Published in final edited form as:

J Am Chem Soc. 2011 December 28; 133(51): 20700–20703. doi:10.1021/ja209240d.

Direct Imaging of Nanoscale Acidic Clusters in a Polymer Electrolyte Membrane

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Abstract

One of the factors hindering development of technologies that rely on the use of proton-conducting polyelectrolyte membrane is the lack of control over the membrane morphology on the nanoscale. Of particular importance is the rearrangement and clustering of acidic groups, which may seriously degrade electrical properties. Although electron microscopy is capable of imaging the morphology of the clusters, images of unmodified membranes with sufficient quality to discriminate between different proposed models have not been presented. Here we show the first determination of the cluster size distribution in a model polymer electrolyte membrane from electron micrographs of individual acidic clusters. Imaging of the sulfur-rich clusters by dark field microscopy was facilitated by the spontaneous formation of thin, cluster-containing layers on the top and bottom surfaces of free-standing films around 35 nm thick.

Keywords

Ionic clusters; polymer electrolytes; fuel cells; electron microscopy

Polymer electrolyte membranes such as Nafion®, comprising nanoscale hydrophilic and hydrophobic domains, are important for a variety of technologies such as purification of sea water ¹, hydrogen fuel cells ², and photo-electrochemical cells ³. Ion transport in these systems is mediated by sulfonic acid groups present in the hydrophilic domains. While scattering experiments have revealed the presence of ionic clusters in both dry and hydrated states, the size and shape of the clusters remain controversial ⁴⁻¹⁰. This controversy impedes both the development of robust fundamental models for ion transport through the membranes, and our ability to develop the next generation of membranes with superior

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transport properties. The purpose of this work is to resolve this controversy by direct imaging of the clusters and measuring the cluster size distribution.

X-ray scattering profiles of Nafion® and other polymer electrolyte membranes (PEMs) contain a broad peak with a characteristic length scale of about 5 nm¹¹. While it is generally assumed that this length scale represents the average distance between the clusters, the scattering data do not provide information about the size and shape of the clusters. The problem lies in the fact that a single broad scattering peak cannot be used to uniquely determine the underlying structure. It is thus not surprising that a variety of different morphologies such as connected spheres⁵, core-shell structures⁶, hard spheres⁷, bundles of rods⁸, parallel cylindrical channels¹⁰, and lamellar channels⁹ are all consistent with the scattering profiles obtained from Nafion®. Electron microscopy can be used to distinguish between these morphologies, but micrographs obtained thus far have not resolved this controversy. Previous electron microscopy studies¹²⁻²⁰ suffer from two limitations: (1) electron micrographs were obtained from films with thicknesses much greater than the cluster size, and overlapping of clusters in projection complicates image interpretation²¹; (2) the contrast between the clusters and the background has always been enhanced by either heavy metal staining agents or by replacing the protons by heavier cations using ion exchange. While the ion exchange procedure is a more controlled process than staining, the fact that ion exchange causes a change in the cluster morphology is well-established²². Thus far, electron micrographs of individual acidic clusters in PEMs have not yet been obtained.

In this work we show electron micrographs of individual ionic clusters in a polymer electrolyte membrane without using heavy element stains or ion exchange. Our experiments were performed on a poly(styrene sulfonate)-*block*-poly(methyl butylene) (PSS-PMB) copolymer synthesized as described in ref.²³. The molecular weights of the poly(styrene sulfonate) (PSS) and poly(methyl butylene) (PMB) blocks were 4.2 kg/mol and 8.1 kg/mol and the volume fraction of the PSS block was 0.27. The PSS block comprises 40 mol % sulfonated monomers. Samples were prepared by dipping lacey carbon-coated electron microscopy (EM) grids into 1 weight % solutions of PSS-PMB in tetrahydrofuran (THF). The wet grids were dried slowly by placing them in a partially sealed vial above a small pool of THF at room temperature. Figure 1 shows typical top and cross section views of an 80 nm thick sample obtained by bright field electron tomography. Here we see alternating lamellae that are similar to those obtained from bulk samples of this copolymer reported in ref.²³. The dark, PSS-rich domains have a smooth structure with relatively little granularity.

Annealing the samples in water vapor produces dramatic changes in morphology. The sample shown in Figure 1 was removed from the microscope, placed above a small pool of water in a partially sealed vial held at 50 °C for 50 hours, and studied by high angle annular dark field (HAADF) STEM. The observed morphology resembles that of a honeycomb. This is most clearly seen in a HAADF image of an untilted film (Figure 2a). The size of the smallest cells in the honeycomb is about 20 nm, similar to the spacing of the lamellar morphologies seen in Figure 1. Careful examination of the honeycomb walls reveals that they consist of concentrated bright spots similar to the spots inside of the honeycomb. The brightness of these spots indicates that they consist of heavier elements sulfur and oxygen,

reflecting the locations of the sulfonic acid groups. The size, high contrast and relatively small number of bright spots make it evident that they represent clusters rather than single sulfur atoms. It is logical to conclude that the honeycomb outlines reflect the sulfurcontaining PSS-rich phase and the nominally dark interior phase is the PMB-rich phase. This is consistent with the fact that PSS is the minor component, although the area fraction of the bright phase in Figure 2a is lower than the bulk volume fraction of PSS. While we show an image of a 35 nm thick sample in Figure 2a, samples with a variety of thicknesses were seen in different portions of the lacey carbon grid. The honeycomb morphology was seen in all cases (we could image films up to 300 nm thick) except films thinner than 25 nm. However, the clarity with which the morphology could be discerned decreased with increasing sample thickness.

Electron tomography was used to clarify the structure seen in Figure 2a. While the resolution of the 3-D reconstruction is slightly lower than the resolution of projection images due to the limited mechanical stability of the film, which causes drift during image recording affecting reconstruction, it is sufficient to reveal the structure of the film. Slices taken from the top, middle and bottom parts of a 3-dimensional reconstruction of the film are shown in Figures 2bcd. The middle section (Figure 2c) shows the honeycomb morphology similar to that seen in Figure 2a except for the absence of bright spots in the dark phase. The top and bottom sections are similar to each other with numerous bright spots and only faint hints of the honeycomb structure. From this 3-dimensional view the structure of the water-annealed membrane in Figure 2 is clear. Exposure to water at 50 °C also results in the formation PSS-rich layers on the top and bottom of the film. This arrangement shields the hydrophobic PMB-rich phase from the surrounding moist air. Such shielding on the surface of the block copolymer with the lower interface energy phase had been discussed earlier²⁴. The walls of the honeycomb are formed by the PSS-rich phase. These vertical lamellae are thinner than expected (based on the bulk volume fraction of PSS) because a substantial fraction of the PSS chains in the sample are covering the top and bottom surfaces. Both horizontal and vertical PSS-rich lamellae contain bright spots due to the presence of ionic clusters. The bright spots seen “inside” the honeycomb in Figure 2a are not due to the presence of ionic clusters in the dark PMB-rich phase but due to the projections of the spotted top and bottom surfaces (Figures 2b and 2d).

Placing the water-treated film back into a THF-containing vial for annealing results in a honeycomb-to-lamella transition. This is established in Figure 3 where we compare TEM tomographic reconstruction images right after casting (Figure 3a) and after first annealing in water and then in THF (Figure 3b). The major difference between the lamellae in Figures 3a and 3b is the presence of dark spots in the PSS-rich lamellae with sizes very similar to those seen in Figures 2. One may ask why the ionic clusters did not form when the sample was originally cast from THF (Figure 1). We propose that the equilibration of the glassy PSS phase is only possible when it is substantially plasticized by a good solvent like water. It is known that THF is a poor solvent for PSS with 40% sulfonation level²⁵⁻²⁶ as used in this work. At the same time THF is an excellent solvent for the PMB phase which swells and reorganizes during the reannealing. As a side effect of reannealing most of the thin films break and only films with thicknesses greater than 100 nm survive. HAADF tomography of

such thick samples produces lower quality reconstructions than TEM bright field tomography.

It is important to establish that the observed clusters were not a consequence of sample rearrangement due to electron beam damage²⁷. We were only able to visualize the clusters using exposures of at least 10^3 e/nm². Series of images with increasing dose showed no change in the cluster morphology. The proof that the clusters we observed are not induced by irradiation below 10^3 e/nm² comes from the fact that none of the samples obtained from the initial THF casting without water vapor annealing showed evidence of clusters (e.g. Figure 1), irrespective of dose.

We used the image in Figure 2a to determine the size distribution of the ionic clusters. The areas within the honeycomb are ideally suited for determining the cluster size due to minimal overlap. We used the integrated intensity of each cluster to determine the cluster size rather than directly measuring diameter, since images of individual clusters are noisy and pixilated. Clusters were sorted into classes according to integrated intensity, and the average of each class was used to determine the scaling between the diameter measured at half maximum and the integrated intensity of the cluster. This scaling was used to determine the diameter of each cluster, and the diameter distribution thus obtained is shown in Figure 5. (See Supplementary Information for more details.) Fitting the experimental distribution to a Gaussian function, $f \sim \exp[-(d-d_{av})^2/2\sigma^2]$, we obtain the average cluster size, $d_{av} = 1.4$ nm, and the standard deviation, $\sigma = 0.25$ nm. The resulting fit is the smooth curve in Figure 5. The estimated uncertainty in d_{av} is about 14 %. This fitting represents the first direct determination of the size distribution of acidic cluster sizes in polymer electrolyte membranes.

To conclude, we have succeeded in obtaining images of nanoscale ionic clusters in a PEM composed of alternating hydrophilic and hydrophobic lamellar domains. Exposing a 35 nm thick free standing electrolyte film to moist air results in the formation of extremely thin cluster-containing layers at the electrolyte/air interfaces and a honeycomb morphology in the interior of the film. This morphology is ideally suited for direct imaging of ionic clusters by electron microscopy. The lamellar morphology with the clusters in the hydrophilic channels is recovered by re-exposing the film to THF-containing air. The shape and size distribution of the clusters that we report allows direct testing of theoretical models for structure formation and transport in PEM. Since proton conductivity in PEMs is intimately linked to the nature of the ionic clusters²⁸, the technique that we have developed will aid in future efforts to design and synthesize more effective PEMs. At this point, we have only identified the nature of clusters in a particular PSS-PMB copolymer. Further work is needed to determine the morphology of ionic clusters in other proton transporting membranes (e.g. Nafion®).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Drs. Robert M. Glaeser and John B. Kerr (Lawrence Berkeley National Lab) for helpful discussions. We also grateful to Dr. Puey Ounjai for the help with analysis of bright field tomography data. Funding for this work was provided by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 through the Electron Microscopy of Soft Matter Program (electrolyte imaging) supported by the Office of Basic Energy Sciences, Materials Sciences and Engineering Division. Part of this work was performed at National Center for Electron Microscopy and the Molecular Foundry at Lawrence Berkeley National Lab, which are supported by the Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02—05CH11231.

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Figure 1. Slices of TEM bright field tomographic reconstruction of an 80 nm thick PSS-PMB film prepared by casting and annealing in THF vapor, showing the lamellar morphology. a) Top view. b) Cross section view along the dashed line shown in (a).

Figure 2.

35 nm thick PSS-PMB film prepared by casting and annealing in water vapor showing the honeycomb morphology and ionic clusters (bright spots). a) HAADF image obtained in projection; b, c, d) Slices of HAADF tomographic reconstruction and diagram indicating position of the slice in cross section of the film b) top slice, c) middle slice, and d) bottom slice. The slices reveal that the ionic clusters are distributed uniformly near the top and bottom surfaces and are concentrated in the honeycomb wall structure.

Figure 3.

Slices from TEM tomographic reconstructions of thin PSS-PMB films prepared by: (a) casting in THF vapor. (b) first casting in THF, then annealing in water vapor, and finally re-annealing in THF. Both samples exhibit lamellar morphology but only sample (b) shows clearly distinguishable ionic clusters in the PSS phase.

Figure 4. Histogram of ionic cluster size distribution (bars) and Gaussian fit (curve).