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Dynamics of Water in a Porous Phosphate Glass

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ABSTRACT

A new series of P_2O_5 doped SiO_2 glasses has been synthesized using a rapid sol-gel process. These materials exhibit proton conduction similar to that of sulphonated fluorocarbon membranes but they are much more resilient to methanol crossover. We have initiated a neutron scattering program to probe the essential differences in water and methanol translational/ rotational dynamics in these glasses on the pico- and nanosecond timescales in an effort to understand these fundamentally different transport properties. We report our initial results on one glass composition at one hydration level.

INTRODUCTION

Commercial methanol fuel-cells typically suffer from reduced capacity due to methanol crossover through the membranes separating reactants and products. A new series of P_2O_5 doped SiO_2 glasses has been synthesized using a rapid sol-gel process. These materials exhibit proton conduction similar to that of sulphonated fluorocarbon membranes but they are much more resilient to methanol crossover. It has also been shown that the highest selectivity (ratio of conductivity to methanol permeability) exists for a molar P_2O_5:SiO_2 ratio of 30:70. The difference between surface water and bulk water transportation mechanisms is thought to be the main reason for the difference in characteristics between the glass and sulphonated fluorocarbon materials [1]. However, the reasons why there is such a difference in transport properties between water and methanol within the glass itself are unclear.

Quasi-elastic neutron scattering (QENS) has been frequently used to study the dynamics of water at various interfaces ranging from the organic [2] to the inorganic [3]. In particular, there have been recent efforts to distinguish the QENS signals arising from inner and outer hydration layers on non-uniform, hydroxyl terminated oxide surfaces [3]. The aim of this paper is to present our initial results for the mobility of surface water in a single phosphate doped silicate glass. Further work is underway to characterize methanol and proton dynamics within the same glass materials.

EXPERIMENT

The glass electrolyte with a nominal molar ratio of 30% P_2O_5 and 70% SiO_2, designated $30P_2O_5$-$70SiO_2$, was prepared using an accelerated sol-gel process [1]. Precursors of tetraethyl-orthosilicate and trimethyl phosphate were partially hydrolyzed in a mixture of ethanol and water and then further hydrolyzed in the presence of formamide. The xerogels were then obtained by gelation at 60 °C for 3 days. The expected cracking from fast shrinkage during gelation was avoided using water/vapor management. The xerogels were then sintered at 250 °C for 2 hours and continuously heated to 700 °C for another 2 hours with a fixed heating rate of 10 °C/hr. The atmosphere was kept saturated in both the gelation and sintering process. A transparent and colorless glass electrolyte was obtained.

The ground glass pore size distribution was measured using a Quantochrome Autosorb 1C and nitrogen gas after 12 hours degassing at 200 °C. The pore size distribution was estimated by applying a nonlinear density functional theory (DFT) kernel supplied by Quantachrome as a part of their software package. The distribution was calculated by fitting the experimental N_2 isotherm with a sum of theoretical isotherms that were computed for the carbon slit-pore model.

Prior to the neutron measurements, the $30P_2O_5$-$70SiO_2$ glass sample was dehydrated at 200 °C for 12 hours with the same sample batch used after hydrating to 13.4 mass percent. Both samples were measured in cylindrical annular geometry (1.66 g of dry sample), sealed with indium o-rings and placed inside a closed-cycle helium refrigerator. Data were collected using the high-flux backscattering spectrometer (HFBS) [4] at the NIST Center for Neutron Research. In this instrument the incident neutron wavelength is varied by Doppler shifting about the mean value of 6.271 Å. Using matching analyzer crystals ensures that only neutrons with a wavelength of 6.271 Å are detected. Elastic scan measurements, with the Doppler drive disabled, were recorded from 5 K to at least 300 K in order to determine the onset of dynamical behavior. QENS experiments were performed at a dynamic range of ±17 μeV for the hydrated sample at 100 K and at temperatures between 220 and 270 K. Data were analyzed from the 12 detectors that are in the backscattering condition. The DAVE software package was used for elements of the data reduction and analysis of the neutron data [5].

DISCUSSION

Nitrogen isotherms obtained at 77 K yield a BET surface area of 310 m^2/g. Further data reduction using the DFT method gives a non-uniform pore size distribution between 20 Å and 55 Å, with a maximum in the distribution at 50 Å as shown in Figure 1. The large pores suggest that a physical methanol pore blocking scenario is unlikely. Assuming an areal density of 9 $Å^2$ for a bulk-like water molecule and the measured 13 mass percent hydration level, one would expect an equivalent of ≈1.3 monolayers. It is likely that due to the non-uniform pores and heterogeneous hydroxyl terminated surface that terminology using monolayers is at best approximate.

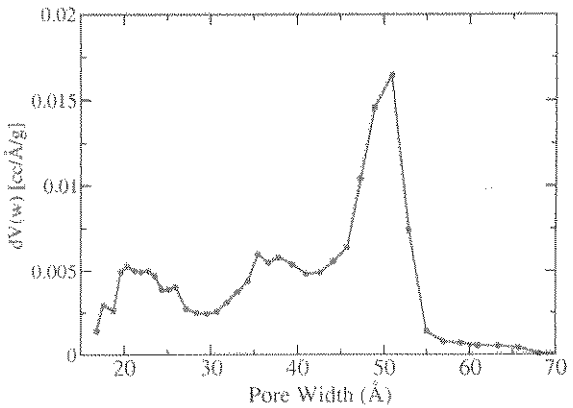


Figure 1. Nitrogen gas derived pore size distribution for the $30P_2O_5$-$70SiO_2$ sample.

An elastic scan can be used to indicate the onset of motion if it occurs within the timescale of the instrument. Figure 2 shows that the hydrated material exhibits super-cooling with a dynamic transition at 195 K. Similar transitions observed on confined water are assigned to the onset of translation dynamics while the rotational component typically is less affected (see for example [3]). The dry glass exhibits no transition to a mobile phase for the temperatures studied yet there is a discernable change in slope of the mean squared displacement at around 110 K. It is not expected that this flattening of the effective mean-squared displacement arises from any residual water content, but it may be influenced by surface hydroxyls.

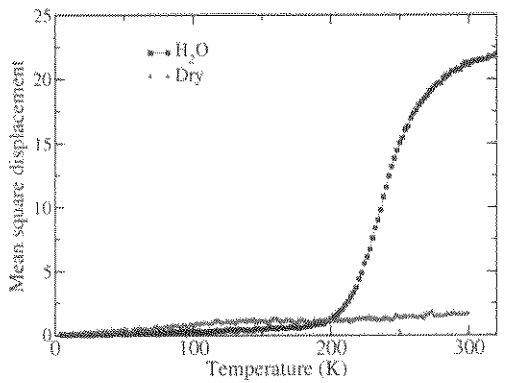


Figure 2. Mean square displacement values derived from elastic scans for the dry and hydrated glasses. The hydrated sample exhibits behavior characteristic of the onset of water dynamics at 195 K.

QENS data which were taken at several temperatures are shown in Figure 3 at a momentum transfer, Q, of approximately 1.1 $Å^{-1}$. The spectra exhibit a broadening compared with the resolution function due to mobile water molecules. The scattering function, $S(Q,\omega)$, for the water sample was analyzed in terms of a translational diffusion model for the dynamic water. The data could be adequately fit to a broad Lorentzian function, a delta function, and a flat background, all convoluted with the instrumental resolution function. An example of such a fit is shown in Figure 3 for the highest temperature (270 K) data. Essentially, this approach implicitly assumes that there is no significant translational-rotational coupling.

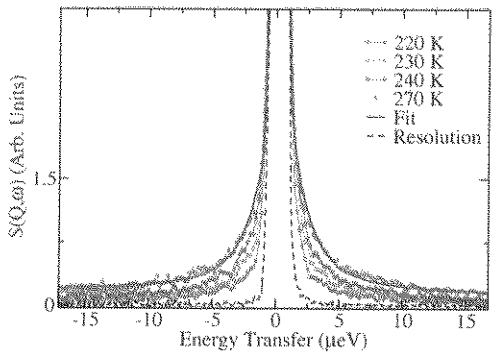


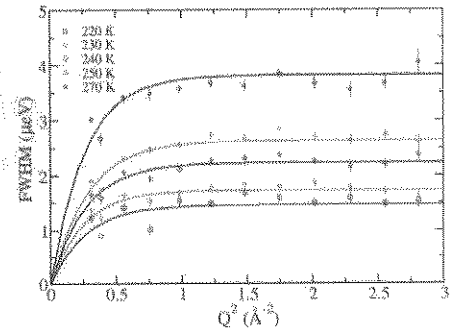
Figure 3. Scattering function measured on HFBS at $Q \approx 1.1$ $Å^{-1}$. Data at 270 K include a fit to a phenomenological model of a Lorentzian, a background and an elastic contribution convoluted with the instrumental resolution.

The Q dependence of the Lorentzian full-width at half maximum (FWHM) is plotted in Figure 4. The Q dependence of the width of the quasi-elastic broadening is indicative of translational jump diffusion with a distribution of jump lengths. We have fitted data to the expression appropriate to a Gaussian distribution of jump length [6],

$$FWHM(Q) = \frac{2h}{\tau_{res}}[1 - e^{-Q^2 \langle r^2 \rangle / 6}], \qquad (1)$$

where $\langle r^2 \rangle$ is a mean-square jump length and τ_{res} is a residence time between jumps. For all temperatures studied the root mean-square jump length is found to be 4.8 Å ± 0.2 Å, a somewhat larger value than the 4.21-4.32 Å cited [3] for the fast water observed on hydrated ZrO_2. This large jump length was explained in terms of a fully hydroxylated surface of silica where one can deduce a distance of 4.66 Å between hydroxyl groups in direct contact with the surface [3] and the same argument is likely to be applicable here.

Figure 4 also shows the temperature dependence of the residency time. There is an Arrhenius temperature dependence of the residency time and no distinguishable glassy behavior. This was also the case for the fast water motion on ZrO_2 [3]. The current activation energy of 9.6(4) kJ/mol is lower than that of 11.38 kJ/mol for the fast water translational motion in ZrO_2.



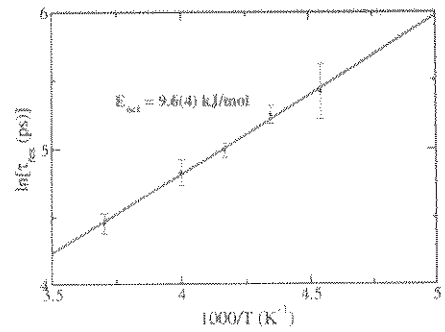


Figure 4. (Left) Width of the Lorentzian component as a function of temperature. Lines are fits to the translational jump diffusion model with a Gaussian distribution of jump lengths. (Right) The residency time for the translational jump diffusion exhibits an Arrhenius dependence with an activation energy of 9.6(4) kJ/mol.

CONCLUSIONS

We have shown that the water dynamics of 13 mass percent water in $30P_2O_5$-$70SiO_2$ can be described using the translation jump diffusion model with a Gaussian distribution of jump lengths within the time- and length-scales of the HFBS spectrometer.

While this may not be the definitive description of the complicated dynamics of water, and may suffer partly from the limitation addressed for water in clays [7], it does serve to compare with the numerous reports which are similar in subject matter. In fact, while we are currently presenting this data interpretation using a simple model, work is progressing to analyze the data in terms of a stretched exponential that more closely represents diffusing species with differing relaxation times. We are also performing measurements on methanol solvated materials and will use different instruments to access longer and shorter timescales that may shed light on the intrinsic water dynamics.

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