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A state-of-charge test for the Li-CuO cell

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The electrochemistry of the Li–CuO cell causes difficulties in the identification of suitable state-of-charge tests for commercial units. The available data has been analysed and a 'best available' test is noted.

1. Introduction

The results of an investigation of the impedance of small lithium-copper oxide primary cells have been presented at the 1981 Anglo-Czech Symposium [1]. A rather crude interpretation of the results was given in terms of rather complicated electrochemistry involving significant impedance contributions from both electrodes and the electrolyte. The electrical network which was found to be generally analogous to the cell [1] is shown in Fig. 1. Such an analogue fairly well represents the main characteristics of the primary cell over most of the states-of-charge, but, the magnitudes of the individual components were observed to change with the time-elapsed between the end of the discharge and the time of the impedance measurement. This variation imposed a severe restriction on our ability to identify a reasonable state-of-charge test. This note records the most satisfactory one.

2. Experimental procedure

The experimental method and apparatus have been fully described [2, 3]. The cells used were of R6 (AA) size (diameter, 13.85 mm; length, 49.5 mm; volume, 7.45 cm^3; mass, 17.4 g) with a rated capacity 200 Wh kg^{-1} when discharging into 120 Ω at 20° C with a mean voltage 1.5 V. The reacting lithium surface was 9.954 cm^2 with an electrolyte volume 2.35 cm^3. When discharging cells were galvanostatted at 37.5 mA (100 h rate) using a Kemitron P-50 potentiostat in conjunction with a Kemitron CM-2 coulometer.

Impedance data was transferred from the punched tape output of the F.R.A. to the PRIME 400 computer for processing as described previously [4, 5].

3. Results

Impedance loci typical of the various states of discharge have already been described [1]. The common feature in all these curves is a high frequency semicircular shape which was generated between 10 kHz and 0.1 kHz. Distortion of the curve from the precise semicircular shape has been investigated and we are now satisfied that it can be ascribed in part to a roughening of the lithium electrode [6]. Nevertheless, it was clear that each locus contained a detectable region between the above frequency limits. This feature is shown in Fig. 2. Figure 2 shows the characteristic magnitudes which were found to vary fairly regularly with the state-of-charge of the cell.

A feature of the behaviour of the cells was the variation of the magnitudes of the impedances with the open circuit stand time (after the end

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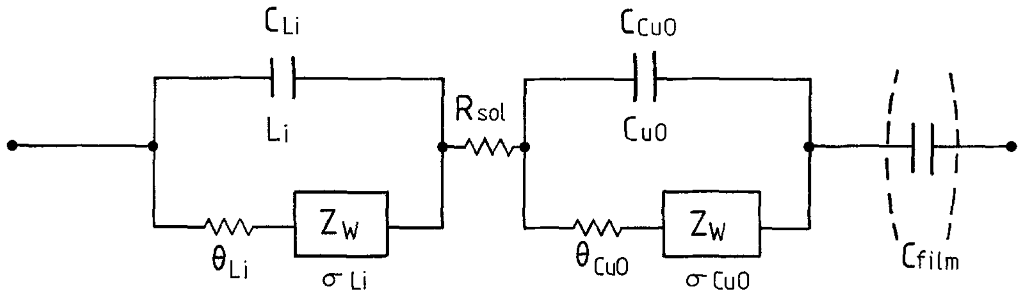

Fig. 1. Analogue proposed for the Li–CuO cell.

of the discharge) before the measurement was taken. The extent of this variation is shown by the data of Table 1 for the 5% discharged cell. There is a very slow increase in the magnitudes of all the in-phase impedance components during 55 days although it is clear that the rate of increase is decreasing as time goes on. Coupled with this variation is a monotonous increase in the cell voltage. Interpretations of these open circuit time variations recognise the progressive development of a film of solid lithium perchlorate or possibly lithium oxide across the electrode surface [1]. Although such films could increase the high frequency resistance and the semicircle diameter, they cannot explain the increasing cell potential. In the short term increasing open-circuit voltages arise from the diffusion of lithium in the porous copper oxide, which distributes Li in the intercolate CuO Li_x, more uniformly. Diffusion is, however, likely to be complete after a day or so. In addition to the filming of the lithium, the development of intermediates in the positive CuO electrode, which cause a local polarization, could provide a long term potential change as they become transformed to more stable compounds.

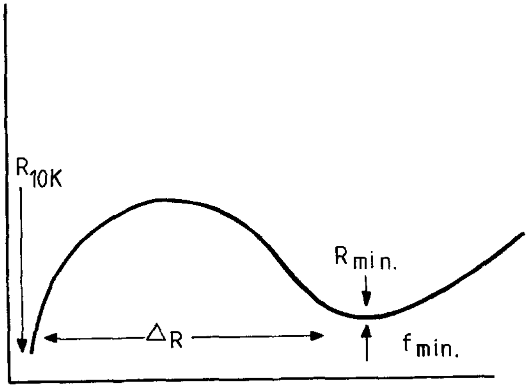

Fig. 2. Characteristics of high frequency shape in the impedance spectrum.

Thus reactions of the type:

$$4CuO + 2Li^+ + 2e^- \rightarrow Li_2O_2 + 2Cu_2O \tag{1}$$

$$E = 1.87\,V$$

which occur at the copper oxide electrode during the discharging reaction, further react on standing to remove the peroxide;

$$Li_2O_2 + 2Cu \rightarrow Li_2O + Cu_2O \tag{2}$$

Reaction 1 is feasible since the corresponding reversible potential is above the on-load potential of the cell when discharging at the 100 h rate employed here. Reaction 2 occurring on open-circuit (when no current flows) removes Li_2O_2 with the production of final cell reaction products (Cu_2O is transformed to cathode reactant, CuO and product Cu by simple disproportionation). Hence Reaction 2 returns the cathode to the initial state at the reversible potential for the Li–CuO cell (~ 2.4 V). The comprehensive data on the cell tested in a fairly random manner is shown in Table 2. The most consistent data which we have been able to identify were obtained by allowing a 24 h stand between the completion of a period of discharge and the test. As we have suggested in the case of the Zn/HgO cell [6] the diameter of the high frequency semi-circle provides the best parameter on which to base a state-of-charge test. This semicircle represents the charge-transfer process and is connected most intimately with the electrochemical concentrations within the cell so that a great deal of confidence naturally attaches to a test founded well in theory. However, a further test is clearly

Table 1. Variation of impedance magnitudes with open circuit stand time

time (h)	*Run*	R_{10k} (Ω)	R_{min} (Ω)	ΔR	f_{min} (Hz)	*Open circuit voltage* (V)
1	242	0.804	1.0208	0.2168	495	1.785
19	341	0.879	1.74	0.861	124	1.894
25	346	0.872	1.711	0.839	124	1.903
92	641	0.8822	2.088	1.206	124	1.936
119	742	0.882	2.279	1.397	98.8	1.942
164	942	0.882	2.553	1.671	78.5	1.941
187	1041	0.8935	2.808	1.915	62.36	1.957
240	2241	0.979	5.816	4.837	24.8	1.973
600	2742	0.917	3.997	3.08	39.31	1.975
601	2744	0.909	3.877	2.97	39.31	1.975
1320	2751	0.921	4.636	3.715	31.20	2.00

necessary in addition to a subtractive two-frequency test. The possibility of a high cell resistance due to contact clearly exists. This can readily be taken into account by fixing a limit for the high frequency reading. This factor was also time dependent, however, the 24 h stand again provided a satisfactory stabilization time at which quite reasonable values could be predicted for a satisfactory cell.

Figure 3 shows the 24 h value of ΔR plotted against state-of-charge in the 100–90% charged range. A quite well defined relationship is shown in the form

$$\Delta R/\Omega = 1.14 - 0.03s \qquad (3)$$

Table 2. Results of a series of experiments on a test cell

Percentage discharge	*Run**	R_{10k} (Ω)	R_{min}(Ω)	f_{min}(Hz)	ΔR	*Open circuit voltage* (V)
0	1631	1.267	4.401	62.36	3.134	2.38
1	2331 (69)	0.982	3.096	62.36	2.114	2.09
2	2431 (17.5)	0.943	2.279	62.36	1.336	1.963
3	2531 (17.5)	0.925	1.838	98.8	0.913	1.926
4	3032 (120)	0.942	2.746	39.31	1.804	1.951
5	141 (22)	0.998	2.225	62.3	1.227	1.878
6	342 (23)	0.947	1.784	98.8	0.837	1.837
7	642 (68)	0.956	2.186	62.36	1.23	1.890
8	841 (19)	0.993	1.987	62.36	0.994	1.829
9	2341 (336)	1.035	3.577	24.8	2.542	1.905
10	2844 (24)	0.996	1.815	62.36	0.819	1.814
20	551 (96)	1.097	1.999	62.36	0.902	1.819
20	1153 (240)	1.048	2.035	62.36	0.987	1.863
30	1851 (120)	1.073	1.849	62.36	0.776	1.802
40	2651 (168)	1.047	1.521	124.	0.474	1.796
50	961 (120)	0.7826	1.019	248.	0.2364	1.725
60	1561 (120)	1.039	1.343	248.	0.304	1.702
70	2361 (96)	3.597	3.910	312.	0.313	1.667
80	2561	14.07	flat			1.525
90	271	32.0				1.508
100	671	19.0				1.402

* Values in parentheses are run durations in hours

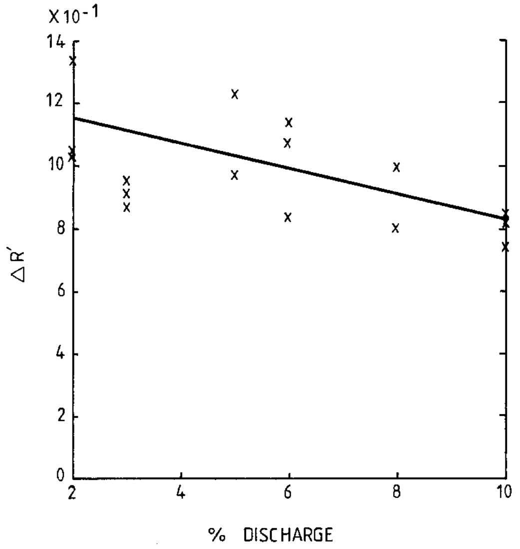

Fig. 3. The variation of ΔR from Fig. 2 with state-of-charge after a 24 h open circuit period.

where s represents the percentage discharge in the limited range down to 90% charged. The Pearson Correlation Coefficient for the above relationship is -0.57.

Table 3 shows the values of the high frequency resistance in this limited range and it is clear that if a value of R_{10k} equal to 1.36 Ω is fixed as a maximum, then, the test protects against unacceptably high resistances outside two standard deviations within the cell.

It should be emphasised that our 'best test' is somewhat contrived since the difficulty of arranging for a minimum 24 h stabilization period after any use is unsurmountable. The test would, however, provide a suitable state-of-charge and quality check on undischarged cells when the 24 h requirement is clearly achieved.

Acknowledgements

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Table 3. The variation of the cell high frequency (10 kHz) resistance value, with state-of-charge

Resistance at 10 kHz (Ω)	*State-of-charge* (%)
0.943	98
0.906	98
0.887	98
0.925	97
0.896	97
0.877	97
0.998	95
0.92	95
0.947	94
0.935	94
0.906	94
0.993	92
0.979	92
0.996	90
0.993	90
1.051	90
0.959	90
0.924	90

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