The temperature dependence of the electrochemistry of the lithium–sulphur dioxide system

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Value for the activation energy, ΔU^{act}, and the entropy change, ΔS, for the reaction $2Li + S_2O_4^{2-} \rightleftharpoons Li_2S_2O_4 + 2e$ in acetonitrile have been found to be 72 kJ mol^{-1} and $-0.3 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively, by a combination of impedance techniques and the use of a temperature-controlled environment on commercially manufactured cells which acted as constant volume containers.

1. Introduction

We have recently reported [1] on the electrochemical behaviour of the lithium–sulphur dioxide system. We then showed that the electrochemistry was apparently dominated in the high frequency domain by the charge transfer characteristics of the lithium electrode. The SO_2–carbon electrode system, which has an enormous surface area, behaved fairly reversibly and contributed relatively little to the impedance of the cell. We were able to estimate the exchange current density and charge transfer coefficient for the lithium exchange in the acetonitrile solution. The energetics of the processes and indeed of the whole cell reaction were not studied and, in fact, a search of the literature failed to yield any information on these aspects of the Li/SO_2 combination.

The Li/SO_2 cell is becoming very important in commerce and a number of industrial companies are in quantity production. Manufacture generally involves lithium foil (with a suitable separator) depolarized at a carbon electrode by SO_2 in acetonitrile; solution conductivity is obtained by addition of LiBr to the acetonitrile. It is of interest to estimate the energetics of the reaction which determine the very desirable low temperature properties of the cell discharge reaction. In this paper, we present results of experiments made in order to supplement the

original work and to extend the range of the investigation in the 'temperature plane'.

2. Experimental procedure

The cells used in this investigation were the Vidor Eternacell (Crompton Parkinson Ltd, South Shields UK), of Size G4 equivalent size $\frac{1}{2}$AA, capacity 0.4 Ah, rated load 18 mA, weight 8 g, diameter 14.2 mm, height 27.9 mm, volume 4.4. cm^3 and size G52 equivalent size C, capacity 3.2 Ah, at a current of 135 mA, weight 44 g, diameter 25.6 mm, height 49.5 mm, volume 25.6 cm^3. The cell consists of a lithium anode, separator and an inert cathode current collector spirally wound with the anode connected to the outer can and the cathode current collector to the metal pin in the glass to metal seal. The current collector consists of carbon material, acetylene black (specific surface area 76 $\text{m}^2 \text{ g}^{-1}$) on an aluminium mesh with a PTFE binder, at which the cathodic reaction

$$2SO_2 + 2e \rightleftharpoons S_2O_4^{2-} \qquad (1)$$
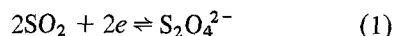
takes place. The electrolyte consists of LiBr and SO_2 dissolved in acetonitrile which results in an internal cell pressure of approximately 60 PSI at room temperature. The SO_2 forms a protective film of lithium dithionite $Li_2S_2O_4$ on the lithium which inhibits any reaction with the acetonitrile

and parasitic corrosion of the anode on open circuit and accounts for the extremely long shelf-life of these cells. A further consequence of this dithionite film is a voltage delay on discharge after a period of storage.

All cells investigated were in the new, undis-charged state. The impedance spectra of these cells were obtained using the Solartron 1250 Frequency Response Analyser (FRA) in conjunction with the 1186 Electrochemical Interface in a manner similar to that described previously [2]. The FRA was controlled by a Kemitron 3000 computer, also used for the acquisition of data, which was then stored on disc for subsequent plotting and analysis. None of the integration facilities of the FRA was used so each measurement was taken over just one cycle and the frequency sweep was continued until the first semicircular part had been completed after, typically, only a few minutes. This procedure gave sufficient accuracy as only the diameter of the semicircle was required for the eventual analysis of results. Each cell was placed in a constant temperature environment and left for several hours to equili-brate before any measurement was made. The impedance spectra of the cell was then recorded in the manner described above and when this had been completed the open circuit voltage was measured. The temperature was then changed by a few degrees and allowed to equilibrate again before the whole procedure was repeated.

3. Results and discussion

Fig. 1 shows how the impedance spectra of various cells change with temperature and Fig. 2 shows how the open circuit potential varies over the same temperature range.

The charge transfer resistance, θ, is obtained from the diameter of the semi-circular shapes in the impedance spectra. These shapes were slightly flattened semi-circles which is probably due to the fact that the lithium electrode has some roughness and is not ideally smooth [3]. Regarding the curves as circular sections, the diameter and hence θ can be readily obtained graphically using simple geometric techniques. This does not give an abolsute value for θ, but it is sufficient for our purposes here.

For the reaction

$$O + Ze^- \longrightarrow R \qquad (2)$$

the exchange current density i_0 is given by

$$i_0 = ZFk_0 C_0^{1-\alpha} C_R^{\alpha} = \frac{RT}{ZFR_{CT}} \qquad (3)$$

where Z is the valence charge number; F the Faraday constant; k_0 the specific equilibrium rate constant; C_O concentration of O in Reaction 2;
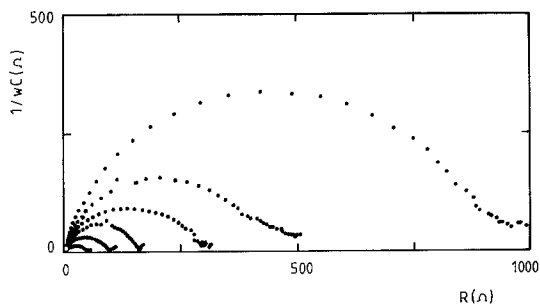

Fig. 1. Impedance loci for the same cell at six different temperatures showing how the diameter of the semi-circle increases with decreasing temperature. In all loci the frequency sweep goes from 60 kHz to 60 mHz with ten steps per decade. The temperature for the largest locus is $-1.8°$ C and the temperatures are in the order 4.2, 7.6, 14.0, 20.0 and 24.4 as the loci decrease in size.
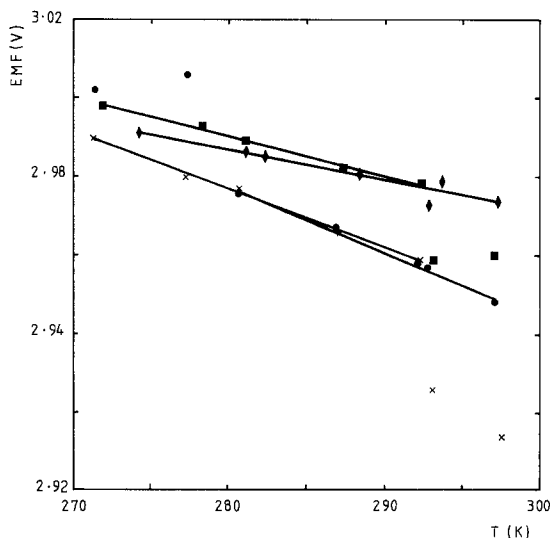

Fig. 2. Plots of E vs T for several cells. The slopes were calculated using the linear portions where possible but it can be seen that the plots give neither good straight lines nor parallel slopes.
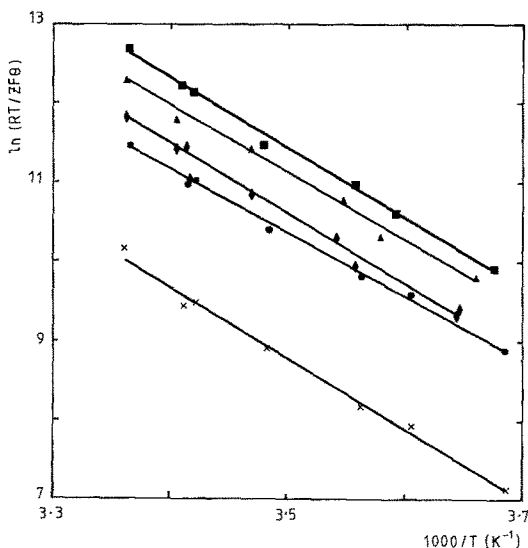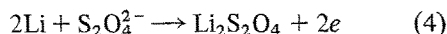
Fig. 3. Plots of ln $(RT/ZF\theta)$ vs $1/T$ for five cells all showing good fits to a straight line and nearly parallel slopes.

C_R concentration of R in Reaction 2; R_{CT} specific charge transfer resistance ($R_{CT} = \xi \times \theta$); α charge transfer coefficient and ξ surface area of electrode. The anodic reaction can be written as

$$2Li + S_2O_4^{2-} \longrightarrow Li_2S_2O_4 + 2e \qquad (4)$$

and Equation 3 becomes

$$i_0 = 2F\underset{\leftrightarrow}{k}C_{Li_2S_2O_4}^{1-\alpha}C_{Li}^{2\alpha}C_{S_2O_4^{2-}}^{\alpha} = \frac{RT}{2F\theta\xi} \qquad (5)$$

where $\underset{\leftrightarrow}{k}$ is the specific equilibrium rate constant. As $\underset{\leftrightarrow}{k}$ is a rate constant, an Arrhenius equation

$$\underset{\leftrightarrow}{k} = A \exp\left\{-\frac{\Delta U^{act}}{RT}\right\} \qquad (6)$$

can be written where A is the pre-exponential factor and ΔU^{act} is the activation energy at constant volume. Since the cell is a closed vessel, the pressure is certainly not constant but varies from 10 to 60 psi in the temperature range used. Equations 5 and 6 are then combined and the logarithm is taken to give

$$\ln \{2FAC_{Li_2S_2O_4}^{1-\alpha}C_{Li}^{2\alpha}C_{S_2O_4^{2-}}^{\alpha}\}$$
$$-\frac{\Delta U^{act}}{RT} = \ln\left\{\frac{RT}{2F\theta}\right\} - \ln\xi \qquad (7)$$

For the same cell in the same state of charge the only variables are T and θ. So Equation 7 indicates that a plot of ln $\{RT/2F\theta\}$ vs $(1/T)$ should give a straight line of slope $-(\Delta U^{act}/R)$. The results of this plot for each cell are shown in Table 1 and the plots themselves in Fig. 3. The slopes for each cell are in fairly close agreement with a mean value of -8600 ± 500 which gives a value of ΔU^{act} as 72 ± 4 kJ mol^{-1}.

The variation of the open circuit potential with temperature (from which the thermodynamics of the reaction is obtained) was also investigated and the results are shown in Fig. 2.

Since

$$\left(\frac{\partial A}{\partial T}\right)_v = -S \qquad (8)$$

and

$$\Delta A = -ZEF \qquad (9)$$

where A is the Helmholtz free energy, S is the entropy and E is the equilibrium potential we have

$$\left(\frac{\partial E}{\partial T}\right)_v = \frac{\Delta S}{2F} \qquad (10)$$

So plotting E vs T should give a straight line of slope $(\Delta S/2F)$ for the present $2e$ process. The results of this plot are shown in Table 1. The mean value of these slopes is $(-1.6 \pm 0.2) \times 10^{-3}$ V K^{-1}. So $\Delta S = -300 \pm 40$ J mol^{-1} K^{-1}. As can be seen, these plots have linear portions. Occasionally the potential was observed to drop suddenly and then recover. This was interpreted as corresponding to the rupturing of the passivating film caused by the performing of the impedance experiment (experimental programme,

Table 1. Summary of slopes of the plots of E vs T and ln (RT/ZFθ) vs 1/T for five cells: cells A, B and C are G52 size and D and E are G4 size

Cell	E vs T (×10⁻³ V K⁻¹)	ln (RT/ZFθ) vs 1/T
A	-0.77 ± 0.3	-8900 ± 800
B	-1.02 ± 0.1	-8800 ± 700
C	-3.29 ± 0.7	-8600 ± 1800
D	-1.68 ± 0.2	-7900 ± 500
E	-1.47 ± 0.1	-8900 ± 900
Mean	-1.6 ± 0.2	-8600 ± 500

see above) followed by a slow repassivation. This is supported by observations of the low frequency electrode impedance. The slope of the Warburg line coming off from the high frequency semicircle was observed to fall when the potentials dropped and then increased when the potential recovered to a value greater than $45°$ which indicates the presence of a film [4]. It was not possible to ascertain the cause for the behaviour in this sequence of experiments. The outcome of this is that the values of the slopes for each cell are not always in very close agreement and this reduces the confidence which can be placed in the values of ΔS calculated.

It is interesting that, in spite of the uncertainties inherent in the thermodynamic estimations, the kinetic charge transfer resistance, θ, is independent of these variations in potential as all the cells gave very good straight line plots defining the characteristic activation energy; moreover, these energies agree very well with each other.

4. Conclusion

Results indicate that, although the open circuit potential is occasionally uncertain due to film formation and subsequent disturbance on the anode, the charge transfer resistance, θ, seems to be relatively insensitive to these variations and this indicates that the properties of the cell in use, i.e. when current is being drawn, will have considerable predictibility over an extended temperature range.

References

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