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A.C. IMPEDANCE STUDY OF LITHIUM IN SULFUR DIOXIDE ELECTROLYTES

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Summary

The kinetics of lithium passivation in SO_2-containing electrolytes has been studied using the a.c. impedance technique. Assuming an equivalent circuit of a solid ionic conductor on a non-blocking metal substrate, the resistance, thickness, and specific conductivity of the passive film on lithium have been evaluated. It has been found that the temperature of passivation has little effect on the rate of film growth.

The influence of SO_2 concentration and lithium surface pretreatment on the impedance parameters during the storage of electrodes has also been investigated.

From Arrhenius plots of the conductivity of the film, two activation energies have been calculated, namely, 0.3 eV in the temperature range −30 to −9 °C, and 0.45 eV from −9 to 25 °C.

Introduction

The passivation of lithium in SO_2 electrolyte solutions, although of practical interest, has not been studied in detail. Measurements of a.c. impedance offer a convenient means for studying the kinetics of lithium passivation. To date, a.c. impedance measurements have been predominantly applied in the study of practical Li/SO_2 cells [1 - 3] where the impact of the carbon cathode on the impedance parameters, especially in a wider frequency range, cannot be neglected.

The present paper aims at investigating the kinetics of lithium passivation in SO_2 electrolyte solutions, both at room and at elevated (55 °C) temperatures.

Experimental

The design of the test and counter electrodes, as well as the cells for the impedance measurements, have been described earlier [4]. The lithium

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test electrodes (0.125 cm^2) were cut in the dry box with a scalpel. This operation was carried out immediately before immersion of the electrodes into the test solution, so that the fresh lithium surface was only exposed to the dry-box atmosphere (30 ppm of H_2O and O_2) for less than 5 s. The electrolyte solution was 1 M LiBr in acetonitrile (AN) saturated with 30 wt.% of SO_2, with a moisture content less than 100 ppm.

The test electrodes were stored in the measurement cells at two temperatures, 22 and 55 °C. Prior to each impedance measurement they were thermostatted at 20 °C. The ratio of the lithium electrode surface area (in cm^2) to the volume of the electrolyte (in cm^3) in the test cells was 2:1; this is almost 5 times lower than that in practical Li/SO_2 cells.

The impedance spectra were recorded by a Solartron 1174 Transfer Function Analyzer connected to a Hewlett Packard computer and printer. The frequency range was from 10^5 to 0.1 Hz. It was found that lower frequency measurements led to destruction of the passive film.

Results and discussion

Effect of storage time and temperature on impedance parameters

Figure 1 illustrates the development of the a.c. impedance diagram of lithium electrodes stored for 120 h at 55 °C in the SO_2 electrolyte.

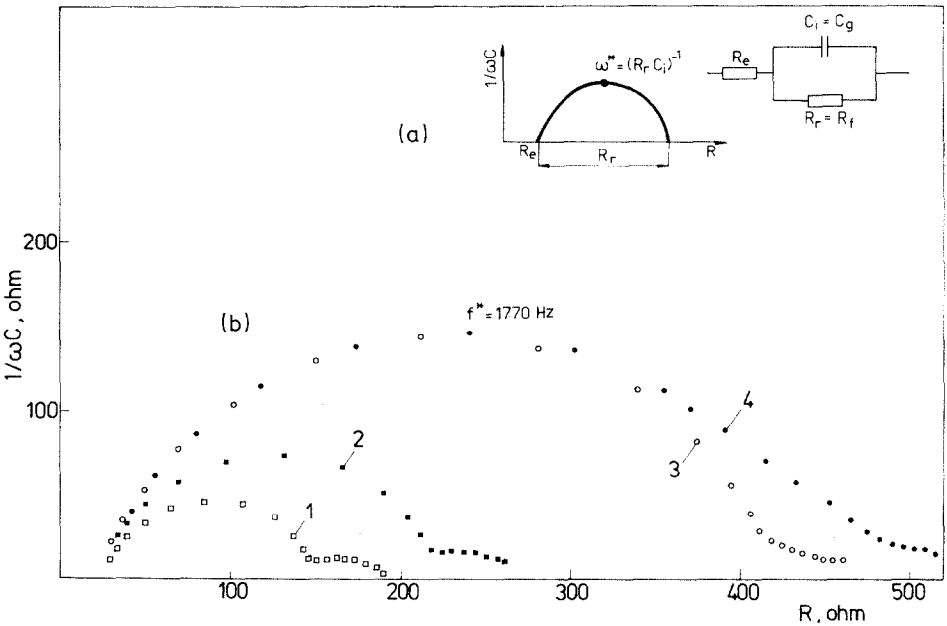

Fig. 1. (a) Equivalent circuit of a passivated lithium electrode: R_f, film resistance; C_g, geometric capacitance; ω^*, radial frequency of impedance arc maximum. (b) Complex plane impedance plots of lithium electrodes for (1), 0.5, (2), 2, (3), 64, (4), 110 h of storage at 55 °C in electrolyte containing 33% SO_2.

TABLE 1

Electrolyte	κ ($10^9 \times ohm^{-1}\ cm^{-1}$)	References
$AN/SO_2/LiBr$	5	This study
PC/1 M $LiClO_4$	1.34	5, 9
PC/1 M $LiAsF_6$	5.3	5, 9
$SOCl_2$/1 M $LiAlCl_4$	0.64 - 1.0	9

The initial value of R (3 - 5 ohm cm^2), obtained by preliminary experiments on clean Li surfaces [4], probably reflects the charge transfer resistance R_d, and agrees well with similar data from previous authors [4, 6]. During passivation, R increases markedly with time because of the formation and growth of the passive film with a resistance R_f and a characteristic frequency, f^*. When R becomes appreciably larger than R_d, the latter can be neglected and the values of R_f and f^* can be used to estimate, as a first approximation, the thickness of the film and its growth with time.

Assuming that the film is a dense, solid ionic conductor, and using the equation of a plane-parallel capacitor, the film thickness can be calculated from:

$$y = \frac{8.85 \times 10^{-14} \epsilon}{C_g} \tag{1}$$

where ϵ is the dielectric constant of the film, and C_g is the geometric capacitance related to the film resistance R_f and the characteristic frequency f^* according to:

$$C_g = \frac{1}{2\pi f^* R_f} \tag{2}$$

The specific conductivity, κ, of the film is equal to:

$$\kappa = y/R_f = \frac{8.85 \times 10^{-14} \epsilon}{R_f C_g} \tag{3}$$

Using eqn. (2):

$$\kappa = 5.56 \times 10^{-13} \epsilon f^* \tag{4}$$

From Fig. 1, it can be seen that while the film resistance grows with time, the characteristic frequency, f^*, remains constant at 1770 Hz during the entire experiment. With this value of f^*, and assuming an arbitrary value of 5 for ϵ, the specific conductivity of the film is found to be 5×10^{-9} $ohm^{-1}\ cm^{-1}$. This value is close to those found by other methods used to study passive films on lithium in $SOCl_2$ and PC electrolyte solutions (Table 1).

The growth kinetics of the passive film can be represented by:

$$y = k\tau^n \tag{5}$$

where n yields information on the growth mechanism in operation.

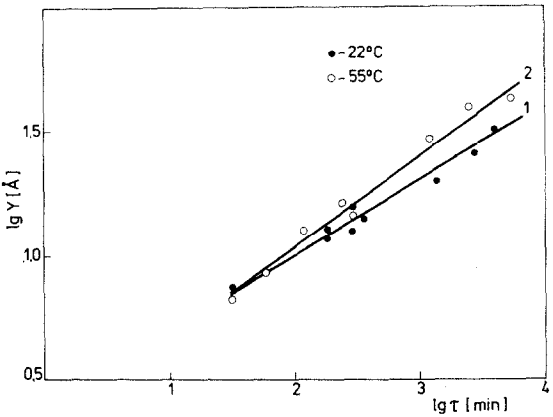

Fig. 2. Log y —log τ plots of film growth of lithium electrodes stored at open circuit at (1), room temperature; (2), 55 °C.

Figure 2 presents the averaged lg y — lg τ dependences obtained from a series of lithium electrodes kept at room temperature (plot 1) and at 55 °C (plot 2). The film thickness is calculated from eqn. (3) with $\kappa = 5 \times 10^{-9}$ ohm^{-1} cm^{-1}. The slopes of the plots are similar (0.3 and 0.4), implying that the temperature of passivation has only a small effect on the rate and mechanism of the growth of the passive film. This small temperature dependence is surprising in view of the strong temperature influence on the growth rate in the case of passive films found on lithium in other liquid oxidants, *e.g.*, $SOCl_2$ [7]. However, it should be noted that the work reported in ref. 7 involved measurements of the overall film thickness, and thus included that of the much thicker porous film that grows much faster on the top of the thin, but dense, primary passive film.

The present data (Fig. 2) are based on the thickness of the primary film only, the growth of which is usually determined by the transport of point defects in the lattice of the ionic crystals or, as supposed by Povarov *et al.* [8], by the diffusion of electrons. In both cases, a parabolic growth law can be expected [9], as demonstrated experimentally by the slopes of the lg y — lg τ relations, which are close to 0.5.

The passive film of lithium in SO_2-containing solutions is rather thin (40 - 50 Å) and has no significant impact on the initial overvoltage of lithium, even at high current densities or low temperatures. This is illustrated by the data in Fig. 3 that show the decay of lithium electrode overvoltage during destruction of the passive film by continuous anodic polarization at 5 mA cm^{-2} and —30 °C. The film was obtained by keeping the lithium electrode in the test solution at the open-circuit potential (OCP) for 120 h at 55 °C. The impedance spectra of the electrode for several intervals during the film destruction are also shown in Fig. 3. It is seen that the lithium overvoltage (ϕ) decays in concert with decrease in the film resistance (R). After an initial sharp fall, the decrease in the film resistance is very small. At 6 C cm^{-2}, R reaches a value of 270 ohm cm^2; this value is close to that,

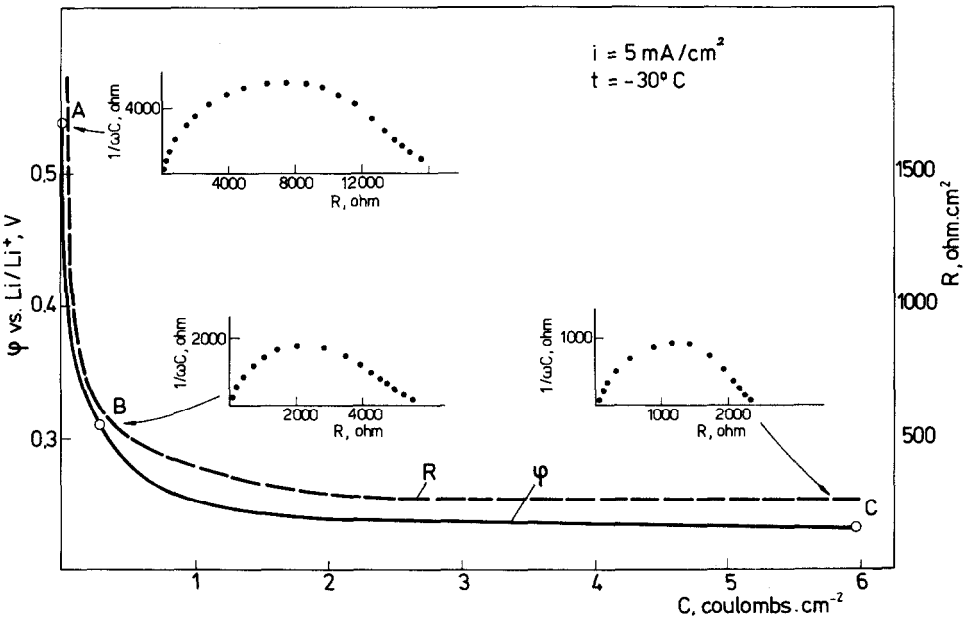

Fig. 3. Decay of overvoltage (ϕ) and resistance (R) during anodic polarization with i = 5 mA cm^{-2} at —30 °C of a lithium electrode stored for 120 h at 55 °C. Impedance plots are: (A), immediately before polarization; (B), after 1 min; (C), after 20 min of polarization.

calculated by extrapolation to —30 °C, of the temperature dependence of the exchange current density of a lithium electrode cleaned by anodic polarization [10]. This agreement in values suggests that, in this case, R is close to the charge-transfer resistance measured on the film-free lithium surface.

As shown by the data of Li/SO_2 battery manufacturers [11], the decay of overvoltage at the beginning of discharge, under similar conditions of cells stored for 30 days at 71 °C, is close to that shown in Fig. 3. This indicates that even after prolonged storage at higher temperatures, the passive film on lithium is easily destroyed by anodic polarization. This is in contrast to behaviour observed in $SOCl_2$ electrolyte solutions, where the thick, porous film, which has considerable effect on the lithium overvoltage, cannot be easily eliminated by anodic polarization.

Effect of SO_2 concentration on impedance of lithium during storage

It is generally accepted [12, 13] that the decrease of SO_2 concentration below certain limits in the electrolyte (*e.g.*, during discharge) can result in undesirable characteristics, especially during overdischarge conditions when lithium sponge can be formed on the cathode. Hence, it is essential to gain a knowledge of the SO_2 concentration that is critical for passivation of lithium.

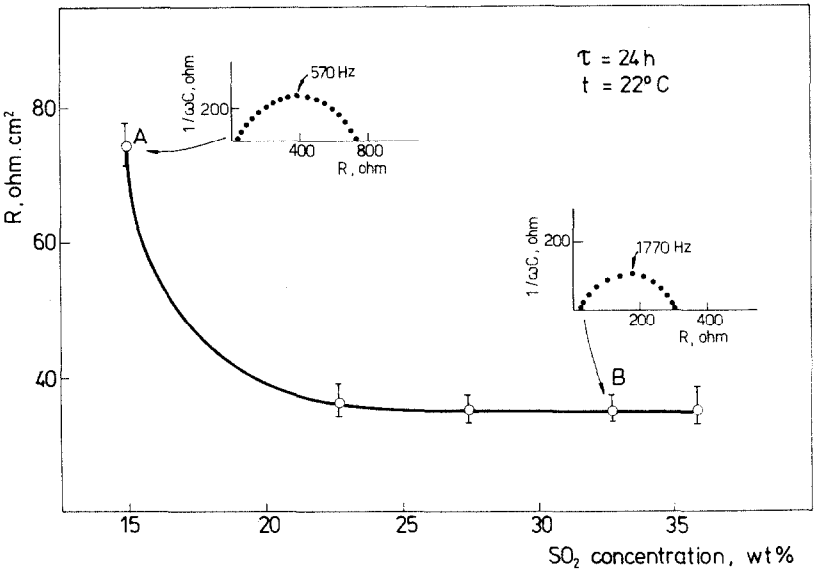

Fig. 4. Effect of SO_2 concentration on film resistance (R) after 20 h storage. Impedance plots are for (A), 15 wt.% SO_2; (B), 33 wt.% SO_2.

As shown by Delnick and Jaeger [14], the film resistance after 45 min storage in the electrolyte decreases linearly with increase in the concentration of SO_2 in the range 6 - 25 wt.%. Our investigations using the galvanostatic pulse technique have shown [15] that the film resistance is virtually unaffected by changes in SO_2 concentration above 15 wt.%.

Figure 4 shows experimental data for the film resistance after 24 h storage at room temperature in the electrolyte as a function of SO_2 concentration. It can be seen that increase in the SO_2 concentration above 20 wt.% has no significant effect on the film resistance. At 15 wt.% SO_2, the film resistance is almost twice as large as that at 35 wt.% SO_2. The characteristic frequency, however, in this case decreases from 1770 Hz at 35 wt.% SO_2 to 570 Hz at 15 wt.% SO_2. This suggests that the films formed at low SO_2 concentrations have different compositions and different dielectric properties implying the formation of a porous organic film in the pores of which lithium dithionate is deposited.

Effect of lithium surface treatment on impedance parameters during storage

Whereas all laboratory operations with lithium are performed in dry boxes (H_2O = 30 ppm), the production of lithium cells is carried out in dry rooms where the moisture can reach 1 - 3% relative humidity (RH). Under the latter conditions, lithium is immediately covered by a hydroxide and/or a carbonate film. It is of interest to evaluate the effect of such hydroxide/carbonate films on the kinetics of lithium passivation after its immersion in the electrolyte of Li/SO_2 cells.

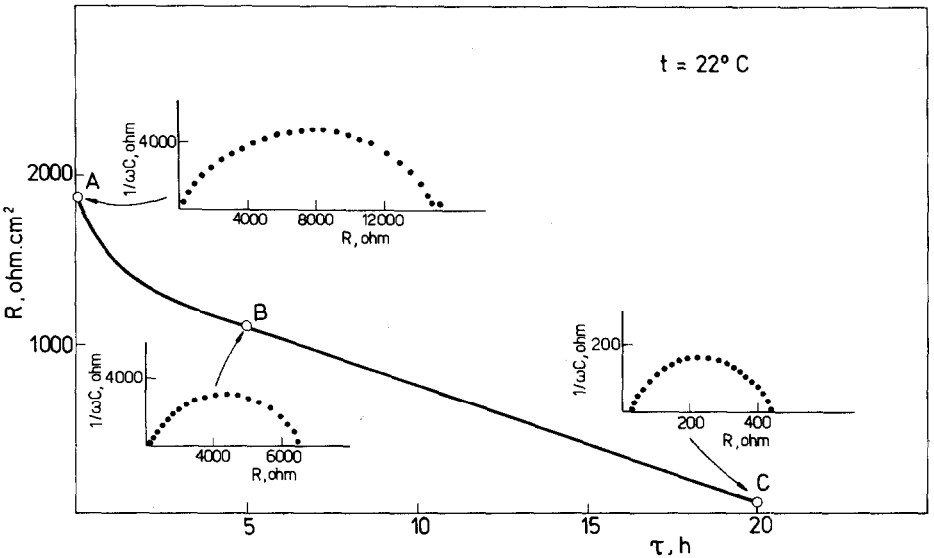

Fig. 5. Development of the resistance (R) of a lithium electrode (kept for 2 h in a dry room with 3.2 R% RH) with time of storage in SO_2 electrolyte. Impedance plots are after storage periods of: (A), 10 min; (B), 5 h; (C), 20 h.

TABLE 2

τ (h)	R (ohm cm^2)	C (μF cm^{-2})
0.166	1854	0.179
5	1151	0.190
20	54.26	0.612

Figure 5 shows the resistance of a lithium electrode kept for 2 h in a dry room with 3.2% RH, and then stored at room temperature in an electrolyte solution containing 35 wt.% SO_2. The impedance diagrams recorded 10 min, 5 h, and 20 h after immersion in the solution are also given in Fig. 5. The a.c. impedance diagram for 10 min of electrode immersion is asymmetric and has parameters that are basically different from those of electrodes prepared in a dry box. The values of the impedance parameters as a function of storage time are listed in Table 2. The resistance of the electrode treated in the dry room (3.2% RH) after 10 min in the electrolyte is two orders of magnitude greater than that of the electrode kept for several min in the dry box (*cf.* Fig. 2), this suggests that a much thicker film is produced in the former case. However, as the storage time is increased, the film resistance gradually decays, and after one day it reaches the values of the electrodes prepared in the dry box. It is likely that the hydroxide/carbonate film

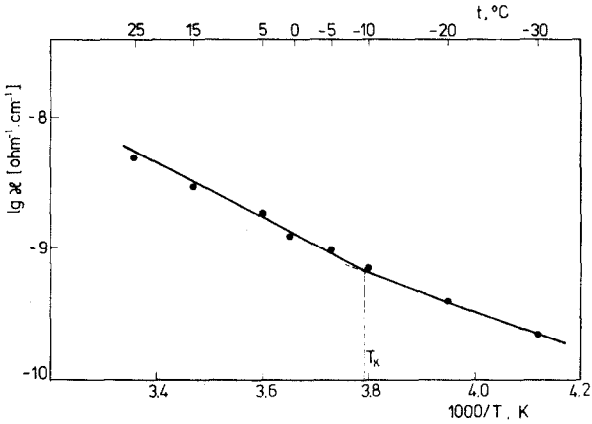

Fig. 6. Arrhenius plot of the conductivity of a film grown for 110 h at 55 °C in an electrolyte containing 35 wt.% SO_2.

(alkaline in character) is dissolved by SO_2, whereafter the usual dithionate film, with a lower resistance and probably smaller thickness, is formed.

Temperature dependence of film conductivity

The temperature dependence of the film conductivity was studied using lithium electrodes stored for different times in the test solution either at 55 °C or at room temperature. The Arrhenius plot (Fig. 6) of the conductivity of the film grown for 110 h at 55 °C has two slopes, implying two activation energies, namely, 0.3 eV in the range −30 to −9 °C and 0.45 eV from −9 to 25 °C. It is found that both the temperature (T_k) at which the slope changes and the values of the activation energies, are practically independent of the temperature and time of passivation. A similar temperature dependence of the conductivity is observed with lithium electrodes kept for 120 h at room temperature in 1 M $LiClO_4$–propylene carbonate solution. The activation energies for the same temperature ranges are 0.2 and 0.45 eV, respectively, with $T_k = -7$ °C [16].

From the above results, two conclusions can be drawn:

(i) there are probably two mechanisms of ionic transport across the film and these depend on the temperature range;

(ii) the change in the transport mechanism occurs at one and the same temperature, irrespective of the anion of the Li^+ conductor and the nature of the organic solvent.

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