

A.C. IMPEDANCE STUDIES OF THE ANODIC PASSIVATING LAYER IN LITHIUM-SOCl₂ BATTERIES

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Summary

Using the a.c. impedance method, two types of low current Li/SOCl₂ batteries were studied. The a.c. response of an anodic film is described by an empirical equation: $H = R/(1 + (i\omega\tau)^\alpha)$, often referred to as the dispersion equation. Although only three parameters are involved, this equation fits in with the experimental data. We offer a qualitative explanation for the time dependence of these parameters. The results presented here form a basis for a quantitative model which should explain the disagreement between the values of film thicknesses calculated from the equation for the capacitance of a parallel-plate capacitor and the values observed by scanning electron microscopy (SEM).

Introduction

Passivation of lithium in SOCl₂ is usually explained according to a generally accepted mechanism, *e.g.*, the SEI model introduced by Peled [1].

In the last decade several papers have been published in which the Li/SOCl₂ system was studied using the a.c. impedance method [2 - 7]. Interpretation of the measurements involving the anodic passivating layer have not been unusual, however, and at least three methods are available for making the measurements:

(a) a simple treatment whereby mainly qualitative characteristics of the impedance responses are observed and only the time dependence of the layer resistance is presented quantitatively [2];

(b) a treatment where the parameters of the growing layer (thickness, resistance, etc.) are calculated using the equation for the capacity of a parallel plate capacitor [5 - 7];

(c) a treatment where equivalent circuits, having characteristics that agree with those of the passivating layer as closely as possible, are studied [3, 4].

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Treatment (a) quantitatively takes into account only one of the many data that can be obtained from an impedance response; (b) assumes homogeneity of the layer's electrical properties and that the depressed semicircle approximates to the ideal; (c) enables one, in principle, to construct equivalent circuits with responses which will be as close to that of the measured system as necessary although their physical backgrounds can sometimes be questionable.

In the studies of superionic conductors [8], porous electrodes [9], and double layers [10], responses have been obtained which include one or more depressed semicircles, each appearing in a particular frequency range. It has been found that such semicircles can be suitably described by the following empirical equation:

$$H(\omega) = \frac{R}{1 + (i\omega\tau)^\alpha} \quad (1)$$

where R and τ are the resistance and the average relaxation time [13], respectively, that can be ascribed to the a.c. impedance response of the measured system. ω is the angular frequency of the superimposed voltage, and α is a dimensionless parameter which is related to the ratio (d) between the maximum value of the imaginary part and half the value of the section cut on the real axis by the semicircle (Fig. 1):

$$\alpha = \frac{4}{\pi} \arctan(d) \quad (2)$$

Equation (1) is sometimes referred to as the dispersion equation and was proposed by Cole and Cole [13] to describe depressed semicircles obtained in studies of the frequency dependence of dielectric constants of some substances.

In this paper we discuss the agreement between eqn. (1) and experimental data for certain Li/SOCl₂ systems, and the relationship between our own and earlier studies involving the passivating layer conductivity mechanism.

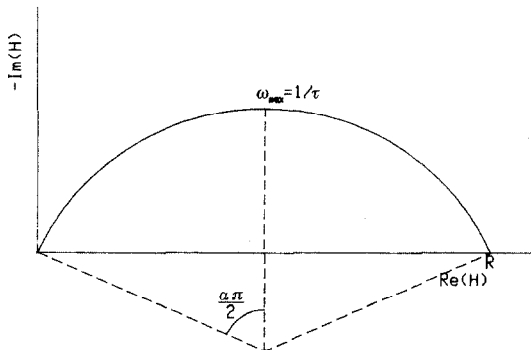


Fig. 1. Transfer function, determined by the dispersion equation, represented in the complex plane.

Experimental

Two different electrolytes were used in the manufacture of the batteries:

(a) 1.5 M LiAlCl₄, prepared as described elsewhere [6],

(b) 3 M AlCl₃/SOCl₂ solution, neutralized with 50% excess of Li₂CO₃ which had been previously dried for 72 h under vacuum at 70 °C. The solution contained 0.6 M SO₂. To this solution 1% of LiAl(SO₃Cl)₄ was added.

Both electrolytes contained less than 1 ppm of Fe and Na. The batteries were tested within the frequency range 1 - 65 000 Hz with 10 measurements per decade. The amplitude of the applied overvoltage ranged from 6 to 10 mV and depended on the magnitude of the film resistance. The values of the amplitudes seem to be rather high and may imply the nonlinearity of such measurements. It was found, however, that the response of a moderately passivated anode remained unchanged, even at amplitudes of 100 mV.

The initial measurements were made 2 h after the batteries had been filled with electrolyte and then two or three times per day. The a.c. impedance response of the passivating layer was described by eqn. (1). Precise values of the parameters in that equation were evaluated by a least square analysis:

$$\sigma = \sum_{i=1}^N \{ [\operatorname{Re}(H(\omega_i)) - \operatorname{Re}(Z_i)]^2 + [\operatorname{Im}(H(\omega_i)) - \operatorname{Im}(Z_i)]^2 \} \quad (3)$$

where N is the number of the data points, $\operatorname{Re}(H(\omega_i))$ and $\operatorname{Im}(H(\omega_i))$ are the calculated values of the real and imaginary part, respectively. $\operatorname{Re}(Z_i)$ and $\operatorname{Im}(Z_i)$ are the corresponding measured values. As the resistance of the layer changed from one measurement to another it was necessary to normalize eqn. (3):

$$\tilde{\sigma} = \sum_{i=1}^N \left\{ \left[\frac{\operatorname{Re}(H(\omega_i)) - \operatorname{Re}(Z_i)}{R} \right]^2 + \left[\frac{\operatorname{Im}(H(\omega_i)) - \operatorname{Im}(Z_i)}{R} \right]^2 \right\} / N \quad (4)$$

R being the resistance corresponding to eqn. (1). $\tilde{\sigma}$ will be referred to as the "error-of-fit".

Results and discussion

According to Macdonald [14] the passivating layer (*i.e.*, an ionic conductor) should respond in at least three different frequency ranges: the electrochemical reaction and the diffusion processes taking place at the metal-passivating layer interface should appear at low frequencies, while the migration of ions (vacancies) through the bulk usually occurs at the highest frequencies. Our system also includes a layer-electrolyte solution interface and an electrolyte/cathode interface. An important feature of the bulk response is that, in contrast to the others, it is extensive and can easily be identified in the time-dependent impedance spectra. The electrolyte

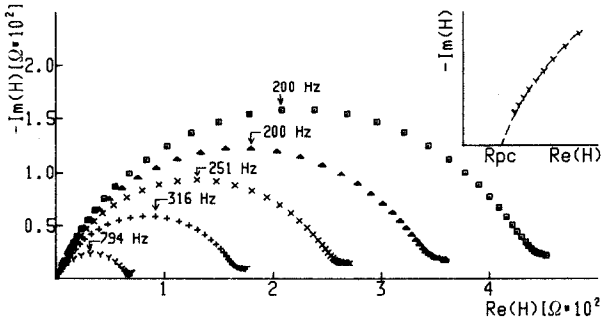


Fig. 2. Time dependence of extensive transfer functions for the batteries containing electrolyte type 'a'. Frequency range: 1 - 65 000 Hz. R_{pc} (real part correction) represents a series resistance which was subtracted from the measured values of the real part of the a.c. responses. γ , $t = 8$ h, R_{pc} = 1.65 Ω ; +, $t = 45$ h, R_{pc} = 2.31; \times , $t = 71$ h, R_{pc} = 1.35; \blacktriangle , $t = 116$ h, R_{pc} = 0.51; \square , $t = 221$ h, R_{pc} = 0.63.

solution should have a purely ohmic resistance which should not be time dependent.

Figure 2 shows the typical time dependence of an a.c. response for batteries filled with the electrolyte type 'a'. It can be seen that there are significant changes in the sizes of the depressed semicircles as well as in the frequency at which the imaginary part has its maximum value (ω_{\max}). While the size increases with time, ω_{\max} decreases. Thus, the responses in the observed frequency range are extensive, which means that they correspond to ionic migration through the bulk.

An approximate description of the impedance response presented in Fig. 2 can be obtained by using the equation for a parallel plate capacitor. This can be regarded as a special case of eqn. (1) (with $\alpha = 1$). The dielectric constant of the film is assumed to be about 11 [5 - 7], whereas the resistivity of the dielectric (layer) is thought to be position independent (*i.e.*, it does not change through the layer cross-section). On the basis of these assumptions the layer thickness is evaluated [6, 7].

Recently, SEM photographs of the passivating layer have been published [11], which clearly show the coarse film surface and the inhomogeneity of the film cross-section. It was also shown that the thickness of the layer reached orders of micrometres within 24 h of the immersion of lithium into the electrolyte. According to the calculations such a thickness should not be reached until the cells were several months old. No satisfactory explanation for this discrepancy has yet been found.

Using the dispersion eqn. (1), a better, although not necessarily an exact, description of the measured semicircles is possible. In Table 1 the experimental and calculated data for the real and the imaginary parts of the impedance response for the batteries containing electrolyte type 'a' are given. There is good agreement between the data within the frequency range 50 - 5000 Hz. Outside this range, however, wide discrepancies appear due to the influence of other processes in a battery (at low frequencies) and due to

TABLE 1

Experimental (Z) and calculated (H) impedance data for a battery with electrolyte type 'a'. Every second measurement is presented. The "error-of-fit" equals 6×10^{-6}

f (Hz)	Re(Z) (Ω)	Re(H) (Ω)	Im(Z) (Ω)	Im(H) (Ω)
1.000	358.81	343.68	18.65	4.76
1.585	355.65	342.89	18.73	6.81
2.512	350.58	341.71	19.43	9.73
3.981	346.04	339.96	22.34	13.84
6.310	340.80	337.29	25.96	19.61
10.000	334.97	333.18	32.36	27.59
15.849	327.55	326.78	41.74	38.40
25.119	316.67	316.77	54.53	52.55
39.811	300.86	301.21	70.92	70.03
63.096	277.53	277.75	89.62	89.62
100.000	244.98	244.57	107.71	108.09
158.489	203.22	202.31	120.10	120.39
251.189	156.37	155.58	122.32	122.00
398.107	111.78	111.50	112.66	112.25
630.957	75.61	75.65	95.00	94.91
1000.000	49.03	49.68	75.06	75.21
1584.893	31.81	32.22	56.45	56.97
2511.886	20.89	20.92	41.14	41.89
3981.072	14.01	13.70	29.44	30.21
6309.573	9.81	9.07	20.84	21.53
10000.000	7.01	6.08	14.71	15.22
15848.932	4.88	4.11	10.37	10.70
25118.864	3.70	2.80	7.35	7.50
39810.717	2.62	1.92	3.71	5.25
63095.734	2.33	1.33	2.93	3.66

electrical noise (at high frequencies). For example, if two or more processes having different relaxation times exist (*e.g.*, their ratio is more than 200) they can be regarded separately. This means that the parameters of an equation ascribed to a certain process can be determined from the a.c. response of that process without the responses of other processes being known. Neglecting the other processes, however, results in an error in the parameters determined from a specific semicircle: the larger the ratio between the relaxation times, the smaller is this error.

There are two other sources of error:

- (a) inaccuracy of the instruments;
- (b) the system has not stabilized: especially significant for freshly made batteries when the resistance varies slightly during the measurement.

As the processes occurring in our system are loosely coupled (the relaxation times are wide apart, Fig. 2) it is possible to refine the approximate values of the parameters acquired from the graphs by using the method described in the Experimental Section above. It should be emphasized that this method does not result in a classical fitting, but is only a refinement of

TABLE 2

“Errors-of-fit” ($\bar{\sigma}$) and the corresponding frequency ranges of fitting for two typical batteries

Battery No. 4 (electrolyte ‘a’)			Battery No. 6 (electrolyte ‘b’)		
Age (h)	$\bar{\sigma} \times 10^{-6}$	Freq. range (Hz)	Age (h)	$\bar{\sigma} \times 10^{-6}$	Freq. range (Hz)
8	8.8	50 - 8000	2	9.2	250 - 50000
12	6.7	40 - 8000	4	6.4	160 - 50000
19	4.9	50 - 8000	10	15	250 - 50000
45	4.3	40 - 8000	17	20	126 - 10000
71	1.3	40 - 8000	22	15	80 - 8000
116	5.8	20 - 2500	27	19	80 - 8000
187	4.5	12 - 2500	41	19	80 - 8000
221	4.5	12 - 2500	51	20	80 - 8000
267	1.9	12 - 8000	65	19	80 - 8000
			135	14	80 - 8000
			184	19	80 - 8000
			239	16	50 - 5000

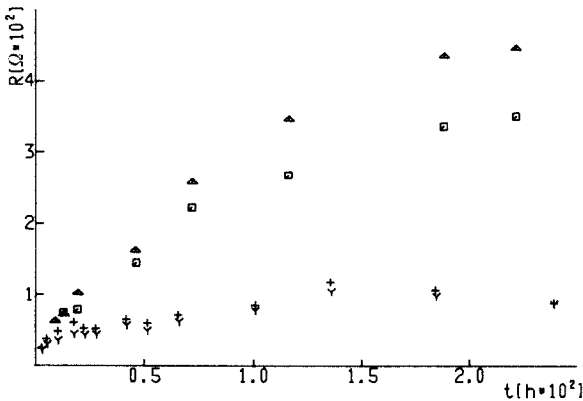


Fig. 3. Time dependence of the resistance. ◻, Battery No. 3, electrolyte ‘a’; ▲, battery No. 4, electrolyte ‘a’; +, battery No. 6, electrolyte ‘b’; ∇, battery No. 9, electrolyte ‘b’.

the values. In Table 2 the “errors-of-fit” and the corresponding frequency ranges of fitting for two typical batteries are shown.

Figure 3 shows the time dependence of the resistance of batteries containing electrolyte type ‘a’ (“normal” electrolyte) and electrolyte type ‘b’ (with the additive). It can be seen that the resistance values are much larger in the former case.

The relaxation times (Fig. 4) change in a similar manner to the resistances (Fig. 3) although the relative magnitudes of the changes are smaller.

Figure 5 shows two typical time dependence curves of α for each system. For the batteries filled with electrolyte type ‘a’, α falls within the

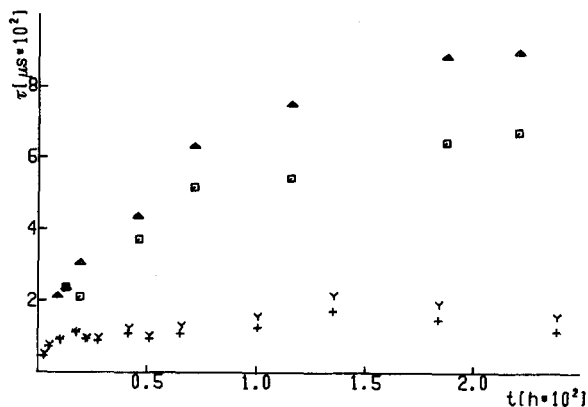


Fig. 4. Time dependence of the relaxation time. □, Battery No. 3, electrolyte 'a'; ▲, battery No. 4, electrolyte 'a'; +, battery No. 6, electrolyte 'b'; γ, battery No. 9, electrolyte 'b'.

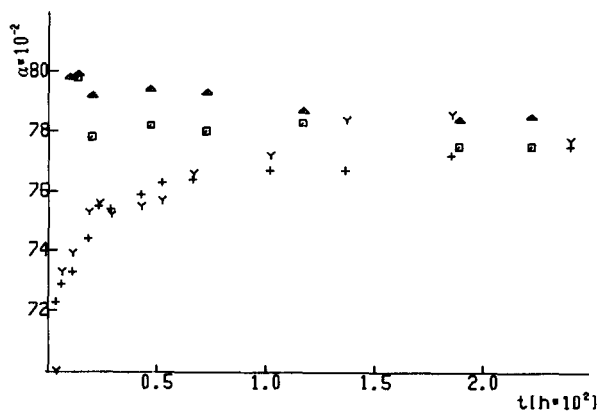


Fig. 5. Time dependence of the dimensionless parameter α . □, Battery No. 3, electrolyte 'a'; ▲, battery No. 4, electrolyte 'a'; +, battery No. 6, electrolyte 'b'; γ, battery No. 9, electrolyte 'b'.

error range and changes may not, therefore, be significant. On the other hand, for electrolyte type 'b' the value of α exhibits a real increase with time and tending to the value for the batteries without additives.

Some authors report on the two extensive semicircles pertaining to ionic migration [12]. The lower frequency semicircle is usually ascribed to the conductivity of grain boundaries (*i.e.*, intergranular conductivity), whereas the higher frequency response pertains to the bulk conductivity (*i.e.*, intragranular conductivity).

In both cases it is difficult to explain the observed increase in relaxation time.

If we assume that measured semicircles are due to the intergranular conductivity then the bulk response should occur at frequencies above 65 000 Hz. In this case the intragranular resistance would be less than the

R_{pc} (real part correction) which was always below 3 ohms and showed no tendency to increase during the film growth (Fig. 2).

We propose a qualitative model where it is assumed that the measured semicircles are due to position-dependent intragranular resistivity *i.e.*, each newly formed sheet of the layer has a higher resistivity than the former one. This assumption should explain the growing relaxation time and the disagreement between the layer thicknesses observed by SEM and the values calculated from impedance measurements using the traditional model [6].

Conclusions

(i) The a.c. response of the anodic passivating layer in Li/SOCl₂ batteries has been described using the dispersion equation of the Cole-Cole type. Good agreement between the measured and the calculated values was found in the frequency range 50 to about 5000 Hz.

(ii) The a.c. response of the passivating layer has been ascribed to intragranular conductivity.

(iii) The time dependence of R , α and τ has been presented for two types of Li/SOCl₂ batteries.

(iv) The increase in relaxation time is assumed to be due to position dependent resistivity of the passivating layer (assuming the dielectric constant of the layer has a constant value).

(v) The position dependence of resistivity has up to the present been neglected in calculations of layer thickness, which may be one of the reasons for obtaining extremely low values compared with those obtained from SEM studies.

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List of symbols

d	The ratio between the extreme value of the imaginary part and the half of the value of the section which is cut on the real axis in complex plane
$H(\omega)$	Transfer function
i	Imaginary unit
N	Number of measured points used in the analysis
R	Total resistance of the passive layer
$\text{Re}(H)$, $\text{Im}(H)$	The real and imaginary part of the calculated transfer function, respectively

$\text{Re}(Z), \text{Im}(Z)$	The real and imaginary part of the measured transfer function
α	Dimensionless parameter in Cole–Cole dispersion equation
σ	Sum of squares by which the difference between two transfer functions was measured
$\tilde{\sigma}$	Error of fit
τ_0	Mean relaxation time
ω	Angular frequency

References

- 1 E. Peled, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, p. 43.
- 2 M. Mogensen, *J. Power Sources*, 14 (1985) 123.
- 3 Ju. M. Povarov and I. V. Vorobeva, *Elektrokhimiya*, 1 (1982) 1963.
- 4 V. E. Kazarinov and V. S. Bagotzky, *J. Power Sources*, 20 (1987) 259.
- 5 M. Mogensen, *J. Power Sources*, 20 (1987) 53.
- 6 R. V. Moshtev, Y. Geronov and B. Puresheva, *J. Electrochem. Soc.*, 128 (1981) 1851.
- 7 J. Phillips and J. Gibbard, in H. V. Venkatesetty (ed.), *Proc. Symp. Lithium Batteries*, Vol. 4, The Electrochemical Society, Pennington, NJ, 1981, p. 54.
- 8 J. R. Macdonald, in G. D. Mahan and W. L. Roth (eds.), *Superionic Conductors*, Plenum Press, New York, 1976, p. 81.
- 9 S. H. Liu and T. Kaplan, in L. Pietronero and E. Tossati (eds.), *Fractals in Physics*, Elsevier, Amsterdam, 1986, p. 383.
- 10 E. R. Brown and J. R. Sandifier, in B. W. Rossiter and J. F. Hamilton (eds.), *Physical Methods of Chemistry*, Vol. II: *Electrochemical Methods*, Wiley, New York, 1986, p. 354.
- 11 J. W. Boyd, *J. Electrochem. Soc.*, 134 (1987) 18.
- 12 P. G. Bruce and R. W. West, *J. Electrochem. Soc.*, 130 (1983) 662.
- 13 K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 9 (1941) 341.
- 14 J. R. Macdonald, *J. Chem. Phys.*, 58 (1973) 4982.