Reaction in the silver zinc cell

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An adiabatic calorimeter was used to measure the thermodynamics of the silver zinc cell. The charge and discharge reactions were shown to take place in two stages involving the production of argentous oxide and argentic oxide respectively. No thermal evidence was found to suggest the existence of a higher oxide of silver. The cell reactions were

\[ 2\text{Ag} + \text{ZnO} \rightleftharpoons \text{Ag}_2\text{O} + \text{Zn}, \Delta H = 158.7 \text{ kJ} \cdot \text{mol}^{-1} \quad (1) \]

\[ \text{Ag}_2\text{O} + \text{ZnO} \rightleftharpoons \text{Ag}_2\text{O}_2 + \text{Zn}, \Delta H = 176.1 \text{ kJ} \cdot \text{mol}^{-1} \quad (2) \]

If the cell was left on open circuit for a long period, or the positive electrodes heated, reaction (2) was suppressed and the discharge took place via reaction (1), without any reduction in capacity.

Introduction

Although batteries containing silver positive electrodes have been studied for many years, the mechanisms of their reactions are still not fully established. Luther and Pokorny [1] showed that three potential plateaux were formed when a silver electrode was charged anodically in potassium hydroxide solution. The potentials of these plateaux were 0.34 V, 0.57 V and 0.74 V measured against a hydrogen electrode in normal potassium hydroxide solution. They associated the first plateau at 0.34 V with the formation of argentous oxide, Ag\textsubscript{2}O, the second plateau at 0.57 V with the conversion of argentous oxide to argentic oxide, Ag\textsubscript{2}O\textsubscript{2}, and the third plateau at 0.74 V was attributed to 'silver peroxide', Ag\textsubscript{2}O\textsubscript{3}, which then decomposed to form argentic oxide. Hickling and Taylor [2] extended this work to suggest that during the formation of the first argentous oxide plateau there may have been some absorption of oxygen or the possible formation of a silver sub-oxide. Jones, Thirsk and Wynne-Jones [3] did not agree that 'silver peroxide' could possibly exist by considering the oxides of silver to be formed by the introduction of oxygen into the octants of a face centred cubic silver lattice. The compound Ag\textsubscript{2}O\textsubscript{3} could then be regarded as an intermediate between AgO with half-filled octants and a hypothetical AgO\textsubscript{2} with completely filled octants.

Pleskov [4] has also suggested the formation of silver peroxide at high anodic potentials and the silver peroxide potential has been reported by Radlein [5] and Nagel, Ohse, and Lange [6]. Jones et al [3] however, examined the oxidation products of silver using X-ray diffraction techniques but found no evidence for oxides higher than argentous oxide and this work has been confirmed by Wales and Burbank [7, 8] again using X-ray diffraction methods.

All previous measurements on the silver oxide system have been carried out using either potential measurements or X-ray diffraction studies, but no thermal measurements have been reported. A new approach has been made to the subject in these laboratories by making thermal measurements, in an adiabatic calorimeter [9] where it was shown that the sum of the electrical energy and the heat absorbed by a working galvanic cell was constant, and equal to the change in enthalpy, at all charge and discharge currents. Preliminary experiments in this calorimeter showed that the charge reaction took place...
in two stages, the oxidation of elementary silver to argentous oxide, and its subsequent oxidation to argentic oxide. The accuracy of the calorimeter was insufficient, however, to distinguish between the charge reactions which involved cell cooling, but it has now been modified to measure decreases in cell temperatures, allowing the charge and discharge reactions of the silver oxide zinc system to be studied in detail.

Experimental

The adiabatic calorimeter [9] was modified to follow decrease in temperature and is shown in Fig. 1. Air was circulated through a ducting (A) by a fan (B) which gave a complete change of air every five seconds. The ducting contained an electrical heater (C) and a cooling coil (D) which was connected to a heat exchanger (E) via a pump (F). The coolant liquid circulating through the heat exchanger was a mixture of ethyl alcohol and castor oil and the heat exchanger itself was immersed in a mixture of either ice and water or solid carbon dioxide and ethanol. A maximum cooling rate of 2°C per minute was obtained inside the calorimeter. The cooling circuit was operated continuously and heat was supplied to the system when required by the electrical heater (C) by comparing the output of two thermistors (G) as described previously [9]. The cell temperature was measured with a thermistor thermometer which covered a range of 15°C–45°C and was sensitive to 0.01°C, its response time being faster than the conventional mercury thermometer because of its much lower thermal capacity. The cell voltage was measured with a potentiometer accurate to 0.1%.

A 15 Ah silver oxide zinc cell incorporating cellophane separators was filled with 33 ml of 7 N potassium hydroxide electrolyte and allowed to stand on open circuit for 72 hours. The thermal capacity of the cell was measured using cooling curves and found to be 221.8 J/°C. No significant change in thermal capacity was measured when the cell was in both a charged and discharged condition.

Charge and discharge cycles were carried out at various currents and the temperature and voltage of the cell was measured at regular intervals. Although the cell was initially at room temperature between 18°C and 21°C, it operated at between 25°C and 35°C depending on the experimental conditions for most of the time. Both the electrical and thermal energy which was either absorbed or evolved from the cell was calculated from this data. The change in enthalpy for the system, ΔH, was then found by adding these quantities. Similar measurements were carried out on a cell which had been stored in a dry charged condition for four years.

Fig. 1. Adiabatic calorimeter.