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Free Volume and Percolation in S-SEBS and Fluorocarbon  
Proton Conducting Membranes

Prepared for publication in Solid State Ionics.

by

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13. ABSTRACT (Maximum 200 words)

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Proton Conducting Membranes

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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  $^1\text{H}$  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. The activation volume results are shown to be consistent with free volume considerations.

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## 1. 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 its properties [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  $^1\text{H}$  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 a reasonable representation of the data. In addition it is shown that previously published activation volume results are consistent with free volume theory.

## 2. Discussion

### 2.1. Percolation

Fig. 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:

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

where  $V_{\text{water}}$  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, ( $C \approx 0.05$ ) 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,  $D_\sigma$  and  $D$  are plotted vs. water uptake in S-SEBS and Nafion 117 in wt-%.  $D_\sigma$  is the diffusion coefficient determined from conductivity using the Nernst-Einstein relation while  $D$  was measured using  $^1\text{H}$  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  $D_\sigma$  and  $D$  for S-SEBS and Nafion 117 show a threshold at  $C \approx 0.05$ .

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]:

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

$C_o$  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  $\log \sigma$  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 ( $1.5 \pm 0.2$ ) 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  $C_0$ . 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, [18] 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  $C_0$  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:

$$C_A = \frac{V_{water}}{V_{water} + V_d - V_p} \quad (3)$$

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  $2.3 \text{ g/cm}^3$ , 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  $1.0 \text{ g/cm}^3$  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:

$$\sigma = \sigma_{A_0} (C_A - C_{A_0})^{n_A} \quad (4)$$

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,  $C_{A_0}$ , is 0.105 for S-SEBS, 0.11 for Nafion 117, and 0.14 for Dow 800. These values are closer to the expected volume fraction for continuum percolation than are the values of equation 2. 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.

As is apparent from Fig. 4, below the threshold volume water fraction the polymers continue to conduct. Furthermore, the electrical conductivity at low water content exhibits other interesting characteristics. For example, Fig. 6 of reference 3, the effect of pressure on the conductivity, as evidenced by the apparent activation volume;

$\Delta V_{APP}$ , defined by

$$\Delta V_{APP} = -kT \frac{\partial \ln \sigma}{\partial p} \quad (5)$$

exhibits a linear dependence vs.  $\ln(\sigma)$  for both Nafion and S-SEBS. The slope of the lines are different for the two materials, the slope for Nafion being about 2.6 times larger than for S-SEBS. These results can be understood from the viewpoint of free volume.

## 2.2. Free Volume

Free volume theory as developed by Cohen and Turnbull [23], predicts that transport occurs when a diffusing species encounters a hole that exists with a volume greater than a critical volume,  $v^*$ . The diffusion coefficient,  $D$ , in this model is as follows [23]:

$$D = g a^* u \exp(-\gamma v^* / v_f) \quad (6)$$

where  $g$  is a geometrical factor,  $a^*$  is approximately equal to the volume of the transported species,  $u$  is the velocity with in the volume,  $\gamma$  is a geometrical factor that accounts for the overlap of holes and  $v_f$  is the average free volume. Further, thermodynamic considerations predict that the velocity,  $u$ , is proportional to the square root of the absolute temperature,  $T^{1/2}$ .

Bamford et al. used the Nernst-Einstein equation to relate the diffusion coefficient to the ionic conductivity for polymers [24]. Following this procedure the conductivity may be expressed as

$$\sigma_{FV} = A_1 T^{1/2} \exp(-\gamma v^* / v_f) \quad (7)$$

where  $A_1$  is a constant.

This form of the conductivity may be used with eq. (5) to derive the following theoretical expression for the apparent activation volume,  $\Delta V_{APP,FV}$

$$\Delta V_{APP,FV} = -kT\chi_f \ln \sigma + A_2 \quad (8)$$

where  $A_2$  is a constant and  $\chi_f$  is the compressibility of the free volume defined by

$$\chi_f = -\frac{1}{v_f} \frac{\partial v_f}{\partial p} \quad (9)$$

Clearly, eq. (8) predicts the experimental result that  $\Delta V_{APP}$  vs.  $\ln(\sigma)$  is a straight line. Further, eq. (8) predicts that the slope of the straight line is equal to  $-kT\chi_f$ . This is important because it provides an explanation of the difference between Nafion and S-SEBS. Specifically, as mentioned above, the slope of the straight line for Nafion is about 2.6 times larger than that for S-SEBS. This result is explained if the ratio of the free volume compressibility,  $\chi_f$ , for Nafion to that for S-SEBS is about 2.6. This trend is reasonable because of the difference in structure of the two materials. Specifically, since the sulfonate groups in Nafion are connected via fluorocarbons vs. benzene rings for S-SEBS, it would be expected that S-SEBS would have a stiffer structure and be less compressible.

Next, the values of  $\chi_f$  calculated from the slopes are 0.52 and 1.36  $\text{GPa}^{-1}$  for S-SEBS and Nafion, respectively. The values for the free volume compressibilities are significantly larger than the bulk compressibility of the dominant components of the material, such as teflon ( $0.288\text{GPa}^{-1}$ ), poly(styrene) ( $0.22\text{GPa}^{-1}$ ) or water ( $0.45\text{GPa}^{-1}$ ) [10]. That the free volume compressibility is larger than bulk compressibilities is not surprising since the free volume is composed of voids in the material and it would be expected that the voids would be more easily affected by pressure. This result is reminiscent of the effect of pressure on activation volumes of point defects in alkaline earth fluorides where it is found that the compressibility of point defect activation volumes is much larger than the bulk compressibility of the material [25]. While this result is reasonable, theoretical studies concerning this point would be valuable.

Next, it is clear that free volume theory (eq. (8)) accounts for all of the activation volume data, even those at high water contents. Specifically, as  $\ln(\sigma)$  increases,  $\Delta V_{app}$  passes smoothly through  $\ln(\sigma)=-7$ , the critical water content for both materials. This suggests that free volume is involved with ion transport both at low and high water contents. This is interesting since, in the case of Nafion at least, it is thought that the transport mechanism is different at low and high water contents [8,10,11]. This is not unreasonable since free volume theory is independent of transport mechanism.

Because of the success of free volume in explaining the variation of the electrical conductivity with pressure (activation volume data), an attempt was made to use free volume considerations to explain the variation of the electrical conductivity with water content. Specifically, an attempt was made to determine whether the abrupt change in dimensions of the sample that occur in the vicinity of the critical water content [Zawod & us ref 3] coupled with free volume theory can account for the rapid increase in electrical conductivity previously explained in terms of percolation. Changes in the volume with water content were obtained from ref. 3. The geometrical factor,  $\gamma$ , and critical volume,  $v^*$ , were assumed to be approximately constant. The resultant theoretical electrical conductivity predicted from eq. (7) did not reproduce the rapid increase in the electrical conductivity above the critical concentration that is observed experimentally.

Consequently, if the free volume scales with the bulk volume, an additional phenomenon such as percolation is necessary to explain the experimental results. Of course, it may be that the free volume increases more rapidly with water content than does the bulk volume in which case the experimental results might be explained. Consequently, further work concerning this point is necessary.

### **3. Conclusions**

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. Activation volume results are shown to be consistent with free volume considerations.

### **Acknowledgments**

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## 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  $D_0$  vs. volume fraction water for S-SEBS and Nafion 117.

**Figure 4.**  $\text{Log}_{10}$ - $\text{Log}_{10}$  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.

**Table 1.** Percolation Fit Parameters.

	$C_0$	$n$	$\sigma_0$ [S/cm]	$C_{A0}$	$n_A$	$\sigma_{A0}$ [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

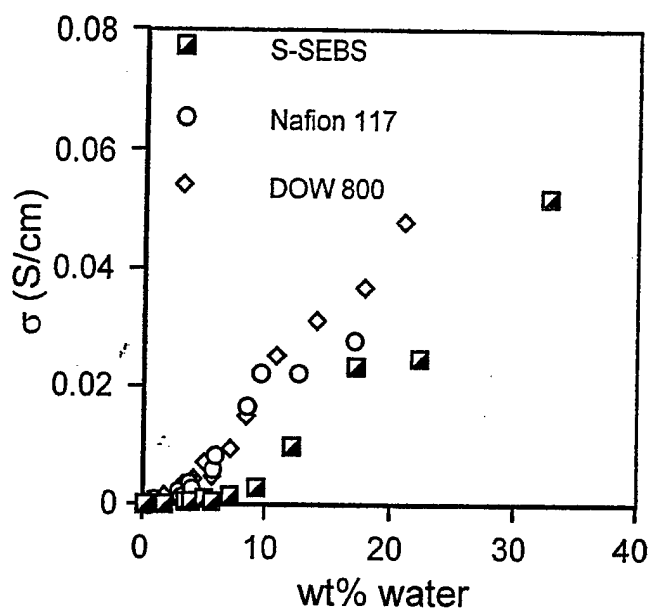


Figure 1

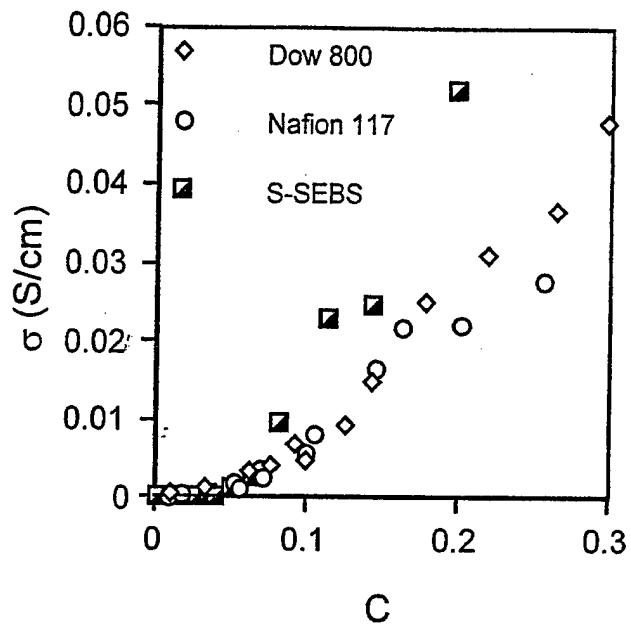


Fig 2

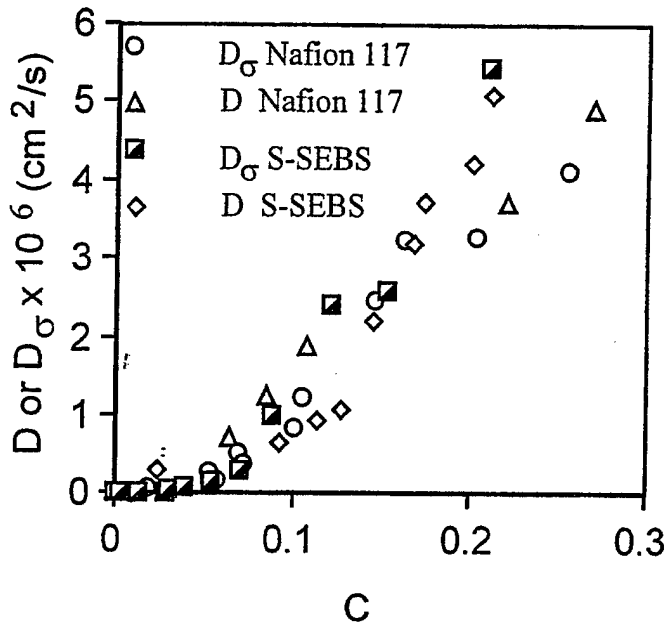


Fig 3

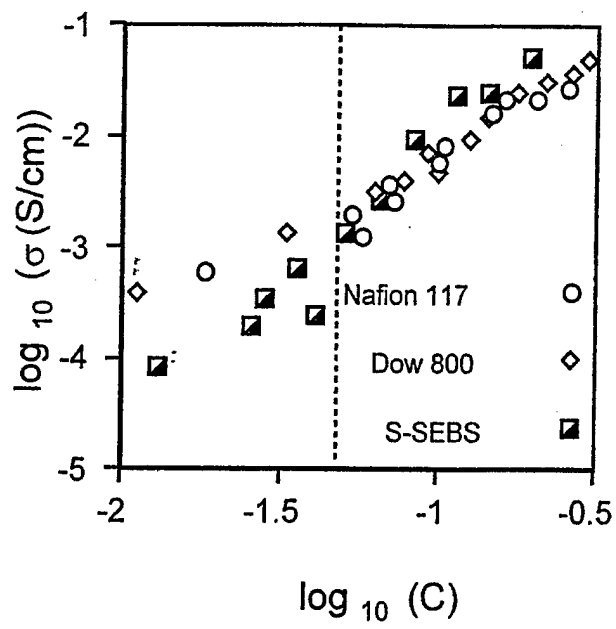


Fig 3

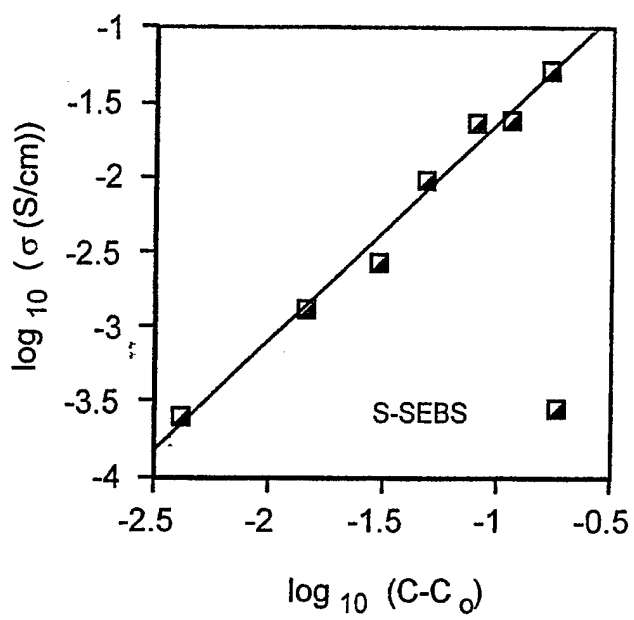


Fig. 5

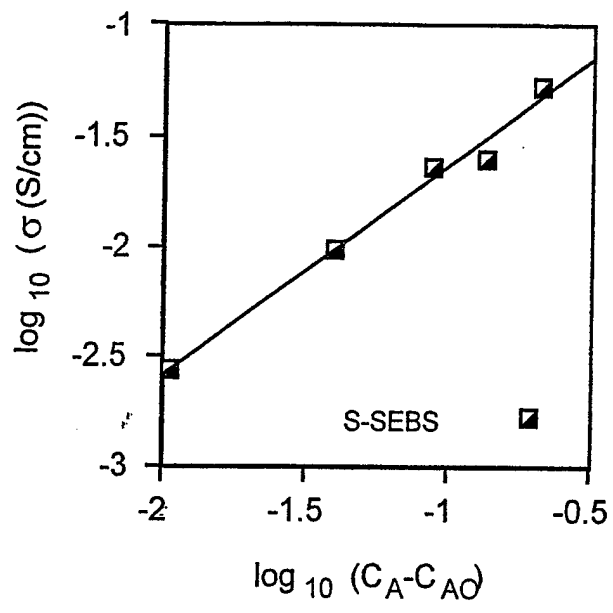


Fig 6