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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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ELECTROLYTES FOR RECHARGEABLE LITHIUM BATTERIES

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ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

SEP
1981

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ELECTROLYTES FOR RECHARGEABLE LITHIUM BATTERIES

INTRODUCTION

One of the concerns in the development of rechargeable lithium batteries is the choice of a stable electrolyte system. In earlier investigations, electrolyte systems like LiClO_4 -PC proved to be unsuitable for rechargeable lithium batteries.¹ Although the efficiency of the plating step is nearly 100%, inefficiencies are realized in the stripping process. This is due to passivating films of lithium-electrolyte reaction products. In our investigations we have observed strong increases in the ohmic cell resistance during the second discharge of the lithium electrode.² In addition to this ohmic polarization, a high anodic polarization, free of the ohmic iR component, was observed, probably caused by a loss of active electrode surface due to blocking film formation.

DISCUSSION

Theoretical Considerations Concerning the Stability of Solvents Versus Lithium

Recently, cyclic ethers such as dioxolane and tetrahydrofuran have been used successfully as solvents in organic electrolytes for rechargeable lithium batteries.^{3,4,5} The choice of cyclic ethers as electrolyte solvents was based on the following considerations. Organic solvents in general are thermodynamically not stable against lithium.⁶ This reactivity with lithium is due to the presence of molecular dipoles in polar solvents.⁷ The C-O bond in ethers is less polar than the C=O bond in propylene carbonate and consequently more stable against lithium; everything is a question of degree. J. Eisch showed that cyclic ethers such as tetrahydrofuran react with lithium,⁸ n-butanol is the product of reductive cleavage, followed by hydrolysis.

V. R. Koch described the lithium-tetrahydrofuran chemistry and its significance with respect to the lithium electrode stability.⁹ It is based on the basic considerations of Eisch and a postulated mechanism explains the tetrahydrofuran ring opening via a dianionic specie.

Further improvements in the ring stability can be made by utilizing inductive effects caused by deliberate structural changes in the cyclic ether. According to E. S. Gould, inductive, electrostatic effects transmitted through chains of atoms can affect the reactivity of molecules.¹⁰ If a more electronegative atom or group is substituted for a less electronegative one, the electron density increases at that atom or group and diminishes at the nearby atoms. The methyl group, as well as any other alkyl group, is slightly less electronegative than hydrogen (<2.1).

The pK , the negative decadic logarithm of the dissociation constant of aliphatic acids, increases with the size of the substituted alkyl group (Table 1).

TABLE 1. pK OF ALIPHATIC ACIDS

<u>Acid</u>	<u>pK</u>
H-COOH	3.77
CH ₃ -COOH	4.8
CH ₃ -CH ₂ -COOH	4.88

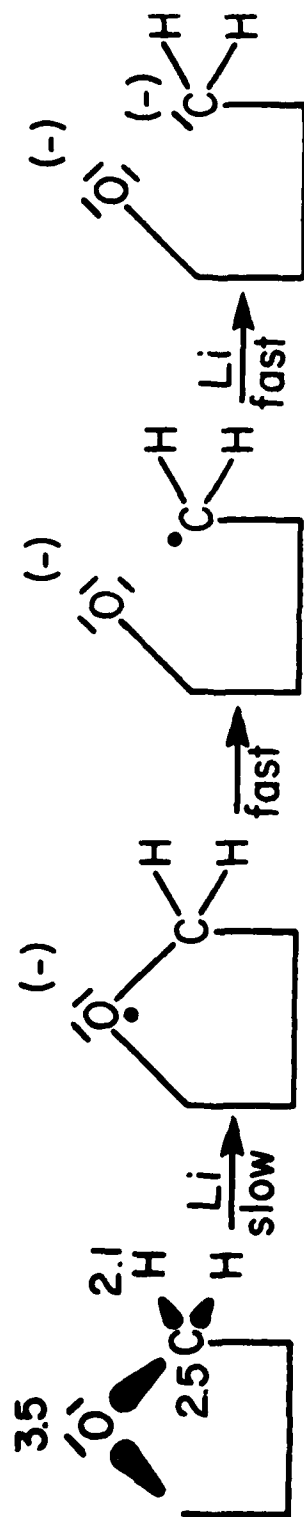
This means that the dissociation of the carboxyl group is decreasing.

In general, groups which are more electronegative than the hydrogen atom are said to have a negative inductive effect and groups which are less electronegative than hydrogen show positive inductive effects. Alkyl groups, as methyl and ethyl groups, all show positive inductive effects and are electron repelling or better electron donating. These inductive effects affect all reactions including heterocyclic reactions like in cyclic ethers.

The oxygen atom in a cyclic ether or ether in general has a given electronegativity (3.5) as compared to the neighboring carbon atoms (2.5). The electronegativity of the hydrogen atom is 2.1 (See Fig. 1a). Substituting one hydrogen atom by an alkyl group will introduce a less electronegative character around the carbon atom and increase the electron density around the oxygen atom (Fig. 1b). The strongest effect will be exerted by substituting hydrogen by a methyl group since the positive inductive effect, although transmitted through a chain of atoms, is attenuated through aliphatic C-C bonds like in the ethyl or propyl group. Consequently, substitution in 2 position has a stronger effect than substitution in 3 position.

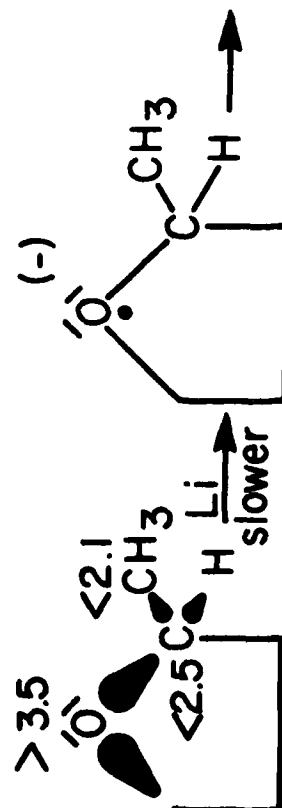
The reductive cleavage of C-O bonds with lithium proceeds apparently along the reaction path shown in Fig. 1a. One electron from lithium enters the molecule and thereby creates an instable configuration. The rate of this step will depend upon the electronegative character of the oxygen atom and require a certain activation energy. It is probably the rate determining step. Koch calls it the transfer of an electron from lithium to the lowest unfilled molecular orbital centered on the oxygen atom.¹¹ The instable anion radicals C-O bond splits in the next step and the ring opens. Another anion radical is the reaction product. This step is probably fast because of the radical nature of the reactant. In the next step, another electron from a lithium atom completes the octet at the carbon end atom and leads to a dianionic specie. This step involving the capture of an electron by a radical has to be fast. The electron configuration at the negatively charged carbon atom is that of a carbanion (R:)⁻, such as (H₃C:)⁻, the methide ion, which is the basis of the reactivity of methyl lithium. The dianionic specie is very reactive because of its carbanion nature and can react further with the original cyclic ether. This leads to a series of further reaction products, depending upon the nature of the cyclic ether.

FIG. 1a. REDUCTIVE CLEAVAGE OF C-O BONDS WITH LITHIUM.



3

FIG. 1b. 2 CH₃ SUBSTITUTION



If a methyl group is substituted for one hydrogen in the 2 position next to the oxygen atom (Fig. 1b), the electronegative character of the oxygen atom will increase. The accession of an electron from lithium will become slower, compared to the non-substituted ether, because of the changed electronegativity of the oxygen atom. The activation energy of the first step will increase. The following steps, the split of the C-O bond, and the takeup of a second electron from lithium, will be fast, since radicals are participating as reactants.

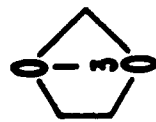
Figure 2 compares various cyclic ethers and aliphatic diethers and we arrive at the following results as far as stability against reductive cleavage by lithium is concerned (Fig. 2). 1,3 dioxolane has been reported to be a practically stable electrolyte solvent.¹² Up to 200 cycles were obtained in Li/TiS₂ cells. Methyl substituted dioxolanes, however, should show a higher degree of stability due to the positive inductive effect (Fig. 2). The symmetrical 2 methyl 1,3 dioxolane has a somewhat higher boiling point than 1,3 dioxolane itself. Higher methyl substituted dioxolanes would definitely be desirable from a stability point of view. The melting and boiling points of these compounds are expected to be elevated too much for practical use as solvents.

Methyl substituted tetrahydrofurans show higher stability versus lithium than plain tetrahydrofuran.¹³ Both 2 methyl tetrahydrofuran and 2,5 dimethyl tetrahydrofuran are expected to be more stable because of the positive inductive effect. The latter compound should have theoretically a higher stability than the first one. Heterocyclic 6 ring structures are also promising solvents, e.g., tetrahydropyrane. Again 2 methyl tetrahydropyrane promises higher stability against ring opening.

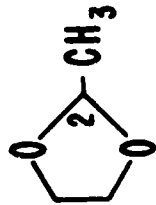
Another group of potential solvents is aliphatic diethers. They have known stability toward alkaline metals and their polar character should make them relatively good electrolyte solvents. 1,1 dimethoxymethane is known to dissolve LiClO₄ well and its low melting point would make it excellent for low temperature operation (Fig. 2). A better choice would be 1,1 dimethoxyethane which should show a positive inductive effect and a higher stability versus lithium. 1,2 dimethoxyethane is another promising diether. 2,2 dimethoxypropane has two methyl groups at the carbon atom next to the oxygen atoms and should be quite stable versus lithium.

Conductance and Rate Limitations of Electrolytes with Ether Solvents and Mixed Solvents

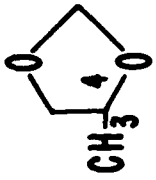
The electrolyte stability versus lithium and the structural characteristics of solvents and solutes are of great importance to the conductance of the electrolytes and rate capability of the total electrochemical system. We have observed previously that the rate characteristics of lithium intercalating cathodes, such as MoO₃, TiS₂, and many other compounds, are both in the anodic and cathodic mode limited by mass transport of lithium ions.¹⁴ Since the rate of the cathodic reduction of molybdenum oxide is limited by diffusion processes, the electrolyte solvent viscosity will strongly influence the diffusion. It could be shown that the cathodic reduction of MoO₃ occurs at a much faster rate in 1M LiClO₄-AN than in 1M LiClO₄-PC.¹⁵ The rate increase could be related to the reduction of the solvent viscosity by one order of magnitude. This finding gave a direction but not a solution since lithium is not stable in acetonitrile.



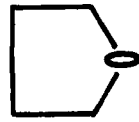
1,3 DIOXOLANE



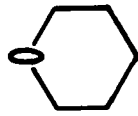
2 METHYL 1,3 DIOXOLANE



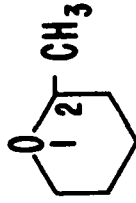
4 METHYL 1,3 DIOXOLANE



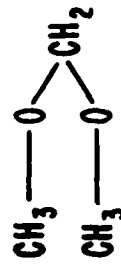
TETRAHYDROFURAN



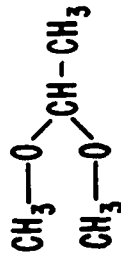
TETRAHYDROPYRANE



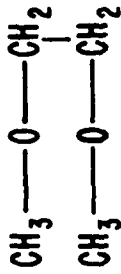
2 METHYL TETRAHYDROPYRANE



1,1' DIMETHOXY-
METHANE



1,1' DIMETHOXY-
ETHANE



1,2 DIMETHOXY-
ETHANE



2,2 DIMETHOXY-
PROPANE

FIG. 2. CYCLIC ETHERS AND DIETHERS.

A new concept for the choice of the electrolyte arises from the theoretical considerations and experimental findings. Cyclic ethers or diethers with low viscosity and methyl group substitution form a class of compounds providing both stability and good rate characteristics. With respect to solute selection, one solute, LiAsF_6 , has become a preferred one with ether solvents since it can apparently form a protective conducting film at lithium. Koch¹⁶ showed that AsF_3 , the reduction product of LiAsF_6 with lithium, can react with lithium butanolate, a reaction product of the reductive cleavage of tetrahydrofuran with lithium, to form polymeric As_2O_3 films on lithium.

In Table 2 the viscosities of various solvents are given.

TABLE 2. VISCOSITIES OF SOLVENTS USED IN LITHIUM BATTERIES

<u>Solvent</u>	<u>Viscosity (cp)</u>
Propylene Carbonate (PC)	2.48
Dioxolane	1.0
Tetrahydrofuran (THF)	0.46
1,2 Dimethoxyethane (DME)	0.4
Methylacetate (MA)	0.38
Methylformate (MF)	0.339
Acetonitrile (AN)	0.336

The last three solvents react with lithium because of their strong polar bonds. The first one in the table with low viscosity and good stability is DME. In order to improve the rate capability of rechargeable lithium batteries, we studied the rate limits given by this diether solvent and compared it with other solvents.

A cell was prepared as described previously.¹⁷ It consisted of a lithium anode, a lithium reference electrode, a molybdenum trioxide cathode, a paper separator, and an electrolyte consisting of an 0.5M solution of LiAsF_6 in 1,2 dimethoxyethane. The solvent, obtained from Pfalz & Bauer, was first tested for peroxide content by the use of Jorissen Reagent which was prepared by dissolving 0.4g of vanadium pentoxide in 4 ml of concentrated sulfuric acid, which was then added to 100 ml water. Although the test was negative, the ether was purified by passage through a column of activated alumina in the dry box. The electrochemical instrumentation used was the periodically interrupted sine wave pulse current circuit¹⁸ which permits ohmic iR free measurements of electrode potentials.

MoO_3 cathodes underwent a step discharge at 1, 5, 10, and 50 mA for five minute duration of each current step. The geometrical area of the cathode was 10 cm^2 . In Fig. 3 the iR free cathode potentials are shown as a function of the current density and compared with step discharges in other electrolytes.

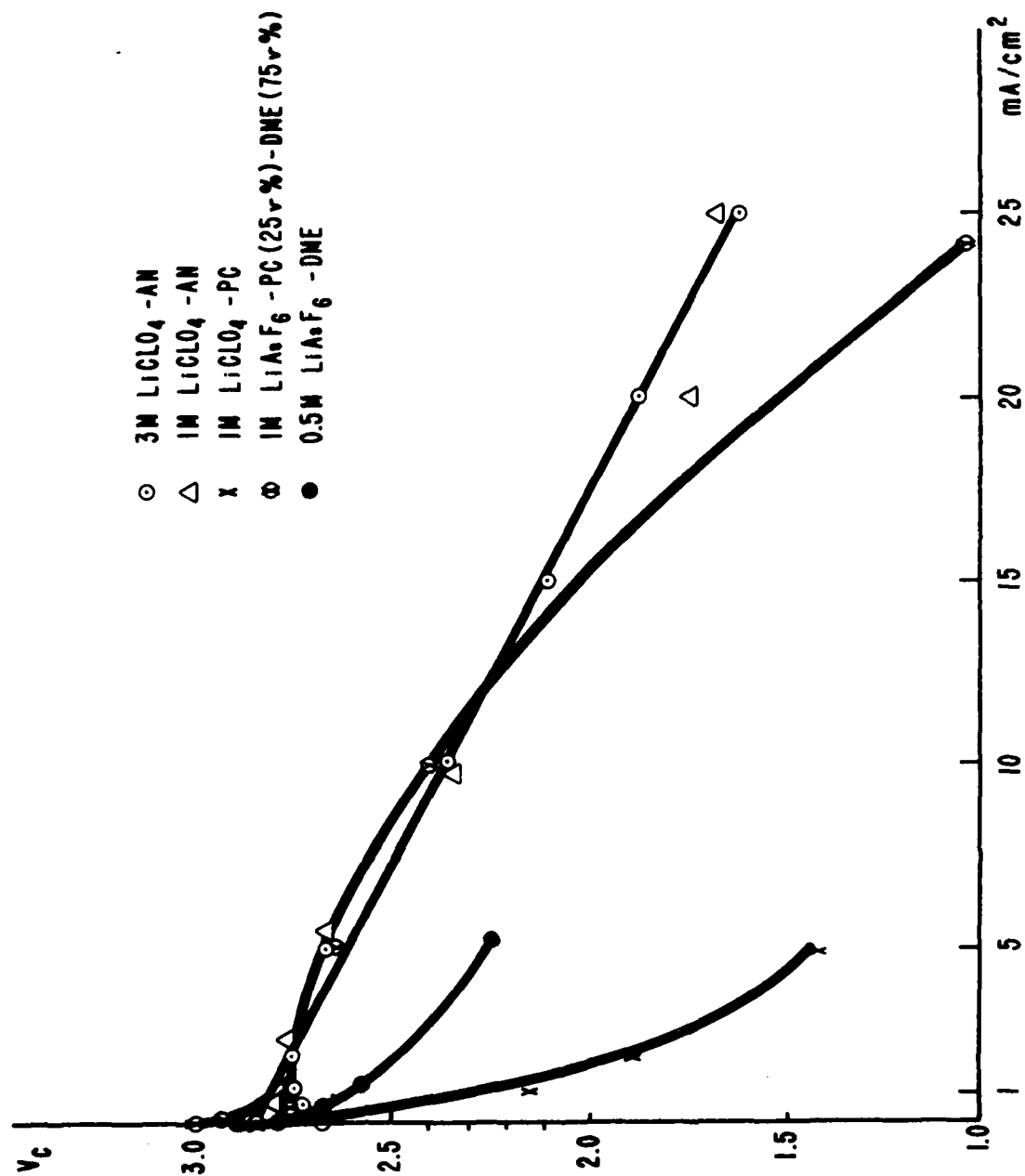


FIG. 3 MoO₃ CATHODE POTENTIAL VERSUS CURRENT DENSITY. VARIOUS ELECTROLYTES. T = 25° C.

At a potential of 2.25 V versus lithium, the rate was 5 mA/cm² as compared to 1 mA/cm² for propylene carbonate electrolyte, a five-fold increase. The viscosity of DME is about 1/6 of that of PC. Current densities above 5 mA/cm² led to high cathode polarizations, probably due to the relatively low number of lithium ions in the 0.5M electrolyte. Therefore, a way was sought to obtain a diether solvent system with higher solute solubility, perhaps a mixed solvent system.

Matsuda¹⁹ investigated the synergistic effect of the organic solvents PC-DME containing sodium perchlorate with respect to electric conductance and viscosity. The conductance of each mixture was higher than that of the individual solvents. A flat maximum was obtained between 25 and 50 V% PC. The specific conductance of 1M NaClO₄ in DME was about $7.10^{-3}\Omega^{-1}\text{cm}^{-1}$ and of 1M NaClO₄ in 25 V% PC and 75 V% DME was about $1.25.10^{-2}\Omega^{-1}\text{cm}^{-1}$. The viscosity of the mix increased with addition of PC. It is about 0.4 cp for DME, about 0.6 cp for 25 V% PC plus 75 V% DME, and about 1.4 cp for the electrolyte.

We prepared an electrolyte consisting of 1M LiAsF₆ in 75 V% DME and 25 V% PC in order to study the influence of the synergistic effect on the polarization characteristics of cathodically step discharging MoO₃ electrodes. In Fig. 3 the MoO₃ cathode potentials are shown as a function of the current densities. The solvent mix gave a superior rate characteristic to the cathode as compared to PC or DME by itself. At 2.4 V cathode potential, 10 mA/cm² were obtained as compared to 3 for DME and 0.7 for PC. The data points lie close to the 1 and 3M LiClO₄-AN curve, but 25 mA/cm² could not be sustained for 5 minutes without the cathode potential dropping below 1.0 V.

Margalit²⁰ recently reported conductance and density data for the solvent mix system in 1M LiAsF₆ in PC and DME. He observed a synergistic effect for the conductance and a specific conductance maximum of $1.7.10^{-2}\Omega^{-1}\text{cm}^{-1}$ for 25 to 30 weight percent PC. The latter figure corresponds to our 25 V% PC.

The synergistic effect on conductance is also reflected in the cathodic rate characteristics of MoO₃ electrodes. A ratio of 1 molecule LiAsF₆ to 2.4 molecules propylene carbonate, in an environment of 8.3 molecules DME as the low viscosity dilutant, is descriptive for the structure of the electrolyte and the transport of ions. In the next table (Table 3), we summarize the influence of synergistic effect (S. effect) and positive inductive effect (P.I. Effect) on the conductance of the electrolytes. The synergistic effects increase the conductance and the positive inductive effects decrease the specific conductance σ . It can be seen from the second half of Table 3 that conductance and current density (mA/cm²), at a given cathode potential, V_c, are proportional to each other. The value of the synergistic effect to increase the rate capability of rechargeable, lithium intercalating cathodes can be recognized.

TABLE 3. INFLUENCE OF METHYL GROUP SUBSTITUTION AND OF MIXED SOLVENT EFFECT ON ELECTROLYTE CONDUCTANCE AND CATHODE KINETICS

Electrolyte	$\sigma \Omega^{-1} \text{cm}^{-1}$	P.I. Effect	S. Effect	$\frac{\text{mA/cm}^2}{V_c}$ at	
				$V_c=2.4$	$V_c=1.9$
1.5M LiAsF_6 -THF	$1.64 \cdot 10^{-2}$				
1.5M LiAsF_6 -2-Me-THF	$0.39 \cdot 10^{-2}$	$-1.25 \cdot 10^{-2}$			
1M LiAsF_6 -THF	$1.26 \cdot 10^{-2}$				
1M LiAsF_6 -2-Me-THF	$0.30 \cdot 10^{-2}$	$-0.96 \cdot 10^{-2}$			
1M NaClO_4 -DME	$0.70 \cdot 10^{-2}$				
1M NaClO_4 -PC, DME (25 V%, 75 V%)	$1.25 \cdot 10^{-2}$		$+0.55 \cdot 10^{-2}$		
0.5M LiAsF_6 -DME	$0.60 \cdot 10^{-2}$			2.5	
1M LiAsF_6 -PC, DME (25 W%, 75 W%)	$1.70 \cdot 10^{-2}$		$+1.1 \cdot 10^{-2}$	10.0	17.0
1M LiClO_4 -PC	$5.12 \cdot 10^{-3}$			0.7	2.0
1M LiClO_4 -AN	$3.19 \cdot 10^{-2}$			10.0	20.0

SUMMARY AND CONCLUSIONS

Electrolyte solvents with C=O bonds, as in propylene carbonate, methyl acetate, and methyl formate, react with lithium and are not suited for use in rechargeable lithium batteries. Cyclic ethers as dioxolane and tetrahydrofuran, however, have been used successfully in such batteries showing good cycle life. Theoretical considerations show that the C-O bond is more stable against lithium. Further improvements in the stability can be made by deliberate structural changes in the cyclic ether such as 2 methyl substitution.

Increased stability is predicted on the basis of the positive inductive effect and has been demonstrated experimentally by increased cycle life when using 2 methyl tetrahydrofuran as the solvent in combination with LiAsF_6 as solute. Increased ring stability is due to a slowing down of the first step, the rate determining step, of the reductive cleavage of C-O bonds with lithium. This positive inductive effect applies to all cyclic ethers and aliphatic diethers. The latter group of solvents is of interest, because of their relatively low solvent viscosity which is desirable for high rate characteristics of the batteries.

Experimental studies were performed with LiAsF_6 -dimethoxyethane electrolyte but solute solubility was too low to permit current densities at MoO_3 cathodes above 5 mA/cm^2 .

Synergistic effects of related mixed solvent electrolytes have been observed recently with respect to increased electrolyte conductance at certain mix ratios. We investigated the synergistic effect on the polarization characteristics of cathodically discharging MoO_3 cathodes. In a 1 M LiAsF_6 , 75 V% dimethoxyethane, 25 V% propylene carbonate electrolyte cathodic rates of 10 mA/cm^2 were obtained at 2.4 V vs Lithium. Thus, the synergistic effect on conductance is also reflected in the cathodic rate characteristics of MoO_3 electrodes. The value of the synergistic effect of mixed solvents for improving the rate capability of rechargeable lithium batteries can be recognized.

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