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Percolation in S-SEBS and Fluorocarbon Proton Conducting Membranes

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Electrical conductivity results at a variety of pressures, temperatures and water contents are evaluated for sulfonated styrene/ethylene-butylene/styrene (S-SEBS) triblock polymer, Nafion 117, and Dow 800 proton conducting membranes. In addition, room temperature and atmospheric pressure diffusion coefficients determined from conductivity and ^{1}H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies are considered. While the S-SEBS and fluorocarbons exhibit a percolation threshold at 10 and 4 wt-%, respectively, all materials exhibit this phenomenon at a volume water fraction of $C \approx 0.035$. Above the threshold the conductivity exhibits a power law behavior. When the volume of the hydrophobic portion of the membrane is subtracted the threshold occurs at the adjusted volume fraction of $C_A \approx 0.12$ which approaches that expected for continuum percolation.

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Abstract—Electrical conductivity results at a variety of pressures, temperatures and water contents are evaluated for sulfonated styrene/ethylene-butylene/styrene (S-SEBS) triblock polymer, Nafion 117, and Dow 800 proton conducting membranes. In addition, room temperature and atmospheric pressure diffusion coefficients determined from conductivity and ^1H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies are considered. While the S-SEBS and fluorocarbons exhibit a percolation threshold at 10 and 4 wt-%, respectively, all materials exhibit this phenomenon at a volume water fraction of $C \approx 0.035$. Above the threshold the conductivity exhibits a power law behavior. When the volume of the hydrophobic portion of the membrane is subtracted the threshold occurs at the adjusted volume fraction of $C_A \approx 0.12$ which approaches that expected for continuum percolation.

INTRODUCTION

Sulfonated styrene /ethylene-butylene /styrene (S-SEBS) triblock polymer is employed by Dais-Analytic Corporation as a low cost proton conducting membrane for use in hydrogen fuel cells. S-SEBS is a relatively new material, with few papers describing the properties of this material .[1-3] S-SEBS is particularly interesting because of the structural differences between it and the widely studied Nafion and Dow materials.[4-13] The important differences are both the composition of the backbone, hydrocarbon vs. fluorocarbon, and nature of the sulfonate ion (connected via a benzene ring vs. fluorocarbon).

In a recent paper[3] the authors presented a variety of experimental data for S-SEBS, Nafion 117 and Dow 800 including complex impedance/electrical conductivity and ^1H pulsed gradient spin-echo nuclear magnetic resonance (NMR) studies. Most of the data for both S-SEBS and the fluorocarbon-based material show the existence of a critical water content. This suggests the possibility that a percolation threshold exists. In fact, percolation theory has been applied to Nafion, albeit with limited success.[14,15] In the present paper a detailed discussion of the application of percolation theory to S-SEBS and fluorocarbon based proton conductors is given. It is shown that when the water is properly accounted for, percolation theory results in an excellent representation of the data.

DISCUSSION

Figure 1 is a plot of electrical conductivity vs. water content from reference 3 for three proton conducting membranes. The general behavior is the same for each of the polymers and may be considered in terms of two regions. In the first region the conductivity is high for high water content and decreases approximately in proportion to the water volume fraction until a critical value is reached. Below the threshold, in the second region, the conductivity is low. Of particular interest is that the threshold differs significantly between S-SEBS (approximately 10 wt%) and the two fluorocarbon polymers (approximately 4 wt%). The existence of a threshold suggests the applicability of percolation theory.

Percolation theory is usually discussed in terms of the volume fraction of water, C, which is given by:

$$C = \frac{V_{water}}{V_{total}} = \frac{V_{water}}{V_{water} + V_d} \qquad (1)$$

where V_{water} is the volume of the water and V_d is the volume of the dry polymer.[15]

Figure 2 is a plot of the electrical conductivity vs. C for the three proton-conducting polymers. While the general behavior is the same as in figure 1, a significant difference is observed in that the threshold is about the same, ≈0.05, for all three polymers. However, each of the materials exhibits a slightly different dependence on C above the critical concentration.

The existence of this threshold can be further demonstrated by considering the behavior of the diffusion coefficient as a function of water content. In figure 7 of reference 3, D_σ and D are plotted vs. water uptake in S-SEBS and Nafion 117 in wt-%. D_σ is the diffusion coefficient determined from conductivity using the Nernst-Einstein relation while D was measured using ^{1}H pulse gradient spin-echo nuclear magnetic resonance.[3] For S-SEBS both techniques yielded a threshold value of approximately 10 wt-% water and for Nafion 117 the value was approximately 4 wt%. Figure 3 is same data plotted vs. the volume fraction of water, C. Both D_σ and D for both S-SEBS and Nafion 117 show a threshold at C≈0.05.

Figure 4 is a log-log plot of electrical conductivity vs. water content for the three proton conducting membranes. Again the data are taken from reference 3. The vertical dashed line represents the logarithm of the approximate threshold (C=0.05). To the right of this line the approximately linear behavior at high water content suggests that a power law, and hence percolation, should be considered when attempting to explain the results.

The reason, of course, is that in percolation theory the conductivity is expected to obey the following law:[16]

$$\sigma = \sigma_o (C - C_o)^n \qquad (2)$$

C_o is the critical volume fraction required for ions to percolate and n is referred to as a critical exponent which controls the scaling behavior.

To test the theory, C_o initially was arbitrarily chosen and log σ vs. log(C-C_o) was best fit to the data for $C > C_o$. This procedure was repeated for various values of C_o until a maximum in the linear correlation coefficient was achieved. The results of the linear regression analysis are listed in Table 1 and the data and best-fit curve for S-SEBS are shown in figure 5.

The three polymers yield C_o values that range from 0.03 to 0.04 and n values that range from 1.3 to 1.5. In lattice percolation theory, where the conducting elements occupy a well defined periodic lattice, the expected value for n is well defined and is a function of system dimensionality. The observed values of n fall in the expected range (1.5 ± 0.2) for a theoretical 3D lattice.[15,17] In continuum percolation theory, where no periodic lattice exists, the value for n is not as well defined but seem to follow those of conventional lattice percolation.[16] However, in all theories, C_o, is well defined and the observed values ($C_o \approx 0.035$) are much lower than the values that are typical of percolation. For example, for continuum percolation on a random close pack structure a value of C_o=0.16 is expected.[16]

There are several possible causes of the anomalously low values of C_o. Hsu et al. have suggested that if the water is spread into a more extended, uniform network then a lower critical concentration would be expected.[15] However, as is discussed by Pourcelly and Gavach,[14] a number of experimental results for Nafion suggest a non-uniform distribution of water. Even though there is doubt concerning the original model of spherical clusters of water in Nafion,[19,20] because of the distribution and effect of the sulfonate ions, it is unlikely that sufficient uniformity can be achieved to explain the results.

Another possible cause of the anomalously low values of C_o would be a very large coordination number. This decreases the percolation threshold by increasing the number of conduction paths. However, x-ray evidence suggests that the coordination number for water is approximately 4.4 at room temperature, a vestige of the tetrahedral structure of ice.[21] Consequently, it is unlikely that a large coordination number exists in these materials.

A more reasonable explanation can be given by reconsidering the way in which the volume fraction is calculated. In percolation theory, all quantities refer to the conducting phase. However, in the case of the proton-conducting membranes a fraction of the material is inert. For example, the hydrophobic regions of Nafion have nothing to do with the conduction process i.e. when water is added to the polymer, the polymer is not replaced. Consequently, a more appropriate approach is to only consider the volume that is available to the water. In this case the volume fraction is given by:

$$C_A = \frac{V_{water}}{V_{water} + V_d - V_P} \qquad (3)$$

where V_P is the volume occupied by the polymer that is not available to water. It is assumed that the sulfonate group is not included in V_P.

An estimate of V_P was made as follows. For Nafion 117 and Dow 800, the density of the polymer was taken to be 2.3 g/cm^3, which is the value for poly(tetrafluoroethylene).[22] For S-SEBS, since the density of each of the constituents is within approximately 7% of that for water, a value of 1.0 g/cm^3 was used. Using these approximations, the revised volume fraction available to water, C_A, was calculated. Using the previous fitting technique, the parameters in the following equation:

$$\sigma = \sigma_{Ao}\left(C_A - C_{Ao}\right)^{n_A} \qquad (4)$$

were evaluated and the results are listed in Table 1. The data and best fit curve for S-SEBS are shown in figure 6. The parameter of interest, C_{AO}, is 0.105 for S-SEBS, 0.11 for Nafion 117, and 0.14 for Dow 800. These values approach the expected volume fraction for continuum percolation. The critical exponent for the available volume, n_A, ranges from approximately 1 to 2.1. While these values cover a broader range than the total volume critical exponent, n, they are not unreasonable for continuum percolation.

It is important to note that present model neglects the swelling of the polymer which would tend to increase the available volume. It will be of interest to investigate the effect of swelling on the percolation model.

CONCLUSION

In summary, proton transport in these membranes depends on the volume water fraction and exhibits a percolation threshold. Above the threshold the conductivity vs. volume water fraction follows a power law. When the volume available to the water is properly accounted for percolation theory may be used to describe the observed conductivity.

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Table 1. Percolation Fit Parameters.

	C_o	n	σ_o (S/cm)	C_{Ao}	n_A	σ_{Ao} (S/cm)
S-SEBS	0.04	1.47	0.685	0.105	0.96	0.207
Nafion 117	0.03	1.38	0.272	0.11	2.1	0.115
Dow 800	0.035	1.31	0.259	0.14	1.75	0.125

FIGURE CAPTIONS

Figure 1. Conductivity vs. weight percent water for Nafion 117, S-SEBS and Dow 800.

Figure 2. Conductivity vs. volume fraction water for Nafion 117, S-SEBS and Dow 800.

Figure 3. The Diffusion Coefficients D and D_σ vs. volume fraction water for S-SEBS and Nafion 117.

Figure 4. Log_{10}-Log_{10} plot of the conductivity vs. volume fraction water for Nafion 117, S-SEBS and Dow 800. The vertical dashed line represents the approximate threshold of C=0.05.

Figure 5. Best fit results for conductivity vs. volume fraction water minus the percolation threshold for S-SEBS.

Figure 6. Best fit results for conductivity vs. volume fraction available to water minus the percolation threshold for S-SEBS.

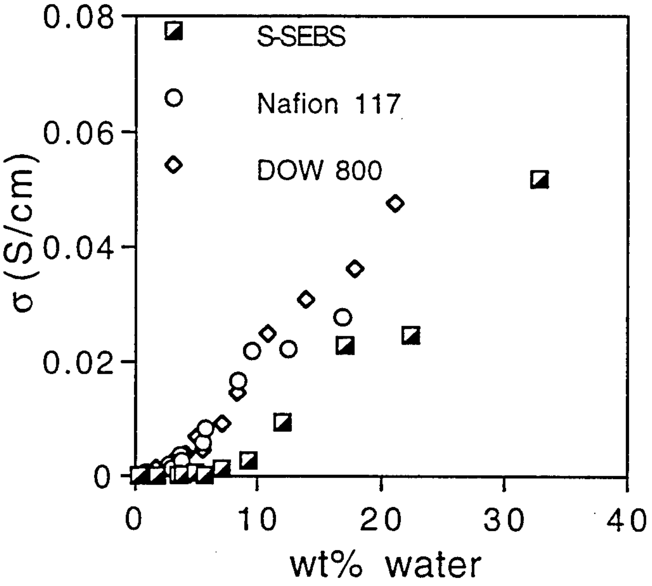
0.08
0.06
0.04
0.02
0
σ (S/cm)
0
10
20
30
40
wt% water
S-SEBS
Nafion 117
DOW 800

Fig. 1

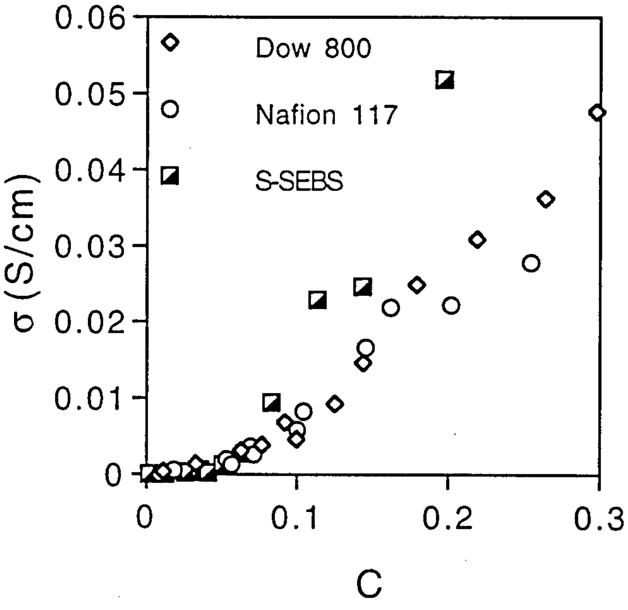
0.06
0.05
0.04
0.03
0.02
0.01
0
σ (S/cm)
0
0.1
0.2
0.3
C
Dow 800
Nafion 117
S-SEBS

Fig. 2

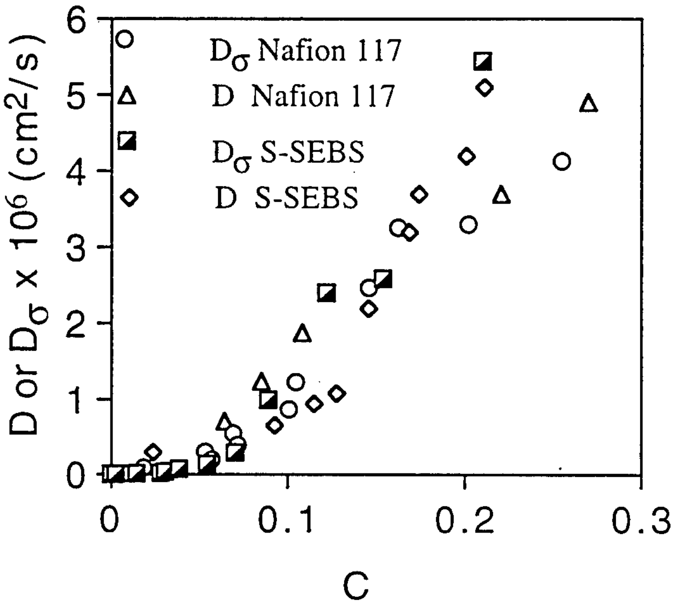
6
5
4
3
2
1
0
D or D_σ x 10^6 (cm^2/s)
0
0.1
0.2
0.3
C
○ D_σ Nafion 117
△ D Nafion 117
◪ D_σ S-SEBS
◇ D S-SEBS

Fig. 3

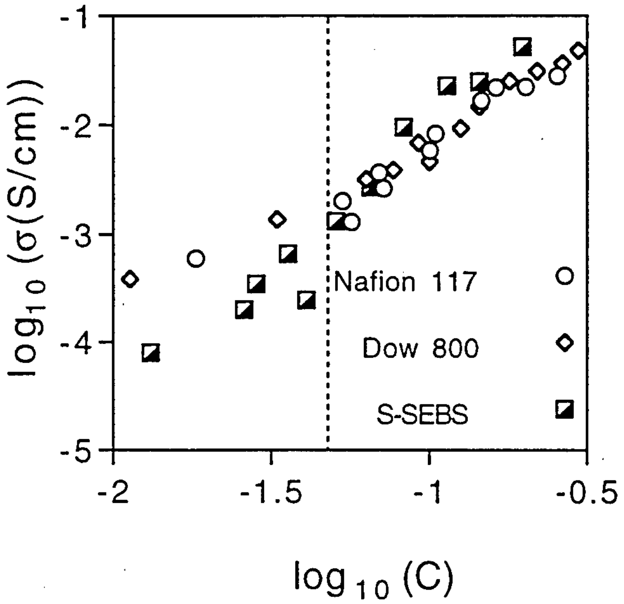
-1
-2
-3
-4
-5
$\log_{10}(\sigma(S/cm))$
-2
-1.5
-1
-0.5
$\log_{10}(C)$
Nafion 117 ○
Dow 800 ◇
S-SEBS ◪

Fig. 4

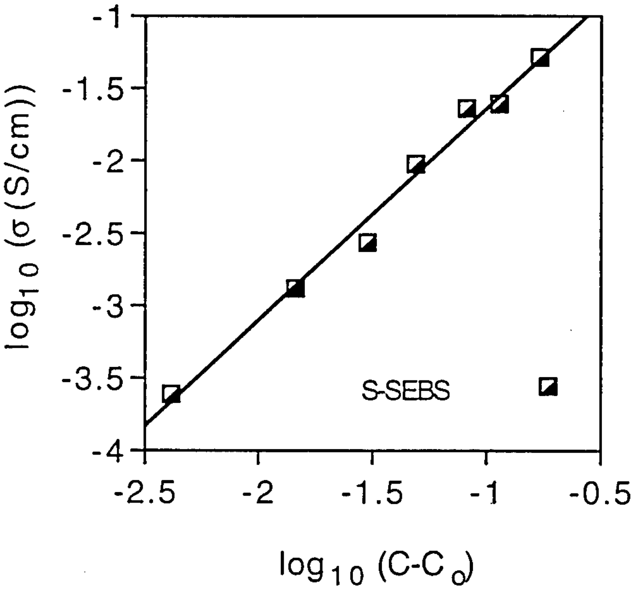

Fig. 5

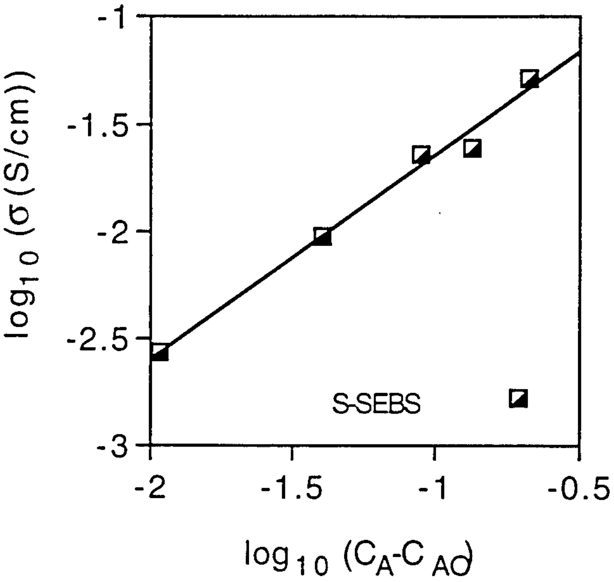

Fig. 6