

Characterization of lithium-thionyl chloride cells by impedance techniques

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Abstract

The main contributor to voltage drop observed on initial discharge of lithium-thionyl chloride cells is the resistance of the passive layer on the lithium anode, as can be determined from the Nyquist plot of a lithium-thionyl chloride cell. At extremely low discharge currents, initial voltage drop corresponds to the value found from the impedance measurements; at higher current, an empirical correction based on the experimental results is required. The dispersion in the values of the impedance parameters and thus in initial voltage drop of individual cells was analyzed. The condition of the lithium surface after assembly was shown not to be the only reason for high dispersion in impedance parameter values. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-thionyl chloride cells; Impedance techniques; Nyquist plot

1. Introduction

The voltage drop during initial polarization of lithium-thionyl chloride cells results from the high resistance passive layer formed on the lithium metal surface during reaction of lithium with the electrolyte [1–3]. The Nyquist plot of the lithium electrode in thionyl chloride solution includes a semicircle characterizing the passive layer and the diameter of this semicircle correlates with the voltage drop during initial polarization of cells [4]. During storage, the impedance of a thionyl chloride cell, as well as its voltage drop under load, increase due to the growth in thickness or density of the passive layer [5–7]. The ability to predict accurately the voltage drop of thionyl chloride cells after prolonged storage would be beneficial in practical applications. However, this analysis is complicated by high dispersion of parameter values used to characterize the impedance of cells; this dispersion may result from effects of extended storage time and temperature variation on the characteristics of the passive layer. In this paper, we discuss the extent of dispersion observed as a function of storage time.

2. Experimental

All experiments were performed on two types of lithium-thionyl chloride cells. Both types had a porous carbon

cathode, lithium foil as anode, and were filled with 1.8 M $\text{LiAlCl}_4/\text{SOCl}_2$. Porosity of the carbon electrode was about 85% (Table 1).

Impedance measurements were performed on a Solartron 1280 with 10 mV amplitude in 0.05–20 000 Hz frequency range. Polarization consisted of 1 min discharge on 110 Ω load for Type A cells and 10 s discharge on 15 Ω for Type B cells. The minimum load voltage was determined from measurements made every 0.1 s after load application. The temperature of cells during all tests was 20°C. Cells were stored at room temperature.

3. Results and discussion

A typical Nyquist plot of a thionyl chloride cell is shown on Fig. 1. It includes a slightly depressed semicircle in high to medium frequency range and a small distorted semicircle at low frequency.

Centers of both semicircles are often located below the real axis. The large semicircle corresponds to the resistance of the passive layer formed on the surface of lithium as a result of reaction of lithium with atmospheric components during cell assembly and consequent reaction of this surface layer with thionyl chloride after filling. The diameter of the semicircle grows with storage and can be used to calculate the resistance of the passive layer on the anode. Extrapolation of this larger curve on the Nyquist plot to infinite frequency gives us the Ohmic resistance of the cell,

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Table 1
Cell characteristics

Cell type	A	B
Lithium surface area (cm ²)	47.7	103.3
Weight of carbon electrode (g)	2.5	8.1
Weight of electrolyte (g)	28.6	128.5
Weight of lithium (g)	2.1	11.8

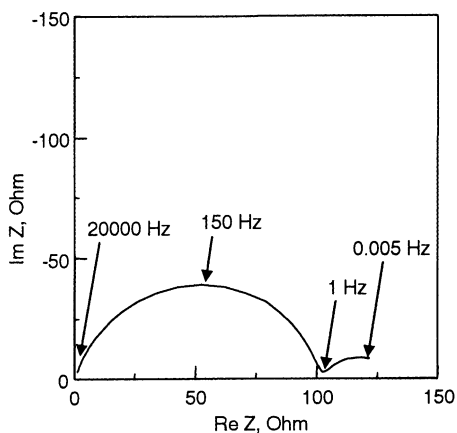


Fig. 1. Typical Nyquist plot of a lithium-thionyl chloride cell.

R_0 . The high frequency part of the cell impedance can be nicely fitted (Fig. 2) by the equivalent circuit presented on Fig. 3.

When a constant current polarization is applied, the voltage drop is equal to the current multiplied by the cell internal resistance. This internal resistance at the beginning of discharge includes Ohmic resistance of electrodes, electrolyte, and tabs, and the resistance of the passive layer formed on the lithium surface. Polarization of the carbon electrode is assumed to be negligible. The resistance of the passive layer, R_{pl} , is a projection of the first semicircle from the Nyquist plot on the real axis. The resistance of the passive layer, R_{pl} , is a good approximation of cell internal

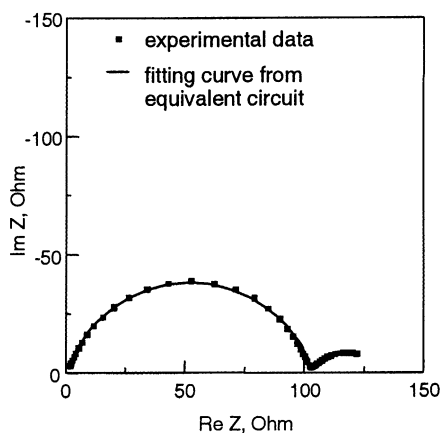


Fig. 2. Fitting of experimental data.

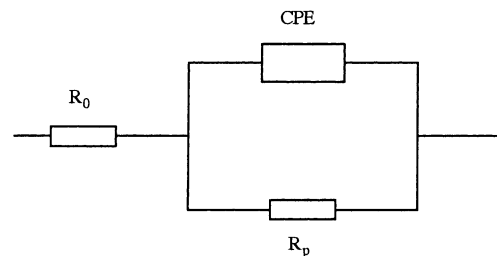


Fig. 3. Equivalent circuit of the impedance of a thionyl chloride cell. CPE: constant phase element, corresponding to the capacitance of passive layer; R_0 : Ohmic resistance of the cell; R_p : the resistance associated with the passive layer.

resistance, because the Ohmic resistance of the cell, R_0 , is much smaller as compared to R_{pl} as can be seen from Fig. 3: a projection of the semicircle on the real axis is about two orders of magnitude bigger than a segment from zero to the high frequency intercept of the first semicircle with real axis.

Provided in Table 2 are the values of the experimentally determined minimum voltage under constant current polarization, V_{min} , and the calculated minimal voltage $V_{min\ calc}$, where $V_{min\ calc}$ is obtained from R_{pl} based on Ohm's law, and V_0 is the open circuit voltage of a cell:

$$V_{min\ calc} = V_0 - IR_{pl} \tag{1}$$

As shown in Table 2, when low currents are applied, $V_{min\ calc}$ is practically equal to the experimental value of V_{min} , e.g. the voltage drop can be calculated from the results of the impedance measurements. When the current is increased, minimum voltage under load, V_{min} , is higher than expected based on R_{pl} but still remains proportional to the impedance of the cell (Table 2; current values 1, 5 and 10 mA). The difference between V_{min} and $V_{min\ calc}$ is, probably, caused by rapid destruction of the primary passive film during the first moments when current is applied.

Table 2
 V_{min} and $V_{min\ calc}$ at different polarization currents for Type A cells

I (mA)	V_0 (V)	R_{pl} (Ω)	V_{min} (V)	$V_{min\ calc}$ (V)	Difference (%)
0.01	3.7006	754	3.6932	3.6931	0.0
0.01	3.7025	545	3.6970	3.6970	0.0
0.1	3.7015	750	3.6293	3.6266	0.1
0.1	3.7026	563	3.6456	3.6463	0.1
0.5	3.7003	740	3.3752	3.3303	1.3
0.5	3.7072	574	3.4653	3.4202	1.3
1	3.6974	390	3.5003	3.3074	5.5
1	3.7003	337	3.5032	3.3636	4.0
1	3.7036	931	2.9678	2.7723	6.6
1	3.6834	143	3.5420	3.5408	0.0
1	3.7036	1210	2.8546	2.4936	12.6
1	3.7026	1191	2.9544	2.5116	15.0
5	3.6973	292	3.2314	2.2371	30.8
5	3.6997	268	3.2589	2.3595	27.6
10	3.6978	306	2.2415	0.6370	71.6
10	3.6996	252	2.9338	1.1796	59.8

In our experiments, polarization was applied as a resistive load, and the values of R_{vd} and $V'_{min\,calc}$ can be calculated using the following equations:

$$R_{vd} = \left(\frac{V_0 R_{load}}{V_{min}} \right) - R_{load} \tag{2}$$

$$V'_{min\,calc} = IR_{load} = \frac{V_0 R_{load}}{R_{vd} + R_{load}} \tag{3}$$

where R_{load} is the load resistance: 110 Ω for Type A cells and 15 Ω for Type B cells; V_0 the open circuit voltage of a cell (3.7 V); and V_{min} is the minimum voltage under the load found from the polarization curve. R_{vd} is the calculated resistance of the passive film at the moment when voltage reaches its minimum value.

In Figs. 4 and 5 the impedance parameter R_{pl} is plotted versus R_{vd} for the two types of cells.

The relationship between R_{vd} and R_{pl} for these two cell types can be described by the following equations:

$$\text{Type A : } R_{vd} = 0.2021R_{pl} + 18.126 \tag{4}$$

$$\text{Type B : } R_{vd} = 0.3392R_{pl} + 1.1019 \tag{5}$$

Using Eq. (3) and taking into account that the open circuit voltage $V_0 = 3.7$ V, resistance R_{load} is 110 Ω for Type A cells and 15 Ω for Type B cells, and expressing R_{vd} in terms of R_{pl} (Eqs. (4) and (5)) the value of the minimum voltage

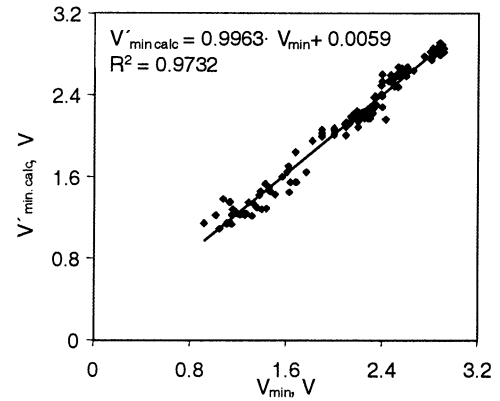


Fig. 6. Calculated minimum voltage $V'_{min\,calc}$ vs. V_{min} found from experiment.

during polarization ($V'_{min\,calc}$) can be calculated as:

$$\text{Type A : } V'_{min\,calc} = \frac{2003}{R_{pl} + 633} \tag{6}$$

$$\text{Type B : } V'_{min\,calc} = \frac{162.7}{R_{pl} + 47.5} \tag{7}$$

Based on these equations, it is possible to predict the voltage drop of cells from the results of impedance measurements with reasonable accuracy (Fig. 6) over the current range of the data presented in Table 2.

It is well known that the resistance of the passive layer in a thionyl chloride cell, and thus the voltage drop of the cell grows with time. The rate of change in passive layer resistance is high in the beginning and then becomes slower [4–8]. Actual magnitude of the resistance depends on the type of the cell and the conditions of storage [4,5,7,8].

The distribution of R_{pl} shortly after cell filling is close to a Normal distribution (Fig. 7). The distribution for both types of cells after initial polarization becomes wider with the time of storage (Figs. 8 and 9). However, when a second polarization was carried out 2 weeks after the first polarization, it causes the absolute value of R_{pl} and its distribution to decrease again (Fig. 10).

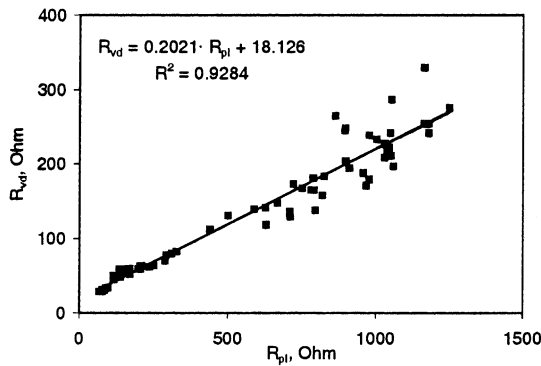


Fig. 4. R_{vd} vs. R_{pl} for Type A cells.

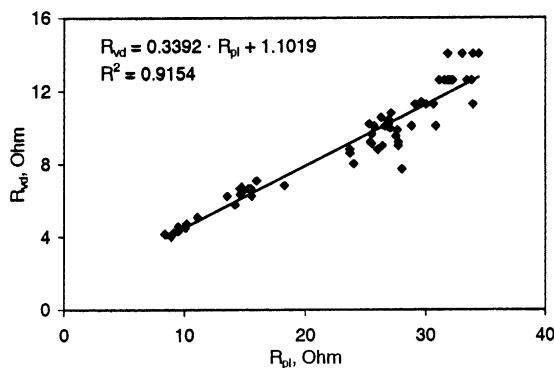


Fig. 5. R_{vd} vs. R_{pl} for Type B cells.

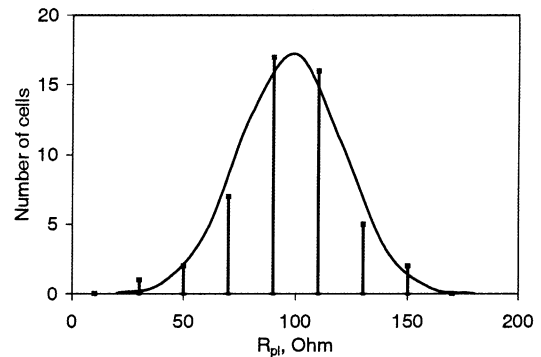


Fig. 7. Histograms showing distribution of impedance of Type A cells after filling.

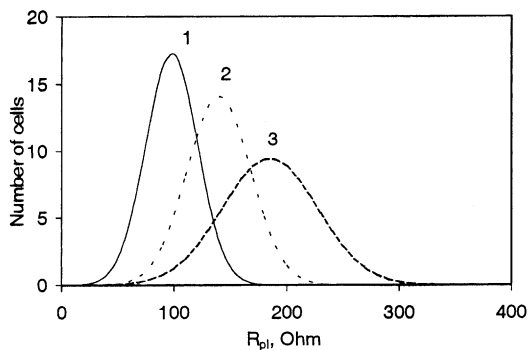


Fig. 8. Distribution of R_{pl} for Type A cells as a function of storage time: (1) 1 day after filling; (2) 1 week after polarization; (3) 2 weeks after polarization.

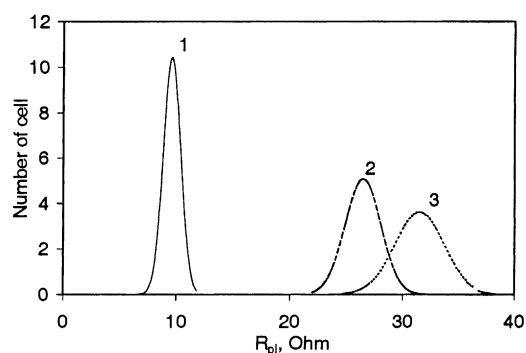


Fig. 9. Distribution of R_{pl} for Type B cells as a function of storage time: (1) 1 week after filling; (2) 2 weeks after polarization; (3) 5 weeks after polarization.

The relationship between the distribution of R_{pl} , expressed as the standard deviation of R_{pl} , and the average value of R_{pl} is shown on Fig. 11 for cells stored from 1 week to 1 year with both single and double polarization. The data show that this relationship is linear even after two polarization events.

Polarization destroys or, at least, significantly changes the passive layer. For example, the average value of R_{pl} for

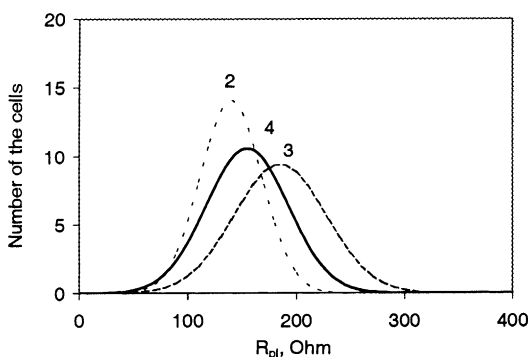


Fig. 10. Effect of the second polarization on R_{pl} for Type A cells: (2) 2 weeks after the first polarization; (3) 5 weeks after the first polarization; (4) 9 days after the second polarization.

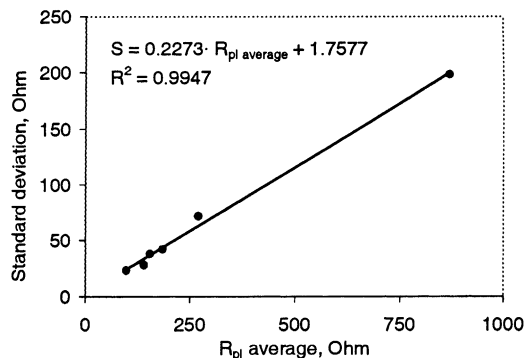


Fig. 11. Standard deviation of R_{pl} for Type A cells vs. average value of R_{pl} .

Type A cells after 1 year storage is 870Ω . Its magnitude 1 min after polarization was approximately 20Ω . At the same time the narrow distribution of R_{pl} for cells after polarization indicates that the characteristics of the passive layer of such cells has become similar. However, the relationship between R_{pl} and the standard deviation of R_{pl} on storage is shown not to change despite multiple prior polarizations (Fig. 11). If the distribution is a function of surface impurities introduced during cell assembly, then the relationship between R_{pl} and its standard deviation should not be independent of repeated polarizations unless the surface impurities are crystal nucleating sites in the passive layer.

The passive layer, which forms after multiple polarizations, should be similar in different cells because it was formed under similar conditions in electrolyte having the same bulk composition in all cells. Further analysis of individual cells (Fig. 12) after polarization shows that the rate of growth of R_{pl} is not equal after the first and the second polarization. These data suggest that nucleating sites obtained in cell assembly do not alone control the rate of change of R_{pl} . Other factors may include local concentration of SO_2 formed during polarization and inclusion in the layer of other crystal forms formed from reaction of polarization products with electrolyte impurities.

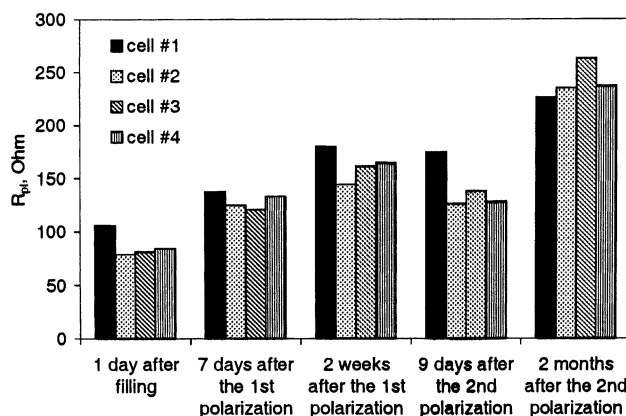


Fig. 12. Changes R_{pl} for individual cells during the experiment.

4. Conclusions

Based on impedance measurements it is possible to predict the voltage drop of lithium-thionyl chloride cells. For small currents, initial voltage drop can be calculated from the value of impedance parameter R_{pl} , which corresponds to the passive layer resistance. At higher currents a correction based on experimental parameters related to cell type must be used.

Polarization of lithium-thionyl chloride cells decreases the voltage drop and narrows its distribution. Average value of R_{pl} and, thus, magnitude of the voltage drop, however, grows during storage at approximately the same rate as it did before the polarization.

Dispersion of the impedance parameter R_{pl} grows with its average value. Its distribution remains to be close to a Normal distribution.

Localized impurities at the anode surface formed during assembly appear not to be the only reason for high dispersion in initial voltage drop of thionyl chloride cells.

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