Pt with water (●) 2M H_2SO_4 (■) and 2M $HClO_4$ (▲)

5. Conclusion

^{1}H spin-lattice relaxation rates of the platinum-carbon black catalyst particles and the CLM showed strong Larmor frequency dependence approximated by a power law due to surface relaxation. The CLM showed larger relaxation rates at higher frequencies which was attributed to acidity of the ionomer. The results show that the FFC-NMR method can provide a unique way to probe the dynamics of diffusing protons in porous materials with complex internal structures like the CLM for which other spectroscopic methods cannot readily be applied.

References

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