

## THE STABILIZATION OF $\text{LiAsF}_6/1,3\text{-DIOXOLANE}$ FOR USE IN RECHARGEABLE LITHIUM BATTERIES

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### Summary

The use of highly conductive  $\text{LiAsF}_6/1,3\text{-dioxolane}$  (DIOX) electrolytes in rechargeable Li batteries is precluded by the ease with which this electrolyte undergoes polymerization. By adding 0.5 - 1.0 vol.% 2-methylfuran (2-MeF) to  $\text{LiAsF}_6/\text{DIOX}$  electrolytes, excellent shelf and cycle life may be obtained in  $\text{Li}/\text{TiS}_2$  cells. Stability tests indicate that 2-MeF acts on the  $\text{TiS}_2$  cathode and the bulk electrolyte as well as on the Li anode.

### Introduction

One of the best electrolytes reported on to date for use in ambient temperature rechargeable Li batteries is the  $\text{LiClO}_4/\text{DIOX}$  system developed by Exxon in concert with their  $\text{TiS}_2$  cathode [1]. Figures of Merit (FOM) in excess of 40 were reported for cycling from 40 - 60 C  $\text{cm}^{-2}$  Li at discharge current densities of 2.5  $\text{mA cm}^{-2}$  [2]. Unfortunately, the propensity of this electrolyte to detonate both on impact and overdischarge precluded further work on this system by the Exxon group [3]. Efforts to cycle  $\text{Li}/\text{TiS}_2$  cells by substituting  $\text{LiPF}_6$  [3],  $\text{LiAsF}_6$  [4], and either  $\text{LiB}(\text{Ar})_4$  or  $\text{LiBR}_4$  [5] for  $\text{LiClO}_4$  have largely failed. For the  $\text{MF}_6^-$  anions, DIOX polymerization was the rule. For the tetraalkyl and phenylborates, the best reported FOM for the Li electrode was 13 [5].

As part of our ongoing electrolyte development program we have considered substituting stabilized  $\text{LiAsF}_6/\text{DIOX}$  electrolyte for  $\text{LiAsF}_6/\text{tetrahydrofuran}$  (THF) and/or 2-methyltetrahydrofuran (2-MeTHF) in  $\text{Li}/\text{TiS}_2$  cells.  $\text{LiAsF}_6/\text{DIOX}$  by itself, and blended with other ethers, may have the potential to provide better conductivities and lower temperature performance than current  $\text{LiAsF}_6^-$ -based ether electrolytes.

While a variety of stabilizers for  $\text{LiAsF}_6/\text{DIOX}$  electrolytes has been proposed [6], no work on the interaction of 2-methylfuran (2-MeF) with the components of the  $\text{Li}/\text{LiAsF}_6\text{-DIOX}/\text{TiS}_2$  battery has been presented in the open literature. Because 2-MeF is able to extend greatly the cycling in tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF)/ $\text{LiAsF}_6$  systems [7], we have studied the chemical stability of the  $\text{LiAsF}_6/\text{DIOX}/2\text{-MeF}$  elec-

trolites via 70 °C storage tests, and have cycled this electrolyte containing the 2-MeF additive in full Li/TiS<sub>2</sub> cells.

## Experimental

1,3-Dioxolane (DIOX) (>99.98% purity) was obtained from Grant Chemical (Baton Rouge, LA) stabilized with 10 ppm of a proprietary preservative. DIOX and THF (Fisher HPLC grade) were stirred over Li/Hg amalgam in a Vacuum Atmospheres Corp. glove box and filtered through 0.7 μm Whatman GF/F glass filters to remove reduced impurities. Lithium hexafluoroarsenate (LiAsF<sub>6</sub>) (LaRoche Industries, Inc., Decatur, GA) was added to DIOX at 0 °C with stirring. 2-Methylfuran (2-MeF) (Aldrich) was distilled over CaH<sub>2</sub> and passed through alumina (Fisher, neutral Activity 1) prior to use.

Samples of DIOX and other cell components were incubated in Teflon-lined, screw-cap culture tubes (Corning, C9826) at 70 ± 2 °C. Visual observations of electrolyte condition were made on a day-to-day basis.

Li/TiS<sub>2</sub> cells were assembled as previously reported [8]. The TiS<sub>2</sub> (Degussa, battery grade) was mixed with 8% Shawinigan carbon, 50% compressed and 8% Teflon which was then pressed onto expanded Ni screen (Delker) at 8000 psi. The cells were cathode limited to 260 mA h capacity and contained a Li/TiS<sub>2</sub> ratio of 3.8 to 1. The electrolyte consisted of 1.5 M LiAsF<sub>6</sub>/DIOX containing 0.5 vol.% 2-MeF. The 20 cm<sup>2</sup> electrode area prismatic test cells were vacuum backfilled with 10 ml of electrolyte. We cycled the cells at 40% depth of discharge between 2.8 and 1.7 V at current densities of 1.0 mA cm<sup>-2</sup> on charge and discharge.

## Results and discussion

### *Cycling studies*

As a control, two cells were prepared without 2-MeF. Upon filling the control cells, the resistances climbed from the usual 2 - 3 Ω to over 30 Ω within 30 min of filling. Owing to the high resistance these cells were uncycleable and, upon opening, contained solid polymerized electrolyte. However, the best data obtained for cells containing 0.5% 2-MeF reached 155 cycles before cathode utilization fell below 40%, as shown in Fig. 1. The minimum Li FOM (Li turnover number) was found to be 18.9. By comparison, the 1.5 M LiAsF<sub>6</sub>/THF electrolyte with, and without, 0.5% 2-MeF reaches 90 - 100 cycles (FOM ~14) and 15 - 20 cycles (FOM ~2.5), respectively [9]. Thus, the addition of 2-MeF to DIOX yields better cycling performance than when added to THF.

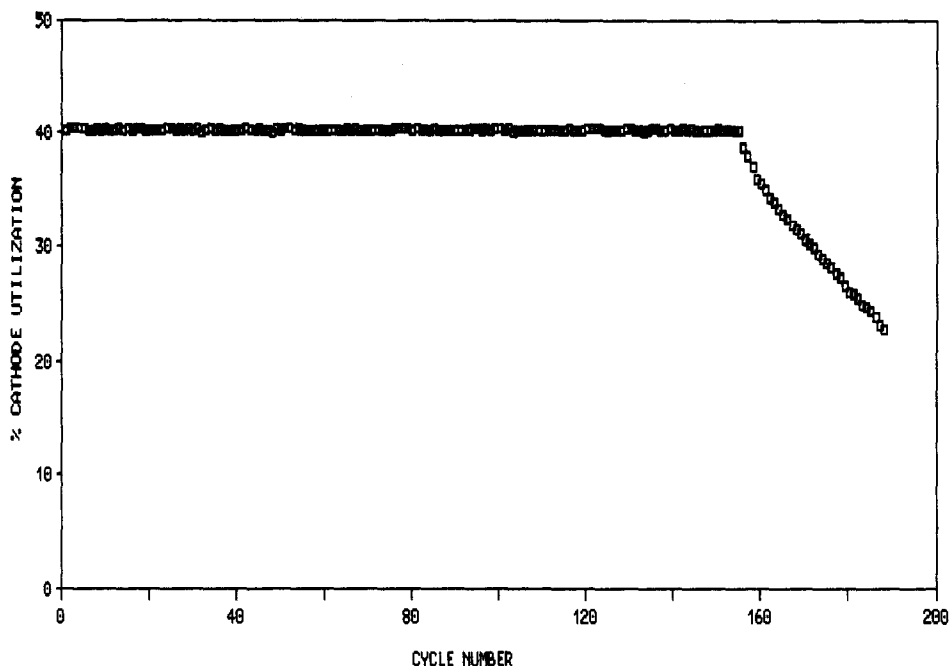


Fig. 1. Cathode utilization vs. cycle number for an Li/TiS<sub>2</sub> cell containing 1.5 M LiAsF<sub>6</sub>/dioxolane + 0.5% 2-MeF.

TABLE 1  
DIOX stability study<sup>a</sup>

Components	Observations	# Days	Temp. (°C)
DIOX	clear, colorless, no sign of polymerization	60	70
DIOX/LiAsF <sub>6</sub>	clear, colorless, viscous	30	25
DIOX/LiAsF <sub>6</sub>	clear, colorless, polymeric gel	60	25
DIOX/LiAsF <sub>6</sub>	clear, colorless, viscous	1	70
DIOX/TiS <sub>2</sub>	clear, colorless, solid polymer	2	70
DIOX/LiAsF <sub>6</sub>	clear, colorless, solid polymer	<1	25
+ TiS <sub>2</sub>		<1	25
DIOX/LiAsF <sub>6</sub>	clear, light yellow, no polymer	4	70
+ 2-MeF	opaque, dark red, viscous	8	70
	opaque, dark red, solid polymer	59	70
DIOX/LiAsF <sub>6</sub>	clear, yellow, no polymer	1	70
+ 2-MeF + TiS <sub>2</sub>	opaque, dark red, viscous	4	70
	opaque, dark red, solid polymer	29	70

<sup>a</sup>No Li present.

### Storage tests

Table 1 summarizes the results of the DIOX stability study. Each tube contained 2 ml of either purified DIOX or 1.5 M LiAsF<sub>6</sub>/DIOX with, or without, 1 vol% of 2-MeF. Several tubes also contained 0.1 g of TiS<sub>2</sub>.

The results indicate that not only does TiS<sub>2</sub> initiate the polymerization of DIOX but also LiAsF<sub>6</sub> does too. The addition of 2-MeF to help reduce DIOX polymerization indicated that 2-MeF may contribute to increased Li cycling by effects other than simple anode film formation. We believe that the formation of catalytically active species as a result of the electrolyte's intrinsic instability indicates that *no amount of purification will ever eliminate all chemical degradation pathways*. Accordingly, high cycle life in lithium cells will be dependent on additives which intercept reactive species *in situ*. In this regard we are currently working on other additives that, in concert with 2-MeF, provide more highly cycleable LiAsF<sub>6</sub>/DIOX electrolytes.

### Conclusions

The work to date on 1.5 M LiAsF<sub>6</sub>/DIOX stabilized with 0.5 - 1.0 vol.% 2-MeF shows:

- TiS<sub>2</sub>, or impurities therein, can initiate rapid polymerization of DIOX while the presence of LiAsF<sub>6</sub> results in a slower polymerization rate. These findings confirm earlier studies in DIOX-based electrolytes lacking 2-MeF [4, 6].
- 2-MeF stabilizes the electrolyte by scavenging reactive impurities and/or electrode/electrolyte reaction products. 2-MeF enhances Li cycling efficiency by effects other than simple anode film formation.
- Li FOMs in excess of 18 may be obtained by cycling full Li/TiS<sub>2</sub> cells with 2-MeF stabilized electrolyte.

### Acknowledgement

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