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# ELECTROCHEMICAL INVESTIGATIONS OF NOVEL SOLID REDOX POLYMERIZATION ELECTRODES

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## Abstract

Electrochemical investigations of a group of novel solid redox polymerization electrodes, recently discovered in our laboratory, indicate that these materials are excellent candidates for all-solid-state, thin-film, energy-storage systems. Some of the advantages offered by the batteries based on these solid cathodes include high energy density and rate capability, extensive utilization of cathode capacity, ease of fabrication, low cost, and superior reliability and safety. In addition, these materials are reversible to lithium and sodium (as well as many alkaline earth and transition metals), allowing for a much greater choice of anode materials, in stark contrast to cells based on analogous intercalation compounds. Further, and in particular, a great advantage of redox polymerization electrodes is the ability to alter the physical, chemical, and electrochemical properties of these materials in a very predictable manner through manipulation of various functional groups, electron-withdrawing heteroatoms, and the molecular architecture.

## 1. Introduction

The elegance of all-solid-state batteries as a means of energy storage has been well recognized (1). The use of polymeric electrolyte as a means of fabricating thin-film solid-state batteries has been pursued by a number of groups (1). The attractive properties of such solid-state cells include high energy density, high reliability, superior shelf life, and excellent electrochemical integrity of the electrolyte/electrode interface

(2). The rationale for using intercalation compounds as cathodes includes relatively low equivalent weights, high reversibility towards lithium insertion, and lack of phase nucleation (pure diffusion of guest ions in the host lattice) during charge/discharge. Among the drawbacks of batteries based on intercalation compounds, however, are their low power capability and low utilization of cathode capacity, particularly at ambient temperatures. It has generally been claimed in the literature that the low observed rate capability of these cells is due to insufficient conductivity of the polymeric electrolyte (transport of  $\text{Li}^+$  in the composite cathode was assumed to be sufficiently fast). Accordingly, many researchers have concentrated on improving the ionic conductivity of polymer-based electrolytes. However, dramatic results with a novel class of solid redox polymerization electrodes (SRPE's), recently discovered in our laboratory, have suggested that the transport properties and electrode kinetics of the cathodes contribute significantly to the overall performance of these solid-state cells, particularly at temperatures above the  $T_g$  of the electrolyte.

Electrochemical properties of the novel class of solid redox polymerization electrodes were characterized in this laboratory to evaluate the viability of using these materials as cathodes for all-solid-state thin-film batteries.

## 2. Experimental

Synthesis of the solid redox polymerization electrodes will be described in detail elsewhere (3). Anhydrous solvents acetonitrile, chloroform, tetrahydrofuran, and crystalline polyethylene oxide (PEO) of various molecular weights ( $3 \times 10^5$ ,  $9 \times 10^5$ ,  $4 \times 10^6$ ,  $5 \times 10^6$ ) were obtained from Aldrich and used as received. Battery grade lithium foil (with thickness of  $125 \mu\text{m}$ ) was obtained from Lithco Co. and stored in an argon atmosphere dry box.

Thin films of PEO-based electrolytes (10 to  $100 \mu\text{m}$ ) were cast from mixtures of a solution of PEO in acetonitrile and a solution of appropriate lithium salts (for lithium cells) or sodium salts (for sodium cells) in the solvent. Thin films of SRPE cathodes (6 to  $15 \text{ mg/cm}^2$ ) with surface capacities of 1 to  $6 \text{ C/cm}^2$  were cast from solutions of PEO and redox polymers (with or without electrolyte salts) in an appropriate solvent or mixed solvents with dispersed carbon black. The solvent was evaporated under vacuum and the thin film complex electrolytes or composite cathodes were subsequently dried under vacuum at  $50^\circ\text{C}$  for 2 days and then kept under vacuum.

All-solid-state, thin film, alkali metal/SRPE cells were constructed by sandwiching a polymeric electrolyte between a thin film cathode and a thin foil of alkali metal.

**Na/ $\beta$ "-alumina/SRPE Cells:** Sodium  $\beta$ "-alumina disks (from Ceramtec) were first chemically etched with phosphoric acid at 150°C for 20 minutes, followed by ultrasonic cleaning in methanol, then baked at 900°C to drive off any trace amount of water, and finally glass-sealed onto  $\alpha$ -alumina tubes at 750 °C and annealed at 530 °C. Reagent grade sodium was treated with sodium oxide at 350°C to remove calcium and then scavenged with titanium sponge at 350-400°C to remove oxygen. The purified molten sodium was then electrochemically filled into the  $\alpha$ -alumina tube through the  $\beta$ "-alumina disk to ensure that the sodium was ultra-pure and the Na/ $\beta$ "-alumina interface was well wetted. Before assembly of each Na/ $\beta$ "-alumina/SRPE cell, the sodium electrode and the  $\beta$ "-alumina disk were well conditioned in molten sodium and their electrochemical behavior was completely characterized in a Na/ $\beta$ "-alumina/Na cell.

Since the Na/ $\beta$ "-alumina interface is both stable and well characterized, the use of a Na/ $\beta$ "-alumina/SRPE cell eliminates complications introduced by the anode/electrolyte interface and hence isolates the performance of the solid redox polymerization cathodes ( $\beta$ "/PEO interface was assumed to be stable). In addition, comparison of the performance of Na/PEO/SRPE cells and Na/ $\beta$ "-alumina/SRPE cells not only allows estimation of the stability of the Na/PEO interface but also provides information on  $\text{-SRS-}$  transport through the PEO-based electrolyte ( $\beta$ "-alumina is a cation selective electrolyte).

Battery performance was evaluated using controlled current techniques. Cells having SRPE cathodes were galvanostatically controlled by an IBM-PC/AT computer interfaced with a DT2801A data translation board and a PAR 273 Potentiostat/Galvanostat using a program written in ASYST (4). The measured cell current, closed-cell voltage (CCV), number of coulombs passed, and cell temperature were simultaneously monitored and acquired by the computer. In addition, open-cell voltages (OCV) were periodically monitored by the computer during charging and discharging by transient termination of the cell current (4). Furthermore, pulse polarization techniques (5) have been successfully applied to estimate cell internal resistance, electrode kinetics, and transport properties.

### 3. Electrochemical Properties

#### 3.1. Stability, reversibility and cyclability

Cyclic voltammetric studies have shown that the redox behavior of these macromolecular redox materials is electrochemically reversible, similar to the analogous organodisulfides (6). However, the stability and cyclability of the all-

solid-state cells using redox polymers with PEO-based electrolytes is much better than that of the cells using organodisulfides dissolved in nonaqueous organic solvents. The instability of the latter system often resulted from complications brought about by liquid solvents (12).

### **(1) Polymers containing carbon-sulfur bonds (-C-S-S-C-)**

Representative polymers with carbon-sulfur bonds are derived from the polymerization of dimercapto dithiazole (X1) and trithiocyanuric acid (X5). The cycling profile and charge/discharge curves of a Na/ $\beta$ "-alumina/X1 cell are shown in Figure 1. This cell was continuously cycled at various discharge/charge rates at temperatures from 80 to 130 °C for 32 cycles. Shown in Figure 2 are several cycling curves of a Na/ $\beta$ "/X5 cell at temperatures from 110 to 130°C. As is evident from Figure 2, there was very little deterioration in performance for both cells (even under abusive cell polarization) with cycling. The performance of these cells indicates that the cathode materials based on -C-S-S-C- monomers are both electrochemically reversible and cyclable.

In addition, the absence of visible deterioration in performance of cells cycled at temperatures from ambient to 145°C indicates that the thermal stabilities of these SRPE materials are quite good in this temperature range.

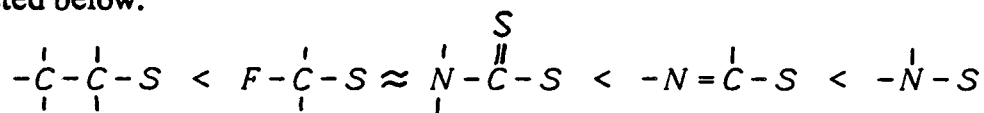
### **(2) Polymers containing nitrogen-sulfur bonds (-N-S-S-N-)**

The polymers with nitrogen-sulfur bonds which have been evaluated include X2, X3, X4, and X6. The synthesis of these materials will be described in a future publication (3). Observed performance of several cells based on these polymers have shown very good rate capability. However, there was apparent degradation in cell performance after a small number of cycles; this may be due to the presence of impurities as the synthetic approach to these materials is still being refined. The rapid electrode kinetics observed for these electrodes imply they may be useful for high power applications. However, further investigations are necessary to elucidate the stability of purified materials.

## **3.2. Electrode kinetics**

The exploration of various organodisulfides and organosulfur redox polymers through impedance spectroscopy (10) and pulse polarization measurements (5) have shown that the electrode kinetics of these materials depend critically on substituents attached to the polymer backbone. Certain electron withdrawing heteroatoms, such

as N, S, and F, greatly accelerate the electrode kinetics, as reported previously in the kinetic studies of organodisulfides (7). The standard rate constant for the redox reaction of the materials evaluated is a strong function of the atoms in the  $\alpha$  and  $\beta$  positions adjacent to the sulfur-sulfur linkage and generally increases in the order as listed below:



It has been observed that the electrode kinetics of the macromolecular organosulfur polymers follows the same trends as the small-molecular organodisulfides.

### 3.3. Ionic transport and cathode utilization

The transport properties of complex or composite cathodes (SRPE + polymer electrolyte) is largely controlled by the diffusion of cations through the polymer electrolytes.

Characterization of Na/ $\beta$ "-alumina/SRPE cells with cathodes modified by electrolyte salts of different concentration indicated that small amounts of appropriate electrolyte salts enhanced ionic transport and hence the rate capability, while excessive salt led to saturation and significant polarization on discharge, and consequently reduced the percentage of cathode utilization. In addition, 4-probe polarization measurements on Li/PEO/SRPE cells indicated that ionic transport is faster in electrodes based on linear organosulfur polymers than in electrodes composed of highly cross-linked polymers.

### 3.4. Rate capability

Rate capability is determined by both electrode kinetics and transport properties. Slow electrode kinetics are manifested by the instantaneous polarization of the positive electrode as a function of current density, whereas slow mass transport is evident in the time-dependant polarization of the electrode (which also is a function of current density; particularly at currents approaching the limiting current). Since the ionic conductivity of  $\beta$ "-alumina electrolyte is sufficiently high, ohmic losses across the electrolyte were insignificant at the current densities studied. Consequently, polarization losses seen in the voltage vs. capacity curves in Figure 3 are dominated by mass transport and electrode kinetics in the composite cathodes.



Shown in Figure 3 are several discharge/charge curves for a Na/beta/X1 cell at 130 °C. The spikes seen in the Figures 3 (a) and (b) show where the computer turned off the cell current to approximate the open cell voltage of the cell as a function of state of charge. The rate capability displayed here, in fact, exceeds the limiting performance predicted for solid-state cathodes based on intercalation compounds (11). This supports our observations that transport of Na<sup>+</sup> in this cathode material is much faster than Li<sup>+</sup> in composite cathodes based on intercalation compounds. Accordingly, SRPE-based cells have much higher rate capabilities than the corresponding systems using intercalation cathodes (13).

Figure 4 shows the trends of the rate capability over the temperature range from 110°C to 130°C. This observation indicated that either the activation energy for Na<sup>+</sup> transport in the composite cathode materials is fairly high or the solubility of sodium salts in the composite cathode decreases considerably as temperature decreases.

Shown in Figure 5 are some representative discharge curves for Na/β"/X5 cells at 130°C. Although the demonstrated rate capability is not as high as that of Na/β"/X1 cells, the discharge curves are very encouraging. Due to the exceptionally low equivalent weight of the X5 polymers (58g/equiv.), solid-state batteries based on this polymer should be useful for very high energy density, medium rate, applications.

### 3.5. Freedom in selection of anode

The performance of the Na/SRPE cells clearly demonstrated that the organosulfur redox polymers are reversible with respect to sodium, in stark contrast to most intercalation compounds which show good reversibility only with respect to lithium. The advantages of sodium electrodes as opposed to lithium electrodes for energy storage are two-fold: (i) sodium is more economical than lithium and (ii) sodium transport is faster than lithium in most polymer-based electrolytes (8), implying higher rate capability. The detailed description of all-solid-state, thin-film sodium cells based on solid redox polymerization electrodes will be addressed in a subsequent communication (9).

In principal, a wide diversity of electro-negative materials, including alkali metals, alkaline earth, and transition metals, can be used as negative electrodes for batteries based on SRPE materials.

#### 4. Conclusions

The unique capability of organosulfur redox polymerization electrodes to undergo reversible polymerization-depolymerization reactions with electron-transfer has been successfully used for advanced energy storage. Electrochemical investigations of the redox polymers further indicate that the molecular design of a diverse spectrum of high performance redox polymerization electrodes can be accomplished through modifying the molecular architecture and by appropriate choice of functional groups and electron-drawing heteroatoms.

Solid redox polymerization electrodes are unique cathode materials for all-solid-state, thin-film, energy-storage systems. The high gravimetric and volumetric energy densities attainable with SRPE materials makes them very attractive for energy storage applications. Furthermore, the fast mass transport and electrode kinetics demonstrated by SRPE's promise superior rate capability, while the demonstrated thermal and chemical stability of these electrodes should result in reliable solid-state cells. Additional advantages offered by these cathodes include ease of fabrication, low cost, and excellent electrochemical reversibility and cyclability (implying long service life). Also, their demonstrated reversibility with respect to sodium metal (as well as many other metals) makes it possible to construct solid-state thin-film sodium batteries, as well as a broad spectrum of cells having various negative electrodes.

#### Acknowledgment

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Table 1. Organosulfur Redox Polymers Evaluated

Notation	Name	Formula	EW*	OCV**
X1	dimercapto dithiazole polymer	$\left( \begin{array}{c} \text{N} - \text{N} \\ \parallel \quad \parallel \\ -\text{S} - \text{C} \quad \text{C} - \text{S}- \\ \quad \quad \quad   \\ \quad \quad \quad \text{S} \end{array} \right)_n$	74	2.81
X2	dimethyl ethylenediamine polymer	$\left( -\text{S} - \overset{\text{CH}_3}{\underset{ }{\text{N}}} \text{CH}_2 \text{CH}_2 \overset{\text{CH}_3}{\underset{ }{\text{N}}} - \text{S} - \right)_n$	75	2.56
X3	ethylenediamine polymer	$\left( \begin{array}{c} -\text{S} \quad \quad \quad \text{S}- \\ \diagdown \quad \quad \diagup \\ \text{NCH}_2 \text{CH}_2 \text{N} \\ \diagup \quad \quad \diagdown \\ -\text{S} \quad \quad \quad \text{S}- \end{array} \right)_n$	46	2.48
X4	polyethylene imine derivative	$\left( \begin{array}{c} -\text{CH}_2 \text{NCH}_2 - \\ \quad \quad \quad   \\ \quad \quad \quad \text{S} \\ \quad \quad \quad   \\ \quad \quad \quad \text{S} \\ \quad \quad \quad   \\ -\text{CH}_2 \text{NCH}_2 - \end{array} \right)_n$	74	2.61
X5	trithiocyanuric acid polymer	$\left( \begin{array}{c} \text{S} \\   \\ \text{C} \\ \diagdown \quad \quad \diagup \\ \text{N} \quad \quad \quad \text{N} \\ \diagup \quad \quad \diagdown \\ -\text{S} - \text{C} \quad \quad \text{C} - \text{S}- \\ \quad \quad \quad \diagdown \quad \quad \diagup \\ \quad \quad \quad \text{N} \end{array} \right)_n$	58	2.82
X6	piperazine polymer	$\left( -\text{S} - \text{N} \begin{array}{c} \diagup \quad \quad \diagdown \\ \diagdown \quad \quad \diagup \end{array} \text{N} - \text{S} - \right)_n$	74	2.56

\* Equivalent weight of the redox polymers, X

\*\* Open cell voltage of Na/ $\beta^{\text{Al}}\text{-alumina}$ /X cells

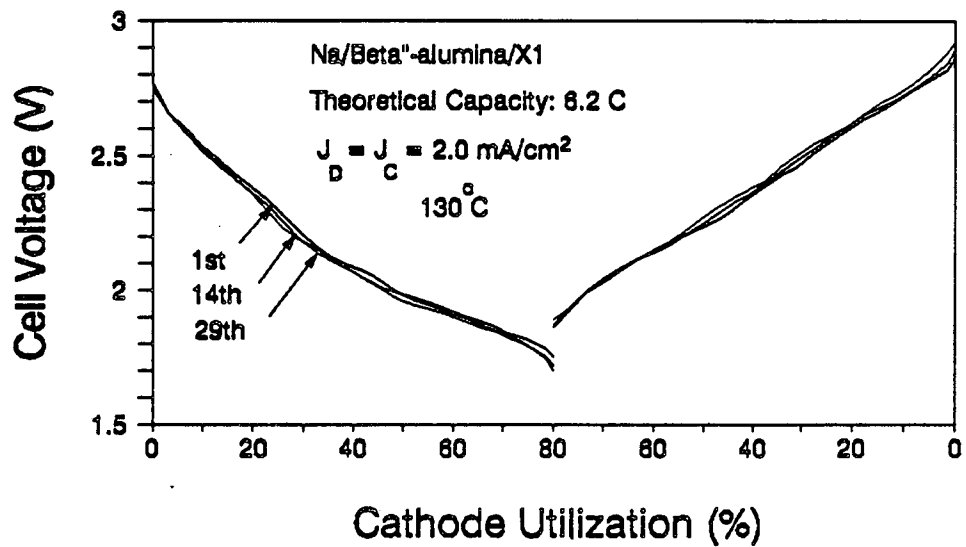


Figure 1. The 1st, 14th, and 29th cycling curves of a Na/beta''-alumina/X1 cell

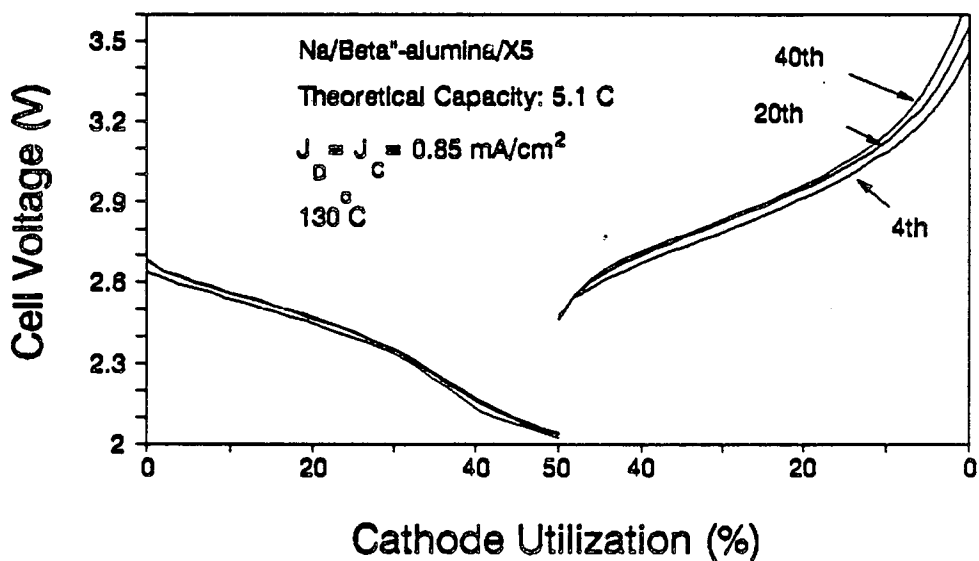


Figure 2. The 4th, 20th, and 40th cycling curves of a Na/beta''-alumina/X5 cell

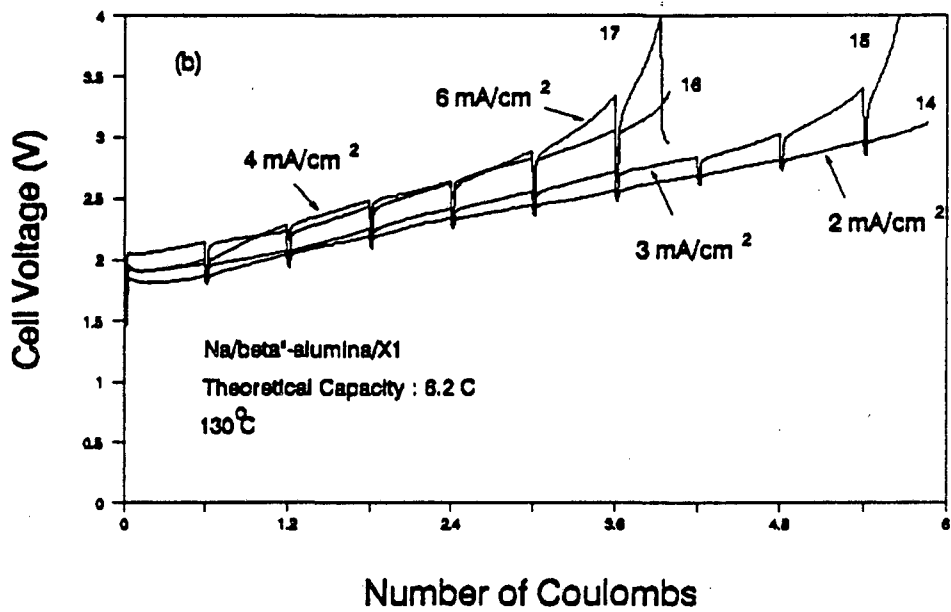
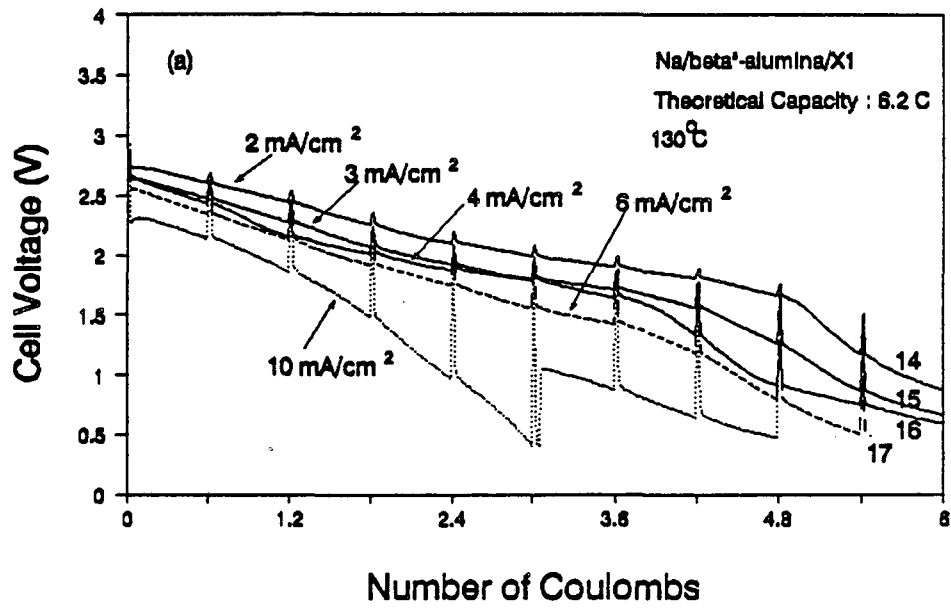


Figure 3. (a) Discharge and (b) recharge curves of a Na/beta'-alumina/X1 cell.  
The numbers by the curves represent the cycle numbers.

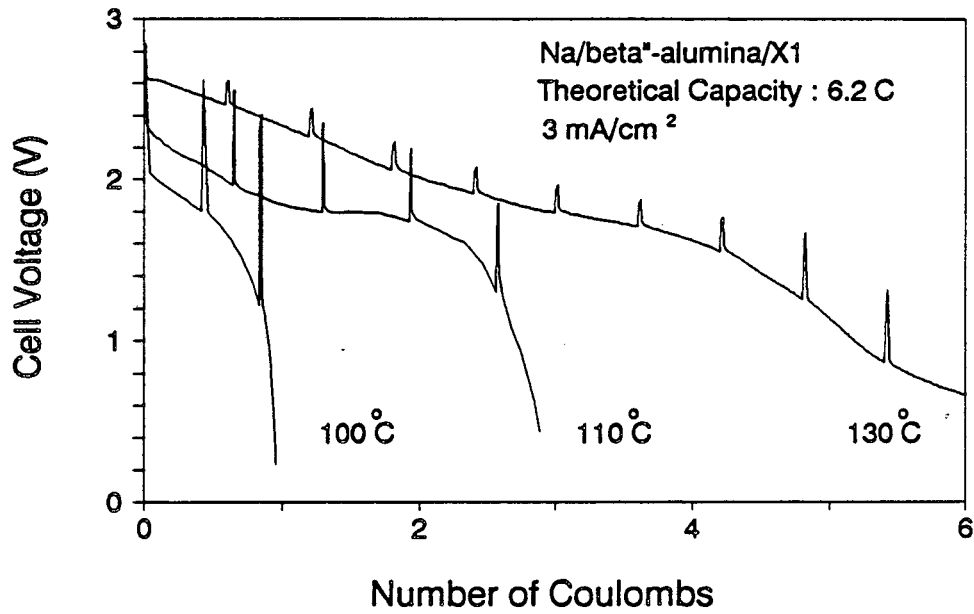


Figure 4. Discharge curves of a Na/beta\*/X1 cell at different temperatures.

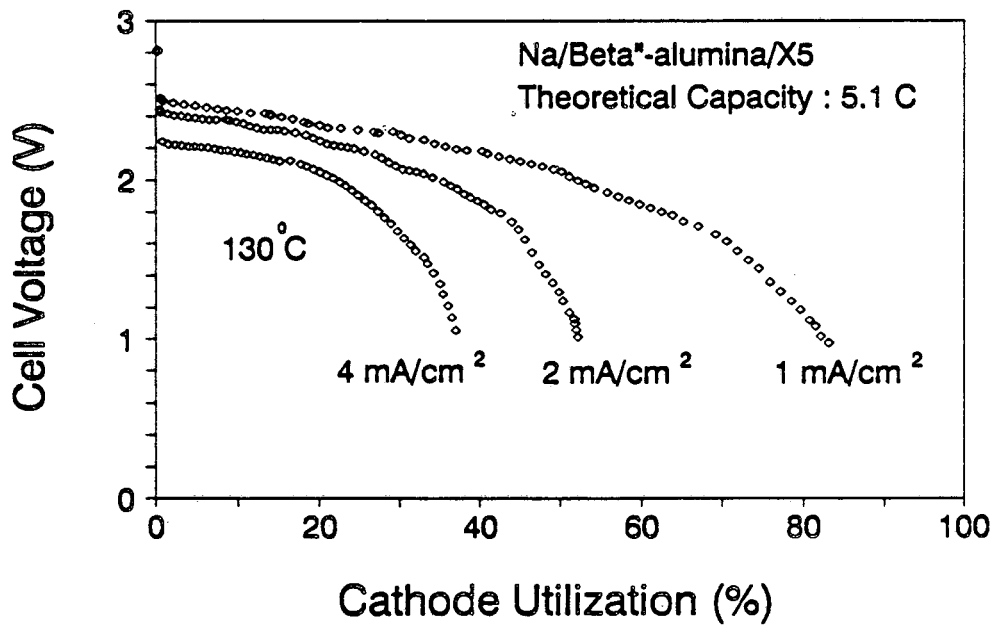


Figure 5. Discharge curves of a Na/beta\*-alumina/X5 cell at 130°C.

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