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TRANSITION METAL COMPOUNDS AS CATHODIC MATERIALS IN RECHARGEABLE LITHIUM CELLS

Herbert F. Hunger

Joseph E. Ellison

Electronics Technology & Devices Laboratory

February 1977

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Item 20. ABSTRACT - Continued.

the energy efficiency and the energy content of the system were determined.



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TRANSITION METAL COMPOUNDS AS CATHODIC MATERIALS IN RECHARGEABLE LITHIUM CELLS

INTRODUCTION

The objective of this study is to compare the theoretical and practical coulombic capacities, energy densities, rate capabilities, and kinetics of cathodes composed of transition metal oxides or chalcogenides. The ultimate objective is a high rate, low overvoltage positive electrode for secondary lithium nonaqueous electrolyte batteries with optimum reversibility and high cycle life. This report covers only the initial phase of the study.

SURVEY OF POTENTIAL CATHODIC MATERIALS

Before any selection of potential, rechargeable cathodic materials could be made, a survey of materials was made on the basis of the following premise: "materials are to be considered which intercalate lithium reversibly without breakdown of the crystal structure of the cathodic material and maintenance of the chalcogenide and oxide bonds during the charge-discharge processes." It appeared that numerous transition metal chalcogenides and oxides would fulfill this requirement.

General Structure

There is sufficient evidence that transition metal chalcogenides with a layer type structure can intercalate inorganic or organic molecules or alkali metal ions. The basic form of these layer compounds comprises a sandwich of anion and cation sheets separated by a Van der Waals gap. A result of the weak Van der Waals binding is that the sandwich gap will open up to accept alkali metal ions. The coordination units are either trigonal prismatic or octahedral. Several stacking polytypes exist. Looking at the IV through VIII B groups of the periodic system, two thirds of the dichalcogenides assume layer structure. They are mostly diamagnetic semiconductors, but some are metallic and show superconductivity.^{1,2}

The group V B and VI B transition metal oxides are known to form alkali metal intercalation or interstitial compounds (vanadium and tungsten bronzes). While some of the compounds show perovskite structures, molybdenum trioxide has a layer structure.^{3,4}

¹J. A. Wilson and A. D. Yoffee, "The Transition Metal Dichalcogenides," *Adv. Phys.* 18, 193 (1969).

²C. Jorgensen, J. B. Neilands, R. S. Nyholm, D. Reinen, and R.J.P. Williams, Structure and Bonding (Springer Verlag, Berlin 1968), Vol. 4, pp. 83-229.

³M. J. Sienko, Advances in Chemistry Series No. 39 (Academic Press 1964) Chapter 21, p. 224.

⁴A. F. Wells, Structural Inorganic Chemistry (Oxford At The Clarendon Press 1962), p. 468.

Nonstoichiometric Phases and Reversibility

Table 1 shows the compositions of lithium intercalates of group IV B through VI B transition metal chalcogenides and oxides with maximum lithium content as cited in the literature.

Table 1. Compositions of Lithium Intercalates of Transition Metals*

<u>Group IV B</u>	<u>Group V B</u>	<u>Group VI B</u>
LiTiS ₂	LiVS ₂	LiCrS ₂
LiTiS ₃	Li _{0.7} ^V 1.25S ₂	LiMoS ₂
LiTiSe ₂	LiVSe ₂	Li ₂ MOO ₃
LiZrS ₂	LiV ₂ O ₅	Li _{0.56} ^{WO} 3
LiZrSe ₂	LiNbS ₂	
LiHfS ₂	Li _{0.78} ^{Nb} 1.09S ₂	
LiHfSe ₂	Li _{1.38} ^{Nb} S ₃	
	LiNbSe ₂	
	Li ₃ NbSe ₃	
	Li ₄ NbSe ₄	
	LiTaS ₂	
	LiTaSe ₂	

*These compounds have maximum lithium content.

With respect to the preparation of these compounds, Whittingham et al.⁵ have found that reaction of transition metal compounds with n-butyl lithium, dissolved in a non-polar solvent such as hexane, leads to lithium intercalation compounds. In general, the group IV B metal disulfides and diselenides react within two days with n-butyl lithium to LiMeS₂ or LiMeSe₂.⁶

⁵M. S. Whittingham, R. R. Chianelli, and M. B. Dines, "A Non-Electrochemical Test for Cathode Activity in Lithium Cells," Abstract, Electrochemical Society Meeting, Dallas, Texas, 5-10 October 1975 (Extended Abstract No. 35).

⁶M. S. Whittingham and F. Gamble, Jr., "The Lithium Intercalates of the Transition Metal Dichalcogenides," Mat. Res. Bull. 10, 363 (1975).

From the V B group, V_5S_8 reacts slower with n-butyl lithium than the IV B compounds to form $Li_{0.7}V_{1.25}S_2$. $Nb_{1.09}S_2$ reacts slowly with n-butyl lithium (15 days). Transition metal in the Van der Waals gap is apparently impeding lithium diffusion. In general, V B compounds show about one order of magnitude slower intercalation than the IV B group compounds. Group VI B compounds, with the exception of molybdenum disulfide, react much more slowly with n-butyl lithium than the other layered dichalcogenides.

In particular, titanium trisulfide is reversible for less than one lithium.⁷ The amount of structural disruption in titanium trisulfide makes it less reversible. Further, the polysulfide bonds must be broken and reformed for reversibility. Titanium trisulfide contains one sulfide sulfur and one polysulfide group, TiS (S-S).

Zirconium disulfide and diselenide are expected to behave similar to the titanium compounds. The structure of zirconium triselenide is known,⁸ but no lithium intercalation compounds are reported in the literature.

Hafnium disulfide and diselenide are known to form lithium intercalates. Vanadium disulfide per se has not been found to be stable, but the structure is stabilized by lithium so that the compound $LiVS_2$ is known.⁹ Vanadium diselenide shows instability due to crystallographic distortion.¹⁰ $LiVSe_2$ can react with excess n-butyl lithium causing a degradation of the lattice.

Vanadium pentoxide forms a stable phase LiV_2O_5 .¹¹ The vanadium is in a highly distorted octahedron of oxygen. For small amounts of lithium ($x \leq 0.13$) in $Li_xV_{2-x}^{5+}V_x^{4+}O_5$, this structure is maintained. These are the α alkali vanadium bronze phases. For the bronzes, the distorted square pyramids have a different orientation to that found in vanadium pentoxide itself. In the reaction of lithium with vanadium pentoxide, the vanadium is reduced from the plus five valent state to the plus four valent state and the vanadium oxygen bond is presumably broken.

Niobium triselenide and tetraselenide are reversible for three and four lithium atoms, respectively.¹² The reversibility involves only an expansion

⁷R. R. Chianelli, M. B. Dines, and M. S. Whittingham, "The Reversibility Question of the Transition Metal Trichalcogenides," Abstract, Electrochemical Soc. Meeting, Dallas, Texas, 5-10 October 1975 (Extended Abstract No. 31).

⁸Von W. Kroenert and K. Plieth, "Die Struktur des Zirkontriselelide," *Allgem. Chem.* 336, 207 (1965).

⁹B. Van Laar and D. J. W. Ijdo, "Preparation, Crystal Structure, and Magnetic Structure of $LiCrS_2$ and $LiVS_2$," *J. Solid State Chem.*, 3, 590 (1971).

¹⁰M. S. Whittingham and F. Gamble, Jr., *Mat. Res. Bull.* 10, op. cit., p.2.

¹¹P. Hagermuller, J. Galy, M. Pouchard, and A. Casalet, "Recherches Recentes Sur Les Bronzes de Vanadium," *Mat. Res. Bull.* 1, 45 (1966).

¹²R. R. Chianelli, M. B. Dines, and M. S. Whittingham, Extended Abstract No. 31, op. cit.; D. W. Murphy, F. A. Trumbore, and J. N. Carides "New Niobium Selenide Cathode for Nonaqueous Lithium Batteries," Electrochemical Society Meeting, Las Vegas, Nevada, 17-22 October 1976 (Extended Abstract No. 70).

and contraction of a lattice which remains essentially undisrupted, the ideal fulfillment of the requirement for good rechargeability. The Se-Se bond is considerably weaker than the S-S bond and is, therefore, more easily reversible.^{13,14} Tantalum disulfide and diselenide form lithium intercalates.¹⁵

Like vanadium, chromium does not form a disulfide, but the compound LiCrS_2 is known.¹⁶ Stable compounds of the type LiMoS_2 are not formed.¹⁷ If formed, they would disproportionate to lithium sulfide and molybdenum, due to the very low free energies of formation of the VI B and later group dichalcogenides. Molybdenum disulfide is on the borderline of stability for intercalation formation. At low lithium contents, Li_xMoS_2 is expected to be stable, but at higher values of X, the intercalation compound becomes unstable to lithium sulfide formation. Molybdenum diselenide probably reacts to form lithium selenide. Molybdenum trioxide and lithium form ternary phases (Li_2MoO_3) as expected from its layered structure.^{18,19} Tungsten disulfide, tungsten diselenide, and rhenium diselenide show no evidence for lithium intercalation. Tungsten trioxide with lithium yields an average stable phase $\text{Li}_{0.56}\text{WO}_3 = \text{LiW}^{\text{VI}}\text{O}_3 (\text{W}^{\text{VI}}\text{O}_3)_{0.77}$. Pure LiWO_3 does not exist.²⁰ Breaking of tungsten-oxygen bonds diminishes reversibility; slow diffusion of alkali ions in the cubic perovskite structure of tungsten trioxide does not promise good rate characteristics.²¹

Comparison Between Rechargeable Lithium Batteries and Nickel-Cadmium Batteries

A comparison was made between rechargeable lithium batteries, based on formation of lithium intercalation or lithium interstitial compounds, and nickel-cadmium batteries. In this comparison we considered: (a) the composition of lithium intercalates of transition metal compounds with maximum lithium content (from Table 1), (b) the rate of lithium intercalation, (c) bond breaking during intercalation (which negatively influences the reversibility and expected coulombic efficiency), and (d) known instability of compounds. The coulombic capacity was expressed in A·h/g; also, initial

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- ¹³J. Broadhead and F. Trumbore, "A Lithium-Niobium Selenide Secondary Battery," Abstract, Electrochemical Society Meeting, Chicago, Illinois, 13-18 May 1973 (Extended Abstract No. 178); also, J. Electrochem. Soc. 120, 102C (1973).
- ¹⁴D. W. Murphy and F. A. Trumbore, "The Chemistry of NbSe_3 and TiS_3 Cathodes," J. Electrochem. Soc. 122, 68C (1975); also, J. Electrochem. Soc. 123, 960 (1976).
- ¹⁵M. S. Whittingham and F. Gamble, Jr., Mat. Res. Bull. 10, op.cit., p.2.
- ¹⁶B. Van Laar and D. J. W. Ijdo, J. Solid State Chem., 3, op. cit., p. 3.
- ¹⁷M. S. Whittingham and F. Gamble, Jr., Mat. Res. Bull. 10, op.cit., p.2.
- ¹⁸F. W. Dampier, "The Cathodic Behavior of CuS , MoO_3 , and MnO_2 in Lithium Cells," J. Electrochem. Soc. 121, 656 (1974).
- ¹⁹N. Margalit, "Discharge Behavior of Li/MoO_3 Cells," J. Electrochem. Soc. 121, 1460 (1974).
- ²⁰M. E. Strausmanis and S. S. Hsu, "The Lithium Tungsten Bronzes," J. Amer. Chem. Soc. 72, 4027 (1950).
- ²¹M. S. Whittingham, "Free Energy of Formation of Sodium Tungsten Bronzes, Na_xWO_3 ," J. Electrochem. Soc. 122, 713 (1975).

component cost expressed in $\$/A\cdot h$, neglecting cost of lithium, were considered; minimum prices of compounds were taken from commercial products catalogs.^{22,23,24,25} The computation of data for nickel-cadmium batteries was based on the prices of nickel hydroxide and cadmium hydroxide. Table 2 shows data for comparing lithium intercalation compound cells with nickel-cadmium cells.

In order to select cathodic materials potentially suitable for rechargeable lithium organic electrolyte batteries, we screened first for higher $A\cdot h/g$ and less $\$/A\cdot h$ than nickel-cadmium. Since all tellurides and most selenides are at a considerable disadvantage, only a few are included in the table. Lithium-molybdenum trioxide, titanium trisulfide, molybdenum disulfide, niobium tetra and triselenide, niobium disulfide, zirconium disulfide, titanium disulfide, and niobium trisulfide showed a higher $A\cdot h/g$ ratio than nickel-cadmium. Lithium-molybdenum trioxide, vanadium pentoxide, and molybdenum disulfide showed a lower $\$/A\cdot h$ ratio than nickel cadmium.

The comparison between rechargeable lithium batteries and nickel-cadmium batteries was continued introducing the electrochemical data shown in Table 3. Table 4 shows a comparison of the rechargeable lithium batteries with the nickel-cadmium batteries on a $W\cdot h/kg$ and $\$/W\cdot h$ basis.

Molybdenum trioxide appears more promising as cathodic material, considering both energy content and cost; also, its rate capability appears adequate. Its cycle efficiency, however, is reported to decrease continuously during 30 cycles in $LiAlCl_4$ -BL electrolyte. Niobium tetra and triselenide should be excluded, in our opinion, from further consideration because of high toxicity. Zirconium disulfide has not been investigated so far as our knowledge. We estimate that it should be about equal in energy density to titanium trisulfide. Niobium trisulfide and titanium disulfide are also promising, considering energy content. The latter also shows good cycle life; however, most chalcogenides are higher in initial component cost than the oxides or the nickel-cadmium cell. Lithium-molybdenum disulfide should equal the nickel-cadmium system in cost, but would be inferior in energy content due to instability of the intercalate, causing also poor cycle life. The poor reversibility, expressed in the coulombic efficiency, of the lithium titanium trisulfide system is due to breaking of polysulfide bonds during lithium intercalation. If the intercalate LiV_2O_5 could be obtained electrochemically, the lithium-vanadium pentoxide system would be superior to nickel-cadmium both in energy density (about $280 W\cdot h/kg$) and cost.

In accordance with the conclusions derived from Tables 1 through 4, it was decided to explore, at first, the lithium-molybdenum trioxide system and then the lithium-zirconium disulfide system. Preliminary experimental work with lithium-molybdenum trioxide cells is reported in the following section. No optimization of electrodes or electrolytes has been attempted so far.

²²Alfa Catalog (74-75 & 75-76), Ventron Corporation, Alfa Products.

²³Inorganic Chemicals 72-73, Research Organic Inorganic Chemical Corp.

²⁴Catalog G-8, November 1974, PRC, Inc.

²⁵Apache Chemicals, Inc.

Table 2. Data for Comparing Lithium Intercalation Compound Cells with Nickel-Cadmium Cells

Cathode Material	Rate of Lithium Intercalation	Bonds Broken	Instable Compound Formed	F _{theor.}	A·h/g	Initial Component Cost \$/A·h
TiS ₂	H			1	0.226	5.32
TiS ₃		B		1.8	0.32	
TiSe ₂	H			1	0.126	15.55
TiTe ₂				1	0.087	19.13
V ₅ S ₈	M			0.7	0.129	
VSe ₂			I	1	0.125	9.97
V ₂ O ₅		B		1	0.142	0.30
ZrS ₂	H			1	0.165	14.30
ZrSe ₂	H			1	0.105	21.00
NbS ₂	M			1	0.164	11.20
NbS ₃				2.4	0.192	
NbSe ₂	M			1	0.104	5.00
NbSe ₃				3	0.229	
NbSe ₄				4	0.263	
MoS ₂			I	1.8	0.288	0.21
MoO ₃				2	0.340	0.08
HfS ₂	H			1	0.108	25.50
HfSe ₂	H			1	0.078	
TaS ₂	M			1	0.106	18.50
TaSe ₂	M			1	0.078	35.00
WO ₃				0.56	0.064	0.98
Ni-Cd Cell				2	0.162	0.37

Symbols: H..... High B.....Some Bonds Broken
M..... Medium I.....Partly Instable

Table 3. Electrochemical Characterization of Cells With Lithium Intercalates²⁶⁻³⁶

Cathode Material	Open Circuit Voltage (V)	F _{exp} or % Discharge	Average Discharge Voltage (V)	Discharge Current Density (mA/cm ²)	Number of Cycles
TiS ₂	1.88 - 2.4	0.6 F	2.2	0.67 - 3.0	300 1,100
TiS ₃	2.17	1.0 F	2.0	0.67	16 300
V ₂ O ₅	3.5 - 3.75	25%	1.5	1.00	375
ZrS ₂	----	-----	---	----	---
NbS ₂	3.11	0.4 F	2.0	0.67	9
NbS ₃	2.95	1.38 F	2.0	0.67	48
NbSe ₃	2.6	3.0 F	---	----	---
NbSe ₄	2.0	4.0 F	1.75	0.40	50
MoS ₂	2.5	0.5 F	1.15 - 1.55	0.67	15
MoO ₃	2.85	1.5 F	2.0	2.00	30
Ni-Cd Cell	1.31		1.24	7.8	

Remarks: 1,100 cycles were obtained with TiS₂, however, only at shallow cycles at 4 percent of its full capacity.
The discharge rate of the nickel-cadmium cell is C/10.

- ²⁶G. 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., February 1976.
- ²⁷M. S. Whittingham, "Electrical Energy Storage and Intercalation Chemistry," *Science*, 192, 1126 (1976).
- ²⁸J. Broadhead and F. Trumbore, op. cit., p. 4.
- ²⁹D. W. Murphy and F. A. Trumbore, op. cit., p. 4.
- ³⁰G. L. Holleck and J. R. Driscoll, "Titanium Sulfides as Cathodes for Secondary Lithium Batteries," Abstract, Electrochem. Society Meeting, Dallas, Texas, 5-10 October 1975, (Extended Abstract No. 32).
- ³¹A. N. Dey, "Lithium-Metal Oxide Organic Electrolyte Primary Batteries," Abstract, Electrochemical Society Meeting, Boston, Mass., 7-11 October 1973, (Extended Abstract No. 54).
- ³²C. R. Walk and J. S. Gore, "Li/V₂O₅ Secondary Cells," *J. Electrochem. Soc.* 122, 68C (1975).
- ³³G. L. Holleck, S. B. Brummer, and F. S. Shuker, "Sulfur-Based Lithium-Organic Electrolyte Secondary Batteries," 3rd Quarterly Report, Contract DAAB07-74-C-0072 (ECOM), EIC, Inc., December 1974.
- ³⁴N. Margalit, op. cit., p. 4.
- ³⁵L. Campanella and G. Pistoia, "MoO₃: A New Electrode Material for Non-Aqueous Secondary Battery Applications," *J. Electrochem. Society* 118, 1905 (1971).
- ³⁶O. Wagner, private communication.

Table 4. Comparison of Rechargeable Lithium Batteries With Nickel-Cadmium Batteries

Cell	$W \cdot h / kg_{\max}^*$	$W \cdot h / kg_{\bar{V}}^{**}$	$\$/W \cdot h$
Li-MoO ₃	1,020	510	0.05
Li-NbSe ₄	526	460	
Li-NbSe ₃	595	458	
Li-TiS ₃	694	356	
Li-ZrS ₂		330	7.15
Li-TiS ₂	542	271	4.10
Li-NbS ₃	566	222	
Ni-Cd	212	200	0.30
Li-NbS ₂	204	141	5.60
Li-MoS ₂	720	108	0.27
Li-V ₂ O ₅	533	71	0.40

*Based on O.C.V. and F_{theor} .

**Based on Average Discharge $\bar{V} = 2 \text{ V}$
(Except Ni-Cd, Li-NbSe₄, and Li-MoS₂)

EXPERIMENTAL INVESTIGATION OF MoO₃ CATHODES

Electrode Preparation

Two types of molybdenum trioxide cathodes were fabricated, so far, and studied in 1M LiClO₄-PC electrolyte versus lithium working and reference electrodes. The first type was a Teflon bonded electrode. A dry cathodic mix of 75 weight percent molybdenum trioxide (PCR, Inc.), 10 weight percent graphite (1651 Microcrystal Graphite, Southwestern Graphite Co.), and 15 weight percent Teflon powder was prepared. About 0.28 g of that mix, containing about 0.215 g molybdenum trioxide (which corresponds to 80 mA·h capacity, considering 2F per mole molybdenum trioxide) were dry pressed on one side into a matrix of foametal (square cross-section area = 10 cm²) of

pure nickel. The second type was an electrode without a Teflon binder. The cathodic mix contained 70 percent molybdenum trioxide and 30 percent graphite. Only one electrolyte, namely, 1M LiClO₄-PC, has been used so far in the investigation.

Preparation of lithium electrodes, the electrochemical cell arrangement, and the electrochemical instrumentation have been described previously.³⁷

Polarization Behavior of MoO₃ Cathodes

The current-cathode potential curves for the two electrodes are shown in Fig. 1. The cathode potential was measured free of any ohmic iR drop versus a lithium reference electrode. In a new Li/1M LiClO₄-PC/MoO₃,C cell with non-Teflon bonded electrodes, the open circuit voltage was at first about 2.0 V. By standing overnight, the open circuit voltage increased to 2.97 V. Teflon bonded electrodes showed an open circuit voltage of 2.85 V. Thus, the open circuit voltage of the cells is larger for a 100 percent state of charge than the EMF predicted from thermodynamic data for a change in oxidation state from MoO₃ to MoO₂ (2.2 V). The formation of intercalation compounds is the explanation for the experimental findings.

From Fig. 1 it can be seen that Teflon bonded electrodes showed mixed activation-concentration polarization up to a current of 5 mA. This was followed by another electrode reaction at higher polarizations. Gassing at the cathode is observed at about 50 mA. The oxidation potential of propylene carbonate lies around 2.56 V.³⁸ This is about the potential region where the second electrode reaction, probably solvent reduction, commences. This means that the cathodic discharge process at such potentials would include lithium intercalation in molybdenum trioxide and reduction of propylene carbonate at the same time. The shape of the curve for electrodes without Teflon indicates mixed activation - concentration polarization up to 20 mA. We would expect that high cathode reversibility could be observed up to 10 mA with Teflon bonded electrodes and up to higher currents with non-bonded electrodes.

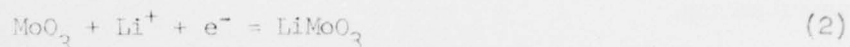
In Fig. 2 the cathodic polarization, η_c , of both electrode types is plotted versus the log of the current density. Both electrodes show a similar Tafel behavior up to $5 \cdot 10^{-4}$ A/cm² with a Tafel slope b of about 0.11. At higher current densities there are strong deviations from Tafel linearity, probably due to concentration polarization effects. At these current densities, the electrode processes seem to be diffusion limited. From the Tafel slope and the open circuit cathode potential E_0 , estimates of the exchange current densities I_0 of the electron transfer reaction can be made.

$$E_0 - E_I = b \log I - b \log I_0 \quad (1)$$

³⁷H. F. Hunger and J. E. Ellison, "Determination of the State of Discharge of Lithium/Organic Electrolyte/Graphite Fluoride Cells," R&D Technical Report ECOM-4391, March 1976.

³⁸H. F. Hunger and J. E. Ellison, "Rate Capability and Electrochemical Stability of Carbon Fluorine Compounds in Organic Electrolytes," J. Electrochem. Soc. 122, 1288 (1975).

We obtain for $E_c = 2.85 - 2.97$ V, $E_I = 2.64 - 2.73$ V, $b = 0.11$ and $I = 5 \cdot 10^{-4}$ A/cm² an estimated I_0 of $3.17 - 6.17 \cdot 10^{-6}$ A/cm². This indicates that the first electron transfer reaction, e.g.,



is probably fast, but that the diffusion of Li^+ ions at higher current densities is probably rate limiting. The Tafel slope $b = 0.11$ V/decade of current density, corresponding to a $\alpha n = 0.5$, indicates a one electron charge transfer process as rate determining in the Tafel region.

Preliminary Charge-Discharge Experiments

Teflon bonded cathodes were chosen for the first charge-discharge experiment, since it was assumed that the mechanical stability of these electrodes would be superior to that of non-bonded electrodes. The cathode contained 0.215 g molybdenum trioxide and had a theoretical capacity of 80 mA·h. The discharge current chosen was 10 mA, which includes, according to Fig. 1, the reversible part of the current voltage curve. The initial open circuit voltage was 3.0 V. After six hours of deep discharge (75% of theoretical capacity), the cathode potential dropped to 1.15 V. Figure 3, Curve 1, shows the initial discharge curve ($T = 24^\circ\text{C}$). There are two plateaus recognizable in the first discharge curve. After 16 hours of rest, the open circuit voltage of the 75% discharged cell was 2.05 V. Thus, we can see that the open circuit voltage of the cell and the cathode potential are strong functions of the state of charge of the cathode and could be used for determination of the state of charge of such cells. After the first discharge, the cathode was charged from 25 percent to 100 percent of the theoretical capacity during 6 hours at 10 mA ($T = 23 - 24^\circ\text{C}$). The cathode potential rose from 2.06 V to 3.30 V. No gassing was observed. The charge curve is shown in Figure 3, Curve 2. After charging and after 16 hours of rest, the open circuit potential of the cathode was 2.65 V, which is considerably less than the initial open circuit potential (3.0 V). The reason for this could be that we did not consider in discharging and charging possible charge consuming side reactions, such as reduction and oxidation of the solvent.

The second 75 percent discharge (Figure 3, Curve 3), at 10 mA for 6 hours, led to a cathode potential of 0.93 V ($T = 23 - 24^\circ\text{C}$). This discharge curve was far lower in the 0-50% region of theoretical capacity than the first one and had an average discharge potential of 1.5 V. The attainment of the open circuit voltage (rest potential) after interruption of the load was similar to that after the first discharge. The second charge (Figure 3, Curve 4) led to a cathode potential of 3.13 V. No gassing was observed at the cathode during the charging process. The cathode having been charged to 100 percent assumed, after 16 hours, a rest potential of 2.55 V. The third discharge (Figure 3, Curve 5) was quite similar to the second discharge, leading, after 6 hours, to a cathode potential of 1.25 V (24°C). During the third charge (Figure 3, Curve 6), the cathode potential reached, after 6 hours, 3.05 V (100% charge). After 7 hours of charging (12.5% theoretical overcharge), the cathode potential was essentially the same, but gassing was observed at the cathode. The fourth discharge

(Figure 3, Curve 7) showed extensive loss of cathode capacity. After 4 hours of discharge at 10 mA, only 50 percent of the theoretical capacity was obtained, while the cathode potential dropped to 0.3 V (23°C). Gassing at the cathode was observed already after 2 hours, starting visibly at 0.9 V. The reasons for this dramatic capacity loss are not known at present, but could be connected with the deep discharges during the first 3 cycles or the overcharge at the end of the third cycle.

The open circuit voltage of the cell and the open circuit cathode potential showed a steady decrease from the first to the fourth discharge: 3.0, 2.68, 2.6, and 2.5 V, respectively, indicating perhaps some change in the capability of the electrodes to intercalate lithium. An accumulation of solvent oxidation products during charge or solvent reduction products (e.g., Li_2CO_3) during discharge could also account for the loss in capacity. Cycling at lower depth of discharge, with control measurements of the current-potential relationship in between, should shed some light on this problem. Also, the influence of electrolytes and solvents would have to be studied closer in this respect.

From these charge-discharge experiments (C/8 rate) with preset coulombic efficiencies of 75 percent, the energy efficiency of non-optimized cathodes is 50.4%. This value was derived from the second and third charge-discharge cycles. Since the average discharge voltage is about 1.5 V at the C/8 rate, 382 W·h/kg of active cell components ($\text{MoO}_3 + \text{Li}$) can be obtained from a non-optimized system.

SUMMARY AND CONCLUSIONS

A survey of potentially rechargeable cathodic materials for lithium batteries was made. Some transition metal chalcogenides and oxides show promise since they intercalate lithium on discharge and release lithium ions on charge. The rate of lithium intercalation is highest for the IV B group compounds. Most of the VI B group intercalates are chemically instable. Bond breaking during intercalation occurs with trisulfides, vanadium pentoxide, and tungsten trioxide. However, several compounds appear suitable as cathodic materials; namely, molybdenum trioxide, niobium tetra and triselenide, titanium trisulfide, zirconium disulfide, titanium disulfide, and niobium trisulfide. They show, in combination with lithium, a theoretically higher A·h/g ratio than nickel-cadmium cells. Further, molybdenum trioxide, vanadium pentoxide, and molybdenum disulfide have a lower, initial material cost ratio, expressed in \$/A·h, than nickel-cadmium. The W·h/kg ratios are especially high for the lithium-molybdenum trioxide, niobium tetra and triselenide, zirconium disulfide, and titanium trisulfide and disulfide systems. The initial material cost for the disulfides, however, are high. The rate capabilities of the systems seem to be adequate for at least C/10 discharge rates and cycling capability has been demonstrated in all cases. Since the open circuit voltages of these systems range from 1.88 to 3.75 V, electrode side reactions involving the organic electrolyte systems have to be expected during both charge and discharge. To what degree they are influencing reversibility and cycle life cannot be predicted at the present. Preliminary experimental work was done with the lithium-molybdenum trioxide system using two types of molybdenum trioxide

cathodes, one bonded with Teflon, the other one without Teflon binder. Marked performance differences were noted. The maximum open circuit voltages obtained so far were 3.0 V (for 100 percent theoretical charge) and 2.05 V (for 25 percent theoretical charge). Thus, the open circuit voltage is a strong function of the state of charge of the cathode (degree of lithium intercalation). The polarization characteristics of both types of cathodes show a mixed activation-concentration polarization, followed by another electrode reaction, probably solvent reduction, at higher polarizations. From the Tafel slope of the polarization - log current density relationship, estimates of the exchange current density show a fast electron transfer reaction. Strong deviations from Tafel linearity at higher current densities indicate diffusion limitation (probably lithium ions). Charge-discharge experiments at the C/8 rate with 75 percent depth of discharge show marked differences between the first charge and discharge curves and the following ones. During the fourth discharge, an extensive loss in cathode capacity was noticed. This irreversible loss could be the consequence of the deep discharges or overcharging. Decrease in open circuit cathode potentials during the cycles indicates a change in the capability of the electrode to intercalate lithium. The loss in capacity could be connected with accumulation of solvent oxidation or reduction products at the cathode. The cycling experiment showed energy efficiencies of about 50 percent from the cathodes; an energy content of 382 W·h/kg of active cell components was obtained from the non-optimized system.

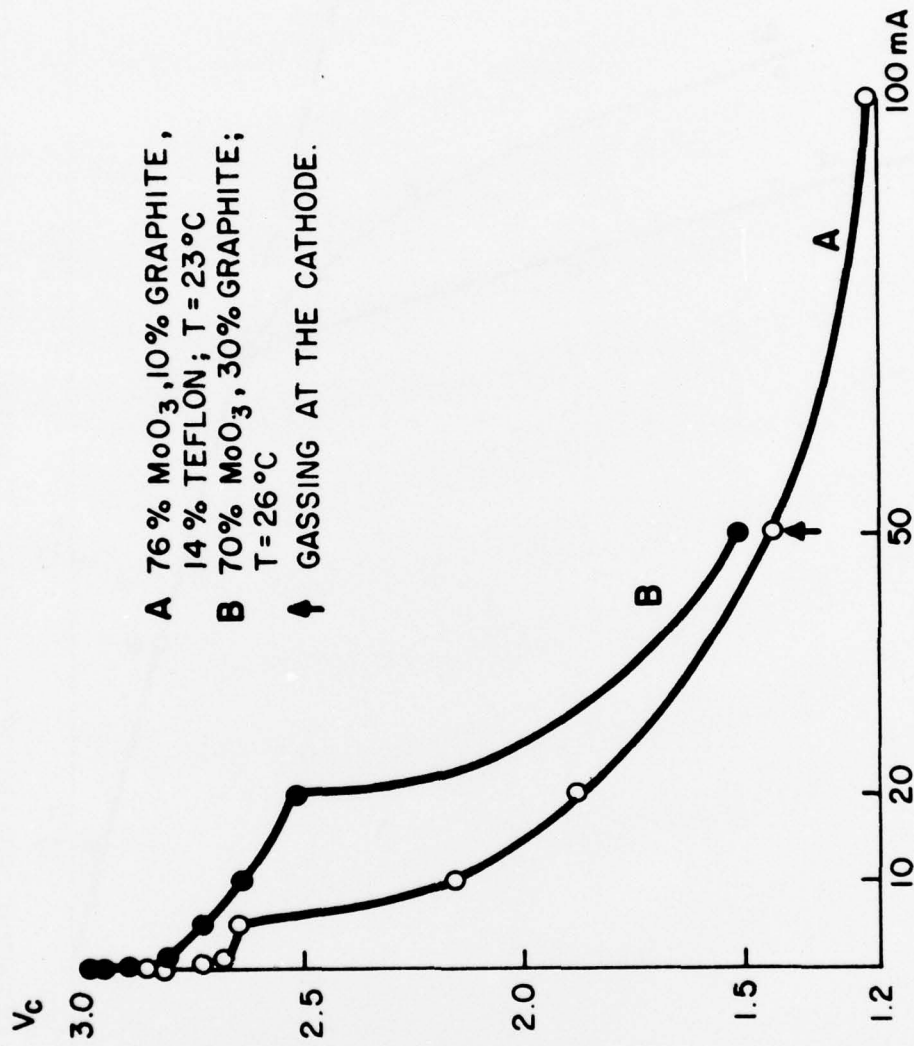


FIG. 1 CURRENT-CATHODE POTENTIAL CURVES OF MoO₃ CATHODES.

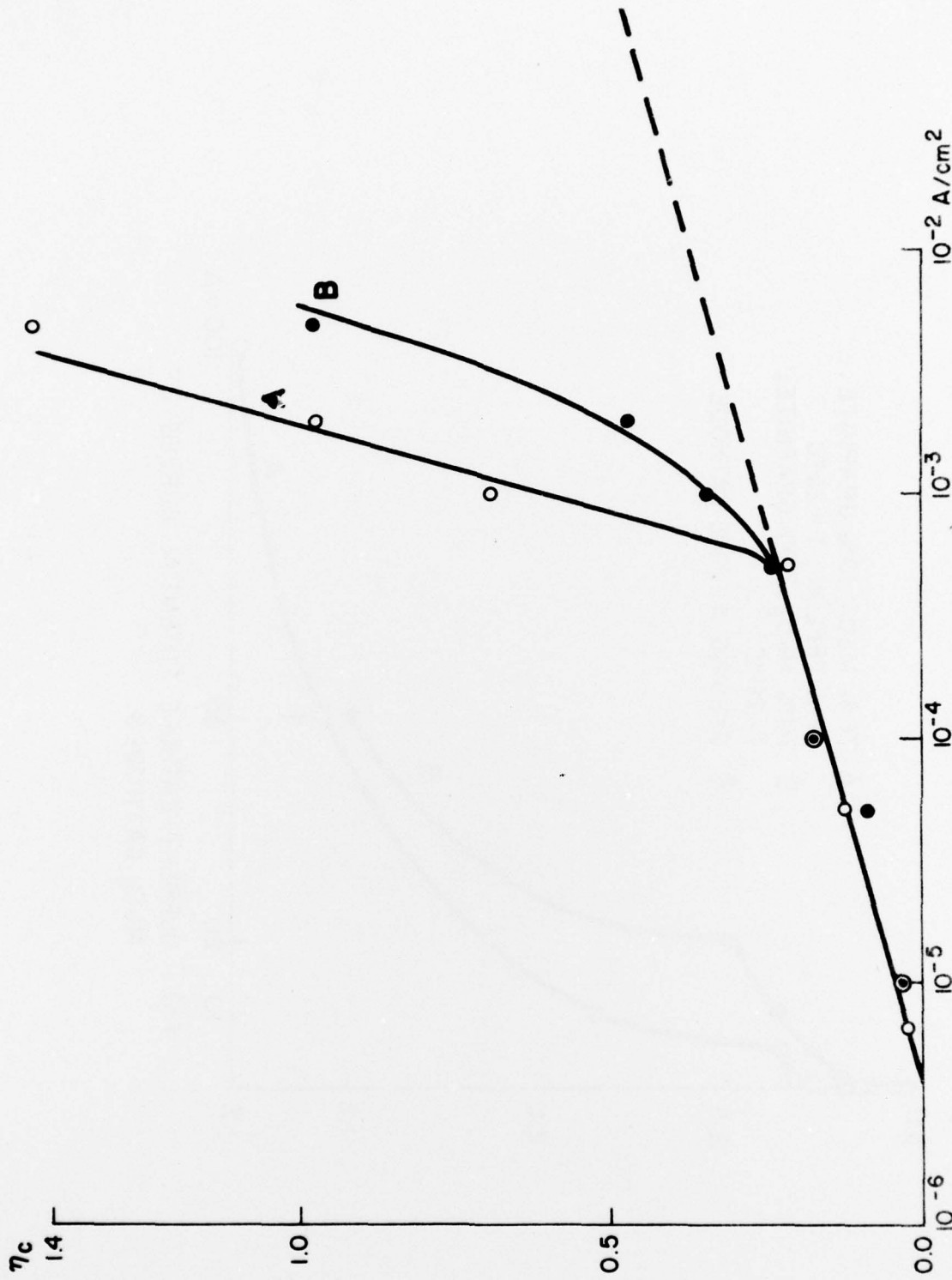


FIG. 2 CATHODIC POLARIZATION VERSUS CURRENT DENSITY OF MoO₃ ELECTRODES (SYMBOLS A & B EXPLAINED IN FIG. 1)



FIG. 3 DISCHARGE AND CHARGE CURVES OF MoO_3 CATHODES AT C/8 RATE (10mA), $T = 23 - 24^\circ\text{C}$, SEQUENCE OF DISCHARGES AND CHARGES : 1-7.