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Determination of the thermodynamic parameters of Zn/ 60Li₂SO₄:40Li₂CO₃/V₂O₅:P₂O₅ electrochemical cells

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Abstract

Zn + El/Li₂SO₄:Li₂CO₃ (60:40)/V₂O₅:P₂O₅ (60:40) + El + GR cells have been fabricated using the simultaneous pressing method. The voltage versus temperature response of the cells after 0%, 25% and 50% depth of discharge at 300 °C was measured. The data were then used to determine the Gibb's free energy, enthalpy and thermoneutral potential of the cell. For 0% and 25% discharge of the cells, the positive values of the thermoneutral potential indicates an exothermic chemical cell reaction, while for 50% discharge it is negative, indicating an endothermic chemical reaction. This confirms that the nature of the chemical reaction taking place inside the cell during the discharge process depends upon the discharge region, which is in accordance with earlier reports.

Keywords: Electrochemical cells; Solid electrolyte; Enthalpy

1. Introduction

High-temperature electrochemical power sources (thermal batteries) originated in the 1940s and were developed mainly for weapons applications [1,2]. More than 10 million such thermal batteries have been produced since Catalyst Research Corporation first made them in 1947 [3]. Their characteristics are ideally suited for military ordnance. They are widely used as a power source in projectiles, bombs, mines, missiles, jammers and torpedoes. Solid-state thermal batteries are advantageous due to:

1. Very long shelf life (longer than 10 yr) in a 'ready

ammunition' state without degradation in performance.

2. 'Instant' activation-fast start design can be activated and can provide useful power.
3. High peak power.
4. Very high demonstrated reliability and ruggedness following long-term storage at extremes of ambient temperatures, and severe stockpile-to-target environments.
5. No maintenance or servicing required.

In the past, extensive efforts have been made to investigate electrochemical systems suitable for a batteries with operating temperatures of about 425 °C and service lifetimes of several days. Recently, a number of solid-state electrochemical cells have been

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fabricated and studied using Li_2SO_4 -based solid electrolytes [4]. Lithium sulphate-based solid electrolytes differ in 1 important aspect from the other 3 groups of crystalline solid electrolytes namely: (1) alumina, (2) calcia stabilized zirconia, and (3) AgI type; the difference is that in sulphates the high ionic mobility is not limited to 1 or 2 species; instead many mono- and di-valent cations have high mobilities in fcc- Li_2SO_4 . This is a clear advantage since it means that a number of metals can be used as the anode in electrochemical cells.

Research and development on such types of batteries have also been in commission, where the environment itself supplies the heat to activate and maintain battery at its operating temperature. For the design and construction of such batteries the heat generated during the discharge process is an important factor as it directly affects the cell lifetime and performance. The importance of the thermoneutral potential (E_H) for the heat generation during the discharge process and its derivation may be found elsewhere in the literature [5,6]. To have a quantitative analysis of heat generation a knowledge of the thermodynamic parameters of the cell is essential. The thermodynamic parameters dS , dG , dH and E_H can be calculated by using the following equations [7]:

$$dS = nF \times (dE/dT), \quad (1)$$

$$dG = -nEF, \quad (2)$$

$$dH = -nEF + nFT \times (dE/dT), \quad (3)$$

$$E_H = E - T \times (dE/dT), \quad (4)$$

where, E_H is the thermoneutral potential, dH is the change in enthalpy, dG is the change in Gibb's free energy, F is Faraday's constant, dS is the change in entropy, E is the open-circuit voltage of the cell, T is the temperature in K and n is the valency of anode.

The preliminary results on Li_2SO_4 -based systems showed promising results from the thermal battery application viewpoint [8]. In this paper the open-circuit voltage versus temperature of $\text{Zn}/\text{Li}_2\text{SO}_4:\text{Li}_2\text{CO}_3$ (60:40)/ $\text{V}_2\text{O}_5:\text{P}_2\text{O}_5$ cells were recorded for various degrees of discharge (0%, 25% and 50%). The data were then used for the de-

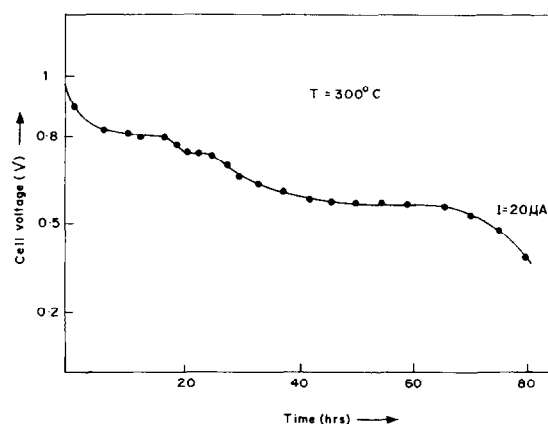


Fig. 1. Discharge characteristic curve for $\text{Zn} + \text{El}/\text{El}/60\text{V}_2\text{O}_5:40\text{P}_2\text{O}_5 + \text{El} + \text{Gr}$ cell at 300°C .

termination of the thermodynamic parameters and the thermoneutral potential of the cell.

2. Experimental

The $\text{Li}_2\text{SO}_4:\text{Li}_2\text{CO}_3$ (60:40) electrolyte and the $\text{V}_2\text{O}_5:\text{P}_2\text{O}_5$ (60:40) cathode were prepared by using the conventional quenching technique [9]. The initial ingredients Li_2SO_4 , Li_2CO_3 , V_2O_5 and $\text{NH}_4\text{H}_2\text{PO}_4$ (A.G. Fluka, Germany) were dried in a porcelain crucible for 12 h at 200°C . The complete drying of the materials was confirmed by following repetitive cycles of heating and weighing. The weighing of the well-dried ingredients was performed with an accuracy of 0.00001 g, using a Mettler AE163 balance. The 60:40 mole ratio of Li_2SO_4 and Li_2CO_3 was mixed thoroughly in an agate mortar under acetone. This mixture was well dried and then carefully transferred into a porcelain crucible. This mixture was melted and allowed to soak at 20°C above the melting point for 3 h so as to achieve complete homogeneity of the melt. The homogenized molten mass was then quenched using an aluminum mould at room temperature. A similar technique was employed to prepare $\text{V}_2\text{O}_5:\text{P}_2\text{O}_5$ (60:40) cathode material.

The weighed amount of cathode mixture was pressed to obtain a pellet of diameter 13 mm. Later, a weighed amount of electrolyte was pressed over the pre-pressed cathode at about the same pressure. Finally, a weighed amount of anode material was

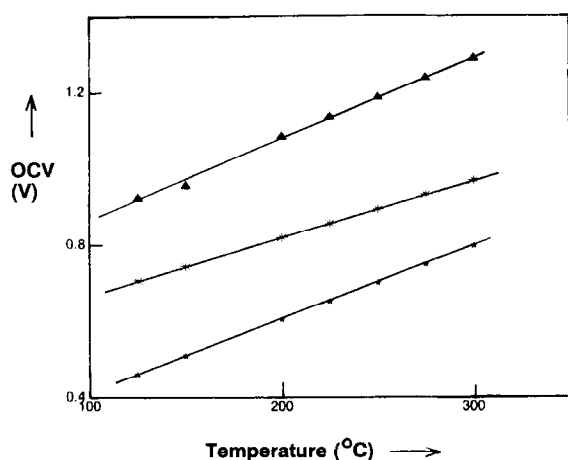
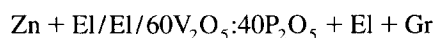


Fig. 2. Variation of OCV with temperature for Zn+El/El/60V₂O₅:40P₂O₅+El+Gr cells (Δ) 0% discharge, (*) 50% discharge, (★) 25% discharge.

pressed at 5 ton/cm² over the pre-pressed electrolyte. The cell configuration is



El = Li₂SO₄:Li₂CO₃ (60:40) powder.

Cells obtained in this way were then loaded in a sample holder having a silver foil spot welded with silver wire as the current collectors. A good mechanical contact was established by using a spring action arrangement. These cells, while loaded in the sample holder, were placed in an electric furnace. The temperature of the furnace was controlled using a Eurotherm PID temperature controller with ± 1 °C accuracy. Before the discharge, the variation of the open-circuit voltage (OCV) was recorded at an interval of 50 °C using a digital Panel Meter with an input impedance of 10 M Ω . The cell was then allowed to discharge through a constant 20 μ A current at 300 °C to 25% of its original OCV, and

again we recorded the OCV as a function of the temperature, as described above. Finally, the cell was discharged to 50% of its original OCV and we repeated the OCV measurement. From the temperature dependence OCV data the thermodynamic parameters of the cell were calculated for the 3 depths of discharge.

3. Results and discussion

Fig. 1 shows a typical discharge characteristic curve for a cell at a constant 20 μ A current drain. The initial sharp drop in emf is due to the high internal impedance. A careful look at the curves reveals the discharge in steps indicating various degrees of intercalation in the V₂O₅:P₂O₅ cathode during the discharge process, i.e. at every transition point the structure of the cathode changes, and thereafter intercalation takes place in different sites.

In general for all cells, the OCV and the short-circuit current are found to increase with an increase in the temperature for all 3 depths of discharge. The increase in the current with the temperature is mainly due to the strong temperature dependence of the conductivity of the electrolyte. On the other hand, enhancement in the OCV is obviously independent of the conductivity but is strongly governed by the thermodynamics of the cell. The linear least-squares fitting of the OCV versus temperature is shown in Fig. 2. Evidently, the OCV of the cell at all temperatures reduces on discharge to different depths. This behaviour of the cell is mainly attributed to the change in the cathode stoichiometry (composition as well as structure) as a result of intercalation.

A detailed complex impedance analysis indicated an enhancement in the overall internal impedance of the cell. The increase in the internal resistance of the cell could be due to the formation of an intermediate

Table 1
Thermodynamic parameters of Zn+El/El/60V₂O₅:40P₂O₅+El+Gr

Discharge Extent	(dE/dT) $\times 10^{-3}$	dG (kJ/mole)			dH			E_H
		200 °C	250 °C	300 °C	200 °C	250 °C	300 °C	
0%	2.046	220	239	258	-33.20	-32.79	32.35	+0.17
25%	1.507	158	171	187	-20	-19.6	-18.6	+0.11
50%	1.92	113	133	150	+61.4	+60.63	+59.85	-0.31

phase across the electrode–electrolyte interface. The values of dE/dT calculated from the figure have been used to obtain the Gibb's free energy (dG), enthalpy (dH) and the thermoneutral potential for 3 depths of discharge, and they are shown in Table 1. Table 1 indicates that for 0% and 25% discharge the enthalpy is negative and the thermoneutral potential is positive (exothermic chemical reaction) while for 50% discharge the enthalpy is positive and the thermoneutral potential becomes negative (endothermic chemical reaction). Unfortunately, there are no reports on the thermodynamic studies of high-temperature batteries in general, and sulphate based in particular, for comparative study. However, the results given in Table 1 indicate that the nature of the chemical reaction taking place inside the cell during the discharge process depends upon the discharge region which is in accordance with earlier reports in the literature [9]. The steps in the discharge curve (Fig. 1) are in good agreement with the above findings.

Acknowledgments

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