

THERMODYNAMIC MEASUREMENTS ON THE Li/SOCl₂ COUPLE

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Summary

As part of an effort to characterize the heat generation rates of lithium-thionyl chloride (Li/SOCl₂) cells, the fundamental thermodynamic parameters of a commercial SAFT Li/SOCl₂ "D" cell and a laboratory cell were obtained over a temperature range of -10 to 35 °C. Results are reported in terms of reversible cell potential (E_r), the temperature dependence of the reversible cell potential (dE_r/dT), and the thermoneutral potential (E_h). Results yielded $E_{r, 25^\circ\text{C}} = 3.68$ V, $dE_r/dT = -0.60$ mV °C⁻¹, and $E_h = 3.86$ V for the commercial cell, and $E_{r, 25^\circ\text{C}} = 3.66$ V, $dE_r/dT = -0.32$ mV °C⁻¹, and $E_h = 3.75$ V for the laboratory cell.

Introduction

Two approaches to the determination of the heat generation characteristics of an electrochemical couple are direct measurement of heat generation by calorimetry and measurement of fundamental thermodynamic parameters, the reversible cell potential (E_r) and the temperature dependence of the reversible cell potential (dE_r/dT). Results for the Li/SOCl₂ cell using both techniques have appeared in the literature, but they have been contradictory. Selected results from the literature are given in Table 1 [1 - 5].

In the present work, the temperature dependence of the reversible cell potential is measured. Most measurements of E_r are performed by assuming that the open circuit potential and E_r are the same. However, in the present work, the load potential at small overpotentials is extrapolated to zero current to obtain E_r . Schlijker [5] used a similar technique, but the load data were not presented and the extrapolation method was not explained. The extrapolated load potential rather than the open circuit voltage may be more indicative of the true equilibrium potential, because it is the potential of the reaction of interest; open circuit potentials are more likely to be controlled by impurities or other reactions that may occur at the electrode surface.

In the present work, linear extrapolations of the voltage to zero current are utilized. The basis for the extrapolations lies in the Butler-Volmer

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TABLE 1

Selected thermodynamic values for the Li/SOCl₂ couple taken from the literature [1 - 5]

Reference	Technique	dE_r/dT (mV °C ⁻¹)	E_h (V)
Gibbard [1]	Calorimetry	-0.81	3.925
Gibbard [1]	dE/dT	-0.53 to -0.61	3.85 - 3.87
Godshall [2]	Calorimetry	-0.20 to -0.60	3.71 - 3.83
Godshall [2]	dE/dT	-0.228	3.72
Bro [3]	Calorimetry	-0.44 to -0.87	3.66 - 3.79
Hansen and Frank [4]	Calorimetry	-0.777	3.877
Schlaikjer [5]	dE/dT	+1.026	3.33
Present work, commercial cell	dE/dT	-0.60	3.86
Present work, laboratory cell	dE/dT	-0.32	3.75

equation [6], which describes the relationship between the current i and the overpotential η for a single electrode reaction

$$i = i_0 \{ \exp(-\alpha n F \eta / RT) - \exp([1 - \alpha] n F \eta / RT) \} \quad (1)$$

where i_0 is the exchange current, α is the transfer coefficient, n the number of electrons transferred, F the Faraday constant, R the gas constant, and T the temperature. The two parts of this equation refer to the forward and reverse reactions; near equilibrium, the forward and reverse reactions will be comparable, whereas at high discharge currents, the reverse reaction will be negligible. According to eqn. (1), at sufficiently small overpotential, the current is linear with voltage

$$i = i_0 (n F \eta / RT) \quad (2)$$

Equation (2) may be rewritten to apply to a two electrode couple, where the total overpotential η_t is the sum of the anode overpotential η_a and the cathode overpotential η_c

$$i = \eta_t (n F / RT) \{ (i_{0,a} \cdot i_{0,c}) / (i_{0,a} + i_{0,c}) \} \quad (3)$$

where $i_{0,a}$ and $i_{0,c}$ refer to the anode and cathode exchange current densities. At small overpotentials, eqns. (2) and (3) indicate that a linear extrapolation of the voltage to zero current would provide the potential at zero overpotential, or the equilibrium potential.

Once the equilibrium potentials are obtained, the temperature dependence of the equilibrium potential, dE_r/dT , can be calculated. Then the thermoneutral potential, E_h , the potential at which no heat is generated, can be obtained by

$$E_h = E_r - T dE_r/dT \quad (4)$$

Finally, heat generation rates, $-dQ/dt$, can be easily calculated from a knowledge of E_h , the load voltage E_1 , and the current I

$$-dQ/dt = (E_h - E_1)I \quad (5)$$

Experimental

A commercial SAFT "D" Li/SOCl₂ cell (model #LSH2-OST) and a laboratory-built cell were used for the thermodynamic measurements. The laboratory cell has been described previously [7]. Temperature control was achieved to ± 0.01 °C by using a Haake model A82 temperature bath; the cell was enclosed in a water-tight poly(ethylene) bag and submerged in the bath. The electrical leads were brought out of the top of the bag, above the liquid level, so that no liquid was permitted to contact the cell case or lead connections.

The cell was discharged potentiostatically by using a PAR model 273 potentiostat; the voltage was measured by using a Hewlett-Packard model #3478A multimeter. The current was measured by the potentiostat to 0.1 μ A.

At each temperature, the cell was allowed to equilibrate in the bath for a minimum of 1 h. The open circuit voltage was then recorded, and the potentiostat was set to control the cell to that voltage. After 1.5 h, the voltage was stepped down 5 mV and the current recorded over a 1.5 h period. The cell was stepped down through successive 5 mV steps for a total of 10 steps, or a total of 50 mV below the open circuit voltage. After each new voltage was applied, the cell was allowed to stay at that voltage and the current was monitored for 1.5 h.

Results and discussion

At each temperature, the voltage was stepped down from the open circuit value by 5 mV increments. At each voltage step, current was measured as a function of time. A typical current-time curve is given in Fig. 1, and indicates that a steady-state was reached after the 1.5 h wait period.

For each temperature, the voltage *versus* current curves were extrapolated to zero current by a linear fit. In order to determine the points that corresponded to the linear region described by eqn. (3) for low overpotentials, linear regressions were performed for the first three points, the first four points, and so on, until all ten points were included in a linear regression.

Analysis of the linear fits, including the correlation coefficients, indicates the most appropriate linear fit regions at low currents (Butler-Volmer kinetics). An example is given in Fig. 2.

The voltages extrapolated to zero current at low currents represent the true equilibrium voltages. These values are plotted as a function of

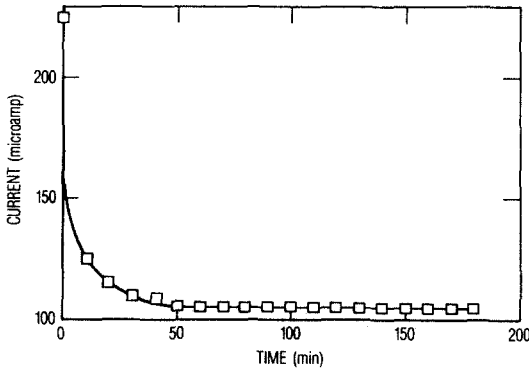


Fig. 1. Dependence of current on time after potentiostatic step from 15 to 20 mV below the open circuit voltage at 10 °C.

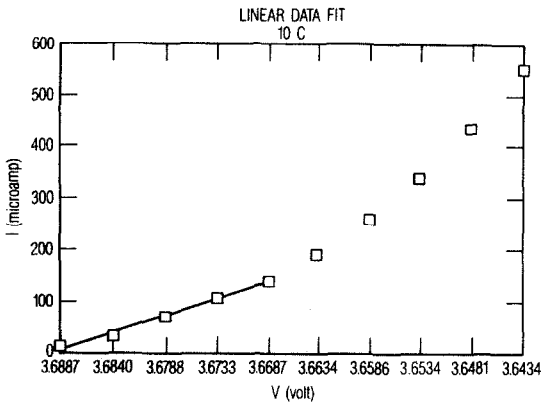


Fig. 2. Linear fit of current vs. voltage for 10 °C.

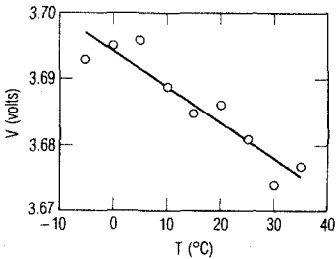


Fig. 3. Temperature dependence of reversible cell potential for Li/SOCl₂ commercial cell.

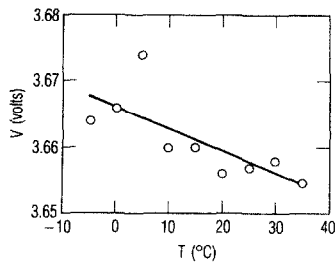


Fig. 4. Temperature dependence of reversible cell potential for Li/SOCl₂ laboratory cell.

temperature in Fig. 3 for the commercial cell and in Fig. 4 for the laboratory cell. A linear fit of the points for the commercial cell yields $dE_r/dT = -0.60 \text{ mV } ^\circ\text{C}^{-1}$ and $E_{r, 25^\circ\text{C}} = 3.68 \text{ V}$, with a correlation coefficient of 0.893; from eqn. (4), $E_h = 3.860 \text{ V}$. For the laboratory cell, $dE_r/dT = -0.32 \text{ mV } ^\circ\text{C}^{-1}$, $E_{r, 25^\circ\text{C}} = 3.66 \text{ V}$, and $E_h = 3.75 \text{ V}$.

The differences between the thermodynamic values obtained for the commercial and laboratory cells are probably due to differences in the electrolyte solutions. The highly-purified electrolyte used in the laboratory cells should have a lower concentration of Cl_2 , SO_2 , and S_2Cl_2 than the commercial cell. The reduction in Cl_2 concentration would be expected to reduce the reversible potential for the cell, as observed. However, the commercial cell also contains an additive which is reported to reduce the voltage delay in this cell after long-term storage. Since such an additive must influence the lithium-electrolyte interface, this additive would likely influence the reversible potential.

The thermodynamic values obtained in this work are compared with values obtained from other work in Table 1. Results from the present work on the commercial cell are in excellent agreement with thermodynamic measurements (dE_r/dT) of Gibbard [1] and with the calorimetric measurements of Godshall [2]; they are in reasonable agreement with the calorimetric results of Hansen and Frank [4]. Results from the present work on the laboratory cell are in excellent agreement with the thermodynamic measurements of Godshall [2]. The present results do not agree with the thermodynamic results of Schlaikjer [5], who reported a positive slope in dE_r/dT . Schlaikjer's results yielded a value for E_h of 3.33 V, which would predict an endothermic reaction at load voltages above 3.33 V. The present results predict that the cell discharge would be exothermic at all load voltages, because the open circuit voltage is below the E_h . The discrepancy between the present results and those of Schlaikjer cannot be fully explained. A number of factors may influence the thermal characteristics of the Li/SOCl_2 cell, including impurities and cell history.

Conclusions

Results from the present work provide an accurate means of predicting the heat generation rates of Li/SOCl_2 cells. The agreement of the present results with key results in the literature substantiates these results. However, different discharge conditions and different cell chemistries may result in different thermal characteristics. Further work will be performed to measure calorimetrically the heat generation of Li/SOCl_2 cells of various manufacturers over a range of discharge rates.

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