

Microcalorimetric studies on lithium thionyl chloride cells: temperature effects between 25 °C and –40 °C

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Abstract

Microcalorimetry studies were performed on commercial lithium thionyl chloride cells to investigate whether there was a change in reaction mechanism in the temperature range between 25 °C and –40 °C. The entropy change associated with cell discharge was calculated from the calorimetry data and was also determined from the temperature dependence of the open-circuit potential. The entropy changes determined by the two methods are compared and discussed in terms of the electrolyte composition variable.

Introduction

Although lithium thionyl chloride cells are commercially available, they still exhibit some unexplained phenomena which tend to vary in degree between the products of different manufacturers and even different dates of manufacture from the same company [1]. The major problems reported are: (i) venting or explosion when the cells are subjected to overdischarge or polarity reversal, particularly at low temperatures (–20 °C and below) [1–4]; (ii) capacity losses when discharged at low temperatures due to long-term storage at room temperature [4]; (iii) cell overheating during warm up, following discharge at low temperatures, with possible venting or explosion [5]. The variation in severity of thermal events involving different manufacturers' cells suggests a dependence on subtle differences in chemistry and/or cell design [1–4]. With the aim of improving operation, reliability and safety at temperatures down to –40 °C, several groups have been investigating the cell chemistry. Detailed analyses of the cell discharge products have been carried out [5, 6] and electrochemical studies have been made using linear sweep voltammetry, rotating disk electrode techniques and a.c. impedance spectroscopy [7–13].

Microcalorimetry and the variation of cell potential with temperature (dE/dT) have been reported by several groups and quasi-fundamental thermodynamic parameters calculated, such as entropy change of the cell reaction (ΔS), thermoneutral potential (E_H), and enthalpy change (ΔH) [11–16]. The reported values of entropy change for lithium thionyl chloride cells are listed in Table 1. The entropy changes were determined

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TABLE 1

Previously-reported experimental entropy values for the lithium thionyl chloride cell reaction

| Author(s) (ref.) | Technique | Temperature (°C) | Experimental ΔS (J K ⁻¹ Eq ⁻¹) |
|-----------------------------|-------------|---------------------|--|
| Bittner <i>et al.</i> [16] | dE/dT | -10 to +35 | -30.9 ^a , -57.9 ^b |
| Gibbard [11] | dE/dT | -23 to +40 | -48 ^c , -59 ^d |
| Godshall and Driscoll [13] | dE/dT | -15 to +75 | -22.0 |
| Takeuchi <i>et al.</i> [15] | dE/dT | -10 to +50 | -62.7 |
| This work | dE/dT | -40 to +25 | -54 ± 3 ^e , -61 ± 3 ^f |
| Bro [12] | calorimetry | +25, +45 | -97.1, -60.7 |
| Godshall and Driscoll [13] | calorimetry | +25 | -19.4 ^g |
| Hansen and Frank [14] | calorimetry | +25, +65 | -75 ± 1, -71 ± 1 |
| This work | calorimetry | -30 to +25 -40 | -56 ± 6 -75 ± 9 |

^aLaboratory cell.^bCommercial cell.^cGTE cell.^dTadiran cell.^eUndischarged.^fPartially discharged.^gCorrected for heat flux due to corrosion of lithium, assuming a 98% current efficiency during discharge ($\Delta S = -32.4$ J K⁻¹ Eq⁻¹ before correction).

from either calorimetry or dE/dT measurements. A theoretical value of the entropy change has also been reported as -54 J K⁻¹ Eq⁻¹ [13]. This theoretical value was calculated for the overall reaction:



However, the calculation was only approximate because the absolute entropy of liquid thionyl chloride was not known, so the gas phase entropy was used. Also, the sulfur dioxide produced during discharge remains in solution, solvated to the lithium ions, so use of the gas phase entropy of sulfur dioxide is inaccurate as well. The necessary corrections have been done. The heats of formation of both gaseous and liquid thionyl chloride have been reported [17], so these were used to calculate the entropy of vaporization and hence the absolute entropy of liquid thionyl chloride. The entropy of sulfur dioxide in the liquid state was similarly calculated. The theoretical entropy change for the cell reaction was then determined as -19 J K⁻¹ Eq⁻¹, which is appreciably less negative than -54 J K⁻¹ Eq⁻¹. This corrected value will also be slightly in error because of solvation effects in the electrolyte; that is, the displacement of thionyl chloride from the lithium ions by the sulfur dioxide [18].

An examination of the data presented in Table 1 reveals that: (i) there is a large spread in entropy values and those obtained from dE/dT measurements are generally less negative than those obtained using calorimetry; (ii) no calorimetry data have been reported for temperatures below 0 °C; (iii) apparent temperature dependences of the calorimetrically-determined entropy are not consistent. Measurements of the temperature dependence of the cell potential have also been reported by Schlaikjer *et al.* [10]. Their measurements were made with the cell under load and yielded an entropy change of $+99$ J K⁻¹ Eq⁻¹. The reason for this apparently, erroneous value would appear to arise from using currents that produced appreciable polarization at the

electrodes; however, the data presented also indicated that there could be a change in cell discharge reaction mechanism between $-20\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$. Knowing that these cells can be subject to thermal problems upon discharge or overdischarge at low temperatures, the present study was initiated to determine the entropy change of the cell reaction at temperatures between $+25\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$. A change in the cell reaction at a particular temperature should manifest itself as a sudden change in ΔS . At the same time, the present calorimetry measurements are the first to be reported on Li/SOCl_2 cells discharged below $0\text{ }^{\circ}\text{C}$.

Experimental

All the calorimetric and electrochemical measurements were performed on spirally wound 'D'-size, lithium thionyl chloride cells manufactured by SAFT (France). The cells are belonged to the same production batch (F88301A) and were manufactured in 1988. The electrolyte was 1.35 M lithium tetrachloroaluminate in thionyl chloride containing approximately 0.5 M sulfur dioxide. Further details of the cell composition, such as other electrolyte additives, protective coatings on the lithium electrode, and the composition of the carbon electrode, were not available to us. The cells were matched for voltage and internal resistance, the internal resistance measurements being performed using a milliohmmeter (Hewlett Packard model 4328A). This instrument makes an impedance measurement at 1 kHz, the value given being the real part of the impedance which mainly comprises the solution resistance of the cell. These measurements are employed routinely in our laboratory and cells are rejected from a batch if they have unusually small or large resistances compared to the average value. The cells were between one and two years old when the experiments were performed.

A heat conduction calorimeter (Hart Scientific, Model 7704) was used for the calorimetric measurements. Data were collected using a Keithley Digital Multimeter (Model 199 system with scanner) interfaced to a personal computer via an IEEE bus. In a typical experiment, the test cell was inserted into the calorimeter cavity with the two lead wires (tinned copper, 16 gauge) coming out through a hole in the cavity lid and taped to the cooling block. The reference cavity was left empty and the test cell equilibrated for at least 24 h prior to discharging. Discharging was carried out at constant current using an Anatek model 25-2S power supply and 3 to 18 mA (7.5 to $45\text{ }\mu\text{A cm}^{-2}$).

Calibration of the calorimeter was achieved by applying a constant current to a standard resistor positioned inside the calorimeter test cavity. For this technique, a nominal $1000\text{ }\Omega$ resistor with a tolerance of 5% was inserted into a hole in the middle of a solid aluminium cylinder which had been machined to the size of the experimental 'D'-size cells. Good thermal contact between the resistor and the aluminium cylinder was achieved using a silicone heat sink compound. The cylinder had a heat capacity similar to that calculated for the test cells [19] and the same lead wires were used for both the calibration and the cell discharge experiments so that any heat loss from the cavity via the leads cancelled out. The resistance of the nominal $1000\text{ }\Omega$ resistor was measured at each temperature so that an accurate power dissipation could be calculated. A resistive heating power of 6.5 mW was chosen for the calibration which covered the range of heat output in the cell discharge experiments. A calibration curve was generated between $25\text{ }^{\circ}\text{C}$ and $-40\text{ }^{\circ}\text{C}$.

Measurement of the temperature dependence of the open-circuit voltage of cells was made using a thermostatically-controlled environmental test chamber (Thermotron

model S4). The cells were allowed a minimum of six hours to equilibrate at each temperature and the voltages were sampled manually.

Heat analysis

The total heat flux during cell discharge, \dot{q}_T , is given by:

$$\dot{q}_T = \dot{q}_p + \dot{q}_s + \dot{q}_{\text{other}} \quad (2)$$

where \dot{q}_p is the heat flux due to cell polarization, \dot{q}_s is the heat flux from entropy effects and \dot{q}_{other} arises from sources such as self discharge (lithium corrosion). The heat flux due to cell polarization depends upon the difference between the open-circuit potential (E) and that under load (E_L) and is given by:

$$\dot{q}_p = i(E - E_L) \quad (3)$$

$(E - E_L)$ arises from the overpotentials at the anode and cathode and also the ohmic potential drop from the solution. The solution resistance and \dot{q}_p both increase significantly with decreasing temperature. \dot{q}_{other} arises from the effects of impurities, from the decay of long-lived intermediates and from corrosion. The most significant of these should normally be corrosion at the lithium surface [12]. During discharge the passivating film on the lithium surface is disrupted to a greater or lesser extent, depending on the current density. At higher current densities the heat flux due to corrosion of the underlying or exposed lithium may be appreciable. One way to correct for this effect is to do separate experiments in which a known amount of fresh lithium is totally discharged at a given current density and the ratio of experimental to theoretical charge is determined, being expressed as a percentage current efficiency. Godshall and Driscoll [13] have determined a current efficiency of 98% for lithium discharged in neutral 1.6 M $\text{LiAlCl}_4/\text{SOCl}_2$ electrolyte at 21 °C, using current densities in the range 2.5 to 120 mA cm^{-2} . This 2% corrosion may appear to be a minor effect, but it must be remembered that all the energy of the corrosion reaction is released as heat, unlike in the faradaic discharge reaction. In the present work the current density was kept small in order to minimize corrosion of the lithium. The corrosion reaction is also responsible for the majority of the heat flux at open circuit (\dot{q}_{oc}) so some of this error is subtracted away with the baseline data during the analysis. At low temperatures the corrosion rate will be much slower so, in principle, the entropy changes calculated for discharge at low temperatures should be true values. From rearrangement of eqn. (2) we have:

$$\begin{aligned} \dot{q}_s &= \dot{q}_T - \dot{q}_p - \dot{q}_{\text{other}} \\ &\approx \dot{q}_T - \dot{q}_p - \dot{q}_{\text{oc}} \end{aligned}$$

but,

$$\dot{q}_s = \left(\frac{i}{nF} \right) T \Delta S \quad (4)$$

Consequently, a plot of \dot{q}_s versus i should yield a straight line from which ΔS can be calculated for each experiment at constant temperature.

Results and discussion

Calorimetry results

The measured heat flux was plotted in Fig. 1 as a function of elapsed time for two different cells. Each cell was discharged at the temperature and rate as indicated

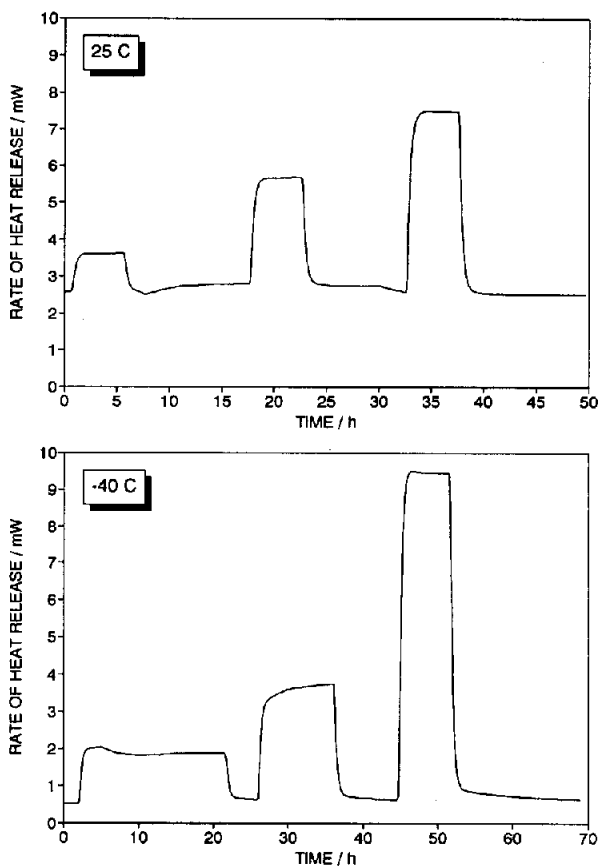


Fig. 1. Heat flux profiles for two 'D'-size, Li/SOCl₂ cells discharged at constant currents: at 25 °C (top, 4, 10 and 16 mA) and at -40 °C (bottom, 3.5, 7 and 16 mA).

and with intervening open-circuit rest intervals. All discharges were exothermic. A considerable length of time was required for the heat flux and the cell potential to attain a relatively steady value both at the start of a discharge and after interruption of the current. It is apparent from Fig. 1 that the rate of release of heat was greater at -40 °C than at 25 °C at comparable discharge rates. The heat flux on open circuit did not change appreciably as a function of the amount of charge withdrawn, because the current was intentionally kept small.

Figure 2 shows plots of \dot{q}_s (or $\dot{q}_T - \dot{q}_{oc} - i(E - E_L)$) and $\dot{q}_s + \dot{q}_p$ (or $\dot{q}_T - \dot{q}_{oc}$) as a function of the current for cells discharged at 25 °C and -40 °C. These data points were abstracted from plots like those of Fig. 1. \dot{q}_p can be seen to be the major component of the overall heat flux during discharging at -40 °C, even at low currents. All the ΔS values, as calculated from \dot{q}_s using eqn. (4), were plotted against temperature in Fig. 3. Despite some scatter in the data, the points obtained at -40 °C were all consistently more negative, even after allowing for an estimated random error of $\pm 9 \text{ J K}^{-1} \text{ Eq}^{-1}$ at low temperatures, compared with $\pm 6 \text{ J K}^{-1} \text{ Eq}^{-1}$ at room temperature. The increased error at -40 °C arises from the large values of \dot{q}_p . The average ΔS values obtained are included in Table 1.

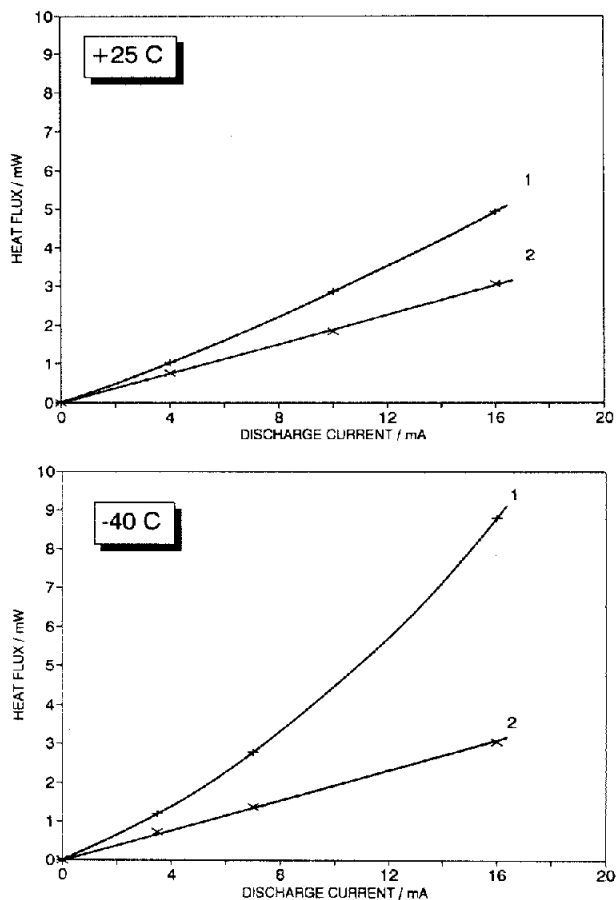


Fig. 2. A comparison of different components of the total heat flux for Li/SOCl₂ cells discharged at 25 °C and -40 °C with increasing currents: curves 1 are $\dot{q}_T - \dot{q}_{oc}$, which is equal to $\dot{q}_p + \dot{q}_s$; curves 2 are $\dot{q}_T - \dot{q}_{oc} - i(E - E_L)$, which is equal to \dot{q}_s . Note the much larger contribution of \dot{q}_p at -40 °C.

Results derived from cell open-circuit voltage data

There was a problem with measuring the cell open-circuit voltage needed for the calculation of \dot{q}_p , particularly at -40 °C. Following a shallow discharge of 0.07 A h at 3 mA at -40 °C, the open-circuit voltage decreased by 0.10 V to 0.11 V for different cells. This difference was obtained after allowing the cells to thermally equilibrate for 10 h. At room temperature the open-circuit voltage recovered to its initial value, but only after 6 to 8 h. This behaviour must reflect very slow processes such as the breakdown and subsequent regrowth of the passivating layer on the lithium. Film growth may be rapid at room temperature, but not at -40 °C. For example, we used impedance spectroscopy to measure the lithium electrode film resistance in a Li/SOCl₂ cell that had been partially discharged at -31 °C. One hour after discharge, this resistance was 1.0 Ω and the cell voltage was 3.563 V. After 4 days the resistance

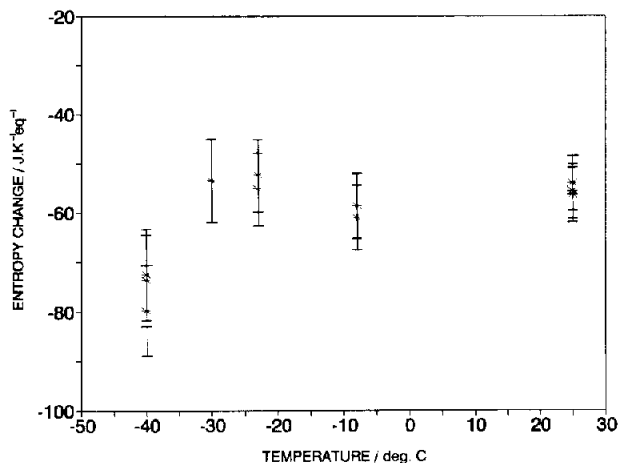


Fig. 3. A plot of calorimetrically-determined entropy of reaction for 'D'-size lithium thionyl chloride cells discharged at different temperatures. The data are significantly different at -40°C , indicating a changed reaction below -30°C .

had risen to $14\ \Omega$ and the potential to $3.657\ \text{V}$. The difficulty in the present work was when to measure the open-circuit voltage. For the results shown in Fig. 3, the open-circuit voltages used were the relatively constant values measured 4 to 10 h after going to open circuit. However, it could be argued that the potential as measured a few minutes after going to open circuit might have been more appropriate, in that the regrowth of film on the lithium electrode would not have perturbed the potential, but provided that the rest of the cell constituents had equilibrated. By example, when ΔS was recalculated from calorimetric data obtained at 25°C and -40°C using voltages measured only 15 min after going to open circuit, the results yielded $\Delta S = -62\ \text{J K}^{-1}\ \text{Eq}^{-1}$ (cf. $-56\ \text{J K}^{-1}\ \text{Eq}^{-1}$) at 25°C and $\Delta S = -94\ \text{J K}^{-1}\ \text{Eq}^{-1}$ (cf. $-74\ \text{J K}^{-1}\ \text{Eq}^{-1}$) at -40°C . Therefore, according to this example, there was a substantial systematic error associated with the choice of the appropriate open-circuit voltage data; however, the difference between the ΔS values at 25°C and -40°C was seen to be increased by changing these values. Consequently, it is suggested that there is a modification or perturbation of the cell discharge reaction below -30°C , that gives rise to a changed ΔS .

Comparison of entropy changes from various sources

The average value of ΔS obtained from calorimetric experiments at 25°C was $-56\ \text{J K}^{-1}\ \text{Eq}^{-1}$. This value of ΔS will be used in the proceeding discussion. The data listed in Table 1 require some discussion because of the large disparity in reported ΔS and also, the generally less negative values reported from measurements of the temperature dependence of the cell potential, (dE/dT) . The spread in ΔS values reported from dE/dT measurements was -22.0 to $-62.7\ \text{J K}^{-1}\ \text{Eq}^{-1}$. There may be several reasons for this spread. First, the experiments were performed on cells from different manufacturers or on cells of different design, but from the same manufacturer. Consequently, the cells will have had different electrolyte formulations, carbon electrodes

made from carbon of differing trace metal composition, and different additives or impurities which adsorb on the electrode surfaces and affect the cell potential. An example of a variation between cells of different manufacturers was reported by Gibbard [11] in which ΔS for a cell manufactured by Tadiran was $-48 \text{ J K}^{-1} \text{ Eq}^{-1}$, while that for a GTE cell was $-59 \text{ J K}^{-1} \text{ Eq}^{-1}$. Secondly, all the experiments reported were performed in slightly different ways. Bittner *et al.* [16] measured dE/dT at low discharge currents (from 0.03 to $1.875 \mu\text{A cm}^{-2}$), extrapolating the data to zero current in order to obtain a closer approximation to the true reversible potential. This technique should be more accurate than simply measuring the open-circuit voltage which may be perturbed by the accumulation of impurities at the electrode surfaces. The data of Takeuchi *et al.* [15] were obtained from a large number of cells whose open-circuit voltages were measured at different degrees of discharge; the ΔS value of $-62.7 \text{ J K}^{-1} \text{ Eq}^{-1}$ was obtained from fresh cells but, for partially discharged cells this value was less negative and ranged between -36 and $-54 \text{ J K}^{-1} \text{ Eq}^{-1}$ for discharges of up to 90%, with no consistent trend. Consequently, the variation in ΔS was taken to arise from experimental uncertainties. Takeuchi *et al.* [15] did not indicate whether the cells were left to stand at all after partial discharging and before commencing the dE/dT measurements, so it is possible that the different rates of regrowth of the anodic film (and presumably increase in potential) which are, of course temperature dependent, could be a factor.

Godshall and Driscoll [13] made their dE/dT measurements at open circuit, but first performed a partial discharge of 8% of capacity in order to destroy the thick anodic film. The cells were then held at room temperature for 20 h before measuring potentials. Gibbard's measurements [11] were made at open circuit, but the cell history prior to the experiments was unclear, so it was assumed that a partial discharge was not performed.

From the limited data available in Table 1 it may be implied that undischarged Li/SOCl₂ cells could yield a more negative ΔS than partially discharged cells. In order

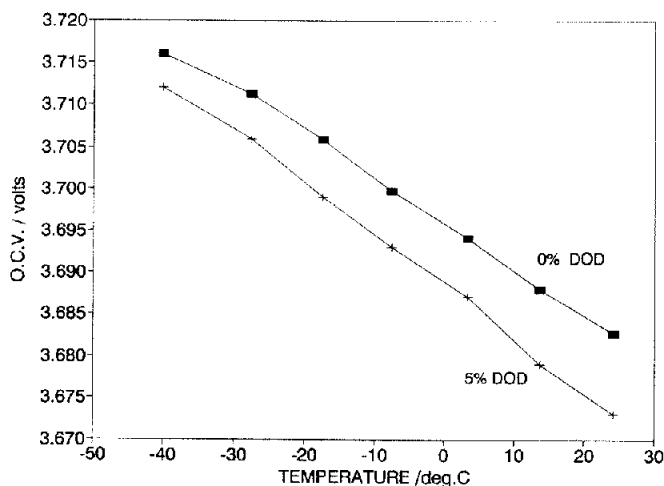


Fig. 4. Temperature dependence of the open-circuit voltage of a 'D'-size lithium thionyl chloride cell, before and after a 5% discharge (see text). The sequence of measurements was from high to low temperature, with the cell equilibrated for a minimum of 6 h at each temperature.

to verify the existence of such a trend, dE/dT experiments were performed between 25 °C and -40 °C. The open-circuit voltage was measured for a group of seven cells, before discharging and also after they had been subjected to a partial discharge of 5% of their nominal capacity. This was followed by a 20 h stand at room temperature. The resulting plots of cell potential against temperature were linear (see Fig. 4), although the points at -40 °C was slightly lower than the extrapolated line. In agreement with the calorimetry results, the cell potential data also indicated a change below -30 °C. For the undischarged cells ΔS was found to be $-54 \pm 3 \text{ J K}^{-1} \text{ Eq}^{-1}$ and that for the partially discharged cells $-61 \pm 3 \text{ J K}^{-1} \text{ Eq}^{-1}$. Therefore, the trend to a less negative apparent ΔS with discharging, using this method, was not supported. A small hysteresis was apparent in the dE/dT data obtained for a complete set of data in which the temperature was cycled, but this was not enough to perturb the gradient of the plot. However, when a second and subsequent temperature cycles were performed, a larger hysteresis was observed. This behaviour will be the subject of a future publication [20].

The generally more negative values of ΔS , reported from calorimetric experiments are probably due to increased corrosion of lithium during discharging, which leads to a higher heat flux and consequently, a more negative apparent ΔS . The spread in calorimetrically-determined ΔS can be attributed to a mixture of experimental uncertainties; lithium corrosion by thionyl chloride and the presence of different impurities in the cells. Hansen and Frank [14] used reserve cells in their experiments, so impurities that might accumulate at the lithium surface were considered to be less of a problem. Those authors also used currents as small as 10 μA so their results are expected to be accurate. Bro [12] reported a change in entropy with temperature, from $-97.1 \text{ J K}^{-1} \text{ Eq}^{-1}$ at 25 °C to $-60.7 \text{ J K}^{-1} \text{ Eq}^{-1}$ at 45 °C. This change was discussed in terms of formation of the radical SO^\cdot as an intermediate in the discharge reaction and of corrosion of the lithium anode. Those experiments were done during a continuous discharge, whereas the present work was done using the heat flux differences between current on and current off, so that the effect of heat dissipated from the decay of long-lived intermediates is cancelled. Godshall and Driscoll [13] discharged cells at rates between 1 and 20 mA cm^{-2} , which is too high for deriving meaningful equilibrium data (the highest current density used in the present work was 0.05 mA cm^{-2}); therefore their data are likely to be in error. However, those authors did correct the measured heat flux for accompanying corrosion of lithium during discharge, using a current efficiency of 98%.

The scatter in ΔS values obtained in the present work indicates that several experiments should be performed in order to obtain a reliable data point and that without such a procedure no accurate temperature versus entropy plot can be generated.

The temperature dependencies of ΔS implied from the data in Table 1 are for data from one or two cells in each case, and should therefore be suspect. The present calorimetrically-determined ΔS values would be expected to be slightly more negative than the true value due to parasitic heat flux from corrosion of lithium. However, the values of -54 and $-61 \pm 3 \text{ J K}^{-1} \text{ Eq}^{-1}$ obtained from dE/dT measurements are comparable with the average calorimetrically-determined value, $-56 \pm 6 \text{ J K}^{-1} \text{ Eq}^{-1}$, so the parasitic heat flux must be small. In this sense it is difficult to reconcile the calculated, theoretical entropy change of $-19 \text{ J K}^{-1} \text{ Eq}^{-1}$ with the results from the above two methods, unless the cell discharge reaction is incorrect as written in eqn. (1).

Calorimetry of partially-discharged cells

Further calorimetric measurements were made at room temperature in order to determine whether there was any effect from the depth-of-discharge (DOD) on the value of ΔS so determined. A small change in ΔS was expected, because of the composition variable for the electrolyte due to accumulating discharge products. Fresh electrolyte contains the solvated cationic species $\text{Li}(\text{SOCl}_2)_2^+$, but the SO_2 that is produced during discharge displaces the thionyl chloride to produce first, $[\text{Li}(\text{SOCl}_2, \text{SO}_2)]^+$ and then, $\text{Li}(\text{SO}_2)_3^+$ [18]. The presence of the solvated cation is the reason why the pressure above the electrolyte of a discharging Li/SOCl₂ cell remains low until near the end of discharge. In addition, a solid adduct can be isolated of composition $\text{LiAlCl}_4 \cdot 3\text{SO}_2$ which has a melting point of 24 °C [18], although solutions of this composition tend to be subject to a large supercooling effect and freeze around 0 °C.

Considering a fresh electrolyte of composition 1.35 M SOCl₂ plus 0.5 M SO₂ (the SO₂ being present to reduce corrosion of lithium), the mole ratios of these components are 1 LiAlCl₄:8.80 SOCl₂:0.37 SO₂. In order to solvate all the lithium cations with SO₂ it is needed to produce 2.63 mole of SO₂, which is electrochemically produced from the reduction of 5.26 mole of SOCl₂. This represents a hypothetical DOD of 60% with respect to SOCl₂. Given that the SO₂ solvates the lithium cations very strongly, then a less negative apparent ΔS is to be expected when all the lithium cations have been solvated. However, if all the SOCl₂ were to be consumed to yield a solution of composition, $\text{LiAlCl}_4 \cdot 4.77\text{SO}_2$, the vapour pressure of such a solution would still only be around 1 atm [21], because the excess 'free' SO₂ would nevertheless be solvated, although not as strongly as in $\text{Li}(\text{SO}_2)_3^+$. The consequent change in ΔS during discharging to less negative values, when all the lithium cations have been strongly solvated by SO₂, may be small and difficult to unambiguously detect by calorimetry. (Note that in the above discussion the presence of elemental sulfur has been ignored, its effect on the electrolyte properties being taken to be negligible in relationship to the present context).

The following results were obtained from calorimetric measurements on three cells at different DOD: 10–15%, $-56 \text{ J K}^{-1} \text{ Eq}^{-1}$; 80–85%, $-59 \text{ J K}^{-1} \text{ Eq}^{-1}$; and 90–95%, $-60 \text{ J K}^{-1} \text{ Eq}^{-1}$. Therefore, within the experimental uncertainty of $\pm 6 \text{ J K}^{-1} \text{ Eq}^{-1}$ there was no conclusive evidence for a change in ΔS ; however, it did appear to become more negative with discharging which agrees with the dE/dT data reported above. With certainty, ΔS did not become less negative as was speculated above on the grounds of solvation effects. Hansen and Frank [14] have reported that ΔS was constant down to 70% DOD. The heat fluxes observed in the present work, from the constant current discharges at 90–95% DOD, were found to be about 25% greater than those from fresh cells, but this was because of the increased polarization near the end of discharge.

Returning to the original objective of identifying a change in discharge reaction at low temperatures, there did appear to be a perturbation. This was exemplified by a trend to a more negative entropy change below -30 °C , but this was not associated with a large increase in heat flux. The major heat flux was shown to be from the cell polarization (see Fig. 2). In addition, no potentially hazardous behaviour was observed when the cells used in the present investigation were warmed up to room temperature, following a discharge at low temperature. It is suggested that previous safety phenomena [5] may have arisen from specific cell design features which strongly influenced the cell chemistry. Hazardous behaviour that arises from the warming up of lithium thionyl chloride cells which have been overdischarged into polarity reversal at low temperature,

has been related to the deposition of metallic lithium. These deposits of lithium are very fine and fragile and have been seen to fall off the carbon electrode during warm up [22] and so could produce a short circuit and consequent hazardous behaviour.

Conclusion

Results from this work indicate that under low rate discharge conditions the Li/SOCl₂ cells showed evidence for a perturbation in reaction mechanism below -30 °C. This is based on a more negative calorimetrically-determined entropy of reaction, for discharges carried out at -40 °C. The average value of the calorimetrically-determined ΔS , between -30 °C and +25 °C was $-56 \pm 6 \text{ J K}^{-1} \text{ Eq}^{-1}$, while the average value at -40 °C was $-75 \pm 9 \text{ J K}^{-1} \text{ Eq}^{-1}$. The values of ΔS determined from dE/dT measurements on 5% DOD cells was $-61 \pm 3 \text{ J K}^{-1} \text{ Eq}^{-1}$. Both figures were appreciably more negative than the theoretically derived value of $-19 \text{ J K}^{-1} \text{ Eq}^{-1}$. No unambiguous change in ΔS was found with DOD.

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