

Novel Solid Redox Polymerization Electrodes

All-Solid-State, Thin-Film, Rechargeable Lithium Batteries

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ABSTRACT

Lithium batteries using solid redox polymerization electrodes (SRPEs) maintain the inherent advantages of all-solid-state, thin-film systems while overcoming some of the limitations of using intercalation compounds as positive electrode (i.e., insufficient rate capability and capacity utilization). Laboratory Li/PEO/SRPE cells have demonstrated higher power capability, energy density, and capacity utilization than analogous Li/PEO/TiS₂ cells. One of the Li/PEO/SRPE cells has achieved 350 cycles from 50 to 93°C with a sustained energy density of 160 Wh/kg (190 Wh/l), power density of 120 W/kg (140 W/l), and 40–75% capacity utilization of the polymerization electrode. At 100°C, power densities of over 1800 W/kg (2200 W/l) at energy densities of 140 Wh/kg (170 Wh/l) have been achieved with up to 96% utilization of cathode capacity. At ambient temperatures (35°C), the cells can be discharged at a current density of 250 μA/cm², achieving a film capacity of 0.5 C/cm².

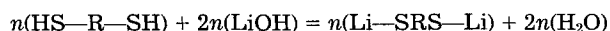
All-solid-state energy-storage systems have attracted worldwide attention and are currently being pursued by a number of battery developers (1). To date, the majority of positive electrode materials used in these systems have been intercalation compounds, with Li/PEO/TiS₂ cells demonstrating the highest levels of performance (2, 3). Although these batteries have many advantages over similar lithium cells involving liquid electrolytes, their limited rate capability and low utilization of cathode capacity have hindered their practical application. Recent investigations of alternative positive electrode materials in our laboratory have indicated that the rate capability of solid-state lithium batteries can be substantially improved by replacing costly intercalation materials with novel, inexpensive positive electrodes which demonstrate far improved electrochemical properties (4, 5).

A number of lithium cells based on a group of solid redox polymerization electrodes (SRPEs), as listed in Table I, have been constructed and tested from ambient to 100°C at various current densities to evaluate the characteristic performance of these systems. Many of these polymeric materials are exceedingly inexpensive and of very low toxicity. The mercaptan precursor to one of the high-performance polymers, dimercaptodithiazole, has a rated toxicity (LD50) approximately equal to that of caffeine.

Experimental

Materials.—Battery-grade lithium foil (with a thickness of 125 μm) was obtained from Lithco Company and stored in an argon atmosphere dry box. Anhydrous lithium salts LiSO₃CF₃ and LiClO₄ were obtained from Alfa, and stored under vacuum several days prior to use. Anhydrous LiN(SO₂CF₃)₂ was used to improve electrolyte conductivity and permit cell operation at temperature approaching ambient (35°C). Battery-grade intercalation compound TiS₂ powders were obtained from Cerac and used as received. Reagent grade sulfur monochloride, iodine, chloroform, mercaptans, and other precursors for solid polymerization electrodes were obtained from Aldrich.

Preparation of polymers.—*Polymers containing carbon-sulfur bonds (6).*—A class of redox polymerization electrode materials based on carbon-sulfur bonds, —C—S—S—C—, were synthesized by a number of routes including aqueous oxidation of the mercaptans or lithium thiolate salts by iodine or other appropriate oxidants. At room temperature many disulfide polymers of this type were prepared by first converting the insoluble mercaptans to soluble lithium salts



Aqueous solutions of the lithium thiolate salts are then rapidly converted to polymeric disulfides upon oxidation by stoichiometric amounts of iodine or soluble tri-iodide species

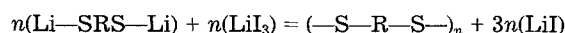


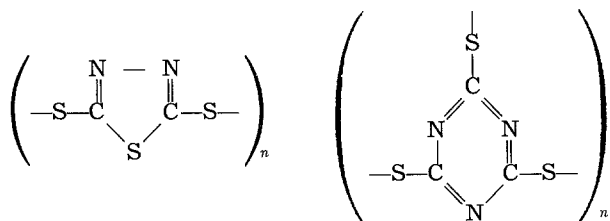
Table I. Notation for organosulfur redox polymers.

Notation	Name	Formula
X0	2-mercaptoethyl ether	$(-\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{S}-)_n$
X1	dimercapto dithiazole	$\left(\begin{array}{c} \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \right)_n$
X2	dimethyl ethylenediamine	$\left(\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{S}-\text{NCH}_2\text{CH}_2\text{N}-\text{S} \end{array} \right)_n$
X3	ethylenediamine	$\left(\begin{array}{c} \text{S} \quad \text{S} \\ \diagdown \quad \diagup \\ \text{NCH}_2\text{CH}_2\text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \right)_n$
X4	polyethylene imine derivative	$\left(\begin{array}{c} -\text{CH}_2\text{NCH}_2- \\ \\ \text{S} \\ \\ \text{S} \\ \\ -\text{CH}_2\text{NCH}_2- \end{array} \right)_n$
X5	trithiocyanuric acid	$\left(\begin{array}{c} \text{S} \\ \\ \text{C} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{N} \\ \diagup \quad \diagdown \\ \text{S} \quad \text{S} \end{array} \right)_n$
X6	piperazine	$(-\text{S}-\text{N} \begin{array}{c} \diagdown \quad \diagup \\ \diagup \quad \diagdown \end{array} \text{N}-\text{S}-)_n$
X7	2,4-dithiopyrimidine	$\left(\begin{array}{c} \text{N} \\ \\ \text{S} \quad \text{S} \\ \quad \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{N} \end{array} \right)_n$
X8	1,2-ethanedithiol	$(-\text{SCH}_2-\text{CH}_2\text{S}-)_n$
X9	2-mercaptoethyl sulfide	$(-\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}-)_n$

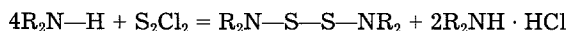
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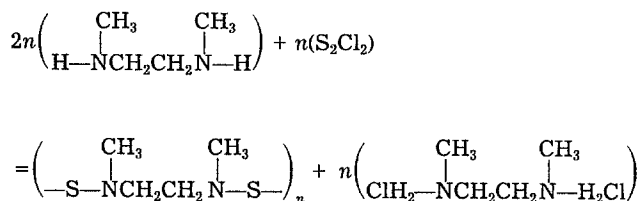
In aqueous solution at slightly elevated temperatures, polymeric disulfides can be made by direct oxidation of the mercaptan by iodine. In all cases, the reaction yield was close to 100% of the theoretical. The polymeric products were thoroughly rinsed to remove any trace of residual mercaptan or other reaction products. Two examples of polymers prepared in this manner were dimercapto dithiazole polymer (X1) and trithiocyanuric acid polymer (X5)



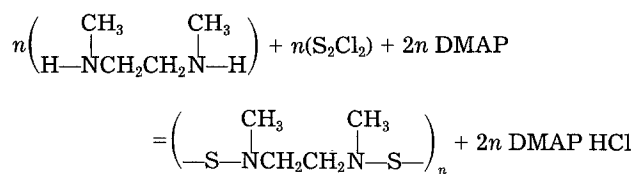
Polymers containing nitrogen-sulfur bonds (6).—Disulfide polymers based on $-N-S-S-N-$ linkages were prepared by the reaction of primary or secondary amines with sulfur monochloride in chloroform. Morpholine disulfide, a commercially available product is prepared by the reaction of the secondary amine morpholine (R) with sulfur monochloride



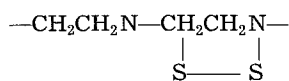
In similar fashion, related polymeric disulfides were prepared by the reaction of monomers having multiple amine sites for reaction, as is the case for dimethylethylenediamine



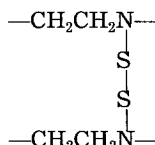
In some cases the reaction was facilitated by the addition of dimethylaminopyridine (DMAP) to scavenge the HCl generated by the reaction



A number of interesting materials can be prepared in this manner; the reaction of linear polyethylene imine with sulfur monochloride could react in a complex fashion, generating polymers with $-CH_2CH_2N-$ backbones and either inter or intra molecular $-S-S-$ cross-links



or



Polymers prepared by the above route include derivatives of dimethylethylenediamine (X2), ethylenediamine (X3), polyethylene imine (X4), and piperazine (X6). These

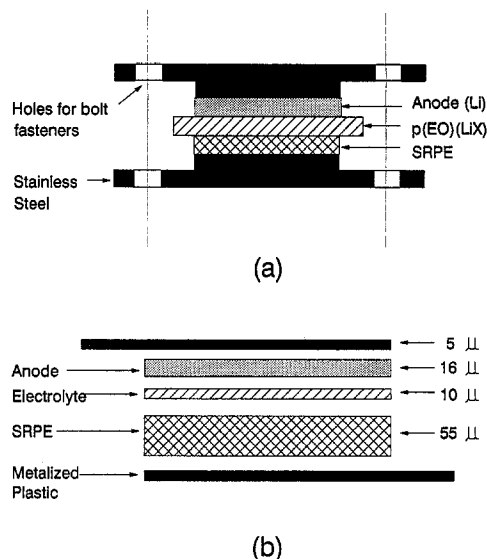


Fig. 1. A schematic view of (a) a laboratory test cell and (b) a model cell used for estimation of energy and power densities.

syntheses were not as straightforward as for the oxidation of mercaptans. The product prepared with ethylenediamine showed evidence of decomposition under vacuum, and elemental analysis confirmed only the piperazine derivative (X6) to be a relatively pure product.

Cell assembly and characterization.—Preparation of thin-film electrolyte and composite positive electrode, assembly of solid-state cells, evaluation of battery performance, and data acquisition were as described elsewhere (4, 5). A schematic view of a test cell used extensively in this study is shown in Fig. 1a. In addition, four-probe polarization techniques were also employed to study electrode kinetics and transport properties as well as to identify the limiting factors to cell performance (7).

Results and Discussion

Rate capability.—Shown in Fig. 2 are several charge/discharge curves of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ cell at various current densities. Based on these data and the actual weight of SRPE films in test cells, the energy and power densities were estimated under the assumption that 5 μm metalized plastic films were used as current collectors (Tables II and III). At 100°C, the cell achieved a power density of 1800 W/kg at an energy density of 140 Wh/kg with

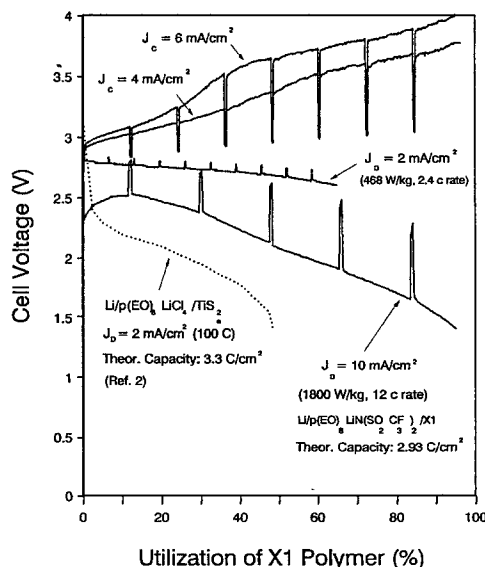


Fig. 2. Typical discharge/charge curves of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ cell at 100°C.

Table II. Sample calculation of energy densities of Li/p(EO)/SRPE cells.

Cell components	Film thickness (μm)	Weight/cm ² (mg)	Density (g/cm ³)
Lithium (12 C/cm ²)	16	0.87	0.544
p(EO) ₈ LiN(SO ₂ CF ₃) ₂	10	1.5	1.5
SRPE (3 C/cm ²)	55	7.8	1.418
Metalized plastic current collector	5 × 2	0.92	0.92
Total	91	11.1	1.22
Energy density	274 Wh/liter	225 Wh/kg	

96% utilization of X1 polymer. At 77-93°C, a sustained energy density of 160 Wh/kg (190 Wh/l) was achieved for over 83 cycles, with an energy density of 80 Wh/kg demonstrated at termination of the test at 350 cycles. This performance exceeds reported data for solid-state systems using intercalation materials (2, 3) or electronically conductive polymers (8). The obtained energy and power densities of this test cell actually meet or exceed the requirements for electric vehicle (EV) application (9). Although a lithium excess of 4:1 was used in the calculation of power and energy densities, thick lithium foils (125 μm) were used in laboratory cells for simplicity.

A striking observation in the performance of these novel batteries is that the rate capability of all-solid-state cells using SRPE materials appears to exceed that of analogous cells using intercalation compounds. In solid-state batteries using composite cathodes of powdered intercalation materials dispersed in a host polymer, mass transport in the positive electrode involves the diffusion of Li⁺ in the host polymer (PEO), across the interfaces between the intercalation particles and PEO, and subsequent diffusion inside the intercalation lattice. Previous studies have indicated that the limiting factor to performance in these systems is the inadequate transport of Li⁺ in the composite positive electrode, either due to the dispersed intercalation powders interfering with the diffusion process in the polymer electrolyte, poor contact between the powders and the host electrolyte, or the slow diffusion inside the intercalation compounds (2). The transport processes in a battery based on intercalation compounds are schematically compared in Fig. 3 with those in a battery based on solid redox polymerization electrodes. For a Li/SRPE cell, the microscopic transport process in the composite positive electrode is quite different, as is discussed below.

Composite positive electrodes in Li/PEO/SRPE cells are inherently far more homogeneous than in the case of intercalation-based composite electrodes. A number of organosulfur redox polymers are soluble in the same solvents in which the polymer electrolytes are dissolved; allowing composite electrodes to be cast from single solutions (with dispersed carbon). Even intractable organodisulfide polymers can be rendered soluble by copolymerization with other disulfides. This intimate mixing of redox polymer with electrolyte allows for the fabrication of highly homogeneous structures, in contrast to the painstaking preparation of homogeneous polycrystalline powders necessary for intercalation-based electrodes. Even in cases where the SRPE material is essentially insoluble in the electrolyte/solvent solution, it was found that the organosulfur polymers were very well dispersed in solution and also formed homogeneous, high-performance, composite positive electrodes. Moreover, upon discharge of the SRPE cathodes the sulfur-sulfur bonds are cleaved, and polyanions are

Comparison of SRPE's and INTERCALATION electrodes

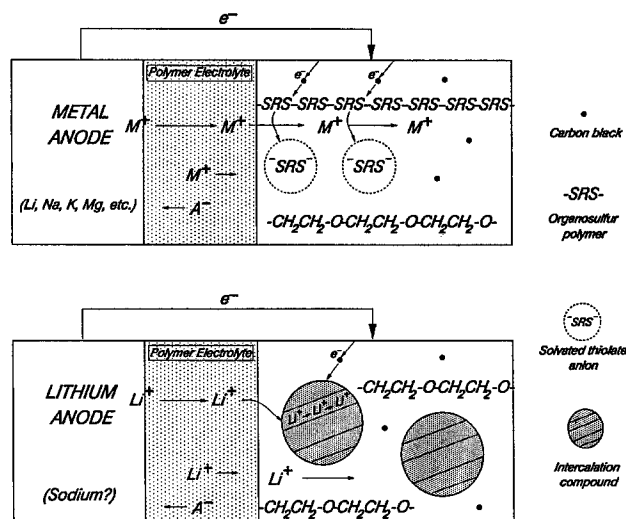


Fig. 3. A schematic view of the transport processes in battery systems based on redox polymerization electrode materials and intercalation compounds.

formed which dissolve into the electrolyte, further enhancing the homogeneity of the SRPE composite electrode. Presumably, the only transport process involved in the SRPE composite electrode is the diffusion of the alkali cations in the homogeneous polymer matrix (the solvated polyanions appear to be quite immobile in the polymeric electrolyte).

In addition, cation transport through a SRPE-based composite positive electrode can be enhanced by improving the conductivity of the polymeric electrolyte. This may not be the case for composite cathode using intercalation materials since the rate-limiting step of the transport process is often diffusion of Li⁺ through the intercalation compounds.

Stability and cyclability.—A prominent feature of the solid-state organosulfur batteries is their excellent stability and reversibility, implying long cycle life and reliability. Shown in Fig. 4a are the first 83 continuous cycles of a Li/p(EO)₈LiN(SO₂CF₃)₂/X1 cell. The first 19 cycles were charged and discharged to equal capacities, while the following cycles were slightly overcharged to 2-4% of available capacity to compensate for possible shorting due to microdendrites of lithium formed during charging. As is clear from Fig. 4a, the performance of the cell was remarkably constant over the first 83 cycles (cell internal resistance stayed relatively constant). The cycle curves do show a slight downward shift with increased number of cycles; this is believed to be due to the formation of microdendrites. In fact, a previous study of reversibility and cyclability of the positive electrode based on Na/β'-alumina/SRPE cells (where dendrite formation is not possible) showed no observable deterioration of cell performance with cycling or extensive cell polarization (4). It should be possible to improve the cyclability of lithium by introducing additives to aid lithium plating, or by the use of a lithium alloy. The utilization of X1 polymer in the cell was

Table III. Energy and power density of operating cell.

Operating conditions	Energy density		Power density	
	Gravimetric (Wh/kg)	Volumetric (Wh/liter)	Gravimetric (W/kg)	Volumetric (W/liter)
100°C				
10 mA/cm ²	140	170	1800	2200
2 mA/cm ²	200	240	468	570
80°C				
First 83 cycles	160	190	120	140
350th cycle	80	95	120	140

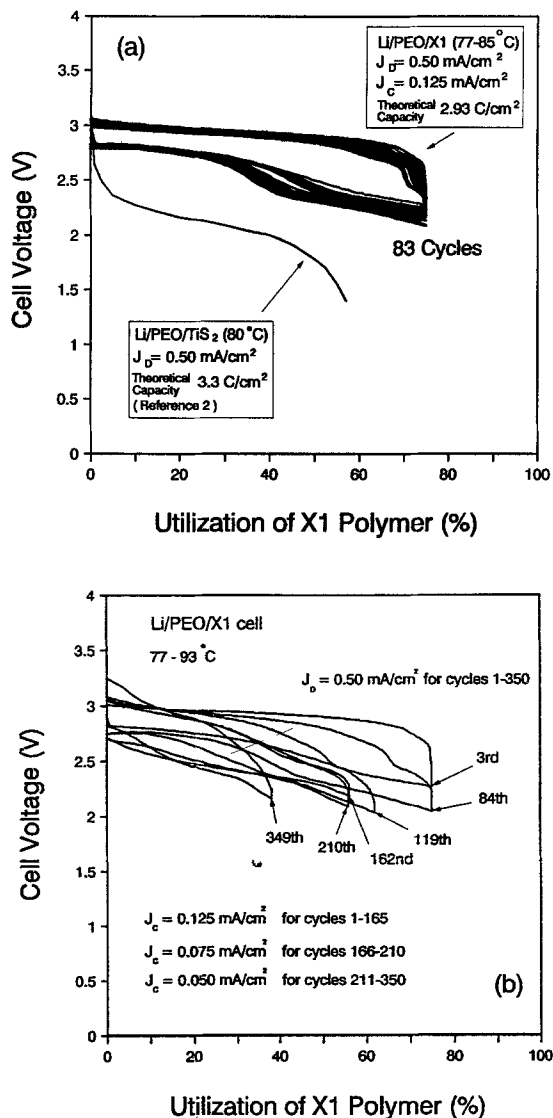


Fig. 4. (a) The first 83 discharge/charge curves of a $\text{Li/p}(\text{EO})_8\text{Li}(\text{SO}_2\text{CF}_3)_2/\text{X1}$ cell operated at $77\text{--}85^\circ\text{C}$, and (b) cycling profile of the cell.

gradually reduced after the first 83 cycles, as shown in Fig. 4b.

It was also observed that the reversibility and cyclability of SRPEs were a function of the synthesis approach used to prepare the polymeric disulfides, as well as subsequent purification of the resulting polymer. For example, it was observed that the presence of unreacted mercaptan as a contaminant in SRPEs in some cases led to poor utilization and cycling of positive electrode.

Utilization of redox polymers and energy density.—Theoretical energy densities of batteries based on SRPE materials are higher than those of intercalation compounds due to the low equivalent weight and high electro-positive character of organosulfur redox polymerization materials (4). For example, the theoretical energy density of a $\text{Li}/\text{X1}$ cell is 990 Wh/kg , approximately double that of a Li/TiS_2 cell, 560 Wh/kg .

Furthermore, the improved capacity utilization of positive electrodes based on SRPEs with respect to intercalation compounds further increases the obtainable energy and power densities of these systems. Figure 5a shows the direct comparison in capacity utilization of positive electrode in a $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{X1}$ cell and a $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{TiS}_2$ cell. These two cells were constructed and tested in exactly the same manner except that the electrochemically active material X1 was substituted with TiS_2 .²

² However, more recent laboratory tests with TiS_2 positive electrode have shown similar utilization to SRPE materials.

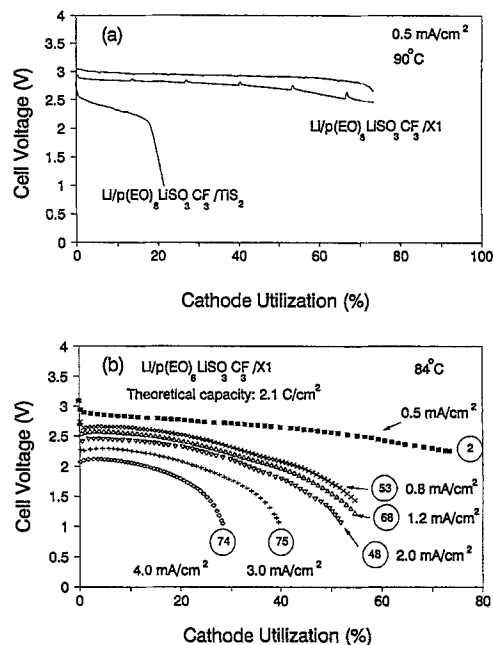


Fig. 5. (a) Capacity utilization of the positive electrode for a $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{TiS}_2$ and a $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{X1}$ cell at 90°C ; (b) utilization of X1 polymer in a $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{X1}$ cell as a function of discharge current density at 84°C . The circled number by each curve represents the cycle number.

Shown in Fig. 5b is the capacity utilization of X1 polymer in a $\text{Li/p}(\text{EO})_8(\text{LiSO}_3\text{CF}_3)/\text{X1}$ cell as a function of discharge current density. As might be expected, it was observed that capacity utilization depends not only on the nature of the redox polymer but also on the supporting electrolyte used as well as the details of processing the composite SRPE films. Typically, the performance of the prepared composite increased with the homogeneity of the microstructure.

Molecular architecture.—The tremendous chemical flexibility of SRPEs has been outlined previously (4). In addition to modification of the chemical properties of $(-\text{SRS}-)_n$ polymers with the organic group R, the physical properties of the polymer can be altered through cross-linking or copolymerization of dissimilar disulfides (10). Although details of the structure of cross-linked and/or copolymerized disulfides were not established for this study, idealized polymer structures are shown in Table I (X3, X4, X5) for the purpose of discussion.

A number of lithium batteries using a variety of organosulfur polymers, including linear (X0, X1, X2, X6, etc.), ladder (X3 and X4), and cross-linked polymers (X5), have been characterized. Cells based on linear polymer X1 and cross-linked polymer X5, in particular, were investigated extensively. Shown in Fig. 6 are representative discharge curves of $\text{Li/p}(\text{EO})_8\text{LiSO}_3\text{CF}_3/\text{X5}$ cells. The performance of a cell based on X5 operated at 80°C , as shown in Fig. 6a, can be directly compared with that of a cell based on X1 operated at the same temperature, as shown in Fig. 4. Similarly, the performance of a cell based on X5 operated at 100°C , as shown in Fig. 6b, can be further compared with that of a cell based on X1, as shown in Fig. 2. Comparison in performance of these cells indicates that both rates capability and capacity utilization of cells having linear SRPEs are better than those with highly cross-linked polymers or ladder polymers. It is possible that cross-linked polymers inhibit lithium cation transport in the positive electrode; further investigation of this relationship is still in progress.

Temperature dependence.—An additional asset of solid-state batteries based on the X1 polymer is the minimal dependence of cell performance on temperature. Shown in Fig. 7a are several discharge curves of a $\text{Li/p}(\text{EO})_8\text{Li}(\text{SO}_2\text{CF}_3)_2/\text{X1}$ cell at various temperatures. As can be inferred from the observed trends shown in Fig. 7a,

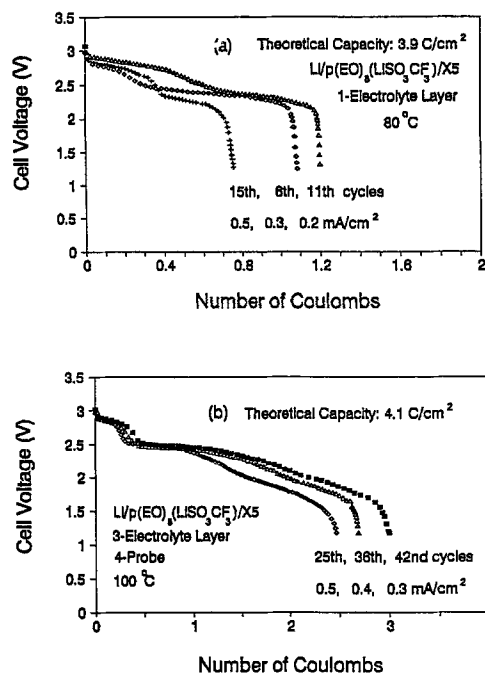


Fig. 6. Performance of $\text{Li}/\text{p}(\text{EO})_2\text{LiSO}_3\text{CF}_3/\text{X5}$ cells (a) with one electrolyte layer at 80°C and (b) with three identical electrolyte layers at 100°C . The voltage presented in (b) was anode-cathode voltage and the internal probes were not involved in this measurement.

the activation energy for ionic transport in this composite electrode is much lower than that in a composite electrode with intercalation compounds, as referred from a previous study on the system (2). Consequently, the performance of the cell is not as dependent on temperature as for systems based on intercalation compounds. Accordingly, $\text{Li}/\text{PEO}/\text{SRPE}$ cells can match the performance of solid-state intercalation batteries operating at higher temperatures.

Shown in Fig. 7b is the observed temperature dependence of the $\text{Li}/\text{p}(\text{EO})_3\text{LiSO}_3\text{CF}_3/\text{X5}$ cells. These trends indicate that the activation energy for the transport process in positive electrode with cross-linked polymers is higher than those with linear polymers.

Overcharge or overdischarge characteristics.—In one instance, the cell described in Fig. 4 was accidentally overcharged at $0.125\text{ mA}/\text{cm}^2$ for 1.4 C , about 48% of the capacity of the positive electrode (2.94 C), bringing the open cell voltage to 3.2 V . In another instance, the same cell was accidentally overdischarged to an open cell voltage of 0.7 V . In both cases, surprisingly, there was no clear evidence of deterioration in cell performance in the following cycles. The exact protection mechanism for overcharge or overdischarge of this system, however, has not been identified and is still a matter of investigation.

Conclusions

All solid-state, thin-film, rechargeable lithium batteries using redox polymerization electrode have demonstrated higher energy density and power capability, better capacity utilization, and lower temperature dependence than the highly developed systems based on intercalation materials or electronically conductive polymers. The demonstrated high performance of this system makes it attractive for a diverse array of applications, ranging from consumer electronics, to satellites, and to electric vehicles.

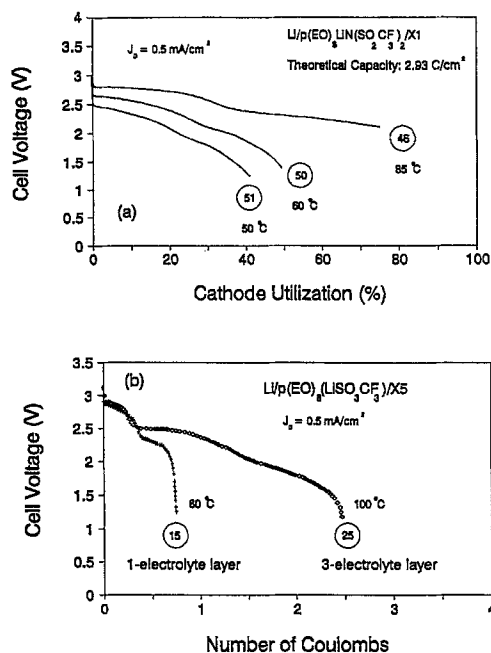


Fig. 7. Temperature dependence of cells using (a) linear polymer (X1) and (b) cross-linked polymers (X5). The circled number by each curve corresponds to the cycle number.

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