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November 1990

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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LBL-29829

SOLID POLYMER ELECTROLYTES FOR RECHARGEABLE BATTERIES

Final Report

November 1990

by

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This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Deputy Assistant Secretary for Utility Technologies, Office of Energy Management, Advanced Utility Concepts Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4557010 with the Lawrence Berkeley Laboratory.

EXECUTIVE SUMMARY

SRI International has synthesized novel solid polymer electrolytes for high energy density, rechargeable lithium batteries. We have systematically replaced the oxygens in PEO with sulfur to reduce the strong hard-acid hard-base interaction, while retaining the favorable helical conformation of the polymer backbone. The best polymer electrolyte produced so far is suitable for a medium power battery.

In another effort, we have synthesized single ion conducting polymer electrolytes based on polyethyleneimine, polyphosphazene, and polysiloxane backbones. The single ion conducting polymer electrolytes will allow greater depth of charge and discharge by preventing dc polarization. The best conductivity so far with single ion conductors is 1.0×10^{-3} Scm^{-1} at room temperature. Further optimization of electrical and mechanical properties will allow the use of these polymer electrolytes in the fabrication of rechargeable lithium batteries.

SRI International is developing advanced ion-conducting polymers that can be used as solid polymer electrolytes (SPEs) in high energy density, rechargeable solid state batteries. Batteries of this type, for example, the Li/SPE/TiS_2 or Li/SPE/V_6O_{13} 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) Low mobility of Li^+ in the SPE.

(2) Difficulty of maintaining intimate contact between the SPE and the lithium negative and TiS_2 intercalation positive electrodes.

(3) Occasional growth of a 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., TiS_2).

(5) 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 originally observed the ionic conductivity of complexes of alkali metal salts with poly(ethylene oxide). Armand and coworkers 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 (T_2GT_2G) conformation. This structure is similar to the complexes between Li^+, Na^+, K^+, and crown ethers. However, PEO and PPO complexes exhibit suitably high ionic conductivities only above 100°C. Recently, Blonsky et al. synthesized poly(phosphazene)-based ionic conductors that show good ionic conductivity at room temperature. However, the ionic conductivites are still too low to meet the power density requirements (>100 W kg^{-1} sustained power) for high density, rechargeable battery applications.

Because SPEs, such as those based on poly(ethylene oxide) and polyphosphazene, are flexible, maintenance of intimate contact with the solid anode and cathode is less of a problem than with rigid solid electrolytes (e.g., Li-conducting glasses). However, the extent to which contact can be maintained depends on the membrane thickness and the dimensional changes that occur in both the negative (Li) and positive (e.g., TiS_2, V_6O_{13}) electrodes on charging and discharging.

These problems would be greatly alleviated if it were possible to use relatively thick (>500 μm) SPE films rather than films of <100 μm as currently used. The thin films now in use are dictated by the low lithium ion conductivities of existing SPEs. Therefore, the principal goal in developing SPE batteries should be to increase the cation conductivity. This can be done only by synthesizing and evaluating new polymer systems having the necessary structural properties to ensure high and stable cation (Li^+) conductivities under the conditions of interest.

Two factors are critical to the transport of ions in polymer electrolytes: (1) liquid-like character of the polymer and (2) sites in the polymer that loosely bind with the ion to permit diffusion. Thus, having "floppy" polyether pendant groups on the polyphosphazene elastomer greatly reduces the glass transition temperature (T_g) of the polymer. Consequently, when complexed with salts, this polymer 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. The activation energy necessary for "hopping" between sites can be lowered by replacing the hard base (oxygen) with a soft base like sulfur. Additionally, the conductance of the polymer complexes can be enhanced by organizing the pendant basic sites so that the "hopping" is stereochemically unhindered.

We have synthesized and characterized several sulfur-containing polymers, $[(C_2H_4S)(C_2H_4O)_x]_n$ (x = 4, 5, 7, 9, 11, and 13), with sulfur content from 7% to 20%. Polymer salt complexes have been prepared with lithium trifluoromethane sulfonate in tetrahydrofuran (THF). Films of these complexes have been prepared by evaporating the solvent slowly and drying the film thoroughly. Ionic conductivities of these films were measured, as shown in Table 1. As the sulfur content in the polymer decreases from 20% to 10%, the conductivity increases to a value of 7×10^{-6} S cm^{-1} at ambient temperature. Further decrease of sulfur content drastically reduces the conductivity. This observation indicates that the polymer electrolyte having 10% sulfur content may have the ideal structure for the transport of ions in the polymer matrix in these new class of polymers.

When the above films were exposed to MeCN vapor, the conductivity increased to the order of 10^{-3} S cm^{-1} (Figure 1). Conductivity with the same order of magnitude was observed

Table 1

ELECTRICAL RESPONSE OF $LiCF_3SO_3$ COMPLEX OF $[(C_2H_4S)(C_2H_4O)_x]_n$

x	%S	Ratio of ether O+S to Li^+ ion	σ at RT(S cm^{-1})	σ after exposure to MeCN (S cm^{-1})
4	20.0	16	4.0×10^{-6}	
		8	1.6×10^{-7}	
5	16.7	16	4.9×10^{-6}	1.1×10^{-3}
7	12.5	16	1.5×10^{-6}	2.1×10^{-3}
9	10.0	16	7.0×10^{-6}	1.7×10^{-3}
11	8.3	16	2.3×10^{-6} /40°C	1.7×10^{-3}
13	7.1	16	3.3×10^{-8} /40°C	4.5×10^{-4}
		Oxidized form of S		
4	20.0	16	1.4×10^{-7}	
9	10.0	16	5.0×10^{-7}	1.2×10^{-5}

when the films were treated with propylene carbonate (PC). Two of the above polymers were oxidized to the corresponding sulfones with m-chloro-peroxybenzoic acid. Upon oxidation, the conductivity is lowered by an order of magnitude as shown in Table 1. Even after exposure to MeCN vapors, the conductivity increases to only 10^{-5} S cm^{-1}.

We decided to synthesize new higher molecular weight, low vapor pressure plasticizers that can be compatible with the polymer backbone and can provide high ionic conductivity.

The plasticization of sulfur-containing polymer salt complexes and poly (ethylene oxide) salt complexes has been carried out with new plasticizers $Me(OC_2H_4)_m$ CN (m = 2 and 8.23) and PC. These results are shown in Tables 2 through 4. As the amount of $Me(OC_2H_4)_2$ CN increases, the conductivity increased to a value of 3.8×10^{-4} S cm^{-1}. Further addition of $Me(OC_2H_4)_2$ CN decreases the conductivity. The salt content may become very dilute under these conditions. In general, as the molecular weight of the nitrile increases, the conductivity decreases as can be seen for the poly (ethylene oxide) system as shown in Table 3.

Upon treatment with either MeCN or PC, the polymer electrolytes give liquid-like electrolytes. To improve the mechanical stability, poly(arylonitrile) (PAN) was added and ionic conductivity was measured. The results are shown in Tables 5 and 6. Addition of PAN greatly improves the mechanical stability with little loss of conductivity.

We have also prepared a sulfur-containing polymer (10.8%) from poly (epichlorohydrin) (PECH) in which the hetero atom sulfur is introduced into the side chain having ethylene oxide repeating units as shown in Scheme I. PECH was treated with $Me(OC_2H_4)_{7.23}$ SH in the presence of Me_4N^+ OH^+ in boiling NMP. The resulting polymer was purified by dialysis against deionized water. Ionic conductivity of $LiCF_3SO_3$ complex was found to be 6.7×10^{-6} S cm^{-1}. This value is comparable to that of poly (ethylene oxide) containing 10% sulfur content as discussed above. After exposure to MeCN vapors, the conductivity increases to a value of 5.9×10^{-4} S cm^{-1}. This polymer was also oxidized to the corresponding sulfone with m-chloroperoxybenzoic acid. As expected, the conductivity of this sulfone was lowered to a value of 1.4×10^{-7} S cm^{-1}. Surprisingly, when this polymer salt complex was exposed to MeCN vapors, the conductivity increased to the order of 10^{-3} S cm^{-1}, but on treatment with PC, the highest conductivity was found to be 1.7×10^{-4} scm^{-1}. Although PECH reacts with thiols, no reaction occurs with alcohols. The reaction of PECH with $Me(OC_2H_4)_{7.23}$ SH gives soluble polymer, whereas the same reaction with $Me(OC_2H_4)_3$ SH gives only insoluble polymer under identical experimental conditions.

Table 2

EFFECT OF $Me(OC_2H_4)_2CN$ ON 16.7% SULFUR POLYMER SALT COMPLEX WITH $LiCF_3SO_3$

Amount of $Me(OC_2H_4)$ CN (mg)	Ratio of Ether O + S to Li^+ Ion	σ at RT (S cm^{-1})
37.8	21.3	3.1 x 10-5
48.7	22.8	9.4 x 10-5
107.3	31.0	1.7×10^{-4}
135.8	35.0	2.1×10^{-4}
184.0	41.8	2.1×10^{-4}
233.9	48.8	3.8×10^{-4}
288.8	56.4	1.1×10^{-4}
536.1	91.0	4.4×10^{-5}

Table 3

PLASTICIZATION EFFECT ON THE POLYMER SALT COMPLEX $[(C_2H_4O)_{16}\ (LiCF_3SO_3)]_n$

Plasticizer	Amount of Plasticizer (mg)	Ratio of Ether Oxygen to Li^+ Ion	σ at RT (S cm^{-1})
Me(OC2H4)2CN	66.8	25.0	2.7×10^{-5}
	100.5	29.4	1.5×10^{-4}
	128.3	33.0	1.4×10^{-4}
$Me(OC_2H_4)_{8.23}CN$	72.7	28.8	2.4×10^{-5}
	99.3	33.4	2.1×10^{-5}
	154.5	40.2	2.7×10^{-5}
	199.6	51.0	2.6×10^{-5}
	275.1	64.3	2.1×10^{-5}

Table 4

PLASTICIZATION EFFECT OF PC ON THE SALT COMPLEX
$[(C_2H_4O)_{16}\ (LiCF_3SO_3)]_n$ (100 mg)

Amount of PC (mg)	σ at RT (S cm^{-1})
34.5	1.1×10^{-4}
48.9	1.8×10^{-4}
65.2	3.2×10^{-4}
107.1	7.3×10^{-4}
166.3	9.2×10^{-4}

Table 5

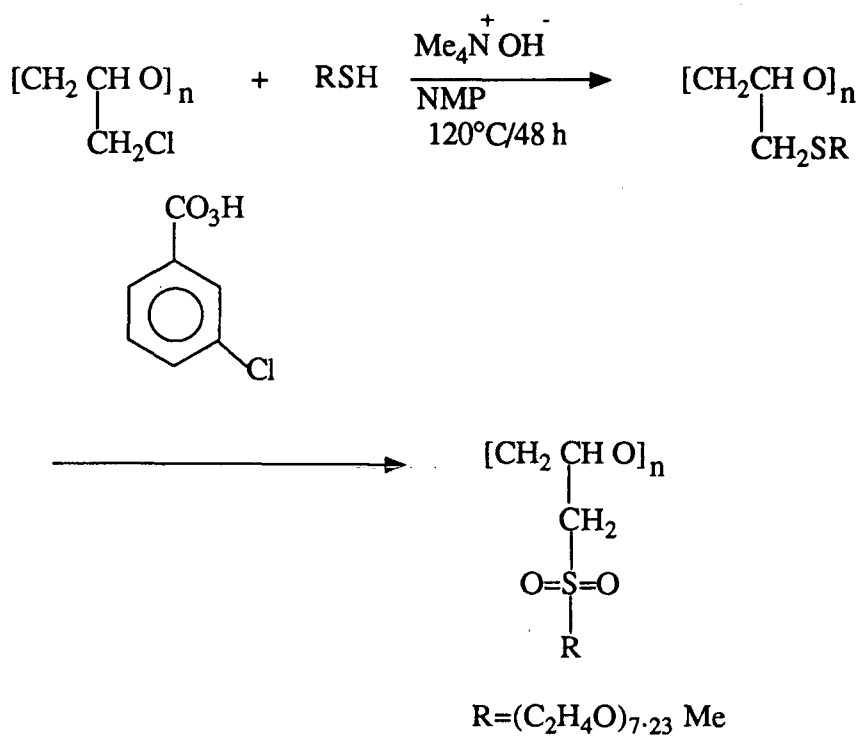
EFFECT OF PAN AS STIFFNER ON 100 mg OF POLYMER SALT COMPLEX $[\{(C_2H_4S)\ (C_2H_4O)_5\}_{16/6}\ (LiCF_3SO_3)]_n$ CONTAINING PC

Amount of PAN (mg)	σ at RT (S cm^{-1})
0	1.0×10^{-3}
46	4.3×10^{-4}
70	2.2×10^{-4}

Table 6

EFFECT OF PAN AS STIFFNER ON 100 mg OF THE POLYMER SALT COMPLEX $[(C_2H_4O)_{16}\ LiCF_3SO_3]_n$ CONTAINING PC

Amount of PAN (mg)	σ at RT (S cm^{-1})
0	3.1×10^{-4}
50	5.7×10^{-4}
60	6.7×10^{-4}
85	2.4×10^{-4}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+
RSH
Me4N+ OH-
NMP
120°C/48 h
[CH2CH O]n
CH2SR
CO3H
Cl
[CH2 CH O]n
CH2
O=S=O
R
R=(C2H4O)7.23 Me

Scheme I

High conductivity was achieved with salt complexes of sulfur-containing polymers. Since these electrolytes are bi-ionic conductors, their ionic conductivity decreases with continued charge and discharge. This problem is attributed to concentration polarization. To avoid dc polarization, we have prepared single-ion conducting polymers with ethyleneimine, phosphazene, and siloxane repeating units in which the mobile ion is either Na^+ or Li^+ ion. Accordingly, the anion is covalently attached to the polymer backbone so that the ion transport is limited to the alkali metal ion. The synthesis strategy adopted to prepare these new polymers and their electrical conductivity are discussed below.

ETHYLENEIMINE-BASED POLYELECTROLYTES

These polyelectrolytes were prepared by side chain modification of polyethyleneimine.

$$[(C_2H_4\underset{\substack{|\\ COR}}{N})_x \quad (C_2H_4\underset{\substack{|\\ R'CF_2SO_2F}}{N})_{i-x}]_n$$

The ionic conductivity of these new polyelectrolytes is poor, but upon exposure to MeCN vapors or by the addition of plasticizers like $Me(OC_2H_4)_mCN$ (m = 2,3, and 7.23) and PC, the conductivity increases on the order of 10^{-5} S cm^{-1} at ambient temperature.

PHOSPHAZENE-BASED POLYELECTROLYTES

Phosphazene-based polyelectrolytes are prepared by the nucleophilic displacement of chlorine atoms from linear poly (dichlorophosphazene) by reaction with alkoxides containing perfluorosulfonate groups.

The electrical response of these new polyelectrolytes is shown in Table 7. In general, Na^+ ion conductivity is higher than the Li^+ ion conductivity.

Table 7

ELECTRICAL RESPONSE OF $[NP(ORCF_2SO_3^-M^+)_x \{(OC_2H_4)_{7.23}OMe\}_{2-x}]_n$

x	M	σ at RT (S cm^{-1})	σ at RT After Exposure to MeCN (S cm^{-1})
0.05	Na	Too low	1.6×10^{-5}
0.10	Na	3.9×10^{-8}	8.7×10^{-5}
0.20	Na	3.2×10^{-7}	2.7×10^{-5}
0.05	Li	5.0×10^{-8}	7.6×10^{-6}
0.10	Li	8.2×10^{-8}	2.2×10^{-5}
0.20	Li	Too low	1.8×10^{-5}

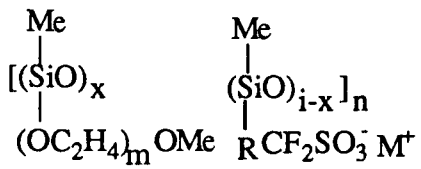
SILOXANE-BASED POLYELECTROLYTES

Siloxane-based new polyelectrolytes containing perfluorosulfonate groups were prepared.

The electrical response of these polyelectrolytes is shown in Table 8. As can be seen, the conductivity of these polyelectrolytes is much higher than for ethyleneimine- or phosphazene-based polyelectrolytes. This observation reflects the separation of ion-pairs in the polymer aggregate having $-COCF_2SO_3^-$ groups in the siloxane polymers compared with that of $-CH_2CF_2SO_3^-$ groups in the case of ethyleneimine- or phosphazene-based polymers.

Table 8

ELECTRICAL RESPONSE OF



m	M	Ratio of Ether Oxygen to M^+ Ion	σ at RT (Scm^{-1})	σ at RT After Exposure to MeCN ($S\ cm^{-1}$)
3	Na	8	$<10^{-8}$	7.3×10^{-6}
		24	3.7×10^{-8}	1.0×10^{-3}
		48	3.6×10^{-8}	5.4×10^{-5}
3	Li	24	1.1×10^{-6}	5.5×10^{-4}
		48	8.9×10^{-7}	1.8×10^{-4}
7.23	Li	41	5.1×10^{-7}	
		89	1.4×10^{-6}	2.2×10^{-5}*

*After treatment with an equal amount of PC.

In conclusion, we have achieved the highest known conductivity for a single ion conductor. Further incremental improvement in conductivity and mechanical properties should allow us to use these single ion conductors in rechargeable lithium batteries in the near future.

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