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LITHIUM CYCLING IN POLYMETHOXYMETHANE SOLVENTS.(U)

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LITHIUM CYCLING IN POLYMETHOXYMETHANE SOLVENTS

by

J. S. Foos and J. McVeigh

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Solutions of $LiAsF_6$ in dimethoxymethane (DMM) and trimethoxymethane (TMM) are shown to be conductive and capable of cycling Li in high efficiency in half-cells. Inspection of electrolytes stored at 70°C in the presence and absence of Li indicated that TMM is more stable than DMM. However, DMM cycles Li much better than TMM after storage.

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LITHIUM CYCLING IN POLYMETHOXYMETHANE SOLVENTS

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Introduction

During the past few years several Li battery electrolytes have been reported which allow the plating and stripping of Li in greater than 95% efficiency at 25°C. Newman reported the use of $LiClO_4$ in dioxolane in Li/TiS_2 cells (1). The cycling efficiency in these cells is very good but unfortunately they are susceptible to detonation (2). Koch has reported the use of 2-methyltetrahydrofuran (2Me-THF) (3) and diethyl ether blends (4) as solvents for $LiAsF_6$ in Li half-cells. The conductivity of these electrolytes is low.

The solution of $LiAsF_6$ in dioxolane is an electrolyte with good conductivity but is reported to polymerize readily (5). Ring strain may contribute to the reactivity of dioxolane. It might be anticipated that the open-chain analogues of dioxolane might be less reactive. Dimethoxymethane (DMM)I and trimethoxymethane (TMM)II were investigated as solvents for possible use with $LiAsF_6$ in Li batteries.

$CH_2(OMe)_2$	$CH(OMe)_3$
I	II

We wish to report that these solvents produce conductive solutions with $LiAsF_6$, show good stability at 70°C, and cycle Li well in half cell tests.

Experimental

The solvents, DMM and TMM (trimethyl orthoformate), were obtained from the Aldrich Chemical Company. Before use the solvents were purified first by preliminary drying using $MgSO_4$ and/or molecular sieves (3A or 4A) for DMM; and molecular sieves (3A or 4A) only for TMM. Subsequently they were distilled from Na benzophenone ketyl (6). Some difficulty was encountered in forming the blue ketyl in TMM. This was attributed to surface films on the Na which can be disrupted by placing the reaction flask in an ultrasonic bath.

The electrolytes for cycling and storage tests were prepared using $LiAsF_6$ (U.S. Steel, as-received) with cooling using Cu shot previously cooled by dry ice. The solvents, if treated with alumina, were passed through a column of activated alumina (Woelm N-Super 1) and the first 10% discarded. Where applicable, pre-electrolyses were done by passing a current (1 mA/cm^2) between two Li metal electrodes ($\sim$30 cm^2) suspended in the electrolyte (100 ml) for $\sim$16 hrs.

Conductivities were obtained using dried distilled DMM and TMM. The conductivities were determined in conductivity cells with cell constants determined using aqueous KCl. An AC conductivity bridge (YSI Model 31) was used to measure the cell resistance. The conductivities were determined at, or corrected to, 25°C with a precision of $\sim$5%.

The storage tests were done in screw cap (Teflon-lined) glass vials. These were stored at 70°C.

The Li cycling was done in prismatic glass cells containing 15-20 ml electrolyte. This experiment, described previously (7), involves making a pre-plate of 4.5 C/cm^2 of Li on a Ni substrate (Ni shim) followed by stripping and then re-plating 1.1 C/cm^2 on the pre-plated Li. The average efficiency per cycle $\bar{E}$, is calculated in Eq. (1):

$$E = \frac{Q_s - \frac{Q_{ex}}{n}}{Q_s} \qquad (1)$$

where n is the number of apparent "100%" cycles, Q_s is the charge stripped (1.1 C/cm^2), and Q_{ex} is the charge in the excess Li (3.4 C/cm^2) at the start of the experiment.

Solution preparation and the electrochemical experiments themselves were conducted at room temperature under an Ar atmosphere in a Vacuum-Atmospheres Corporation dry box equipped with a Model HE-493 Dri-Train.

Results

Conductivity of Electrolytes. In order to minimize electrolyte IR drop, the electrolyte in a battery should show maximum conductivity. The solvents I and II give electrolytic solutions with greater conductivities than most other non-cyclic ethers.

The conductivities of solutions of $LiAsF_6$ in ethers are generally high as compared to solutions of other salts such as $LiClO_4$, $LiBF_4$, etc. For instance, the maximum conductivity of $LiAsF_6$ in THF is 0.017 Ω^{-1} cm^{-1} (7) as compared to 0.006 and 0.004 for $LiClO_4$ (8) and $LiBF_4$ (9), respectively. The ethereal solutions of $LiAsF_6$ previously known to cycle Li with high efficiency, i.e., 2Me-THF and DEE blends, have maximum specific conductivities in the 0.002-0.004 Ω^{-1} cm^{-1} range.

Conductivity vs. concentration profiles for $LiAsF_6$ in DMM and TMM are shown in Figure 1. The conductivity profiles are typical for solutions of $LiAsF_6$ in ethers and show maximum conductivities of $\sim 0.0065\ \Omega^{-1}\ cm^{-1}$ for DMM and $\sim 0.008\ \Omega^{-1}\ cm^{-1}$ for TMM.

Lithium Cycling in Half-Cells. The plating and stripping of Li at 25°C is a rigorous test of electrolyte stability. Electrolytes were evaluated for half-cell cycling efficiency using electrolytes prepared using distilled solvent (D), distilled solvent treated with alumina (DA), and electrolytes that were additionally pre-electrolyzed (DP).

The freshly plated Li, generated during pre-electrolysis, should be especially reactive. It was hoped that this Li would react with impurities in the electrolyte giving insoluble reaction products and thereby purify the electrolyte. The results for DMM and TMM electrolytes are shown in Table 1. This table shows representative cycling efficiencies which illustrate the effect of different purification on Li cycling. In these tests, both electrolytes show high cycling efficiency.

Electrolyte Stability at 70°C. The cycling test above allows the evaluation of room temperature stability of the electrolyte towards freshly plated Li over the period of the experiment, one or two days. An accelerated test for long term stability is the storage of electrolytes at 70°C in the presence and absence of Li. A solvent, 2Me-THF, which has proved useful in Li/TiS_2 cells shows excellent stability when stored with Li at 70°C (7).

Stability tests were conducted by storing samples of 1.5M $LiAsF_6$ in DMM and TMM in the presence and absence of Li at 70°C. The results are shown in Table 2. The TMM appears more stable with no apparent reaction noted at 20 days at 70°C. These tests may be somewhat misleading. Although no reaction was observed visually, the TMM electrolyte stored at 70°C with Li subsequently failed completely to cycle Li. The DMM results were variable, with the results reported typical of several tests. Despite the apparent lack of stability in DMM electrolytes, the samples stored with Li retained moderate cycling ability.

Discussion

The conductivity of the electrolytes studied make them interesting candidates for Li battery use. However, the stability of the electrolytes under actual cell conditions is of primary concern. This includes stability towards reduction by Li and to thermal decomposition in the bulk electrolyte. The half-cell cycling results indicate a relatively high degree of stability of electrolyte towards Li. However, this test is somewhat insensitive to electrolyte decomposition due to the large excess of electrolyte present. The variation of the cycling efficiency with purification appears to be reproducible. It is attributed to variations of the levels of impurities. What is not clear is the nature of the impurities and whether they improve half-cell and storage test behavior. It may be that the electrolyte containing only pure solvent and salt would give the best results. On the other hand, perhaps small amounts of impurities may scavenge undesirable reactive intermediates. Differentiating between these possibilities is difficult.

In this work, electrolytes which were optimized in half cell work were chosen for storage tests and cycling after storage. The DMM electrolytes (D and DA) gave similar cycling efficiencies before storage and similar, though decreased, efficiencies after storage. The electrolyte purified with alumina (DA) gave contradictory results in that it appeared more stable than the DMM (D) in the presence of Li and less stable in the absence of Li. The TMM electrolyte also gave contradictory results by showing no apparent reaction in stability tests and yet failing to cycle after storage.

The above observations illustrate the difficulty in evaluating electrolytes for Li batteries half-cells and the appearance of storage tests. Further investigation of these electrolytes in Li/TiS_2 test cells as well as a more thorough chemical analysis of the storage tests is in progress.

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FIGURE CAPTION

Fig. 1. Conductivity of $LiAsF_6$ solutions in DMM and TMM (25°C).

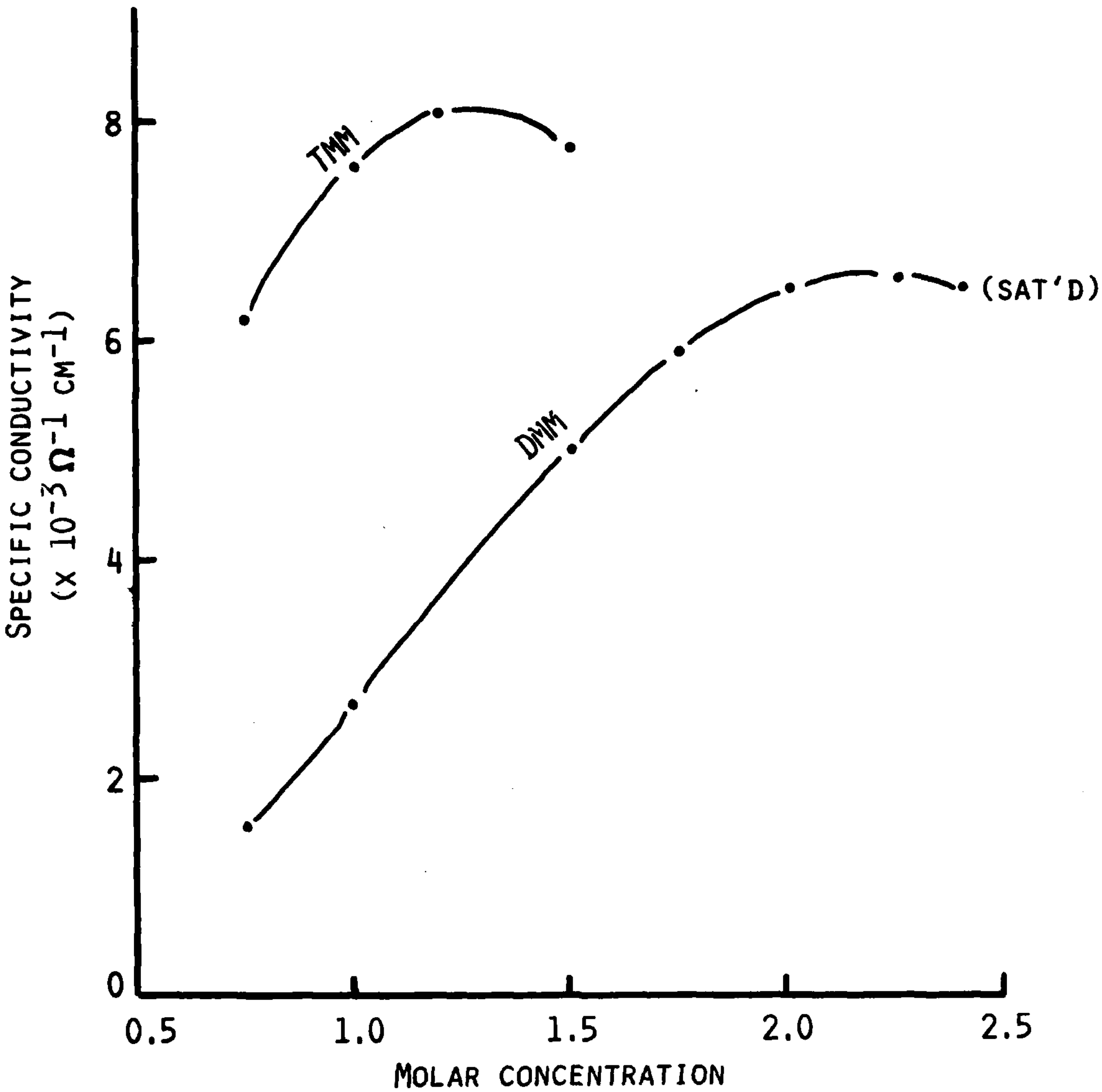
SPECIFIC CONDUCTIVITY
(x $10^{-3}\,\Omega^{-1}$ CM^{-1})
8
6
4
2
0
0.5
1.0
1.5
2.0
2.5
MOLAR CONCENTRATION
TMM
DMM
(SAT'D)

TABLE 1

HALF-CELL CYCLING TESTS USING DMM AND TMM ELECTROLYTES

1.5M $LiAsF_6$ in DMM	(D)	97.3%
	(DA)	97.5%
	(DP)	96.5%
1.5M $LiAsF_6$ in TMM	(D)	93.2%
	(DP)	95.1%

TABLE 2

STORAGE TESTS AND CYCLING AFTER STORAGE USING DMM AND TMM ELECTROLYTES AT 70°C

Solvent	With Li	Without Li
DMM (D)	Electrolyte clear with a small amount of Li corrosion at 10 days.	Electrolyte clear >10 days then darkened rapidly.
DMM (D)	Cycled after 10 days storage with Li → 87.5%.	
DMM (DA)	Electrolyte clear with a small amount of Li corrosion, > 1 month.	Electrolyte dark at 6 days.
DMM (DA)	Cycled after 10 days storage with Li → 86.9%.	
TMM (D)	No reaction at 20 days.	No reaction at 20 days.
TMM (DP)	Cycled after 14 days with Li (no reaction) → 0%.	

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