

INVESTIGATION AND PRODUCTION CONTROL OF Li/SO₂ CELLS BY THE GALVANOSTATIC PULSE METHOD

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Summary

A fast and nondestructive method for production control and development research on Li/SO₂, Li/SOCl₂, and Li/SO₂Cl₂ cells is described. Employing the galvanostatic pulse technique, the method yields useful data for the IR drop in the cell, the passivation state of the Li anode, and eventual cathode defects. It can also be applied to the study of the effect of variations in the electrolyte and the cathode on the performance characteristics of cells during storage under various conditions. The applicability of the method is exemplified by data on fresh and stored Li/SO₂ cells.

Introduction

The power characteristics of Li/SO₂ cells are assessed by polarization tests. The simplest of these, often applied in production control, is the short circuit test. When properly performed it is practically nondestructive, but it does not reveal the actual state of the cell since the strong current immediately destroys the passive film on the Li anode. More accurate and extensive data for the actual state of the cell can be obtained by a.c. impedance measurements which, however, require very sophisticated equipment along with a profound knowledge of the theory and interpretation of impedance diagrams. A simpler, faster, and nondestructive method employing more readily available instrumentation is the galvanostatic pulse method (GPM) which has been used in the study of passive films on Li [1 - 4]. The potentialities of the GPM as a tool for rapid production control as well as for development and research on Li/SO₂ cells will be presented in this paper.

Theory

The technique of the GPM has been described previously [2]. It rapidly gives the high frequency capacitance, C , and the micropolarization resistance, R_p , of the cell as well as the voltage drop between the electrodes R_e . In prac-

tical cells without a reference electrode, the R and C values of the anode and cathode cannot be determined separately. In most cases of interest, however, an approximate evaluation of the individual R and C values, sufficient for practical purposes, is feasible. The high frequency impedance of the cell can be represented approximately by the general equivalent circuit (Fig. 1), where C_g denotes the geometric capacitance of the solid film on the electrode, C_d the double layer capacitance at the film/solution interface, R_b the bulk resistance of the film and R_t the charge transfer resistance. The suffixes "c" and "a" stand for the cathode and anode, respectively.

The value of the ohmic drop resistance, R_e , comprising the resistance of the electrolyte, the separator, the metal conductors, and contacts is readily assessed from the jump in the overvoltage response obtained upon application of a short (5 - 10 μ s) galvanostatic pulse. The high frequency capacitance of the cell, C , is estimated from the initial slope of the same transient. When films of appreciable thickness are formed on the electrodes we may write

$$C^{-1} = C_{g,a}^{-1} + C_{g,c}^{-1}. \quad (1)$$

Excluding the special case when a cell is deeply discharged below 1.5 V, the carbon cathode is practically free from coverage by a dense film. On the other hand, the Li anode, except for a short period immediately after filling the cell with the electrolyte or immediately after a strong activation, is always covered by a dense primary film with a thickness proportional to C^{-1} [1 - 3]. Hence, as a first approximation we have

$$C^{-1} = C_{g,a}^{-1}. \quad (2)$$

It is only in the extreme case immediately after activation of the cell by a strong current pulse, when the film on the anode is completely destroyed, that we can neglect the geometric capacitance of the film on the anode. Hence,

$$C^{-1} = C_{d,a}^{-1} + C_{d,c}^{-1}. \quad (3)$$

The cell resistance, R , is obtained from the horizontal portion of the overvoltage transient when a low amplitude but longer (2 - 10 ms) pulse is applied such that the steady state overvoltage does not exceed 10 - 15 mV. Basically, R corresponds to a value measured at very low frequency. Neglecting the concentration polarization in the electrolyte solution, which is insignificant under these conditions, we can write for the general case

$$R = R_{p,a} + R_{p,c} + R_e \quad (4)$$

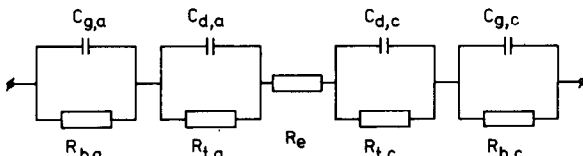


Fig. 1. General approximate equivalent circuit for an Li/SO₂ cell.

with $R_{p,a}$ and $R_{p,c}$ the polarization resistance of the electrodes,

$$R_{p,a} = R_{b,a} + R_{t,a} \quad (5)$$

$$R_{p,c} = R_{t,c}. \quad (6)$$

Here again, it is assumed that the carbon cathode is film-free. Bearing in mind the larger surface area of the cathode we may write for the total cell resistance

$$R = R_{p,a} + R_e = R_{b,a} + R_{t,a} + R_e. \quad (7)$$

As shown by numerous experiments, however, the film on the anode, even for freshly prepared cells, is sufficiently thick that $R_{b,a} \gg R_{t,a} \ll R_e$ and consequently

$$R = R_{b,a} + R_e, \quad (8)$$

where $R_{b,a}$ is proportional to the film thickness.

From the value of R determined by the GPM one can accurately estimate the initial voltage drop of a cell when the discharge current is switched on. The rate of the voltage recovery to the nominal value will depend on the level of the anode passivation and the discharge c.d.

Results and discussion

A number of D-size Li/SO₂ cells, some of which were obtained in the open market and others that were prepared in this laboratory were tested by the GPM. Typical examples of experimental results for undischarged cells are given in Table 1. In all cases, the value of R_e did not exceed 30 - 40 ohm cm². Higher R_e values will indicate poor metallic contacts, improperly prepared electrolyte solution, or low porosity separator material.

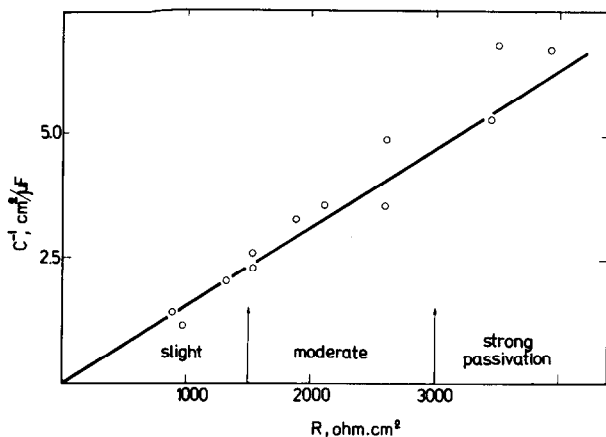
As seen from Table 1 both R and C^{-1} begin to increase immediately after the cell is filled with the electrolyte (1 (a), (b), (c)). Very high values of R and C^{-1} in fresh cells or in stored cells after their activation are evidence of defects in the cathode. Improperly prepared active carbon materials can give higher polarization as well as a lower capacity on discharge. Another, less probable, defect might be insufficient wetting of the cathode by the electrolyte solution, leading to gas inclusions.

A series of 12 cells (regular product of a leading battery company) was tested after 2.5 years storage at room temperature. As shown by Table 1 the degree of passivation of these cells varies considerably, although they originate from one and the same production batch. Figure 2 presents a C^{-1} vs. R plot of the data for these cells. The linear dependence reveals, in agreement with previous similar measurements in 3 electrode glass cells [1 - 4], that the predominant component of R is the bulk resistance of the film on the Li anode. The slope of this plot gives a figure of 2×10^{-9} ohm⁻¹ cm⁻¹ for the specific conductivity, close to values reported earlier for this film [4].

TABLE 1

Typical values of R and C^{-1} for undischarged Li/SO₂ cells

No	State of cell	C^{-1} (cm ² /μF)	$R - R_e$ (ohm cm ²)
1	Fresh cells		
	(a) 3 - 4 h after preparation	0.1 - 1.0	60 - 120
	(b) 1 month later	1.2 - 1.4	200 - 300
	(c) 3 months later	1.6 - 2.0	800 - 1000
2	Cells stored for 2.5 years at room temperature		
	(a) slightly passivated	< 2.5	< 1500
	(b) moderately passivated	2.5 - 5.0	1500 - 3000
	(c) deeply passivated	> 5	> 3000
3	Repassivation of activated cells		
	(a) immediately after activation	< 0.15	~ 0
	(b) 2 h after activation	0.7 - 0.9	100 - 200
	(c) 1 month after activation	1.4 - 1.6	600 - 700

Fig. 2. R vs. C^{-1} relation obtained from undischarged Li/SO₂ cells stored for 2.5 years at room temperature.

Undischarged passivated cells are readily activated by shorting for ~ 1 s, whereby the film on the Li anode is completely destroyed so that $R \cong R_e$. Immediately after the activation both R and C^{-1} increase steeply. This is exhibited in the semilog plots of R and C^{-1} vs. t (Fig. 3) for a moderately passivated cell (R before activation was 1200 ohm cm²) during its repassivation after a shorting pulse of ~ 100 mA/cm² for ~ 1 s. The plot reveals two slopes reflecting, probably, two stages of repassivation, e.g., film formation followed by film thickening. It should be pointed out that the rate of film formation and subsequent growth in a real cell is much higher than in experimental glass cells with a large excess of electrolyte solution. One of the main

reasons for this difference in the rate of film growth is probably the different ratio of Li anode surface area to electrolyte volume, which is $\sim 25 \text{ cm}^{-1}$ in the first case and only $\sim 10^{-2} \text{ cm}^{-1}$ in the second case.

A deeply passivated cell ($R = 3200 \text{ ohm cm}^2$) was activated continuously by a slow discharge current (0.9 mA/cm^2). The voltage-time curve was used to estimate the cell resistance, R , after correction for the ohmic drop R_e . Figure 4 presents the semilog plot of R vs. time. Here, again, two different slopes are observed. The initial, steeper slope probably reflects the perforation and cracking of the film, while the second slope is associated

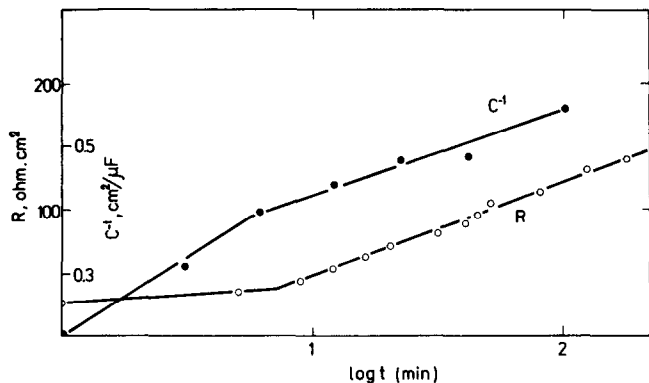


Fig. 3. Increase of R and C^{-1} of an Li/SO_2 cell with time after activation by shorting.

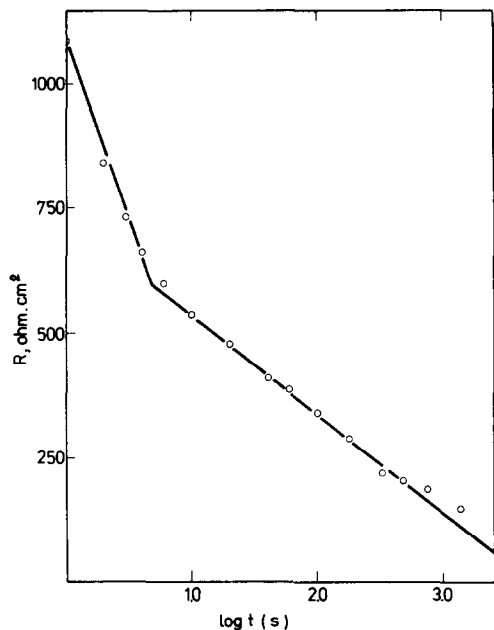


Fig. 4. Activation of a deeply passivated Li/SO_2 cell by slow discharge at 0.91 mA/cm^2 . Decrease of R with time.

with the removal of the film from the metal surface. The initial voltage drop in this particular case exceeded 1.0 V so that the discharge voltage remained below 2.0 V for 1 - 2 s. This is only a minor voltage delay, but more severe delays could be expected after longer storage times and at lower temperatures. The nominal voltage of this cell, 2.8 V, was attained after 48 min of discharge, while for fresh cells this time should be less than 12 min. These findings indicated that Li/SO₂ cells are not totally exempt from voltage delay problems. Voltage delays in excess of 10 s are also reported by Gabano [5] for Li/SO₂ cells stored for 3 months at 70 °C.

The growth of the cell resistance upon deep discharge is illustrated in Fig. 5. The final discharge was performed at a comparatively low c.d., 0.64 and 0.32 mA/cm², in order that a deeper impregnation of the cathode with reaction products could be achieved. It is seen that a normal discharge to 2.0 V has a small effect on both R and C^{-1} .

At the lower discharge rate to cut-off voltages below 1.5 V very high cell resistances are obtained. This is a result of the strong cathode passivation, since it is well known that during discharge the anode remains active. Besides this, at the end of the cell discharge, when the SO₂ concentration is reduced below 15 wt.%, the Li anode cannot be passivated, even on OCV [4]. The exceptionally high resistances of discharged cells exemplified in Fig. 5 imply that if a lower capacity cell is connected in series in a battery, it may develop dangerously high temperatures long before its reversal.

As seen in Fig. 5, the reciprocal capacitance, C^{-1} , remains constant down to a cut-off voltage of 1.7 V despite the substantial increase in R . This could be attributed to the porous character of the layer formed on the cathode. It might be supposed that at lower cut-off voltages (~ 1.7 V) the film becomes so dense and impermeable to the solution that C^{-1} begins to grow proportionately with R . The ohmic drop R_e , on the other hand, remains constant down to 1.0 V (~ 30 ohm cm²), whereafter it increases to 40 ohm cm².

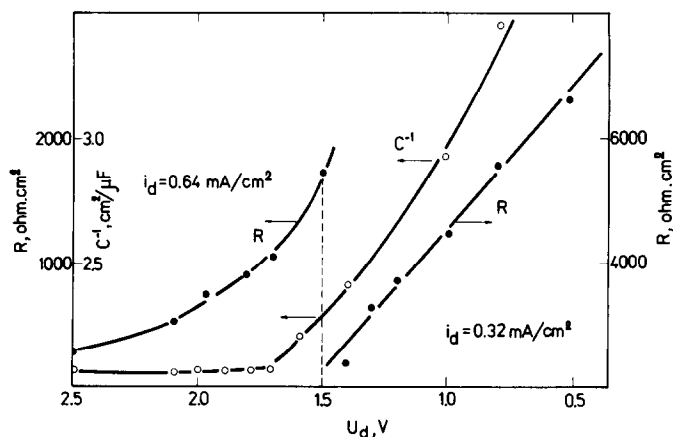


Fig. 5. Increase of R and C^{-1} of an Li/SO₂ cell during a slow overdischarge as a function of cut-off voltage, U_d .

The above few examples clearly demonstrate that the galvanostatic pulse method could be a very useful tool both in production control and in research and development on Li/SO₂ cells. Further tests on the basis of this method could be developed both for Li/SO₂ cells and other Li cells, especially Li/SOCl₂ and Li/SO₂Cl₂, and eventually for other primary cells.

More accurate measurements by the GPM with practical Li/SO₂ cells provided with a reference electrode are under way. It is expected that they will yield a better insight into the processes occurring during storage, passivation, activation, discharge, and overdischarge of the Li/SO₂ cell.

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