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THE FARADAIC IMPEDANCE OF THE LITHIUM–SULPHUR DIOXIDE SYSTEM. A FURTHER EXAMINATION OF COMMERCIAL CELLS

N F HARMAN*, N A HAMPSON and P J. MITCHELL

Chemistry Department, Loughborough University of Technology, Loughborough, Leics, LE11 3TU (U K)

D EYRE

Crompton Parkinson Ltd, Vidor Works, South Shields, Tyne & Wear (U K)

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Summary

Impedance measurements have been made on Li/SO_2 (C) cells (manufactured by a U.K. Company) at various states of charge. The individual electrode impedances have been measured against a lithium reference electrode using a transfer function analyser. A model for the cathode behaviour is presented. From the values of the analogue circuit elements it is shown that there is a film on the undischarged cathode which initially impairs the behaviour. Over a large range of residual capacities the charge transfer resistance is relatively constant. There is evidence for the presence of adsorbed intermediates at the carbon matrix.

Introduction

The lithium–sulphur dioxide cell is one of the most successful of the newly developing lithium primary systems. It is capable, for example, of a very high energy density (330 W h kg^{-1}) coupled with a very long shelf life. Recently, we undertook an impedance study of small Li/SO_2 (C) cells (LO 32S units manufactured by Duracell Batteries, Ltd.) containing an acetonitrile-based electrolyte solution over a range of states of charge.

The cell behaviour was described on the evidence of a relatively simple impedance locus (out-of-phase component of the electrode impedance displayed against the in-phase component). The assumption that the lithium

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*Author to whom correspondence should be addressed

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was the more irreversible of the two electrodes was considered to be correct, since the impedance data conformed to a simple Randles conversion for charge transfer followed by diffusion in solution. Moreover, the changes in the impedance with reactant concentration varied in the manner expected for a system in which the lithium dominated the cell behaviour Specifically, from the change in the charge transfer resistance, θ (corrected for the effective anode area), as the cell discharged, an estimation of the charge transfer coefficient for the Li^+/Li exchange in the acetonitrile–SO_2 solution (0.37) was made (The product θC_L, of the apparent charge transfer resistance θ and the double layer capacitance C_L, was found to be a very good assessment of the residual capacity of the cell [1, 2])

It has since emerged, from monitoring the performance of other commercially produced $Li–SO_2(C)$ cells, that the previously reported behaviour [1] is not consistent throughout the range of manufacturers For example, differences in the impedance of comparable units produced by Crompton Parkinson Ltd included an elongation in the charge transfer semicircle This, together with the appearance of an additional shape in the complex plane plot, suggested that the controlling mechanism of these cells' behaviour might be consistent with a porous electrode at which adsorption was a significant process It was decided that the most convenient way to obtain a detailed study of the system was to incorporate a third (reference) electrode within the cell and so obtain the component (impedance) behaviour of both electrodes This paper records the results of such a study

Experimental

The experimental procedures for obtaining the impedance data, isolating the component processes, and matching with numerical values have been described previously [3, 4].

The cells used were Vidor Eternacell, size G20 (capacity 7.5 A h, rated load 1000 mA) specially modified to contain a lithium reference electrode. This was introduced into the cell via glass seals on the plane end of the cylindrical unit so that it lay tightly sandwiched between the anode and cathode but isolated from both by the microporous polypropylene separator. As such, it formed a rather complex thin layer cell

The cells were discharged galvanostatically at 1 A for periods of 30 min and allowed to equilibrate for three days before any impedance measurements were made.

The impedance spectra of the anode with respect to the reference electrode, and the cathode with respect to the reference electrode, were obtained after each discharge step. In this way, 15 states-of-charge were investigated In order to confirm that the third electrode was behaving as a true reference electrode, the two spectra were added together point by point, vectorially, and compared with the impedance of the whole cell. Figure 1 for the undischarged cells shows this to be the case.

Results and discussion

Figure 1 shows that the anode and cathode impedances which go to form the total cell impedance are of the same order of magnitude although, in general, that of the cathode was somewhat greater. Thus these particular cells were rate-controlled by both anode and cathode and it is not possible to ignore either electrode in a consideration of the cell behaviour.

The impedance plots of the cathode with respect to the reference were fitted to a model using the Taylor theorem approach [5]. The model consisting of a Randles circuit modified for electrode roughness and porosity, and used by Hughes [1], did not give a sufficiently good fit in the present cases. The best fit was found by modifying this model to incorporate adsorption on the cathode surface [6]. The presence of a dielectric film on the surface [4] was represented by a series capacitance C_s. It was not found necessary to associate a resistance parallel with C_s in order to decompose our results (for an electrode perturbation greater than the 3 mV used in these experiments or for frequencies approaching d.c. operation, this would have been necessary). A series inductance was also added to account for effects which arise from the cell geometry and internal connections. A circuit analogue for this model is shown in Fig. 2.

The isolation of the 9 circuit elements demanded that as many frequency values as (reasonably) possible be investigated. We have used 60, which gives sufficiently precise values of the components to be estimated, with an acceptable least squares variance of the computed values.

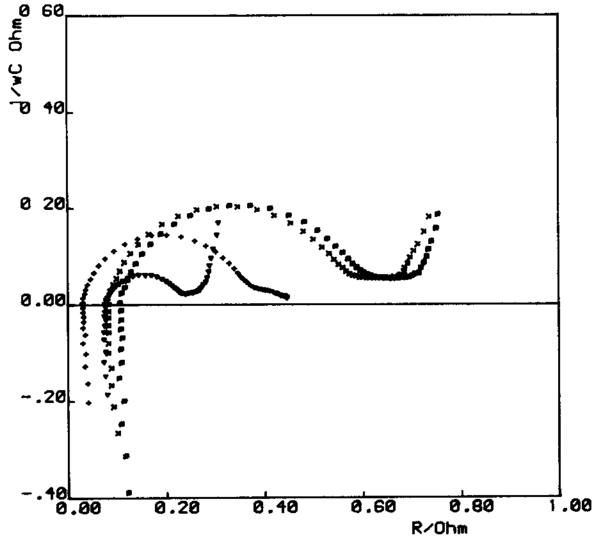

Fig 1 Cell and electrode impedances +, Li/Ref, ▽, C/Ref, ×, Li/C cell, □, impedance sum Li/Ref + C/Ref (Slight difference from link cell impedance due to experimental self perturbation)

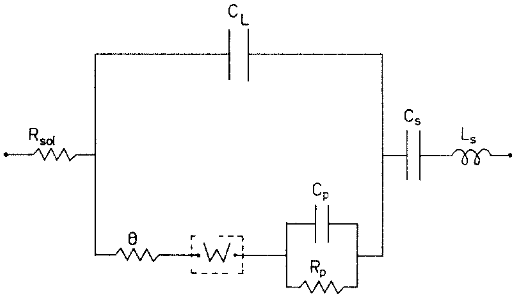

Fig 2 The analogue for the carbon electrode θ, charge transfer resistance, C_L, double layer capacitance, R_{sol}, solution resistance, W, Warburg impedance, C_S, film capacitance, L_S, contact inductance, C_P, "intermediate" reaction capacitance, R_P, "intermediate" reaction resistance

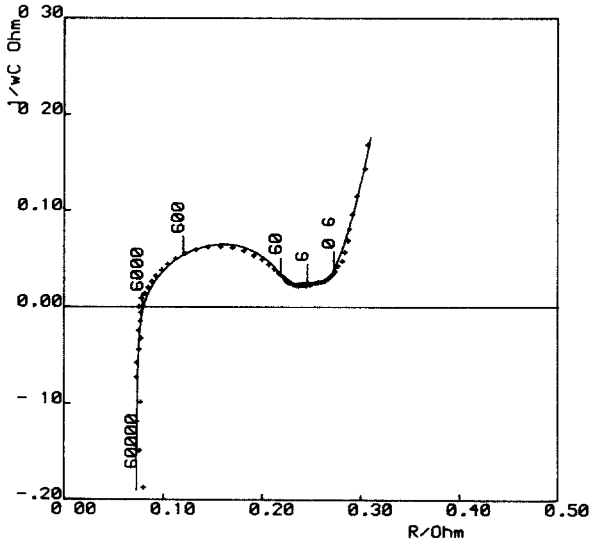

Fig 3 Typical curve fitted to the experimental data for the cathode +, experimental points, ——, computed curve

Figure 3 shows a typical example of the experimental data with a fitted curve. The validity of the model was confirmed by the excellence of the fits obtained for all states of charge.

Computed equivalent circuit component values are given in Table 1

The variations of the components as charge is withdrawn from the cell is interesting and yields information regarding the cathodic processes. The double layer capacitance, C_L, has an initially low value corresponding to the presence of an intruding film of lithium dithionite on the surface This masking film very rapidly breaks on discharge to yield a relatively constant, active surface The value of C_L rises to a maximum of $\sim 4 \times 10^{-2}$ F just before the cell is completely discharged, then falls to a value of 3×10^{-3} F. This great increase in electrode capacitance towards the cell exhaustion point

TABLE 1

Charge removed (A h)	R_{sol} ($10^2\ \Omega$)	θ (Ω)	θC_L (10^3 F)	σ ($10^2\ \Omega\ s^{-1/2}$)	Roughness factor (γ)	C_s (F)	L_s (10^8 H)	R_p ($10^2\ \Omega$)	C_p (F)	θC_L (10^4 S)
0	3 3	0 62	0 5	13 4	0 620	33 0	68 3	13 5	0 1	3 6
0 5	5 5	0 11	8 5	3 6	0 460	16.0	68 0	1 5	2 1	9 9
1 0	7 5	0 05	14 0	2.0	0 540	14 5	56 0	1 0	0 5	7 5
1 5	6 6	0 07	8 5	2 4	0.685	16 5	57 2	1 5	0 3	6 0
2 0	6 1	0 07	9 5	2 2	0 665	15 0	59 2	1 5	0 55	7 2
2 5	6 7	0 08	3 0	3 0	0.885	18 0	65 0	3 0	0 01	2 7
3 0	6 2	0 07	10 0	2.8	0 700	18.0	53 5	1 5	0 7	7 3
3 5	8 5	0 05	10 0	2 2	0 710	18 5	54 4	1.0	0 8	6 0
4 0	6 4	0 05	10.5	2 8	0 700	19 0	54 4	1.0	1 2	6 1
4 5	6 6	0 035	12.0	2 0	0 685	20 5	56 4	0 5	2 3	5 1
5 0	7 1	0 06	11 0	2 9	0 680	17 5	53 5	1 5	1 5	7 2
5 5	6 8	0 03	16 5	2 2	0 640	21 5	55 2	1 0	2 7	4 7
6 0	6 3	0 06	16.5	4 4	0 585	19 0	62 2	3 0	1 7	10 1
6 5	6 4	0 02	41 0	4 8	0 475	21 5	61 2	2 0	7 3	7 0
7 0	8 2	0 035	3 0	29 4	0 700	63 0	51 8	31 0	1 6	1 1

possibly indicates the breakup of the cathode — the intrusion into the inner regions of the carbon crystallites leading to the final passivation of the electrode This picture is supported by the parameters C_s, R_p, C_p, which all indicate the break-up of the cathode structure as available charge in the cell is exhausted.

The charge transfer resistance, θ, is complimentary to the series and double-layer capacitances C_s and C_L Initially high, indicating the presence of a retarding film, θ rapidly falls on the removal of charge from the cell, becoming more or less constant at 0.05 Ω throughout the whole of the region of useful discharge. This, again, suggests that the initially protective film is readily removed and that the reduction of SO_2 occurs at a surface of approximately constant active area The Warburg coefficient, σ, which for

$$O + ne \rightleftharpoons R$$

is·

$$\sigma = (\sqrt{2}/2)(RT/n^2F^2)[(C_O\sqrt{D_O})^{-1} - (C_R\sqrt{D_R})^{-1}] \tag{1}$$

provides further confirmation, in the present system, in which $Li_2S_2O_4$ is fairly insoluble and the other reactants are in excess, it becomes

$$\sigma = (1/\sqrt{2})(RT/n^2F^2)(AC_R\sqrt{D_R})^{-1} \tag{2}$$

where C_R and D_R represent the concentration and diffusion coefficient, respectively, of $S_2O_4^{2-}$ and A is the effective area of the electrode. In the present case the diffusing area of the electrode is, initially, relatively low and on discharge it rises to a fairly constant value

The inductive component of the electrode impedance is clearly a complex quantity This, in our opinion, is most likely linked to physical geometric modifications within the cell which occur as a consequence of volume changes within the carbon This material is disposed on an aluminium mesh and it is reasonable to ascribe the major part of the inductive component to this source.

The need for the parallel (R_p–C_p) circuit in the analogue representation is interesting, for it was not needed in the earlier investigation [1]. It represents the presence of some process in the cathode reaction which exerts a significant current control in the experimental frequency range The presence of an adsorbed intermediate such as SO_2^- or SO_2^{2-} at the electrode, or reactions of the type

$$SO_2 + e^- \longrightarrow SO_2^-{}_{ads} \tag{3}$$

$$SO_2^-{}_{ads} + SO_2^-{}_{ads} \longrightarrow S_2O_4^{2-} \tag{4}$$

or

$$SO_2 + e^- \longrightarrow SO_2^-{}_{ads} \tag{5}$$

$$SO_2^-{}_{ads} + e^- \longrightarrow SO_2^{2-}{}_{ads} \tag{6}$$

$$SO_2 + SO_2{}^{2-}{}_{ads} \longrightarrow S_2O_4{}^{2-} \qquad (7)$$

would imply the observed reaction model. It is not possible in this investigation, however, to decide which of these (or others) is the appropriate mechanism. The interest lies in the qualitative differences between this and the previous investigation which indicate significant behaviour differences among the various available carbons (and catalysed carbons). A final point which arises from the work is that, while the product θC_L was a useful parameter for residual capacity assessments for certain cell types, it was very insensitive in this case. (Table 1).

Conclusions

(i) The impedances of both anode and cathode are of the same order.

(ii) The cathode could be represented by a complex model based on charge transfer and diffusion, with allowance for adsorption and electrode films.

(iii) At high frequencies the geometry of the system gives rise to an inductive branch in the impedance locus.

(iv) Initially, the cathode is covered by a thin layer, probably of $Li_2S_2O_4$ This is partially removed on discharging.

(v) There is evidence of serious cathode disruption when the cell has been drained of useful charge.

(vi) There is strong evidence for adsorbed intermediates on the porous carbon cathode matrix.

Acknowledgement

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