



NMR Characterization of Composite Polymer Membranes for Low-Humidity PEM Fuel Cells

Isabella Nicotera,^a Tao Zhang,^{b,*} Andrew Bocarsly,^{b,**} and Steven Greenbaum^{c,**,z}

^aDepartment of Chemistry, University of Calabria, 87037 Rende, CS, Italy

^bDepartment of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

^cDepartment of Physics, Hunter College, New York, New York 10021, USA

Composite membranes prepared by incorporating SiO₂, TiO₂, or Zr(HPO₄)₂ particles into Nafion exhibit enhanced performance in proton exchange membrane (PEM) fuel cells tested at elevated temperatures compared to filler-free Nafion when operating under lower relative humidity. Water-transport properties of these membranes were investigated by nuclear magnetic resonance (NMR) methods, including pulsed-field-gradient spin-echo diffusion, spin-lattice relaxation, and spectral measurements. At least two distinct water environments are observed in all materials, and the enhanced water uptake of the composites, relative to filler-free Nafion, is attributed to alteration of the pore structure of the membrane.

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Proton exchange membrane fuel cells (PEMFCs) utilizing hydrogen as a fuel source provide clean and efficient energy-conversion systems for automobiles, portable devices, and stationary power generation. The development of a high-performance proton-conducting PEM is critical to achieving optimal power density and efficiency, because membrane ohmic loss is a major component of total cell overpotential loss.

PEMFCs operating in the typical 60–80°C temperature range face problems including poor carbon monoxide tolerance and heat rejection. These drawbacks can be overcome by increasing the operating temperature range up to 110–150°C.¹ In this temperature range two opposite effects come into play: (i) improved electrocatalytic kinetics and (ii) decreased proton conductivity of the electrolyte.² PEMFC performance is critically dependent on the membrane water content. However, too much humidification causes flooding of the electrodes and consequently, the diffusion overpotential increases due to insufficient oxygen and hydrogen supply. In order to reduce these overpotentials, properties such as stable water uptake and high proton conductivity are essential for the electrolyte.

At the moment, Nafion is the most widely used polymer electrolyte due to its unique mix of chemical inertness, mechanical and thermal stability, and high proton conductivity. Nafion is a perfluorosulfonate ionomer membrane consisting of a hydrophobic fluorinated long main chains and short side chains which are terminated by a sulfonic acid group. These constituents are also responsible for the morphological structure of the membranes. Structurally, Nafion is complex, and although the exact structure is not known, many studies^{3,4} have been performed since the 1970s on this type of membrane (concerning the macroscopic transport properties and the molecular-level structure of the solute) and several models have been proposed to describe the way in which ionic groups aggregate within the polymer network. Most of these studies converge on the fact that as a result of hydrogen bonding, the acid groups tend to aggregate to form tightly packed regions referred to as clusters^{5,6} and reveal that the molecular-level structure plays a very important role in mass transport in the electrolyte. A widely known model of Nafion is due to Gierke,^{7,8} who proposed an inverted micellar structure in which the ionic clusters are interconnected. Two different water environments in the membrane can be distinguished. A certain amount of water is needed for the solvation of the SO₃⁻ groups. This water is tightly bound close to the inner pore surfaces. The uptake of additional water fills the volumes of pores and behaves more like bulk water. Another well-known model is the three-phase model

membrane structure suggested by Yeager and Steck,⁹ and several mathematical models have also been proposed in order to explain the extraordinary transport properties of this ion exchange membrane based on the characteristics of the electrolyte structure.¹⁰

The present work focuses on two objectives. One is to study the water transport properties of Nafion membranes and to correlate this with fuel cell performance. The other goal is to examine the effects of adding an inorganic particle phase such as SiO₂, TiO₂, or Zr(HPO₄)₂ to the membrane. Composite membranes prepared by the addition of high surface area ceramic oxides to the Nafion matrix provide a promising alternative to pure perfluorosulfonic acid membranes for elevated-temperature PEMFC operation (>100°C).¹¹

Pulse-field-gradient spin-echo-NMR (PFGSE-NMR) techniques were employed in this work to obtain a direct measurement of water self-diffusion coefficients in Nafion and Nafion composite membranes. This technique has been shown to provide valuable information on water transport in PEM materials.¹² NMR spin-lattice relaxation time (T_1) and ¹H-spectra were also taken as a function of temperature and water content. Moreover, all the Nafion composite membranes studied by NMR were assembled in membrane electrode assemblies (MEAs) and tested in a fuel cell. Voltage-current polarization data were recorded under different temperature and humidity conditions. Thus, a direct comparison of fuel cell characteristics and NMR dynamics was available.

Experimental

Membrane preparation.— Nafion/SiO₂, Nafion/TiO₂, and Nafion/Zr(HPO₄)₂ organic-inorganic composite membranes were prepared by the following: (i) 3 wt % (by Nafion solute weight) inorganic particles were sonicated for 2 h and stirred for another 2 h in isopropyl alcohol (IPA); (ii) 15 wt % Nafion solution was added followed by stirring for 1 h. The mixture was then transferred into a cylindrical mold on a glass substrate. Solvent evaporation was carried out in an oven at 50–60°C for about 12 h. The membrane was then heated to and maintained at 80°C for 1 h to remove the residue solvent. The membrane was subsequently transferred into a high-temperature oven and annealed at 145°C for 15 min. The membrane was removed from the glass substrate by soaking in deionized water after cooling to room temperature.

All composite membranes produced by casting were subsequently treated by rinsing in (i) boiling H₂O₂ (3 vol %) for 40 min, (ii) boiling deionized H₂O for 40 min, (iii) boiling H₂SO₄ (0.5 M) for 40 min to remove any metallic impurities, and (iv) boiling deionized H₂O for 40 min twice to remove excess acid. Extruded Nafion 112, used as a control, was also treated by following the same procedure. Identical procedure was followed to prepare membrane samples for both NMR and fuel cell experiments.

* Electrochemistry Society Student Member.

** Electrochemistry Society Active Member.

^z E-mail: steve.greenbaum@hunter.cuny.edu

NMR measurements.—NMR measurements were performed using a Chemagnetics CMX-300 spectrometer with a ^1H operating frequency of 300.02 MHz. Spectra were obtained by transforming the resulting free-induction decay (FID) of single $\pi/2$ pulse sequences. The $\pi/2$ pulse width was about 10 μs . Spin-lattice relaxation time (T_1) was measured by both saturation-recovery and inversion-recovery sequences. Finally, self-diffusion coefficients of water in filler-free Nafion and in the Nafion composite membranes were measured using a PFGSE method first proposed by Stejskal and Tanner,¹³ consisting of a Hahn-Echo pulse sequence ($\pi/2 - \tau - \pi$) with two identical magnetic field gradient pulses, the first applied between the 90 and 180° radio frequency (rf) pulse (during the dephasing) and the second after the 180° rf pulse (during the rephasing) but before the echo. Following the usual notation, the gradient pulses have magnitude g , duration δ , and time delay Δ . The attenuation of the echo amplitude is represented by the Stejskal-Tanner equation

$$A(g) = \exp\{-\gamma^2 g^2 D \delta^2 [\Delta - (\delta/3)]\} \quad [1]$$

where D is the self-diffusion coefficient and γ is the nuclear gyromagnetic ratio. Note that the exponent in the equation is proportional to the mean-squared displacement of the molecules over an effective time scale ($\Delta - \delta/3$). For the investigated samples, the experimental parameters Δ and δ were 10 and 1 ms, respectively, and the gradient amplitude, g , varied from 10 to 300 Gauss cm^{-1} . The uncertainty in the self-diffusion measurements was $\sim 3\%$.

Prior to the NMR measurements, membranes were dried over P_2O_5 for about 10 days. The dried membranes were then immersed in distilled water for different times (from 2 h up to 2 days) at room temperature. Upon being removed from the water they were quickly blotted dry with a paper tissue (to eliminate most of the free surface liquid). The water content value was determined using a microbalance and recorded as

$$\text{uptake}\% = \frac{(m_{\text{wet}} - m_{\text{dry}})}{m_{\text{dry}}} \times 100 \quad [2]$$

At this point the membranes were loaded into a 5 mm NMR Pyrex tube and hermetically sealed. In order to minimize the evaporation of the solvent from the membrane with increased temperature, a “cap” of Teflon was placed just above the membrane. Thus, the free volume available to the evaporated water was minimized.

PEMFC experiments.—Membranes to be tested were hot pressed between two 5 cm^2 ETEK LT140EW ELAT electrodes by placing the MEAs between two Teflon sheets at 140°C under a pressure of 20 Mpa for 1 min. MEAs were tested in a single cell block using Globetech Inc. GT-1000 fuel cell test station. The test station was equipped with independent humidification control of the reactant gases (H_2 , O_2) by changing temperatures of the humidifier and the cell. The humidified reactant gas was maintained at a temperature higher than the humidification bottles to avoid water condensation before the cell. The gas-flow rates were regulated using mass-flow controllers and the total pressure of the gases was controlled using backpressure regulators. The cell was allowed to run at 30°C with humidifier bottles at 50°C under hydrogen and oxygen at atmospheric pressure for an hour before the cathode gas was switched to nitrogen. The cathode was then cycled between 0.1 and 1.0 V vs anode used as a reversible hydrogen electrode at a scan rate of 100 mV/s for an hour before polarization curves were obtained. Current-voltage (I - V) polarization curves were recorded using an Amrel FEL 60-1 electronic load. The cell was maintained at a constant current of 1 A before each polarization curve was taken. All MEAs were tested following an identical procedure.

Results and Discussion

NMR investigation.—PGSE-NMR experiments were carried out on membranes with different water content. As shown in the Arrhenius plots of Fig. 1, it is evident that the diffusion coefficients (D)

strongly depend on the water content of the membranes, with the diffusion coefficient for each membrane increasing with increased water content. Additionally, we note that the highest water uptake values are different for each membrane: 37 wt % for Nafion, 50 wt % for TiO_2 composite, 46 wt % for SiO_2 composite, and 60 wt % $\text{Zr}(\text{HPO}_4)_2$ composite. Some of the membranes exhibit a decrease in the diffusion coefficients at very high temperatures when the actual water content is below the starting value, and the drop is more accentuated when the starting water content value is lower. For example, in the $\text{Zr}(\text{HPO}_4)_2$ composite with 14% uptake, the diffusion starts to decrease above 60°C, and at 140°C its value is approximately 1 order of magnitude smaller than the value at room temperature. From this point of view, the filler-free Nafion at the maximum water content and the TiO_2 composite (at 50% and 42% water content) show the best self-diffusion performance because the diffusion coefficients continue to increase up to 140°C. No considerable difference in the overall magnitude of self-diffusion coefficient is observed between Nafion composites and filler-free Nafion under corresponding conditions.

Figure 2 shows the T_1 Arrhenius plots of all the samples. The longitudinal relaxation time gives information about the local environment and dynamics, including both translation and rotation, of the water molecules on a time scale comparable to the reciprocal of the NMR angular frequency (~ 1 ns). Because the molecular correlation time τ_c depends on temperature, when doing variable temperature measurements, one often observes a minimum in T_1 when $\omega\tau_c \sim 1$, where ω is the NMR frequency.¹⁴ The systems exhibit some temperature dependence but no T_1 minimum in the temperature range investigated. The T_1 trends are consistent with the diffusion trends observed in Fig. 1: T_1 increases when self-diffusion coefficient increases, and we find approximately the same reduction in T_1 and D at higher temperatures. However, in contrast to the diffusion results, all composite membranes studied exhibit higher T_1 values than filler-free Nafion. Also, compared to diffusion results, the magnitudes of T_1 drop with temperature for all membranes are much smaller. Higher T_1 values reflect more facile water molecular rotational and translational motion in the so-called extreme narrowing limit well above the T_1 minimum, i.e., $\omega\tau_c \ll 1$. To understand what happens when the temperature increases, it is useful to consider the proton NMR spectra collected on partially swelled membranes with about 20% of water uptake at various temperatures (Fig. 3). These spectra were referenced against pure water set at 0 kHz. Most of the spectra were acquired with the same number of scans, but in cases where the scan numbers were different, intensities have been normalized. Plots of one type of membrane for different temperatures were rescaled to one figure. Two peaks were observed. The primary peak (1–3 kHz) was attributed to the bulk water. The intensity of this peak decreases with increasing temperature. Therefore, there is some water loss from the membrane at the high temperatures, despite the presence of the Teflon cap. The second peak (< 0 kHz) which emerges beside the primary peak at high temperatures has a constant intensity. This peak, attributed to the tightly bound water as is discussed later, is more pronounced when the bulk water signal decreases at high temperatures with water loss from the membrane. No decay of this peak was observed in the course of the PGSE measurements, indicating that the diffusion coefficient corresponding to these tightly bound water molecules was lower than 10^{-8} cm^2/s , nor did application of a stimulated echo diffusion sequence¹⁵ yield D values for this peak. A downfield shift of the primary resonance during the heating was noticed. In addition, this second signal has the same temperature shift as the primary peak. The observed spectra shape is independent of the initial water content; however, as the water content increases, the relative intensity of the second signal decreases.

Figure 4 displays the chemical shift values vs temperature at all the water contents for all the samples. The reported chemical shift values were referenced to the shift of distilled water at the same temperature as the membrane data. By comparing the self-diffusion

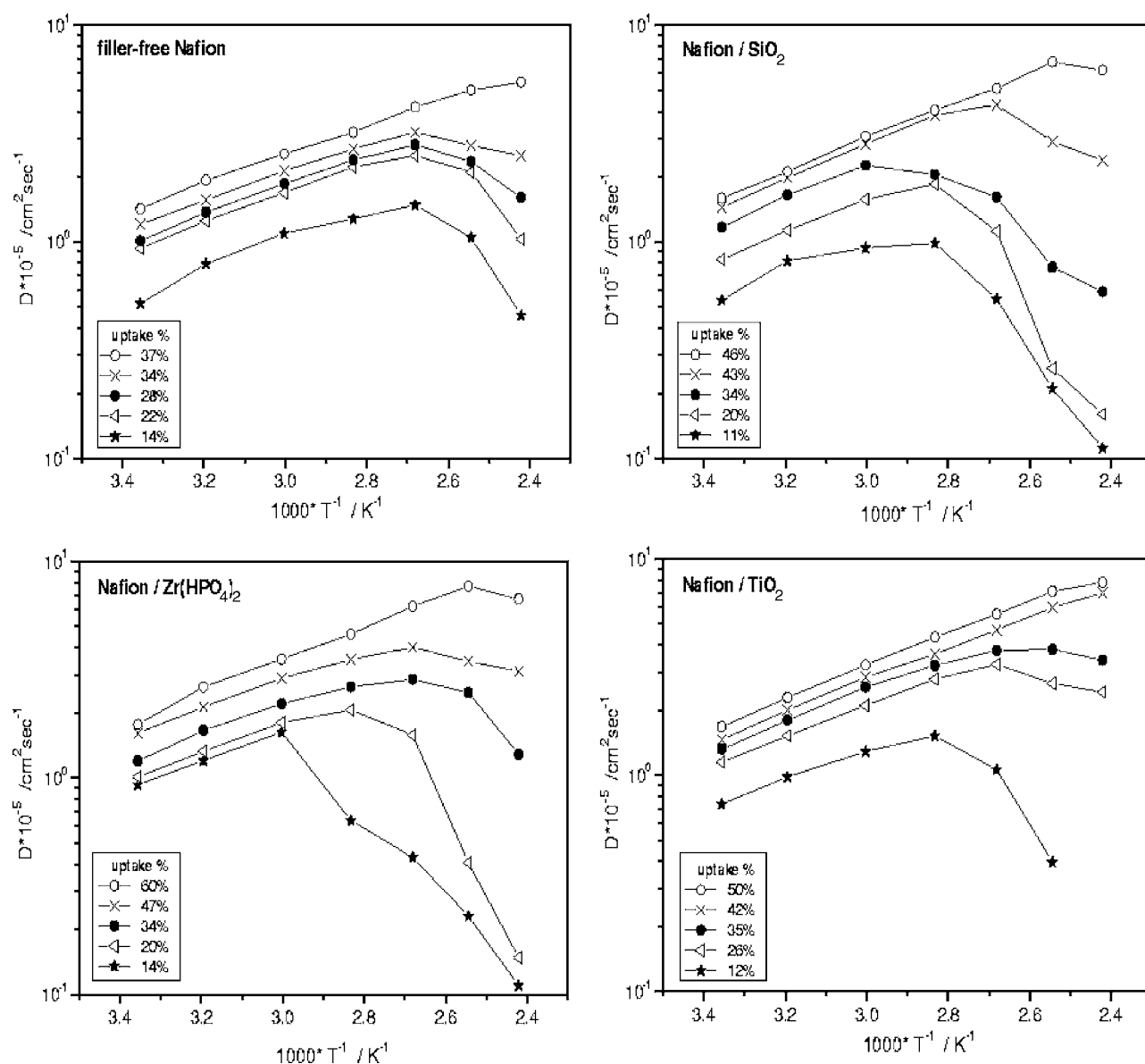


Figure 1. Arrhenius plots of the water self-diffusion coefficients in filler-free Nafion and Nafion composite membranes at different water contents.

coefficient and T_1 trends of Fig. 1 and 2 with chemical shift trends, a certain similarity is discovered. For example, at the highest water content the diffusion curve shows a linear Arrhenius behavior almost up to the maximum temperature (140°C) and the corresponding chemical shift trend is essentially temperature independent. At lower water contents of the membranes, where the diffusion coefficient falls steeply, the corresponding chemical shift increases. This is particularly noticeable in the composites with low water content and is attributed to the departure of the average water molecular environment from that of bulk water. Such chemical shift development is also observed on the second water signal in the spectrum (Fig. 3), even though the corresponding tightly bound water remained inside the membrane. Two notable exceptions are the behaviors of the 34 wt % Nafion and the 47 and 34 wt % $Zr(HPO_4)_2$ composite (which is not understood at this time).

The Gierke⁷ and Yeager¹⁰ models both indicate that in the water-swelled Nafion membrane two different water environments can exist. The two spectral features shown in Fig. 3 are attributed to these two aqueous environments. The higher frequency, more intense peak has been used here to determine the D values presented. The water associated with this signal is different from free water because the

peak is broad (~ 1 kHz), typical of confined water, and the diffusion coefficients are at least 1 order of magnitude less than that of free water. The lower frequency signal is more visible as the primary absorption feature becomes smaller due to water content decrease. It is broader and with less defined shape than the primary signal, and with a (not-measurable in the current apparatus) diffusion coefficient of less than 10^{-8} cm²/s, as mentioned previously. Thus, the water molecules associated with this signal are strongly bound. In fact, even the shape of the main peak in some of the spectra suggests multiple water environments that are not in rapid (on the NMR time scale) equilibrium with each other. Such observations are consistent with the cluster-model described by Gierke,⁷ where most of the water is associated with clusters filling the pore volumes, and some of the water solvates the SO_3^- groups, the latter portion being strongly confined by the relatively large electrostatic and hydrogen bonding forces in the vicinity of the inner-pore surfaces.

The presence of inorganic particles does not qualitatively change the water transport mechanism just described because the behavior of the composite spectra is not much different from that of the filler-free Nafion. It is clear that the effect of the particles is to

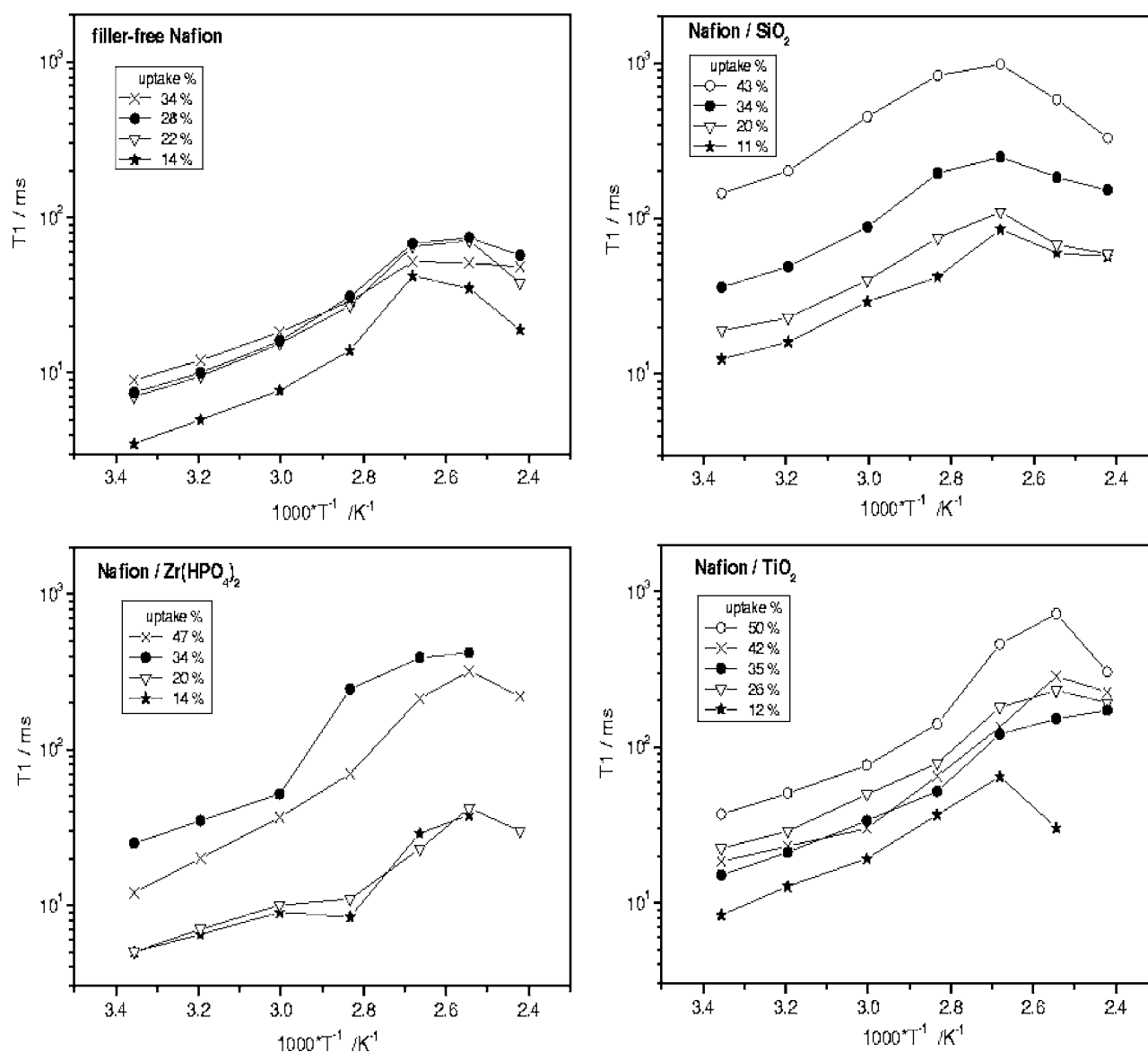


Figure 2. Arrhenius plot of water longitudinal relaxation time (T_1) in filler-free Nafion and Nafion composite membranes at different water contents.

improve the water uptake of the membranes, at least from the liquid water preparation procedure employed for these studies. It has been previously reported that Nafion/ $Zr(HPO_4)_2$ composite membrane exhibited improved elevated temperature PEMFC performance compared to filler-free Nafion membrane even though ex situ proton conductivity was not enhanced by the addition of the inorganic phase.¹⁶ In that work, it was suggested that the $Zr(HPO_4)_2$ phase altered the Nafion membrane structure by providing cavity structures, which were critical to improved performance under PEMFC constrained conditions. In our view the enhanced absorption is not merely a consequence of the fact that SiO_2 , TiO_2 , or $Zr(HPO_4)_2$ particles are hygroscopic but is also attributable to their effect on the pore structure, creating larger cavities where more water molecules can be hosted in cluster form. It is surmised that if a significant fraction of the “extra” water in the composites were associated with surface groups on the particles, the NMR would exhibit corresponding variations in spectral appearance and/or general diffusive and relaxation behavior. In fact, no such variation is observed.

The abrupt decrease of the diffusion coefficients of the $Zr(HPO_4)_2$ and SiO_2 composite membranes when the water content is low is hypothesized to be related to the pore/channel structure of

the membrane, where the $Zr(HPO_4)_2$ or SiO_2 particles block part of the hydrophilic polymer channels through which water migrates. The overall similarity in self-diffusion coefficients between Nafion composites and filler-free Nafion indicates that the beneficial effects on water translational motion from the inorganic particles counterbalance the hypothesized blocking effects at high water content. The diffusion coefficients start decreasing at low water content and high temperature when blocking effects dominate water transport, partially due to membrane water loss. However, in the case of T_1 measurements, the particle blocking effect is less important as T_1 reflects more localized motions, including rotation as well as translation. This is consistent with the much smaller magnitude of T_1 value drop than that of D at the highest temperature. This finding, along with the higher T_1 values associated with Nafion composites, supports the conclusion that the beneficial effects of Nafion composite membranes result from a structure change in Nafion polymer matrix upon addition of the inorganic particles, which facilitate more water motions with improved water-retention ability.

Performance in PEMFC.— All the membranes characterized by NMR were also tested in a H_2/O_2 fuel cell. Fuel cell polarization

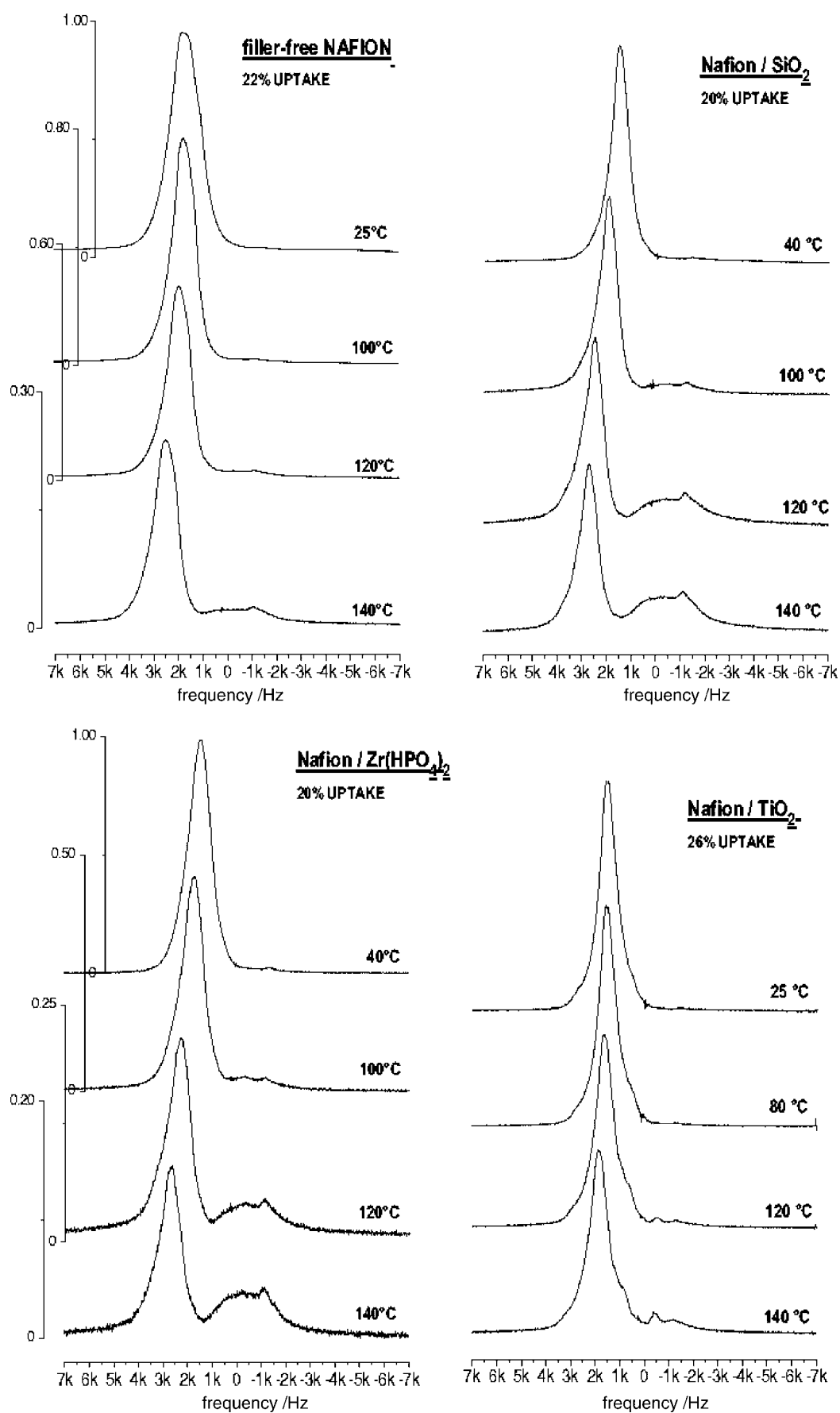


Figure 3. ^1H -NMR spectra of filler-free Nafion and Nafion composite membranes with about 20% of water uptake.

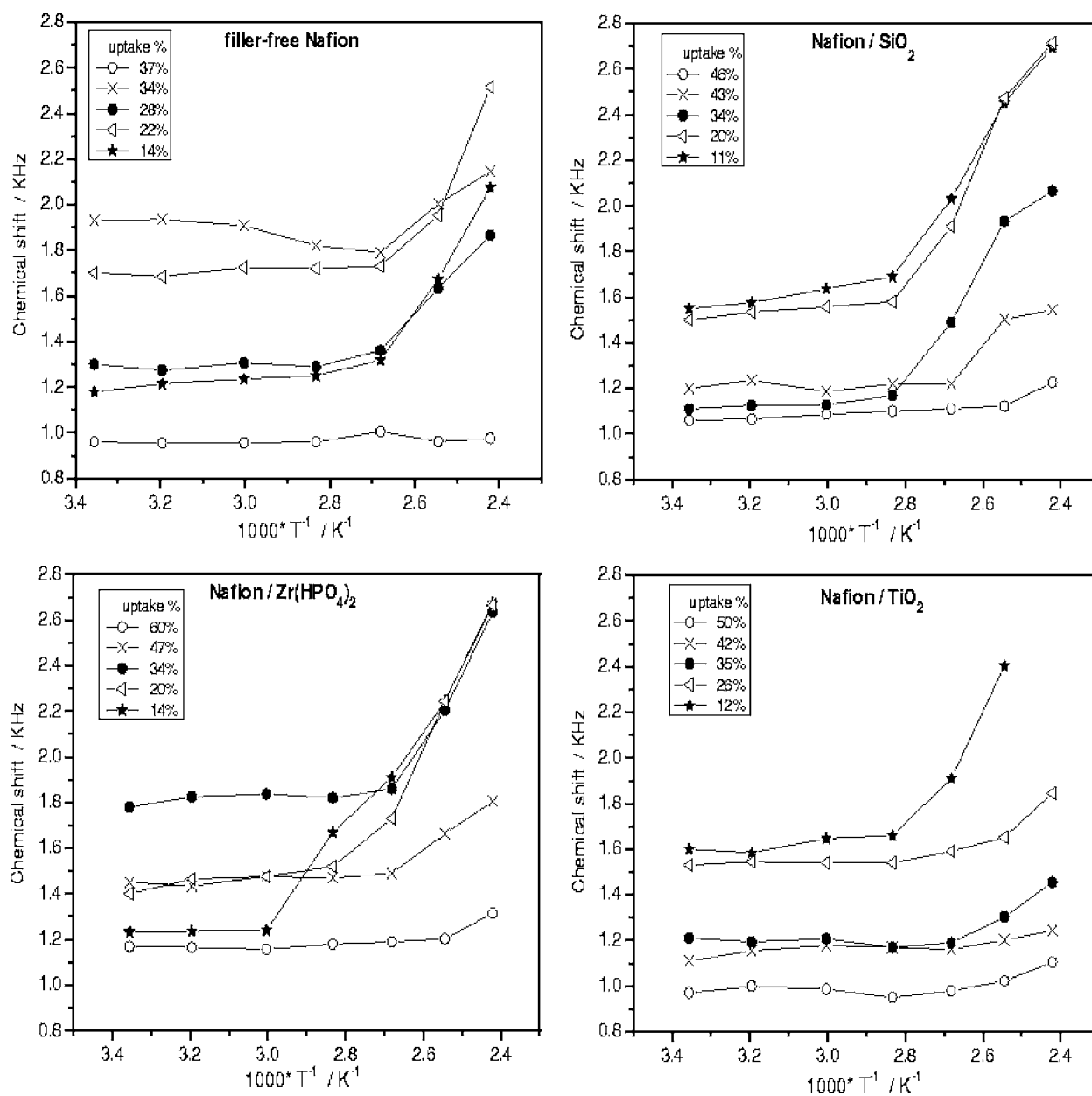


Figure 4. Inverse temperature plot of the chemical shift relative to the ^1H -NMR spectra main peak of the in filler-free Nafion and Nafion composite membranes at different water uptake.

curves under different temperature and humidity conditions are shown in Fig. 5 and 6. The temperatures are denoted as anode feed humidifier/cell/cathode feed humidifier temperature in Celsius. The indicated pressure is the total pressure, including water vapor and reactant gas pressure. When the humidification bottle temperatures are higher than the cell temperature, 100% relative humidity (RH) is obtained and the membrane performances are optimal, with the polarization curves exhibiting small slopes in the linear (ohmic) region. At both temperatures, composite membranes exhibit slightly enhanced performance compared with Nafion 112. It has been reported² that addition of inorganic particles to Nafion shows little beneficial effects when the fuel cell is operating under fully humidified conditions. The improvement in this case is attributed to smaller membrane thicknesses of composite membranes.

To evaluate the under-humidified performances of filler-free and Nafion composite membranes, the temperatures of humidification bottles were reduced and polarization curves under various RH conditions were recorded. Membrane performances under three differ-

ent RH conditions are illustrated in Fig. 6 (a) 72, (b) 61, and (c) 51%, respectively. When the feed gas humidity is decreased by reducing the humidifier temperature while maintaining cell temperature constant, the PEMFC performance degrades with higher ohmic slope due to severe water loss of the membrane. All composite membranes tested under these conditions show considerably higher fuel cell performances than filler-free Nafion. As previously reported,² the addition of an inorganic phase to Nafion membranes significantly improves the membrane performance in a PEMFC under low RH conditions. The improvement of composite membranes over Nafion 112 is larger at lower RH. This indicates that the enhanced PEMFC performance of composite membranes is attributed to their improved water-retention ability under these low-humidity operational conditions. Following the same trend as the NMR results, Nafion/SiO₂ membrane exhibits the lowest performance of all composite membranes, which is more evident at lower humidity. This indicates that the nature of inorganic particles is critical to the

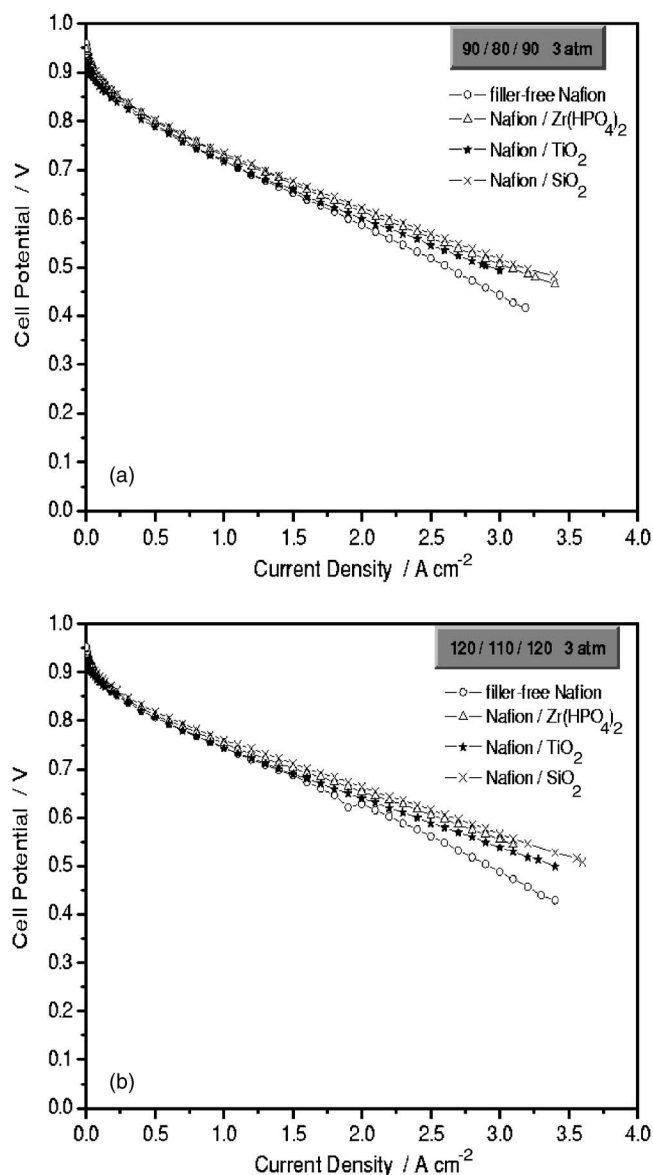


Figure 5. Fuel cell polarization curves of MEAs composed of a filler-free Nafion or Nafion composite membrane under fully humidified conditions: (a) 90/80/90°C (temperature of the anode humidifier/cell/cathode humidifier), 3 atm (total cell pressure), and (b) 120/110/120°C, 3 atm.

water retention ability and therefore fuel cell performance under low humidity conditions. All composite membranes outperform Nafion 112 control when tested at reduced humidity in fuel cell experiments.

Given the sharply reduced water diffusivity in the composites at low water content and high temperature, it is clear that the relationship between the NMR results and the fuel cell performance is not necessarily a straightforward one. One difficulty in direct comparison between NMR diffusion and membrane performance is that for NMR, there is a known and roughly constant (except at the highest temperatures) amount of water, which was added by exposing the membranes directly to liquid water, in the samples, whereas in the fuel cell, the water content can be very different among samples equilibrated under the same RH condition. For example, the actual water content in the membrane under low RH operating conditions of the fuel cell could well be higher than the values corresponding to the ex situ membranes exhibiting low water NMR diffusion.

The results of Fig. 6 in fact suggest that composite membranes

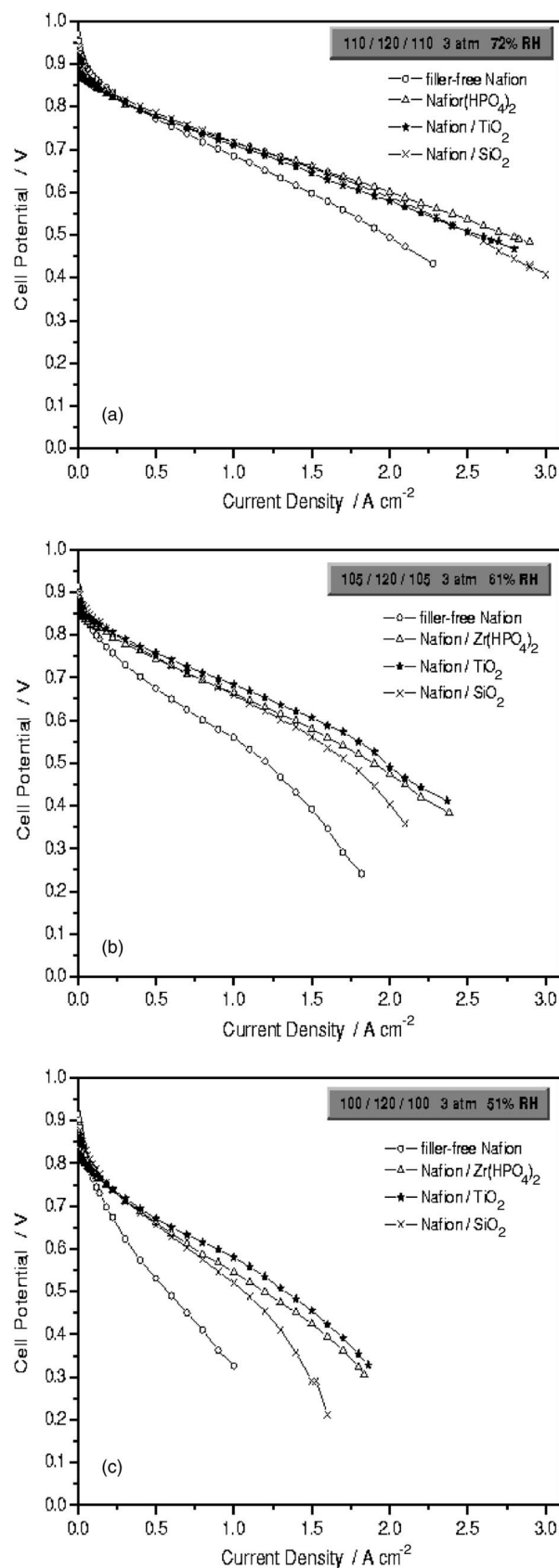


Figure 6. Fuel cell polarization curves of MEAs composed of a filler-free Nafion or Nafion composite membrane under low RH conditions: (a) 110/120/110°C (temperature of the anode humidifier/cell/cathode humidifier), 3 atm (total cell pressure), 72% RH (relative humidity of the feed gas), (b) 105/120/105°C, 3 atm, 61%RH, and (c) 100/120/100°C, 3 atm, 51% RH.

are able to retain more water in fuel cell at low humidity. As discussed earlier, this may be attributed to the changing pore/channel structure of Nafion produced by the introduction of an inorganic phase. The improved PEMFC performance of Nafion composite membranes is consistent with the NMR T_1 results because PEM proton conduction as well as T_1 is more associated with localized water motion, including molecular rotation. The well-known strong correlation between water diffusion and proton conductivity in Nafion notwithstanding,¹² proton transport rate in water-swollen Nafion membranes by hopping is limited by the reorientation step of the water molecule to accept the proton from neighbor water molecule.¹⁷ This effect is more pronounced in fuel cell experiments because composite membranes can hold more water without considerable volume expansion, which is restricted under the constrained conditions associated with the fuel cell test fixture.

Conclusion

An NMR analysis of the water transport properties inside filler-free and inorganic Nafion composites has been carried out. The ^1H NMR spectra indicate a cluster-type structure with at least two types of water: water forming clusters filling the pore volumes and water solvating the SO_3^- groups, the latter strongly bound. One effect of the inorganic particles is to improve the water uptake of the membranes. The NMR results demonstrate that the amount of water absorbed in excess from the composite membranes with respect to the filler-free Nafion is not simply due to the hygroscopic nature of the SiO_2 , TiO_2 , or $\text{Zr}(\text{HPO}_4)_2$ particles but to an alteration of the polymeric matrix structure, creating larger cavities where the water molecules can be hosted in cluster form. This result suggests that the structure of the composite plays a key role in fuel cell performance of the membrane.

Self-diffusion coefficients are strongly dependent on the water content of the membrane. $\text{Zr}(\text{HPO}_4)_2/\text{Nafion}$ membrane reveals the highest diffusion together with the maximum water uptake. However, the diffusivity of the $\text{Zr}(\text{HPO}_4)_2$ and SiO_2 composites drops sharply when the membrane water content is low, which is attributed to the particles physically blocking part of the hydrophilic polymer channels through which water migrates. This is distinct from the enhanced performance of the composites at low RH, which may

have a higher water content in the fuel cell than they do in the NMR sample tube, and in which it is surmised that localized water molecular motion probed by T_1 measurements, including rotation, plays a more prominent role in the proton transport mechanism.

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