The impedance of the Li/SOCl₂, BrCl primary cell

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Impedance measurements show that the Li/SOCl₂, BrCl cell has, to a first approximation, a relatively simple electrical behaviour. The chemistry of the cell is itself complicated and together with the very low interelectrode separation, this leads to the impedance behaving erratically as charge is withdrawn. It seems to be impossible to identify a suitable state-of-charge test.

1. Introduction

We have recently reported on the impedance of the lithium–thionyl chloride cell [1]. This cell has a very high operating voltage level at high current loadings which makes it attractive as a high rate source of electrical energy. It has been reported that interhalogen compounds acting as co-depolarizers result in an enhanced voltage level during discharge [2–4] and an improved resistance to abuse due to the combination of bromine species with product sulphur and an improved breakdown of the cathode film. Recently cells containing the mixed depolarizers have become established as energy sources. This note records the impedance characteristics of a typical cell.

2. Experimental details

The cell used was type BCX72 (Electrochem. Industries Inc., New York) which was nominally capable of delivering 1 Ah at a current of 1 mA with an average load voltage of 3.6 V from an initial open circuit voltage of 3.9 V. The cell was in disc format (7.54 mm thick: 25.35 mm diameter) and weighed 13 g. Details of the SOCl₂:BrCl electrolyte solution are given in a paper from the manufacturers laboratory [2, 3].

The experimental technique by which the impedance of the cell on open circuit conditions was estimated after various amounts of charge had been removed, has been described [5]. In this case the charge was removed at the 40 h rate (25 mA).

3. Results

Figure 1 shows the impedance locus for the new (undischarged) cell. It consists of a high frequency semicircular shape which goes into a further loop which returns to the real axis at low frequency.

Discharging produced shapes which were broadly similar at the different states-of-charge investigated (Figs. 2 and 3). It was found that charge in excess of the nominal (20%) could be obtained from the cell. The shape generated still exhibits the higher frequency semicircle, but, the tail is of very complex form (Fig. 4).

4. Discussion

There are a number of possible mechanisms which can be invoked to generate an impedance locus similar to that of Fig. 1 and for the cell at succeeding states of charge. We have examined the totality of these and none completely describe the system throughout the whole range. The best 'universal' fit is that of mixed rate-control by charge-transfer and a diffusion process between narrowly spaced electrodes. We have fully discussed this model in connection with the HgO/Zn cell [6]*. Figures 1–4 show examples of this approximate fit using the values of

$$\xi = \left(\frac{2a^2}{D}\right)^{1/2} \qquad (1)$$

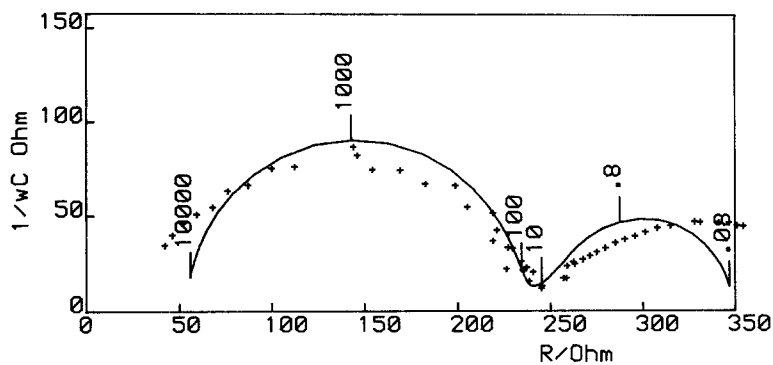* Note: In the earlier paper [6] a printing error was left uncorrected: Equation 1 given here is correct.

Fig. 1. Impedance locus generated by a Li/SOCl$_2$, BrCl cell. Fully charged. experimental points, calculated (see discussion).
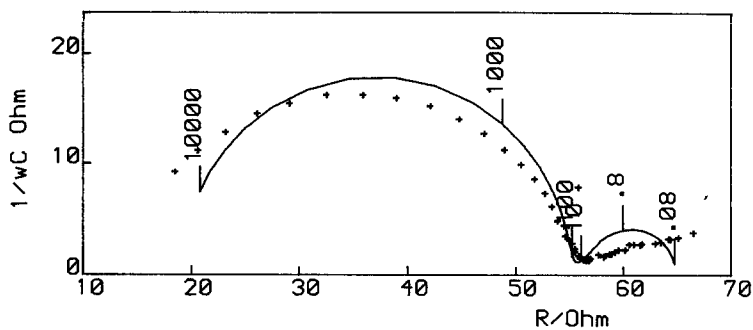
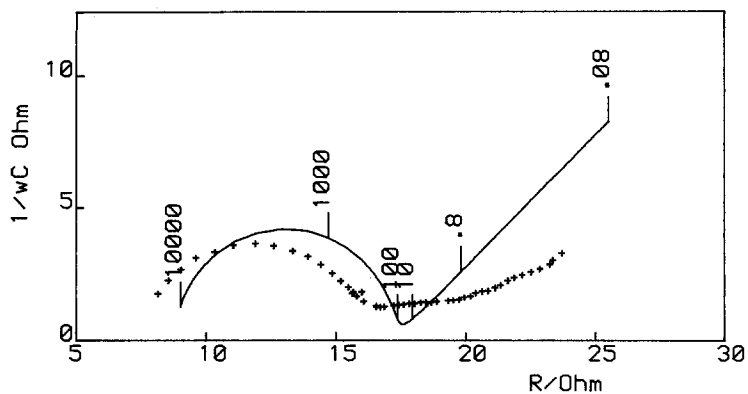Fig. 2. As Fig. 1, but containing 99% nominal capacity.

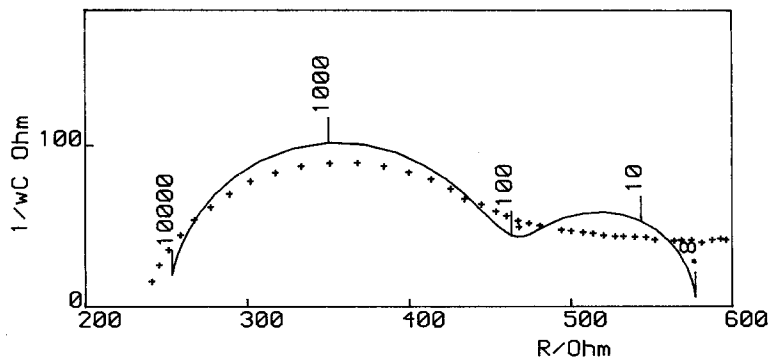Fig. 3. As Fig. 1, but containing 70% nominal capacity.

Fig. 4. As Fig. 1, but over-discharged by 20%.

Table 1. The parameters obtained by the computations are shown in Table 1 for the mathematical least squares fitting on the resistive data.

% Charge	$R_{\Omega}(\Omega)$	$\theta\,(\Omega)$	$C_{DL}(\mu F)$	$\sigma\,(s^{-1/2})$	$\xi\,(s^{1/2})$
100	54.17	178.8	0.90241	98.82	1.168
99	19.17	35.8	2.0554	8.837	1.118
90	23.25	92.130	2.925	5.427	10
70	8.814	8.390	12.358	5.831	10
40	33.87	48.91	3.7052	238.1	0.7648
20	60.54	58.33	3.2792	211.8	1.23
0	93.63	130.9	0.45261	152.8	0.1160
−20	251.6	196.2	0.78860	563	0.23

where a is the interelectrode spacing, D is the diffusion coefficient of the diffusing species and other parameters shown in Table 1 (symbols have their conventional meanings).

As the roughness factor in these cells was unity, this suggests to us that the behaviour of the cell is dictated by the anode which must be relatively smooth *vis-à-vis* the cathode which is adsorbed onto carbon black and is porous in character.

The magnitudes of the modelled circuit elements show no well-defined trends – with the exception of the 'electrolyte' resistance parameter which as shown in Fig. 5 shows a progressive increase after about 10% of the available charge has been withdrawn. Attempts to 'normalize' the parameters by compensating for increased electrode area or electrolyte resistance using double layer capacitance or electrolyte resistance did not produce satisfactory relationships with the state-of charge.

With the exception of statements that the bromides and chlorides of lithium are formed there are no published reaction sequences for the electrochemical behaviour of this cell on discharge [8]. What is clear is that the BrCl (rather than chlorine which might be produced as a by-product, or by ionization of the BrCl) must react with the lithium. It has been suggested [3] that the reacting species might be a complex formed between BrCl and SOCl₂. This at least would explain the higher reversible potential (3.9 V) of this particular cell than is obtained with the Li/Br₂ cell which has an OCV of 3.5 V. There is no doubt that the cell reactions are complex, and this is reflected in the fit of the simple model to the cell behaviour. A critical examination of the calculated behaviour shown in Figs. 3, 4, and 5 forces one to the conclusion that the model is only correct to a first approximation.

In general the Li/BrCl, SOCl₂ cell has two advantages over the Li/SOCl₂ cell: one is the higher potential and the other is the enhanced safety [2]. This latter aspect is apparently derived from the by-product bromine which combines with by-product sulphur and avoids the potentially explosive character of the lithium–sulphur combination.
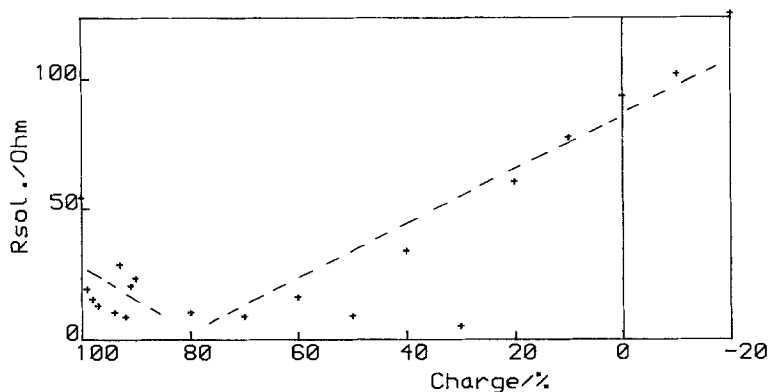

Fig. 5. R_{Ω} plotted against state-of-charge.

The interplay of these reactions together with the complex build-up of lithium chloride species at the anode serve to produce a very convoluted behaviour. The impedance behaviour is more complex than that of the $Li/SOCl_2$ [1] cell and the difference must reside in the addition of BrCl.

We can conclude that the cell impedance is controlled mainly by the anode, and that the very small interelectrode separation contributes to an erratic impedance behaviour as charge is withdrawn from the cell.

The resistance parameter of Fig. 5 was the only parameter to provide some indication of the state-of-charge, but we believe that it can not be used as the basis for an accurate state-of-charge measurement, especially at states-of-charge between 100% and 90%.

References

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