SOLID POLYMER ELECTROLYTES FOR RECHARGEABLE BATTERIES

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by

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EXECUTIVE SUMMARY

Under Subcontract No. 4569110 with Lawrence Berkeley Laboratory, SRI International has synthesized and tested new, dimensionally stable polymer electrolytes for high energy density rechargeable lithium batteries. We have prepared semi-interpenetrating networks of sulfur-substituted polyethyleneoxide with tetraethylorthosilicate (TEOS). The *in situ* hydrolysis of TEOS produces a mechanically stable three-dimensional network that entangles the polymer electrolytes and makes the film dimensionally flexible and stable. With this approach, the best dimensionally stable polymer electrolyte of this type produced so far, has a room temperature lithium ion conductivity of $7.5 \times 10^{-4} \text{ S cm}^{-1}$.

Another type of solid polymer electrolytes, polydiacetylene-based single-ion conductors with high room temperature proton conductivity were also developed. The best conductivity of these polymers is two orders of magnitude higher than that of Nafion® under comparable experimental conditions. With further appropriate chemical modification, the new polymers could be used in fuel cells.

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INTRODUCTION

The objectives of this project under Subcontract No. 4569110 with Lawrence Berkeley Laboratory were to develop new solid polymer electrolytes (SPEs) with improved mechanical properties for use in high-energy-density batteries and to fabricate and evaluate test cells using the most promising polymers.

SRI International is developing advanced ion-conducting polymers that can be used as SPEs in high-energy-density, rechargeable solid state batteries. Batteries of this type, for example, the Li/SPE/TiS₂ or Li/SPE/V₆O₁₃ systems, promise virtually maintenance-free, reliable operation over many thousands or tens of thousands of cycles if certain physico-chemical problems can be overcome. The most important problems are summarized as follows:¹

- (1) Low mobility of Li⁺ in the SPE.
- (2) Difficulty of maintaining intimate contact between the SPE and the lithium negative and the intercalation positive electrodes.
- (3) Occasional growth of lithium dendrite that penetrates the SPE on recharging.
- (4) Low positive electrode usage on rapid charging. This problem is not due to the SPE itself but reflects a limitation of existing intercalation positive electrodes (e.g., TiS₂).
- (5) Poor long-term thermal stability at the temperatures at which SPE batteries may operate (e.g., 80°-100°C).

Research has expanded considerably in the development of solid polymer electrolytes for applications in high-energy-density batteries, specific ion sensors, and electronic displays. Wright and coworkers^{2,3} originally observed the ionic conductivity of complexes of alkali metal salts with poly(ethylene oxide). Armand and coworkers⁴⁻⁶ developed a detailed understanding of the ionic conductivity of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) salt complexes and proposed their use as solid polymer electrolytes in high-energy-density batteries. For the PEO-salt complexes, it has been suggested that the alkali metal cations reside in the helical tunnel of PEO, which is in a (T₂GT₂G) conformation. This structure is similar to the complexes between Li⁺, Na⁺, K⁺, and crown ethers. However, PEO and PPO complexes exhibit ionic conductivities suitably high for high-density, rechargeable battery applications only above 100°C. In the past few years polymer electrolytes that have better ionic conductivity than PEO at room temperature, such

as polyphosphazene-based ionic conductors have been developed.⁷ However, their ionic conductivities are still too low to meet the power density requirements ($>100 \text{ W kg}^{-1}$ sustained power) for high-density, rechargeable battery applications, and these electrolytes do not provide flexible, dimensionally stable films, as needed for application in batteries.

Two factors are critical for enhancing the transport of ions in polymer electrolytes: (1) polymers with a liquid-like character, and (2) sites in the polymer that loosely bind with the ion to permit diffusion. For example, having "floppy" polyether pendant groups on the polyphosphazene elastomer greatly reduces the glass transition temperature (T_g) of the polymer,⁷ with the result that when this polymer is complexed with salts, it shows substantially higher room temperature conductivity than the corresponding PEO complexes. However, the ionic conductance exhibited by the polyphosphazene electrolyte at room temperature is still too low for application in batteries. In addition, the polyphosphazene/lithium salt complex does not provide flexible, pinhole-free films.

The interaction between the alkali metal ion and the ether oxygen in the polymer complexes is a strong hard-acid/hard-base interaction as defined by the hard/soft-acid/base (HSAB) principle.⁹ The activation energy necessary for "hopping" between sites can be lowered by replacing the hard base (oxygen) with a soft base like sulfur.^{10,11} Additionally, the conductance of the polymer complexes can be enhanced by organizing the pendant basic sites so that the "hopping" is stereochemically unhindered. Using these principles, SRI International has synthesized dimensionally stable novel polymer electrolytes with enhanced room temperature lithium ion conductivity. The best performing polymer electrolyte, a semi-IPN of sulfur substituted polyethylene oxide (16.7% sulfur substitution) with tetraethylorthosilicate showed a conductivity of $7.5 \times 10^{-4} \text{ Scm}^{-1}$ when tested in a Li/Li cell.

Additionally, partially fluorinated polymer electrolytes with unique transport properties for protons have been synthesized. The best performing polymer showed a room temperature proton conductivity two orders of magnitude higher than that of Nafion® when the two polymers were tested under the same conditions.

RESULTS AND DISCUSSION

DIMENSIONALLY STABLE SULFUR-SUBSTITUTED POLY(ETHYLENE OXIDE) AND MEEP CONDUCTORS

Polymer electrolyte films with high dimensional stability and good ionic conductivity were prepared by adding tetraethylorthosilicate (TEOS) to a lithium complex of 16.7% sulfur-containing poly(ethyleneoxide) (PTE_{16.7}) in the presence of a catalytic amount of acid. The sulfur-containing poly(ethyleneoxide), lithium triflate (LiTf), TEOS, and a catalytic amount of acid were dissolved in tetrahydrofuran, and gelation of TEOS was carried out by heating the solution at 70°C for two hours. Films of the polymer salt complexes were thoroughly dried, and their conductivities were measured. Some of the films were plasticized by adding propylene carbonate (PC). Table 1 shows the lithium ion conductivities at room temperature for variable amounts of TEOS and PC. A lithium ion conductivity (σ) of $1.1 \times 10^{-4} \text{ S cm}^{-1}$ was measured for the polymer electrolyte film TEOS/PTE_{16.7}-LiTf/PC (relative molar ratios = 1:2:4). *In situ* hydrolysis of TEOS produces a mechanically stable three-dimensional network that entangles the polymer electrolytes and makes the film dimensionally flexible and stable. Moreover, the addition of PC does not affect the mechanical stability of the film. In the absence of TEOS, the polymer films had a tendency to flow.

The mechanical stability of MEEP electrolyte films was similarly improved by addition and *in situ* hydrolysis of TEOS (Table 2). MEEP₁₆/LiTf films without TEOS have poor dimensional stability and a high tendency to flow. Their conductivity at room temperature is $4.41 \times 10^{-6} \text{ S cm}^{-1}$ in the presence of PC (MEEP/PC 1:2 by weight), but without any plasticizer, the films show conductivities lower than $10^{-7} \text{ S cm}^{-1}$. By optimizing the amount of TEOS, we were able to prepare polymer electrolyte films with high ionic conductivity of $7.60 \times 10^{-4} \text{ S cm}^{-1}$. Increasing the TEOS content resulted in more rigid films with lower conductivity. The MEEP/TEOS films, however, showed partial phase separation and their mechanical properties were not as good as those of the PTE_{16.7}/TEOS films. The partial phase separation indicates incomplete formation of the semi-IPN under these experimental conditions.

Because the silicate network in these films is formed in the presence of a second polymer (i.e., the polymer electrolyte), we have indeed made a semi-interpenetrating network (semi-IPN). Interpenetrating polymerization is unique because it represents a mode of blending two or more

Table 1

LITHIUM ION CONDUCTIVITY OF 16.7% SULFUR SUBSTITUTED
POLY(ETHYLENEOXIDE) LITHIUM TRIFLATE COMPLEXES
WITH IMPROVED MECHANICAL PROPERTIES*

Additions to the PEO/LITF Complex		Ionic Conductivity at RT (S cm ⁻¹)
TEOS (mol/mol polymer)	PC Plasticizer (wt/wt polymer + TEOS)	
0	0	4.9 x 10 ⁻⁶
0	2	1.3 x 10 ⁻³
1	0	1.3 x 10 ⁻⁷
1	2	9.2 x 10 ⁻⁵
0.5	0	1.1 x 10 ⁻⁶
0.5	2	1.1 x 10 ⁻⁴

*In all the experiments, the lithium ions were 1/16 (mol/mol) of the sum of ether oxygen and sulfur in the polymer.

Table 2

LITHIUM ION CONDUCTIVITY MEEP LITHIUM COMPLEXES
WITH IMPROVED MECHANICAL PROPERTIES

Composition				Ion Conductivity at RT after PC plasticizer (1:2 by wt) added (S cm ⁻¹)*
MEEP (mg)	LiTf (mg)	Ether Oxygen/Li ⁺	TEOS ^a (mL)	
150	37.5	8	0.018	1.46 x 10 ⁻³
300	75.0	8	0.14	4.39 x 10 ⁻⁴
300	75.0	8	0.07	5.49 x 10 ⁻⁴
450	56.0	16	0.21	7.60 x 10 ⁻⁴
300	37.5	16	0.42	4.55 x 10 ⁻⁷
300	37.5	16	0.28	1.76 x 10 ⁻⁶

*MEEP complex with LiTf (16 ether oxygen/Li ion) but no TEOS exhibited a conductivity of 4.41 x 10⁻⁶ S cm⁻¹ at RT. In the absence of PC as plasticizer, all the films showed conductivity << 10⁻⁷ S cm⁻¹ at RT.

polymers to produce a mixture in which phase separation is not as extensive as it would be otherwise. In this regard, semi-IPNs are more advantageous than normal blends, in which sometimes multiphase morphology can be present. Because no phase separation takes place in semi-IPNs, we expect these polymer electrolytes to have longer life time and better performance than polymer electrolytes prepared from blends. Moreover, with semi-IPNs, the electrolyte film flexibility and mechanical strength as well as the electrical characteristics can be controlled by proper selection of the polymer components and their relative ratio.

PHOSPHAZENE-BASED SINGLE-ION CONDUCTORS

Phosphazene-based polyelectrolytes are prepared by nucleophilic displacement of chlorine atoms from linear poly(dichlorophosphazene) by reaction with alkoxides containing perfluorosulfonate groups ($\text{OC}_2\text{H}_4\text{C}_2\text{F}_4\text{SO}_3\text{M}$, $\text{M} = \text{Li}$ or Na) and alkoxides of monomethylether ethyleneglycol oligomers. Table 3 shows the electrical response of these phosphazene-based electrolytes functionalized with variable amounts of PC added. In general, the sodium ion conductivity is higher than the lithium ion conductivity.

The conductivities of this new class of phosphazene-based single-ion conductors are comparable with those of phosphazene-based polyelectrolytes functionalized by $\text{OCH}_2\text{CF}_2\text{SO}_3\text{Li}$, as we previously reported.

SILOXANE-BASED SINGLE-ION CONDUCTORS

The electrical response of siloxane-based polyelectrolytes with variable amounts of PC added is shown in Table 4. The highest lithium conductivity, $5.27 \times 10^{-5} \text{ S cm}^{-1}$, was measured for a polymer electrolyte film containing 50% (wt/wt) PC. Accordingly, siloxane-based single-ion conductors appear to perform better than the phosphazene-based analogs.

POLYDIACETYLENE-BASED PROTON CONDUCTORS

We have synthesized sulfonated polydiacetylenes that show proton conductivity two orders of magnitude higher than that of Nafion, when tested under the same experimental conditions (Table 5). Both partially fluorinated and nonfluorinated sulfonate polydiacetylene-based

Table 3 ELECTRICAL RESPONSE OF $\left[\text{NP(OR)}_x (\text{OC}_2\text{H}_4\text{OC}_2\text{F}_4\text{SO}_3\text{M})_{1-x} \right]_n$		
Polyelectrolyte/PC Plasticizer (wt/wt)	Ion Conductivity at RT (S cm^{-1})	
	Na ⁺	Li ⁺
1:0	$< 10^{-7}$	$< 10^{-7}$
1:3	4.53×10^{-5}	8.50×10^{-6}
1:6	6.67×10^{-5}	1.08×10^{-5}
1:9	4.59×10^{-5}	1.33×10^{-5}
1:13	-	1.11×10^{-5}

*R = (C₂H₄O)_{7.23}CH₃; x = ~1.74.

Table 4
IONIC CONDUCTIVITY OF

PC Plasticizer (wt/wt%)	Lithium Ion Conductivity at RT (S cm ⁻¹)
0	4.14×10^{-7}
0.5	5.27×10^{-5}
1.0	5.05×10^{-5}
2.0	5.52×10^{-6}

electrolytes were prepared and their conductivities tested with varying humidities (Tables 5 and 6), respectively.

Diacetylene monomers carrying a sulfonic group were synthesized and then polymerized by topochemical thermal polymerization in the form of thin films or pellets. The structure of the monomers is as follows:

(Nonfluorinated)

(Partially Fluorinated)

Monomer (1) was prepared by base-catalyzed ring-opening reaction of 1,3-propane sultone with 2,4-hexadiyn-1,6-diol, followed by conversion to the monomer H^+ form through ion-exchange chromatography. The monomer synthesis is shown as follows.

The partially fluorinated monomer (2) was synthesized by reaction of 2,4-hexadiyn-1,6-bis(tosylate) with 2-fluorosulfonyl perfluoroethoxide, which was prepared *in situ* by ring-opening of tetrafluoroethane- β -sultone with potassium fluoride.

The polymer conductivity increases with exposure of the films to increasing humidity (Tables 5 and 6). This increased conductivity is likely due to shielding of the protons by the water molecules from the oppositely charged polymer backbone.

ELECTROCHEMICAL STUDIES

Electrochemical impedance spectroscopy was used to characterize the discharge/charge cycle behavior of two Li cells. The first cell contained a polymer electrolyte consisting of a semi-IPN of PTE_{16.7} with TEOS, and propylene carbonate (PC) as plasticizer. For convenience, lithium foil was used for both the anode and cathode. The electrolyte was 0.406 mm thick and 0.5 cm² in area. The second cell contained only PC as electrolyte. This cell used a Li anode and a

Table 5
PROTON CONDUCTIVITY OF
NAFION AND SRI's POLYELECTROLYTE PREPARED FROM
 $\text{HO}_3\text{S}-\text{CF}_2\text{CF}_2\text{OCH}_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$

Testing Conditions*	H ⁺ Conductivity at RT (S cm ⁻¹)	
	Nafion	Polydiacetylene-based Polyelectrolyte
Dry sample, tested in air	1.9 x 10 ⁻⁷	1.9 x 10 ⁻⁷
Sample exposed to moisture	2.1 x 10 ⁻⁴	1.3 x 10 ⁻²

*Polymer films were tested.

Table 6
PROTON CONDUCTIVITY OF SRI's POLYELECTROLYTE PREPARED FROM
 $\text{HO}_3\text{S}-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$
UNDER VARIABLE HUMIDITY

Testing Conditions*	H ⁺ Conductivity at RT (S cm ⁻¹)
Dry sample tested in air	6.5 x 10 ⁻⁶
Sample exposed to 50% RH	1.4 x 10 ⁻⁵
Sample exposed to 90% RH	6.9 x 10 ⁻⁴
Sample exposed to 98% RH	1.1 x 10 ⁻³

*Polymer pellets were tested. RH = Relative humidity.

TiS₂ cathode. The electrolyte was 1.42 mm thick and 0.5 cm² in area. Both cells were galvanostatically discharged at current densities from 20 to 30 $\mu\text{A cm}^{-2}$, usually for four hours and then recharged at the same current density. The impedance of the cell was measured over the range 1 mHz to 1 MHz using a Solartron 1255 Frequency Response Analyzer. Data were obtained periodically during each discharge over 10 charge/discharge cycles.

The impedance data are presented here in the form of complex plane (often referred to as Nyquist) plots. Figure 1 shows the variation in the impedance of the PTE_{16.7} cell with respect to the degree of discharge of the cell. The impedance locus in the complex plane typically exhibited two semicircles at all degrees of discharge. The major semicircle spanned the high frequency region from about 20 kHz down to 2 Hz, while the minor semicircle appeared at frequencies below about 2 Hz. It is apparent that the radius of the major semicircle decreases with degree of discharge. A corresponding decrease in the low frequency intercept of the impedance locus with the real axis results from this change. The radius of the minor semicircle and the frequency distribution around both semicircles are independent of the degree of discharge of the cell.

Figure 2 shows the effect of cycling on the impedance of the Li/PTE_{16.7}, TEOS, PC/Li cell for a constant depth of discharge (approximately 50%, or 20 μAh). The impedance locus typically exhibited the two semicircles seen in Figure 1. The radius of the major semicircle decreased during the first three cycles but increased during later cycles. The radius of the minor semicircle and the frequency distribution around both semicircles appear to be independent of the cycle number.

The impedance of the Li/PC/TiS₂ cell at various degrees of discharge during the first discharge is shown in Figure 3. In this case, the impedance locus follows a distorted semicircle from approximately 20 kHz down to about 2 Hz. The distortion at high frequency probably indicates the presence of a second capacitive-type feature; this is particularly so in the case of the spectrum for 55 μAh . At lower frequencies the data were affected by scatter due to noise, and no useful results could be obtained below 2 Hz. The radius of the semicircle decreased from its initial value of 1500 Ω to 1000 Ω at 40 μAh , then increased to 1750 Ω at the end of the discharge. The high frequency intercept remained effectively constant at 250 Ω throughout the entire discharge.

The data from the PTE_{16.7} cell were deconvoluted in terms of both the impedance and admittance, and it became evident that the major semicircle was in fact *two* semicircles, which (as discussed below), we believe are related to the charge transfer processes at the two electrodes. The third (low frequency) semicircle is probably associated with the cathode during discharge.

Figure 1. Change of impedance of Li-PTE-Li cell with degree of discharge.
(Second discharge; $i_{dc} = 20 \mu A \text{ cm}^{-2}$; $\Delta i_{ac} = 0.4 \mu A \text{ cm}^{-2}$).

Figure 2. Change of impedance of Li-PTE-Li cell with cycle number at constant degree of discharge ($20\ \mu\text{Ah}$). ($i_{dc} = 20\ \text{mA cm}^{-2}$; $\Delta i_{ac} = 0.4\ \mu\text{A cm}^{-2}$).

Figure 3. Change of impedance of Li-PC-TiS₂ cell during initial discharge.
($i_{dc} = 30 \mu A cm^{-2}$; $\Delta i_{ac} = 0.4 \mu A cm^{-2}$).

The high frequency intercept obtained in the complex plane at ~45 kHz provides the resistance of the polymer electrolyte. The value of the intercept is about 86 Ω , irrespective of the degree of discharge of the cell or the cycle number. From this intercept, we calculate a conductivity of $7.5 \times 10^{-4} \text{ S cm}^{-1}$, which is consistent with the results of the conductivity measurements performed earlier in this study.

Since three semicircles appeared to be present, the impedance data were analyzed in terms of an equivalent circuit model in which three impedances are in series, with each impedance consisting of a resistance and a capacitance in parallel. The capacitance in two cases (C_1 and C_2) was about $0.2 \mu\text{F cm}^{-2}$, while the resistances, R_1 and R_2 , were about 1000 and 4500 Ω for the initial cycle. These two R-C pairs in combination give rise to the major semicircle in the impedance spectra above. During discharge and in subsequent cycles, C_1 , C_2 , and R_1 remained effectively constant. However, R_2 decreased by about 700 Ω during discharge and by a similar amount during the first three cycles for a given degree of discharge. During subsequent cycles, R_2 was larger at a given degree of discharge.

C_1 and C_2 are considered to be associated with the Li-polymer double layer since (1) their values are close and (2) double layer capacities are typically on the order of microfarads per square centimeter. Accordingly, R_1 and R_2 are thought to correspond to charge transfer for Li oxidation and reduction, respectively; the higher resistance is linked with Li reduction because it is viewed as the slower reaction. Hence, the lack of change in R_1 and C_1 with discharge and cycling indicates that the lithium did not react with the electrolyte to form a passivating film under the test conditions; if a passivating film is present, it must form rapidly after the lithium makes contact with the electrolyte.

The changes in the impedance spectra with respect to degree of discharge and cycle number seem to be largely due to the resistance R_2 . This finding suggests that the resistance associated with Li reduction decreases as the cell is discharged, possibly because of a higher surface area and therefore a more intimate contact between the electrode and the electrolyte. On this basis, the increase in R_2 during later cycles implies that the contact area decreases, which in turn suggests partial separation of the solid electrolyte from the lithium foil.

The origin of the third capacitance, C_3 , is uncertain. Its value of 5 mF cm^{-2} is far higher than expected for a double layer and is more in line with an adsorption pseudocapacitance. Thus, we have tentatively proposed that C_3 is associated with adsorption of reduced Li ions. On this

basis, the corresponding resistance, R_3 , which has a value of $800\ \Omega$, is presumably related to the removal of adsorbed lithium, for example, by surface diffusion from deposition sites to other sites.

CONCLUSIONS

We have fabricated polymer electrolyte films with appropriate mechanical properties for their utilization in rechargeable lithium batteries, as well as other electrochemical devices. The mechanical properties of the polymer electrolytes have been improved by preparing semi-IPNs of sulfur-substituted polyethyleneoxide with tetraethylorthosilicate. The resulting polymer electrolyte film is dimensionally stable and flexible, and plasticizers can be added to it.

The electrochemical performance of the Li anode/PTE_{16,7}, TEOS polymer interface during discharge appears to be independent of both depth of discharge and cycle number. Thus, no progressive formation of a passivating film on the lithium surface was observed during the test; however, it is possible that a passivating film is formed rapidly after the lithium is brought into contact with the electrolyte.

Novel partially fluorinated polymers with enhanced room temperature proton conductivity in comparison with Nafion® have also been synthesized. These novel polymers open new avenues for the development of polymer electrolyte fuel cells.

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