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Nanoscale metal sulfides in perfluorinated ionomer membranes

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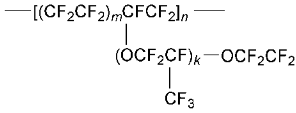
The preparation and characterization of nanoscale metal sulfide particles in perfluorinated ionomer membranes, including Nafion and those based on the sulfonimide ionomer and the bis(sulfonyl)methane ionomer, are reported. The results suggest that these membrane films all contain hydrophilic structural cavities and that the nanoscopic structures of the sulfonimide ionomer and bis(sulfonyl)methane ionomer membranes are quite similar to that of the commercial Nafion film. Properties of the nanoscale particles in the ionomer membranes are presented, and their implications for the understanding of membrane nanoscopic structural details are discussed.

1 Introduction

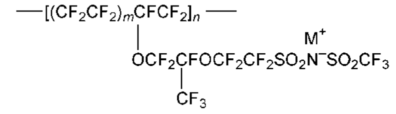
The structural details and properties of perfluorinated ionomer membranes have attracted much attention.[1–9] The current understanding of ionomer membrane structures is based largely on the results from studying Nafion, the commercially available ionomer membrane film. It was proposed about 20 years ago[3] that the Nafion membrane microstructures could be understood in terms of a reverse micelle-like ion cluster model. The model assumes the presence of essentially three distinctive structural regions: the perfluorinated polymer network, water cores, and the interfacial domain between the two regions, where the water cores in neighboring clusters are presumably interconnected through channels. Supporting evidence for the model came from small-angle X-ray diffraction studies of Nafion, which also provided an estimate for the ion cluster size of *ca.* 4 nm in diameter.[1,3,5] The model has been used successfully in explaining bulk properties of ionomer membranes that are closely related to their microstructures. However, issues such as the size and morphology of the hydrophilic ion clusters, the significance and dimension of the interfacial region, and even the organization of the hydrophilic and hydrophobic structural domains remain subjects of debate.[6–9]

Ionomer membranes have been used as templates for the preparation of nanoscale particles.[10–16] In fact, properties of the nanoparticles thus formed in the membranes provide valuable information for the understanding of the membrane structural details. For example, Wang and Mahler reported the formation of CdS nanoparticles in a Nafion membrane film *via* exposure of the film loaded with cadmium acetate to H_2S gas.[11] According to the results from their X-ray diffraction and transmission electron microscopy analyses,[11–13] it appears that the particles in the membrane film are of the same dimension as the reverse micelle-like ion clusters. Here we report a study of nanoscale metal sulfide particles in perfluorinated ionomer membranes, including Nafion (**I**) and those based on the sulfonimide ionomer (**II**) and the bis(sulfonyl)methane ionomer (**III**).[17–21] Our results suggest that these membrane films contain similar hydrophilic structural cavities, which are suitable for the preparation of nanoparticles. The properties of the nanoscale particles in the ionomer membranes are reported, and their implications for the understanding of the nanoscopic structural details of membranes are discussed.



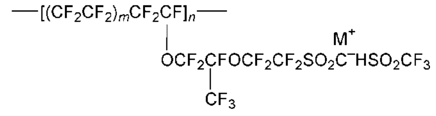
$$-[(CF_2CF_2)_mCFCF_2]_n-$$
$$(OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}F)_k-OCF_2CF_2SO_3^-M^+$$

Nafion (**I**)



$$-[(CF_2CF_2)_mCFCF_2]_n-$$
$$OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2SO_2\overset{M^+}{N^-}SO_2CF_3$$

Sulfonimide Ionomer (**II**)



$$-[(CF_2CF_2)_mCF_2CF]_n-$$
$$OCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2CF_2SO_2\overset{M^+}{C^-}HSO_2CF_3$$

Bis(sulfonyl)methane Ionomer (**III**)

2 Experimental

2.1 Materials

Cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$] and sodium sulfide (Na_2S) were purchased from Aldrich; and lead nitrate [$Pb(NO_3)_2$] was obtained from Fisher Scientific. Spectroscopy grade organic solvents were used as received. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

Nafion ionomer (**I**) membrane with an equivalent weight of 1100 was provided by Du Pont Co. The sulfonimide ionomer (**II**) was prepared *via* the copolymerization of tetrafluoroethene with the sulfonimide monomer.[17,18] The membrane was obtained by wet casting from a solution of the sulfonimide ionomer in dimethylformimide, followed by careful annealing at high temperature. The equivalent weight of the sulfonimide ionomer membrane was estimated to be *ca.* 1200 in terms of titration. Similarly, the membrane of bis(sulfonyl)methane ionomer (**III**) was prepared and characterized *via* the same procedures,[17,18,21] with an equivalent weight of *ca.* 1170. Details on the characterization of the ionomer membranes **II** and **III** and on related structural parameters are reported separately.[19–21]

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2.2 Sample preparation

The ionomer **I–III** membrane films were purified to remove colored impurities in the films using a uniform treatment procedure. In the purification, the films were immersed in concentrated nitric acid while stirring at 60 °C for 24 h. The acid was then decanted and the films were placed sequentially in aqueous solutions of 60%, 40%, and 20% nitric acid, each for 1 h with stirring, followed by washing thoroughly with clean water. The treated ionomer membrane films are clear and optically transparent down to 200 nm. Converting the membrane films to the sodium form was achieved by soaking the treated films in a 0.1 M aqueous solution of sodium hydroxide with stirring for 24 h, followed by washing thoroughly with clean water until neutral. The membrane films in the sodium form are also clear and optically transparent down to 200 nm.

2.3 Measurements

Absorption spectra were measured on a computer-controlled Shimadzu UV-2101PC spectrophotometer. A mask with a 5 mm diameter hole in the center was used in absorption measurements of the ionomer membrane films to insure that all of the transmitted light passed through the sample. Steady-state fluorescence spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450 W xenon source and an R928 photomultiplier tube (PMT). Fluorescence measurements were made in the front-face geometry using a lab-built sample stage.

Powder X-ray diffraction measurements were carried out on a Scintag XDS-2000 powder diffraction system. TEM images were obtained on either a Hitachi 600AB transmission electron microscope or a Hitachi 7000 transmission electron microscope.

3 Results and discussion

3.1 CdS in Nafion

For the preparation of CdS nanoparticles in the hydrophilic cavities of Nafion membrane film, the film in sodium form was soaked in a 0.5 M aqueous solution of $Cd(NO_3)_2$ for 24 h, rinsed with water, and then dried in a vacuum oven at 70 °C for 2.5 h.[22] The Cd^{2+}-containing film was soaked in a 0.2 M aqueous solution of Na_2S for the formation of CdS nanoparticles, followed by soaking in fresh water for the removal of unreacted reagents and $NaNO_3$. The X-ray diffraction data for the film show the typical CdS pattern, which matches the reference in the JCPDS database, on top of an extremely diffuse diffraction peak due to the Nafion membrane background. The broadness in the CdS diffraction peaks is characteristic of particles with dimensions of a few nanometers. The results are in general agreement with those reported in the literature.[11–13]

For the TEM analysis of the CdS nanoparticles–Nafion film sample, ultra-thin cross-sectional slices of the film were prepared. In the preparation, the film was placed in an epoxy resin which was allowed to harden, and then cut using an ultra-microtome with a diamond knife. The TEM image of such a slice corresponds to a cross-sectional view of the Nafion membrane film loaded with CdS nanoparticles. The dark spots in the image are due to CdS particles; and a statistical analysis of more than 100 particles that can be identified from the TEM image yields an average particle size of 6.5 nm, with a size distribution standard deviation of 1.2 nm (Table 1). The lighter areas of the TEM image show network-like structures which, according to a comparison with the TEM image of a blank Nafion film, can be attributed primarily to the perfluorinated polymer chains that make up the Nafion membrane. In addition, there may also be some small CdS particles in these largely hydrophobic or interfacial domains of the membrane structure.

Absorption and luminescence spectral measurements were carried out for the CdS nanoparticles in Nafion film when soaked in fresh water; and the results are shown in Fig. 1. The absorption onset is at *ca.* 525 nm; and the spectrum shows a shoulder at *ca.* 425 nm. The luminescence spectrum was obtained with excitation at 350 nm in a front-face geometry to minimize self-absorption effects. The spectrum consists of two overlapping luminescence bands that are associated with exciton emission (peaking at *ca.* 460 nm) and the emission due primarily to particle surface defects (centered at *ca.* 600 nm).[12,13] The defect luminescence is intense, which might be a result of significant amounts of intrusion by polymer branches into the CdS nanoparticles.

3.2 PbS in Nafion

For the preparation of PbS nanoparticles, a piece of Nafion membrane film was soaked in a saturated aqueous solution of $Pb(NO_3)_2$. Then, after the film surface was washed with water and blotted dry, the film containing Pb^{2+} was immersed in a solution of Na_2S to form PdS nanoparticles in the structural cavities of the Nafion film. The unreacted reagents and $NaNO_3$ were removed by soaking the film in fresh water. The nanoparticles were identified by the X-ray diffraction pattern, which matches the PbS reference in the JCPDS database.

Ultra-thin cross-sectional slices of the Nafion film with PbS nanoparticles were prepared. The TEM image of such a thin slice is shown in Fig. 2. The largely irregular dark regions in the TEM image represent PbS particles embedded in the Nafion membrane structure, which correspond to an average particle size of 6.3 nm, with a size distribution standard deviation of 1 nm (Table 1). Since the nanoscale PbS particles are most likely formed in the hydrophilic cavities, the uniformity of the nanoparticles suggests the presence of similar sized ion clusters in the Nafion membrane structure. In the TEM image, it appears that the PbS nanoparticles are somewhat diffuse, with a sponge-like morphology. Such a morphology for particles incorporated in ionomer membranes was also suggested by Gierke and co-workers.[3,5] The TEM image also shows regions that can be characterized as channel-like structures connecting the PbS particles in ion clusters (Fig. 2). The largely blank network-like regions in the TEM image can be assigned to the perfluorinated polymer backbone structures in the Nafion membrane.

Table 1 Parameters of the metal sulfide nanoparticles in the ionomer membranes

Membrane	Particle	Average particle size/nm		σ^b/nm
		X-Ray[a]	TEM	
Nafion (**I**)	CdS	14	6.5	1.2
Nafion (**I**)	PbS	11	6.3	1
Sulfonimide (**II**)	PbS	15	4.4	0.6
Bis(sulfonyl)methane (**III**)	PbS	12	5.5	1

[a] Calculated from the X-ray peak broadening using the Debye-Scherer equation.[23] [b] Size distribution standard deviation obtained from the Gaussian statistical analysis of TEM results.

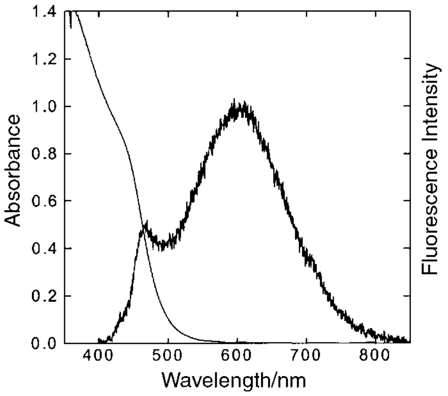

Fig. 1 Absorption and fluorescence spectra of the CdS nanoparticles in Nafion membrane film.

The properties of the embedded nanoscale CdS and PbS particles in Nafion membrane are consistent with the membrane structure being composed of fairly uniform reverse micelle-like hydrophilic cavities, as proposed in the ion cluster model.[1,3,5] The ion clusters are distributed randomly in the perfluorinated polymer network, which serves as the backbone of the membrane film. In addition, there are likely substantial nanoscopic regions in the Nafion membrane structure that may be characterized as channels connecting the ion clusters. The structural details of the channels are unclear; but, despite the limited resolution, the TEM results seem consistent with the suggestion that the channels are composed of heterogeneous mixtures of water and perfluorinated polymer branches.[8,9]

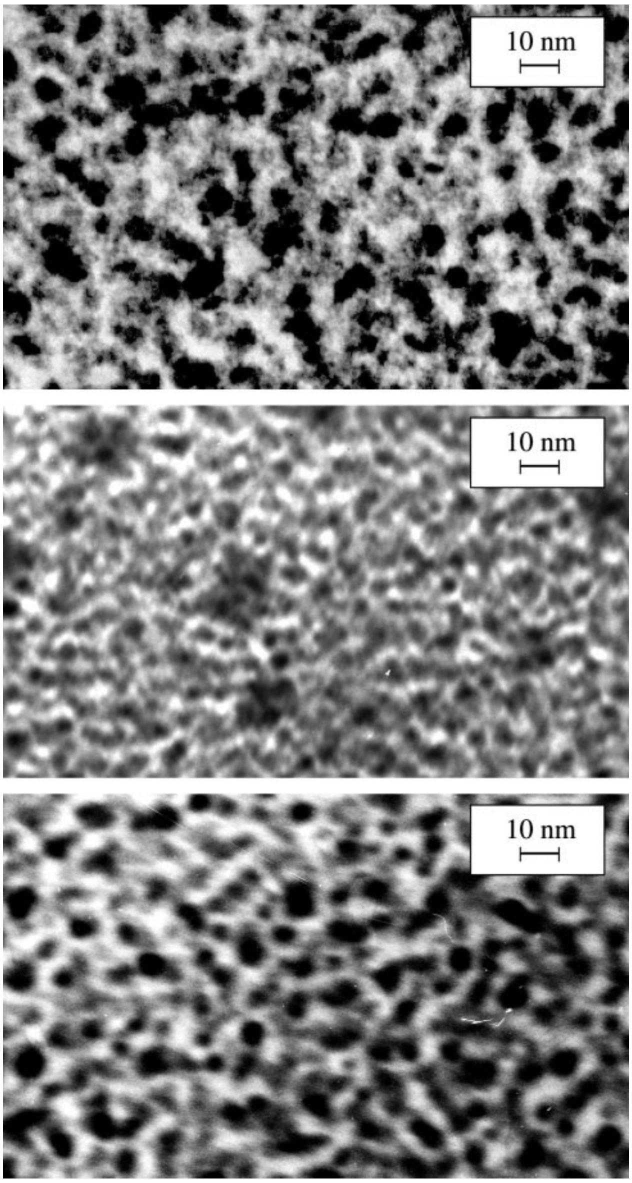

Fig. 2 A comparison of the TEM images of the ionomer membrane films loaded with PbS; Nafion (top), sulfonimide ionomer (middle), and bis(sulfonyl)methane ionomer (bottom).

3.3 PbS in other membranes

Nanoscale PbS particles were also prepared in other perfluorinated ionomer membranes, including films of sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**),[17–21] which have the same physical appearance as the commercial Nafion film. In the preparation, the ionomer membrane films were exchanged for Pb^{2+} ions in a saturated aqueous solution of $Pb(NO_3)_2$. The films were then rinsed with water and blotted dry, and were immersed in an aqueous solution of Na_2S to form PbS nanoparticles in the membrane structural cavities. The unreacted reagents and $NaNO_3$ were removed by soaking the film in fresh water. The nanoparticles were again identified in the X-ray diffraction analysis; and the diffraction patterns thus obtained match the PbS reference in the JCPDS database (Fig. 3, Table 1).

A direct observation of the PbS particles embedded in the sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**) membranes was again achieved *via* TEM measurements of ultra-thin cross-sectional slices of the PbS-loaded films. The TEM images thus obtained are compared in Fig. 2; they also show essentially three structural elements. The dark regions due to PbS nanoparticles are more regular in shape and more uniform in distribution in these two membrane films than those in the Nafion film (Fig. 2). The results may be explained in terms of differences in the rigidity of the ion cluster structures in the three different membrane films. The ion clusters in the sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**) membranes might be somewhat more flexible, allowing the formation of PbS particles in a more spherical shape. Otherwise, similar to those in the Nafion film, blank areas due to the perfluorinated polymer network can be clearly identified in the images of both sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**) membranes. The TEM images of these two membrane films loaded with PbS particles also show channel-like structures, which, again, can be assigned to the intrinsic hydrophilic or interfacial channels in the membrane structure stained with smaller PbS nanoparticles.

According to the X-ray and TEM results, the nanoscopic

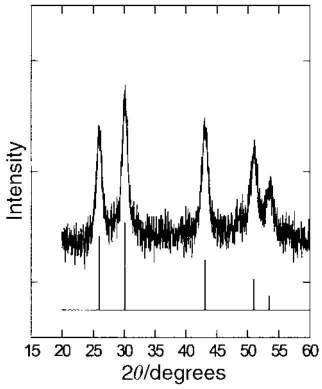

Fig. 3 The powder X-ray diffraction pattern of the bis(sulfonyl)-methane ionomer membrane loaded with PbS is compared with the reference in the JCPDS database. The peak indices (from low to high angles) are (111), (200), (220), (311), and (222), corresponding to a cubic cell of $a = 6.1468$ Å.

structures of the sulfonimide ionomer (**II**) and bis(sulfonyl)-methane ionomer (**III**) membranes are rather similar to that of the commercial Nafion film. This is also consistent with the results from spectroscopic investigations of these membrane films using extremely environmentally sensitive luminescent molecular probes.[8,9] The nanoscopic structural similarities of these films validate the development effort, in which the sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**) membranes are considered as alternatives to the commercial Nafion film for potential applications in fuel cells and electrochemical devices. On the other hand, the sulfonimide ionomer (**II**) and bis(sulfonyl)methane ionomer (**III**) membranes may be used to prepare nanoscale materials that are somewhat different from those hosted in the hydrophilic cavities of the Nafion membrane.

The hydrophilic structural cavities in the membranes serve as templates for conveniently producing semiconductor nanoparticles of reasonably narrow size distributions. The method is potentially applicable to a variety of materials. These nanoparticle–ionomer membrane composites may find unique applications in areas such as photocatalysis and the development of novel nonlinear materials.

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References

1 S. C. Yeo and A. Eisenberg, *J. Appl. Polym. Sci.*, 1977, **21**, 875.
2 M. Falk, *Can. J. Chem.*, 1980, **58**, 1495.
3 T. D. Gierke, G. E. Munn and F. C. Wilson, *J. Polym. Sci.*, 1981, **19**, 1687.
4 H. L. Yeager and A. Steck, *J. Electrochem. Soc.*, 1981, **128**, 1880.
5 W. Y. Hsu and T. D. Gierke, *J. Membr. Sci.*, 1983, 13.
6 C. Heitner-Wirguin, *J. Membr. Sci.*, 1996, **120**, 1.
7 M. H. Litt, *Polym. Prepr.*, 1997, **38**, 80.
8 C. E. Bunker, B. Ma, K. J. Simmons, H. W. Rollins, J.-T. Liu, J.-J. Ma, C. W. Martin, D. D. DesMarteau and Y.-P. Sun, *J. Electroanal. Chem.*, 1998, **459**, 15.
9 C. E. Bunker, H. W. Rollins, B. Ma, K. J. Simmons, J.-T. Liu, J.-J. Ma, C. W. Martin, D. D. DesMarteau and Y.-P. Sun, *J. Photochem. Photobiol.*, 1999, **126**, 71.
10 M. Krishnan, J. R. White, M. A. Fox and A. J. Bard, *J. Am. Chem. Soc.*, 1983, **105**, 7002.
11 Y. Wang and W. Mahler, *Opt. Commun.*, 1987, **61**, 233.
12 E. F. Hilinski, P. A. Lucas and Y. Wang, *J. Chem. Phys.*, 1988, **89**, 3435.
13 Y. Wang, A. Suna, J. McHugh, E. F. Hilinski, P. A. Lucas and R. D. Johnson, *J. Chem. Phys.*, 1990, **92**, 6927.
14 E. S. Smotkin, R. M. Brown, L. K. Radenburg, K. Salomon, A. J. Bard, A. Campion, M. A. Fox, T. E. Mallouk, S. E. Webber and J. M. White, *J. Phys. Chem.*, 1990, **94**, 7543.
15 J.-M. Zen, G. Chen, F.-R. F. Fan and A. J. Bard, *J. Chem. Phys. Lett.*, 1990, **169**, 23.
16 A. Albu-Yaron and I. Arcan, *Thin Solid Films*, 1990, **185**, 181.
17 D. D. DesMarteau, *J. Fluorine Chem.*, 1995, **72**, 203.
18 D. D. DesMarteau, US Patent No. US 5,463,005, 1995.
19 J. J. Sumner, S. E. Creager, J. J. Ma and D. D. DesMarteau, *J. Electrochem. Soc.*, 1998, **145**, 107.
20 S. E. Creager, J. J. Sumner, R. D. Bailey, J. J. Ma, W. T. Pennington and D. D. DesMarteau, *Electrochem. Solid State Lett.*, 1999, **2**, 434.
21 G. J. Shafer and D. D. DesMarteau, unpublished results.
22 The vacuum drying process is not necessary for the formation of nanoparticles. Similar results were obtained in the preparation without the drying step.
23 H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures*, John Wiley and Sons, New York, 1959.