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TECHNICAL NOTE

Semi-aqueous lithium–mercury oxide battery

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At the present state of research, one of the factors which most limits the performances of cells with organic electrolytes is the unsatisfactory behaviour of the cathode materials used. These tend to polarize markedly in the media studied even at relatively low values of the discharge current density (a few mA/cm^2). In each case, their electrochemical behaviour is definitely inferior to that shown by the lithium electrodes, which can support higher discharge currents when used as anodes in these media [1]. Therefore it is necessary to operate at low current densities, but even under these conditions the coulombic efficiency of the cathode is generally low. These disadvantages should be largely overcome by using the cathodes in aqueous solutions with high conductivity, where satisfactory values for the diffusion rates of the ionic species and of the solubility of the products formed by the reaction at the electrodes create conditions much more favourable than in organic solutions.

We have attempted to combine the advantages derived from the use of a lithium anode (high values of potential and of electrochemical equivalent) with those derived from the use of a cathode in an aqueous solution (limited values of polarization and good coulombic efficiency). Thus a cell was made with a lithium anode in an organic solution and a HgO cathode in aqueous solution; the organic solvent used (dimethylcarbonate, DMC) is insoluble in water, so that a complete separation between the organic phase and the aqueous one is possible so as to keep the lithium anode under the required anhydrous conditions. The cell may be shown as:

$$\mathrm{Li/LiAlCl_4{-}DMC/KOH{-}H_2O/HgO,C} \qquad (1)$$

HgO was chosen as cathode in this preliminary investigation because of its well-studied behaviour in the caustic electrolyte used in the mercury cell [2]. The over-all reaction, occurring through the migration of lithium ions from the anode to the cathode, may be simply shown as:

$$\mathrm{2Li + HgO = Li_2O + Hg}$$

The organic solution of $LiAlCl_4$ in DMC has a satisfactory specific conductivity ($\chi = 13{\cdot}2$ m mho cm^{-1} at 27°C for $c = 19$ g/100 g solvent), greater than that of $LiClO_4$ in the same solvent (6·3 m mho cm^{-1}) [3]. The solution of KOH was 40% by weight and the mercuric oxide (red variety) was mixed with 10% by weight of finely powdered graphite.

The cell was constructed in a button form (Fig. 1), by absorbing the aqueous solution on glass fibre paper (Whatman GF 81) and using a stainless steel tube (internal diameter 2·5 cm) as

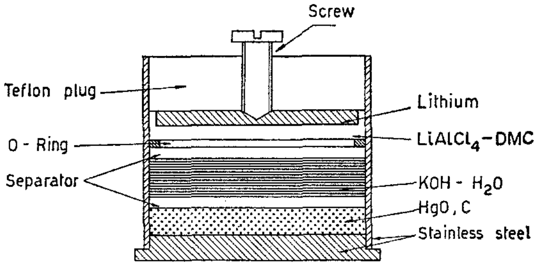

Fig. 1. Construction details of the semi-aqueous button cell. Internal diameter: 2·5 cm. Height (excluding the Teflon plug): 1·0 cm.

the external casing. The organic solution and the lithium electrode were added to the aqueous semi-cell in a dry box under an atmosphere of argon and then the cell was sealed. Thus, a semi-liquid button cell was obtained, similar in structure to that described by Cook [4]. About 1 g of the cathodic mixture was used so that the theoretical capacity of the cell was about 210 mAh (based on a two-electron reduction of the oxide). The lithium anode had the form of a pellet derived from lithium rod. The HgO,C cathode (4·9 cm^2) was in the form of a loose powder.

This cell has an open circuit voltage (OCV) of 2·8–2·9 V at room temperature. A determination of degree of polarization during discharge was carried out at various current densities. As a comparison, a cell of the Mallory type [2]:

$$\text{Zn(Hg)/KOH—H}_2\text{O/HgO,C} \qquad (2)$$

was constructed in our laboratory with the same technique as for cell (1) and subjected to a polarization test (the two cells having the same dimensions and the same capacity). In Fig. 2 curves *I–V* are reported for the two cells; for each value of *I*, the corresponding value of *V* was observed for 30 sec, during which time the potential remained almost constant, showing a slight tendency to increase. As expected in the presence of the organic solvent, the semi-aqueous cell shows higher values of polarization for a given value of *I*. However, it should be noted that, because of the higher OCV value for cell (1) (2·8 V) compared to cell (2) (1·35 V), the semi-aqueous cell always maintains a higher potential than the aqueous one. The increase in cell polarization caused by the organic solvent is therefore acceptable.

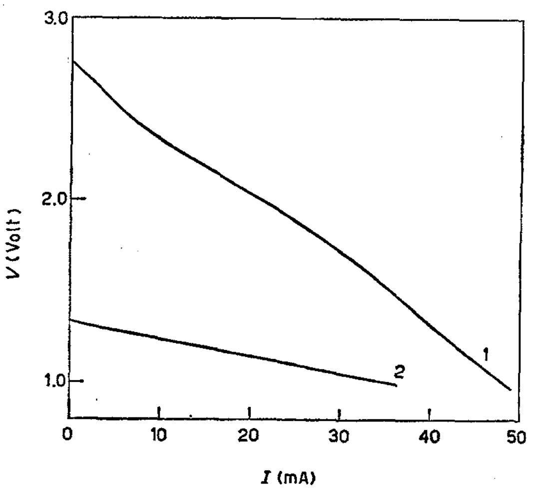

Fig. 2. Cell polarization. Curve 1: cell (1). Curve 2: cell (2).

On the basis of this result, the semi-aqueous cell was subjected to a discharge at 2 mA (which corresponds to a C/100 discharge for a capacity of 200 mAh) up to a 1·3 V cut-off. The discharge curve (Fig. 3) has an average potential of 1·9–2·0 V, substantially higher than that of the aqueous mercury cell (1·3 V). It is reasonable to suppose that higher values may be obtained by improving the non-aqueous semi-cell. The coulombic efficiency is 60%, a satisfactory value considering the use of a lithium anode in an organic solvent and the unsophisticated state of development of the cell. It should be noted that throughout the discharge the cell is capable of recovering its OCV very rapidly. This seems to prove that the decrease in potential on load is mainly attributable to an increase in the internal resistance, i.e. concentration or activation polarizations have minor importance.

At the moment, the major disadvantages seem to be linked to the tendency of DMC to evaporate, thus causing an increase in the resistance of the organic layer. It is therefore necessary to produce a hermetically sealed cell and to limit the empty spaces in which the solvent can evaporate. Examination of some cells after use has not revealed any deterioration of the lithium due to attack by the aqueous solution.

The first results obtained therefore seem to demonstrate the possibility of combining an aqueous semi-cell with a non-aqueous one. Research in this direction is in progress to ascertain primarily: (1) the possibility of using other types of semi-cells (organic and aqueous); (2) the shelf life of these cells; (3) their behaviour as a function of temperature; (4) the possibility of improving their performance by improving the construction from a technological viewpoint; in particular, the energy density practically attainable has to be determined (the theoretical one is 608 Wh/kg, for cell (1), whereas that of cell (2) is 248 Wh/kg).

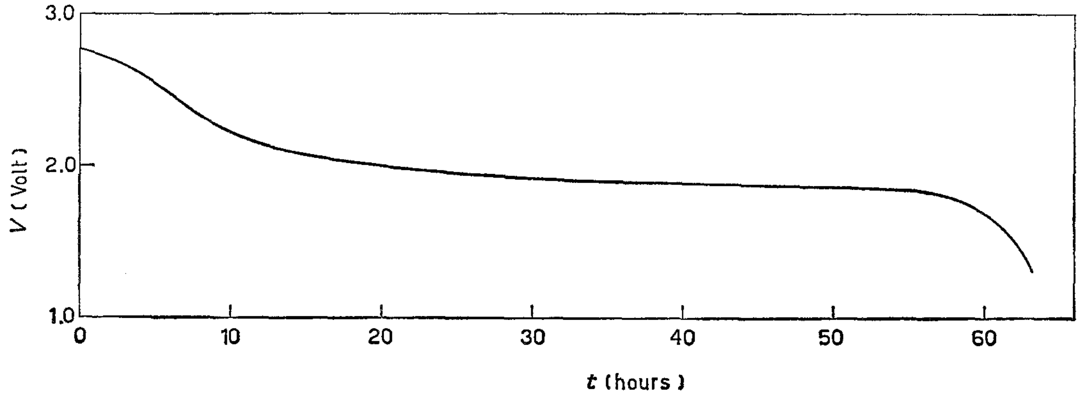

Fig. 3. Cell discharge at 2·0 mA (C/100).

References

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[4] G. Cook, *J. Electrochem. Soc.*, **117**, (1970) 559.