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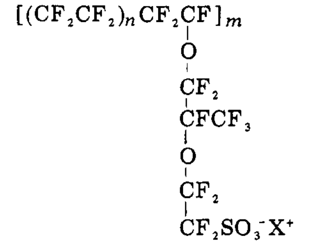
Ion Percolation and Insulator-to-Conductor Transition in Nafion[1] Perfluorosulfonic Acid Membranes[†]

Nafion perfluorosulfonic acid products are made from a copolymer of tetrafluoroethylene (C_2F_4) and a vinyl ether PSEPVE ($CF_2{=}CFOCF_2C(CF_3)FOCF_2CF_2SO_2F$) known as XR resins which are then converted to the ion-exchanged sulfonate form



$$\begin{array}{l} [(CF_2CF_2)_nCF_2\overset{}{C}F]_m \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CFCF_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2SO_3^-X^+ \end{array}$$

by hydrolysis.[2] These materials possess extraordinary electrochemical and mechanical properties and can be used as a membrane separator in a chlor–alkali cell.[2] Their unique transport characteristics are intimately associated with a spontaneous phase separation which occurs in hydrated perfluorosulfonate polymer: the conductive aqueous phase segregates into ion containing clusters which are randomly dispersed in an insulating fluorocarbon matrix.[3,4] In this paper, we apply modern percolation theory[5] to gain insight into the transport processes occurring in this system and identify, for the first time, an (ionic) insulator-to-conductor transition in Nafion. Our theory is very general and can be applied to other ionomeric systems as well.

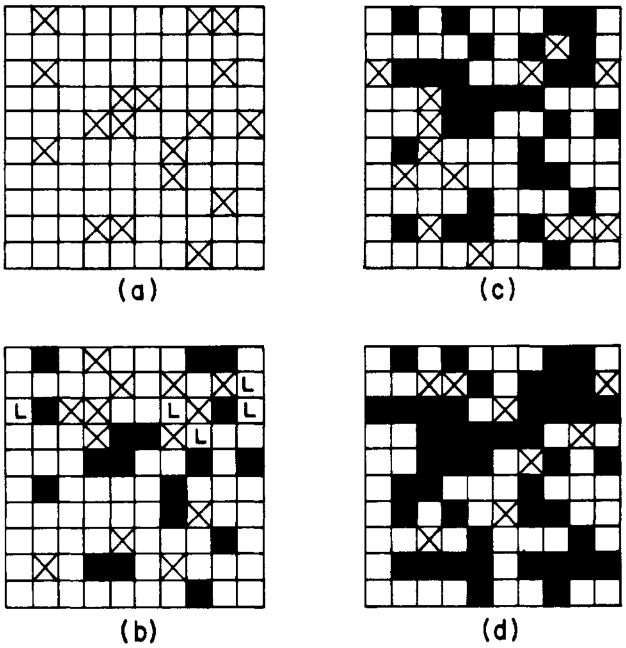


Figure 1. A two-dimensional illustration for the concept of percolation. The shaded and crossed areas correspond respectively to sites that were previously occupied and sites that have just been occupied whereas those marked L in (b) are some empty sites that must be occupied before the onset of ion transport. The percentages of occupancy of the grid for cases (a) to (d) are 18, 31, 45, and 53%, rspectively. For detailed discussions, see text.

The percolation theory has been investigated thoroughly and extensively applied.[5] Its salient features can be conveniently illustrated on a two-dimensional grid with some of its sites randomly occupied as shown in Figure 1a–d. For our purposes, empty and occupied sites would correspond to the fluorocarbon and the ion cluster phases, respectively. At low concentrations, ion clusters are well separated into "islands" (cf. Figure 1a) so that macroscopic ion flow from one side of the grid to the other is impossible. At a higher concentration (Figure 1b), these "islands" grow in size and interconnect to form extended pathways. However, crucial links (such as those marked L in Figure 1b) are still missing here and there; thus, long range ion transport is still impossible. Eventually, above a threshold value of occupancy, which is approximately 44% for our two-dimensional example, some of these links have been filled (as shown in Figure 1c) to form conductive channels through which ions can now flow. Hence, an ionic insulator-to-conductor phase transition occurs at this threshold and simultaneously the average size of the extended pathways, which is the correlation length of our phase transition problem, becomes macroscopic. At even higher occupancies (cf. Figure 1d), percolation channels crisscross the grid engulfing dead ends and filling missing links which lead to progressively higher conductivities.

The principal conclusion that a threshold value (c_0) exists for the volume fraction (c) of the aqueous phase in the polymer below which ion flow is impossible can be established with the renormalization group technique,[6-8] with a mean field theory (for six dimensions),[9,10] or from numerical computations.[5,11-15] In addition, these analyses showed that above and near the threshold, the conductivity σ obeys a simple power law

$$\sigma = \sigma_0(c - c_0)^n \tag{1}$$

where the critical exponent n and the prefactor σ_0 are constants. The exponent n is a universal constant which depends on spatial dimensions only and is applicable to any percolative system regardless of its chemical, mechanical, structural, morphological, and statistical properties.[16] For a three-dimensional (3D) system, n was reported to range between 1.3 and 1.7[5,12-15] with 1.5 probably the most reliable value. In contrast, the threshold volume fraction c_0 depends on both the dimensionality and the manner in which the two components are dispersed.[15] For a 3D continuous random system, c_0 is 0.15 according to recent investigations.[14,17,18] It can, however, be larger if ion clusters flocculate into several well-isolated regions;[15] conversely, it may be smaller if they spread out into an

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extended network. Finally, the prefactor σ_0 depends on the details of the conduction mechanism and can only be computed from specific microscopic models. The important feature of our theory is that dimensional and topological information of cluster connectivity are contained in the factor $(c - c_0)^n$ whereas details of how ions move within a cluster have been separated out into the prefactor σ_0 which can then be determined empirically.

To test this theory, the room temperature conductivity of a perfluorosulfonate polymer at four different equivalent weights[19] (1050, 1100, 1350, and 1500) was measured as a function of the volume fraction of the aqueous phase. Our starting samples were films in the potassium sulfonate form and were ion exchanged into the sodium salt form by soaking in hot, stirred nitric acid, water, and concentrated solutions of sodium hydroxide, in that order, for several days. Equilibration with the sodium hydroxide solution (at room temperature) was considered complete when the wet sample weight stabilized. The volume fraction c of the aqueous phase in a given sample was controlled by varying caustic concentrations from 15 to 50% by weight, and c was obtained from

$$c = \Delta V/(1 + \Delta V) \tag{2}$$

with

$$\Delta V = \frac{\rho_d (w_1 - w_0)}{\rho_c w_0} \tag{3}$$

where ρ_d and ρ_c are the densities of the dry polymer and the caustic solution, respectively, whereas w_0 and w_1 are the dry and wet weights of the sample. Sample conductivity was measured by an ac technique with frequencies between 10^0 and 10^7 Hz and a constant measuring current density of 1.25 mA/cm^2 with the apparatus shown in Figure 2. The sample consists of two halves of a liquid test cell that were separated by a membrane of Nafion. External electrical contacts were provided via platinum screens pressed against opposing surfaces of the membrane. Comparison of cell impedances with and without the polymer indicates that the pure sodium hydroxide impedance is several orders of magnitude less than the cell impedance with the membrane present. Thus, the series impedance of the liquid electrodes is negligible and the membrane impedance is given by:

$$Z = R + iX_c = R_L\{(V_B/V_A)\exp(i\theta) - 1\} \tag{4}$$

where the quantities V_A, V_B, θ, and R_L are defined in Figure 2. Polarization of the electrode/polymer interface was observed as capacitive reactance X_c at the lowest frequencies. This X_c decreases smoothly as f increases. The measuring frequency f required to avoid this polarization is called f_0 (which is typically $\geq 10^3$ Hz), and for $f \geq f_0$, $X_c = 0$ and R $(=R_0)$ is independent of frequency.[20] The sample conductivity is then obtained from R_0 by[21]

$$\sigma = (1/R_0)(t/A) \tag{5}$$

where t and A are the membrane thickness (~0.06 cm) and the electrode area (~1.3 cm^2), respectively. The measured conductivity jumped abruptly from $\lesssim 10^{-6}$ Ω^{-1} cm^{-1} (which is insulative for all practical purposes) at approximately 9% volume fraction of aqueous phase to $\sim 2 \times 10^{-4}$ Ω^{-1} cm^{-1} at about 11%. The threshold volume fraction c_0 as determined from a best fit of eq 1 to our data points is depicted in Figure 3: it is 0.10 which is less than the ideal value of 0.15 for a completely random system. This suggests that these ion containing clusters are not randomly dispersed. In fact, they tend to spread out into an extended conductive network presumably via some narrow channels between clusters as postulated by Gierke.[3] The critical exponent n was also determined from the slope of Figure 3 to be (1.5 ± 0.2) which is well within the theoretical bound of 1.3 to 1.7. The prefactor σ_0 is 0.16 Ω^{-1} cm^{-1}.[22]

In conclusion, the percolative nature of the transport processes and the importance of cluster connectivity as well as an ionic insulator-to-conductor transition have been identified for the first time in Nafion perfluorosulfonic acid

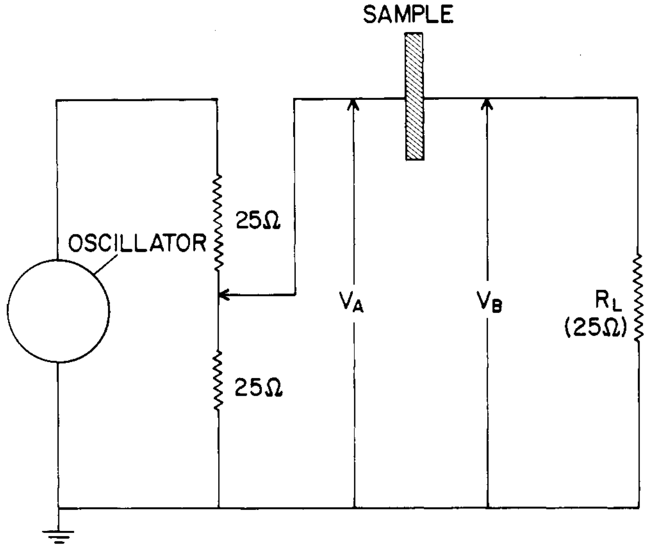

Figure 2. Dielectric measuring apparatus: Oscillator-Wavetek Model 164 (10^0–10^7 Hz); V_A, V_B, and θ (their phase difference) are measured by a Hewlett Packard Model 3575A gain/phase-meter.

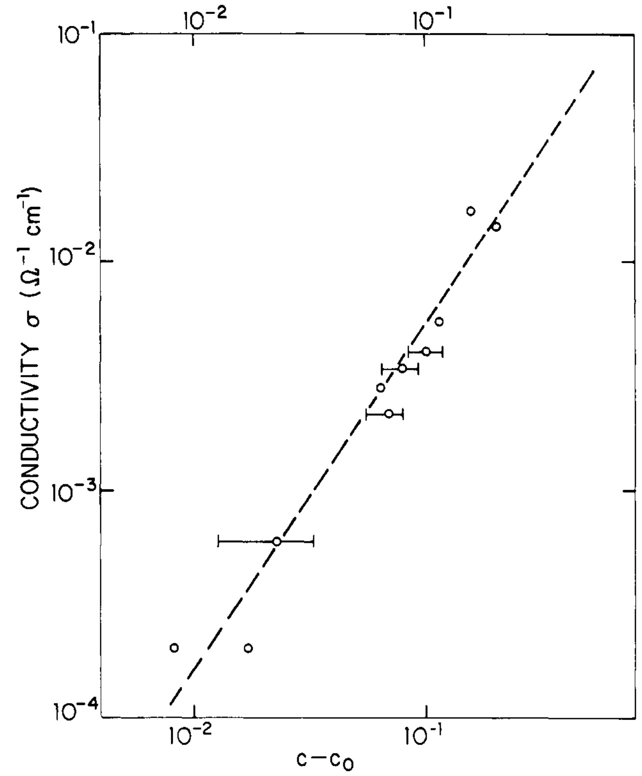

Figure 3. Log–log plot of conductivity σ vs. the excess volume fraction of the aqueous phase $(c - c_0)$. Typical error bars for the determination of volume fraction are shown whereas the corresponding errors for conductivity are smaller and omitted for clarity. The straight line is a fit of the percolation result given in eq 1 to the data points with $n = 1.5$, $c_0 = 0.10$, and $\sigma_0 = 0.16$ Ω^{-1} cm^{-1}.

ion-exchange membranes. Similar transitions are also expected in other ionomeric systems as well.

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(19) The equivalent weight is the mass of the dry polymer in the sulfonic acid form required to neutralize 1 equiv of base.

(20) Normally, R increases slowly for frequencies below f_0 and at ~10 Hz its value is about 30% larger than that at or above f_0. For very conductive samples, however, R may increase by as much as a factor of 2 or 3 (see also ref 21).

(21) The dc conductivity of a pure solution of sodium hydroxide has also been measured by the same method, using a porous poly(tetrafluoroethylene) membrane. At room temperature and for $f \geq f_0 \simeq 1$ kHz, it is 0.32 Ω^{-1} cm^{-1} for a 15% (by weight) solution which agrees well with the literature value of 0.35 Ω^{-1} cm^{-1} [see, for example, "Handbook of Chemistry", 10th ed., compiled and edited by N. A. Lange, McGraw-Hill, New York, 1967, p 1219]. The same interfacial polarization phenomenon discussed in the text and in ref 20 was also observed such that at 60 Hz the apparent conductivity decreased to 0.11 Ω^{-1} cm^{-1}.

(22) Experimental uncertainty for ln σ_0 is ±0.62. Variation in the conductivity σ_s of pure solution of sodium hydroxide is within this limit; otherwise, the measured conductivity σ for wet membranes of Nafion should be properly normalized.

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CORRECTION

Elliot Charney: Dependence of the Electric Field-Induced Orientation of Poly(riboadenylic acid) on Its Polyelectrolyte Properties. Volume 11, Number 5, September–October 1978, page 1059.

The expression in this communication for the fractional charge density is in error. The correct expression is $i = (1 - \kappa - \xi^{-1})$. Figure 1 should therefore be replaced by the accompanying figure. The slope and intercept of the linear plot thus differs slightly from the original, but the essential conclusion of the communication that the orientation in an applied electric field of a high charge density linear polyelectrolyte is linearly proportional to the charge density remains valid.

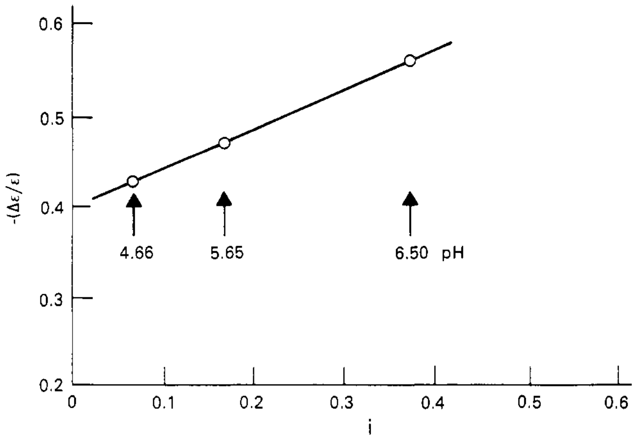

Figure 1.