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CORROSION PHENOMENA DURING OVERCHARGE IN POLYMER
ELECTROLYTE CELLS(U) MINNESOTA UNIV MINNEAPOLIS

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CORROSION RESEARCH CENTER M Z MUNCHI ET AL. 19 MAY 88

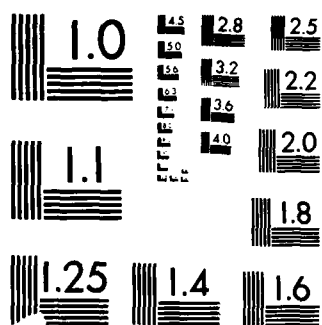
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Corrosion Phenomena During Overcharge
in Polymer Electrolyte Cells

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ABSTRACT

The corrosion behavior of the polymer electrolyte cell, $\text{Li} | (\text{PEO})_8 \cdot \text{LiCF}_3\text{SO}_3 | \text{V}_6\text{O}_{13}$, has been investigated using various surface analytical techniques. The results indicate that under normal cycling conditions, the cell components are perfectly intact with no evidence of any corrosion. However, cells placed on overcharge for prolonged periods showed an inability to discharge.

1. INTRODUCTION

Ionically conducting polymers formed by the reaction of polyethylene oxide (PEO) and various alkali metal salts were first discovered by Fenton and co-workers in 1973[1]. The subsequent use of this material as a solid electrolyte in solid state batteries has aroused considerable interest worldwide[2-6]. Most of the studies have been directed towards secondary batteries utilizing lithium anodes and insertion cathodes. One of the most widely described systems is



Because of the low conductivity of the electrolyte, the cell needs to be operated between 80 and 140°C.

The feasibility of this system has been demonstrated in a variety of research cells. Recent work has shown, however, that the cycling efficiency of these cells deteriorates rapidly during overcharge [7]. For cells utilizing thick cathodes (50-75 μm), overcharge was most detrimental since the cell voltage reached about +5V, sufficient to degrade the polymer electrolyte. This severe degradation was indeed shown by both optical and scanning electron microscopy. In addition, the increased heat generated during the overcharge reaction also resulted in cathode instability. This was recognized not only from physical observation but also by EDAX which indicated vanadium in the electrolyte. This was interpreted as due to a physical migration rather than further oxidation of the vanadium oxide particles. The present paper examines the behavior of thin cathode (10-15 μm) cells during overcharge.

2. EXPERIMENTAL

2.1 Preparation of the Cell Material

All cell fabrication and materials handling have been described previously [8]. The only deviation being the cathode film thickness which were 10-15 μ m.

2.2 Cell Testing

The cycling of all cells was carried out at 100°C in the glove box. The theoretical capacity of the cathode was 1.5 mAh, based on the assumption that 8 Li ions intercalates into the V_6O_{13} unit structure. A constant current discharge (C/10 rate) and a constant voltage charge through a current limiting resistor were used for all cells.

Once the cell capacity reached a stable value with cycling, it was placed on overcharge at C/10 constant current above the nominal open-circuit voltage of 3.2V in the manner described previously[7]. A plateau in the V-t curve was generally observed and at this point the cell would be placed at constant potential and the current-time behavior monitored. After a given time interval the cell would then be discharged at the C/10 rate to obtain the final capacity.

2.3 Microscopy Examination

Post-mortem analysis was made on cells in the charged state using optical, scanning electron and auger microscopy. The cells were dismantled in the dry room atmosphere.

Optical microscopy was carried out using an Olympus SZ III optical microscope equipped with a polaroid camera.

Scanning electron microscopy was carried out using a JEOL 840II microscope. Low accelerating voltages ($\sim 20\text{kV}$) were used in order to avoid beam damage or sample charging.

Auger microscopy was carried out on the cell cross-section using a Scanning Auger Microprobe PHI 595. In this case the accelerating voltage was 3kV .

3. Results and Discussion

Figure 1 shows the cycling sequences for the polymer electrolyte cells. Figure 1a depicts a typical constant current discharge followed by a typical constant voltage charge (Figure 1b) through a current limiting resistor. The constant potential is maintained across the fixed resistor and the cell such that as the cell charges, the voltage drop across it increases with a corresponding decrease across the fixed resistor. The current flowing through the cell decreases until the cell is fully charged. Once the cell has attained stabilization in capacity with cycle number and the coulombic efficiency in the final charging cycle has reached close to 100%, the cell is placed on overcharge at the C/10 rate. A voltage-time profile for cell #1 utilizing a thin cathode is shown in Figure 1c. In this case the cell stabilizes at 3.9V . The behavior appears to be quite different from cells utilizing thick cathodes [7] where the cell reached about $+5\text{V}$, sufficient to decompose the electrolyte.

Here the cell potential was constant even after 5h overcharge. The cell was subsequently discharged at the C/10 rate. The capacity was found to be the same as the original capacity. The cell was re-charged and then again placed on overcharge. After stabilizing to a constant potential of 3.9V , the cell was held

at this potential for one day before discharging. The cell capacity was found to be as before. Overcharging the cell at the C-rate resulted in a voltage plateau at 4.65V. After one day at this potential, the open-circuit voltage of the cell was zero.

Post-mortem examination of the cell using optical microscopy showed the electrolyte and cathode to be severely deteriorated. Figure 2 shows a typical section depicting the electrolyte, lithium and cathode. The white fluffy deposits seen previously in overcharged cells[7] were also found to be present in this cell. EDAX analysis indicated the S content to be considerably higher in this area than in other areas, thus suggesting a strong possibility of Li salt. These areas are more clearly seen in the micrograph of Figure 3. Figure 4 shows a cross-section of this cell depicting mainly the electrolyte and cathode with some remains of the Li and it appears that the deposition of the salt occurs at the electrolyte-cathode interface. This seems reasonable since during overcharge, a large portion of the anions (CF_3SO_3^-) are located at this interface and at the potential of PEO degradation, the salt would be expected to precipitate at this cathode-electrolyte boundary. Figure 4 also provides microscopic evidence that the transport number of the lithium cation is not unity; otherwise the salt would be distributed uniformly throughout the electrolyte.

Figure 5 shows an electron micrograph of the cathode after the overcharge. The material appears somewhat fused with a large number of voids. These may have been caused by the PEO degradation from the cathode. A clearer description of this is provided by an electron micrograph of the PEO electrolyte (Figure 6)

after cell degradation. A comparison with the PEO micrograph in the charged state from a normal cycled cell clearly indicates large changes taking place as a result of overcharge (Figure 7).

Elemental analysis of the electrolyte using EDAX indicated the presence of S, Cl, V and Al. Previously [7] it was reported that the presence of Cl originate from impurities in the PEO whereas V is transported as V_6O_{13} particles during the overcharge. At this stage, the detection of Al was presumed to be due to the Al mounting stub in the microscope.

Auger microprobe analysis was made on the electrolyte cross-section for vanadium. Figure 8 shows such a scan indicating vanadium to be present virtually throughout the electrolyte.

In sharp contrast, EDAX examination of the cell components from a normal cycled cell (cell #2) in the charged state revealed only S in the electrolyte and S, and V in the cathode with traces of Cl. The cell was perfectly intact after several cycles. A cross-sectional view of this cell described in an earlier paper [9] showed good adhesion at the anode/electrolyte and electrolyte/cathode interfaces with no cell degradation. Optical and SEM analysis showed the cathode surface to be highly smooth and the electrolyte maintained its original color and integrity. In addition there were no salt deposits at the cathode-electrolyte boundary.

In order to investigate the overcharge phenomena further, subsequent cells were overcharged only at the C/10 rate.

Cell #3 also reached about +4V during the overcharge. After holding for 15 minutes at this potential, the cell was discharged. The capacity was found to be the same as the original capacity. The time interval was subsequently increased to 30 and 45 minutes in which case the cell capacity was again the same. Examination of the cathode and electrolyte layers indicated a few spots of blue areas visible only under the optical microscope. This was originally thought to be Cr emanating from the stainless-steel. However EDAX analysis did not indicate anything other than the normal constituents. Despite this coloration, the cell was fairly well intact with no evidence of deterioration.

Cell #4 behaved in the same way as cell #3. This cell, however, was held for two days at +4V. The cell capacity was not affected and in addition, post-mortem microscopic examination indicated the electrolyte and cathode to be reasonable well adhered to one another. However, the aluminum backing for the cathode was severely corroded and almost depleted. Figure 9 shows an optical micrograph of this surface adhered to the stainless-steel current collector. The remains of the Al appeared extremely brittle.

Although optical microscopy examination of the cathode at the cathode-electrolyte interface showed the surface to be smooth and fairly uniform, the cathode at the cathode-aluminum interface showed large pittings caused probably by the anodic oxidation of the Al (Figure 10).

In addition, the lithium surface also appeared somewhat porous and brittle. The surface was remarkably different from the lithium surfaces previously examined. Figure 11 shows an electron micrograph of such a surface. EDAX

analysis of this surface indicated the presence of Al, Cl, S and V (Figure 12). A Cl x-ray map of this surface revealed that the Cl was situated in localized areas (Figure 13). More remarkable was that the Al was also only present in these same localized clusters (Figure 14). It is well known that Al has a strong affinity for Cl, but the presence of both elements in the same region may just be coincidental.

The microscopic evidence provided from this cell clearly suggest that at the potential of about +4V, the reactions occurring in the cell during overcharge are mainly based on corrosion from the cathode. In addition to the V_6O_{13} migration, the Al backing for the cathode is corroding and migrating to the Li surface. This is supported not only from physical observation of the Al, but also from evidence provided by elemental Al analysis. The results also support the conclusion that at this potential neither the electrolyte nor the cathode undergo degradation. This explains the constancy in the potential-time curves during overcharge whereby a simple steady-state corrosion of the Al and vanadium oxide take place.

In contrast, cells utilizing thick cathodes [7] reach the potential for PEO degradation (-5V), and this reaction appears to dominate the corrosion of the current collector. This is true also for thin cells operating at high rates. In both cases, the IR drop across the cell is sufficiently large to attain about 5V, resulting in electrolyte degradation.

Calculations based on previous data [7] suggest that these polymer electrolyte cells can only withstand about 15-20% of overcharge. This factor

needs to be taken into account when designing a battery consisting of a large array of cells. Not only must the loading capacity of the individual cells be carefully controlled, but also each cell must be carefully monitored for failures which could lead to overcharge (or even overdischarge) of the other cells.

ACKNOWLEDGEMENT

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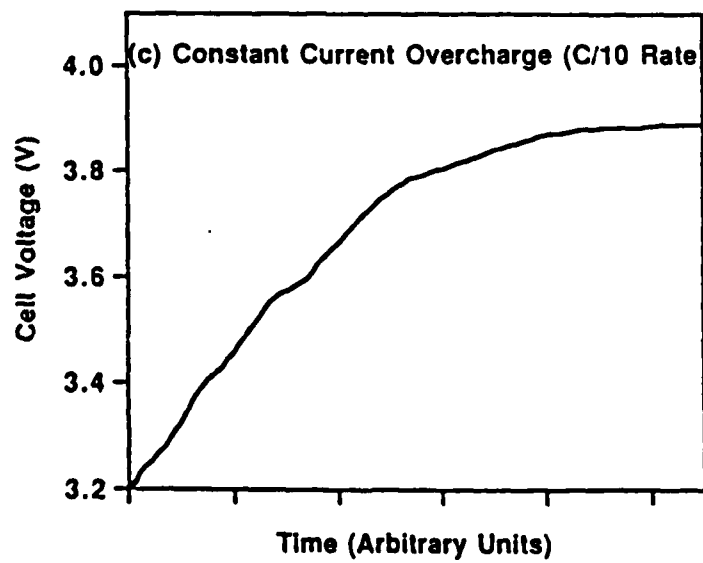
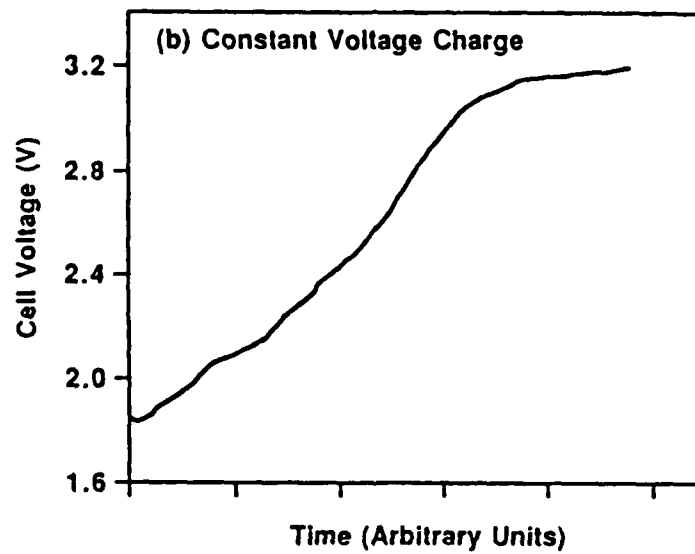
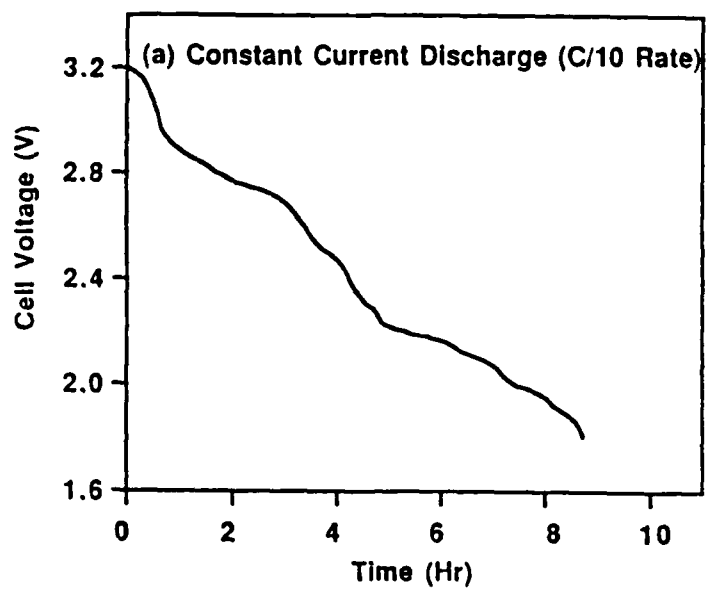


Figure 1. Cycling profiles for the polymer electrolyte cells.

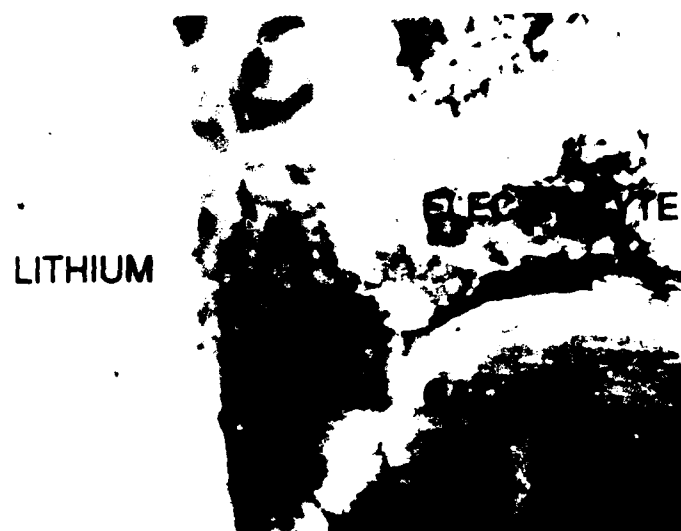


Figure 2. Optical micrograph of the cell components (cell #1) after overcharge.

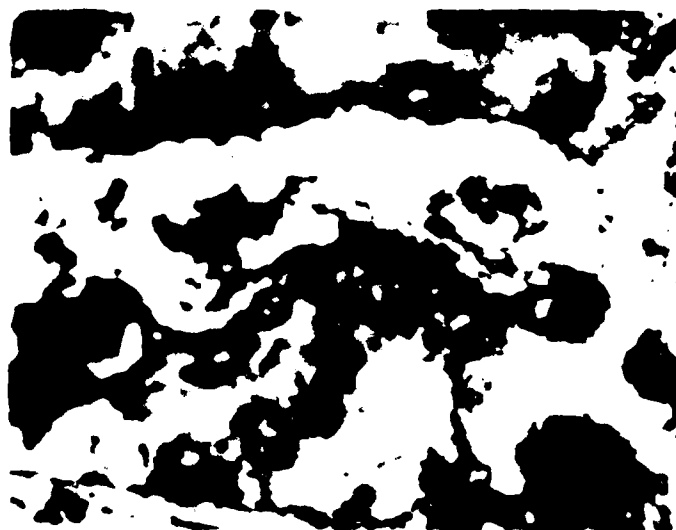


Figure 3. Optical micrograph of the electrolyte (cell #1) at the cathode/electrolyte interface.

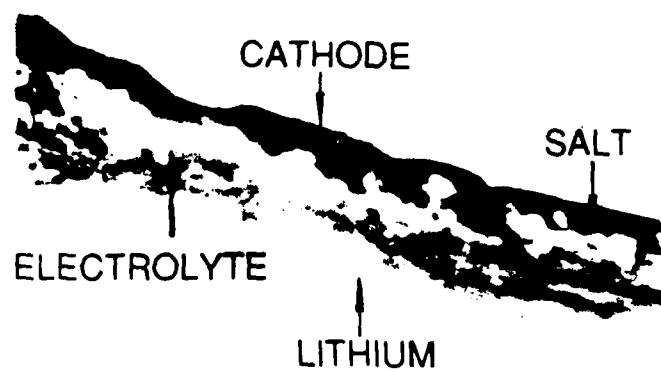


Figure 4. Cross-sectional view of cell #1

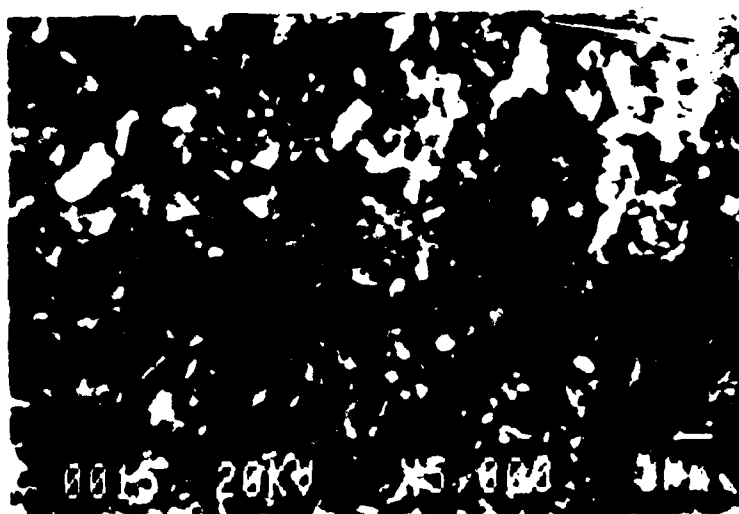


Figure 5. Scanning electron micrograph of the cathode (cell #1) after overcharge.

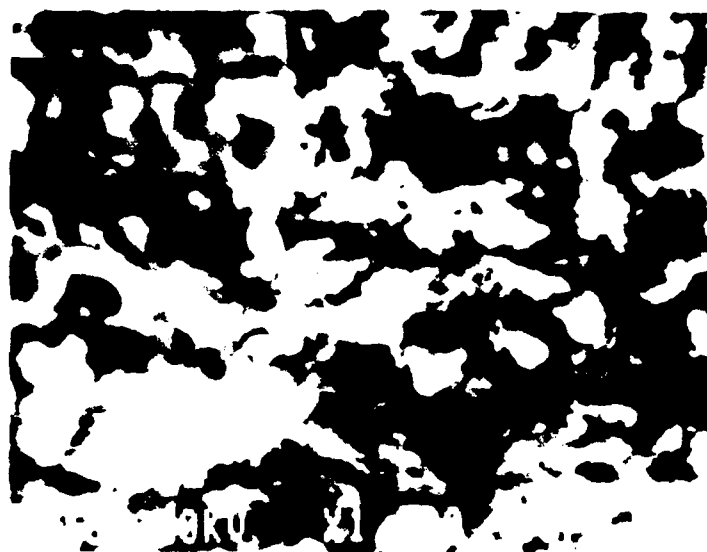


Figure 6. Scanning electron micrograph of the electrolyte (cell #1) after overcharge.

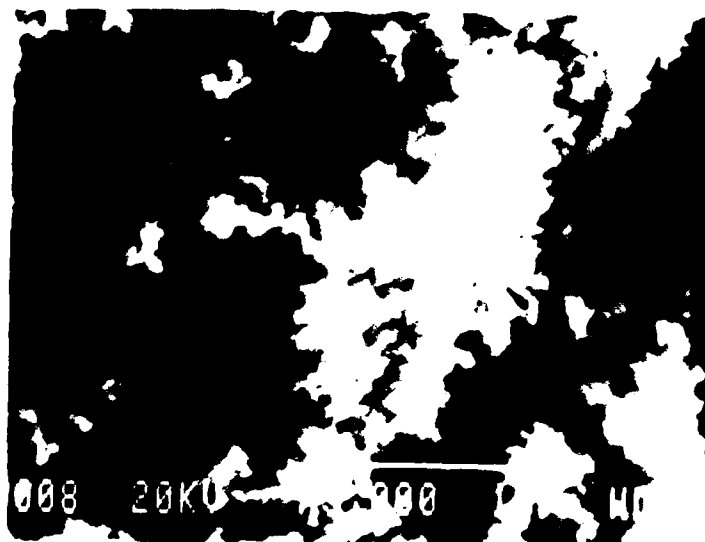


Figure 7. Scanning electron micrograph of the electrode surface after normal charge (ref. 7)

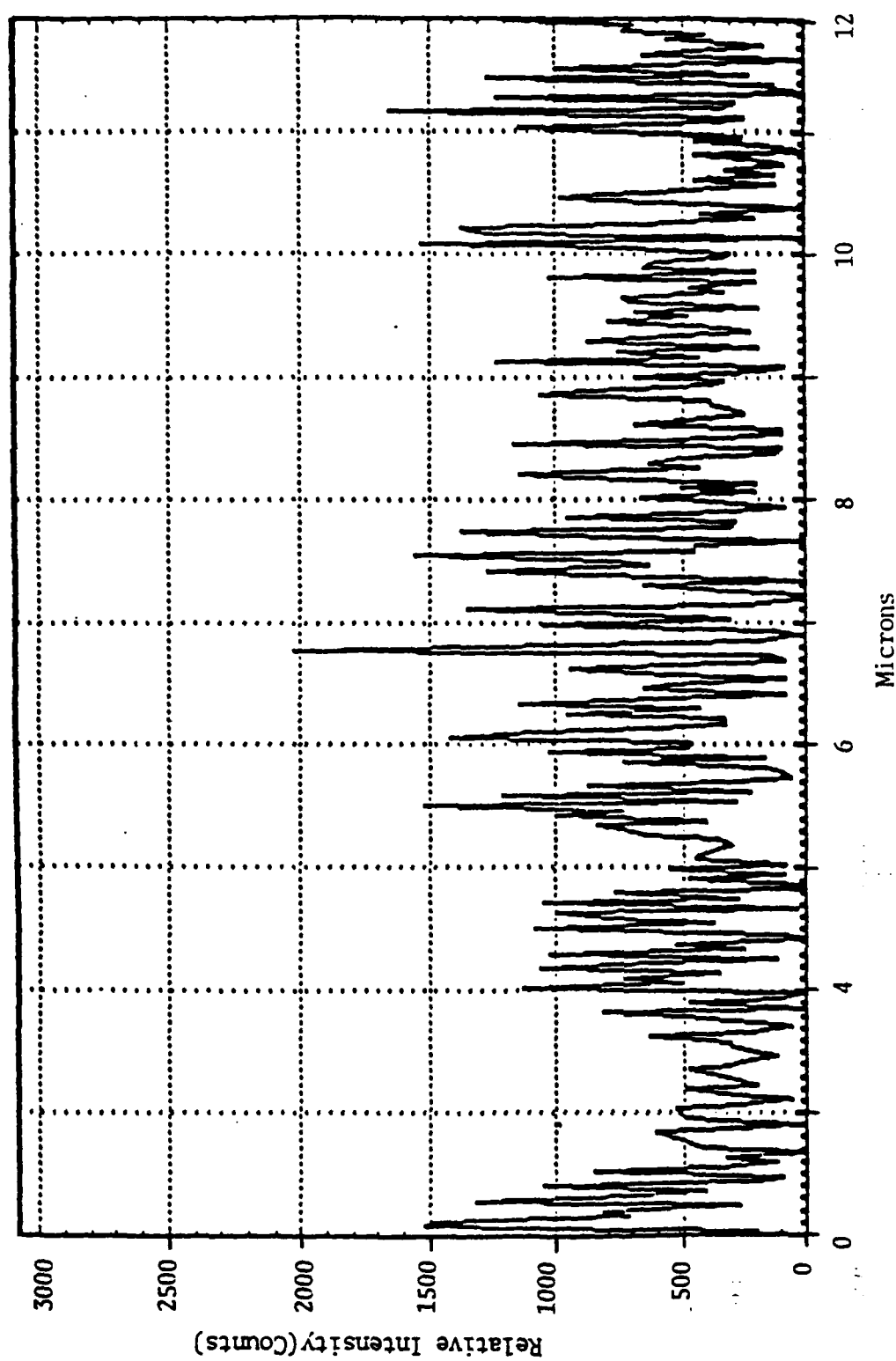


Figure 8. Auger microprobe line scan across the electrolyte cross-section for vanadium.

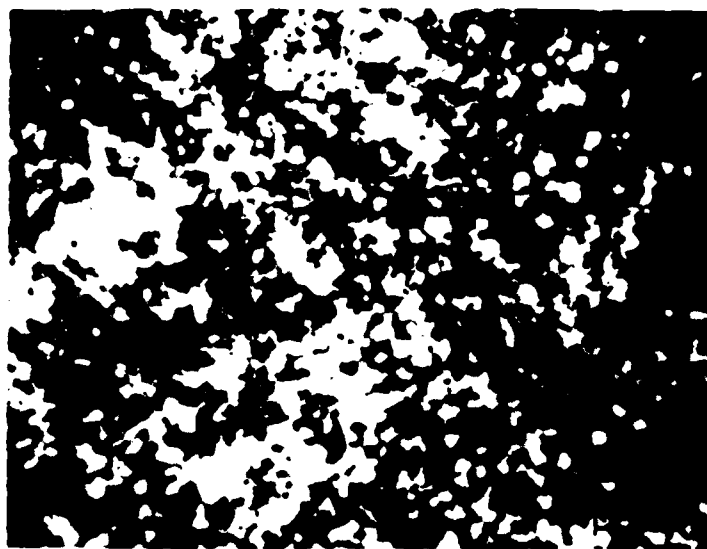


Figure 9. Optical micrograph of the depleted aluminum packing ice #4

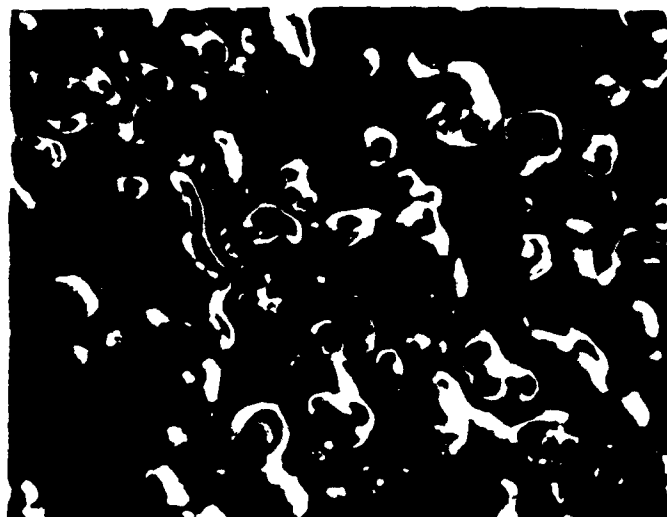


Figure 10. Optical micrograph of the cathode at the cut-off potential of the cell (cell #4).

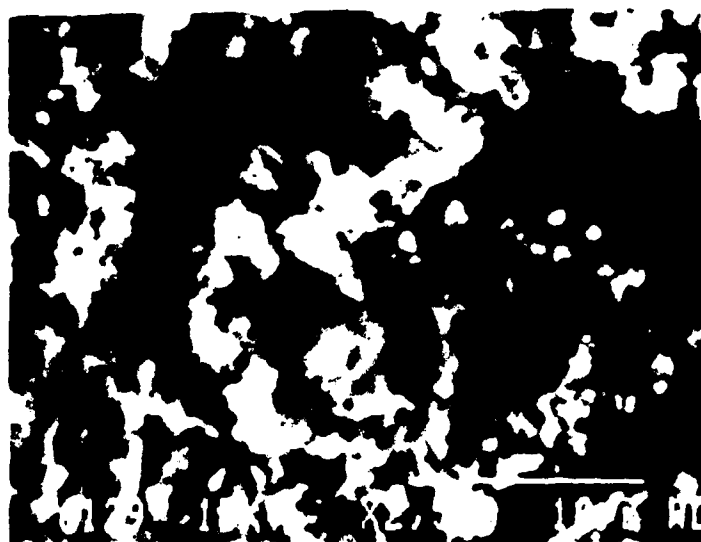


Figure 11. Scanning electron micrograph of the lithium surface (cell #4).

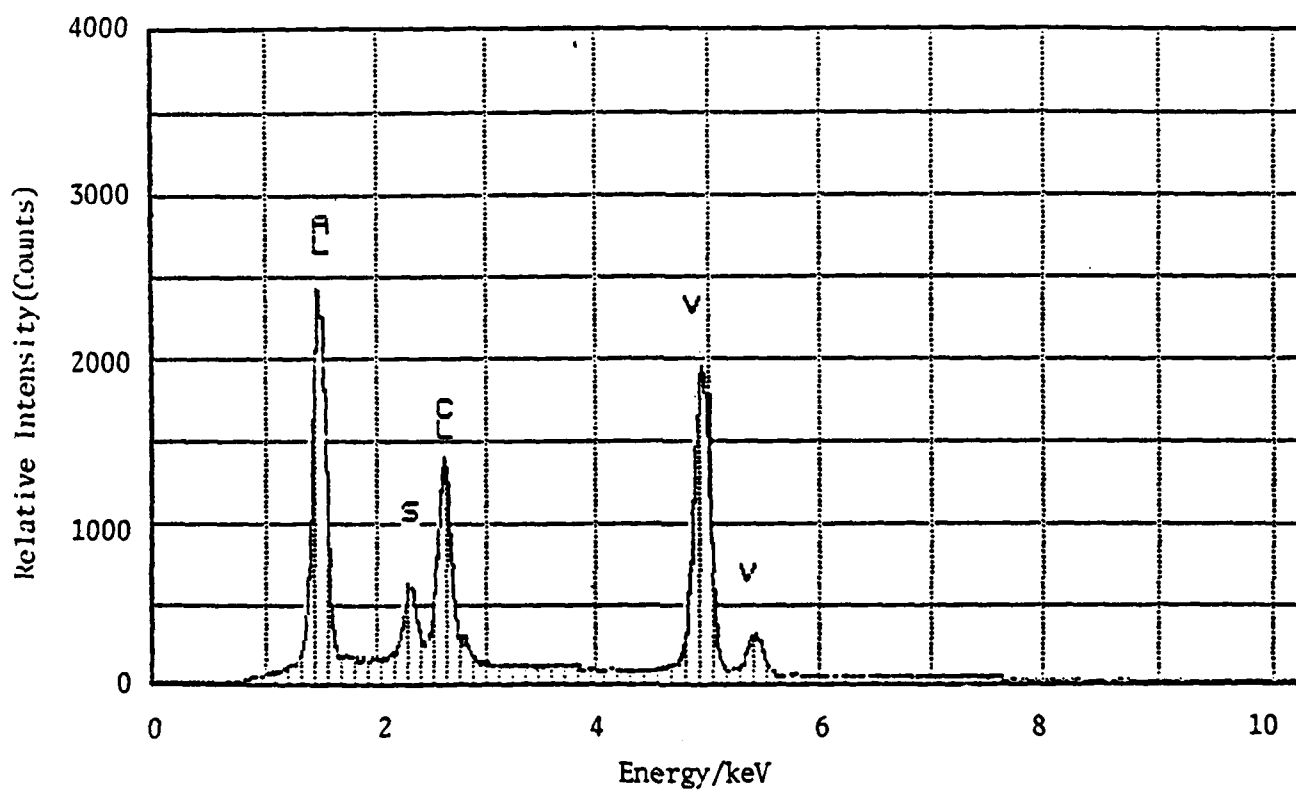


Figure 12. EDAX analysis of the lithium surface (cell # 4).



Figure 13 X - ray mapping of Cl on the lithium surface (cell #4).

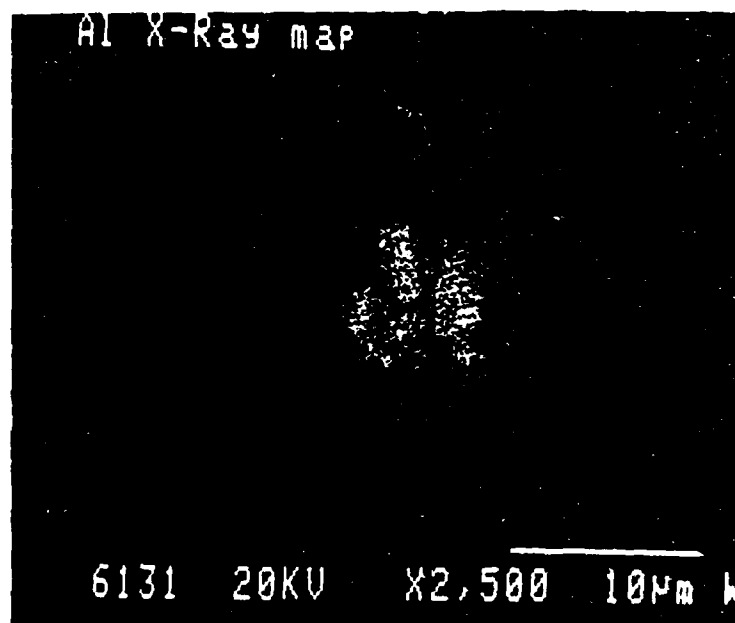


Figure 14. X - ray mapping of Al on the lithium surface (cell #4).

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