The Faradaic impedance of the lithium-sulphur dioxide system. A kinetic interpretation

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Impedance measurements have been made on $Li/SO_2(C)$ cells containing an acetonitrile-based electrolyte in a range of states from newly assembled to completely discharged. The cell behaviour can be explained if it is assumed that the lithium is an irreversible electrode and that the SO_2 electrode is reversible. The nominal exchange current density on the lithium is $0.7 \, mA \, cm^{-2}$ and $\alpha \simeq 0.37$ for the cell $Li/LiBr(2.35 \, mol \, dm^{-3}), CH_3CN, S_2O_4^{-}|SO_2(6.25 \, mol \, dm^{-3})C$

1. Introduction

The lithium–sulphur dioxide system is of importance in the contemporary energy storage scene because of its very high energy density, $330 \, Wh \, kg^{-1}$, and very long shelf life. Consequently the development of the system has reached a relatively high level of sophistication. In this system the reactivity of lithium metal with water makes it necessary to use non-aqueous solvents and to hermetically seal the batteries. Electrode separation is usually at a minimum in keeping with fabrication and electrolyte solution balance and the need to have a medium in which the SO_2 gas can dissolve. One method of achieving these conditions is to use a rolled-up construction with a helical format of the three layers, anode, electrolyte and cathode. It is clearly necessary to physically separate the anode and cathode using an inert separator and also to provide a current collector for the cathode. One typical construction is to use a sheet of lithium metal as the anode and SO_2 in the form of an acetylene black as the cathode. In these circumstances with the large surface available for the cathodic reaction (blacks typically have particle sizes of 10^2 to 10^3 Å) this electrode behaves reversibly. The consequences of this arrangement is that the Li/SO_2 system provides a system in which the lithium electrode can be studied. Data on the lithium electrode in organic solvents are scarce and therefore it was considered of some interest to present the results of an investigation of the Li/SO_2 cell LO32S manufactured by the Mallory Company.

2. Experimental procedure

The experimental procedure for obtaining impedance data and abstracting the kinetic information and system characteristics have been described previously [1, 2]. The cells used in the investigation were type LO32S of 1.65 cm diameter and 3.4 cm high. The dimensions of the lithium anode were 1.91 cm wide and 15.2 cm long. The cell contained 2.8 g of SO_2 which was partially adsorbed on carbon (acetylene black of mean particle size 425 Å; ~ 0.4 g; specific surface $60 \, m^2 \, g^{-1}$). The area of the cathode was about 10^5 times that of the anode. Under these conditions the contribution of the cathode to the overall cell impedance can be regarded as minimal and can certainly be neglected particularly at high frequency when the reaction layer is thin so that the effective electrode area tends to the true value. The cell electrolyte was LiBr ($2.35 \, mol \, dm^{-3}$) in acetonitrile.
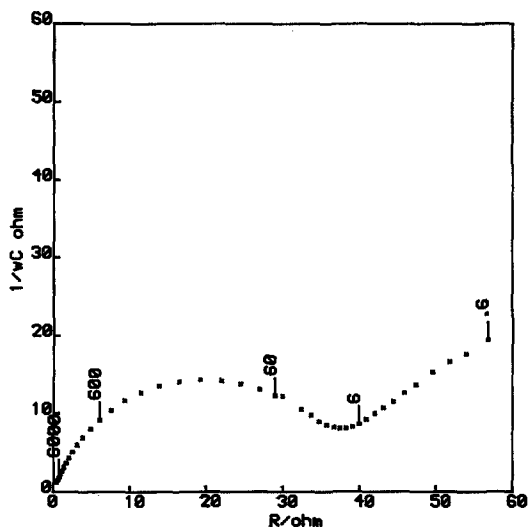
Impedance measurements were made on cells

Fig. 1. Impedance loci for the Li/SO$_2$ cell (type LO32S). Freshly assembled. Room temperature.

Fig. 3. As Fig. 2 but 800 mA h.

poised at the reversible cell voltage. Cells were investigated in the fully charged (new) state and after definite known amounts of charge had been withdrawn from the cells for which the nominal capacity was 10^3 mA h. Data were satisfactorily matched to a Randles model in the frequency range down to 0.6 Hz.

3. Results and discussion

Figure 1 shows the impedance data for a Li/SO$_2$ cell from which no charge had been withdrawn. This plot consists of a very well-defined semi-
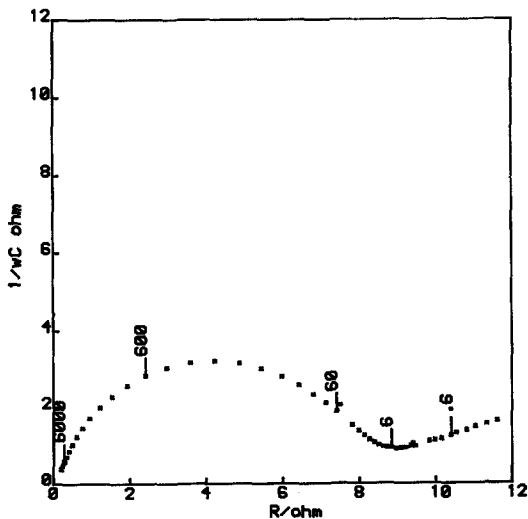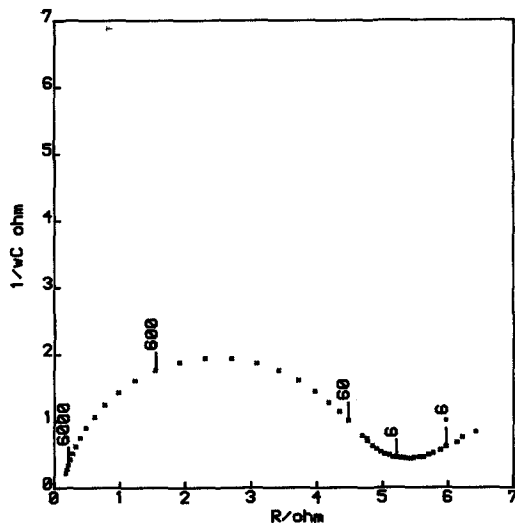
circle which was flattened somewhat and which degenerated into a well-defined Warburg line. The charge transfer resistance, θ, double-layer capacitance, C_L, Warburg slope, σ, and solution resistance, R_Ω, can be readily found by matching the impedance of the cell using the Taylor theorem approach [3]. The results are shown in Table 1 together with those corresponding to other data relating to cells from which varying amounts of charge have been withdrawn (Figs. 2, 3 and 4). The quality of the kinetic data are illustrated by Figs. 5–9 which show the behaviours of the kinetic analogues from Table 1 compared with the experimental points. The data are not

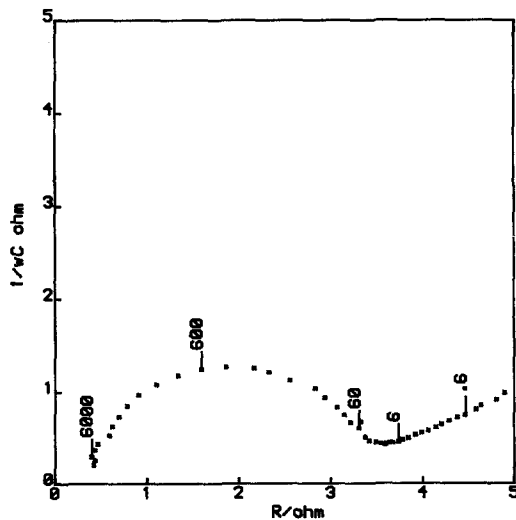Fig. 2. As Fig. 1 but after withdrawal of 50 mA h.
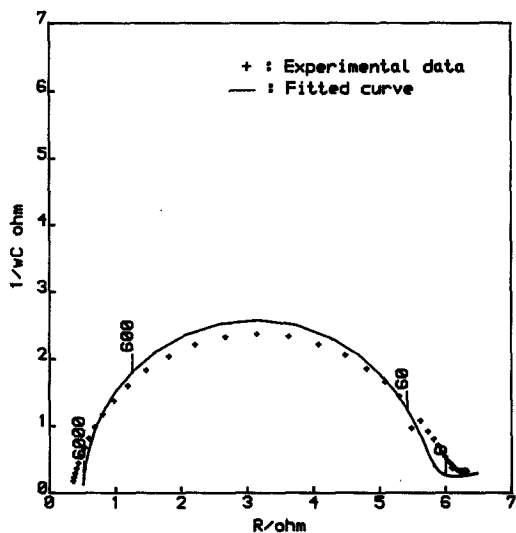
Fig. 4. As Fig. 2 but 900 mA h.

Fig. 5. As Fig. 2 but 80 mA h. The solid line represents the calculated locus.
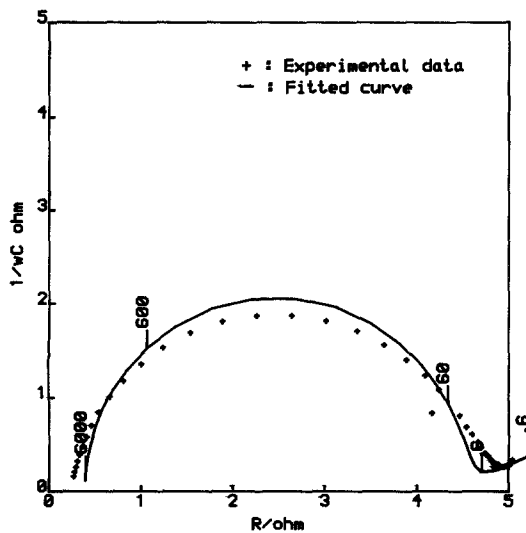

Fig. 7. As Fig. 5 but 200 mA h.

the exact fit which would be expected for the behaviour of a plane smooth electrode at which a redox reaction is occurring. There are several reasons which might account for this fact.

First there is the fact that the lithium electrode is not ideally planar but rough [3]. The extent of this roughness (expressed, for example, as the depth of microgrooves) in comparison with the characteristic length, $(D/\omega)^{1/2}$, where D is the diffusion coefficient of the electroactive species, may vary from porous (when this microgroove depth ratio is greater than 3) to flat. This in itself would lead to an elongation of the semicircle.

Table 1 shows that the double-layer capacitance steadily increases with quantity of charge removed from the cell and after about 25% of the recoverable charge has been removed becomes approximately constant. We interpret this behaviour as a pitting attack on the plane electrode giving rise to well-defined facets, though the relationship between these and the grain structure of the metal is uncertain. With the withdrawal of further charge from the cell the facets grow with consequential increase in surface which are proportional to the charge withdrawn. This is true until overlap of the facets occurs when further removal of
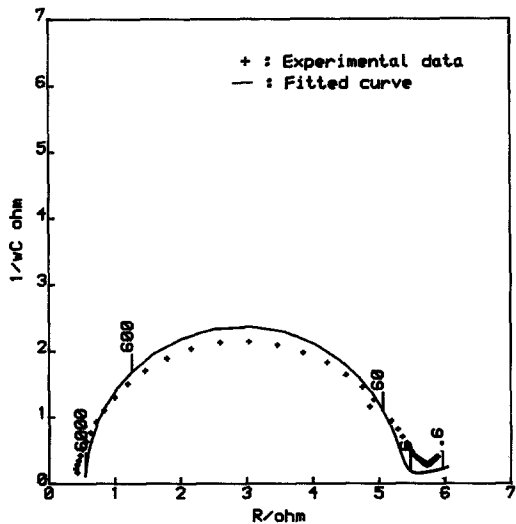

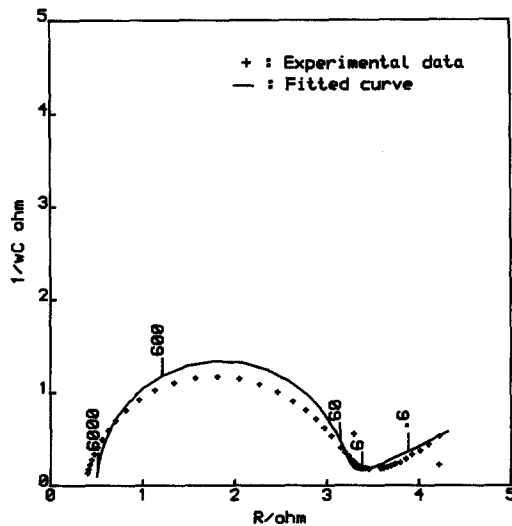
Fig. 6. As Fig. 5 but 100 mA h.

Fig. 8. As Fig. 5 but 400 mA h.

Table 1. Kinetic parameters extracted from the impedance data

Dischg. (%)	Rsol. (Ohms)	Theta (Ohms)	D.L. Cap (Farads)	Sigma $(s^{-1/2})$	Error ($\pm$)
Battery No. 2					
0	0.1848E 01	0.2999E 02	0.2628E−04	0.5012E 02	0.8950E 00
1	0.1225E 01	0.2086E 02	0.3369E−04	0.3359E 02	0.6582E 00
2	0.7934E 00	0.9931E 01	0.4418E−04	0.1417E 02	0.3411E 00
3	0.6450E 00	0.8141E 01	0.4905E−04	0.1143E 02	0.2645E 00
4	0.7459E 00	0.1223E 02	0.5274E−04	0.1523E 02	0.3859E 00
5	0.5346E 00	0.7237E 01	0.6855E−04	0.5211E 01	0.2707E 00
6	0.4931E 00	0.6464E 01	0.7152E−04	0.5572E 01	0.2677E 00
7	0.4624E 00	0.5906E 01	0.7585E−04	0.5112E 01	0.2516E 00
8	0.4274E 00	0.5181E 01	0.8374E−04	0.3691E 01	0.2169E 00
9	0.4031E 00	0.5503E 01	0.8716E−04	0.3288E 01	0.2238E 00
10	0.3599E 00	0.4897E 01	0.9111E−04	0.3023E 01	0.1860E 00
20	0.2734E 00	0.3711E 01	0.1161E−03	0.1889E 01	0.1317E 00
30	0.2339E 00	0.3049E 01	0.1344E−03	0.1185E 01	0.1010E 00
40	0.2249E 00	0.3275E 01	0.1315E−03	0.1409E 01	0.1296E 00
50	0.9966E 00	0.3629E 01	0.1264E−03	0.1718E 01	0.1166E 00
60	0.2455E 00	0.3625E 01	0.1404E−03	0.1549E 01	0.1138E 00
70	0.3028E 00	0.2661E 01	0.1349E−03	0.1452E 01	0.8503E−01
80	0.3213E 00	0.4290E 01	0.1034E−03	0.3113E 01	0.1276E 00
90	0.5016E 00	0.2888E 01	0.1219E−03	0.1788E 01	0.1756E 00
100	0.1369E 01	0.3476E 01	0.8380E−04	0.1467E 02	0.4526E 00
Battery No. 3					
0	0.1601E 01	0.3201E 02	0.4919E−04	0.2353E 02	0.1239E 01
1	0.8320E 00	0.1654E 02	0.6883E−04	0.1195E 02	0.5835E 00
2	0.5765E 00	0.1133E 02	0.8098E−04	0.5183E 01	0.3815E 00
3	0.4354E 00	0.7742E 01	0.9077E−04	0.2684E 01	0.2467E 00
5	0.3708E 00	0.7744E 01	0.1086E−03	0.3340E 01	0.2052E 00
6	0.3366E 00	0.6604E 01	0.1142E−03	0.2105E 01	0.1963E 00
7	0.4714E 00	0.6337E 01	0.1173E−03	0.1554E 01	0.1745E 00
8	0.5243E 00	0.5233E 01	0.1209E−03	0.1408E 01	0.1419E 00
9	0.4538E 00	0.5735E 01	0.1251E−03	0.1605E 01	0.1662E 00
10	0.5491E 00	0.4740E 01	0.1263E−03	0.1256E 01	0.1338E 00
20	0.3826E 00	0.4053E 01	0.1358E−03	0.1821E 01	0.1109E 00
30	0.2244E 00	0.3426E 01	0.1455E−03	0.1099E 01	0.1135E 00
40	0.4978E 00	0.2641E 01	0.1535E−03	0.1571E 01	0.1387E 00
50	0.4765E 00	0.4132E 01	0.1457E−03	0.1472E 01	0.1146E 00
60	0.2795E 00	0.3686E 01	0.1575E−03	0.1455E 01	0.1116E 00
70	0.2274E 00	0.2282E 01	0.1568E−03	0.1728E 01	0.6725E−01
80	0.2804E 00	0.3292E 01	0.1316E−03	0.2257E 01	0.1089E 00
90	0.6329E 00	0.2738E 01	0.1484E−03	0.1441E 01	0.9372E−01
100	0.2040E 01	0.3528E 01	0.7121E−04	0.1508E 02	0.3735E 00

charge, although renewing the surface, does not yield an increase in surface area. If the double-layer capacitance is taken as a measure of surface area (which is reasonable since the electrolyte solution is concentrated) then the observed behaviour is to be expected. A measure of the exchange current, i_o, is obtained as θC_L. The charge transfer resistance, θ, changes with the amount of charge delivered by the cell as shown by Fig. 10 and the area corrected relationship obtained by plotting $\log \theta + \log CL$ versus $\log(\%D)$ as is shown by Fig. 11 in deference to the exchange current equation

$$i_o = ZFk_0 C_0^{1-\alpha} C_R^{\alpha} = RT/ZFi\theta \qquad (1)$$

where Z is the valence charge number, k_0 is the specific equilibrium rate constant and α is the charge transfer coefficient.
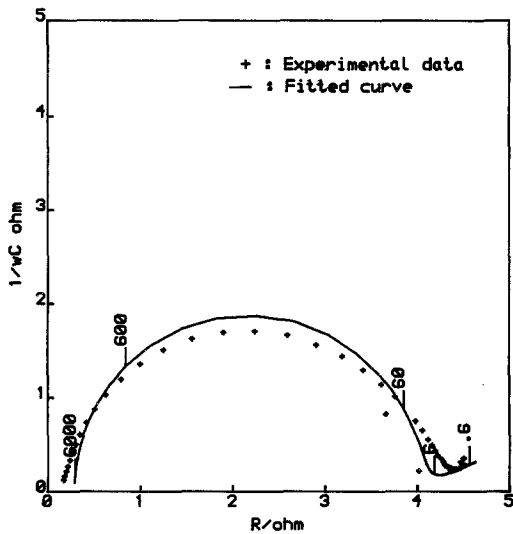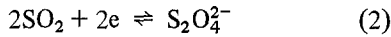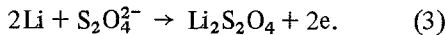
The kinetics of the Li/SO$_2$ cell arise from the

Fig. 9. As Fig. 5 but 600 mA h.

equations connecting the reversible electro-chemistry of the carbon cathode

$$2SO_2 + 2e \rightleftharpoons S_2O_4^{2-} \qquad (2)$$

with the irreversible anodic reaction

$$2Li + S_2O_4^{2-} \rightarrow Li_2S_2O_4 + 2e. \qquad (3)$$

The lithium dithionite dissolves only to a certain very limited extent in the electrolyte solution,

LOG(θ)

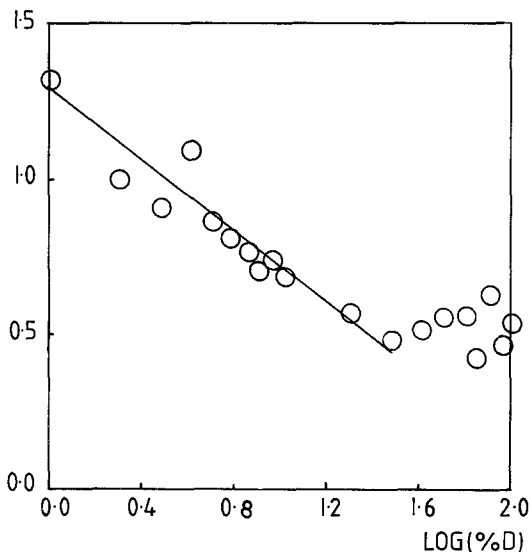Fig. 10. The relationship between θ and charge withdrawl (percentage of nominal capacity);
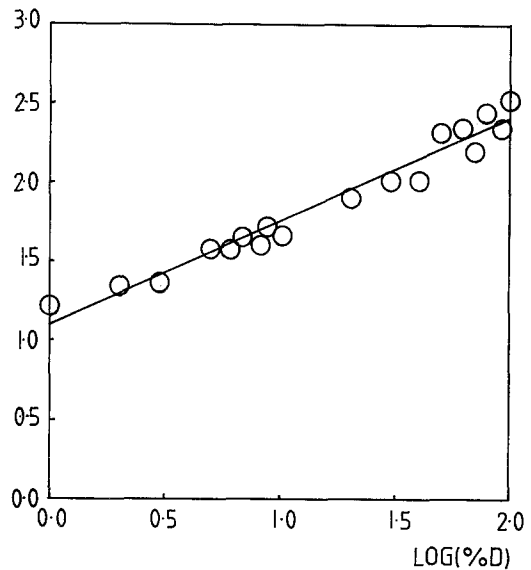

Fig. 11. As Fig. 10 but corrected for area increase.

and, there is some evidence that a solid lithium dithionite phase may be produced near the lithium electrode [4]. This evidence is reinforced by impedance measurements at very low frequency when the Warburg line becomes steeper than 45° in keeping with the conclusion that a series capacitance term must be included due to the presence of a dielectric. A situation equivalent to this one which has been fully investigated in an aqueous sulphuric acid solution arises with a partially discharged lead dioxide electrode [5]. Here the $PbSO_4$ effectively behaves as a capacitive contribution to the cell impedance at low frequency.

From Equation 3 we can write

since

$$i_o = 2F\underset{\leftrightarrow}{k}C_{LiS_2O_4}^{1-\alpha} C_{Li}^{2\alpha} C_{S_2O_4^{2-}}^{\alpha} \qquad (4)$$

$$A = \frac{A}{C_L^0} \cdot C_L \qquad (5)$$

the cell exchange current becomes

$$I_o = 2F \frac{A^0}{C_L^0} C_L \underset{\leftrightarrow}{k} C_{LiS_2O_4}^{1-\alpha} C_{Li}^{2\alpha} C_{S_2O_4^{2-}}^{\alpha} \qquad (6)$$

where $\underset{\leftrightarrow}{k}$ is the specific equilibrium rate constant, A is area and A^0 is the area before charge is withdrawn.

It is certain that the very major part of the lithium dithionite produced is removed progress-
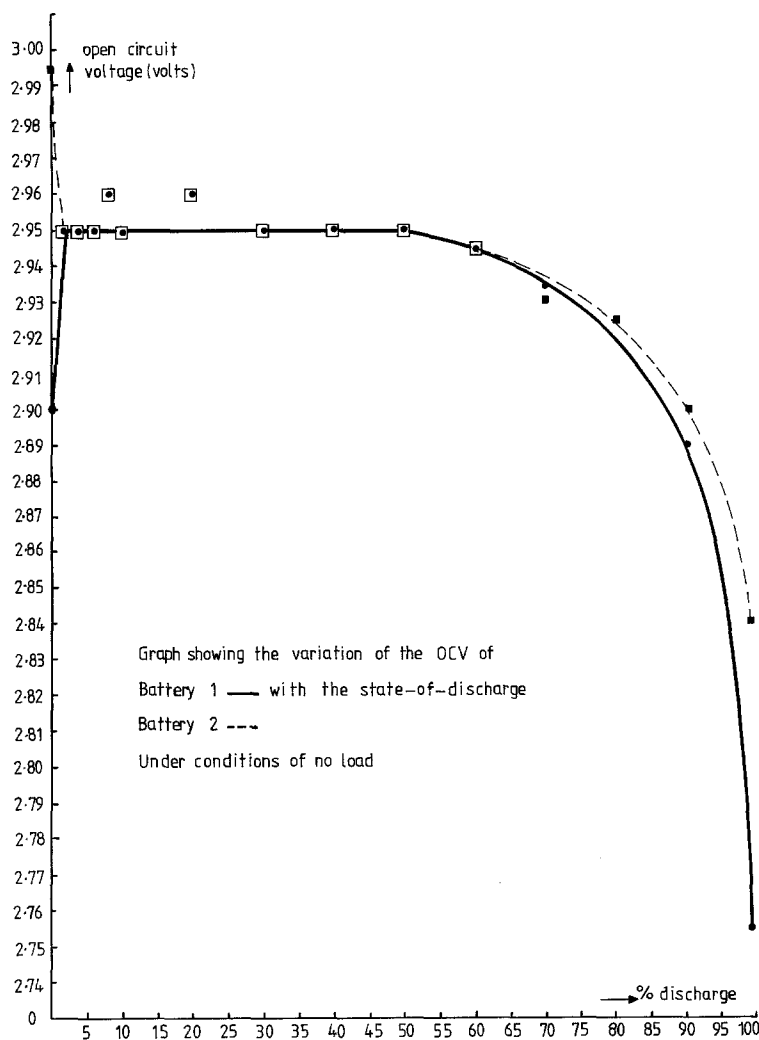
Fig. 12. The relationship between the cell equilibrium potential and the charge withdrawn.

ively by precipitation as it is formed [4] and as a first approximation we have, remembering that C_{Li} is conventionally unity for a solid metal and using Equation 1,

$$\frac{1}{C_L}\theta = \frac{2^2 F^2}{RT}\frac{A^0}{C_L^0}kC_{S_2O_4^{2-}}^{\alpha}. \quad (7)$$

For Equation 2 we can write

$$C_{S_2O_4^{2-}}/C_{SO_2}^2 = -\exp[(E_s - E_s^{\ominus})2F/RT] \quad (8)$$

where E_s is the potential of the SO_2 electrode and $E_s^{\ominus}$ is the standard potential.

We are unable to measure E_s since it is not possible to introduce a third electrode into the cell. However, we can connect $C_{S_2O_4^{2-}}$ with C_{SO_2}

accurately enough if we examine the equilibrium cell voltage curve corresponding to different amounts of charge withdrawn from the cell. This is shown in Fig. 12 and it can be seen that the cell potential varies little throughout the range in which 50% of the total available charge is removed from the cell. Consequently E_s in Equation 8 can be considered sufficiently constant for us to write

$$\frac{1}{C_L}\theta = BC_{SO_2}^{2\alpha} \quad (9)$$

where B is a constant.

A plot of $\log(C_L\theta)$ versus $\log C_{SO_2}$ should be a straight line with slope 2α. Since when the experimental sequence is commenced starting from a new cell the amount of charge available is

equivalent to SO_2 available, such a plot is equivalent (but opposite in sign) to plotting $\log(C_L\theta)$ against log (charge removed). Such a plot is shown in Fig. 11 to be a straight line with a slope of -0.75. It can be concluded that α is about 0.37 within the limits of uncertainty inherent in this argument.

The exchange current for the lithium electrode in the system:

$$Li|LiBr(2.35\,mol\,dm^{-3}), CH_3CN,$$

$$S_2O_4^{2-}|SO_2(6.25\,mol\,dm^{-3})C \qquad (10)$$
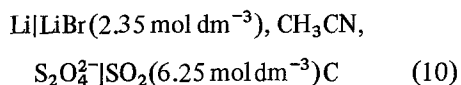
from Equation 1 was found to be 4.3 mA for the total superficial surface area ($0.7\,mA\,cm^{-2}$).

The magnitudes of the Warburg's slopes from Table 1 are interesting because when they are corrected for area the gradual increase in Warburg slope can be interpreted in terms of a decrease in $C_{S_2O_4^{2-}}$ in accordance with

$$\sigma = \frac{RT}{2^{1/2}Z^2F^2}\sum\frac{1}{C_iD_i^{1/2}}. \qquad (11)$$

We can conclude from this work that the lithium electrode in acetonitrile solution in conjunction with the SO_2/C electrode behaves as an irreversible electrode. The charge transfer coefficient is about 0.37 and the nominal exchange current density $0.7\,mA\,cm^{-2}$.

Acknowledgement

References

[1] N. A. Hampson and M. J. Willars, *Surface Tech.* 7 (1978) 247.

[2] S. Kelly, N. A. Hampson, S. A. G. R. Karunathilaka and R. Leek, *Surface Tech.* 13 (1981) 349.

[3] R. de Levie, 'Advances in Electrochemistry and Electrochemical Engineering, Vol. 6 (edited by P. Delahay and C. W. Tobias), Interscience, New York (1967) p. 329.

[4] J. Croft, Duracell Battery Co. (private communication).

[5] S. Kelly, N. A. Hampson, S. A. G. R. Karunathilaka and R. Leek, *Surface Tech.* 13 (1981) 362.