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Self-Discharge in Bimetallic Cells Containing Alkali Metal

A theoretical analysis of self-discharge in a bimetallic thermally regenerative cell is reported (ref. 1). A relation is shown to exist between the current drawn and the rate of discharge under open-circuit conditions.

Thermally regenerative bimetallic cells, with alkali-metal anodes, have been considered as a means for conversion of thermal to electrical energy. In these cells the anode is an alkali metal such as lithium, sodium, or potassium; the cathode consists of a binary alloy of the alkali metal and a more noble metal such as lead, bismuth, or tin. The electrolyte is a mixture of molten halides of the alkali metal of the anode. The open-circuit potentials of such cells have been used for calculation of the thermodynamic properties of binary alloys.

It was noted (ref. 1) that in sodium-bismuth, bimetallic cells having an electrolyte of molten sodium fluoride, sodium chloride, and sodium iodide, a non-faradic or "irreversible" transfer of sodium from the anode to the cathode takes place. Since this transfer occurs without producing an electric current in the external circuit, it is also called a self-discharge of the cell. The self-discharge rate is much too high to be explained simply by diffusion of dissolved sodium atoms through the electrolyte. Moreover, the rate of self-discharge decreases with increase in current drawn from the cell.

For the theoretical analysis, an attempt to explain the observed self-discharge rate and its anomalous behavior with current, it was assumed that (1) the self-discharge of the cell is in part due to electronic conductivity of the electrolyte, which in turn results from and is proportional to dissolved alkali metal; (2) an equilibrium exists between dissolved alkali-metal atoms and alkali-metal ions and electrons; and (3) the activity coefficient of the dissolved metal atoms is consistent with respect to concentration.

The self-discharge rate of a concentration cell is considered to be due to the dissolution and ionization of alkali-metal atoms in the fused-salt electrolyte. On the basis of the outlined assumptions, an expression was derived that relates the self-discharge rate as a function of current. This expression was used for construction of graphs showing the effect of cell current on the self-discharge rate for a variety of conditions. It is demonstrated that the open-circuit potential of such a cell is less than that predicted from theoretical thermodynamic considerations.

Reference:

1. Hesson, J. C.; Foster, M. S.; Shimotake, H.: Self-Discharge in Alkali Metal-Containing Bimetallic Cells. J. Electrochem. Soc., vol. 115, No. 8, Aug. 1968, pp. 787–790.

Notes:

1. This information may interest researchers in electrochemistry or molten-salts chemistry.
2. Inquiries concerning this information may be directed to:

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(continued overleaf)

Patent status:

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