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THE BEHAVIOR OF MOLYBDENUM TRIOXIDE ELECTRODES IN NONAQUEOUS ELECTROLYTES

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→ Experimental work with molybdenum trioxide cathodes in organic electrolytes was aimed at increasing the cathodic rate capability of the electrodes.

Coulombic analysis of cycling experiments suggests a high coulombic efficiency up to 1.5 F per molybdenum atom. The cathode kinetics is characterized by a fast electron transfer step followed by a slow diffusion step which becomes rate determining at practical current densities. Electrolyte solvent optimization led to a considerable increase in rate capability up to 25 mA/cm^2. Sq cm

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THE BEHAVIOR OF MOLYBDENUM TRIOXIDE ELECTRODES IN NONAQUEOUS ELECTROLYTES

INTRODUCTION

In a previous report[1] a comparison was made between rechargeable lithium batteries, based on lithium intercalation or lithium interstitial compounds of transition metal oxides or chalcogenides, and nickel-cadmium batteries. Based on a Wh/kg and \$/Wh basis, the lithium-molybdenum trioxide system appeared superior to the other possible systems. Thus, preliminary experimental work was carried out with lithium-molybdenum trioxide cells.

The objectives of continued study of the system included the determination of the coulombic efficiency and rate capability of the molybdenum trioxide electrode during cycling in 1M $LiClO_4$-PC electrolyte, a diagnostic look at the reaction mechanism, an optimization of the electrolyte with respect to rate, based on the findings of the reaction mechanism study, and an estimate of the practical rate limitations of the system.

Wherever possible, a comparison was made with other cathodic materials, such as Group IV B and V B dichalcogenides and other Group VI B oxides.

EXPERIMENTAL PROCEDURES

The material handling procedures, propylene carbonate (PC) solvent purification, and electrolyte preparation have been described thoroughly before.[2]

In addition to 1M $LiClO_4$-PC, a new electrolyte 1M or 3M $LiClO_4$-AN was used in part of this study. Acetonitrile, from Eastman Organic Chemicals, employed as the solvent, was treated with Molecular Sieve, Type 4A, grains (J. T. Baker Chemical Co.). The molybdenum trioxide sample was obtained from PRC, Inc. (Product No. 10375, Lot No. 4331).

The molybdenum trioxide cathodes were prepared from a cathodic mix containing 70% molybdenum trioxide and 30% graphite (1651 Microcrystal Graphite, Southwestern Graphite Co.). The mix was pressed on one side into a matrix of foametal of pure nickel (area=10 cm^2, originally 2 mm thick, 90% porosity, 20 mil pores), supplied by General Electric, Detroit, Michigan. The compression occurred at room temperature. A compression pressure of about 2,000 psi=$1.38.10^7$ Pa (pascal) was applied. Each electrode contained about 0.28 g of the cathodic mix which corresponds to about 80 mAh capacity, considering a theoretical capacity of 2F per mole MoO_3.

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

The cathode was surrounded by a filter paper (genuine Whatman Filter Paper No. 1) separator. The lithium anode and reference electrode were spaced 5 mm on either side from the cathode with free electrolyte in between. This arrangement was realized in a teflon cell having three parallel grooves for placement of the three electrodes. The cell was described in detail previously.[3]

The lithium anode and lithium reference electrode were prepared by pressing lithium ribbon (15 mils thick, Foote Mineral Co.) onto a nickel screen (Exmet 2/0) with a pressure of 1,000 psi ($=6.9.10^6$ Pa) and cutting 10 cm^2 electrodes. The amount of lithium metal per electrode was equivalent to approximately 0.62 Ah per electrode.

The main electrochemical instrumentation used was the periodically interrupted sine wave pulse current circuit[4] designed to permit ohmic iR free measurements of potentials. This technique is essential for kinetic studies, including the accurate determination of kinetic parameters such as exchange currents and Tafel slopes, to separate the various polarization components from each other.

RESULTS AND DISCUSSION

Coulometric Results of Partial Reduction Experiments During Cycling

A cycling experiment (10 charge-discharge cycles) at the C/8 rate (1 mA/cm^2) with 25% depth of discharge (0.5 F/MoO_3), with control measurements of the current-cathode potential relationship, initially and between the cycles, has been performed. The experiment was designed initially to shed some light on the cathode deterioration problem observed previously[5] during deep cycling (75% or 1.5 F/MoO_3) in 1M $LiClO_4$-PC electrolyte. During deep cycling, the cathode potential versus lithium dropped to 1.0 V. In the new experiment, the cathode potential on discharge never fell below 2.0 V vs lithium.

Figure 1 shows the discharge and charge curves for the first and tenth cycle. It was observed that the cathode potentials decreased by about 0.1 V from the first to the second discharge; thereafter, up to ten cycles, the discharge potentials decreased only slightly. However, the charging curves, which initially ended at about 3.3 V versus lithium, decreased further to about 3.0 V at the end of the tenth cycle. Thus, there is some improvement in the energy efficiency of the cathode after cycling.

The cathode potential-current curves measured initially and between cycles are depicted in Figure 2. They show a strong decrease in cathode potential between the first and fifth cycle, but none thereafter.

---

[3] H. F. Hunger and G. J. Heymach, "Cathodic Discharge of Graphite Intercalation Compounds in Organic Electrolytes," J. Electrochemical Society 120, 1161 (1973).

[4] H. F. Hunger and J. E. Ellison, ECOM-4296, op. cit., p. 1.

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

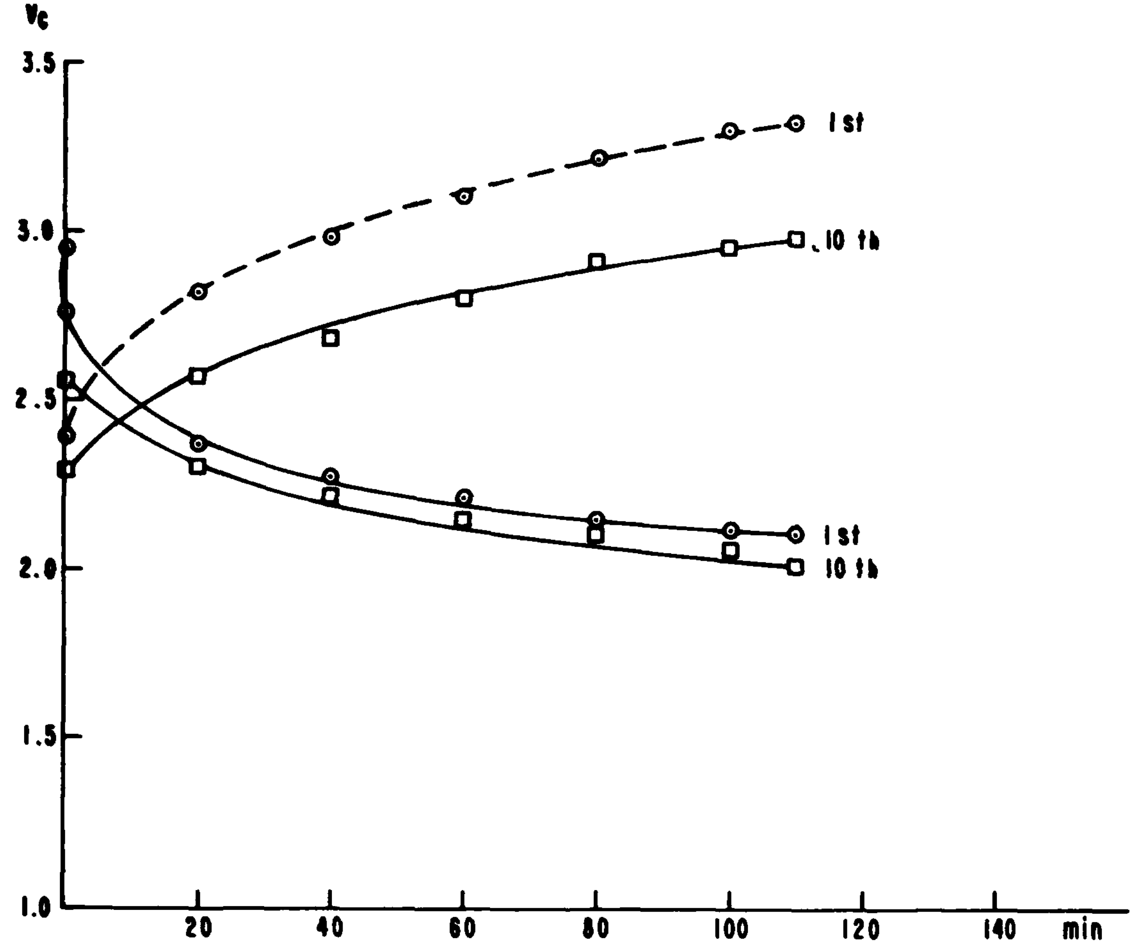

FIG. I MoO_3 CATHODE POTENTIAL VERSUS MINUTES OF DISCHARGE – CHARGE.
25 % DEPTH OF DISCHARGE. i = 10 mA. T = 25° C. 1M $LiClO_4$–PC ELECTROLYTE.

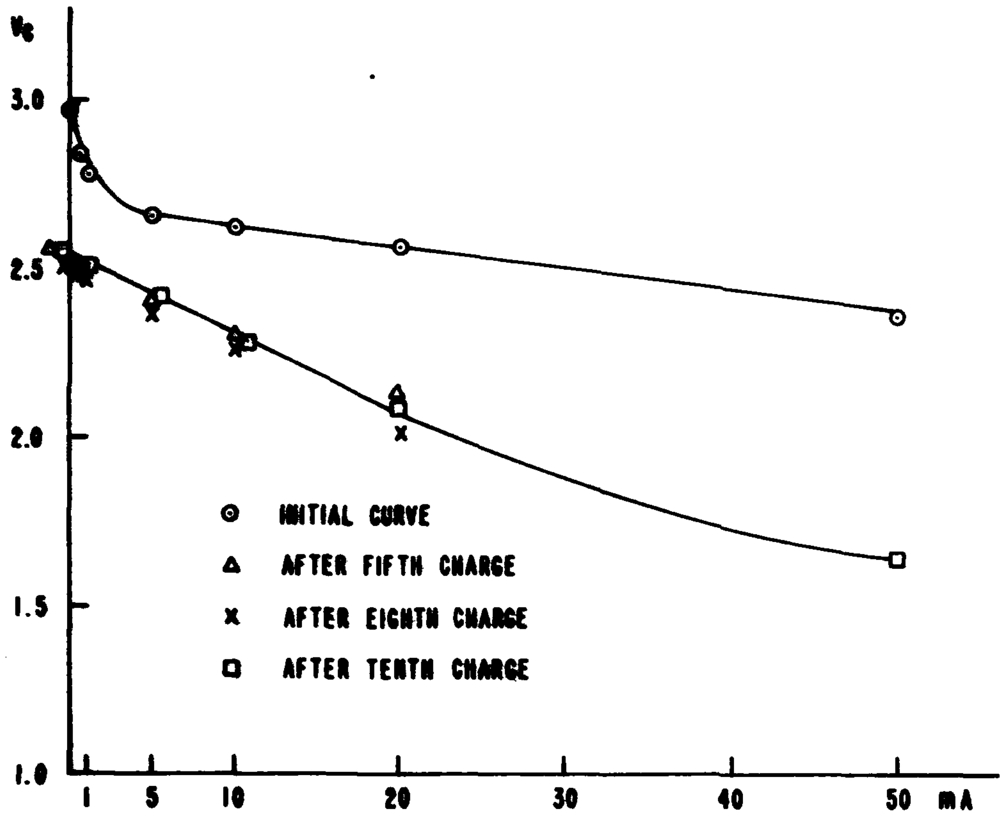

FIG. 2 MoO_3 CATHODE POTENTIAL VERSUS CURRENT CURVES MEASURED INITIALLY AND BETWEEN CYCLES. 25 % DEPTH OF DISCHARGE. T - 25° C. IM $LiClO_4$ -PC ELECTROLYTE.

It is known from the literature that V_2O_5, WO_3, and MoO_3 form mixed valency compounds when lithium intercalation occurs, e.g., LiV_2O_5 and $Li_5Mo_2O_8$ in molten electrolytes.[6,7,8]

Since a decrease in MoO_3 cathode rest potential is connected with an increase in lithium intercalation, a practically constant rest potential around 2.5 V versus lithium after a discharge of 25% of theoretical cathode capacity and recharging up to 100% of theoretical charge acceptance, indicates partial reduction of MoO_3 to a mixed valency compound in which the amount of lithium intercalation is practically constant. This compound does not appear to be reoxidized to MoO_3 during the charge cycles. It is difficult to assess accurately the nature of this compound. A coulometric evaluation of the data suggests, however, that MoO_3 undergoes partial reduction to a compound of the composition $LiMo_2O_6$.

This partial reduction step (Equation 1)

$$2MoO_3 + Li^+ + e^- = LiMo_2O_6 \qquad (1)$$

is irreversible and reoxidation does not occur during charging. The first charging curve constitutes, in our opinion, mainly electrolyte oxidation. During further discharge cycles (25% of theoretical capacity), the compound $LiMoO_3$ is the end product with a series of nonstoichiometric intermediates in between (Equation 2).

$$LiMo_2O_6 + Li^+ + e^- = 2LiMoO_3 \qquad (2)$$

Further charging curves appear different from the first one and represent probably the reoxidation of nonstoichiometric compounds of the general type $Li_{1+n}Mo_2O_6$ (whereby $0 < n \leq 3$) to $LiMo_2O_6$.

If the discharge were continued up to 75% of theoretical capacity, then the product Li_2MoO_3 would be finally formed, which is reported as having the maximum content of lithium intercalation. The rest open circuit potential of a completely lithiated compound lies around 2.0 V. Initial MoO_3 potentials lie around 3.0 V.[9] This perhaps explains why only 1.5F/MoO_3 were found for the total discharge of MoO_3 cathodes by one investigator.[10]

---

[6] P. Hagenmuller, J. Galy, M. Pouchard, and A. Casalot, "Recherches Recentes Sur des Bronzes de Vanadium," Materials Research Bulletin, 1, 45 (1966).

[7] M. E. Strausmanis and S. S. Hsu, "The Lithium Tungsten Bronzes," J. Amer. Chem. Soc. 72, 4027 (1950).

[8] B. N. Papao and H. A. Laitinen, "Electrochemical Reduction of Molybdenum (VI) Compounds in Molten Lithium Chloride-Potassium Chloride Eutectic," J. Electrochem. Soc. 120, 1346 (1973).

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

[10] N. Margalit, "Discharge Behavior of Li/MoO_3 Cells," J. Electrochem. Soc. 121, 1460 (1974).

A similar behavior was found by Holleck et al. where a nonrechargeable capacity (45% of initial capacity), during the initial part of the disulfide (Ti,Nb) reduction, was observed.[11]

Cathode Polarization as a Function of Cycling

In the cycling experiment described in the last chapter, cathode potential current curves were measured initially and between cycles. In Figure 3, MoO_3 cathode polarization versus log current density curves are plotted as a function of the number of cycles. From the figure the following can be seen:

(1) There are no significant changes as far as the Tafel slope is concerned with cycling.

(2) Uncertainties in the exchange current density, I_o, with cycling are probably due to not completely reached cathode rest potentials; e.g., 2.53 V measured after the fifth cycle should be 2.64 V in order to give the same I_o like the initial curve. Another explanation would be that the I_o for the cathodic reduction of MoO_3 is different from that of $LiMo_2O_6$.

(3) The curves between the 5th and 10th cycle are practically identical. Thus, it appears that, in general, the reaction kinetics and reaction rate remain essentially the same.

Diagnostic Indications Concerning the Reaction Mechanism

The polarization behavior of the MoO_3 cathode permits some statements concerning their reaction mechanism. A diagnostic analysis of current density-cathode potential curves in 1M $LiClO_4$-PC electrolyte indicates a mixed activation-concentration polarization, followed by another electrode reaction at cathode potentials below 2.5 V.[12] From the polarization-log current density curves (Figure 3), estimates of the exchange current densities of the electron transfer reaction yield an I_o of about 5.10^{-6}A/cm^2. This indicates a fast electron transfer reaction. The slope ($b=0.11$) of both curves corresponds to a $\alpha n=0.5$, indicating a one electron charge transfer process as rate determining in the Tafel region. Strong deviations from Tafel linearity at higher current densities above 5.10^{-4}A/cm^2 indicate diffusion limitation, probably by Li^+ ions. A reaction mechanism can thus be postulated for initial cathodic discharges and one for subsequent discharges after recharging. Equation (1) postulates the initial charge transfer step which is apparently fast. Equation (3) shows the diffusion step, preceding the electron transfer step which becomes rate determining at higher polarizations.

$$Li^+_{solution} \longrightarrow Li^+_{solid} \qquad (3)$$

---

[11] G. L. Holleck, J. R. Driscoll, and F. S. Shuker, "Sulfur-Based Lithium Organic Electrolyte Secondary Batteries," Final Report, Contract DAAB07-74-C-0072(ECOM), EIC, Inc., March 1976.

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

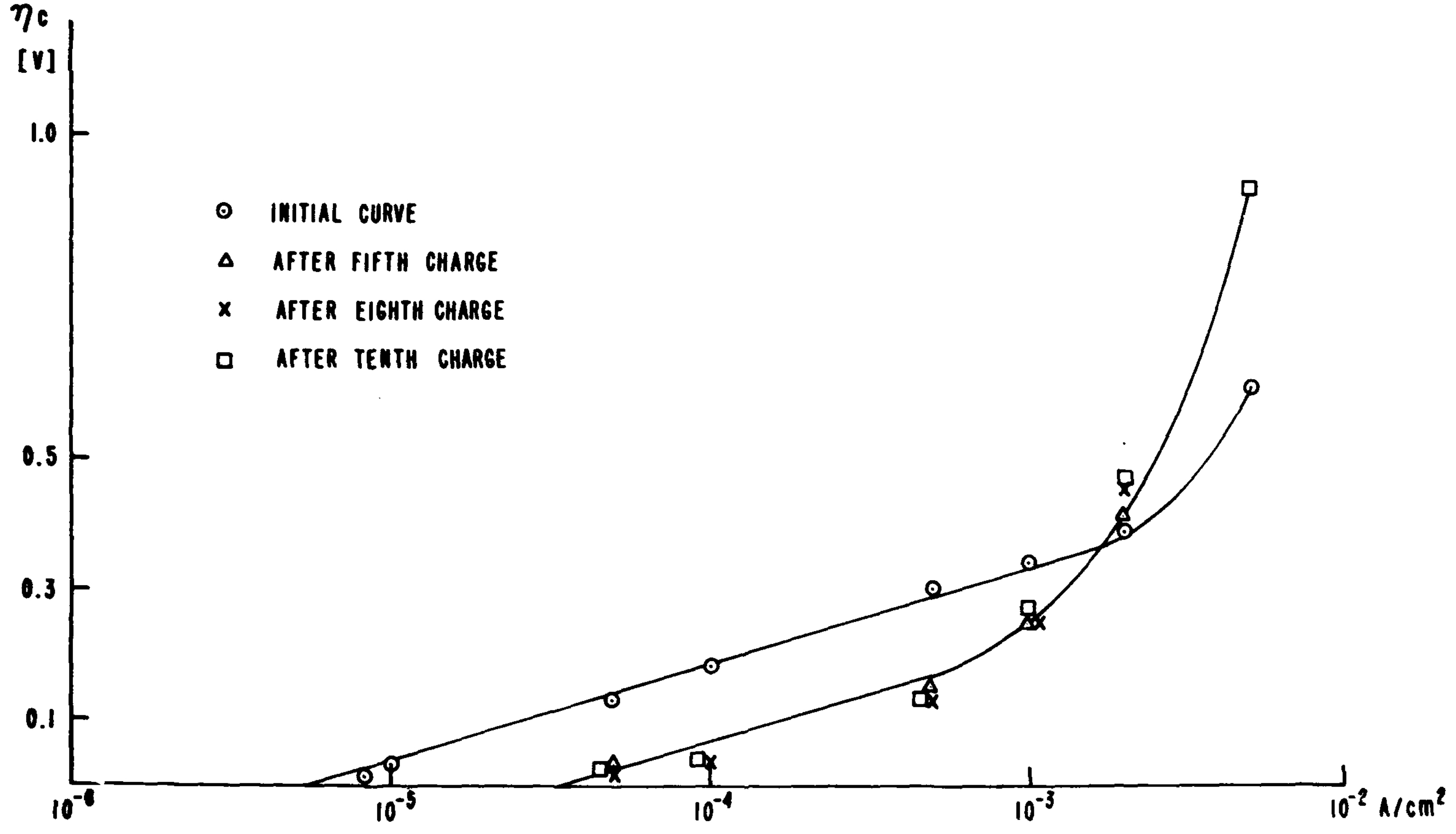

FIG. 3 MoO_3 CATHODE POLARIZATION VERSUS LOG CURRENT DENSITY CURVES AS A FUNCTION OF THE NUMBER OF CYCLES. T = 25° C. 1M $LiClO_4$ -PC ELECTROLYTE.

Equation (2) postulates subsequent cathodic discharges after "recharging." A similar reaction mechanism has been postulated by Besenhard and Schoellhorn for chromium oxides.[13] Equation (4) shows their overall reaction, the formation of a ternary phase such as $LiCr_3O_8$.

$$xLi^+ + xe^- + Cr_nO_m \rightleftharpoons Li_xCr_nO_m \qquad (4)$$

While CrO_3 could not be reduced cathodically, Cr_3O_8, Cr_2O_5, and Seloxcette yield more than one electron per chromium atom. They believe that the polarization is caused by hindered transport of nonsolvated Li^+ ions in the solid phase. Holleck et al. believe that the limiting current density at TiS_2 cathodes in methyl acetate electrolytes is determined not only by diffusion of Li^+ ions in the solid but also by concentration changes in the adjacent electrolyte layer.[14] Further dimensional charges in bonded TiS_2 electrodes, particularly during the first discharge, and large increase in weight of the electrodes during discharge, indicate simultaneous intercalation of lithium and of solvent molecules.

Thus, there appears to be a general behavior during the electrochemical formation of nonstoichiometric ternary phases by lithium intercalation. Diffusion of lithium ions with or without solvent participation appears to be rate limiting at practical current densities.

Electrolyte Optimization With Respect to Rate

Since we had found that the rate of the cathodic reduction of molybdenum oxide was limited by diffusion processes, a strong influence of the electrolyte on the rate capability of the cathode had to be expected. On one hand, the electrolyte solvent itself by its viscosity will strongly influence the diffusion; on the other hand, the lithium ion concentration of the electrolyte will play a significant role. The relatively high viscosity of the electrolyte solvent propylene carbonate, which we used so far in our experimentation is probably slowing down the diffusion of lithium ions in the electrolyte within the porous electrode. A decrease of the viscosity of the electrolyte solvent should lead to a better rate capability of the cathode, higher practical capacity, less side reactions with consequential solvent oxidation and reduction effects, and finally to a better low temperature performance.

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

[14] G. L. Holleck et al., op. cit., p. 6.

Table 1 shows some significant electrolyte characteristics, such as diffusion coefficients, viscosities, and specific conductances.[15,16,17]

It can be seen from the table that the solvent viscosity has a significant influence on conductance. According to Holleck et al.,[18] who worked with titanium disulfide cathodes, a high lithium ion concentration in the electrolyte is desirable. The nature of the solute anion plays apparently only a subordinate role.

Considering electrolyte conductance and solvent viscosity, the following sequence of electrolytes appears suitable in order to attain maximum rate capability at the lithium intercalating cathode in rechargeable lithium-organic electrolyte cells:

$$0.7M\ LiCl - 1M\ AlCl_3 - AN > 1M\ LiClO_4 - AN >$$

$$1.1M\ LiAsF_6 - MF > 1M\ LiClO_4 - MF$$

This sequence considers expected rate characteristics only, it does not take into account the long term compatibility of all cell components with each other. Extensive, individual system studies would have to be made in order to clarify all these questions. Based on this sequence, acetonitrile was used as the electrolyte solvent in further experimentation concerned with establishing rate limitations of the molybdenum oxide cathode. Acetonitrile electrolytes have a high diffusion coefficient for lithium ions and a low solvent viscosity. Their conductance matches that of methyl formate. As solute, we preferred lithium perchlorate over salt mixtures, since our previous experimentation was done with that salt. Both a 3 molar and 1 molar concentration of lithium perchlorate was used in the further experimentation.

Rate Limitations of the Molybdenum Oxide Cathode in Acetonitrile Electrolytes

In order to determine the solvent effect on the rate characteristics of molybdenum oxide cathodes, cells were assembled which can be characterized by the schemes

$$Li/3M\ LiClO_4 - AN/MoO_3,C$$

$$Li/1M\ LiClO_4 - AN/MoO_3,C$$

---

[15] R. Keller and J. F. Hon, "Investigation of Electrolyte Systems for Lithium Batteries," Final Report, Contract NASA CR-72803, Rocketdyne, 26 May 1969 to 25 July 1970.

[16] R. Keller, J. N. Foster, D. C. Hanson, J. F. Hon, and J. S. Muirhead, "Properties of Nonaqueous Electrolytes," Contract NASA CR-1425, North American Rockwell Corporation, Aug. 1969.

[17] J. M. Sullivan, D. C. Hanson, and R. Keller, "Diffusion Coefficients in Propylene Carbonate, Dimethyl Formamide, Acetonitrile, and Methyl Formate," J. Electrochem. Soc. 117, 779 (1970).

[18] G. L. Holleck, et al., op. cit., p. 6.

Table 1. Diffusion Coefficients for Lithium Ions D, Specific Conductances of Solutions σ, and Viscosities η of Solvents and Solutions. 25°C.

Electrolyte	D ($cm^2 sec^{-1}$)	σ ($\Omega^{-1} cm^{1}$)	η solvent ($g\ cm^{-1} sec^{-1}$)	η solution ($g\ cm^{-1} sec^{-1}$)
1M $LiClO_4$-PC	$2.58.10^{-6}$	$5.12.10^{-3}$	2.48	7.08
0.7M LiCl 1M $AlCl_3$-PC	$3.04.10^{-6}$	$6.56.10^{-3}$	----	7.18
1M $LiClO_4$-DMF	$7.3.10^{-6}$	$3.18.10^{-3}$	----	1.89
1M LiCl-DMF	$5.87.10^{-6}$	$8.5.10^{-3}$	0.79	1.83
1M LiCl 0.075M $AlCl_3$-DMF	$5.72.10^{-6}$	$7.78.10^{-3}$	----	2.29
1M $LiClO_4$-BL	----	$1.5.10^{-2}$	1.7	----
1M $LiClO_4$-MA	----	$0.7.10^{-2}$	0.38	----
3M $LiClO_4$-MA	----	$1.4.10^{-2}$	----	----
1M $LiClO_4$-AN	$1.71.10^{-5}$	$3.19.10^{-2}$	----	----
3M $LiClO_4$-AN	----	$3.0.10^{-2}$	0.336	----
0.7M LiCl 1M $AlCl_3$-AN	$1.69.10^{-5}$	$5.1.10^{-2}$	----	----
1M $LiClO_4$-MF	$1.68.10^{-5}$	$3.2.10^{-2}$	0.339	----
1.1M $LiAsF_6$-MF	$1.54.10^{-5}$	$3.36.10^{-2}$	----	----

The first cell had an initial open circuit voltage of 2.83 V, and second cell of 2.98 V. The current-potential curves of the cells were measured using the periodically interrupted sine wave pulse current circuit. Each data point was taken after a five-minute period on drain (pseudo steady state).

In Figure 4 the MoO_3 cathode potential versus a lithium reference electrode are plotted against the current densities in mA/cm^2 of geometrical electrode cross section. The potential-current density curve belonging to the 3M $LiClO_4$-AN electrolyte showed an initial delay phenomenon. The curve for the 1M $LiClO_4$-AN electrolyte shows an initial drop associated with activation polarization and then straightens out indicating mixed activation and concentration polarization without reaching a definite limiting current density at a cathode potential of 1.6 V versus lithium reference electrode. The curve for 1M $LiClO_4$-PC can be interpreted the same way. The numbers assigned to the arrows above the curve for the 3M $LiClO_4$-AN electrolyte indicate the status of theoretical cathode utilization.

The plot shows a considerable increase in rate capability in going from propylene carbonate to acetonitrile. It shows, e.g., that after 5 minutes discharge at 2.0 mA/cm^2, a theoretical cathode utilization at 3.12% was reached, after another 5 minutes at 25 mA/cm^2 - 78%. The surprising finding is that the cathode, e.g., after 60.9% of theoretical cathode utilization, is still capable of a rate of 20 mA/cm^2 at a cathode potential of 1.8 V and after 78% of a rate of 25 mA/cm^2 at a potential of 1.7 V versus lithium. The total coulombic capacity of the cathode in question was $8.4.10^{-2}$ Ah. The data above indicate a 2-3 C rate capability for the experimental cathodes investigated. The rest open circuit potential, after 78% discharge of the molybdenum trioxide cathode in 3M $LiClO_4$-AN, was 2.22 V. Since there is such a strong improvement in the rate capability of the cathode by replacing a viscous solvent by a less viscous one, we postulate that the rate limitation is caused by the diffusion process from the bulk of the electrolyte through the pore-electrolyte to the electrolyte-electrode interface or due to diffusion of solvated lithium ions within the Van der Waals gap between the molybdenum oxide sheets. Schoellhorn et al.[19] claim that nonsolvated alkali cations enter the lattice in aprotic electrolyte solutions in dimethoxyethane (DME) or dimethylsulfoxide (DMSO). Based on our experimental data, it is believed that, in the case of acetonitrile, the solvent participates in the diffusion process.

Effect of Cycling on Rate Characteristics of the Molybdenum Oxide Cathode in Acetonitrile Electrolytes

Recharging of the molybdenum oxide cathode in 3M $LiClO_4$-AN with 1 mA/cm^2 in the open cell design in the dry box led to strong solvent evaporation and temperature decrease of the electrolyte (25°C → 22°C); thus solvent had to be added to the cell. Salt crystallization was noted at the electrodes, both cathode and anode.

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[19] R. Schoellhorn and R. Kuhlmann, "Topotactic Redox Reactions and Ion Exchange of Layered MoO_3 Bronzes," Materials Research Bulletin 11, 83 (1976).

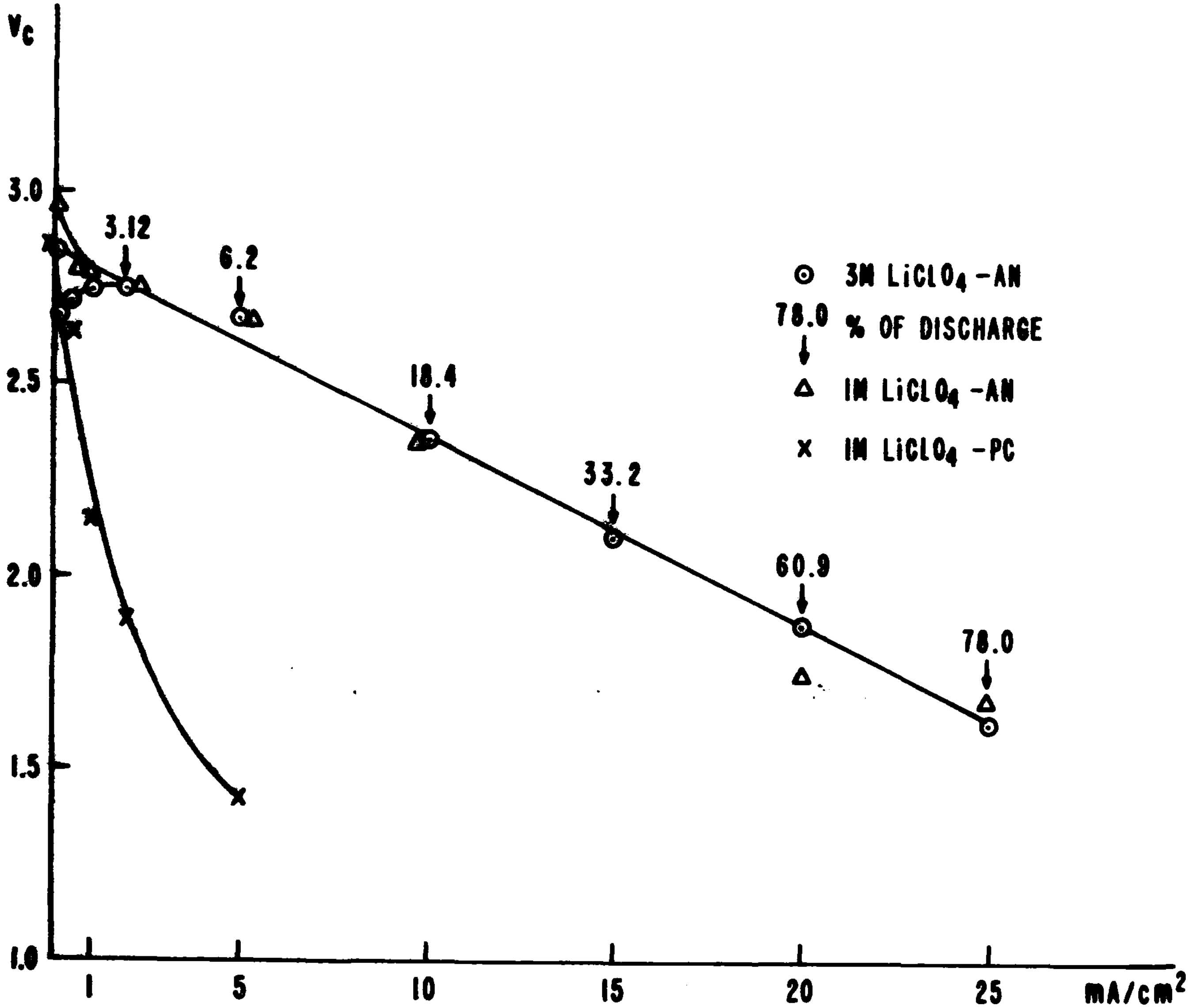

FIG. 4 MoO_3 CATHODE POTENTIAL VERSUS CURRENT DENSITY. VARIOUS ELECTROLYTES. T = 25° C.

The second current-potential curve measured indicated a strong loss in cathode rate capability, obviously by blocking of the cathode with salt crystals. While the cathode could sustain easily 25 mA/cm^2 during the initial discharge, a current density of only 2 mA/cm^2 led to a complete cathode potential breakdown during the second discharge. The problem was not as severe with 1M $LiClO_4$-AN. The first and second cathode polarization versus current-density curves are shown in Figure 5; the initial curve measured in 3M $LiClO_4$-AN is plotted for comparison purposes.

The figure further shows that the Tafel slope in acetonitrile is similar to that in the propylene carbonate electrolyte. The exchange current density for the 3M solution appears, from the graph, to be higher than that of the 1M solution, but data measured at lower current densities indicate that the exchange current densities are of the order of $10^{-6}A/cm^2$, like in the case of propylene carbonate. This has to be expected since the solvent should not have any significant influence on the rate of the electron transfer process. Strong deviations from Tafel linearity are observed above $5.10^{-3}A/cm^2$. This is one order of magnitude higher than in propylene carbonate. This difference of one order of magnitude is comparable to the difference in diffusion coefficients for Li^+ ions in the two solvents, $2.58.10^{-6}$ and $1.71.10^{-5}$. Charging of the cathode was done after the cell was provided with fresh electrolyte and fresh lithium electrodes. The similarity of shape of the second curve with the first one indicates a displacement of the original curve to lower current densities, probably due to a decrease of the electrochemically active cathode area by a factor of ten. All other kinetic characteristics remain essentially the same. The decrease of surface areas could have several causes, namely, salt depositions within the electrolyte structure, deposition of side reaction products, and/or loss of contact between active particles due to irreversible swelling.

Ultimate Choice of Electrolyte Solvents

Although electrolyte solvents like acetonitrile improve the initial rate capability of molybdenum oxide cathodes considerably, the ultimate use of a solvent will be determined by its stability versus lithium and its influence on the rechargeability of the lithium electrode. Acetonitrile does not appear to be the ultimate solvent. Billion[20], e.g., reports reactivity of acetonitrile with sodium (Equation 5).

$$2\ CH_3 - CN + 2Na \longrightarrow NaCN + CH_4 + Na - CH_2 - CN \qquad (5)$$

Lithium perchlorate-dioxolane solutions, used with titanium disulfide electrodes, present explosion hazards probably due to the perchlorate anion.[21]

---

[20] J. P. Billion, "Electrochimie dans L'Acetonitrile," J. Electroanalyt. Chem. 1, 486 (1959/60).

[21] B. M. L. Rao, C. H. Newman, R. W. Franzis, and L. H. Gaines, "Titanium Disulfide Electrode," Abstract, Electrochemical Society Meeting, Atlanta, Georgia, 9-14 October 1977 (Extended Abstract No. 7).

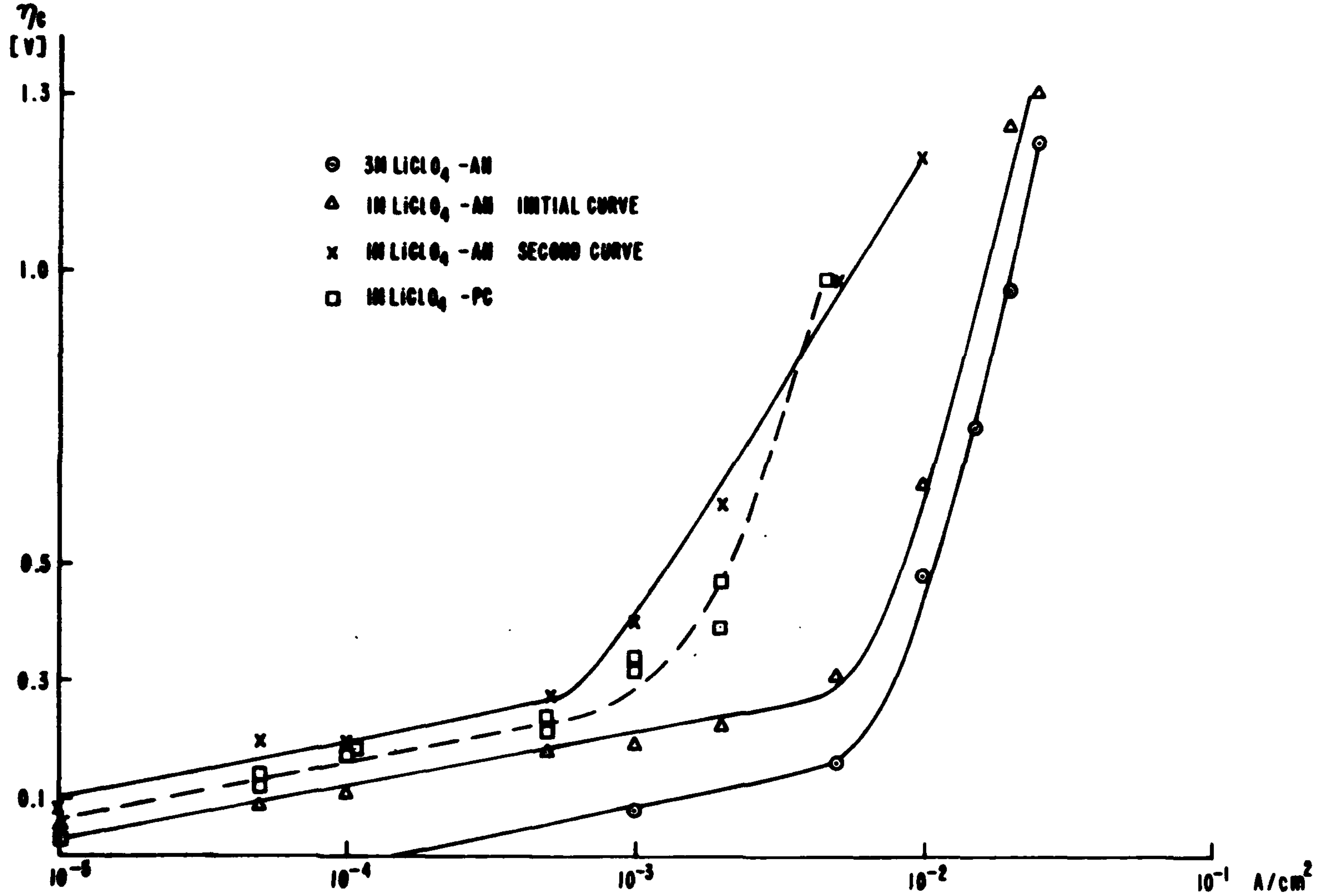

FIG. 5 MoO$_3$ CATHODE POLARIZATION VERSUS LOG CURRENT DENSITY CURVES. VARIOUS ELECTROLYTES. T = 25°C

Problems in recharging the lithium electrode, due to film formations, are reported with propylene carbonate and tetrahydrofurane solvents.[22,23]

An electrolyte consisting of 1M $LiAsF_6$-THF shows an oxidation potential of more than 4.2 V versus the lithium electrode, promising greater protection against overcharge; 1M $LiClO_4$-THF oxidizes already at 3.5 V on platinum.[24]

Several solvent-electrolyte properties have to be observed for proper choice of electrolytes in secondary lithium batteries:

(1) Provide high rate capability for both anode and cathode.

(2) Show chemical stability versus anode and cathode material.

(3) Permit discharging and recharging of anodes and cathodes with high coulombic efficiency without formation of blocking films or deposition of side reaction products.

(4) Show high electrolyte oxidation and low reduction potentials.

Rate Comparison With Other Lithium Intercalation Compounds

A rate comparison of molybdenum oxide cathodes in 1M $LiClO_4$-PC and 1M $LiClO_4$-AN shows that at a cathode polarization of about 0.3 V, which corresponds to the upper end of the Tafel region, current densities of 5.10^{-4} and $5.10^{-3}A/cm^2$, respectively, can be obtained; $5.10^{-3}A/cm^2$ is equal to 5 mA/cm^2. However, at a higher polarization, up to 25 mA/cm^2 were obtained (3C rate - room temperature) with good cathode utilization efficiencies. Various investigators report rate capabilities of other cathodes. Holleck et al.[25] report, e.g., discharges at C/12 and C/1 rates at NbS_2 electrodes with 2 mAh/cm^2 capacity in 1M $LiAlCl_4$-PC electrolytes. These are niobium foil electrodes with active disulfide layers. In comparison, our compressed foametal electrodes have a capacity of about 8 mAh/cm^2 or a total capacity of 80 mAh. Potentiostatic charging and discharging of NbS_2 in 1M $LiClO_4$-PC electrolyte shows peak current densities of about 5 mA/cm^2; NbS_3-Nb foil cathodes in 1M $LiAlCl_4$-PC electrolyte permit discharge rates of 0.5 mA/cm^2 at the 10 hour rate and 2.0 mA/cm^2 at the 1 hour rate. Potentiostatic discharging (1.5 V discharge voltage, 2.8 V charge voltage) shows up to 10 mA/cm^2 initially in 1M $LiClO_4$-PC. Similar potentiostatic tests with TiS_2 permit up to 7.5 - 10.5 mA/cm^2 initially, but the main discharge and charge occur below 5 mA/cm^2 in propylene carbonate. An increase in temperature from 25 to 60°C raises the current density above 10 mA/cm^2. In methyl acetate electrolyte, current densities of 10 mA/cm^2 and above are obtained at room temperature. Potentiostatic tests with TiS_3

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[22] P. J. Rommers and J. R. V. Beck, "Behavior of the Secondary Lithium Electrode in Propylene Carbonate Based Electrolytes," Abstract, Electrochemical Society Meeting, Atlanta, Georgia, 9-14 October 1977, (Extended Abstract No. 1).

[23] V. R. Kock and J. H. Young, "The Reaction of Lithium With Tetrahydrofuran-Based Electrolytes," ibid. (Extended Abstract No. 5).

[24] F. W. Dampier and S. B. Brummer, "Corrosion Resistant Materials for Organic Electrolyte Li Secondary Batteries," ibid. (Extended Abstract No. 14).

[25] G. L. Holleck, et al., op. cit., p. 6.

electrodes show the first reduction step at around 5 mA/cm^2. Thus, the di- and trisulfides of titanium and niobium are capable of 5-10 mA/cm^2 depending upon the nature of the solvent and the operating temperature. Mass transfer limitations are indicative in all cases. Thus, the behavior of these compounds is quite similar to that of MoO_3. Recently, chromium oxides were reported as suitable cathodic materials. Cyclic voltammetry of Seloxcette (approximate composition Cr_2O_5) in $LiClO_4$-DME electrolyte indicates a cathodic reduction rate of over 2 mA/cm^2, the recharging rate being somewhat lower.[26]

SUMMARY AND CONCLUSIONS

Experimental work with molybdenum trioxide cathodes in organic electrolytes was concerned with determination of the Faradaic efficiency and rate capability of the rechargeable system, a diagnostic look at the reaction mechanism, an optimization of the electrolyte with respect to rate capability, and an estimate of the practical rate capability of the cathode.

Coulombic analysis of cycling experiments suggested a high coulombic cathode efficiency at moderate rates (1 mA/cm^2). Molybdenum trioxide is initially partially reduced. This lithiated product cannot be re-oxidized; however, further reduction of this compound up to 1.5F per molybdenum atom is possible. These products can be reversibly oxidized to the partially reduced compound.

The cathode kinetics show a fast single electron transfer step but diffusion processes become rate determining at higher current densities. A similar behavior is observed with certain chromium oxides, with titanium di- and trisulfides and niobium di- and trisulfides as cathode materials.

Cycling at moderate rates (1 mA/cm^2) and 25% depth of discharge show that the cathode performance stabilizes between the first and tenth cycle and the reaction kinetics and reaction rates remain essentially the same.

Since the mechanism studies showed that lithium ion diffusion is rate limiting in electrolytes with viscous solvents, partial optimization of the electrolyte with respect to cathode rate capability was undertaken. On the basis of diffusion coefficient, solvent viscosity, and electrolyte conductance, the electrolytes 1 - 3 molar lithium perchlorate in acetonitrile were chosen. With these electrolytes, about a ten-fold rate capability (25 mA/cm^2) at high coulombic efficiency (up to 78%) was reached. The high rate and/or deep discharge, however, was detrimental to the present cathode and its performance decreased considerably during the second cycle.

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[26] J. O. Besenhard and R. Schoellhorn, op. cit., p. 8.