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## Communication: Nanoscale ion fluctuations in Nafion polymer electrolyte

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Ion conduction mechanisms and the nanostructure of ion conduction networks remain poorly understood in polymer electrolytes which are used as proton-exchange-membranes (PEM) in fuel cell applications. Here we study nanoscale surface-potential fluctuations produced by Brownian ion dynamics in thin films of low-hydration Nafion<sup>TM</sup>, the prototype PEM. Images and power spectra of the fluctuations are used to derive the local conductivity-relaxation spectrum, in order to compare with bulk behavior and hopping-conductivity models. Conductivity relaxation-times ranged from hours to milliseconds, depending on hydration and temperature, demonstrating that the observed fluctuations are produced by water-facilitated hydrogen-ion hopping within the ion-channel network. Due to the small number of ions probed, non-Gaussian statistics of the fluctuations can be used to constrain ion conduction parameters and mechanisms. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892875>]

Understanding the dynamics of ions in disordered or complex materials is a topic of considerable fundamental and technological interest. A broad variety of materials exhibit a quasi-universal behavior<sup>1</sup> of the electrical conductivity that decreases as a power-law with observation time. This so-called sub-diffusive dynamics on short times crosses over to normal diffusion and time-independent conductivity on long times. This behavior could arise from a number of different mechanisms, such as intermittent ion trapping,<sup>2</sup> correlated hopping,<sup>3</sup> spatially heterogeneous mobility,<sup>4</sup> or geometric confinement,<sup>5</sup> among others. Macroscopic measurements average over variations occurring on small length scales, making it difficult to distinguish which microscopic models are most applicable.

Polymer electrolytes are complex ion-conducting materials that can be used in many applications such as in proton-exchange-membranes (PEM), a critical component of fuel cells. As a PEM, they must conduct hydrogen ions efficiently but provide a barrier to anions and electrons. Their proton conduction properties<sup>6,7</sup> are still poorly understood, even in the prototype PEM, Nafion<sup>TM</sup>, which is a fluorocarbon polymer with side-chains containing sulfonic-acid groups. When hydrated, the hydrophilic sulfonates must segregate from the hydrophobic Teflon backbone, but the precise nanostructural organization of Nafion has proven difficult to understand. Early models proposed amorphous networks of weakly connected water-containing micellar domains.<sup>8</sup> Recent evidence suggests that bundles of long tubular channels<sup>9</sup> or ribbons<sup>10</sup> may be prevalent. Near an interface ordered structures may occur<sup>11,12</sup> depending on the surface material, hydration, and heat treatment.<sup>13</sup> Nafion and related materials work well as PEMs when fully hydrated at temperatures below 100 °C. However, fuel cells can be more efficient and durable when operated at high temperatures and lower hydration levels.

In this paper we use non-contact electric-force-microscopy (EFM) to study local surface-potential fluctua-

tions that arise from the Brownian dynamics of ions in a polymer electrolyte. We show that images and power-spectra of the fluctuations can be used to derive the frequency-spectrum of the local ac conductivity. We found that the spectrum of fluctuations for low-hydration material is similar to that of hopping conductivity in disordered materials.<sup>1</sup> High-order statistical properties of the fluctuations are found and can be used to characterize and constrain conductivity parameters and mechanisms.

Proton conductivity in Nafion has been extensively studied at various levels of hydration,<sup>7,14</sup> characterized by  $\lambda$ , the molar ratio of water molecules to sulfonate sites. For Nafion which has been dried in vacuum at room temperature, it is believed that  $\lambda \approx 1$ .<sup>11,13</sup> Various conduction mechanisms contribute at different  $\lambda$ , but it is probable<sup>6</sup> that at low  $\lambda$ , H<sup>+</sup> ions can hop between neighboring SO<sub>3</sub><sup>-</sup> sites, likely facilitated by water molecules and possibly polymer chain dynamics. Local conductivity in well-hydrated Nafion films has been studied<sup>15,16</sup> by contacting the film surface with a Pt atomic-force-microscope (AFM) tip. In this way, both topography and conductance could be imaged. Strong conductance heterogeneity was found, and interpreted as nanometer width conducting channels.<sup>16</sup> However these experiments are mainly probing surface conductance, which may differ from bulk properties due to different surface nanostructure,<sup>12</sup> and are complicated by electrode interfacial effects.

The measurements described here use non-contact EFM techniques to measure spatio-temporal surface-potential fluctuations,  $\delta V_s(x,y,t)$ , which arise from charge or polarization dynamics within the underlying three-dimensional conduction network. This technique, described in more detail previously,<sup>17,18,29</sup> involves applying AC and DC bias voltages (<1 V) to an AFM cantilever with conducting tip (Fig. 1(e)) which is oscillated at its resonance frequency,  $f_{\text{res}}$ , at a height,  $z$ , above the sample surface. The bias-induced tip charge and response of the sample modulates the force gradient on the

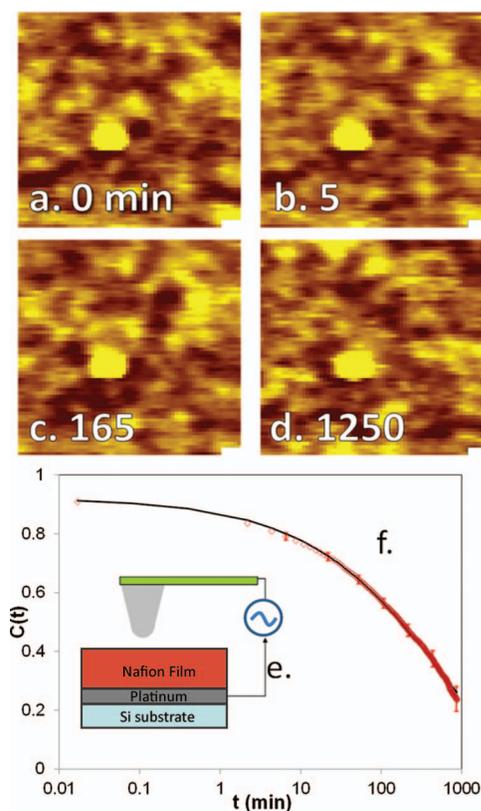


FIG. 1. Surface potential images ( $xy$  range:  $970 \times 970$  nm,  $z$  range:  $\pm 100$  mV) of dried Nafion at  $T = 18^\circ\text{C}$ , and various times in minutes as indicated (a)–(d). The bright spot near the center is a marker used for tracking. The inset (e) shows the EFM tip with AC bias and 60 nm thick Nafion film on platinum. The time auto-correlation function of the images is shown in (f), along with a stretched-exponential fit.

tip, and thereby  $f_{\text{res}}$ , which is measured. The technique can be used to probe local dielectric susceptibility in materials,<sup>30</sup> and is sensitive to depths of 10–100 nm below the surface depending on the tip-radius and film thickness. In this work, we studied 60 nm thick Nafion films of equivalent weight  $\sim 1100$ , spin-cast onto Pt electrodes on oxidized Si,<sup>13</sup> using PtIr coated AFM tips with  $\approx 25$  nm radii. In addition to providing a conducting electrode, the Pt suppresses formation of lamellar interface structures in Nafion that form on other surfaces.<sup>11</sup>

In Figures 1(a) and 1(d) we see images of surface potential on Nafion at  $18^\circ\text{C}$ , which has been annealed in vacuum at  $130^\circ\text{C}$  for 8 h, resulting in an ultra-dry  $\lambda \approx 0$ <sup>11,13</sup> sample. The images show an apparently random pattern of spatial variation in surface potential with an RMS variation of  $78 \pm 4$  mV. A particle is used as a tracking feature to ensure that the same positions are recorded over several hours. Images recorded at various times after the initial image (Figs. 1(a)–1(d)) show that the pattern gradually evolves into a new random pattern, completely uncorrelated with the initial one, after several hours. In Fig. 1(f) we show the temporal auto-correlation function for a series of 500 similar images recorded at 2.2 min intervals. This is fit to a stretched-exponential function,  $C(t) = \exp(-(\frac{t}{\tau})^\beta)$ , with correlation time,  $\tau = 520$  min, and stretching exponent,  $\beta = 0.45$ . Similar images recorded at  $26^\circ\text{C}$  show the same behavior except that the loss of correlation is faster, with  $\tau = 34$  min,  $\beta = 0.45$ . The spatial structure

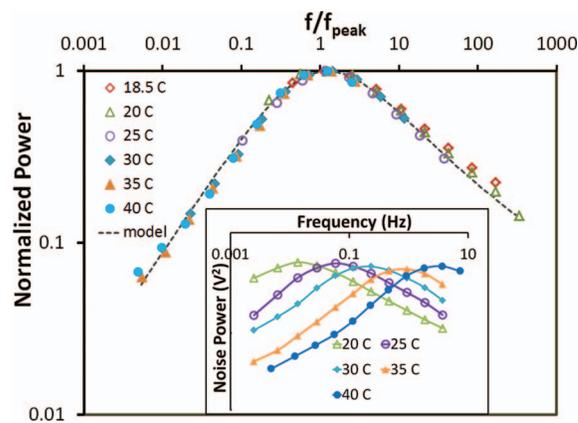


FIG. 2. Inset: Noise spectra,  $P(f)$ , for Nafion annealed to  $40^\circ\text{C}$  in vacuum, for various temperatures as indicated (errors on  $P(f)$ : 7% for low frequency, 0.2% high). Main plot: Master plot of spectra vs.  $f/f_p$ , together with hopping conductivity model spectrum.

in the images has  $\approx 60$  nm correlation length, consistent with the measurement resolution expected for 25 nm radius-of-curvature tips with the force-gradient method. The magnitude of the surface potential variation is consistent with it arising from thermal fluctuations in polarization of the sample,<sup>17,18</sup> as discussed in detail below. If we ascribe the relaxation-time observed to conductivity relaxation,<sup>14</sup> i.e.,  $\tau \approx \epsilon/\sigma$ , we find an exceedingly low conductivity of  $\sigma \sim 1.0 \times 10^{-17}$  ( $\Omega\text{cm}$ )<sup>-1</sup> at  $18^\circ\text{C}$  with  $\epsilon = 3.3 \epsilon_0$ .<sup>14</sup> Measuring local conductivity at these levels in a more conventional way, by making contact with the AFM tip to the film,<sup>16</sup> applying a voltage, and measuring current, is not possible because the currents would be far too low. In addition contact with the tip would lead to interfacial effects which could dominate the measurements.

Freshly prepared and hydrated Nafion films placed in vacuum also showed thermally driven surface-potential fluctuations, with dynamics ( $\tau^{-1}$ ) that were considerably sped up, by a factor of  $\approx 2000$  relative to the  $130^\circ\text{C}$  annealed samples. For these samples, spatial imaging is too slow to capture the temporal dynamics in detail. We instead capture time-series of the surface potential fluctuations with a higher sampling rate at a single spatial position. We then perform Fourier analysis to find the power spectral density,  $S(f)$ . We bin-sum  $S(f)$  over logarithmic intervals,  $f$  to  $2f$ , to obtain the octave power,  $P_o(f)$ , which in-effect scales  $S(f)$  by  $f$  and produces spectra with a characteristic peak frequency. In Fig. 2 well-averaged noise power spectra for Nafion which have been annealed to  $40^\circ\text{C}$  are shown for various temperatures. The spectra all have broadened peaks, whose peak frequencies,  $f_p$ , shift higher with increasing temperature. We can account for the measured noise spectra in terms of the complex conductivity spectrum based on the Nyquist's relation:  $S(f) \sim 4k_B T \text{Re}Z$ ,<sup>18</sup> where  $Z$  is an effective tip-sample impedance. This approach was used previously for polymer films which exhibit dielectric relaxation.<sup>17,19</sup> The effect of charge carrier dynamics on potential fluctuations measured with this method were analyzed in detail.<sup>20</sup> In an organic field-effect transistor the fluctuations were not measurable above other background noise source, were much smaller than predicted,<sup>21</sup> and this was attributed to carrier interactions.<sup>20</sup>

If the sample film has frequency-dependent complex permittivity,  $\varepsilon(f) = \varepsilon'(f) - i\varepsilon''(f) = \varepsilon'(f) - i\frac{\sigma(f)}{2\pi f}$ , and the tip capacitance,  $C$ , is modeled simply as a series combination of a vacuum capacitance and sample capacitance,  $C_0\varepsilon(f)$ , where  $C_0$  is the geometrical capacitance of the portion of the sample directly beneath the tip, then the tip impedance is  $Z = -i/\omega C$  and its real part is  $ReZ \approx \frac{\varepsilon''(f)}{2\pi f C_0 |\varepsilon(f)|^2}$ . Then the Nyquist noise spectrum will have the form,  $P_o(f) \approx 4k_B T \frac{\varepsilon''(f)}{2\pi C_0 |\varepsilon(f)|^2}$ , which has a frequency-dependence reminiscent of the imaginary component of electric modulus,  $M'' = Im(1/\varepsilon)$ . In most ionic conductors at low frequencies,  $\sigma$  becomes nearly frequency-independent as it approaches its dc limit,  $\sigma_{dc}$ . In that case  $M''(f)$  exhibits a peak at  $f_p \sim \frac{\sigma_{dc}}{2\pi\varepsilon'}$ . Here, we can use this relation (which works well in bulk Nafion<sup>14</sup>) to determine dc conductivity from measured noise peak frequencies, and we find that it is still very low for un-annealed samples at room temperature,  $\sigma_{dc} = (5 \pm 2) \times 10^{-14} (\Omega \text{ cm})^{-1}$ . For comparison, from dielectric susceptibility measured in bulk material with  $\lambda = 1$ ,<sup>22</sup> the room-temperature conductivity is  $\sim 1 \times 10^{-13} (\Omega \text{ cm})^{-1}$ . And since conductivity is a very strong function of  $\lambda$  in this low-hydration regime, we determine that the main results discussed here, are for  $\lambda \sim 1$ .

The spectra of Fig. 2 can be analyzed explicitly in order to characterize the local ac-conductivity (conductivity relaxation) spectrum. When plotted on a master plot (Fig. 2), i.e., by dividing  $P(f)$  and  $f$  by their peak values, universal features of the spectra can be seen. The spectra nearly collapse onto a universal form  $p(\nu)$ , for  $p = P/P_p$ ,  $\nu = f/f_p$ . Above and below  $\nu = 1$ , the spectra are found to be power-laws:  $p^+(\nu) \sim \nu^{-0.35}$  and  $p^-(\nu) \sim \nu^{0.7}$ . We quantitatively analyze the noise magnitude and spectral form by using a specific AFM tip capacitance model,  $C(z, \varepsilon, d) = 2\pi\varepsilon_0 R \ln(1 + \frac{R(1-\sin\Theta)}{z+d/\varepsilon})$ , which has been successfully used in force-gradient capacitance-microscopy for a height  $z$ , tip angle  $\Theta$ , over thin films of thickness,  $d$ , and dielectric constant  $\varepsilon$ .<sup>23</sup> Here we replace  $\varepsilon$  with  $\varepsilon(f)$  and assume a frequency-independent  $\varepsilon' = 3.3$ , and a hopping-type<sup>1</sup> conductivity model with two-distinct power-law regimes which gives  $\varepsilon''(f) = \frac{\sigma_0}{2\pi f_0} [(\frac{f}{f_0})^{\alpha-1} + (\frac{f}{f_0})^{\beta-1}]$ , where  $\alpha$  and  $\beta$  are low and high-frequency exponents,  $f_0$  is a crossover frequency, and  $\sigma_0$  is the conductivity at  $f_0$ . We then apply Nyquist's relation to obtain a model noise spectrum,  $P(f)$ . We find that a crossover frequency somewhat larger than the peak frequency produces peaks of similar width to the data. The model spectra that best matches the data, shown in Figure 2, requires  $\alpha = 0.31 \pm 0.03$ ,  $\beta = 0.75 \pm 0.03$ , and  $f_0 \sim (20 \pm 5)f_p$ . We can integrate the model noise spectrum to find the total root-mean-square (rms) surface potential fluctuations,  $V_{rms} = [\int S(f)df]^{1/2}$ , and we find that the measured value of  $V_{rms}$  ( $78 \pm 4$  mV) can be obtained with a quite reasonable tip radius of  $R = 24.5 \pm 1.5$  nm, and tip angle  $23^\circ$ .

The dependence of  $f_p$  with  $T$  is non-Arrhenius, as shown in Figure 3, for various temperatures and annealing histories. It was found that samples limited to  $T < 80^\circ\text{C}$  could be reversibly rehydrated ( $\lambda \approx 1$ ) when re-exposed to humid air (rh = 85%,  $40^\circ\text{C}$ , 12 h). Subsequent annealing to  $60^\circ\text{C}$  in vacuum would slow the dynamics by  $\approx 8\times$  relative to the rehydrated material at  $30^\circ\text{C}$ . Annealing to  $130^\circ\text{C}$  produces very

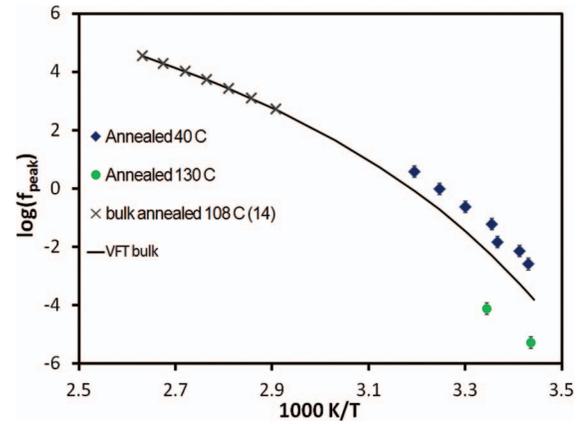


FIG. 3. Arrhenius plot of peak-frequencies of noise spectra vs. inverse temperature are shown for two vacuum annealing temperatures and data from bulk electric-modulus data together with its VFT fit.<sup>14</sup> The blue diamonds are derived from the spectra of Fig. 2.

dry regions ( $\lambda \approx 0$ ) with crystallized fluorocarbon backbones which cannot easily be hydrated,<sup>13</sup> and this produced dramatic, irreversible reductions in  $f_p$  shown in our data. Also shown are peak frequencies derived from bulk  $M''(f)$  measured in bulk Nafion dried in vacuum at  $\sim 108^\circ\text{C}$ <sup>14</sup> and its Vogel-Fulcher-Tamman (VFT) fit. The trend in this data is quite consistent with our results in that it lies between the results for lower and higher annealing temperatures.

All of these results strongly suggest that the dynamics we are observing is that of the  $\text{H}^+$  ions, whose mobility and conductivity is facilitated by the addition of water molecules. The spectra gives similar information about the ion dynamics as bulk electric modulus or ac conductivity, but at a local, nanoscale level. Another way these measurements could be useful for Nafion, or other ion conductors, is to use them to study spatial or temporal variations in the ion dynamics. Because we are sampling a rather small volume of material, it may be possible to detect variations in the ion dynamics that could be useful in characterizing conduction parameters or mechanisms. Various 4th-order statistics, such as kurtosis, can be used as non-Gaussian parameters ( $\Delta_{NG}$ ), which could be used to detect temporal or spatial variations in ion mobility or number, which can then be compared to models. One of these parameters,<sup>24</sup> excess (beyond Gaussian) noise power fluctuations,  $\Delta_{NG} = \delta P_{ex}^2 / \langle P \rangle^2$  has been used to test dynamical models<sup>25</sup> in spin glasses,<sup>26</sup> disordered conductors,<sup>27</sup> among other systems.<sup>28</sup> Some proposed ion conduction mechanisms, which involve intermittent hopping dynamics or significant ion interactions, could be expected to produce large temporal  $\Delta_{NG}$ . Even in the case of nearly stationary dynamics, fluctuations in ion number or mobility could be observed spatially, through the sampling of different ion populations, and will give  $\Delta_{NG} \sim 1/N_i$ , where  $N_i$  the number of mobile probed ions.  $N_i$  can be related to the product of ion density,  $n_i$ , and an effective probed volume,  $V_{eff}$ . The effective volume is found using the spatial correlation function, a finite-element-model for our geometry, and parameters: tip radius  $R = 25$  nm, held at  $z = 0.8 R$ , and film thickness  $d = 2.4R$ , to be  $V_{eff} = 1.7\pi R^2 d = 2.0 \times 10^5 \text{ nm}^3$ . For our ultra-dry Nafion samples, excess spatial, but not temporal, variations of about 7% in noise

power were found in the high-frequency wing of the spectra, giving  $\Delta_{\text{NG}} \sim 0.005$ . This result is consistent with nearly stationary dynamics, with  $N_i \sim 200$  giving an ion density  $n_i \sim 1 \times 10^{-3} \text{ nm}^{-3} = 1 \times 10^{18} \text{ cm}^{-3}$ , which gives an effective room temperature diffusion constant  $D \sim 1.5 \times 10^{-4} \text{ nm}^2/\text{s}$ . This suggests most ions in this regime are hopping in fixed, quasi-localized environments,  $<2 \text{ nm}$  in size, at least in the driest material. Detailed measurements, analysis and implications of  $\Delta_{\text{NG}}$  will be described elsewhere.

Samples were made in part at the NIST CNST Nanofab. Commercial products are identified within to foster understanding which does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor imply that these products are necessarily the best available for the purpose. B.R., M.B., and N.E.I. supported by NSF DMR 1006007. We thank Max Turnquist for assistance with figures.

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