

POLYMER ELECTROLYTES FOR A RECHARGEABLE LI-ION BATTERY

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Abstract

Lithium-ion polymer electrolyte battery technology is very attractive for many consumer and military applications. A $\text{Li}_x\text{C}/\text{Li}_y\text{Mn}_2\text{O}_4$ battery system incorporating a polymer electrolyte separator based upon novel Li-imide salts is being developed under the sponsorship of US Army Research Laboratory, Fort Monmouth, NJ. This paper reports on the work currently in progress in this program on (i) the synthesis of the Li-imide salts, (ii) polymer electrolyte films incorporating these novel lithium salts, (iii) development of electrodes and cells. A number of Li-salts have been synthesized and characterized. These salts appear to have good voltaic stability. PVDF polymer gel electrolytes based on these salts have exhibited conductivities in the range of 10^{-4} to 10^{-3} S/cm.

Introduction

Improvements in microelectronics have led to a massive reduction in size of many electronic products to a point where the rechargeable battery occupies largest amount of space in the product. Li-ion polymer electrolyte or Li-ion batteries, with a possible specific energy and an energy density of 180 Wh/kg and 350 Wh/L respectively, represent the best technology for future portable electronic products [1]. The polymer gel electrolyte separator in these systems is the key component and a variety of polymer gels are being developed for this application. Gelled electrolytes based on polyvinylidene difluoride (PVDF) homopolymer or its copolymer with hexafluoropropylene are an important new class of gel electrolytes [2]. The PVDF polymers swell appreciably in liquid electrolytes based on carbonate esters. A typical polymer gel electrolyte consists of a solution of

LiPF_6 in EC/PC in a matrix of the PVDF-based polymer. The electrochemical, thermal and chemical stability of the inorganic lithium salts, such as LiAsF_6 or LiPF_6 , may not be adequate. The degradation products AsF_6 or PF_6 are strong Lewis acids and can initiate solvent polymerization resulting in rapid capacity loss [1]. The imide salt, lithium *bis*-trifluoromethane sulfonyl imide [3] and the methide salt lithium *tris*-trifluoromethane sulfonyl methide [4,5] have exhibited significantly improved stability compared to AsF_6 and PF_6 [1,6]. These large anions are expected to undergo little ion association with Li^+ cation due to the electron withdrawing properties of the $-\text{CF}_3\text{SO}_2$ groups causing significant charge delocalization of the imide anion. This also increases both the degree of dissociation of the lithium salt and the acidity function of the imide acid. Armand has shown that the imide anion has a plasticizing effect on PEO [3]. This plasticizing effect may also contribute to the improved performance of the salt in fluoropolymer gel electrolytes. Other imides with fluorinated groups bound to the nitrogen atom might be expected to have desirable properties. By careful tuning of the substituents on nitrogen in terms of size and electron-withdrawing properties new lithium salts with improved properties may be possible. A Phase II SBIR program, sponsored by the US Army Research Laboratory, Physical Sciences Directorate, is currently underway at Technochem Company with a subcontracted effort at Brookhaven National Laboratory (BNL). The ongoing effort involves the synthesis and characterization of new lithium imide salts with anions designed to act as plasticizers for fluorinated polymer matrices. Improved polymer electrolytes from this effort will be incorporated in Li-ion cells using $\text{Li}_x\text{C}/\text{Li}_y\text{Mn}_2\text{O}_4$ chemistry. This paper reports the current status on the new lithium salts and the polymer electrolytes prepared from them.

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Experimental

Synthesis and Characterization of Li-salts - The following lithium imide salts were synthesized and characterized at BNL:

- (1) $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{Li}$
- (2) $\text{CH}_3\text{SO}_2\text{NLiC(O)CF}_3$
- (3) $\text{CH}_3\text{SO}_2\text{NLiC(O)C}_3\text{F}_7$
- (4) $\text{CH}_3\text{SO}_2\text{NLiC(O)C}_7\text{F}_{15}$
- (5) $\text{CF}_3\text{SO}_2\text{NLiSO}_2\text{C}_8\text{F}_{17}$
- (6) $\Phi\text{-SO}_2\text{NLiC(O)CF}_3$

Some of the salts such as $\text{R-SO}_3\text{Li}$ (# 1) were relatively simple to prepare. It could be prepared in a pure well crystallized form with high yields, simply by reacting $\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ with Li_2CO_3 in methanol. Preparation of many of the other salts required preparation of precursors and imide acids under a critical set of reaction conditions. The method used to prepare $\Phi\text{-SO}_2\text{NLiC(O)CF}_3$ was typical of most of the syntheses. This method was as follows: $\Phi\text{-SO}_2\text{NHC(O)CF}_3$ was prepared by reacting $\Phi\text{-SO}_2\text{NH}_2$ with $(\text{CF}_3\text{CO})_2$. $\Phi\text{-SO}_2\text{NHC(O)CF}_3$ dissolved in anhydrous ethyl ether, at -78°C under nitrogen, was reacted with stoichiometric amounts of butyl lithium dissolved in hexane. The mixture was warmed to room temperature and filtered to remove trace amounts of solid impurities that formed. The filtrate was evaporated to dryness and the residual solid was recrystallized from ethyl ether. ^1H NMR indicated that product batches were of high purity. The Li-salts were white crystalline powders.

Several methods were used to characterize the product acid and the lithium salt for composition and purity. In most cases ^1H NMR and FTIR measurements were sufficient. In a few cases it was necessary to exchange the acid with CH_3OD and repeat the NMR measurements on the acid. In the case of $\text{CH}_3\text{SO}_2\text{NLiC(O)CF}_3$ determination of the purity of the product was very difficult. Its composition was finally confirmed by a combination of FTIR, ^1H NMR, ^{13}C NMR, ^{19}F NMR and elemental analysis. The NMR results were consistent with a pure product, confirmed by the elemental analysis. The ^{19}F NMR for the imide acid

and the corresponding lithium salt also confirmed the purity of the product.

Conductivity Measurements- The salts, as received, were dried under vacuum at 100°C for five hours and were subsequently stored in an argon atmosphere. Solvents, acetone, ethylene carbonate (EC), diethyl carbonate (DEC), tetrahydrofuran were reagent grade and traces of moisture in the solvents were removed by using thoroughly dried molecular sieves. PVDF homopolymer and copolymers were obtained either from Aldrich or Elf Atochem. All the handling and testing with lithium salts and solutions were conducted in an argon glove box. The solution conductivities were measured using a Jenway Conductivity Meter, Model No. 4020. This instrument and the conductivity setup were calibrated with a 0.01 N KCl solution. The conductivity values of solutions of the synthesized lithium salts were determined in solutions using a solvent mixture of 2:1 mole ratio of ethylene carbonate to diethyl carbonate. PVDF copolymer gel electrolytes were prepared by solution casting using a salt solution to polymer ratio of about 65 to 35 by weight. The starting EC-DEC solvent ratio was 1:4 by weight. The polymer electrolyte films were about $150\mu\text{m}$ in thickness and possessed good mechanical strength. Samples of films were assembled with ion-blocking gold electrodes 0.75 inch in diameter in a stainless fixture. The polymer electrolyte conductivity measurements were carried out using a Hewlett-Packard Impedance Analyzer Model No. 4192A.

Voltammetry Experiments- Single sweep voltammetry scans were carried out using an EG&G Princeton Applied Research Model No. 273 potentiostat/galvanostat. The working electrode was a 0.079 cm^2 area aluminum electrode and counter and reference electrodes were made from lithium foil (FMC- Lithium Division). An aluminum substrate was selected for its relative inactivity in these solvents over the potential range of interest. For all the experiments, a scan rate of 5 mV/s and a voltage range of 2.2 to 4.2 volts were selected. These experiments were carried out in liquid electrolytes using a solvent mixture 2:1 mole ratio of EC to DEC and salt concentrations of 0.5 molal new Li salts and 1.0 molal TFMSI.

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Results and Discussion

Liquid Electrolytes- The conductivities of these salt solutions at molal concentrations of 0.50 and 1.0 in 2:1 mole ratio mixture of EC and DEC are presented in Table 1. The conductivity values of these Li salts in liquid electrolytes are generally lower than those for the lithium bis-trifluoromethane sulfonyl imide (TFMSI) solutions. For example, a one molal solution of TFMSI in 50:50 vol. percent ethylene carbonate: propylene carbonate has exhibited a conductivity value of 5.5×10^{-3} S/cm at 24.2°C. This value compares favorably with that of the literature value for a one molar solution of TFMSI in the same solvent mixture at 5.12×10^{-3} S/cm at 20°C [7]. The two CF_3SO_2 - groups on nitrogen in this compound are probably more effective in delocalization of charge on this anion than the compounds synthesized and evaluated, so far in this effort. Further, the larger groups attached to the imide nitrogen in these salts results in bulkier anions reducing their mobility in liquid electrolytes, in particular when one compares salts 2 to 5. Nevertheless, the conductivity values

of these salts in liquid electrolytes are of similar magnitude to those observed with Li salts with other organic moieties.

Polymer Electrolytes - The conductivity data for the polymer electrolyte films prepared from these new lithium salts are presented in Table 2. The molality of the salt in liquid phase of the polymer electrolyte film is about 0.50 to 0.75. The films made from the highest molecular weight salt # 6 and salt #1 are not as good as those made from salts #'s 2, 3, 4 and 6. The fluorinated side chains on these salts provide a plasticizing effect on the PVDF polymer backbone, although this needs to be confirmed by differential scanning calorimetry. In general, the conductivities of these films were lower than those in liquid electrolytes by factors ranging 0.1 to 0.35. Polymer electrolyte films containing TFMSI salt exhibited a polymer to liquid electrolyte conductivity ratio of 0.30, which is in the same range as these imide salts. The larger anions generally yielded proportionately lower conductivity values in polymer gels compared to those in corresponding liquid electrolytes.

Table 1
Conductivities of Solutions of Li-Salts
in EC-DEC Solvent Mixture

Salt #	Salt Molality	Temperature, °C	$\sigma \times 10^4$ S/cm
1	0.50	21.6	20
	1.00	21.3	15
2	0.50	25.3	9.8
	1.00	26.2	11
3	0.50	28.4	9.4
	1.00	27.6	9.0
4	0.50	27.7	6.5
	1.00	25.8	5.7
5	0.50*	22.0	4.3
6	0.50	23.0	10

* A small amount of THF was necessary to keep the salt in solution

Voltaic Stability of the imide salts- Single sweep voltammograms were recorded after 3-4 scans were taken on the aluminum electrode over the potential range of 2.2 to 4.2 volts with respect to a lithium electrode. The voltage scans obtained for salt #'s 3, 4, 6 and TFMSI are shown in Figure 1 as *a*, *b*, *c* and *d* respectively. The voltage scans for these salts do

Table 2
Conductivity of Polymer Electrolyte Films
Made from Synthesized Lithium Salts

Salt #	Salt Molality	Temp. °C	$\sigma \times 10^4$ S/cm
1	0.59	24	3.4
2	0.75	25	1.6
3	0.60	24	3.2
4	0.50	25	0.96
5	0.50	25	0.42
6	0.60	25	2.5

not show any activity over the studied potential range and characteristically very low currents of a few μA above 4.0 V. The new salts compare favorably with the Li-TFMSI in terms of voltaic stability.

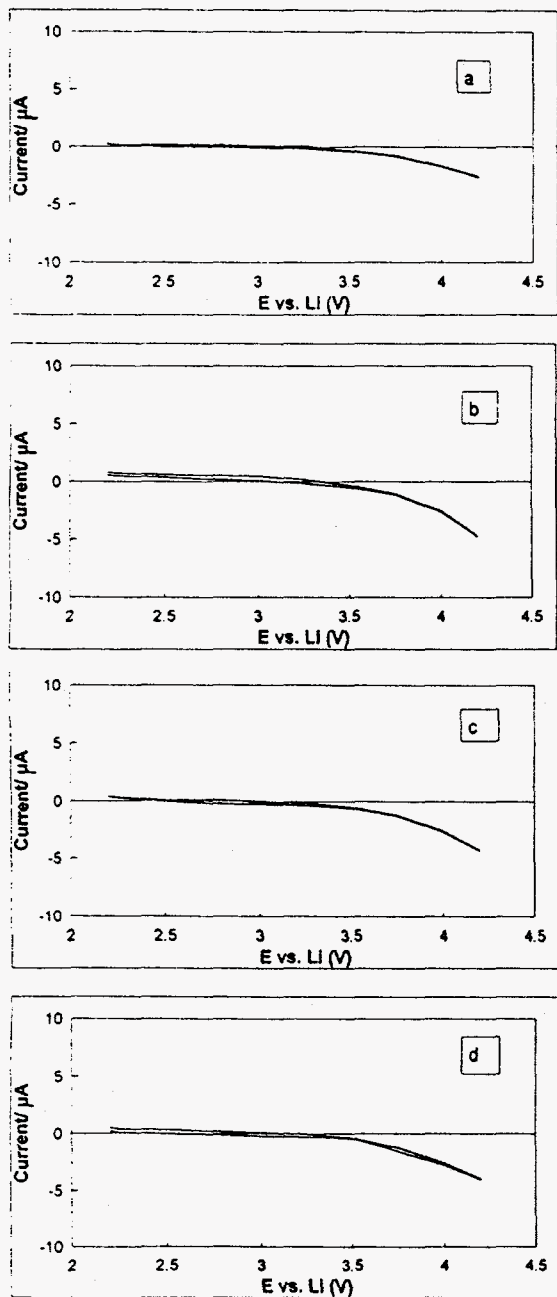


Figure 1 Cyclic voltammograms for LiX in 2:1 mole EC:DEC solvent mixture on a 0.08 cm^2 aluminum electrode. (a) $\text{X} = \text{CH}_3\text{SO}_2\text{N}^-\text{C}(\text{O})\text{C}_3\text{F}_7$, (b) $\text{X} = \text{CH}_3\text{SO}_2\text{N}^-\text{C}(\text{O})\text{C}_7\text{F}_{15}$, (c) $\text{X} = \Phi\text{-SO}_2\text{N}^-\text{C}(\text{O})\text{CF}_3$, and (d) $\text{X} = \text{CF}_3\text{SO}_2\text{N}^-\text{CF}_3\text{SO}_2$ For (a), (b), (c) 0.5 molal and for (d) 1.0 molal concentration.

Conclusions

Synthesis of lithium salts of imides with different groups bound to the nitrogen atom is proven feasible. It is thus possible to develop an anion which will provide a plasticizing effect on a fluoropolymer. The new salts exhibit liquid electrolyte conductivities in EC-DEC of $4\text{-}20 \times 10^{-4} \text{ S/cm}$ at room temperature and in PVDF polymer gel electrolytes $0.4\text{-}3.4 \times 10^{-4} \text{ S/cm}$. The larger anions due to their size and lesser charge delocalization compared to TFMSI do exhibit lower conductivities. A preliminary evaluation indicates that these new imide salts are stable in the range of 2.2 to 4.2 volts against lithium.

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