

Conductivities and Transport Properties of Gelled Electrolytes with and without an Ionic Liquid for Li and Li-Ion Batteries

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Conductivity and transport properties have been determined for gelled polymer electrolytes of three compositions: a base PVdF–polymer gel with organic carbonate solvents as plasticizers and LiN(SO₂C₂F₅)₂ electrolyte, a second polymer electrolyte with 5 mass % 1-ethyl-3-methylimidazolium bisperfluoroethylsulfonfyl imide (EMI–BETI) added to the base polymer electrolyte, and a third PVdF polymer electrolyte using only EMI–BETI as the plasticizer. Conductivities were studied over the temperature range +25 to –40 °C, and for all three gels, the temperature dependence of the conductivities was found to follow the VTF equation, which is consistent with the free volume model for ion transport. For the gel containing 5 mass % EMI–BETI, transport numbers were determined from +50 to –20 °C and were found to decrease as the temperature decreased. Although there are no theoretical models to treat and interpret the temperature dependence of transport numbers, we found that a modified VTF equation resulted in an excellent fit to the temperature dependence of the transport number, which is another confirmation of a free volume model for transport in these gelled polymer electrolytes.

Introduction

Poly(vinylidene fluoride)–hexafluoropropylene copolymers (PVdF–HFP), first introduced by Bellcore¹ and recently reviewed by Nishi,² are the bases for considerable worldwide research on optimization of gelled polymer electrolytes. In this paper, we report new studies on the use of PVdF–HFP gels based on the plasticizing organic solvents ethylene carbonate (EC), propylene carbonate (PC), γ -butyrolactone (γ -BL), vinylene carbonate (VC), and the ionic liquid 1-ethyl-3-methylimidazolium bisperfluoroethylsulfonfyl imide (EMI–BETI). Selection of EC and PC is based on the low vapor pressure PVdF–HFP gel developed by Sony (e.g., see ref 2), and improvement in performance of this base system is achieved by first adding γ -BL to increase conductivities and then the ionic liquid EMI–BETI to improve cross-linking and safety. Because PC, γ -BL and EMI–BETI are known “aggressive” solvents toward graphite anodes in Li-ion cells, small amounts of VC were added to this new formulation to stabilize the passive SEI on graphite.³

On the basis of the above concepts, we prepared three gels of composition given in Table 1 with lithium bisperfluoroethylsulfonfyl imide (LiBETI) as the electrolyte.

The objectives of our initial studies on the gels summarized in Table 1 are to characterize the conductivity and transport properties as a function of temperature. Application of these gels to prototype Li-ion cells will be reported in a future publication.

TABLE 1: Composition of Gels Containing LiBETI

gel no.	mass %						
	ionic liquid (EMI–BETI)	EC	PC	VC	GBL	LiBETI	PVDF 2801
1		15.61	31.15	2.34	31.15	13.09	6.53
2	4.77	14.86	29.72	2.23	29.72	12.48	6.21
3	62.5					18.75	18.75

Experimental Section

Composite Membranes Preparation. Gelled polymer electrolytes involved dissolving the lithium salt (LiBETI) in the appropriate solvent mixtures heated to ~45 °C followed by addition of PVdF–HFP and further heating to 90 °C to ensure complete dissolution of the polymer. The hot solutions were then quenched to room temperature by casting onto Al foil forming films around 250 μ m thick. The following summarizes the sources and purities for each material: EMI–BETI (99% pure, from Strem Chemicals), LiBETI (battery grade, 3M), PVdF–HFP (Kynar PVdF 2801), γ -BL (99%, EM Science), PC (99%, Aldrich), EC (99%, Ferro Corp.) and VC (98%, H.C. Starck). All solids were dried in a vacuum at 90–100 °C overnight, and all liquids were dried with 3A molecular sieves overnight. Fabrication of the gels was carried out in a dry room of 1% relative humidity.

Ionic Conductivity Measurements. The ionic conductivity of all membranes was determined by ac impedance spectroscopy using cells with stainless steel blocking electrodes and Teflon spacers to fix the thickness. Measurements were made from high to low temperature in a forced air Tenny Environmental Chamber controlled to ± 1 –2 °C. The impedance tests were carried out from 100 kHz to 0.1 Hz using a Gamry model PC13/

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300 potentiostat. The specific ionic conductivities, σ , of the gelled electrolytes were determined by using the following equation:

$$\sigma = \frac{t}{(d/2)^2 \pi R_i} \quad (1)$$

where t , d and R_i represent the thickness, the diameter and the ionic resistance (bulk resistance + grain boundary resistance), respectively. The temperature ranges studied for each gelled electrolyte are as follows: for gel number 1, +25 to -30 °C; for gel 2, +25 to -30 °C; for gel 3, +25 to -40 °C.

Transport Number Measurements. Transport numbers were determined by the method of Bruce et al.,^{4–6} which is a direct-current polarization method based on the dc polarization technique of Sørensen and Jacobsen⁷ to determine transference numbers in polymer electrolytes. A two-electrode blocking cell was used: two stainless steel current collectors in close contact with two lithium metal disks sandwiched between the gelled membrane to be analyzed. If a constant dc bias (which must be ≤ 0.03 V to obtain a linear response from the system) is applied to the electrodes of the cell, a current is measured that falls from an initial value i_0 to a steady-state value of i_s , which is reached after 2–6 h. For measurements at -20 , 0 , $+25$ and $+50$ °C, the steady-state current, i_0 , was reached after 4 h. For the -10 °C measurement, i_0 was recorded after 2 h and thus was not quite at steady state. This introduced a small experimental error that is seen in Figures 7 and 8 and is discussed below. With the passage of time, anions accumulate at the anode and are depleted at the cathode and a concentration gradient is formed. At the steady state, the net anion flux falls to zero and only cations carry the current: therefore the cation transference number can be evaluated from the ratio i_s/i_0 . Because the thickness of the passivating film on the electrode will vary over the time required to reach a steady-state current, the values of the intrinsic resistance must be measured shortly before the application of the dc bias potential and immediately after the attainment of steady state to determine the correct cationic transference numbers t_+ , by using the equation

$$t_+ = \frac{i_s(\Delta V - i_0 R'_0)}{i_0(\Delta V - i_s R'_s)} \quad (2)$$

In eq 2, the subscripts 0 and S indicate initial values and steady-state values, respectively, R' is the passivating film resistance R_{film} , ΔV is the applied voltage, and i is the current. The measurement of R'_s and R'_0 was achieved by recording two impedance spectra on the cell in the frequency range between 0.1 Hz and 100 kHz before the application of the bias potential, and after steady state has been reached and the dc bias potential has been removed. The resulting spectrum is typically a semicircle and asymmetric in shape due to convolution of two different contributions, i.e., bulk and grain boundary,⁸ to the ionic resistance of the electrolyte membrane. The deconvolution of the spectra to obtain R_{ct} and R_{film} was made using the nonlinear least-squares (NLLSQ) fit software developed by Boukamp^{9,10} and the equivalent circuit shown in Figure 1, where the processes of charge transfer and of conduction through the passivating layer are treated as two subcircuits of a resistance and a constant phase element (CPE) in parallel (the CPE is more suitable than a pure capacitive element because of the fractal nature of the electrode–solution interface).

The transport number for gel 1 (see Table 1) was determined at 25 °C, and for gel 2, transport numbers were determined over the temperature range -20 to $+50$ °C.

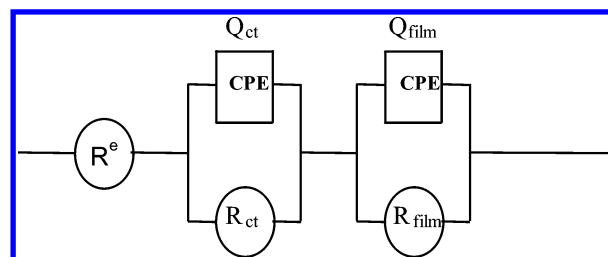


Figure 1. Equivalent circuit used for the transport number cell.

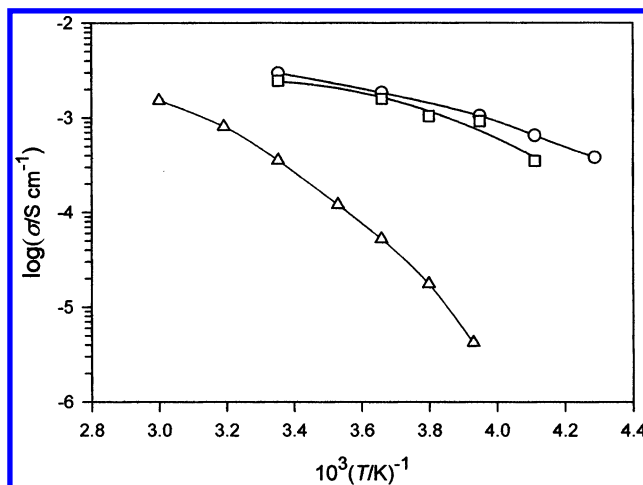


Figure 2. Arrhenius plots for the conductivities of gels listed in Table 1: (□) gel 1; (○) gel 2; (Δ) gel 3.

Results

Conductivities. Figure 2 summarizes the conductivity results for the three gelled membranes on the basis of the Arrhenius equation

$$\sigma = A \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

The Arrhenius equation predicts that a plot of $\log \sigma$ vs $1/T$ should be linear, but as seen in Figure 2, the plots are curved. In view of this behavior, the conductivity data were fitted to the VTF equation:

$$\sigma T^{1/2} = A \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (4)$$

In eqs 3 and 4, σ is the specific conductivity, A is a frequency factor based on the number of charge carriers, E_a is an activation energy, and T_0 is a reference temperature closely related to the glass transition temperature T_g . The VTF equation predicts that a plot of $\log(\sigma T^{1/2})$ vs $1/(T - T_0)$ should be linear, which in fact we observe (Figure 3). Using a curve fitting technique, we have evaluated the VTF parameters, and the results are given in Table 2.

Transport Numbers. Figure 4 shows the chronoamperometric curve obtained for gel 2 at -10 °C: the value of i_s (the steady-state current) is obtained from the end of the curve. To determine the initial value i_0 , about 70 points of the chronoamperometric curve recorded from 0.005 s to the first second (Figure 5), and i_0 was taken from the short extrapolation of current to $t = 0$. Figure 6 shows the impedance spectra in the complex plane recorded at $t = 0$ and $t = t_s$ gel 2 at -10 °C. The diameter of the semicircle is approximately equal to the sum of R_{ct} and R_{film} , the exact value of which is obtained from

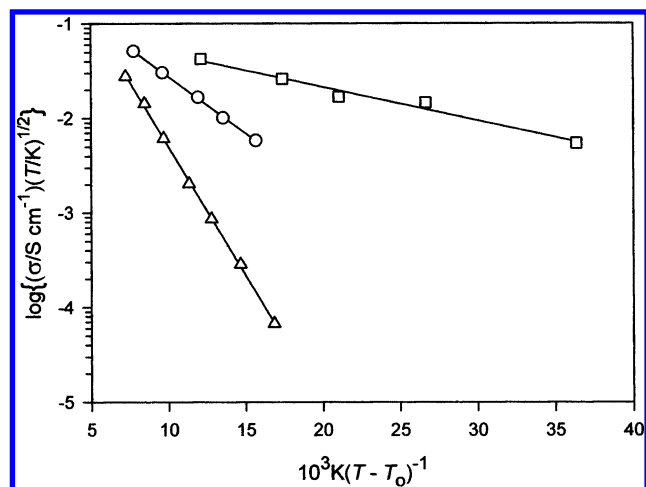


Figure 3. VTF plots for the conductivities of gels listed in Table 1: (□) gel 1; (○) gel 2; (Δ) gel 3.

TABLE 2: Ionic Liquid (IL) Content of Gels and Derived VTF Parameters from Conductivities

gel no.	$A/S \text{ cm}^{-1}(T/K)^{1/2}$	$E_a/\text{kJ mol}^{-1}$	T_0/K	$t_0/^\circ\text{C}$
1 (no IL)	0.109	0.676	215.7	-57.5
2 (5% IL)	0.437	2.293	169.4	-103.8
3 (63% IL)	2.732	5.233	195.1	-78.1

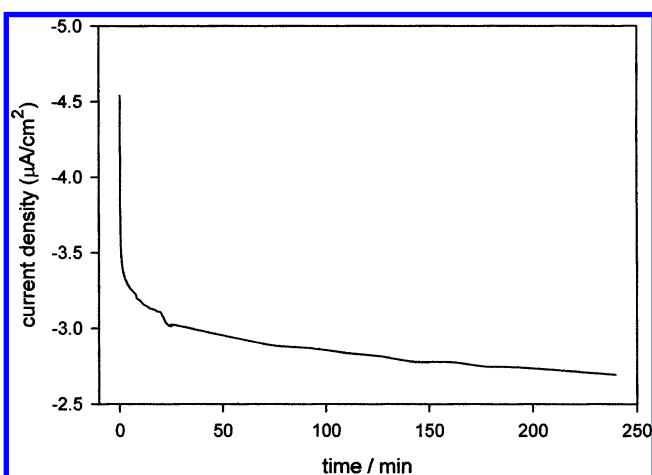


Figure 4. Chronoamperometry of the cell with gel 2 at -10°C .

the deconvolution of the spectrum. Growth of the passivating film on the lithium surface can be deduced from the measured increase of resistance. The results of our measurements are given in Table 3.

Discussion

Conductivity Results. In electrolyte solutions based on a salt dissolved in a liquid (e.g., LiBETI) in EC, PC, EMC and their mixtures, cations and anions are solvated (coordinated to) solvent molecules; e.g., the solvation number of Li^+ in PC is probably 3–4, and for the anion, the solvation number is probably 1 (e.g., see ref 11). When the conductivities for these solutions are studied, it is the mobility of the whole complex (ion + the solvent coordination sphere) that moves under the applied electric field. When the solvent molecules are removed, one is left with a pure salt that, in the liquid state (the “ionic liquid”), is generally more conductive and in which conductivity is based solely on the mobility of ions moving in a viscous environment where there is no solvation sphere. When an ionic salt melts, its volume generally increases by 10–25%, but X-ray

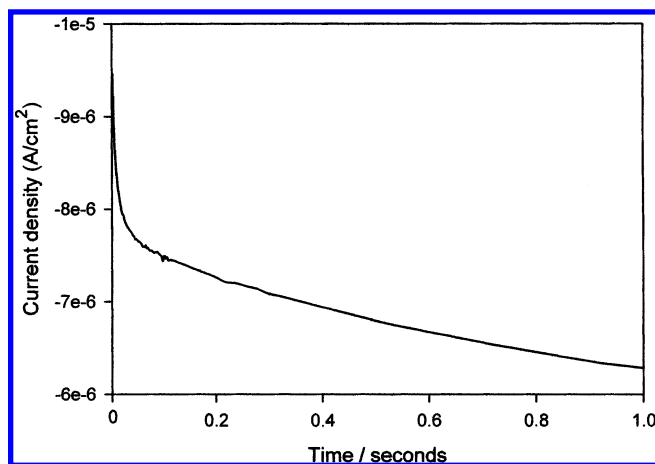


Figure 5. First second of the chronoamperometric curve of the cell with gel 2 at -10°C .

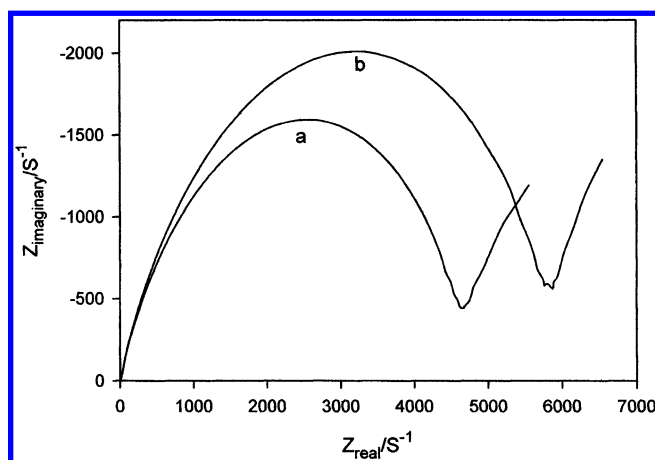


Figure 6. Impedance spectra (from 0.1 Hz to 100 kHz) for gel 2 at -10°C at $t = 0$ (a) and $t = t_s$ (b).

TABLE 3: Transport Numbers for Gels 1 and 2

gel no.	$t/^\circ\text{C}$	T/K	t_+
1	25	298.2	0.41
2	50	323.2	0.66
2	25	298.2	0.47
2	0	273.2	0.38
2	-10	263.2	0.27
2	-20	253.2	0.142

diffraction studies show that the ions in the fused salt are slightly closer to each other than in the solid state.¹² To account for this apparent contradiction of an increase in volume when the inter-ionic distances decrease, it follows that empty volume or “free space” must be introduced into the ionic liquid, and the high mobility of ions in the ionic liquid is due to jumps of ions into vacant sites, i.e., into the free volume. Our results suggest important contributions to the overall conductivity by this free volume effect. The VTF A parameters (eq 4) related to the number of charge carriers are seen to increase significantly as the concentration of EMI–BETI is increased (Table 2) reaching a value of $2.732 \text{ S cm}^{-1}(T/K)^{1/2}$ for the gelled electrolyte 3. Though small additions of 1–5 mass % of the ionic liquid to the baseline gel number 1 slightly improve the conductivities at room temperature and lower the calculated T_0 value, the conductivities of gel 3 are significantly smaller due to the high viscosity of EMI–BETI.

Transport Number Results. The interpretation of transport numbers as a function of temperature is an interesting problem. If ionic mobilities, λ_i° , followed Stokes’ law,

$$\lambda_i \eta = \frac{zeF}{6\pi r_i} \quad (5)$$

the Walden product would be independent of temperature if the ionic radius r_i is constant. However, for aqueous systems where viscosities decrease as the temperature is increased, and assuming r_i is independent of temperature, eq 5 predicts an increase in mobilities. However, for small ions such as K^+ and H_3O^+ the reverse is observed (see below). The temperature dependence of mobilities and transport numbers could also arise from changes in ion solvation (i.e., the ionic radius r_i is not constant), and how this affects the sign of the temperature coefficient of $\delta t_+/\delta T$ is not clear. According to Kay, no quantitative theory exists to relate the temperature dependence of transport numbers.¹³ Because transport numbers are related to mobilities, we sought to determine if the behavior of the gels studied in the present work can be modeled similarly to that used for conductivities, i.e., to a modified Arrhenius equation

$$t_+ = A \exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

or to a modified VTF equation,

$$t_+ T^{1/2} = A \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (7)$$

Figure 7 shows the plot of our transport data as a function of temperature based on the Arrhenius model, and Figure 8 shows the temperature dependence based on the VTF model. Both figures show the small experimental error for the -10°C data point due to the fact that i_0 had not quite reached steady state. On the basis of the excellent fit of the data to eq 7, as shown in Figure 8, we conclude that the transport behavior in our polymer can be described in terms of a free volume model, as we concluded on the basis of our conductivity measurements. When the $t_+(Li^+)$ data for temperatures from -20 to $+50^\circ\text{C}$ were fit to the modified VTF, eq 7 resulted in the following values for the adjustable parameters:

$$A = 18.095(T/K)^{1/2} \quad E_a = 384 \text{ J mol}^{-1} \\ T_0 = 230.9 \text{ K } (-42.3^\circ\text{C})$$

Although the theoretical significance of these adjusted VTF parameters is not resolved at this time, our analysis again confirms that the transport properties of gel 2 are heavily influenced by free volume, as was found from the conductivity measurements. Direct comparison of the VTF parameters for conductivity and for transport is not possible because the former reflects contributions by the two cations Li^+ and EMI^+ whereas the latter VTF parameters for t_+ reflect contributions only by the Li^+ ion. Qualitatively, one can relate the temperature dependence to the mechanism of transport and to solvation effects depending upon the system under study, e.g., polymer vs aqueous. For ionic liquids and many polymer electrolytes, conduction can be related to available free volume,¹⁴ and as the temperature is decreased, the available free volume also decreases, resulting in a decrease in conductivity and transport number, as we observe for the gels studied here. Other than the review by Kay dealing with the effect of temperature on transport numbers for KCl in water¹³ and for silicotungstic acid ($H_4SiO_4 \cdot 12WO_3 \cdot xH_2O$) recently studied by Horky et al.,¹⁵ there are few publications we can cite for comparison to our present results. The cation transport numbers for both K^+ and H_3O^+

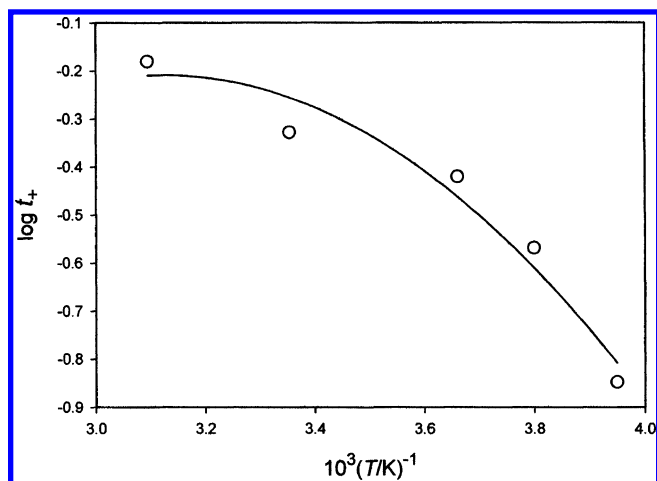


Figure 7. Arrhenius plot for t_+ in gel 2 (eq 6).

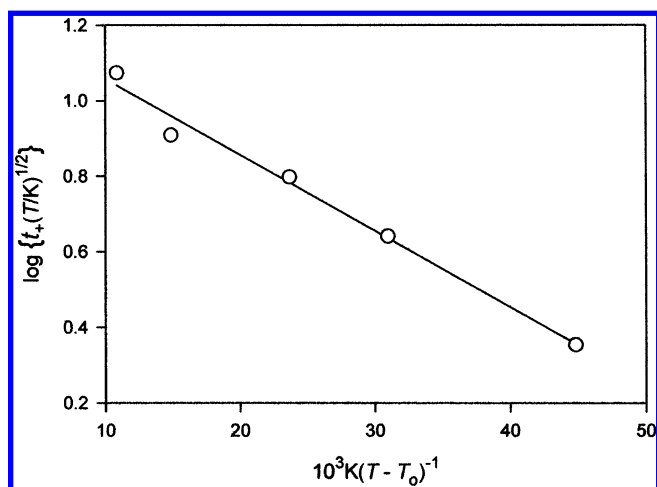


Figure 8. VTF plot for t_+ in gel 2 (eq 7).

were found to decrease as the temperature increases, opposite to the present observation for gelled electrolyte number 2 and opposite to predicted behavior based on the Walden product. Although the observations for t_+ in aqueous solutions are certainly due to solvation effects such as structure-breaking effects on cospheres and electrostriction effects as discussed by Kay, and by change in the conduction mechanism for H_3O^+ (from rapid Grotthus type conduction to a slower hydrodynamic mobility) as discussed by Horky et al., clearly the effect we observed for the gelled polymer electrolytes can be attributed to changes in free volume.

Conclusions

The conductivity and transport number measurements were found to follow VTF equations for ion transport in terms of a free volume model. The results indicating a significant decrease in transport number as the temperature decreases have important implications for the use of gelled polymer electrolytes in Li and Li-ion batteries. It is well-known that the conductivities of gelled polymer electrolytes are generally smaller than their liquid based counterparts and rarely are of practical use for Li-ion cells at temperatures below -20°C (e.g., see ref 2). The fact that we observe $t_+(Li^+)$ decreases from 0.47 at $+25^\circ\text{C}$ to 0.14 at -20°C implies that besides conductivity limitations for gelled electrolytes, Li^+ -ion transport is another significant limitation for use below -20°C in Li and Li-ion batteries.

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