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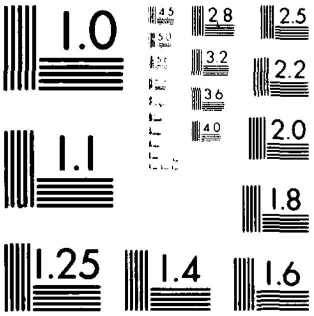

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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

DELET-TR-80-15

THE CHARGE AND DISCHARGE BEHAVIOR OF MOLYBDENUM TRIOXIDE ELECTRODES IN LITHIUM PERCHLORATE-PROPYLENE CARBONATE ELECTROLYTE

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July 1980

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LiClO4

The anodic and cathodic behavior of molybdenum trioxide electrodes in various states of lithiation was investigated in 1M $LiClO_4$-PC electrolytes at room temperature. A comparison was made between the anodic and cathodic rate capabilities of the electrodes. From cycling experiments at various depths of discharge, cycle life data were obtained. Problems observed after deep discharges are discussed.

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THE CHARGE AND DISCHARGE BEHAVIOR OF MOLYBDENUM TRIOXIDE ELECTRODES IN LITHIUM PERCHLORATE-PROPYLENE CARBONATE ELECTROLYTE

INTRODUCTION

In previous reports[1,2] a comparison was made between lithium intercalation compounds of transition metal oxides and chalcogenides, which were considered as potential candidates for the active positive plate material in rechargeable lithium batteries.

In the first report, ECOM-4474, it was concluded that molybdenum trioxide offers a high Wh/kg of active cell component ratio and low initial active component cost, expressed in $/Wh of active cell components. Consequently, molybdenum trioxide was used as a model material in our experimental investigations in order to learn and understand the problems connected with rechargeable lithium batteries.

Several other potential cathode materials have been reported since 1976 and a new comparison of rechargeable lithium batteries with nickel-cadmium batteries is made in Table 1.

Table 1. Comparison of Rechargeable Lithium Batteries With Nickel-Cadmium Batteries

INTERCALATE	Wh/kg theor.*	Wh/kg pract. **	$/Wh
$Li_{4.4}Cr_3O_8$	1,622	1,248	
$Li_{2.8}Cr_2O_5$	1,582	1,220	0.008-0.43
Li_3NiPS_3	1,164	776	
Li_2MoO_3	1,020	510	0.05
$Li_{7.5}V_6O_{13}$	800	550	
$LiCr_{0.75}V_{0.25}S_2$	610	373	
$LiTiS_2$	542	271	4.1
Li_4NbSe_4	526	460	
(Ni-Cd Cell)	212	200	0.3

*Based on open circuit voltage and F_{theor}.

**Average discharge voltage $\overline{V} = 2V$, except $Li\text{-}Cr_2O_5(Cr_3O_8) = 3.0V$, $Li\text{-}V_6O_{13} = 2.2V$, $Li\text{-}NbSe_4 = 1.8V$, $Li\text{-}Cr_{0.75}V_{0.25}S_2 = 2.65V$, and Ni-Cd = 1.24V

---

[1] Herbert F. Hunger and Joseph E. Ellison, "Transition Metal Compounds as Cathodic Materials in Rechargeable Lithium Cells," R&D Technical Report ECOM-4474, February 1977.

[2] Herbert F. Hunger and Joseph E. Ellison, "The Behavior of Molybdenum Trioxide Electrodes in Nonaqueous Electrolytes," R&D Technical Report DELET-TR-78-28, October 1978.

In Table 1 we have entered the lithium intercalate with maximum lithium content, the theoretical and practical energy content, expressed in Wh per kg of active cell components and the $/Wh value whenever the costs of commercial products were available. A lack of this data indicates experimental materials prepared by various investigators. The last item in column "intercalate" has been put in parentheses, indicating a cell without a lithium intercalate.

The following is a brief summary of references concerning compounds not included in the first report, ECOM-4474.

The lithium intercalates of chromium pentoxide[3] show potentially the highest energy content and an attractive price range for initial, active component cost, depending on whether the raw material is CrO_3 or Seloxette ($Cr_2O_{4.92}$); both are commercially available.

The second intercalate, Li_3NiPS_3, has been reported by LeMehaute and Perche,[4] but reversibility is in question because of a multiphase region for $X > 1.5$ in Li_xNiPS_3.

$Li_{7.5}V_6O_{13}$ has been investigated by researchers at Bell Labs; its structure and electrochemical behavior have been described.[5] The structure consists of alternating double and single zig-zag chains of VO_6 octahedra with channels for lithium diffusion, which makes it quite different from the usual layer structures of intercalates with lithium in the Van der Waal's gap.

The intercalate $LiCr_{0.75}V_{0.25}S_2$ is based on a chromium substituted vanadium disulfide. The substitution suppresses the transition from a hexagonal to a distorted phase. In addition to structural data, electrochemical data are presented.[6]

Murphy and Carides[7] found recently that TiS_2 exhibited two discharge voltage plateaus, one at 2.0 V versus lithium for $LiTiS_2$ and the other at 0.5 V versus lithium for Li_2TiS_2. Electrochemical cycling was poor when both plateaus were involved, but improved reversibility was observed when only the lower plateau was involved. Corresponding data are not included in Table 1 because of the low potential of the second plateau.

---

[3] J. O. Besenhard and R. Schoellhorn, "Chromium Oxides as Cathodes for Secondary High Energy Density Lithium Batteries," J. Electrochem. Soc. 124, 968 (1977).

[4] A. LeMehaute and P. Perche, "Utilization of Transition Metal Phosphorus Trisulphides as Battery Cathodes," Preprint from the 11th International Power Sources Symposium 1978, Brighton, England.

[5] D. W. Murphy, P. A. Christian, F. J. DiSalvo, and J. N. Carides, "Vanadium Oxide Cathode Materials for Secondary Lithium Cells," J. Electrochem. Soc. 126, 497 (1979).

[6] D. W. Murphy and J. N. Carides, "Cathodes for Nonaqueous Lithium Batteries Based on VS_2," The Electrochem. Soc., Inc., Fall Meeting, Atlanta, Georgia, October 9-14, 1977. Extended Abstract No. 12.

[7] D. W. Murphy and J. N. Carides, "Low-Voltage Behavior of Lithium/Metal Dichalcogenide Topochemical Cells," J. Electrochem. Soc. 126, 349 (1979).

Table 1 shows that there are several novel intercalates which should be considered as cathode materials if high energy content is desirable in batteries.

In the second report, DELET-TR-78-28, the rate capability of the molybdenum trioxide electrode at room temperature and cycling in 1M $LiClO_4$-PC and 1 M or 3M $LiClO_4$-AN electrolyte was investigated. A comparison was made with other cathodic materials such as group IVB and VB dichalcogenides and group VIB oxides. It had to be concluded that the rate capability of such reversible systems is highly electrolyte dependent.

In this report we complete the study of model system, Equation (1),

$$Li/\ 1M\ LiClO_4\text{-}PC/\ MoO_3 \qquad (1)$$

and summarize its charge and discharge behavior, thereby identifying some of the general problems connected with rechargeable lithium systems.

EXPERIMENTAL PROCEDURES

Material handling, component and cell preparation, and electrochemical measurements were carried out in a dry lab in helium atmosphere. Up to 5 ppm of water were measured in the dry box.

1M $LiClO_4$-PC was used as the electrolyte. The solvent purification and electrolyte preparation have been described previously.[8]

The preparation of the molybdenum trioxide cathodes, lithium anodes, and lithium reference electrodes as well as the cell arrangement were described in detail in a previous report.[9]

The electrochemical instrumentation used in measuring the current-potential curves and in the charge-discharge experiments was based on the periodically interrupted sine wave pulse current circuit, designed to measure ohmic iR free potentials in organic electrolytes with higher ohmic resistance.[10] The polarity arrangement in this circuit made it possible to measure the ohmic iR free cathode potential versus the lithium reference electrode during cathodic discharge of the MoO_3 electrode. During anodic operation of the Li_xMoO_3 electrode, the cell polarity had to be reversed. In this case the ohmic iR free potential of the lithium cathode versus the lithium reference electrode plus the iR free cell voltage could be measured. The Li_xMoO_3 anode potential was computed from these data by Equation (2):

$$V_{cell} = V_{anode} - V_{cathode} \qquad (2)$$

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[8] H. F. Hunger and J. E. Ellison, "Cathodic Reduction of Carbon-Fluorine and Carbon-Nitrogen-Fluorine Compounds in Organic Electrolytes," R&D Technical Report ECOM-4296, March 1975.

[9] H. F. Hunger and J. E. Ellison, DELET-TR-78-28, op. cit., p. 1.

[10] H. F. Hunger and J. E. Ellison, ECOM-4296, op. cit.

RESULTS AND DISCUSSION

Anodic Behavior of Molybdenum Trioxide Electrodes in 1M $LiClO_4$-PC Electrolytes at Room Temperature

In order to observe solute-solvent oxidation, freshly prepared Li/1M $LiClO_4$-PC/MoO_3 cells were charged in 5 minute interval step charges, ranging from 5.10^{-6} A/cm^2 to 10^{-2}. The average cell temperature was 28°C. The amount of active material in the cathode was 0.213 g MoO_3. During each step, the cell voltages and the potentials of the lithium working electrode versus the lithium reference electrode were recorded and the potentials of the molybdenum trioxide anode were computed. Figure 1 shows these potentials versus the anodic current. The upper curve shows the events at a MoO_3 anode. Starting at a potential of 2.85 V versus lithium, the potential rises steeply with increasing anodic current. At 4.03 V, gassing is observed at the anode and the potential-current curve turns into an inclined plateau above 4.2 V. The total charge introduced during step charging amounted to 16.2 mAh. This corresponds to a 30% overcharge if a charge acceptance of 1.5e^-/Mo is taken as a standard. Before gassing occurs, the overcharge is 2.6%. This is probably due to the oxidation of some reduced species in the MoO_3 electrode. However, the major overcharge occurs in the region above 4.0 V.

According to J. O. Besenhard,[11,12] the anodic decomposition voltage of propylene carbonate at platinum is +2.9 V versus SCE. The potential of the SCE is +0.2415 V versus the standard hydrogen electrode (SHE). Thus, the propylene carbonate oxidation potential is +3.145 V versus SHE or since the potential of the reversible lithium electrode in propylene carbonate is -3.265 V versus the SHE potential, the solvent oxidation potential should be +6.4 V versus lithium. Thus, another anodic process must be responsible for the electrolyte oxidation; e.g., the perchlorate anion can be oxidated anodically (Equation (3)) and yield chlorine dioxide and oxygen.[13]

$$ClO_4^- \longrightarrow ClO_2 + O_2 + e^- \qquad (3)$$

From the free enthalpie of formation of the end products and reactant of Equation (3), the free enthalpie of the reaction can be computed from Equation (4).

$$\Delta G^\circ_{react.} = \left(\Sigma \Delta G^\circ_{form.}\right)_{end} - \left(\Delta G^\circ_{form.}\right)_{start} \qquad (4)$$

$\Delta G^\circ_{react} = +31.97$ K cal, indicating an endothermic process.

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[11] J. O. Besenhard, Thesis, TU Munich 1973 (available from NTIS, N 74-30505).

[12] J. O. Besenhard and G. Eichinger, "High Energy Density Lithium Cells. Part I Electrolytes and Anodes," J. Electroanal. Chem. 68, 1 (1976).

[13] F. Beck, Elektroorganische Chemie, Verlag Chemie, Weinheim, 1974,p.110.

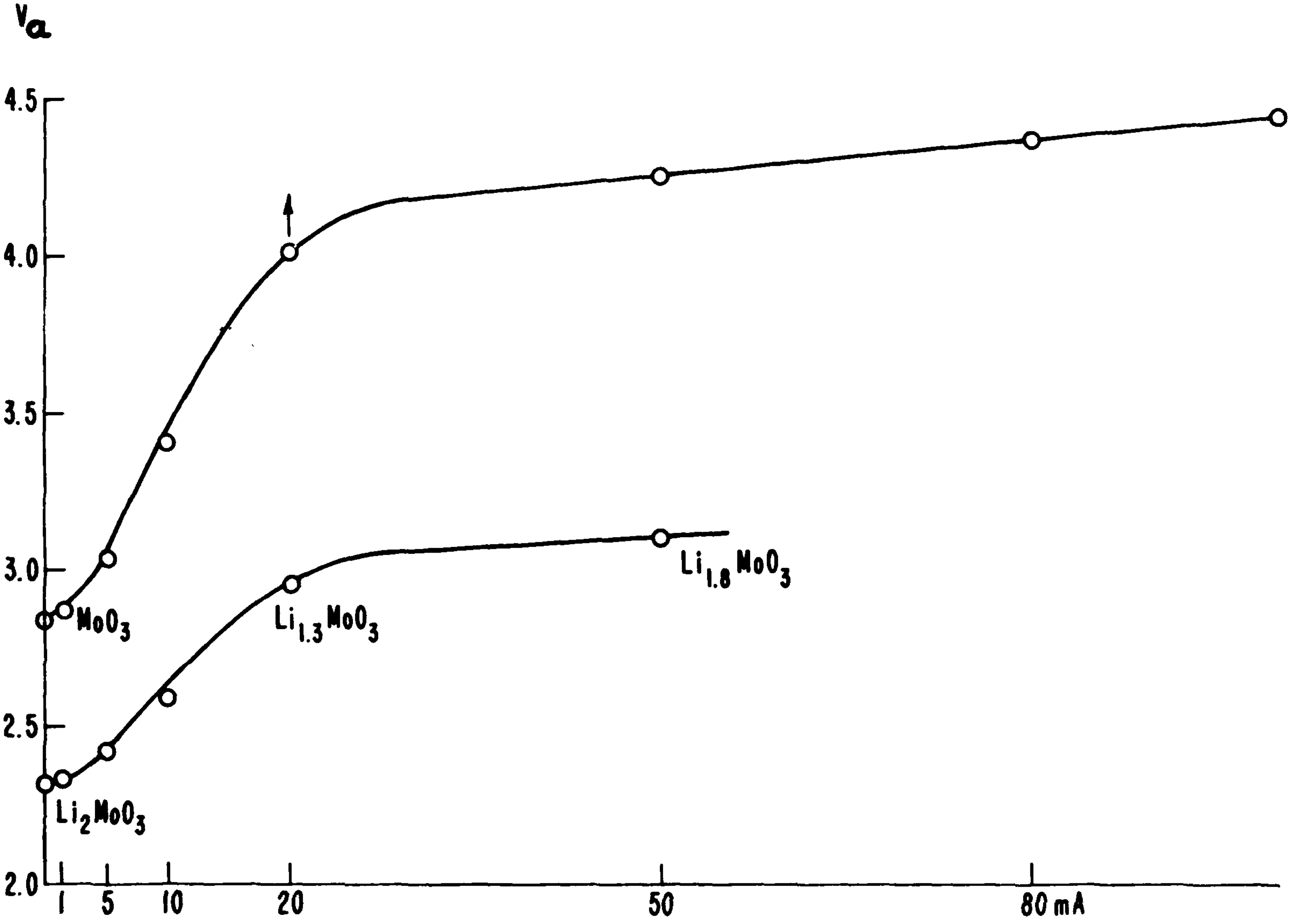

Figure 1. Potential of MoO_3 and Li_xMoO_3 Anodes Versus Anodic Current

Since $\Delta G^\circ_{\text{react.}} = -n\ 23{,}060.E$ (5)

E = +1.385 V versus SHE. Depending upon the lithium potentials, ranging from -3.09 V to -3.432 V versus SHE, a lower oxidation potential of 4.47 V versus lithium can be estimated for the perchlorate anion. The data does not take into account the solvation by propylene carbonate and can only be used as a guidance. Therefore, it is highly probable that the region of the curve above gassing (Figure 1) accounts for perchlorate anion rather than solvent oxidation.

The overcharged molybdenum trioxide electrode was discharged to Li_2MoO_3 ($2e^-$/Mo) at 1 mA/cm^2 to a potential of 1.12 V versus lithium and over-discharged (35.4% theor.) to 0.75 V versus lithium, whereby solvent reduction occurred. Gassing was observed at 0.93 V versus lithium.

Step charging of the Li_2MoO_3 electrode with 5 minute intervals was done over the range of 5.10^{-6} A/cm^2 to 5.10^{-3} A/cm^2 at 28°C. The lower curve in Figure 1 represents the Li_xMoO_3 anode potential versus the anodic current. During the step charging, the composition of the electrode changed in accordance with the charge passed from X=2 to X=1.8. An inclined plateau above 3 V shows the oxidation of Li_xMoO_3 at charging rates of 2-5 mA/cm^2.

Effect of Overcharging

In Figure 2 the effect of overcharging the MoO_3 electrode by 30% is shown by plotting the ohmic iR free polarization of the MoO_3 cathode versus current density. One curve represents an original MoO_3 cathode, the other interrupted curve, an overcharged electrode. It can be seen that at practical current densities above 1 mA/cm^2 a negative effect occurs due to overcharging, which can be seen in the higher cathode polarization. It is possible that the anodic reaction products of Equation (3), namely ClO_2 and O_2, attack the graphite additive to the MoO_3 electrode and break up conducting bridges between active particles, thus damaging the electrode structure.

Anodic and Cathodic Rates of Molybdenum Trioxide Electrodes in Various States of Lithiation

The anodic and cathodic behavior of MoO_3 electrodes in various states of lithiation is shown in Figure 3. The polarization-current density curves for an original MoO_3 cathode, a $Li_{0.5}MoO_3$ cathode after 10 cycles (33.3% depth of discharge), and a Li_2MoO_3 anode during the first cycle are compared. It can be seen that initially all curves show linear slopes up to 5.10^{-4} A/cm^2. The original MoO_3 cathode differs in its tafel slope (b) constant from the lithiated electrodes (b = 0.11 versus 0.025) indicating different mechanisms. Above 5.10^{-4} A/cm^2, strong deviations from linearity are observed for the latter electrodes and diffusion control seems to determine their behavior both in the anodic and cathodic mode. The kinetics of the anodic and cathodic reactions in Equation (6)

$$Li_{0.5}MoO_3 + 1.5\ Li^+ + 1.5e^- \rightleftharpoons Li_2MoO_3 \qquad (6)$$

appear to be quite similar (same b and I_o). Solvated lithium ions seem to play a major role in the mass transport limited mechanism.

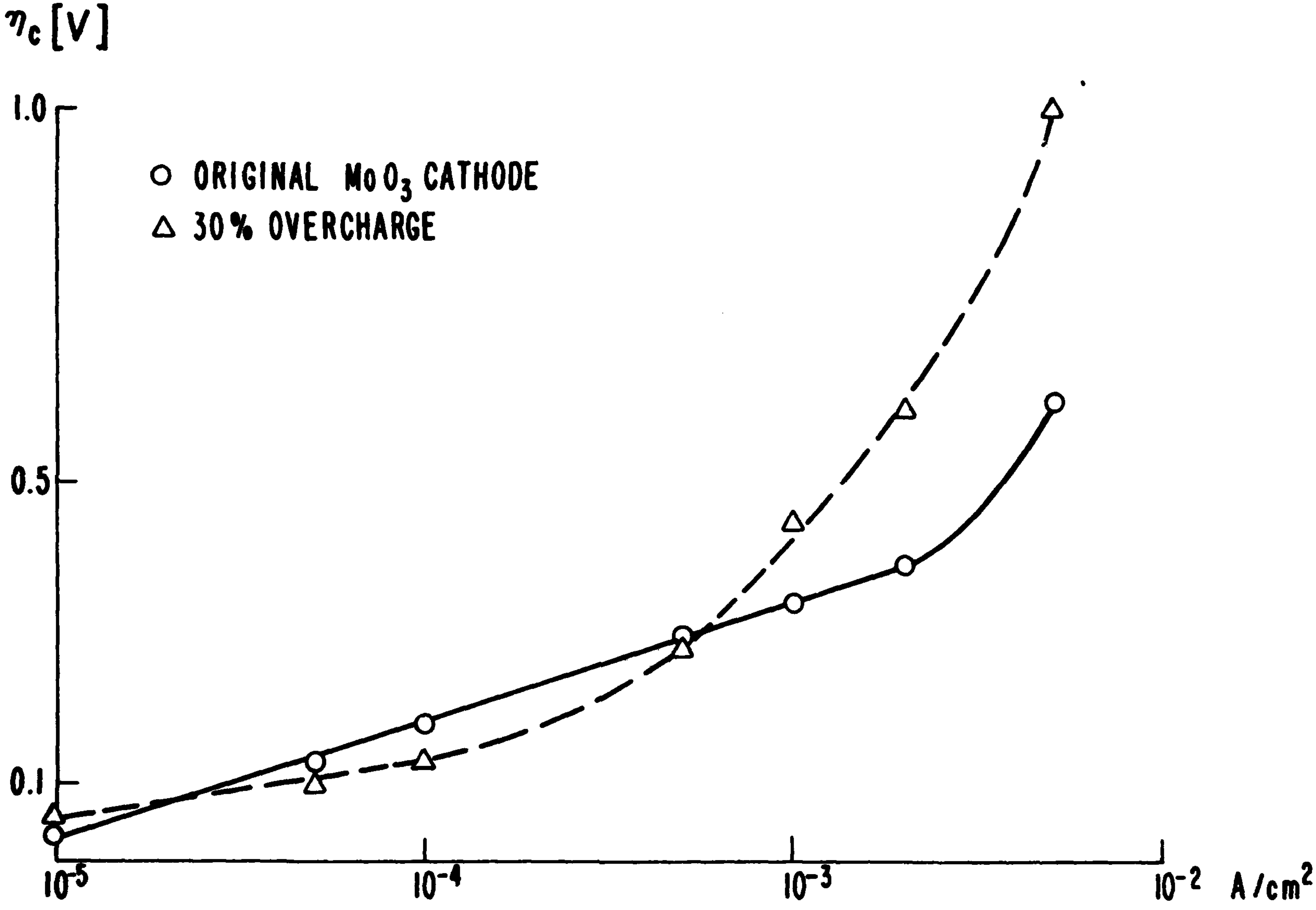

Figure 2. Effect of Overcharging on Polarization of MoO_3 Cathodes

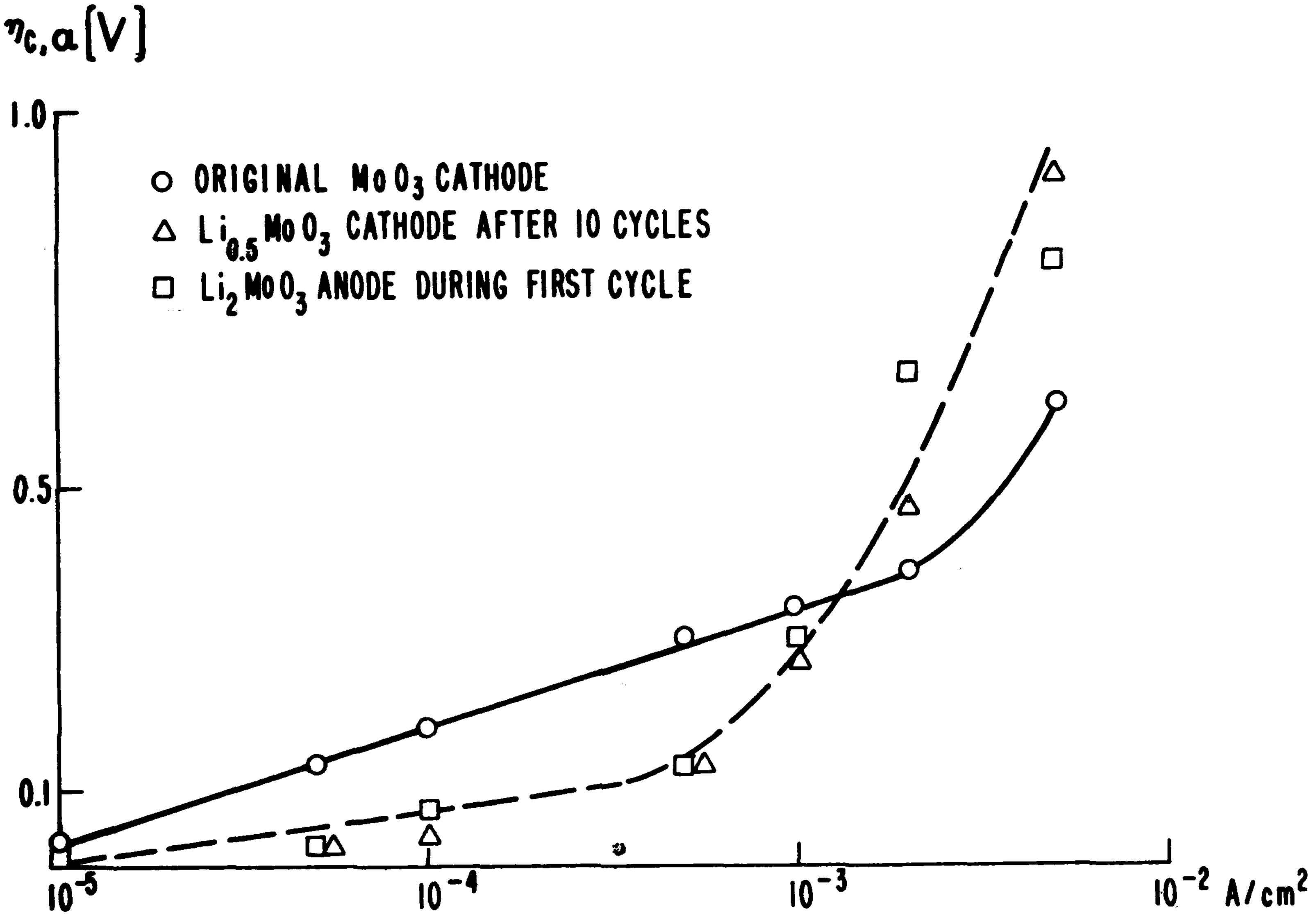

Figure 3. Polarization of MoO_3 Cathode and Li_xMoO_3 Electrodes Versus Current Density

Considering the results reported in a previous technical report,[14] it can be concluded that charge and discharge rates of molybdenum trioxide electrodes in a 1M $LiClO_4$-PC electrolyte at room temperature are of the same order of magnitude (1 mA/cm^2). The relatively high viscosity of the electrolyte apparently causes slow lithium ion transport. Higher discharge current densities have been observed in less viscous media. These results show the direction that has to be taken to increase the rate capability of the lithiated molybdenum trioxide electrodes.

The Rechargeable Compounds

It has been shown previously (R&D Technical Report DELET-TR-78-23) that MoO_3 undergoes partial reduction to a compound of the approximate composition $LiMo_2O_6$. This partial reduction step becomes gradually irreversible and reoxidation does not occur during recharging. Thus, $Li_{0.5}MoO_3$ becomes the actual positive plate material instead of MoO_3. Complete reduction to Li_2MoO_3 ($2e^-$/Mo) appears possible from the data. Thus, if we refer in the following to depth of discharge, we have to define what we mean. The intercalation compound $Li_{0.5}MoO_3$ corresponds to a fully charged electrode, a composition of $LiMoO_3$ to 33.3% depth of discharge, and one of Li_2MoO_3 to 100% depth of discharge. The composition change is proportional to the coulombs passed through the cell. Side reactions are not considered except at potentials below 1.2 V.

The electrode potentials of partially or fully discharged $Li_{0.5}MoO_3$ electrodes are a linear function of the amount of intercalated lithium computed from coulometric data (Figure 4). Initial MoO_3 potentials lie around 3.0 V. The open circuit potentials of rechargeable Li_xMoO_3 electrodes, however, lie between 2.65 and 2.12 V versus lithium. It appears that the composition $Li_{0.5}MoO_3$ is reached gradually during partial discharges (initially 25% theoretical of $2e^-$/Mo) and the potential becomes constant after 9 to 10 cycles. This is shown in Figure 4 by the connotations 2,3,and 10 for the $X = 0.5$ data. At $X = 1.25$, $X = 1.75$, and $X = 2.0$, the constant potential for the $X = 0.5$ composition is reached already after the second recharging and resting overnight.

The linearity of the potential-composition diagram indicates that a single phase exists over the lithium concentration range which is a criterion for good reversibility; e.g., Li_xTiS_2 shows a single phase as a function of x.[15] Single phases are reversible; multiphases are usually poorly reversible. The potential-composition curve for Cu_xTiS_2, e.g., shows a discontinuity due to multiphase existence of the dichalcogenide over the intercalation range.[16]

Cycling at 33.3% Depth of Discharge

In Figure 5 the first discharge of MoO_3 to $Li_{0.5}MoO_3$ is shown. All discharges were done at a current density of 1 mA/cm^2 and the compositions were

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[14] H. F. Hunger and J. E. Ellison, DELET-TR-78-23, op. cit., p. 1.

[15] M. S. Whittingham, "Chemistry of Intercalation Compounds; Metal Guests in Chalcogenide Hosts," Progress in Solid State Chem., 12, 1 (1978).

[16] B. Scrosati, M. A. Voso, and M. Lazzari, "A Cyclable Copper Solid-State Cell Based on Intercalation Electrodes," J. Electrochem. Soc. 126, 699 (1979).

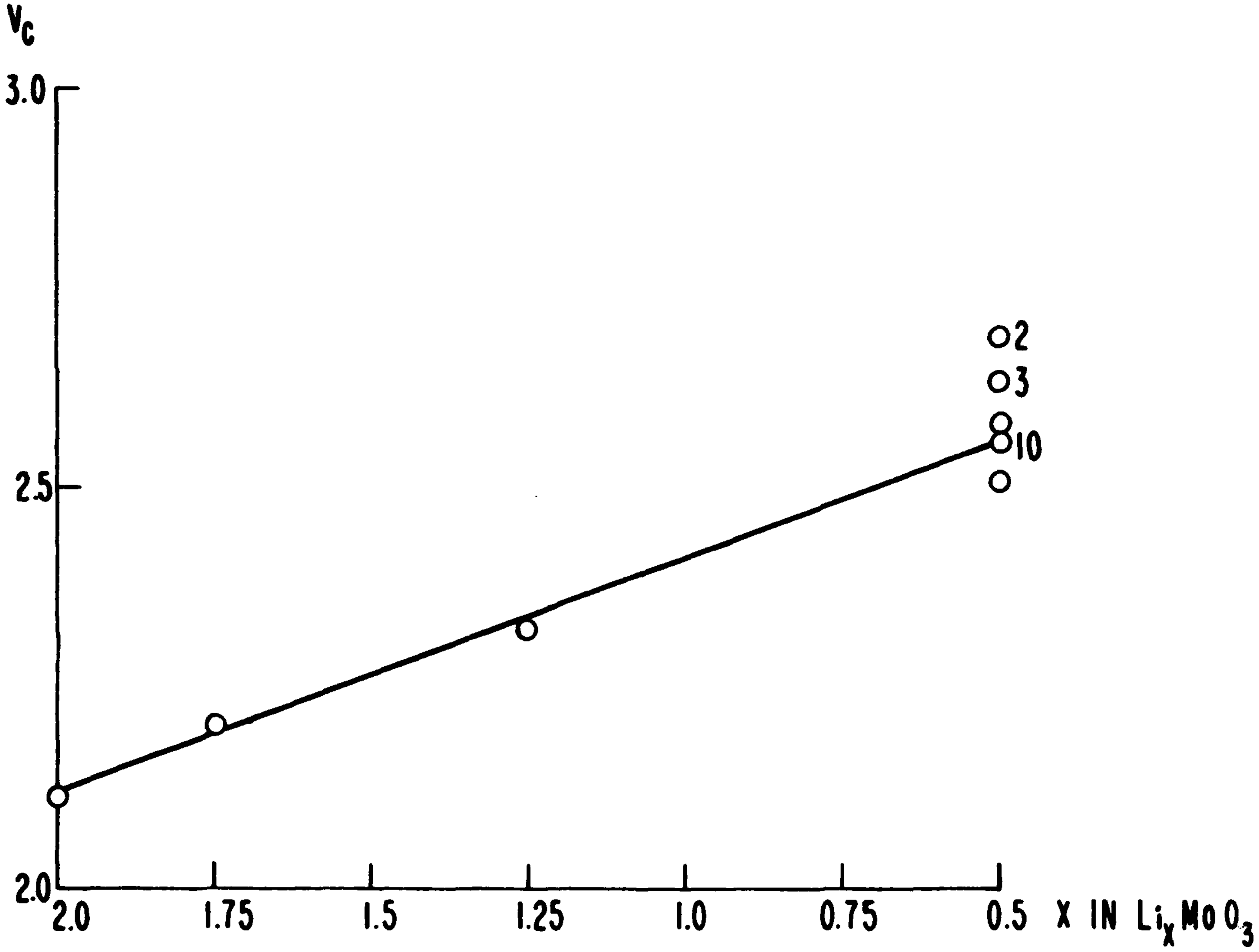

Figure 4. Open Circuit Potential of Li_xMoO_3 Electrodes as a Function of Lithiation

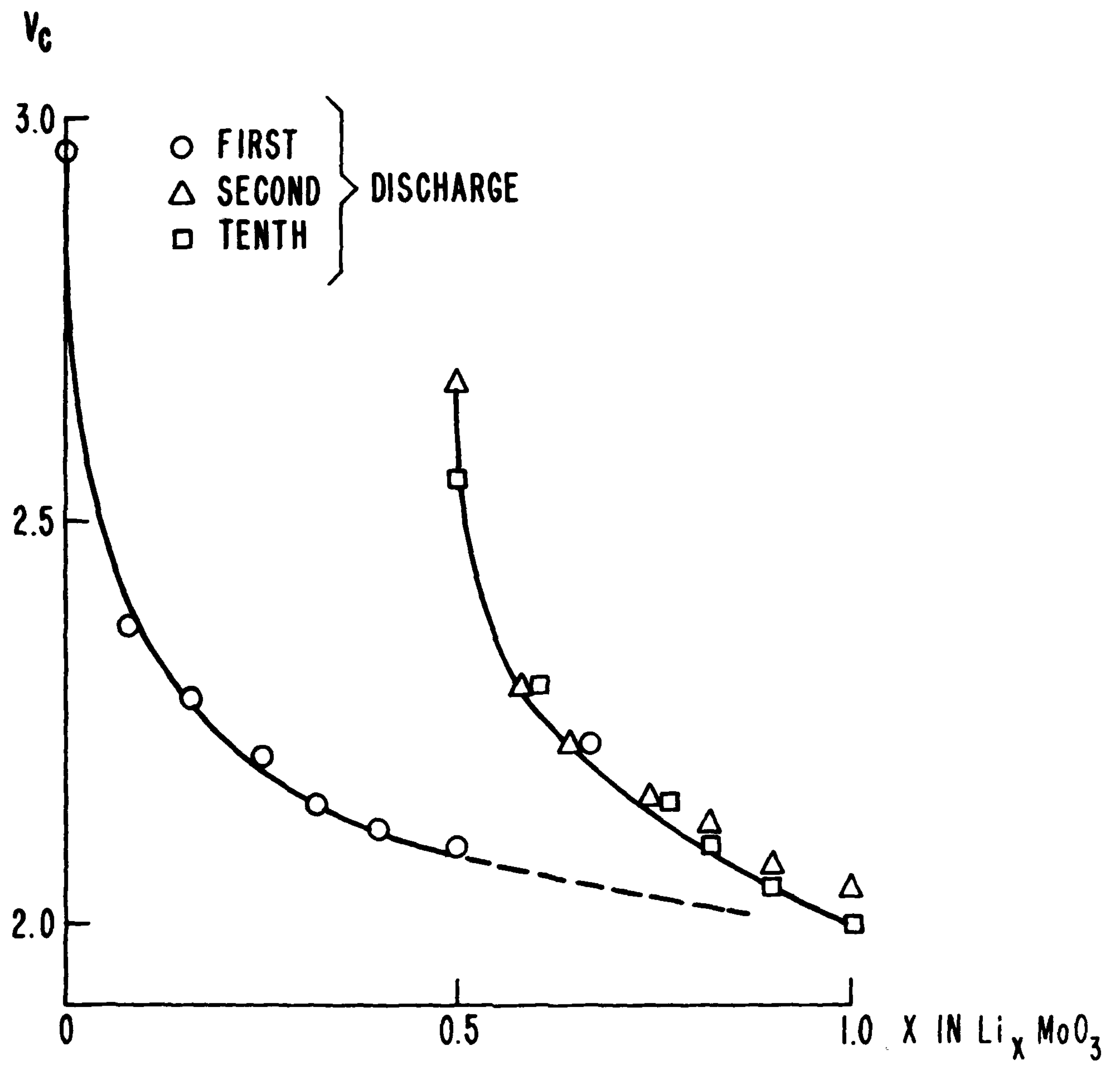

Figure 5. Li_xMoO_3 Cathode Potential as a Function of Progressing Discharge (1 mA/cm^2)

computed on the basis of the coulombs passed. After charging the electrode with the same number of coulombs (the first charge curve is shown in Figure 6), the cathode assumed a rest potential of 2.71 V. This was the initial potential of the second discharge. As can be seen from Figure 5, no significant change in the discharge curve occurred between the second and the tenth discharge. The cathode potentials remained all the time above 2.0 V and no reduction of the electrolyte solvent could occur.

Table 2 shows the cathode utilization efficiency as a function of depth of discharge, cathode potential, and number of cycles. We refer first to the data for 33.3% depth of discharge. During the first cycle the MoO_3 electrode is reduced to $Li_{0.5}MoO_3$ with a cathode utilization efficiency of 100%. During the second through tenth cycle, reduction occurs from a composition of about $Li_{0.5}MoO_3$ to a composition close to $LiMoO_3$ with an average utilization efficiency of 82.3%. At a depth of discharge of 100%, the composition of $Li_{0.5}MoO_3$ is reached already at a potential of 2.0 V during the first cycle. Further reduction to a composition close to Li_2MoO_3 occurs with an average utilization efficiency of 95.3% over 3 cycles. Thereafter a strong loss in cathode capacity is observed.

Table 2. Cathode Utilization Efficiency as a Function of Depth of Discharge, Cathode Potential, and Number of Cycles

33.3% Depth of Discharge

Cycle	1	2	3	9	10	2-10 Average
Cathode Potential						
2.5 V	4%	54%	52%	51%	52%	52.3%
2.25	40	65	62	57.5	64	62.1
2.2	100	88	80	77	84	82.3

100% Depth of Discharge

Cycle	1	2	3	4	Average
Cathode Potential					
2.0 V	50.3%	25%	27.5%	0%	26.3%
1.5	66.7	64	66.9	6	65.9
1.2	92	94	100	14	95.3

In Figure 6 the Li_xMoO_3 anode potentials are plotted versus the state of charge X. Charging was performed at a current density of 1 mA/cm^2 (i = 10 mA). The first charge curve reaches 3.3 V at X = 0. The second curve also reaches 3.3 V, but the third and the following curves reach values below that, becoming fairly steady around 3.0 V for the ninth and tenth charge.

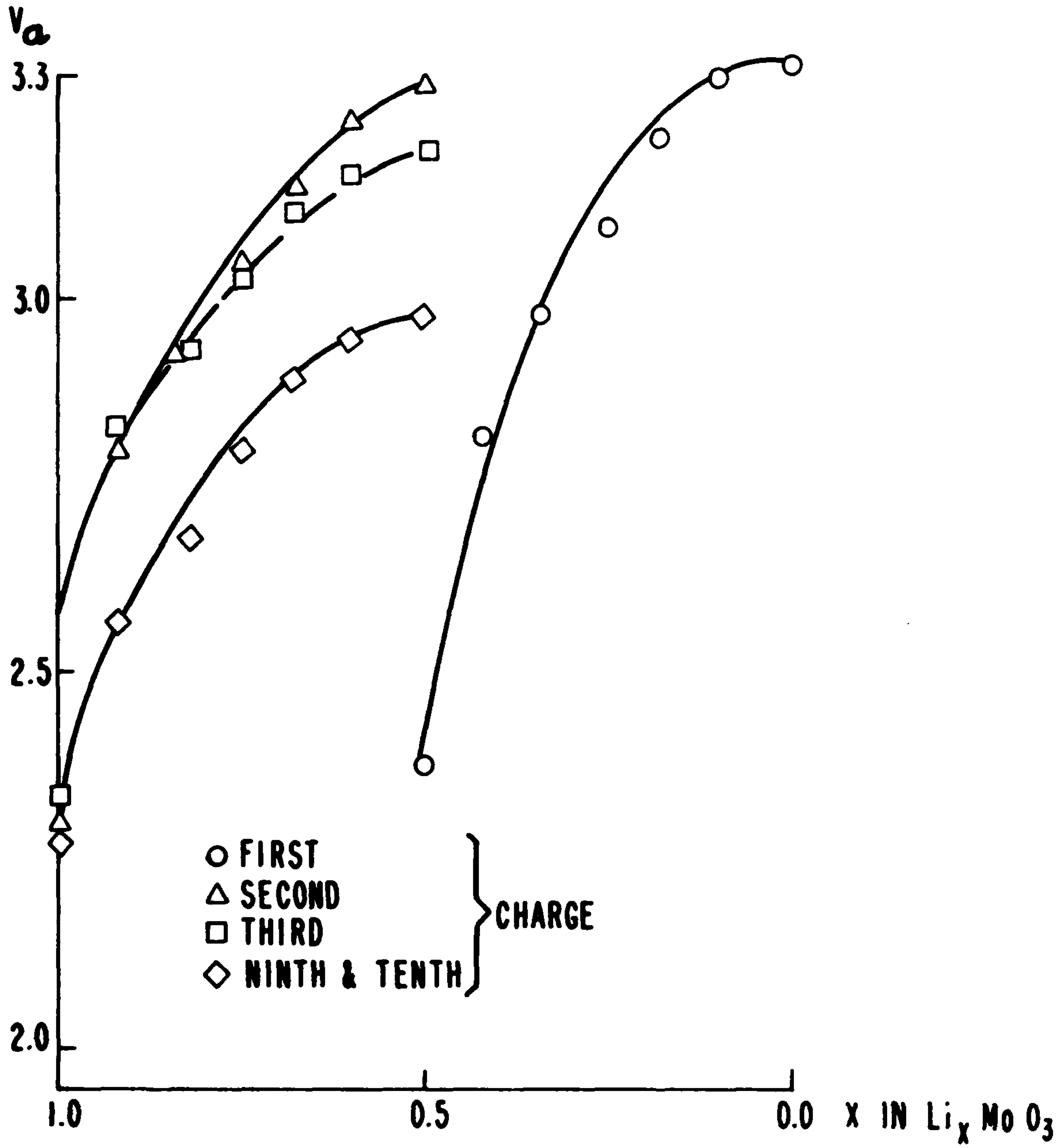

Figure 6. Li_xMoO_3 Anode Potential as a Function of Progressing Charge (1 mA/cm^2)

It is [illegible]ult to explain these inconsistencies completely. It appears that a partial recharging to MoO_3 is possible during the first 5 cycles, but after approximately ten cycles a steady potential belonging to another composition, namely, $Li_{0.5}MoO_3$, is obtained which suggests a slow phase change from the oxide phase to the intercalate phase.

Cycling Up to 100% Depth of Discharge

Figure 7 shows consecutive discharges of MoO_3 to $Li_{1.5}MoO_3$ and of $Li_{0.5}MoO_3$ to Li_2MoO_3. The depth of discharges are 75% based upon MoO_3 during the first cycle and 100% based upon $Li_{0.5}MoO_3$ during the following cycles. Starting with the second cycle at $X = 0.5$, the average discharge potentials for the same composition X form a straight line. When a composition of about $X = 1.5 - 2.0$ is reached at a cathode potential of about 1.2 V versus lithium, solvent reduction is observed at the cathode by the evolution of propylene gas. Such deep depths of discharge are detrimental to the performance of the cathode. Only three charge-discharge cycles could be obtained before strong capacity losses of the positive plates occurred (See Table 2). The failure mechanism is not known, but there are several possibilities considering the chemistry of the system:

(1) Accumulation of insoluble solvent reduction products, such as Li_2CO_3 in the pore structure of the cathode.

(2) Loss of contact between active electrode particles due to irreversible swelling caused by solvent intercalation.

(3) Short circuits due to lithium dendrite formation between anode and cathode.

(4) Trumbore[17] reports that treatment of electrolytes with 4 A type molecular sieves can lead to an ion exchange between Li^+ and Na^+, thus introducing some sodium ions into the electrolyte solution. These ions might be incorporated into the $Li_xNa_yMoO_3$ compounds on deep discharge and adversely affect the performance of the cell, and decrease the capability of the positive plate.

In general, deep depths of discharge, approaching 100%, are unrealistic for operation of practical cells.

Figure 8 presents the three charge curves of the 75% to 100% depth of discharge experiments. Similar to the first charge curve in the 33.3% discharge experiment (Figure 6), the first charge curve reaches about 3.3 V at $X = 0.5$. The charging potential, however, drops at $X < 0.5$. The second and third charging curves show a plateau around 3.0 V, similar to that of the ninth and tenth charging curve in Figure 6. These potentials are well below the oxidation potential of the electrolyte. A possible explanation for the 3.3 V and 3.0 V potential levels was already given in connection with Figure 6.

---

[17] F. A. Trumbore and J. J. Auborn, "On the Purification of Nonaqueous Electrolytes for Lithium Battery Studies," The Electrochem. Soc. Inc., Fall Meeting, Pittsburgh, Pennsylvania, October 15-20, 1978. Extended Abstracts of Battery Division. Abstract No. 22.

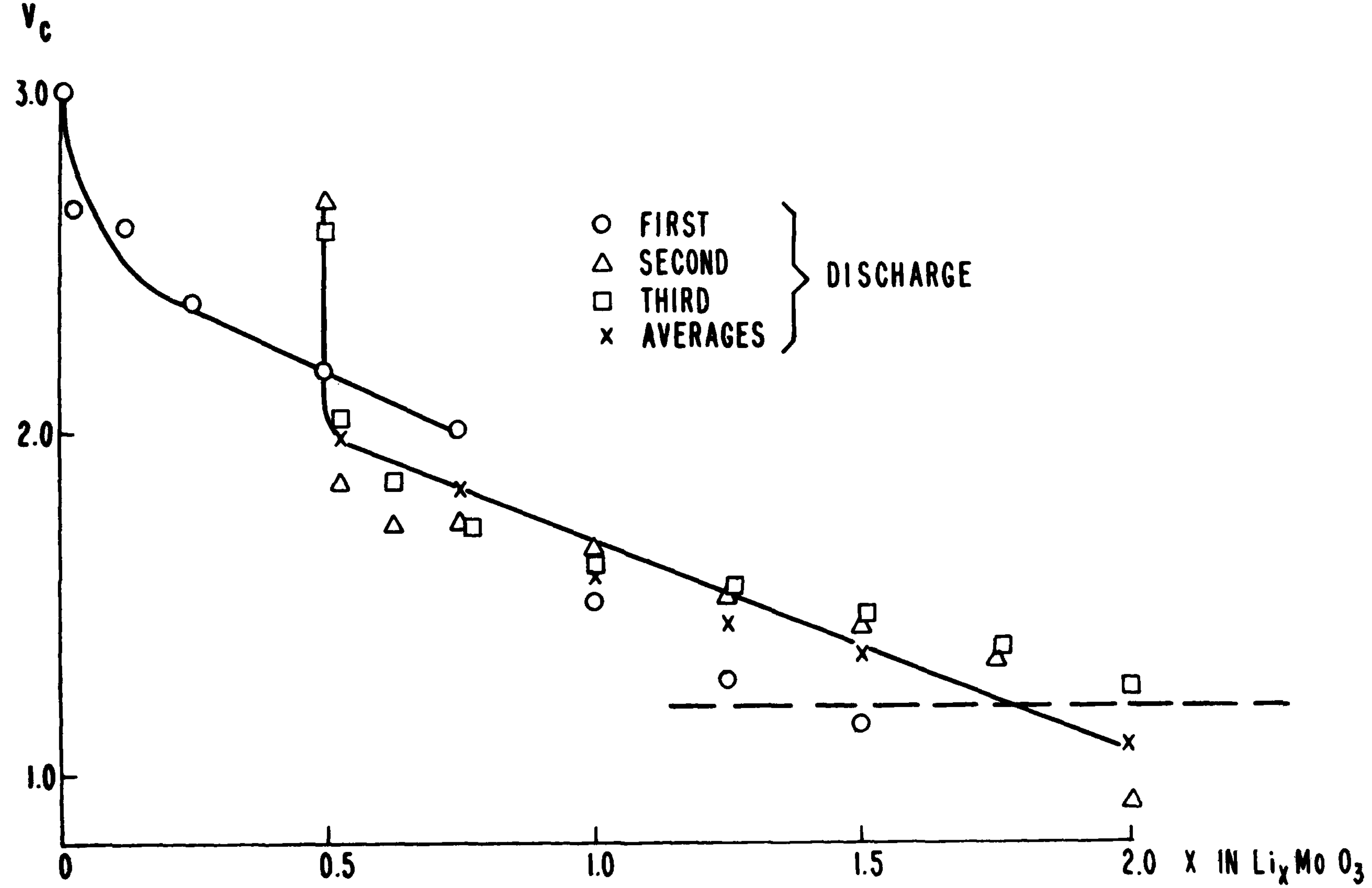

Figure 7. Li_xMoO_3 Cathode Potential as a Function of Progressing Discharge (1 mA/cm^2) - Depth of Discharge 100%

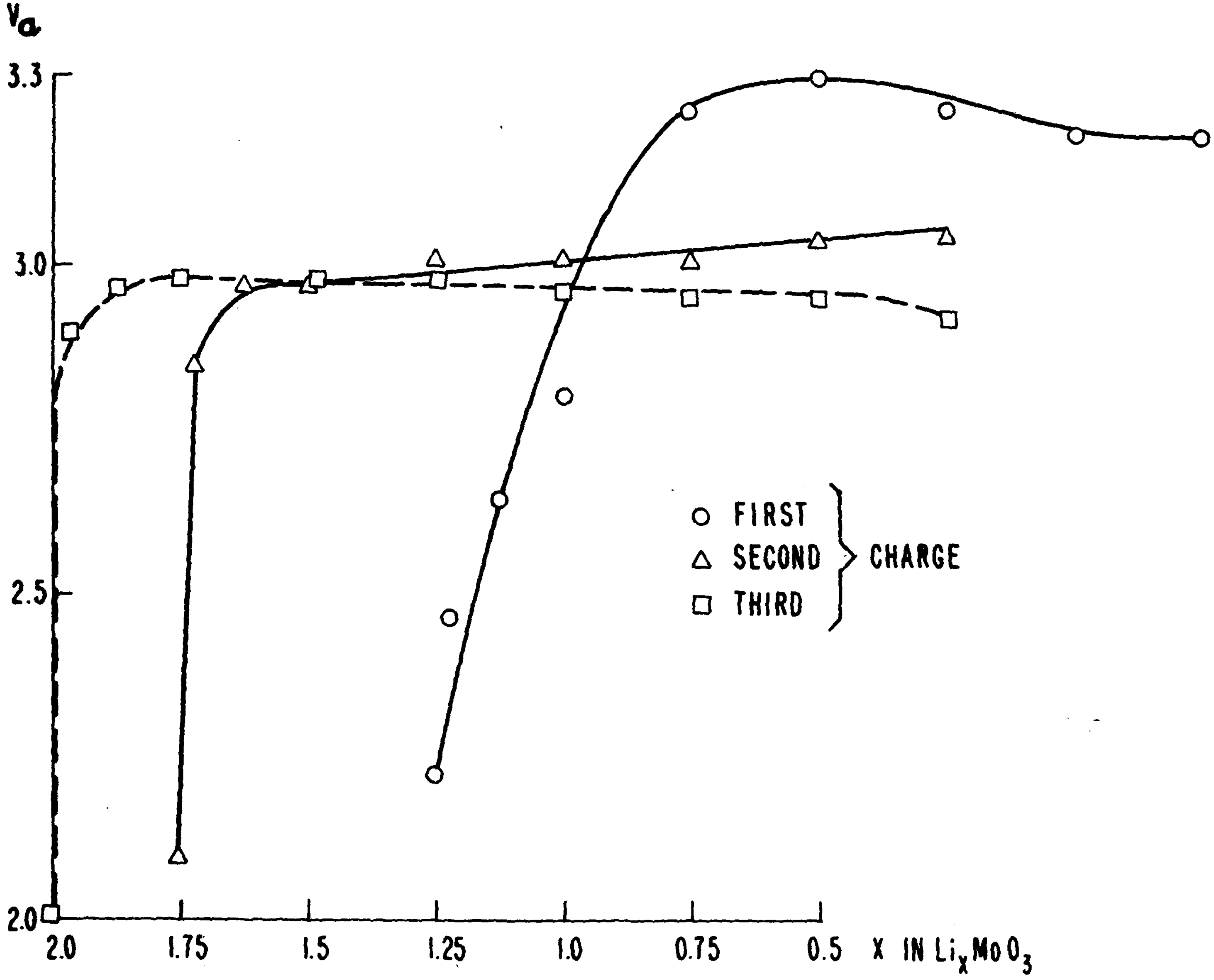

Figure 8. Li_xMoO_3 Anode Potential as a Function of Progressing Charge (1 mA/cm2) - Full Charge

A similar cycling experiment was performed over three cycles, to 50% depth of discharge, based on MoO_3, during the first discharge, and to 66.6% depth of discharge, based on $Li_{0.5}MoO_3$, during the second and third discharge. The results obtained were quite similar to that in the experiment described before.

Conclusions from the Cycling Experiments

(1) 33.3% depth of discharge based on $Li_{0.5}MoO_3$: Ten cycles were obtained with the molybdenum trioxide electrode with practically constant performance since the second cycle. At a current density of 1 mA/cm^2, the discharge potential ranged from 2.5 - 2.0 V, the average being 2.25 V. Three lithium electrodes had to be used during ten cycles, with failure after about three cycles. The lithium electrodes had a capacity of 0.62 Ah per electrode. Only 0.019 Ah were passed during charging and discharging. This corresponds to a depth of discharge of only 3%. About 20% of the free energy of the cell reaction appear as heat during discharge. The charging process is endothermic except the ohmic iR losses. The system has 87 Ah/kg of active components or 196 Wh/kg. This corresponds to the energy capacity, based on active components, of the nickel-cadmium cell.[18]

(2) 66.6% depth of discharge based on $Li_{0.5}MoO_3$: Three cycles were obtained with the cathode. Cathode failure was accepted after the third discharge, when capacity had dropped from about 4 hours of operation to 2 hours. The average cathode potential during discharge was 1.5 V; 174 Ah/kg and 261 Wh/kg of active cell material were obtained. In this experiment there were constant problems with the lithium electrodes. Three had to be used all together. The first lithium electrode operated normally during the first discharge (1 mA/cm^2) at a potential of +0.05 V versus lithium. The depth of discharge at the lithium electrode was 6.7%. The cell resistance was 30Ω. The lithium electrode went well through the first charge but failed during the second discharge (+1.08 V versus lithium). The cell resistance went up to $90\ \Omega$, indicating a strong increase in ohmic resistance, probably due to an insulating film at the lithium electrode. In addition to this ohmic polarization, a high anodic polarization, free of the ohmic iR component, was observed ($\eta = 1.08$ V), probably caused by a loss of active electrode surface due to blocking film formation. It has to be added that the cell had been standing fully charged overnight before discharge, which apparently increased the passivation. Failure mechanisms which apply to lithium electrodes in 1M $LiClO_4$-PC electrolyte have been reported.[19,20] A replacement for the first lithium electrode performed well during the second discharge (+0.05 V versus lithium) but failed gradually during the second charging, with the ohmic resistance increasing to $300\ \Omega$. A third lithium electrode performed normal during the third discharge. Table 3 shows the behavior of lithium electrodes during cycling in 1M $LiClO_4$-PC.

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[18] H. F. Hunger and J. E. Ellison, ECOM-4474, op. cit., p. 1.

[19] R. Selim and P. Bro, "Some Observations on Rechargeable Lithium Electrodes in a Propylene Carbonate Electrolyte," J. Electrochem. Soc. 121, 1457 (1974).

[20] R. D. Rauh and S. B. Brummer, "The Effect of Additives on Lithium Cycling in Propylene Carbonate," Electrochimica Acta, 22, 75 (1977).

Table 3. Lithium Electrode Failures During Cycling at 1 mA/cm^2

Depth of Discharge %	Stand	Cycles Completed	Failure
3	-	3	During 4th Discharge
6.7	Stand Charged Overnight	1	During 2nd Discharge
10	-	3	During 4th Discharge

From the table it can be seen that cycle life depends more on stand time of freshly deposited lithium in the electrolyte than on depth of discharge. Passivation of lithium occurs by reaction with the electrolyte solvent and constitutes a surface not a bulk reaction.

(3) 100% depth of discharge based on $Li_{0.5}MoO_3$: Only three cycles were obtained with the cathode as described before. The lithium electrode withstood three cycles before failing during the fourth discharge. 40% of the free energy of the intercalation reaction were obtained as heat. An energy efficiency of about 50% and 261 Ah/kg and 392 Wh/kg of active cell components were obtained during 3 cycles. The energy capacity is about twice that of the nickel-cadmium cell.

(4) Reason for Energy Losses: The main reason for energy losses is the concentration polarization at the cathode which constitutes the major component of the total polarization; e.g., at a cell voltage of 2.0 V, the polarization at the lithium anode is only 0.05 V and the ohmic drop (5 Ω per cell) is also 0.05 V. Both are small compared to the cathode polarization which is 83% of the total polarization.

SUMMARY

Identification of Anodic Charging Processes

At molybdenum trioxide anodes, oxidation of the lithium perchlorate-propylene carbonate electrolyte occurs above 4.0 V versus lithium at rates above 2.0 mA/cm^2. This is close to the anodic oxidation potential of the perchlorate ion. In order to avoid damages to the electrode by oxidation, anodic potentials above 3.3 V should be avoided when charging Li_xMoO_3 electrodes in 1M $LiClO_4$-PC electrolytes.

Determination of Anode Kinetics

The completely discharged molybdenum trioxide anode permits initial charging rates of 1-5 mA/cm^2 at potentials of 2.7 to 3.1 V versus lithium. The anode kinetics is similar to the cathode kinetics - a fast electron transfer step and a slow diffusion step which becomes rate determining at practical current densities.

Cycling of Molybdenum Trioxide Electrodes at Various Depths of Discharge

At a moderate depth of discharge (33.3%) and moderate rates (1 mA/cm^2), at cathode potentials above 2 V versus lithium, the performance of the cathode is practically constant over ten charge-discharge cycles. The energy capacity, expressed in Wh/kg of cell reactants, corresponds approximately to that of the nickel-cadmium cell.

At deep depths of discharge (66.6% and 100%), the cathode potential drops toward the end of the discharge below 1.2 V versus lithium, a potential region where solvent reduction occurs already. This is apparently detrimental to the performance of the cathode. The energy capacity, expressed in Wh/kg of cell reactants, was twice that of the nickel-cadmium cell. Only three charge-discharge cycles could be obtained. A severe capacity loss was observed at the positive plate after 3 cycles. Therefore, a cutoff potential above 1.2 V versus lithium is required to avoid this detrimental effect.

CONCLUSIONS

In conclusion, the lithium-molybdenum trioxide cell with $LiClO_4$-PC electrolyte is capable of moderate rates in the order of 1 mA/cm^2 and a cycle life of 3 cycles. High concentration polarization at the cathode is the reason for rate limitations on both charge and discharge. Poor lithium electrode rechargeability, due to encapsulation of freshly deposited lithium with lithium-solvent reaction products, is the major reason for limited cycle life. Both problems are due to the solute-solvent interaction with lithium and research in this field will form the basis for further advancements in rechargeable lithium batteries.