

## ANODIC PASSIVATION OF LITHIUM IN ELECTROLYTES FOR Li/SO<sub>2</sub> CELLS AT LOW TEMPERATURES

P. ZLATILOVA, Y. GERONOV and R. MOSHTEV

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, 1113 Sofia (Bulgaria)

(Received April 4, 1984; in revised form August 3, 1984)

### Summary

The anodic passivation of Li in acetonitrile (AN) + 30% SO<sub>2</sub> solutions of LiBr was studied in the temperature range -10 to -30 °C. It was shown that the time of passivation,  $\tau$ , follows the galvanostatic  $i-\tau^{-1/2}$  relation, characteristic for passive phenomena and related to the accumulation of anodic dissolution products at the electrode surface. The slope of the  $i-\tau^{-1/2}$  relation is a function of temperature and the time of the preceding chemical passivation. The experimental constants which were determined (activation energy, critical concentration of the dissolution product LiBr, and the diffusion coefficient of Li<sup>+</sup>) support the validity of the assumed passivation mechanism.

### Introduction

It has generally been assumed that Li could not be passivated by anodic polarization. In a Short Communication, however, James [1] recently reported that Li is passivated anodically in propylene carbonate (PC) and SOCl<sub>2</sub> electrolyte solutions at room temperature. In a second publication [2] the same author concluded that this phenomenon is associated with the accumulation of anodic dissolution products in the pores of a surface layer formed on the metal during storage at open circuit. This type of anodic passivation (AP), preceded by a supersaturation of the reaction products at the metal surface, has been extensively studied in the case of Zn in alkaline solutions [3 - 6] and of Ni [7], Fe, and Cr [8] in acid solutions, *i.e.*, in solvents in which the dissolution products are soluble.

The papers of James were the first to demonstrate that Li can also be passivated in two of the most important electrolytes used in practical Li cells: LiClO<sub>4</sub>/PC and LiAlCl<sub>4</sub>/SOCl<sub>2</sub>. The third important solution, LiBr/AN/SO<sub>2</sub>, was not studied because its low viscosity prevents anodic passivation of Li except at extremely high current densities which are not attainable in practice. Our preliminary experiments revealed that Li is also anodically passivated in this solution, though at low temperatures. Since Li/SO<sub>2</sub>

cells perform reliably at temperatures down to  $-30^{\circ}\text{C}$  it was of interest to determine the limits of this low temperature performance. The present investigation was also carried out in order to elucidate the nature of the anodic passivation of Li and the effect some variables had on this phenomenon.

## Experimental

A hermetically sealed, double walled glass cell was used in the experiments. The test electrodes were cut from 0.5 mm-thick Li foil, which was pressed on one side of a Cu foil (0.2 mm) current collector. The surface area of the test electrode was  $0.5\text{ cm}^2$ , while that of the Ni foil counter electrode, a hollow cylinder, was  $10\text{ cm}^2$ . A Li reference electrode was placed near to the test electrode. The ohmic drop for each cell, which was maintained at a thermostatically controlled temperature, was measured by the galvanostatic pulse method [9].

Two types of Li electrodes were used in the experiments: (i) freshly cleaned Li electrodes, scraped with a blade in the dry box and rapidly immersed in the test solution, and (ii) "passivated" electrodes stored for different periods of time at  $55^{\circ}\text{C}$  in two different conditions ("dry" with about 150 ppm of water or "wet", with about 1200 ppm of water).

Solutions containing 0.5 - 1.25M LiBr were prepared by dissolving the vacuum dried solute in a well-dried mixture of 30 wt.%  $\text{SO}_2$  and 70 wt.% AN. The  $\text{SO}_2$  and AN were dried with molecular sieves to a water content below 10 ppm. After drying the AN was twice distilled. LiBr (Merk p.a.) was dried under vacuum at  $150^{\circ}\text{C}$ . The "wet" solution was prepared by adding water before the LiBr was dissolved.

## Results and discussion

### (i) Anodic passivation of fresh electrodes

A typical galvanostatic voltage-time transient, recorded at  $240\text{ mA/cm}^2$  and  $-30^{\circ}\text{C}$ , is shown in Fig. 1. The transition time determined according to Adams [10], is assumed to be equal to the passivation time,  $\tau_p$ , which is almost equal to the time taken to reach an overpotential of 3.5 V, where the  $\text{Br}^-$  ion is oxidized to  $\text{Br}_2$ . The passivation time,  $\tau_p$ , for freshly cleaned electrodes was reproducible to within  $\pm 5\%$  and, although the surface prepared by scraping produced comparatively rough Li surfaces, it was found that this only had a very limited effect on the experimental results.

Following the current interruption (Fig. 1) the open circuit voltage of lithium quickly recovered. This type of behaviour suggested a temporary passivation due to the accumulation of dissolution products at the electrode surface without the formation of an insoluble phase film as, for example, in the case of Zn in alkaline solutions [3, 4].

It was shown that for the case of Zn [4, 11] and Ni [7] the passivation time is related to the current density, by Sand's equation in the form:

$$(i_a - i_f)\tau_p^{1/2} = (C_{cr} - C)F(\pi D/4)^{1/2} = K \quad (1)$$

where  $i_f$  represents mass transport other than by diffusion,  $C_{cr}$  is the critical concentration of the metal ions at the interface required to cause passivation, and  $C$  is the metal ion concentration in the bulk. This equation has not been applied so far to alkaline metals and nonaqueous solutions.

Figure 2 shows  $i$  as a function of  $\tau_p^{-1/2}$  for the anodic passivation of fresh electrodes at  $-10$ ,  $-20$  and  $-30$  °C. It demonstrates the validity of

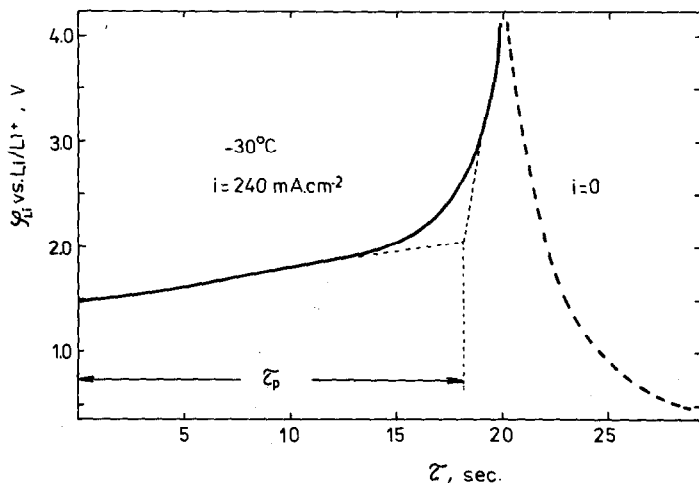


Fig. 1. A typical galvanostatic potential-time curve at  $-30$  °C for a fresh lithium electrode. Electrolyte: 1M LiBr/AN/30%  $SO_2$ .

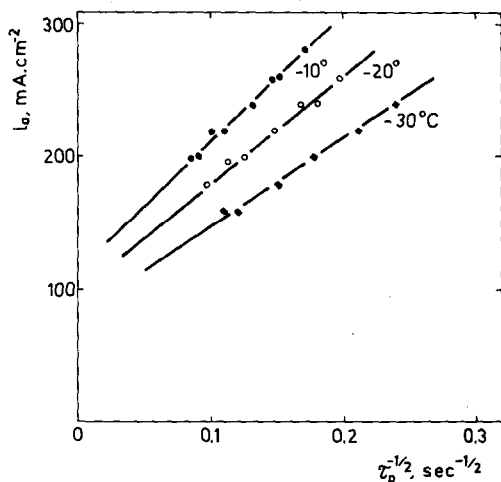


Fig. 2. Passivation current vs.  $\tau_p^{-1/2}$  curves for fresh lithium electrodes at three low temperatures.

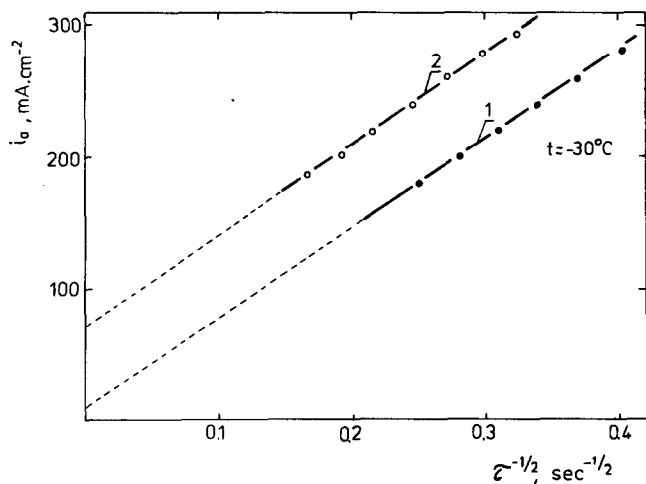


Fig. 3. The effect electrode screening has on the current vs.  $\tau_p^{-1/2}$  plots for fresh Li electrodes: 1, with a separator (see text); 2, without separator.

eqn. (1) with the slope (*i.e.*,  $K$ ) a function of temperature. The intercept on the ordinate,  $i_t$ , is considerable, and additional experiments were performed to determine its origin. For these experiments fresh Li electrodes were tightly wrapped with a layer of polypropylene separator ( $d = 0.12$  mm). The results in Fig. 3 indicate that screening the Li surface leads to a reduction of the intercept, most probably because of the limited convection of the solution at the electrode surface. The slope of the  $i$  vs.  $\tau^{-1/2}$  plots,  $K$ , however, is not affected by the electrode screening. This slope is mainly determined by the current density in the pores of the surface layer (see below). The position of the electrode (vertical or horizontal) had only a very limited effect on  $K$  provided that all other conditions were kept constant.

#### (ii) Effect of chemical passivation on the anodic passivation of lithium

Figure 4 shows  $i$  as a function of  $\tau_p^{-1/2}$  for Li electrodes stored for various periods of time (including fresh lithium) in the test solution at  $55^\circ\text{C}$  and containing 150 ppm of water.

Curves 1 and 2 in Fig. 5 show the decrease of  $K$  with time of chemical passivation,  $t$ , of Li electrodes in two electrolytes with different water contents. Curves 3 and 4 in Fig. 5 illustrate the effect storage has on the anodic passivation, by presenting the current density necessary to passivate the electrode for 10 s,  $i_{10}$ , as a function of  $t$ . As may be seen,  $i_{10}$  falls from 220 to 100 mA/cm<sup>2</sup> after about 3 months of storage in the test solution containing 150 ppm of water (curve 3). The same decrease of  $i_{10}$  is attained after only one month of storage in the "wet" solution (curve 4).

The decrease of  $K$  with respect to  $i_{10}$  during storage is related to the passive film formed as a result of Li corrosion. The film grows in thickness and, during the anodic pulse, it is perforated at all weak points, forming pores filled by the solution. The porosity achieved at a given anodic current

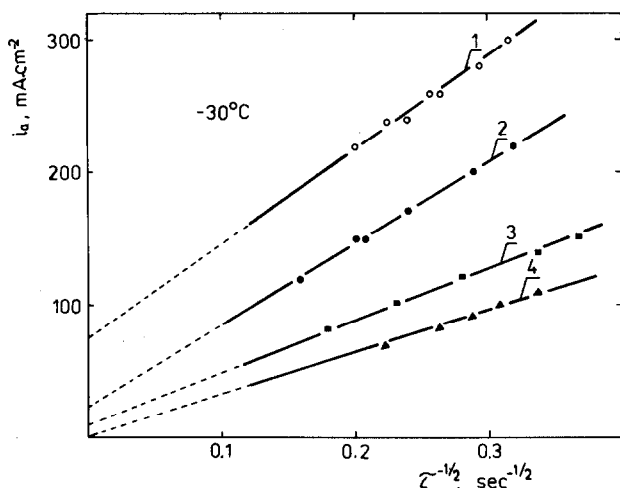


Fig. 4. Current vs.  $\tau_p^{-1/2}$  plots at  $-30^\circ\text{C}$  for Li electrodes after storage at  $55^\circ\text{C}$  for different periods of time in a "dry" electrolyte (150 ppm  $\text{H}_2\text{O}$ ): 1, a fresh electrode; 2, after 170 h of storage; 3, 1000 h; 4, 1500 h.

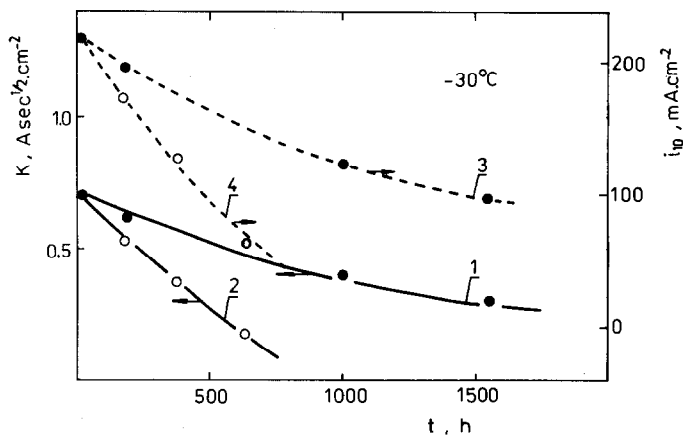


Fig. 5. The effect time of storage in 1M LiBr/AN/30%  $\text{SO}_2$  solutions with different water contents has on the slope,  $K$ , of the current vs.  $\tau_p^{-1/2}$  plots and the passivation current,  $i_{10}$ : 1, 3, 150 ppm  $\text{H}_2\text{O}$ ; 2, 4, 1200 ppm  $\text{H}_2\text{O}$ ; 1, 2,  $K$  vs.  $t$ ; 3, 4,  $i_{10}$  vs.  $t$  plots.

density is most probably a function of the film thickness. Thus, as the film thickens with the time of storage, the true current density will increase, which in turn will reduce the time of passivation,  $\tau_p$ .

As shown earlier [9] the increase of water concentration in LiBr/AN/ $\text{SO}_2$  solutions has a significant effect both on the rate of film growth and on its morphology. It is likely that, at higher water concentration, the dithionate film, having a porous structure (Fig. 6), is converted to a hydroxide film with a coarser and denser structure (Fig. 7). This could explain the effect the water content has on  $i_{10}$  and  $K$  (see Fig. 5). The influence of

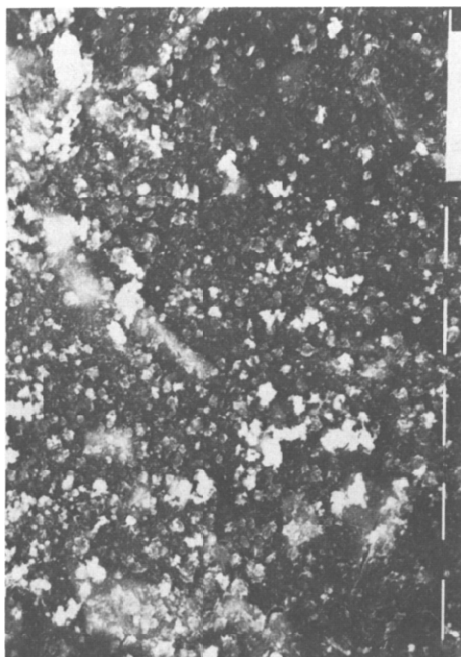


Fig. 6. Scanning electron micrograph ( $\times 1000$ ) of Li electrode after 1500 h storage at  $55^\circ\text{C}$  in a 1M LiBr/AN/30%  $\text{SO}_2$  solution containing 150 ppm  $\text{H}_2\text{O}$ .

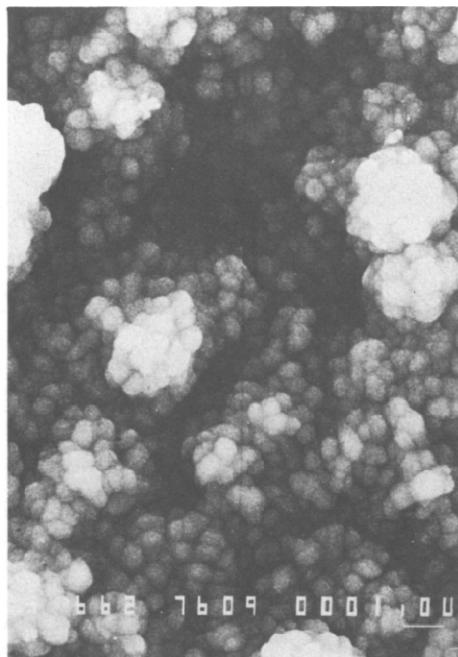


Fig. 7. Scanning electron micrograph ( $\times 6600$ ) of Li electrode after 144 h storage at  $25^\circ\text{C}$  in a 1M LiBr/AN/38%  $\text{SO}_2$  solution containing 2000 ppm  $\text{H}_2\text{O}$  (taken from ref. 9).

storage time on the current  $i_t$  (see Fig. 4) can also be explained by the increase of the film thickness, which acts as a screen limiting the convection at the electrode surface.

### (iii) Mechanism of the anodic passivation

The validity of eqn. (1) with respect to the relation between  $i_a$  and  $\tau_p^{-1/2}$  suggests that the overvoltage during anodic polarization is associated with the accumulation of anodic products at the electrode surface. The latter reach a critical concentration,  $C_{cr}$ , above which a deposit of the Li salt is formed, covering the metal surface. To check the validity of eqn. (1) further, we studied the concentration dependence of  $K$  at  $-30^\circ\text{C}$ , presented in Fig. 8, using only fresh electrodes. The extrapolation to  $K = 0$  yields  $C_{cr} = 3.8\text{M}$ . There are no exact data for the solubility of LiBr in the AN/30%  $\text{SO}_2$  solvent at  $-30^\circ\text{C}$ , but solutions containing up to 1.5M LiBr are easily prepared. So, if a value of 2.0M LiBr is assumed for the solubility, the supersaturation of 1.9 at the moment of the salt sedimentation seems quite reasonable.

From the slope of the plot in Fig. 8 the diffusion coefficient,  $D$ , of the Li cation in the test solution at  $-30^\circ\text{C}$  was estimated to be  $5 \times 10^{-6} \text{ cm}^2/\text{s}$ .

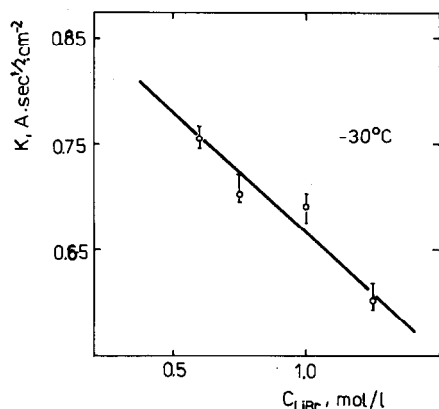


Fig. 8. Dependence of  $K$  on LiBr concentrations in AN/SO<sub>2</sub> solution at  $-30\text{ }^{\circ}\text{C}$ .

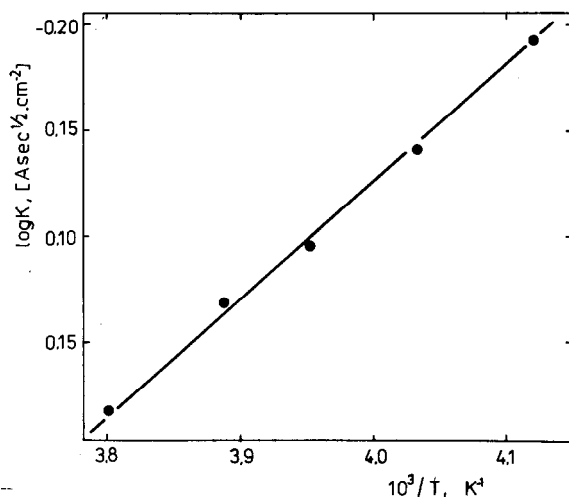


Fig. 9. Arrhenius plot of the process of anodic passivation for fresh Li electrodes in a 1M LiBr/AN/30% SO<sub>2</sub> solution.

There are no data in the literature for the  $D$  of Li in this, or similar solutions, for a comparison, but, with the low viscosity of the solvent and the considerable conductivity of the solution (even at  $-30\text{ }^{\circ}\text{C}$ ), this figure is quite reasonable.

The activation energy of the anodic passivation process in the solution under study was determined from the temperature dependence of  $K$ , assuming no temperature dependence of  $C_{cr}$  in the temperature range studied ( $-30$  to  $-10\text{ }^{\circ}\text{C}$ ).

The slope of the Arrhenius plot in Fig. 9 yields  $2.3 \pm 0.2$  kcal/mol ( $0.10 \pm 0.01$  eV) which is a typical value for a diffusion limited process.

It should be emphasized that, contrary to the passivation of Zn in KOH or Ni in H<sub>2</sub>SO<sub>4</sub> solutions, where the salt deposition after supersaturation

is followed by the formation of insoluble passive films, no such film is formed on Li in the present case. Hence, the initial potential of Li is restored soon after the interruption of the anodic current (Fig. 1). The lack of a true, insoluble anodic film due to the anodic polarization is also demonstrated by the fact that the polarization curves are very closely reproducible immediately after the self-activation, due to the depletion of the electrode surface from the anodic dissolution products, *i.e.*, LiBr.

### List of symbols

$i_a$	Anodic polarization current density ( $A\text{ cm}^{-2}$ )
$i_f$	Current density due to mass transport other than diffusion ( $A\text{ cm}^{-2}$ )
$i_{10}$	Current density necessary to passivate the electrode for 10 s ( $A\text{ cm}^{-2}$ )
$C$	Li ion concentration in the bulk ( $\text{mol dm}^{-3}$ )
$C_{cr}$	Critical concentration of the Li ion at the interface required to cause passivation ( $\text{mol dm}^{-3}$ )
$D$	Diffusion coefficient of $\text{Li}^+$ in the test solution ( $\text{cm}^2\text{ s}^{-1}$ )
$F$	The Faraday ( $C\text{ mol}^{-1}$ )
$K$	Constant in the Sand's equation ( $A\text{ s}^{1/2}\text{ cm}^{-2}$ )
$\tau_p$	Passivation time (Fig. 1)

### References

- 1 S. D. James, *J. Power Sources*, 10 (1983) 105 - 107.
- 2 S. D. James, *Proc. Symp. Lithium Batteries*, Vol. 83-4, Electrochem. Soc., Inc., Newark, NJ, 1983, p. 74.
- 3 R. Landsberg and H. Bartelt, *Z. Elektrochem.*, 61 (1957) 1162.
- 4 T. P. Dirkse and N. A. Hampson, *Electrochim. Acta*, 16 (1971) 2049.
- 5 T. P. Dirkse and N. A. Hampson, *Electrochim. Acta*, 17 (1972) 387.
- 6 M. B. Liu, G. M. Cook and N. P. Yao, *J. Electrochem. Soc.*, 128 (1981) 1663.
- 7 R. Landsberg and M. Hollnagel, *Z. Elektrochem.*, 58 (1954) 680.
- 8 K. I. Vetter, *Elektrochemische Kinetik*, Springer, Berlin, 1961.
- 9 Y. Geronov, B. Puresheva and R. V. Moshtev, *J. Power Sources*, 9 (1983) 273.
- 10 R. N. Adams, *Electrochemistry at Solid Electrodes*, Marcel Dekker, Inc., New York, 1969.
- 11 M. Eisenberg, H. F. Bauman and D. M. Brettner, *J. Electrochem. Soc.*, 108 (1961) 909.