

Problems of manufacturing a magnesium–iodine battery

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Abstract

The present paper deals with problems of manufacturing a magnesium–iodine battery, based on experiences drawn from the lithium–iodine battery. Initial results are outlined, taking into account activation and coating of the magnesium surface.

Introduction

The lithium–iodine battery is a well-known solid-state battery which has successfully been produced since the 1970s for application in heart pacemakers [1]. Within the manufacturing process, anode coating by poly(2-vinyl–pyridine) (P2VP) has been shown to be necessary to guarantee a favourable discharge behaviour over a long working period [2]. As cathode materials, charge-transfer complexes of P2VP and iodine are commonly used. In comparison with the Li battery, there are only a few papers dealing with other reactive light metals such as magnesium [3–5]. This metal has a sufficiently negative standard electrode potential ($E^0 = -2.35$ V) and a high charge density (3.8 A h/cm³, the value for Li being 2.1 A h/cm³) which makes it interesting for application in electrochemical power sources. In ref. 3 an open-circuit voltage of 1.85 V for a Mg/I₂ cell has been calculated from the heat of MgI₂ formation. But, up to now, Li has not been replaced by a different metal in commercial solid-state iodine batteries.

Experimental

With this background, a Mg/I₂ battery was constructed in an analogous way to that described for Li/I₂ batteries in ref. 6, coating the anode with P2VP or mixtures of P2VP and anthracene. For the preceding activation of the magnesium surface, which was supposed to play an essential role for application in electrochemical cells, different methods were applied:

- (i) removal of the oxide layer by abrasion;
- (ii) dissolving the oxide layer by washing with aqueous solutions of hydroiodic acid;
- (iii) anodic dissolution of the magnesium surface by electrolysis, the electrolyte being a Grignard solution in tetrahydrofuran (THF) containing LiBr, and
- (iv) activation by allowing to react with butyl iodide for a short time in the form of a Grignard reaction.

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The activation reactions were followed by rinsing with dry diethyl ether or THF. The magnesium anodes then showed a bright metallic surface (after reaction (i), (ii)) or a velvet like black one (after reaction (iii), (iv)). The anode sheets (surface area: 12 cm²) were dipped into a solution of 1 g P2VP in 10 ml benzene and after evaporation of the solvent it was found that the anodes had been coated by a thin polymer layer (thickness: 20-30 μm). Based on the model reactions for P2VP-coated lithium anodes [6], in some cases anodes were coated by a solution of 1 g P2VP in 10 ml THF saturated with anthracene (0.34 g/10 ml THF). The coated anodes were then mounted into the battery case filled with the cathode material, followed by hermetically sealing the case with polyester resin. The total battery design is described in ref. 6. The theoretical capacity is confined by the anode to 0.83 A h.

As cathode material a mixture of *n*-butylurotropinium iodine (BuUrI) and iodine, partly containing polyiodides, was used [6]. This material with the composition BuUrI_{1.5} is a liquid material, and so it can be easily poured into the battery case. For comparison, some batteries were manufactured applying activated, but uncoated anodes. All experimental steps were carried out in an argon filled glove box.

Mode of battery testing

The discharge characteristics of the batteries were determined (plot of voltage versus discharge time) in the following way: the batteries were allowed to discharge by applying a continuous load of 140 kΩ at 37 °C, and after definite time intervals, the resistor was switched off for 24 h, and then the cell voltage (*U*) was measured under different constant loads, the resistivity being infinite (open circuit), 140 and 5 kΩ, respectively. From the potential drop under load the internal resistance of the cell was calculated. In some cases, the internal resistance was measured by means of an impedance technique, applying a frequency response analyser connected to a galvanostat. The values obtained were in good agreement with those calculated from the potential drop.

Results and discussion

In the case of cells containing uncoated anodes, immediately after dipping the anode into the cathode material the open-circuit voltage (OCV) came to approximately 1 V, but the voltage dropped down rapidly to a value of about 0.6 V, which was then constant for a long period. The values finally reached varied in the range of 1.2 to 1.6 V.

For cells containing coated anodes an initial open-circuit voltage of 0.3 to 0.5 V was obtained, 30 min after manufacturing. These values were nearly constant for a long period. Only after a long storing period of 1000 to 2000 h the voltage began to increase with time and reached a final value of 1.65 V, being constant for many thousand hours, but the load voltages measured at 140 kΩ and 5 kΩ proved to be very much lower (see Fig. 1).

The increase of the OCV is related to a strong increase of the internal resistance up to MΩ values, which means that the batteries are useful for very low current drainage only, to be seen from Fig. 2.

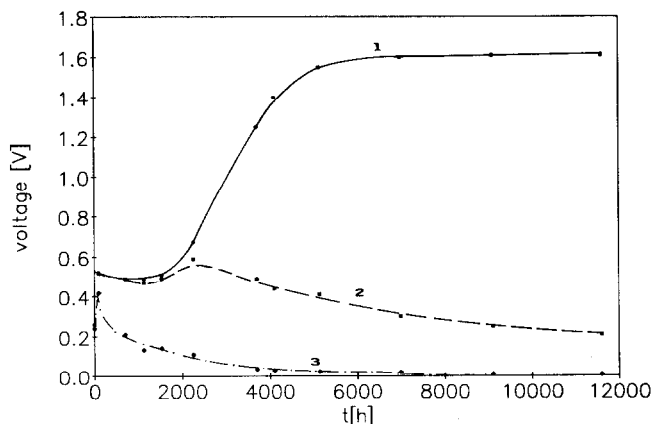


Fig. 1. Discharge curves for batteries with coated anodes (voltage vs. time): (1) open circuit; (2) measured under $140\text{ k}\Omega$ load, and (3) measured under $5\text{ k}\Omega$ load.

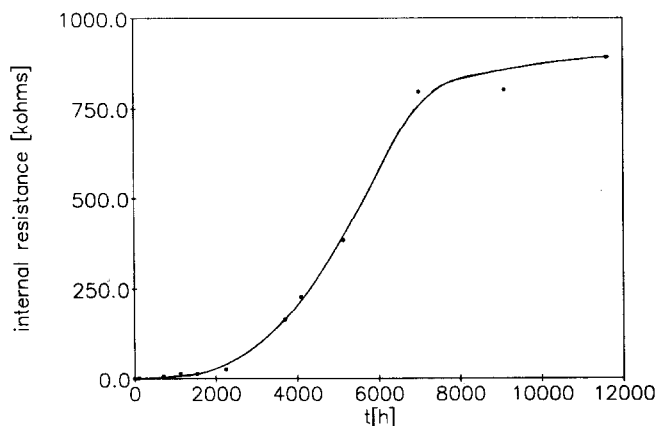


Fig. 2. Course of internal resistance vs. time.

The theoretical OCV of 1.85 V [3] has not been measured in any instance. Possibly, it is built up only for a very short time, immediately after installation of the magnesium anode into the cathode material.

Concerning the mode of activating the magnesium surface, it must be pointed out that there are no significant differences in the discharge behaviour. Also addition of anthracene to the coating layer had no influence on the discharge characteristics. This means that the formation of magnesium-anthracene, as an intermediate product which should react with P2VP forming higher molecular weight products according to the reactions cited in ref. 6, does not play a decisive role.

The effect of moisture is interesting when present on the magnesium/cathode interface. A different discharge characteristic was found for batteries with anodes activated by aqueous hydroiodic acid. Whereas the voltage at the beginning of the discharge process is higher than for dry coated anodes, a stable OCV of 1.2 V is reached which is then constant for a long period (see Fig. 3). If the anodes are rinsed with dry THF after acid washing the normal low initial voltage is found.

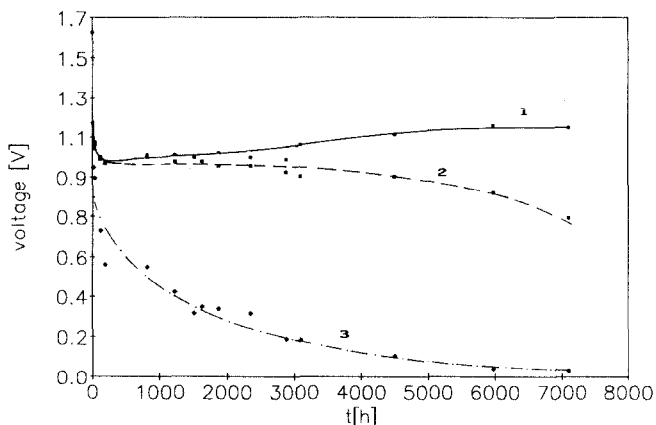


Fig. 3. Discharge curves for batteries with hydroiodic acid-activated anodes: (1) open circuit; (2) measured under 140 k Ω load, and (3) measured under 5 k Ω load.

Conclusions

The present study shows that manufacturing a magnesium–iodine battery is possible in principle, but it takes a long storage time to generate the final open-circuit voltage of 1.65 V. Probably, all processes necessary for the formation of the solid electrolyte need much more time than in the case of Li/I₂ battery. Taking into account the same model reactions as discussed for the Li/I₂ system [6], we have found that these model reactions applied to magnesium occur much more slowly [7]. In particular, the reaction of magnesium with anthracene proceeds in a different way [8] to form a more covalent addition compound. For this reason, the addition of anthracene to the P2VP solution for anode coating is not expected to have a significant influence on the cell performance. As a consequence, contrary to the Li/I₂ cell, no high molecular weight network structure of P2VP on the magnesium anode is built up. Therefore, the conductivity of MgI₂ will not be improved to such an extent as for the Li/I₂ batteries. The insufficient formation of an ion conducting interphase consisting of a complex compound like MgI₂(P2VP)_x accounts for the very low current density under load. The main problem is, therefore, to stimulate the formation of a MgI₂ complex having a sufficiently high ion conductivity.

Acknowledgements

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