A POSSIBLE MECHANISM FOR THE REDUCTION OF VOLTAGE DELAY IN THE Li/SOCl$_2$ SYSTEM VIA CYANOACRYLATE COATINGS ON LITHIUM

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Summary

Scanning electron microscopy and X-ray photoelectron spectroscopy were used to investigate the passivation of lithium treated with alkyl 2-cyanoacrylates in LiAlCl$_4$/SOCl$_2$ electrolyte. Cyanoacrylate coatings reduce anode polarization by affecting the morphology and growth kinetics of the LiCl passivating film. The mechanism for these effects depends on the gradual dissolution of the coating in electrolyte and its subsequent replacement by LiCl. Dissolving either the monomer or polymer form of cyanoacrylate directly into the electrolyte without coating the lithium also affects LiCl film growth and reduces polarization.

1. Introduction

The Li/SOCl$_2$ system [1, 2] is attractive as a battery power source because of its high voltage and energy density, long shelf life, broad operating temperature range, and hermetic sealing. However, a major concern about its successful commercial application is voltage delay. Voltage delay is caused by an excessive build-up of a passivating multilayer LiCl film on anodes in the customary LiAlCl$_4$ electrolyte [1 - 5]. It has two components as shown in Fig. 1: (a) an initial polarization of the anode causing the cell voltage to drop below a predefined cutoff voltage when it is first placed on load, and (b) the time required for the voltage to recover to its operating level. This phenomenon can be conveniently measured in half-cells, as done here, by measuring the anodic polarization of a Li working electrode *versus* a Li reference in response to a galvanostatic step.

Several approaches have been suggested to reduce voltage delay [6 - 11] and have met with varying degrees of success. One successful, but as yet little understood fundamentally, approach is to coat the anode with a polymer of alkyl 2-cyanoacrylate [11].

Recently [12] we characterized the performance of cyanoacrylate coatings as a function of various discharge and processing parameters. In that paper, three possible mechanisms were offered for how cyanoacrylate reduced voltage delay in LiAlCl$_4$/SOCl$_2$ electrolyte. Further work was needed,

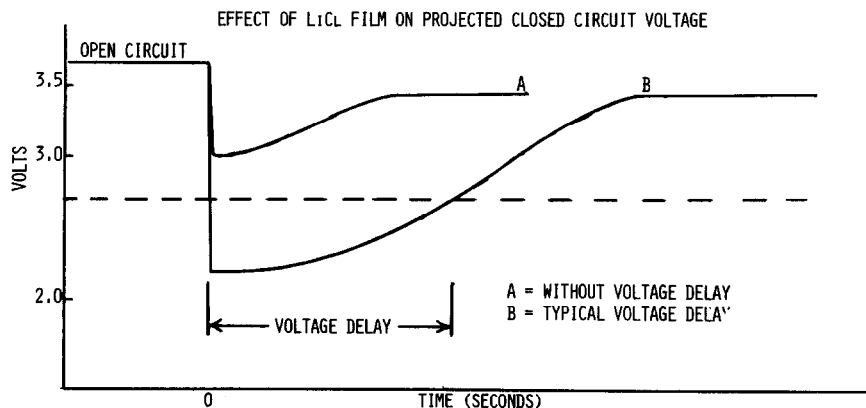EFFECT OF LiCl FILM ON PROJECTED CLOSED CIRCUIT VOLTAGE

Fig. 1. Simulated data showing a Li/SOCl$_2$ cell with and without voltage delay. The two components of voltage delay are shown: the initial polarization and the time required to recover to the operating voltage level.

however, to determine which one, or combination, was most accurate. This paper describes the subsequent work that was performed in an attempt to understand and identify the actual mechanism.

Scanning electron microscopy (SEM) was used to evaluate how the growth and morphology of the passivating anode film of LiCl is affected by the cyanoacrylate treatments. X-ray photoelectron spectroscopy (ESCA) was used to determine the presence of cyanoacrylate on coated lithium substrates after electrolyte storage.

Important processing parameters to consider in discussing the effectiveness of plain cyanoacrylate coatings are the type of alkyl homologue used, the coating thickness, and the extent of surface coverage. These parameters were previously optimized [12] for long-term effectiveness to a 0.0025 cm-thick coating of ethyl 2-cyanoacrylate applied in two applications to the anode. The high solubility of cyanoacrylate in electrolyte [12] is also an important factor in understanding how the material reduces voltage delay.

Alkyl 2-cyanoacrylates [13] are unsaturated monomeric esters which polymerize rapidly at room temperature through the central C atom, as shown below. Weak bases such as traces of water moisture in the air will initiate the polymerization. They have a service temperature of up to about 80 °C.

$$CH_2 = \underset{\underset{COOR}{|}}{\overset{\overset{CN}{|}}{C}} \longrightarrow \left[-CH_2 - \underset{\underset{COOR}{|}}{\overset{\overset{CN}{|}}{C}} - \right]_n$$

2. Experimental

Alkyl 2-cyanoacrylate monomers (necessarily containing polymerization inhibitors in the ppm concentration range) were obtained from Pacer

Technology and Resources, Campbell, California. They were stored at room temperature and shielded from light in a dryroom ($< 1\%$ R.H.). Lithium (Foote Mineral Company) was coated in the dryroom with the material by an optimized solution casting procedure described in ref. 12. The final coating thickness was 0.0025 cm. Treated and untreated lithium samples were then placed in a serum bottle purged with 4.8 grade Ar and capped. This bottle was placed within a second container also purged with the argon. The lithium was then transferred to an Ar filled glove box (1 - 2 ppm H_2O, Vacuum Atmospheres Company) for electrolyte addition and subsequent resealing. The electrolyte was 1.6M $LiAlCl_4$ in $SOCl_2$. In some tests either a cyanoacrylate monomer (1:40 volume ratio) or a polymer (61.5 mg/cm^3) was added to the electrolyte. A polymer coating containing $LiClO_4$ (reagent grade, G. Frederick Smith Chemical Company) was also prepared as in ref. 12. Room temperature storage occurred in the glove box. High temperature (71 °C) storage took place in a Blue M Stabil-Therm gravity oven.

At the end of the storage period the lithium samples were removed from their bottles in the glove box and carefully rinsed with a small amount of straight thionyl chloride. The sample was allowed to dry before being placed in a suitable Ar filled container for transport to the SEM and ESCA instruments. A chamber, which was purged with Ar, was attached to the SEM and ESCA instrument ports so that the lithium samples could be transferred into them in an inert atmosphere. A JEOL Model 35C was used for taking SEM photomicrographs. A Physical Electronics Industries Model 548 ESCA/Auger Spectrometer was used for obtaining ESCA spectra. Spectra were obtained using an Al Kα radiation source (1486.6 eV) working at 500 W (10 kV, 50 mA) and an analyzer pass energy of 200 eV. During the analysis the chamber pressure was about 10^{-8} Torr. Half-cell anode polarization methods were performed as in ref. 12.

3. Results

3.1. SEM micrographs

When untreated Li (as received from Foote) is stored in 1.6M $LiAlCl_4$/ $SOCl_2$ electrolyte a densely packed, cubic LiCl crystal film is formed on its surface as shown in Fig. 2(a), (b). However, when a Li sample which is coated with ethyl 2-cyanoacrylate (E-CA) is stored under identical conditions, a much different film morphology develops, as shown in Fig. 3(a), (b). The room-temperature-formed film on the treated anode is very open with wide spacing between major crystal growths; the crystals themselves are not cubic, but rather angular and irregular-shaped. After high temperature storage, the film formed on the E-CA coated anodes appears mossy and much less dense than the corresponding untreated sample.

An even more open LiCl film (with associated improvements in polarization, Table 1) can be achieved by incorporating a salt into the E-CA cast polymer coating [14]. Figure 4(a), (b) shows the much more open film
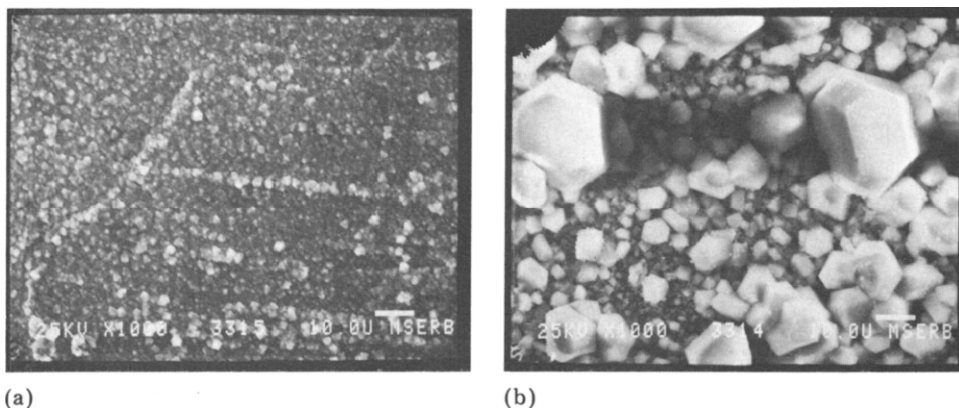
(a)   (b)

Fig. 2. Untreated Li samples stored five days in 1.6M LiAlCl$_4$/SOCl$_2$. (a) room temperature; (b) 71 °C.

(a)   (b)
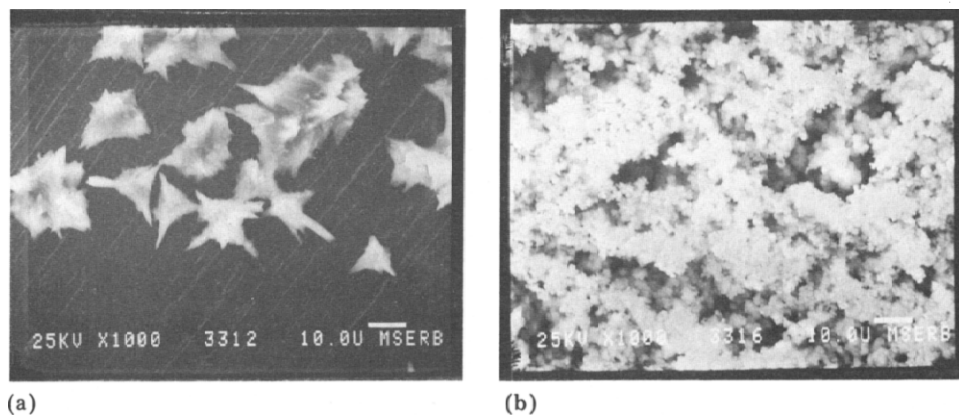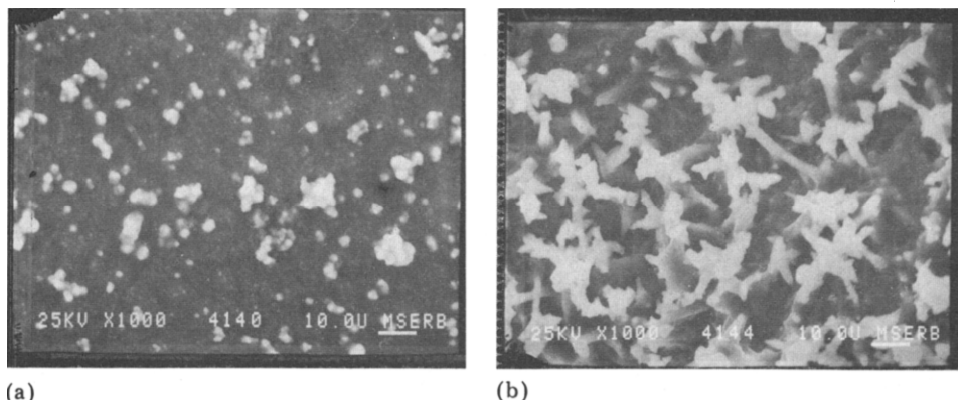
Fig. 3. Lithium samples coated with E-CA (0.0025 cm thick) stored five days in 1.6M LiAlCl$_4$/SOCl$_2$. (a) room temperature; (b) 71 °C.

TABLE 1

Effect of cyanoacrylate treatments on anode polarization
Average of two measurements at 6 mA/cm^2, 24 h storage in electrolyte, at room temperature.

Treatment	Figure number	Max. polarization, V vs. Li
None	2	1.695
I-CA	5	1.341
E-CA	3,5	0.535
E-CA + LiClO$_4$	4	0.370
E-CA monomer additive to electrolyte	6	0.455

(a)   (b)

Fig. 4. Lithium samples coated with E-CA doped with $LiClO_4$ stored five days in 1.6M $LiAlCl_4/SOCl_2$. (a) room temperature; (b) 71 °C.
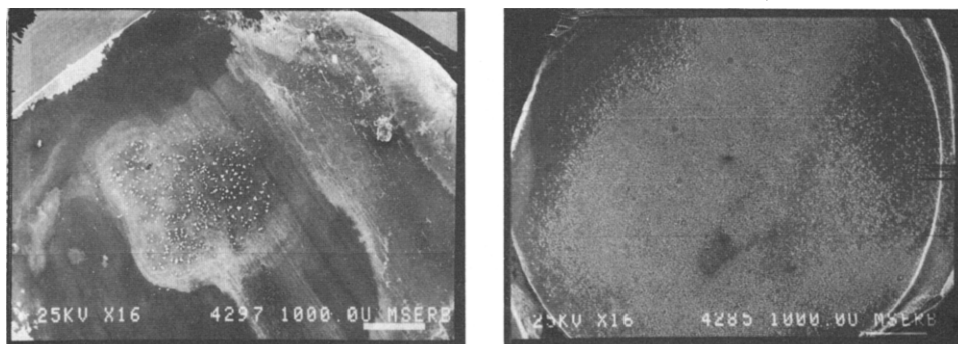
(a)   (b)

Fig. 5. Lithium samples (low magnification) coated and stored five days in 1.6M $LiAlCl_4/SOCl_2$. (a) E-CA, 0.0025 cm thick; (b) I-CA, 0.0025 cm thick.

which was formed (under the same conditions as in Figs. 2 and 3) when $LiClO_4$ was incorporated into the polymer coating. $LiClO_4$ is essentially insoluble in the electrolyte.

The extent of LiCl coverage on treated anodes depends partly on the cyanoacrylate homologue used for the coating. E-CA (5 cps viscosity, 1.07 g/cm^3 monomer) has a faster set time and higher degree of polymerization and density than the slower setting isopropyl cyanoacrylate monomer (I-CA, 5 cps viscosity, 1.00 g/cm^3). The low magnification view in Fig. 5(a), (b) compares the LiCl film which grows on anodes treated with the two homologues. The E-CA treated sample shows only scattered crystal growth, while the use of the isopropyl homologue results in a much more extensive coverage. This difference in extent of coverage manifests itself in the polarization data given in Table 1. Apparently, the denser E-CA polymer coating is more effective in limiting film growth than I-CA.
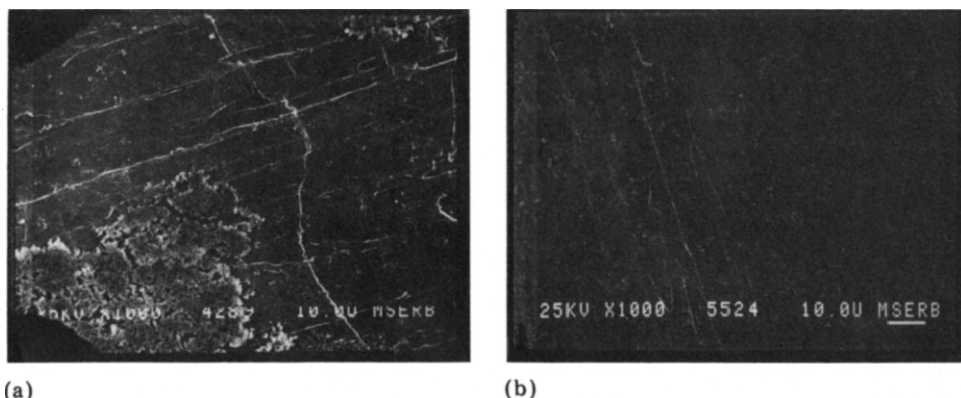
(a)   (b)

Fig. 6. Lithium samples stored five days at room temperature in modified 1.6M LiAlCl$_4$/SOCl$_2$. (a) E-CA monomer added to electrolyte; (b) E-CA polymer added to electrolyte.

SEM photomicrographs have revealed that just dissolving either the E-CA polymer or monomer directly in the electrolyte will also greatly reduce LiCl growth on uncoated anodes at both room and high temperatures as shown in Fig. 6(a), (b). This effect, however, has been seen to diminish with long-term storage.

The differences in LiCl film morphologies achieved by the various cyanoacrylate treatments described above correlate very well with the corresponding half-cell polarization data in Table 1. The trend is for anodes covered by the denser appearing LiCl films to be highly polarized, while those covered with the less dense covering polarize less.

3.2. ESCA spectra

Figure 7 shows the broad scan spectrum for a Li sample coated with E-CA but which had no electrolyte contact. The binding energy data for the detectable elements comprising E-CA (O, N and C) agree well with those
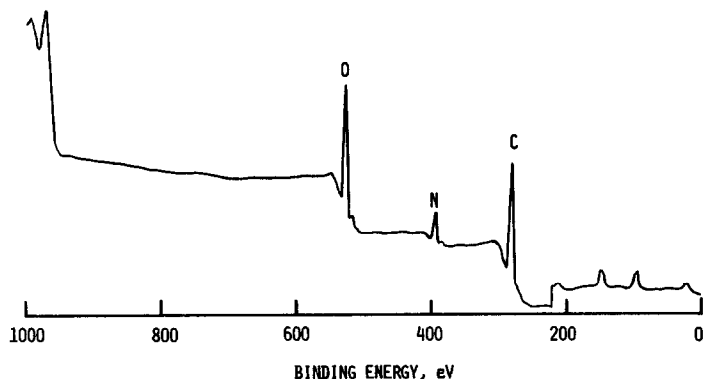

Fig. 7. ESCA spectrum of Li surface coated with E-CA. No electrolyte contact.

cited in the literature [15, 16]. The peak heights in conjunction with the respective atomic sensitivity factors were used to get a rough comparison between the calculated *versus* the theoretical stoichiometry of E-CA. The calculated stoichiometry (24% O, 9% N, and 67% C) is almost identical with the theoretical value. Peak shapes could not be resolved sufficiently to permit identification of different oxygen and carbon bonds [17].

Ion sputtering with Ar at 5×10^{-5} Torr for 10 s created a large, golden area on the sample and probably changed the E-CA chemically, since its calculated post-sputtered stoichiometry showed a decline in the O 1s signal and a large increase in the C 1s peak. Peak shapes and locations of maxima for O and C were not changed by the sputtering.

Figure 8 is an ESCA spectrum of an anode coated as above but now stored in electrolyte before analysis. There are two main differences between it and the previous sample. One is the expected appearance of the Cl signal from the LiCl film that exists on the immersed Li surface. The appearance of the same Cl signal due to LiCl film growth was also reported in ref. 15. (The Cl signal observed here could also be due in part to the possible chlorination of the polymer by thionyl chloride.) The second major difference between the two spectra is the absence of the N 1s peak. Nitrogen, found in the polymer's cyano functional group, is the only unambiguous evidence for E-CA since both the observed O and C signals could be due to other surface species. Oxygen and carbon have been observed on both fresh Li and Li which had contacted both thionyl chloride and LiAlCl$_4$ electrolyte [15]. Therefore, the indicated absence of N in the Fig. 8 sample means that at a minimum, E-CA is still present on Li after electrolyte storage, but in an altered state, and at a maximum that it is absent altogether. As an alternative one could hypothesize that thionyl chloride cleaved the E-CA eliminating the cyano group from the polymer. For instance, poly(ethyl acrylate) would contain theoretically detectable C and O, but no N [16].
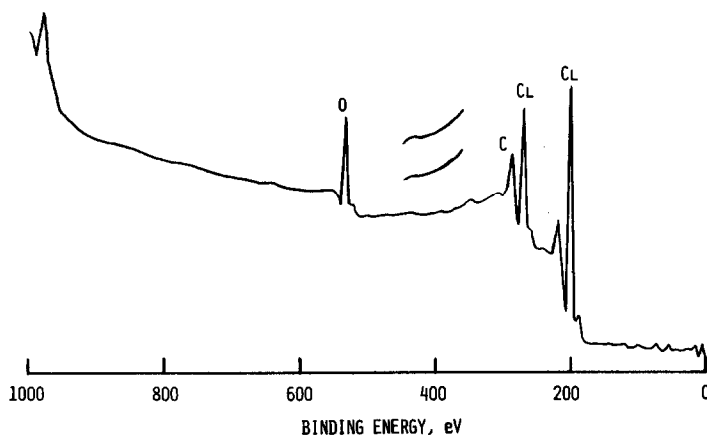

Fig. 8. ESCA spectrum of Li surface coated with E-CA and then stored in 1.6M LiAlCl$_4$/ SOCl$_2$ for five days at 71 °C. High resolution scans (analyzer pass energy of 25 eV) were recorded to confirm absence of N.

A similar spectra as in Fig. 8 was observed for uncoated Li removed from electrolyte containing dissolved E-CA monomer. This was the analogous experiment for the SEM sample of Fig. 6(a). The purpose of this ESCA experiment was to determine if any of the dissolved E-CA was adsorbed onto the Li surface. Although the N signal was absent, the C, O and Cl signals cannot be unambiguously assigned as discussed above and so the experiment was inconclusive.

4. Discussion

There are at least three possible explanations for the reduction of voltage delay in the $Li/SOCl_2$ system via cyanoacrylate coatings on lithium. One is that the cyanoacrylate coating remains on the anode surface in some form as a physical barrier preventing direct contact with the electrolyte. To accommodate the discharge reaction, the coating could incorporate some sort of redox couple to shuttle the electrons and lithium ions across it or act as a type of ion exchange membrane.

A second hypothesis is that as a result of the initial cyanoacrylate coating the LiCl film which is produced passivates less than one formed on untreated anodes. The LiCl film would grow as the coating dissolved off the anode due to the polymer's high solubility in electrolyte (as discussed below), and possibly initially through pinholes in the original coating.

The third considered possibility is that the coating dissolves and acts solely as an electrolyte species. For instance, the dissolved form of the coating could complex with the electrolyte salt creating a species which does not exchange chloride with the initial LiCl film as readily as the plain $AlCl_4^-$ anion [7]. Each hypothesis is considered below individually along with the relevant analytical data.

According to the barrier hypothesis, the cyanoacrylate polymer coating would have to remain on the Li surface after storage in electrolyte. This seems unlikely since the solubility of the E-CA polymer in 1.6M electrolyte is at least 185 mg/cm^3 [12]. At this level, more than three times the amount of coating applied to the samples (and in actual cells, ref. 12) could have theoretically dissolved in the available electrolyte during the storage period. Visual inspection and the ESCA data tend to confirm the absence of bulk E-CA on samples stored in electrolyte. However, a monolayer barrier would still be a possibility. Even though the only certain ESCA indicator for E-CA, the cyano group's N 1s peak, is absent, and the presence of C, O and Cl could be accounted for by other surface species, an altered polymer monolayer composed of C and O (and possibly Cl) cannot be positively ruled out. However, if the improvement is due solely to an undissolved monolayer, then the effect should be independent of the initial coating thickness. Previous work [12] has shown that there is, in fact, a large dependence on coating thickness. In summary, the physical barrier hypothesis does not seem likely.

According to the second stated hypothesis, a LiCl film would replace the original polymer coating on the anode surface. This replacement LiCl film would be less passivating than the type formed on untreated anodes. There are several lines of evidence to support this hypothesis. First, the solubility of the coating is high enough for all of it to dissolve from the anode. Secondly, SEM photos show that the replacement LiCl film has a different crystal structure and reduced density and coverage than the film on untreated samples. These characteristics combine to reduce the passivation polarization, as shown in Table 1. Finally, the different effects of the various cyanoacrylate treatments can be explained in terms of this hypothesis and, more specifically, the direct relationship between extent of surface coverage of the coating and its dissolution rate, and the rate of growth of the replacement LiCl film. A faster dissolution rate or relatively less complete initial surface coverage would result in a faster rate of growth for the replacement film.

The difference in the polarization behavior between I-CA and E-CA coated anodes is probably due to their different physical properties. I-CA polymer, being less dense than E-CA, will probably dissolve more rapidly and provide a lower initial surface coverage leading to a more rapid growth of LiCl. The dependence of polarization on initial E-CA coating thickness can also be explained in these terms. Coating dissolution rate would be a function of initial thickness, and different thicknesses would also offer varying degrees of initial surface coverage. Apparently, the more rapid the growth of the replacement LiCl film, the more passivating it is. Previous studies on untreated Li surfaces have shown that the faster grown LiCl films cause greater passivation than those formed at slower rates [3].

In summary, cyanoacrylate coatings apparently provide a means to change the growth kinetics of the LiCl film. The magnitude of the change will depend mainly on the dissolution rate of the coating, but also on the extent of its initial surface coverage. This impact on growth kinetics results in a LiCl film with a crystal structure, density, and coverage which, together, are less passivating than that of a film formed quickly on an untreated Li anode.

The improvements obtained with doping the polymer film with $LiClO_4$ can also be explained in terms of this hypothesis. Figure 4(a), (b) shows that the replacement film for E-CA + $LiClO_4$ has a different morphology from that for just E-CA alone. The inclusion of the electrolyte insoluble $LiClO_4$ in the initial polymer coating could possibly affect the dissolution rate of the surrounding coating or act as nucleation centers for an imperfect and still slowly formed LiCl film.

The third possible mechanism is that once the cyanoacrylate has dissolved from the Li, it exerts its effect directly from the electrolyte. To test this, Li anodes coated with E-CA were stored for five days at room temperature in electrolyte. They were then removed, carefully rinsed with distilled thionyl chloride, replaced in fresh electrolyte and pulsed at 6 mA/cm^2. The maximum polarization was very low: 0.350 V (average of two measure-

ments). This indicates that for coated anodes, the material that dissolves off the anode into the electrolyte during storage is not necessary for reducing voltage delay. Rather it is strictly the characteristics of the replacement LiCl film which minimize voltage delay.

On the other hand, SEM photos show that the film coverage is greatly reduced for uncoated anodes after storage in electrolyte containing either the monomer or polymer cyanoacrylate additive. Table 1 shows that the electrolyte with the monomer additive reduces the polarization of uncoated anodes. ESCA experiments could not definitely determine whether any of the dissolved material adsorbed onto the uncoated Li surface. Further experiments are needed to tell if the dissolved cyanoacrylate complexes with the electrolyte salt. In summary, the third hypothesis is not valid for coated anodes. However, E-CA dissolved in the electrolyte can reduce film growth for uncoated Li anodes, at least initially.

5. Conclusion

With this work, it was found that cyanoacrylate coatings reduce anode polarization by affecting the morphology and growth kinetics of the LiCl film. The initial cyanoacrylate coating is replaced by a LiCl film which is less passivating than one formed on untreated anodes. The faster the replacement film is formed, the more passivating it is. The growth kinetics of this replacement film depend on the coating's dissolution rate and the initial extent of surface coverage. In practical terms, the dissolution rate and coverage are a function of the density of the polymer and the coating thickness.

Acknowledgements

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