SOME OBSERVATIONS ON THE ATTACK OF ESTERS BY LITHIUM

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Prepared for:
Office of Naval Research
Advanced Research Projects Agency

February 1975

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Some Observations on the Attack of Esters by Lithium

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FEBRUARY 1975

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Deposition and discharge of lithium on an inert (nickel) substrate was studied in an electrolyte composed of 1M LiClO₄ in methyl pivalate (1). As with methyl acetate, cycling efficiencies were less than 10%, and the corrosion rate was greater than 200 μA/cm². In methyl pivalate, the
corrosion rate of the electrodeposited metal was relatively unaffected by SO$_2$ or nitromethane, unlike methyl acetate. The similar behavior of the two pure esters implies a corrosion mechanism involving initial electron transfer to the carbonyl carbon rather than a hydrogen abstraction.

\[
\begin{align*}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{C} - \text{C} - \text{OCH}_3 \\
\text{CH}_3
\end{align*}
\]

(I)
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Previous work in this (1,2) and other laboratories (3,4) has revealed the reactivity of esters with lithium. The reaction is especially noticeable with high surface area lithium formed by electrodeposition from these solvents. From measurement of gas evolution, Dampier and Krouse (3) determined the order of stability of linear esters to be methyl formate > methyl acetate > ethyl acetate. On the other hand, Meyers (4) noted that methyl acetate and methyl formate were more reactive toward lithium than n-butyl formate. In all cases, reactivity was enhanced by addition of lithium salts.

Two mechanisms of reaction of esters are most likely. The first is the abstraction of an acidic a hydrogen to form, initially, the corresponding lithium adduct:

\[ RR'HCOR'' + RR'C = COR'' \rightarrow RR'C = COR'' + \frac{1}{2} H_2 \]

Condensation, etc.

Another possibility is the well-known reduction of carbonyl compounds by alkali metals (5):

\[ 2 \text{RCOR'} + 2 \text{Li} + 2 \text{RCOR'} + 2 \text{Li}^+ \]

(\text{also H abstraction or polymerization})

One experiment to distinguish between these two pathways is to assess the corrosion of electrodeposited lithium using solvents of electrolytes in methyl pivalate (I), which contains no acidic hydrogens, or other hydrogens especially susceptible to abstraction by lithium metal.
Methyl pivalate (Aldrich) was distilled using a Perkin-Elmer 251 spinning band column. The middle 70% fraction was collected at 101°C and a 5:1 reflux ratio and the receiver was backfilled with argon before transferring to the argon atmosphere dry box. Solutions were made up 1M in "anhydrous" LiClO$_4$ (Alfa), and subsequently dried for three, 24 hour periods with fresh portions of activated Linde 5A, 600 mesh molecular sieve.

Electrochemical measurements have been described previously (1,2).

Fig. 1 compares the cyclic voltammograms, measured on a platinum wire electrode (potentials vs. Li/Li$^+$) of methyl acetate and methyl pivalate between +4.5V and +0.8V (Li-It alloying potential). It is evident that if the sweep is limited to the +4.0 to +1.2V range, the voltammograms are quite similar, except for a slightly higher cathodic current for methyl acetate in the 1.0-2.0V region. Methyl acetate is, however, considerably more sensitive at the anodic potential limit than methyl pivalate. Both compounds show some reduction activity below 1.0V which enhances the subsequent oxidation peak at 2.0V.

One interpretation of these results is a higher level of electroactive impurities in methyl acetate than in (I). On nickel, the cyclic voltammograms reveal considerably greater cathodic currents for methyl acetate than for methyl pivalate in the 0 to +1.0V range (Fig. 2). Both electrolytes contained less than 10 ppm H$_2$O, but the presence of other impurities cannot be discounted. A more attractive interpretation, for the present purposes, is that solvent oxidation and reduction at the electrode surface is kinetically more favorable in the less bulky methyl acetate.

Lithium was plated and stripped on a nickel substrate at 10 mA/cm$^2$ using an electrolyte of 1M LiClO$_4$ in methyl pivalate. A polarization between the counter and working electrodes of 3.5V, compared to 0.5V for 1M LiClO$_4$ in methyl acetate, indicates a high iR component. An average efficiency of 7% lithium recovery was obtained over five cycles of 1 coul/cm$^2$. Corrosion experiments (1) allowed the calculation of a 200-400 μA/cm$^2$ corrosion rate for this electrolyte, based on recoverable lithium. This is similar to the attack rate of methyl acetate on electrodeposited lithium (2). Solutions containing 0.05M and 1.6M nitromethane, which favorably improved lithium cycling in propylene carbonate and methyl acetate (2), yielded an average of 65% and 73%
Fig. 1: Cyclic voltammograms of 1M LiClO₄ in methyl pivalate (---) and in methly acetate (-- - - -) on platinum. Sweep speed, 0.1 V/sec. $T = 25^\circ\text{C}$. 
Fig. 2: Cyclic voltammograms of 1M LiClO₄ in methyl acetate (a), and in methyl pivalate (b,c) on nickel. Sweep speed = 0.1 V/sec. T = 25°C.
lithium cycling efficiency over eight cycles on a clean working electrode. Average corrosion rates of 285 μA/cm² and 273 μA/cm² (over the first 4000 sec of the life of the deposit) were obtained for electro-deposited lithium in the 0.04M and 1.6M nitromethane solutions, respectively. Solutions 2M in SO₂ gave an average efficiency of 70% over nine cycles, and an average corrosion rate of 300 μA/cm² over 2400 sec. Passivation of the lithium deposit was not observed for either additive.

The methyl pivalate-based electrolyte, after standing for several days in the presence of electrodeposited lithium, begins to turn yellow. Similar results were obtained for methyl acetate. In both cases, the yellowing reaction was slightly retarded by adding SO₂ or NM.

If a hydrogen abstraction were an important process in the attack of these esters by lithium, electrodeposited lithium should be quite stable to methyl pivalate. However, methyl pivalate is corrosive to such deposits at a similar rate to methyl acetate. These results, along with the general cathodic currents observed between 0 and +1.0V vs. Li/Li⁺ in the cyclic voltammograms, indicate a solvent reduction reaction in which electron transfer to the carbonyl carbon, a center of positive charge, is the first step. Furthermore, the corrosion rate of lithium in methyl pivalate is not lowered by the addition of nitromethane or SO₂, unlike the corrosion rate in methyl acetate. Under these circumstances, there is no advantage to the use of methyl pivalate in secondary lithium batteries.

REFERENCES


5. H. O. House, Modern Synthetic Reactions (New York: W. A. Benjamin, Inc., 1963), Ch. 3.