273

SURFACE FILMS ON LITHIUM IN ACETONITRILE–SULPHUR DIOXIDE SOLUTIONS

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Summary

The growth of the passive film on Li in acetonitrile–sulphur dioxide solutions of LiBr, $LiAsF_6$, $LiAlCl_4$ and $LiClO_4$ with time has been followed by galvanostatic pulse measurements and SEM observations.

It was found that the specific conductivity of the primary film on Li in AN–SO_2–LiBr solutions ($k = 4 \times 10^{-9}$ ohm^{-1} cm^{-1}) is practically insensitive to changes in concentration of SO_2 and LiBr.

The substitution of Br$^-$ by AsF_6^- anions in AN–SO_2 electrolytes significantly changes the properties of the film; the rate of growth and the "steady state" value of the polarization resistance are much higher as compared with those of films obtained on Li in Br$^-$-containing electrolytes.

Water contamination above 1000 ppm enhances the growth of the passive film as compared with that in "dry" electrolytes.

Introduction

The normal passivation of Li in the electrolyte solution of Li/SO_2 cells is indispensable for their long storage life. However, both extremes, the over-passivation causing voltage delay and the depassivation leading to explosion hazards, are obviously undesirable. The recently reported adverse effects of these phenomena [1, 2] have stimulated the present study on the passivation of Li as a function of the electrolyte composition.

Experimental

The growth of the primary passive film with time was followed by galvanostatic pulse measurements [3], which yield the polarization resistance, R_p, and the capacitance, C, of the Li electrode. The electrolyte solutions, consisting of acetonitrile (AN), SO_2 and an Li salt (Br$^-$, ClO_4^-, $AlCl_4^-$, AsF_6^-), contained less than 70 ppm of H_2O ("dry" electrolytes). Sulphur dioxide and AN were dried with molecular sieves to a water content below 10 ppm.

After drying AN was twice distilled. LiBr (Merk p.a.) and $LiAsF_6$ were dried under vacuum at 150 °C; $LiClO_4$ at 200 °C. $LiAlCl_4$ was synthesized by melting the mixture of dried LiCl and resublimed $AlCl_3$ [3].

The Li metal was pressed in a glass tube and its working surface was freshly cut in the dry box immediately before each experiment. The secondary porous films were observed by SEM. The transfer from the dry box, where the samples were stored in the various solutions, to the SEM chamber was performed by a vacuum technique [4].

Results and discussion

(i) Effect of LiBr and SO_2 concentrations

The preliminary tests showed that in AN solutions containing less than 12 wt.% SO_2 and 0.3 - 0.5M LiBr, metallic Li corrodes very rapidly, forming thick, gelatinous surface layers with a low R_p. Hence, all subsequent measurements were carried out in solutions with SO_2 concentrations ranging from 15 to 50 wt.%. The R_p-t curves in Fig. 1 show that R_p is practically independent of the SO_2 concentration. It is seen also that R_p grows substantially only in the first 20 - 40 h (Fig. 1, curve 1). A significant increase in R_p was again observed after 200 h which is explained by the increase in density of the porous film, as confirmed by SEM observations. Figure 2 presents a $1/C-R_p$ plot obtained during the growth of the primary film for 40 - 60 h at various SO_2 and LiBr concentrations. All experimental points are close to the average straight line the slope of which yields the specific conductivity of the film $k = 4 \times 10^{-9}$ ohm^{-1} cm^{-1} (assuming an arbitrary value of $\epsilon = 10$). The
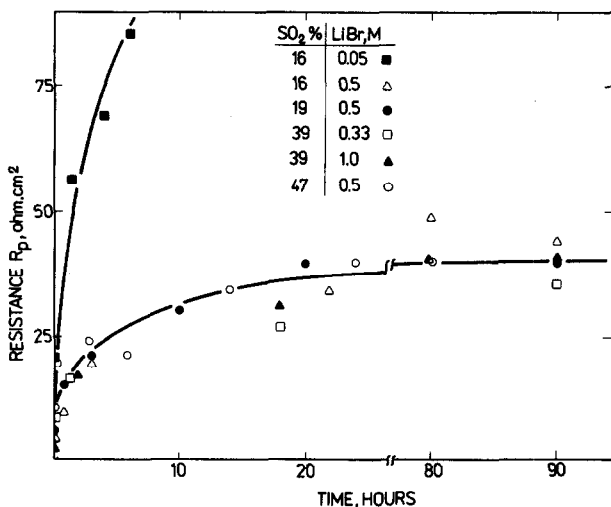

Fig. 1. Polarization resistance vs. time dependence of Li electrodes in AN + SO_2 solutions with various SO_2 and LiBr concentrations.
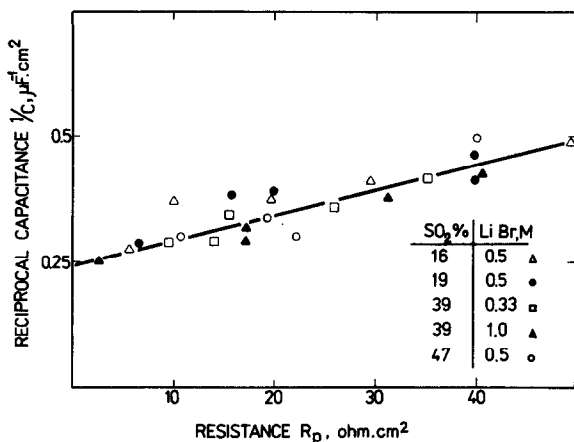
Fig. 2. Reciprocal capacitance *vs.* polarization resistance plot of Li electrodes obtained during 60 h passivation in AN + SO$_2$ electrolytes.
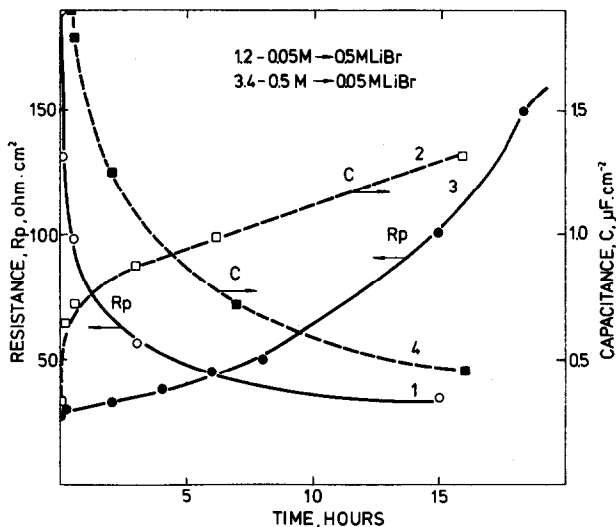

Fig. 3. Polarization resistance and capacitance change with time after transferring a passivated Li electrode from 0.5M to 0.05M LiBr solution in AN + SO$_2$ and *vice versa*: 1, 2, from 0.05 to 0.5M; 3, 4, from 0.5 to 0.05M.

fact that k is practically insensitive to changes in SO$_2$ and LiBr concentrations suggests that the film composition is probably one and the same in all these solutions.

At LiBr concentrations below 0.05M the growth of R_p with time was unexpectedly fast (Fig. 1, curve 2). Additional tests based on transferring a passivated Li electrode from a 0.05M to a 0.5M LiBr solution and *vice versa* (Fig. 3) revealed that the high R_p and low C of Li in the dilute solution is due to the porous layer filled with a low conductivity electrolyte solution. In solutions more concentrated than 0.05M LiBr the resistance of the porous

layer is negligible and the R_p of the dense primary film in series with the porous layer can be measured sufficiently accurately.

It was established that the films formed in LiBr-containing solutions were easily destroyed by current pulses of amplitude greater than 5 mA/cm^2 and a duration longer than 20 ms. Therefore, the Tafel experiments requiring such pulses were not carried out. A possible reason for the film instability could be its thickness or its amorphous structure as compared with passive films in other nonaqueous solutions such as SOCl$_2$ [3, 5].

(ii) Effect of water

It was established that the kinetics of the film formation in AN/SO$_2$ electrolytes is affected substantially by water contaminations above 1000 ppm. The effect is expressed by the higher rates of increase of the polarization resistance R_p, and its higher "steady state" values as compared with the results in the "dry" electrolytes (Fig. 4, *cf.* curves 3 and 1).

SEM observation of Li specimens stored for 144 h in AN/38% SO$_2$/0.5M LiBr solution containing 2000 ppm of H$_2$O showed more coarsely crystalline and denser films as compared with the morphology of the passive films grown for the same time in the "dry" electrolytes (*cf.* Figs. 5 and 6). This relatively fast formation of secondary passive film in water-containing electrolytes could explain why the R_p and C of the Li electrode in the latter solutions change steeply after 80 h of storage (see Fig. 4, curve 3). It is also possible that a film of different composition is formed (*e.g.*, LiOH).

It was found that at a constant water content ($\sim$ 1000 ppm) an increase of the solute concentration in the AN/SO$_2$ solutions inhibits the effect of water on film growth. For example, lithium specimens stored for 144 h in a "moist" electrolyte (2000 ppm H$_2$O) in the absence of salt corroded heavily (rough and matt Li surface) while samples kept in the same solution but

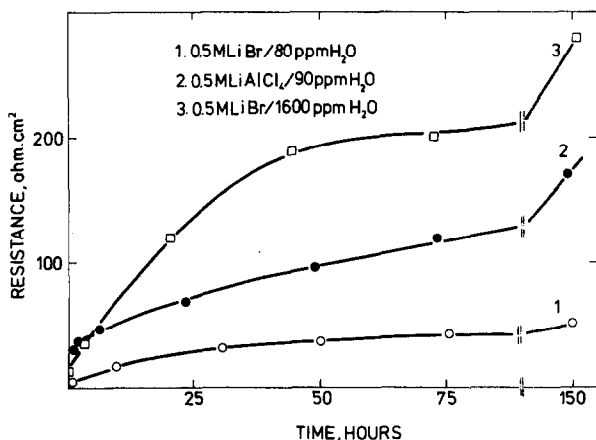Fig. 4. Polarization resistance *vs.* time dependence of Li electrodes in AN + 37 wt.% SO$_2$ with: 1, 0.3 - 1.0M LiBr/80 ppm H$_2$O; 2, 0.5M LiAlCl$_4$/90 ppm H$_2$O; 3, 0.5M LiBr/1600 ppm H$_2$O.
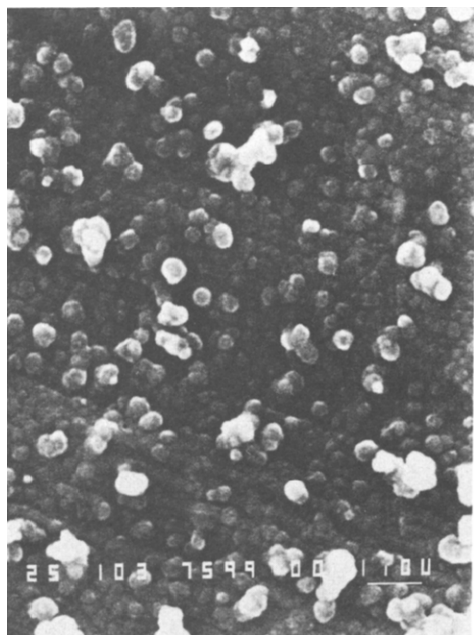
Fig. 5. SEM photograph of Li surface after 144 h storage in a 0.5M LiBr solution in AN + 38 wt.% SO_2 ("dry electrolyte"). (× 7000.)
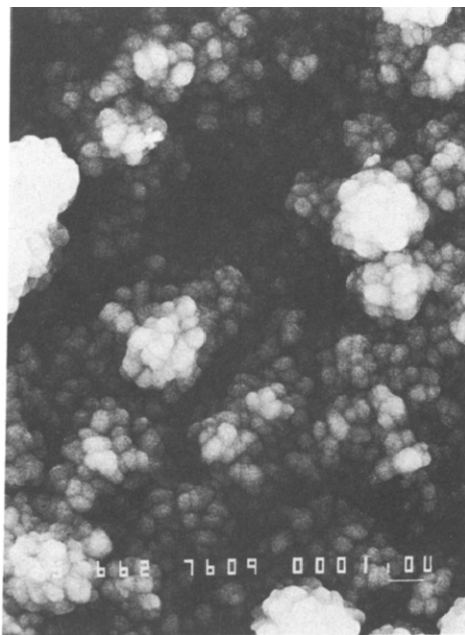
Fig. 6. SEM photograph of Li surface after 144 h storage in a 0.5M LiBr solution in AN + 38 wt.% SO_2 containing 2000 ppm H_2O. (× 4620.)

containing 0.5M LiBr remained unaffected (bright Li). A similar phenomenon was recently reported for Li stored in "moist" $LiClO_4$ and $LiAsF_6$ propylene carbonate electrolytes [4]. The water activity appears to be reduced by the presence of a salt, probably as a result of the formation of solvates or hydrolysis products.

(iii) Effect of the anion

It was found that the substitution of the Br^- anion by ClO_4^- or $AlCl_4^-$ in the $AN-SO_2$ solutions changes, but insignificantly, the kinetics of the film growth (Fig. 4, curve 2). In the presence of the AsF_6^- anion the situation is quite different, as exhibited by the R_p-t plot in Fig. 7 for an Li electrode immersed in a saturated $LiAsF_6$ 0.15M solution with 38 wt.% SO_2. The rate of growth and the final values of R_p are much higher even than those of films obtained in 0.05M LiBr solutions (Fig. 7, curve 1). The specific conductivity of the film formed in $LiAsF_6$ solutions determined both at low electric fields from the $1/C-R_p$ plot and at high electric fields from Tafel plots (Fig. 8) shows one and the same value (4×10^{-10} ohm^{-1} cm^{-1}), which is one order of magnitude lower than that of films formed in LiBr solutions. The SEM pictures of this film revealed no porous layer even after storage for 150 h in the $LiAsF_6$ solution. This implies a very low film corrosion rate, in accordance with its low ionic conductivity.
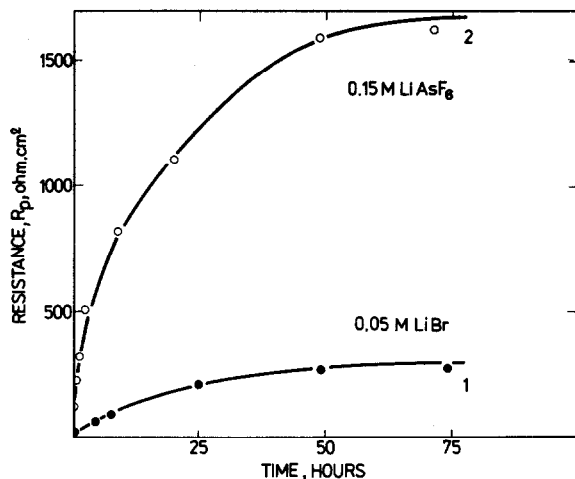
Fig. 7. Polarization resistance *vs.* time dependence of Li electrodes in AN + SO_2 solutions with: 1, 0.05M LiBr; 2, 0.15M $LiAsF_6$.

The transfer of an Li electrode passivated in AsF_6^--containing SO_2 electrolyte to a solution with a higher conductivity (AN/37% SO_2/0.5M LiBr) does not significantly change either R_p or C. This also confirms the assertion that a thin, nonporous film, formed in $LiAsF_6$ solutions, is responsible for the much higher polarization resistance measured in this electrolyte as compared with that observed in LiBr solutions. These findings are in agreement with Dey's conclusions that Li/SO_2 cells with $LiAsF_6$ electrolyte are safer under abuse conditions [2]. Using differential scanning calorimetry measurements, Kilroy [6] has also indicated that $LiAsF_6$ displaces the initiation of the Li–AN reaction in SO_2-containing electrolytes· to higher temperatures as compared with LiBr.

(iv) Effect of temperature
The apparent activation energy of the ionic conductivity was assessed by the temperature dependence of R_p of the passive films grown in AN/SO_2 solutions with different solutes in the range −30 to 50 °C. The Arrhenius plots are presented in Fig. 9 where curve 1 refers to a passive film growing for 66 h in AN/37 wt.% SO_2 in the absence of salt. The measurements were performed immediately after transferring the Li electrode from this solution to another containing 0.5M LiBr.

Curve 2 refers to Li stored for the same time in the 0.5M LiBr solution. Curves 3 and 4 refer to the passive films formed in 0.5M $LiAlCl_4$ and 0.15M $LiAsF_6$ solutions in AN/37 wt.% SO_2, respectively. From the plots lg R_p–$1/T$ the values of the activation energy were estimated, namely, −0.66 eV for LiBr, 0.50 eV for AsF_6^- and 0.53 eV for $AlCl_4^-$.

It can be seen that the nature of the anions does not essentially influence the apparent activation energy value but gives rise to a considerable change in the pre-exponential factor. The latter is about three orders of mag-
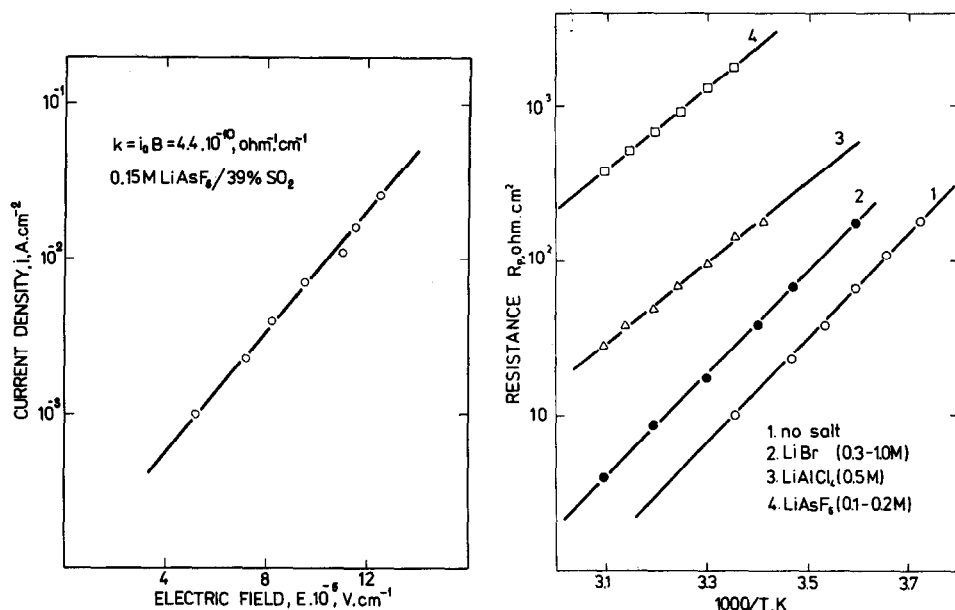
Fig. 8. Tafel plot obtained from cathodic pulse measurements in 0.15M LiAsF$_6$ solution in AN + 38 wt.% SO$_2$.

Fig. 9. Arrhenius plots of Li electrodes obtained after 72 h passivation in AN + 37 wt.% SO$_2$ solutions with different lithium solutes: 1, no salt; 2, 0.3 - 1.0M LiBr; 3, 0.5M LiAlCl$_4$; 4, 0.15M LiAsF$_6$.

nitude higher for the films formed in LiAsF$_6$ electrolytes as compared with that of films obtained in LiBr solutions. This result agrees well with the lower specific conductivity determined in LiAsF$_6$ solutions by low- and high-field measurements (see Section (iii) above).

On the other hand, exactly the same activation energies for the films formed in AN–SO$_2$ solutions with and without LiBr were obtained. The pre-exponential factors are also fairly close. This finding also implies one and the same nature and composition of the passive film in both solutions, probably Li$_2$S$_2$O$_4$ [5].

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