Monitoring voltage fluctuations for the characterization of lithium cells

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Abstract

A technique based on monitoring small voltage fluctuations was applied to the study of Li/SO_2 and $Li/SOCl_2$ cells during their normal resistive discharge. In a purely resistive circuit the cell internal resistance is a key variable which can fluctuate with internal modifications occurring during the cell discharge. By filtering and properly recording the spontaneous electrochemical transients it was possible to reveal some interesting differences between the Li/SO_2 and $Li/SOCl_2$ systems. The electrochemical noise patterns can thus be seen as a characteristic signature that is sensitive to the cell's operation which, in the case of Li cells, is a compromise between a passivated metal with an extra long shelf life and an active state triggered by the galvanic coupling to an ever-ready cathode.

Introduction

Both the lithium–sulphur dioxide and the lithium–thionyl chloride systems are of importance in the contemporary energy storage scene because of their very high energy densities, 330 and 500 W h kg^{-1}, respectively, and very long shelf life. Because of this intrinsic, long lasting power lithium batteries are presently used in large quantities by the military and in increasing numbers in the electronic market. They have only recently been introduced to the consumer market but will probably see growth in this area during the next decades. It is well known, however, that lithium cells are not as tolerant as aqueous cells to design flaws and abuse. In fact, the subject of safety immediately comes to mind when the use of a lithium cell is contemplated.

The observed stability of the Li anode is due to the presence of a protective film covering its surface, thus preventing open circuit shelf discharge. In the last decade several papers have been published on studies made on the passivation mechanisms of both the $Li/SOCl_2$ [1–7] and Li/SO_2 [8–11] systems through the use of electrochemical impedance spec-

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troscopy. Any condition that can lead to the disruption of the protective film, however, may also make the cell potentially hazardous. The same disruption could also induce voltage oscillations that would be characteristic of the internal resistance behaviour.

The study of electrochemical potential or current fluctuations has always fascinated scientists. The early work in this field has been reviewed in 1972 by Tyagai [12] and subsequent publications reviewed by Bezegh and Janata [13] and by Searson and Dawson [14]. Most of the noise investigations carried out to date were focussed on phenomena associated with corrosion studies and used sophisticated data collection and analysis systems [15, 16]. Only a limited research effort has been reported on the study of such fluctuations observed on battery systems [17–20].

Quite recently it was reported [19, 20] that electrochemical noise patterns observed at the early stages of charging sealed lead/acid cells appeared to be related to charging difficulties at the positive electrode, while noise patterns appearing at the end of charge were associated with problems at the negative electrode. A more extensive study of these phenomena concluded [21] that monitoring electrochemical noise would be a valid non-destructive testing technique to discriminate cells with problems.

The present study illustrates, with some characteristic results, how such a technique can be used to reveal the fundamental behaviour of Li/SO_2 and $Li/SOCl_2$ cells during a normal resistive discharge.

Experimental

Figure 1 is a schematic diagram of the system used to monitor voltage noise patterns. The system consists of a discharge circuit and an RC measuring circuit, originally described by Iverson [22], in which a 1 MΩ resistor (R) and a 1 μF tantalum capacitor (C) are used in series to block the d.c. voltage of the cell under study. The current circulating through the RC circuit is monitored by measuring the voltage drop across the resistor every 300 ms with a 5 1/2 digit voltmeter (Fluke model 8840A).

A description of the cells discharged for this study is presented in Table 1. The two Li/SO_2 'C' cells (cells A and B) were discharged completely at a $C/15$ rate (190 mA) through a fixed load resistor (15 Ω).The $Li/SOCl_2$ 'D' (cell C) cell was discharged much more slowly ($C/40$) while the $Li/SOCl_2$ 'AA' (cell D) cell was discharged at close to $C/10$. No effort was taken to control the temperature but thermocouple readings indicated that the cells stayed within one degree of room temperature.

Results

Some typical results obtained during the resistive discharge of two Li/SO_2 'C' cells are presented in Figs. 2 and 3. During the first minutes of
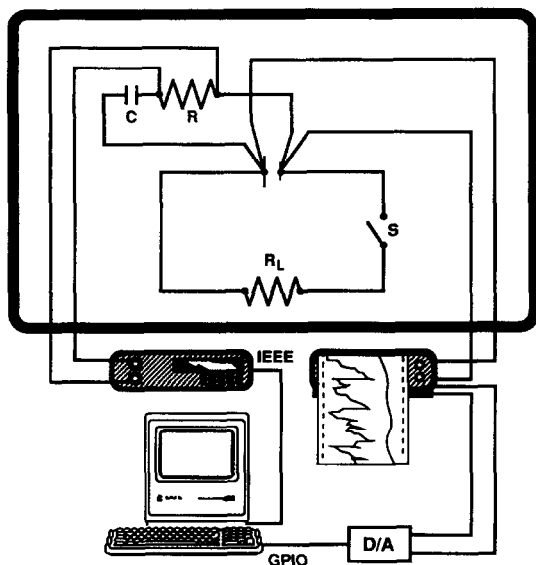
Fig. 1. Experimental set-up for the measurement of potential fluctuations. $R = 1$ MΩ; $C = 1$ μF; R_L = load resistance.

TABLE 1

Characteristics of four lithium cells

Type	Li/SO$_2$		Li/SOCl$_2$	
Cell	A	B	C	D
Company	Duracell[a]	Duracell[a]	SAFT[b]	SAFT
Year produced	1982	1980	1988	1988
Initial OCV(V)	3.01	2.90	3.68	3.68
Characteristic	High rate balanced	Lithium rich	High rate wound	Low rate bobbin
Type	'C'	'C'	'D'	'AA'
Nominal capacity (A h)	3	3	7	1
Real capacity (A h)	2.87	2.86	7.46	0.70
Discharge current (mA)	190	190	190	90
Discharge mode	Interrupted[c]	Continuous	Interrupted	Continuous

Cell chemistry:
[a]5% LiBr, 24% acetonitrile, 71% SO$_2$.
[b]82% SOCl$_2$, 8% LiAlCl$_4$, 0.8% SO$_2$, 0.4% S$_2$Cl$_2$.
[c]Discharge for 8 h/rest for 16 h.

discharge, cell A showed regular voltage fluctuations of approximately 10 μV in amplitude, but with a variable low frequency profile (30 - 70 mHz). The same cell started to show a different type of voltage fluctuation once it was approximately 75% discharged. The negative voltage excursions in
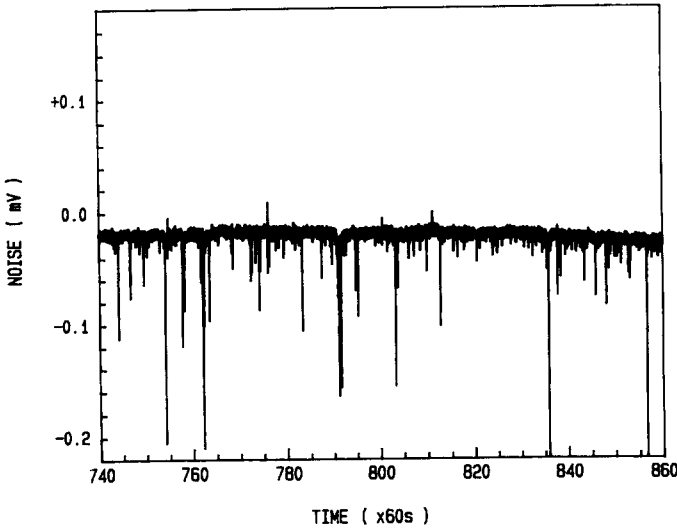
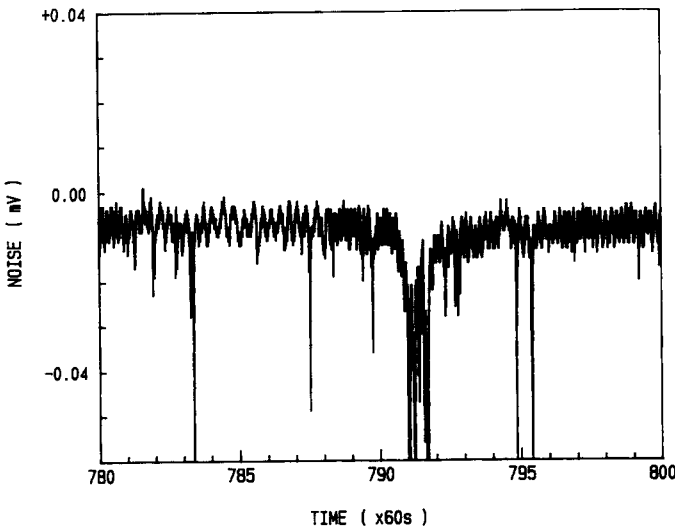Fig. 2. Potential fluctuations observed with an Li/SO$_2$ 'C' cell (cell A) near the end of discharge.

Fig. 3. Magnification of the potential fluctuations observed with an Li/SO$_2$ 'C' cell (cell A) near the end of discharge.

Fig. 2 were themselves superimposed on the more regular, low amplitude background noise, as is better illustrated in the magnification presented in Fig. 3. The second Li/SO$_2$ 'C' cell, which was discharged under similar conditions, always produced a background signature relatively quieter. A striking similitude with the first cell none-the-less started to be visible during

the last phase of discharge (> 75%), when the same moderately large negative voltage fluctuations became an increasingly dominant component of the noise signature.

Once the Li/SO$_2$ 'C' cells (cells A and B) were discharged beyond a finite threshold (< 2.7 V), a tremendous increase in the potential fluctuations was observed for both cells. The background electrochemical noise increased progressively during the following hours and became characteristically random. Such a random electrochemical noise had previously been observed when an attempt was made to recharge fully discharged sealed lead/acid cells after they had been left shorted for a few hours. This type of noise had then been attributed to corrosion phenomena occurring at the positive electrode [21].

The features observed during discharge of the Li/SOCl$_2$ cells used in this study differed remarkably from the results obtained with Li/SO$_2$ cells. Both Li/SOCl$_2$ cells produced potential spikes even during the early part of their discharge.

The Li/SOCl$_2$ potential fluctuations presented in Fig. 4 correspond to a discharge state of 90% of the real capacity. Even at the low discharge rate used for such a high-rate lithium cell, cell C produced a series of positive and negative peaks that were both characteristic and detectable (Fig. 4). The voltage fluctuations' dominance by the positive peaks was also quite visible for the low-rate cell (cell D) prior to being fully exhausted. The transition to a higher level of electrochemical noise was as visible for the high-rate Li/SOCl$_2$ cell upon exhaustion (Fig. 5) as it was for the Li/SO$_2$ cells.
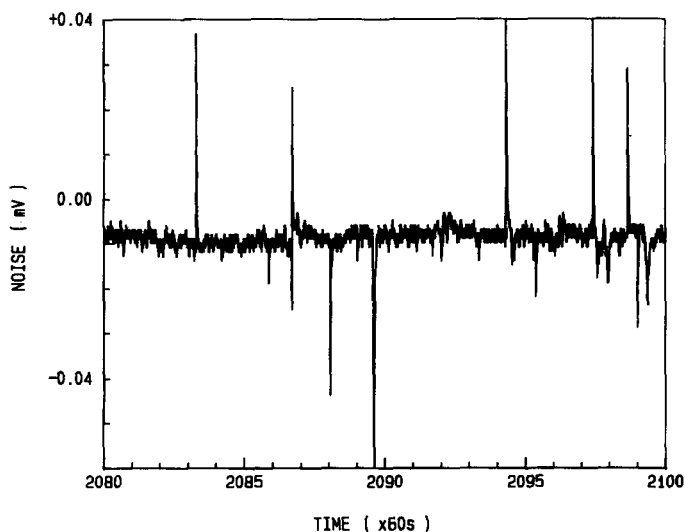

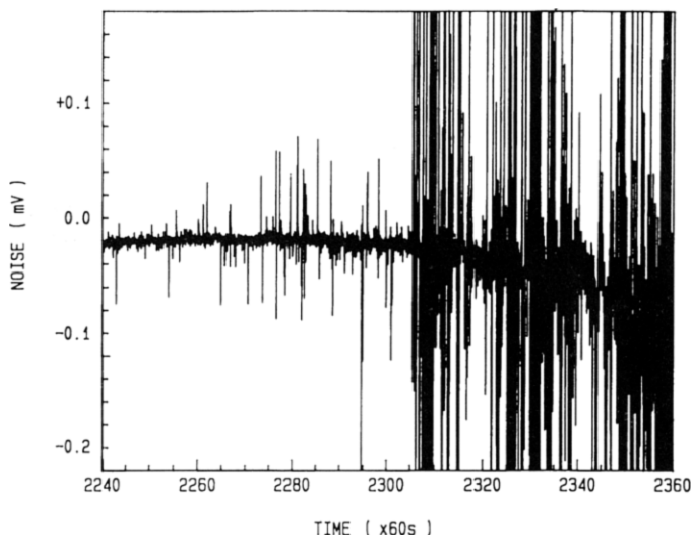Fig. 4. Potential fluctuations observed with an Li/SOCl$_2$ High Rate 'D' cell (cell C) near the end of discharge.

Fig. 5. Voltage noise patterns observed with an Li/SOCl$_2$ 'D' cell (cell C) during its transition to become fully discharged.

Discussion

It is beyond the scope of this paper to explain the mechanisms underlying the potential fluctuations observed so far with both Li/SO$_2$ and Li/SOCl$_2$ cells under normal discharge conditions. It is more appropriate to estimate the relative sensitivity of such fluctuations to basic cell parameters and to highlight the advantages of using such a monitoring technique for routine battery characterization.

The noise data recording have to be interpreted in terms of a current circulating through a high pass filtering circuit which mainly serves to cut off the d.c. component of the battery being tested. Such a filter behaves, more or less, like a capacitor for voltage changes slower than the cut-off frequency. This behaviour explains the negative values presented in Figs. 2–5, which correspond to the negative slope $(dE)/(dt)$ of cells slowly being discharged.

For more rapid voltage fluctuations or, more specifically, for voltage fluctuations faster than the filter cut-off frequency (0.16 Hz), the filter ceases to behave capacitatively and acts as a resistor. It is then possible to estimate the sensitivity of the technique to the only parameter that is variable in such a circuit, i.e., internal resistance (R_{cell}) of the cell under test. Equation (1) expresses the voltage at the cell posts (V) as a function of the cell e.m.f.(E) and the ohmic drop due to the cell internal resistance (IR_{cell}).

$$V = E - IR_{cell} \quad \text{or} \quad I = \frac{(E - V)}{R_{cell}} \tag{1}$$

Since that voltage also corresponds to the voltage drop across the load resistor (R_L), eqn. (2), it is possible to express the cell internal resistance independently of the discharging current, as in eqn. (3).

$$V = IR_L \qquad (2)$$

$$R_{cell} = \frac{(E-V)}{V} R_L \quad \text{or} \quad E = \frac{(R_L + R_{cell})}{R_L} V \qquad (3)$$

By deriving expression (3), where basically only V and R_{cell} can fluctuate at a higher frequency than the filter cut-off frequency, it is possible to evaluate the variation of the cell internal resistance as a function of the observed potential fluctuations, as in eqn. (4) and its subsequent form eqn. (5), obtained by replacing E with its expression in eqn. (3).

$$\frac{dR_{cell}}{R_{cell}} = -\left(\frac{E}{E-V}\right)\frac{dV}{V} \qquad (4)$$

$$\frac{dR_{cell}}{R_{cell}} = -\left(\frac{R_L + R_{cell}}{R_{cell}}\right)\frac{dV}{V} \qquad (5)$$

Using eqn. (5) and approximate values for R_L (20 Ω), and V (3 V), it can be estimated that a rapid excursion of 0.15 mV would correspond to a parallel decrease in the internal resistance of the cell being tested by approximately 0.5% of its absolute value. Such a technique is thus very sensitive to internal changes occurring inside a cell being discharged.

The details of various reaction mechanisms proposed for the reduction of $SOCl_2$ have been extensively discussed in the open literature [23–25]. Thermodynamically, Li and $SOCl_2$ are unstable when put together and should react vigorously. The practical stability of the Li anode in this environment is due to the presence of an LiCl protective film on its surface that prevents further attack by $SOCl_2$ [26]. Hence, any condition that can lead to the disruption of the protective film may render the cell electrochemically unstable and potentially hazardous. A number of incidents are on record involving Li/$SOCl_2$ cells that resulted in physical damage and one fatal accident [27].

Extensive studies have been carried out to evaluate the various chemical and electrochemical processes that govern the safety and performance of these cells [28]. Major voltage instabilities have been observed when some cells were submitted to a forced over-discharge regime that can often lead to the venting of toxic gases or violent rupture of the cell [29, 30]. The voltage oscillations reported in the present study occurred very early in the normal and safe discharge of Li/$SOCl_2$ cells. The amplitude of the recorded noise patterns indicates that the transformations involved are minor and fundamental characteristics of these cells. The presence of positive peaks amid the electrochemical noise patterns can only be explained by a sudden micro-improvement of the cells' internal resistance, since they operate at a voltage inferior to the e.m.f., or by the sporadic faradaic contribution of a chemical species.

It has been generally observed during discharge of the Li electrode in an $SOCl_2$ environment that the formation of holes in the surface layer of protective LiCl allows direct contact between the electrode and the electrolyte [31]. Consequently, under these conditions, the surface layer cannot be described as a simple interphase consisting of a polycrystalline solid electrolyte, as is the case with most Li electrodes. A recent study using impedance spectroscopy [32] proposed a complex model to describe Li electrode behaviour kinetics in a catalyzed $SOCl_2$ electrolyte. In this model, the microworld at the bottom of the holes in the LiCl film lacks natural convection, and is subject to rapid precipitation phenomena that can partially block the already-limited active surface. Such inhomogeneities in surface films have often been the source of electrochemical oscillations during the active–passive transition of passivating metals.

The results obtained with Li/SO_2 cells during most of their discharge (75%) indicate a smoother operation than the $Li/SOCl_2$ cells tested under similar conditions. The cyclic nature of the baseline, which is sometimes quite visible with the instrumental resolution presented in this study, seems to be present at various levels with most lithium cells so far tested. The variations observed both in the amplitude and frequency of these regular oscillations can only be attributed to changes occurring in the internal mechanisms of the cells, which have been described as being quite complex. The characteristics and effects of the lithium passivation layer on the operation of Li/SO_2 cells have recently been studied and discussed in great detail [33]. The effects of long-term, low discharge rates indicated, for example, that low discharge rates modified the lithium passivation layer and favoured subsequent lithium corrosion and self-discharge. The partial discharge of the lithium anode primary passivation layer apparently perturbs the secondary layer, which is more loosely attached to the anode. The Li/SO_2 cell history seems to be a parameter that plays an important role in the delicate balance of the chemical mechanisms that keep such cells on the fine line between a long shelf life and a very active state.

Conclusions

The baseline noise recorded during the simple resistive discharge of lithium cells was found to vary with the cell type and the depth of discharge. It is premature at this point to attempt to relate the frequency or amplitude of the recorded transients with the complex mechanisms that govern the interaction between the various materials involved in a lithium cell discharge. A thorough study of these transients would have to be accompanied by a detailed knowledge of both the history and chemistry of the cells under investigation.

A more direct application of such a monitoring technique would be for a non-destructive evaluation of $Li/SOCl_2$ and Li/SO_2 cells [34], since any cell misbehaviour should be preceded by fluctuations of the electrochemical

signature. A systematic study to verify this principle, and to apply noise monitoring to the non-destructive testing of lithium cells, is presently in progress in an industrial laboratory.

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