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ALL-SOLID-STATE THIN-FILM RECHARGEABLE LITHIUM BATTERIES USING SOLID REDOX POLYMERIZATION ELECTRODES

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Abstract

Lithium batteries using solid redox polymerization electrodes maintain the advantages of all-solid-state thin-film systems while overcoming the limitations of using intercalation compounds as cathodes (i.e., insufficient rate capability and unsatisfactory cathode utilization). Laboratory Li/PEO/SRPE cells have already demonstrated much higher power capability, energy density, and cathode utilization than analogous Li/PEO/TiS_2 cells. One of the Li/PEO/SRPE cells has achieved 350 cycles from 50 ^oC to 93 ^oC with a sustained energy density of 264 Wh/kg (241 Wh/l), power density of 160 W/kg (144 W/l), and 38% to 75% of cathode utilization at 90% voltage efficiency. At 100 ^oC, power densities of over 2400 W/kg and energy density of 200 Wh/kg have been achieved with up to 96% utilization of cathode capacity. At ambient temperatures, the cells can be discharged at a current density of 250 $\mu A/cm^2$, achieving a film capacity of 0.5 coulombs/cm^2.

1. Introduction

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 cathode materials used in these systems have been intercalation compounds, with Li/PEO/TiS_2 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 has hindered their practical application. Recent investigations of alternative cathode 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 cathodes which demonstrate far improved electrochemical properties (4).

A number of lithium cells based on a group of solid redox polymerization electrodes (SRPE's), recently discovered in our laboratory, have been constructed and tested from ambient to 100 ^{o}C at various current densities to evaluate the characteristic performance of these systems.

2. Experimental

Battery grade lithium foil (with a thickness of 125μm) was obtained from Lithco Co. and stored in an argon atmosphere dry box. Anhydrous lithium salts $LiSO_3CF_3$ and $LiClO_4$ were obtained from Alfa, and stored under vacuum several days prior to use. Plasticizing electrolyte salt[1], $LiN(SO_2CF_3)_2$, was used to maintain the polyethylene oxide electrolyte in the amorphous state at ambient temperatures. Battery grade intercalation compound TiS_2 powders were obtained from Cerac and used as received.

Preparation of thin-film electrolytes and composite cathodes, assembly of solid-state cells, and the evaluation of battery performance and data acquisition were as described in a previous communication (4). In addition, 4-probe polarization techniques (5) were also employed to study electrode kinetics and transport properties as well as to identify the limiting factors to cell performance.

3. Results and Discussion

3.1. Rate capability

Shown in Figure 1 are several charge/discharge curves of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ cell at various current densities. Based on cell performance, the corresponding energy and power densities (excluding current

[1] obtained from Michel Armand, ecole nationale superieure d'electrochimie et d'electrometallurgie de grenoble, France.

collectors) were calculated from the actual weight and volume of the thin film electrolyte, cathode, and lithium foil (excess 4:1). At 100 ^{o}C (as shown in Figure 1), the cell achieved power and energy densities of 2400 W/kg and 200 Wh/kg, respectively, with 96% of cathode utilization. At 77-93°C, a sustained energy density of 264 Wh/kg (241 Wh/l) and power density of 160 W/kg (144/l) has been achieved for over 350 cycles. The corresponding Ragone plot of the cell is shown in Figure 1 (b). This performance is far in excess of any existing solid-state systems using intercalation materials (2, 3) or electronically conductive polymers (7), and the obtained energy and power densities meet or exceed the requirements for electric vehicle (EV) application (6). Although a lithium excess of 4:1 was used in the calculation of power and energy densities, thick lithium foils (125μm) were used in laboratory cells for simplicity.

The most striking observation in the performance of these novel batteries is that the rate capability of all-solid-state lithium cells using SRPE materials is much greater than cells using intercalation compounds. In solid-state batteries using composite cathodes of powdered intercalation materials dispersed in a host polymer, mass transport in the cathode involves the diffusion of Li^+ in the host polymer, across the polymer composite cathode interface, 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 cathode, 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). For the Li/SRPE cells, however, the microscopic transport process in the cathode is radically different, as is discussed below.

Depolymerization-Polymerization Processes:

Composite cathodes in Li/PEO/SRPE cells are inherently far more homogeneous than in the case of intercalation-based composite electrodes. Many organosulfur redox polymers are soluble in the same solvents which the polymer electrolytes are dissolved in; allowing composite electrodes to be cast from single-phase solutions (with dispersed carbon). This intimate mixing of redox couple with electrolyte allows for the fabrication of highly homogeneous structures, yet is far simpler in execution than 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 cathodes. Moreover, upon discharge of the SRPE cathodes the sulfur-sulfur bonds are cleaved, and

polyanions are formed which dissolve into the electrolyte, further enhancing the homogeneity of the SRPE composite electrode. Accordingly, the only transport process involved in the SRPE composite cathode 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 rates through composite cathode using SRPE materials can be enhanced by improving the conductivity of the polymeric electrolyte. This is probably not the case for composite cathodes using intercalation materials becaused the rate limiting step of the tranport process is often diffusion of Li^+ through the intercalation compounds.

3.2. 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 Figure 2 (a) is the first 83 continuous cycles of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ 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 micro-dendrites of lithium formed during charging. As is clear from Figure 2 (a), 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 down shift with increased number of cycles; this is believed to be due to the formation of micro-dendrites. In fact, a previous study of reversibility and cyclability of the positive electrode based on Na/β"-alumina/SRPE cells (where dendrites formation is not possible) has shown no observable deterioration of cell performance with cycling or extensive cell polarization (3). The cyclability of lithium can, however, be improved by introducing additives to aid lithium plating. The cathode utilization was gradually reduced after the first 83 sycles, as shown in Figure 2 (b).

3.3. Cathode Utilization and Energy Density

Theoretical energy densities of batteries using SRPE materials are higher than those of systems based on intercalation compounds due to the low equivalent weight and high electropositive character of organosulfur redox polymerization materials (3). For example, the theoretical energy density of Li/X1 is approximately double that of Li/TiS_2.

Furthermore, the improved utilization behavior of positive electrodes based on SRPE's with respect to intercalation compounds further boost the obtainable practical energy and power density of these systems. Figure 3 (a) shows the direct comparison in cathode utilization of a $Li/p(EO)_8LiSO_3CF_3/X1$ cell and a $Li/p(EO)_8LiSO_3CF_3/TiS_2$ 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. The rate capability and the cathode utilization of X1 is shown in Figure 3 (b). The better cathode utilization is a inherent advantage of the polymerization electrodes due to the far greater homogeneity of the composite electrode structure.

3.4. Molecular Architecture and Monomers

A number of cells using a group of organosulfur polymers, including linear (X1, X2, X3, X6), ladder (X4), and cross-linked polymers (X5), have been characterized. Shown in Figure 4 are representative discharge curves of $Li/p(EO)_8LiSO_3CF_3)/X5$ cells (a) with one electrolyte layer at 80°C and (b) with three identical electrolyte layers at 100°C. Comparison in performance of the cells with various SRPE materials indicates that both rate capability and cathode utilization of the cells having linear polymers are better than those with cross-linked polymers or ladder polymers. It is believed that this is closely related to the microstructure of the composite cathode and further investigation of this phenomenon is in progress.

3.5. Temperature dependance

An additional asset of the solid-state batteries based on the X1 polymer is the minimum dependence of cell performance on temperature. Shown in Figure 5 (a) are several discharge curves of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ cell at various temperatures. As can be inferred from the observed trends shown in Figure 5 (a), the activation energy of ionic transport in the composite cathode is much lower than in a composite cathode with intercalation compounds. Consequently, the performance of the cell is not as dependent on temperature as for systems based on intercalation compounds (2). Accordingly, Li/PEO/SRPE cells can match the performance of solid-state intercalation batteries operating at much higher temperatures.

Shown in Figure 5 (b) is the observed temperature dependance of the $Li/p(EO)_8LiSO_3CF_3)/X5$ cells. The observed trends indicate that the activation energy for the transport procerss in cathodes with cross-linked polymers are higher than those with linear polymers.

4. Conclusions

All-solid-state, thin-film, rechargeable lithium batteries using redox polymerization cathode have demonstrated higher energy density and power capability, better cathode utilization, and lower temperature dependence than the highly developed systems based on intercalation materials or conductive polymers. The achieved energy and power densities meet or exceed the requirements for electric vehicle application (6).

Acknowledgment

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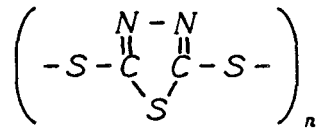
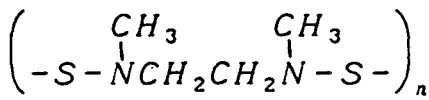
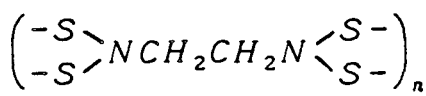
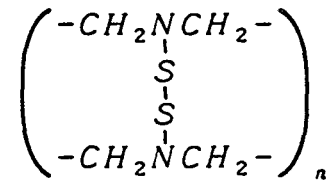
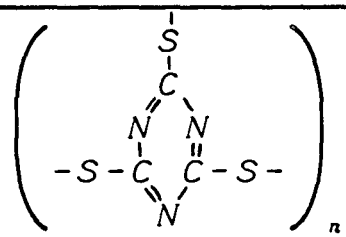
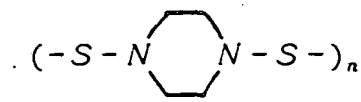
Notation for Organosulfur Redox Polymers

Notation	Name	Formula
X1	dimercapto dithiazole polymer	
X2	dimethyl ethylenediamine polymer	
X3	ethylenediamine polymer	
X4	polyethylene imine derivative	
X5	trithiocyanuric acid polymer	
X6	piperazine polymer	

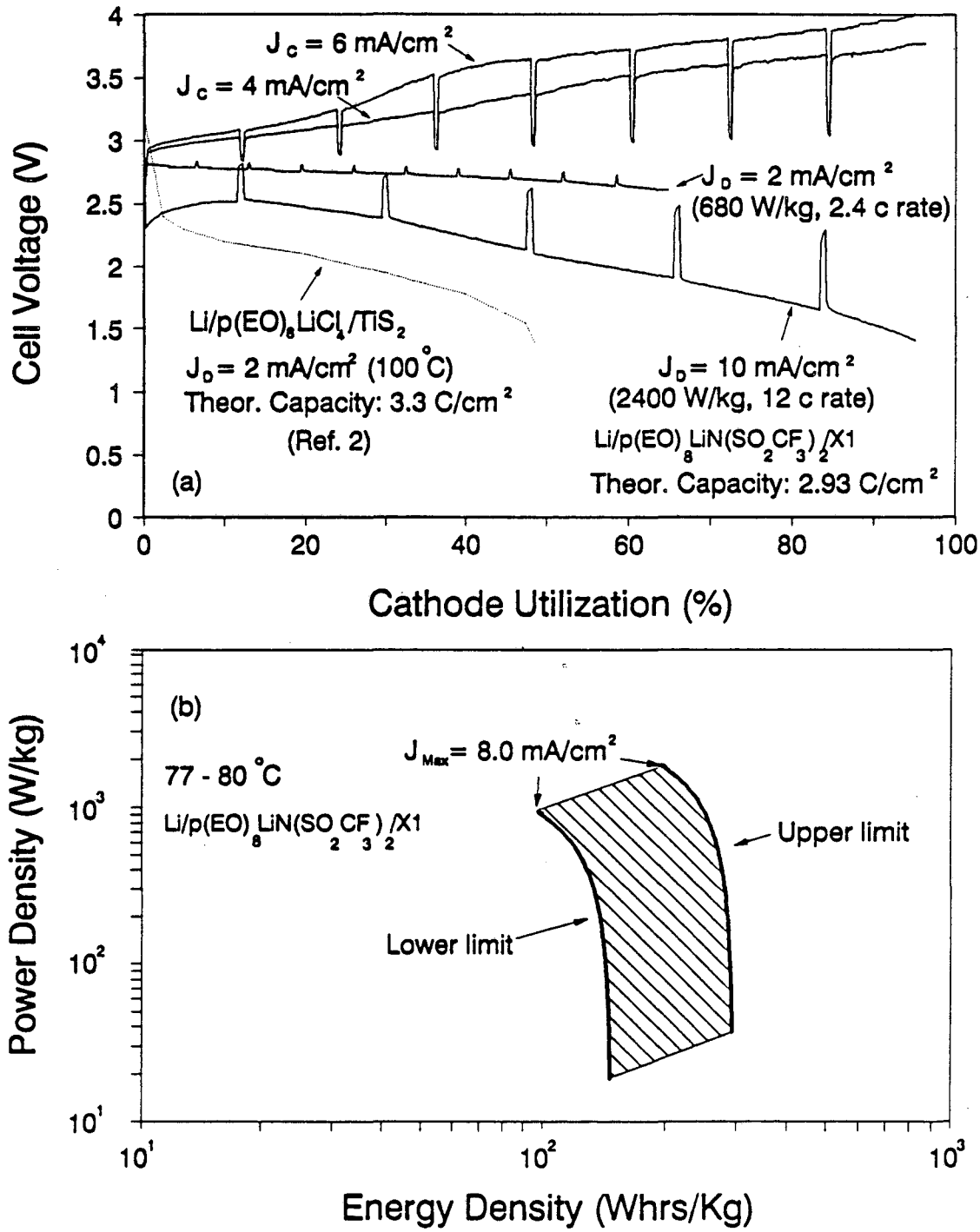


Figure 1. (a) High rate discharge/charge curves of a $Li/p(EO)_8LiN(SO_2CF_3)_2/X1$ cell at 100 °C and (b) Ragone plot for the cell.

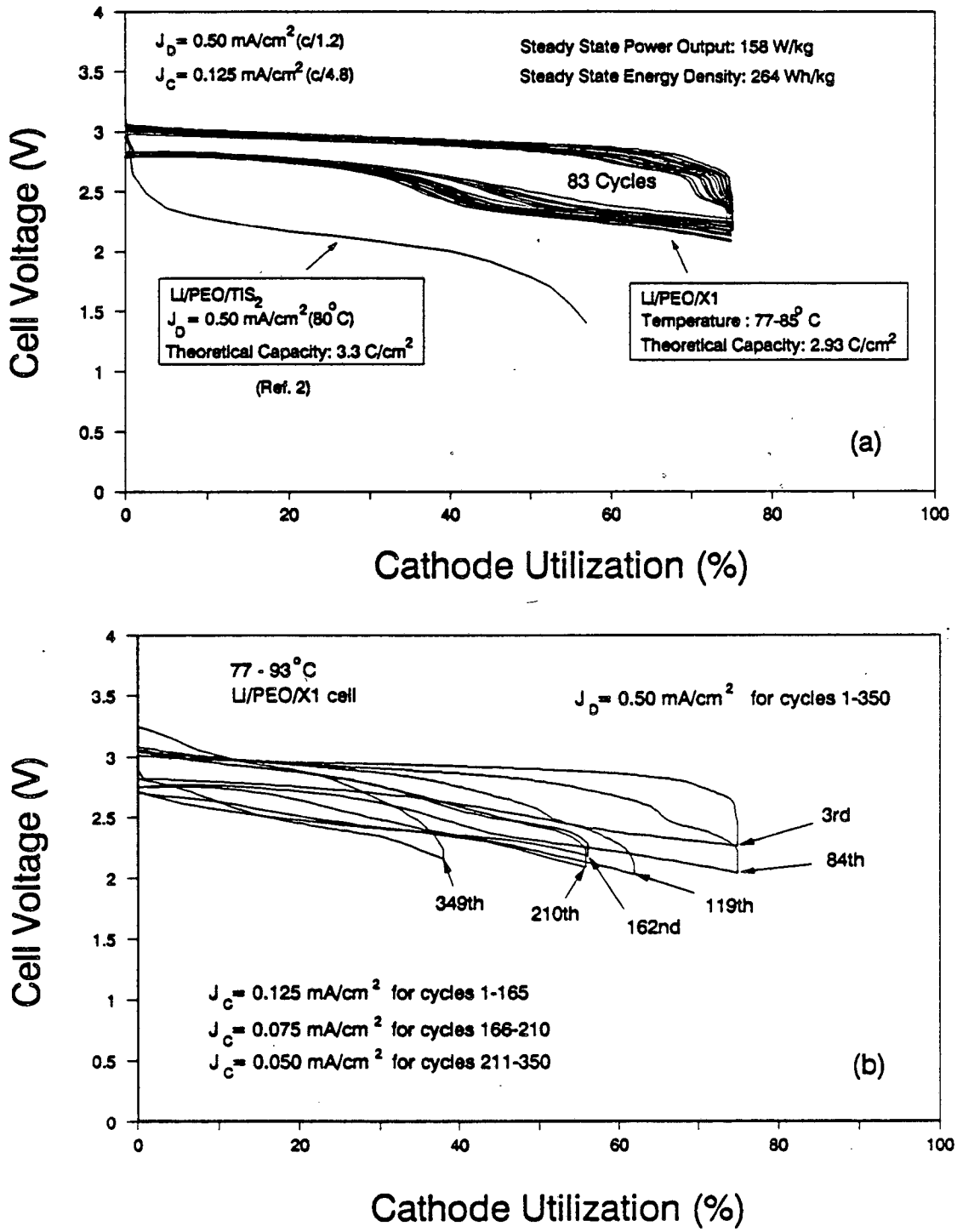


Figure 2. Cycling profile of a Li/p(EO)$_8$LiN(SO$_2$CF$_3$)$_2$/X1 cell.

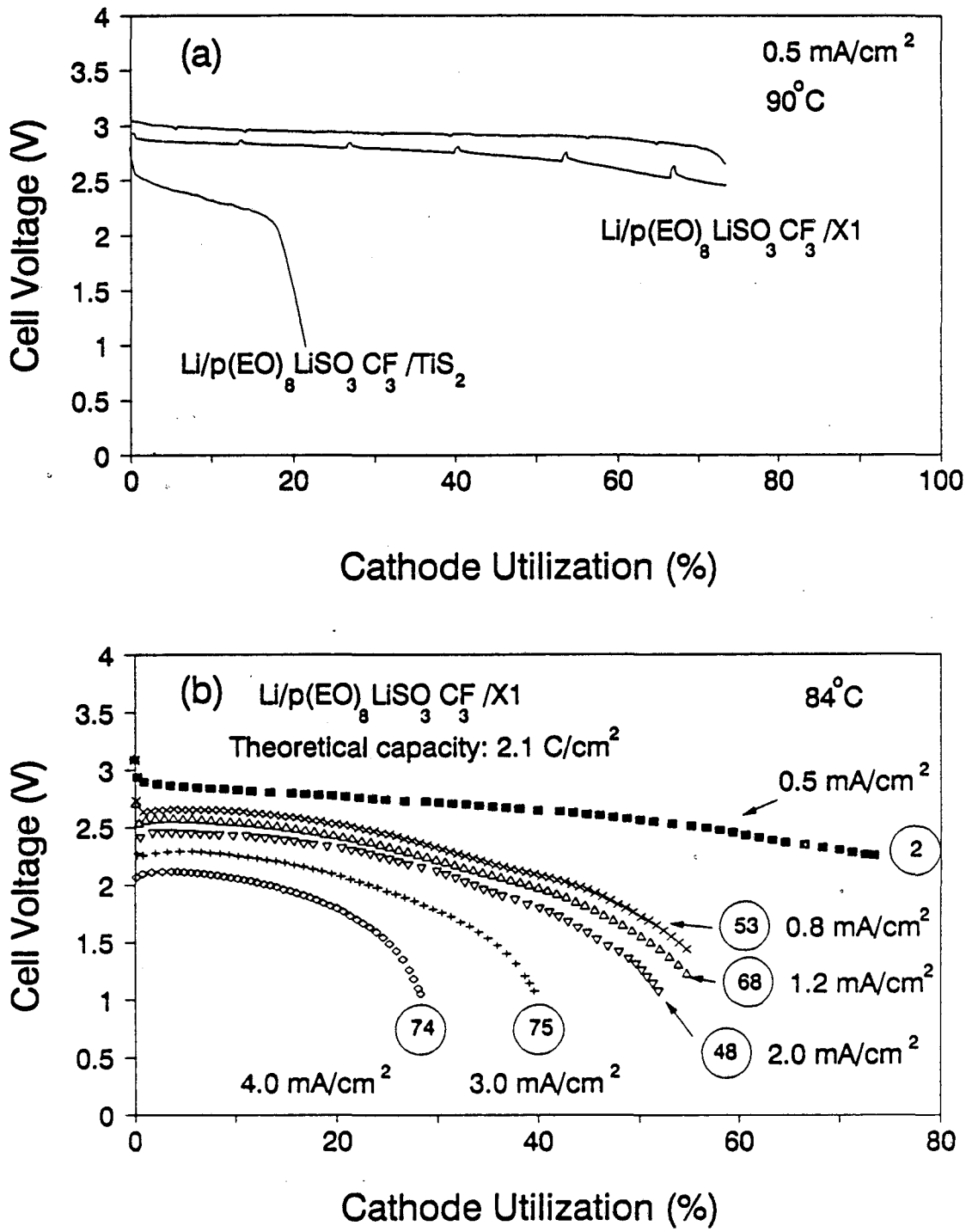
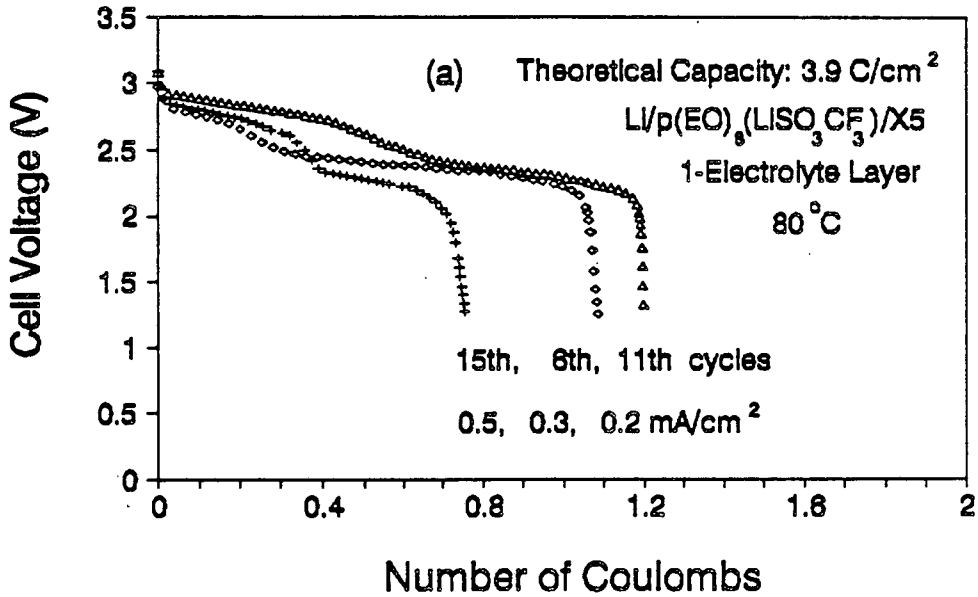


Figure 3. Cathode utilization and rate capability.



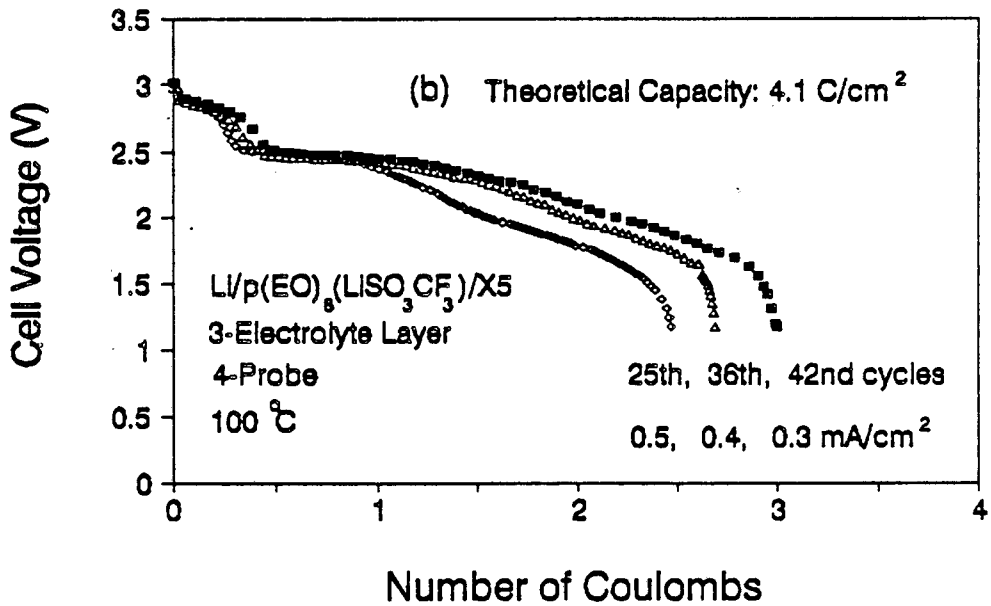
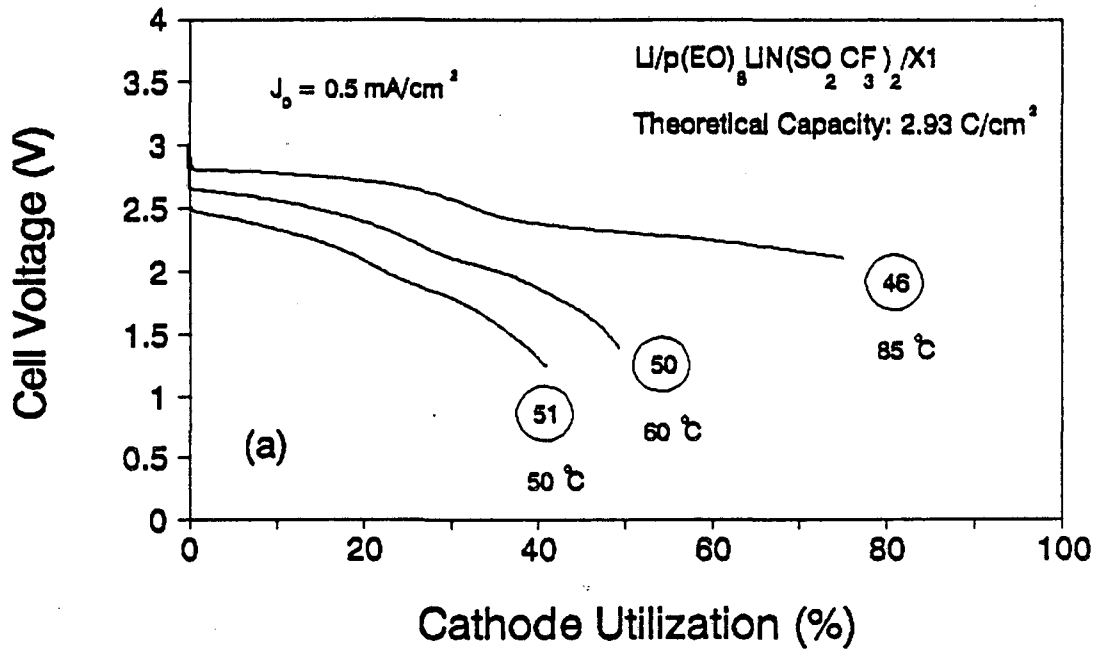


Figure 4. Performance of LI/PEO/X5 cells (a) at 80 °C and (b) at 100 °C.



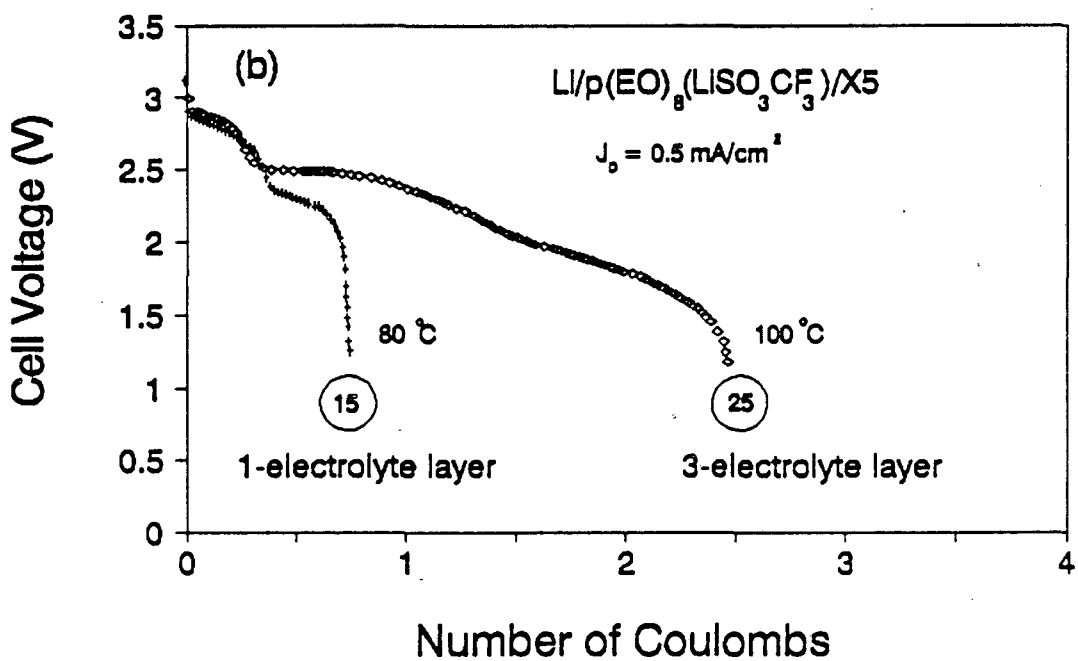


Figure 5. Temperature dependence of cells using (a) linear polymers (X1) and (b) cross-linked polymers (X5).

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