

## A study on novel lithium–iodine and lithium–bromine solid electrolyte batteries

K. Lühder, L. Schmidt, A. Schnittke and H. Füllbier

*Ernst-Moritz-Arndt University of Greifswald, Soldtmannstraße 16, O-2200 Greifswald (Germany)*

(Received February 25, 1992; in revised form May 12, 1992)

### Abstract

This paper deals with the influence of coating the lithium anode on the discharge behaviour of lithium–iodine and lithium–bromine batteries, containing lithium ion conducting solid electrolytes, at different temperatures. In contrast to poly(2-vinylpyridine)/iodine charge-transfer complexes, commonly used as cathodes in heart pacemaker batteries, polyiodides and polybromides bonded to polymers of styrene, which are functionalized by cationic groups, were used. It has been found that addition of anthracene to poly(2-vinylpyridine) as a coating material produces a positive effect on the discharge behaviour.

### Introduction

Recently we reported on a novel coating material consisting of a mixture of poly(2-vinylpyridine) (P2VP) and anthracene for the lithium anode in the lithium–iodine solid electrolyte battery [1]. Using such a mixture for coating the anode, more favourable discharge behaviour of the batteries was achieved than by applying P2VP alone. In the present paper it will be shown that this effect is generally observed, not only by applying a definite cathode material, such as liquid polyiodides [1] or solid polyiodides bonded to functional groups in polymer resins, but also for lithium batteries in which different bromine-containing cathode materials have been used. In this context, the discharge behaviour at different temperatures has been studied.

### Experimental

#### *Battery arrangement, materials, design and mounting procedure*

For testing the different coating layers, the following battery arrangement regarding our novel electrochemical materials, e.g., coating layers on the anode surface as well as iodine- and bromine-containing cathode materials, was chosen:

collector	lithium	coating	cathode	collector
	layer	material		
anode side			cathode side	

As cathode materials novel polyiodides and polybromides bonded to anion-exchange resins based on copolymers of styrene and divinylbenzene (as cross-linking agent),

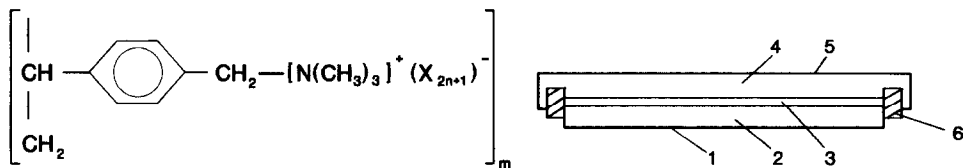


Fig. 1. Structure of applied polymers with X=iodine or bromine.

Fig. 2. Battery design. 1: bottom part of the case stainless steel (anode collector); 2: lithium metal; 3: coating layer; 4: cathode material; 5: top part of the case stainless steel (cathode collector); 6: polypropylene gasket ring.

which are functionalized with tetraalkylammonium cations via the benzene rings in C4 position, were used (Fig. 1). For preparing these substances, commercial anion-exchange resins (Wofatit EA 60, Chemie AG, Bitterfeld, Germany), loaded with chloride, were converted into the iodide and bromide form and then allowed to react with iodine or bromine to form the polyiodide and polybromide (Poly-I, Poly-Br), respectively. The detailed preparation has been described in [2-4].

Besides these materials, in the case of bromine, charcoal was also used as the basic substance for the halogene cathode [3]. For this purpose it was pulverized and loaded with bromine at room temperature (5 g bromine/1 g charcoal), which product will be designated by Ch/Br.

After preparation the substances were stored in sealed ampoules or in 'Schlenk' vessels to exclude atmospheric moisture. They show a sufficiently high conductivity to act as a cathode material, as it can be concluded from the following values: Poly-I:  $3.1 \times 10^{-4}$  S/cm, Poly-Br:  $1.2 \times 10^{-4}$  S/cm, Ch/Br: 40 S/cm.

As coating materials for the lithium anode, a solution of P2VP in benzene (1 g P2VP in 10 cm<sup>3</sup> benzene) and a solution of P2VP in tetrahydrofuran (THF) saturated by anthracene (1 g P2VP + 0.3 g anthracene in 10 cm<sup>3</sup> THF), respectively, were used.

The batteries were constructed as button cells, using the commercially-produced parts of the cell R 2032, which have been shown to be more useful for the evaluation of the cathode materials, described above than conventional cells LiS 2300 (Litronik GmbH, Pirna, Germany), as they are used in heart pacemakers. The battery design can be seen from Fig. 2.

Assembly of the different parts was carried out in a glove box under an argon atmosphere. First, a lithium disk (diameter: 16 mm, thickness: 1 mm) was cut out of a lithium foil. The lithium had previously been remelted for cleaning and had a purity of 99.99%. The disk was pressed into the bottom part of the cell. The lithium surface was then coated by dropping a few drops of the solution onto the metal surface, followed by evaporating of the solvent. The cathode material was then placed on the coated surface, either in the form of a powder or as a tablet which had been separately pressed before mounting. The powder was slightly pressed by means of a piston, either by hand or machine. Finally, the top part of the cell case was put on top of the cathode material and flanged, by means of a special device, the gasket placed around the bottom part acting as an isolating material. In this way the battery case was made air-tight.

#### Mode of battery testing

After having produced the batteries as described above, their discharge characteristics were determined by plotting voltage ( $U$ ) versus time. For this purpose the

batteries were discharged by applying a continuous load of 140 k $\Omega$  at 25 °C (standard experiment), being the load commonly applied in heart pacemakers. At definite time intervals the cell voltage was measured by using different loads. As, in most cases, there was only a very slight difference between the values of voltage at 140 k $\Omega$  and the open-circuit voltage, the last values are omitted in the following section.

Furthermore, in some experiments the batteries were tested above and below ambient temperature. To perform these tests the batteries were stored in a drying chamber and a refrigerator, respectively, at the desired temperature. These devices were provided with a supply pipe for cables to carry out the measurements externally.

## Results and discussion

### *Polyiodide as cathode material*

Before testing the influence of different anode coating layers on the discharge behaviour, it was to be shown that such a layer is in general necessary. From Fig. 3, it can be seen that application of anode coating is necessary, as was already found in a previous paper [1]. Without any coating of the lithium surface the discharge curves show a continuously downward tendency from the beginning of the discharge. Addition of anthracene to P2VP as a coating material, compared with the application of pure P2VP, improves the discharge behaviour slightly.

In Fig. 4, discharge curves of batteries whose anodes were coated with pure P2VP and a mixture of P2VP and anthracene are compared. Discharge temperatures were 80 °C and 130 °C. It is seen that coating anodes with P2VP/anthracene produce higher and more constant discharge voltages than coatings of P2VP only.

At lower temperatures, +1 °C and -20 °C, the beneficial effect of anthracene addition is not as significant as in the case of higher temperatures (Fig. 5). Within the first discharge period up to 2000 h, the anthracene-containing layer seems to be

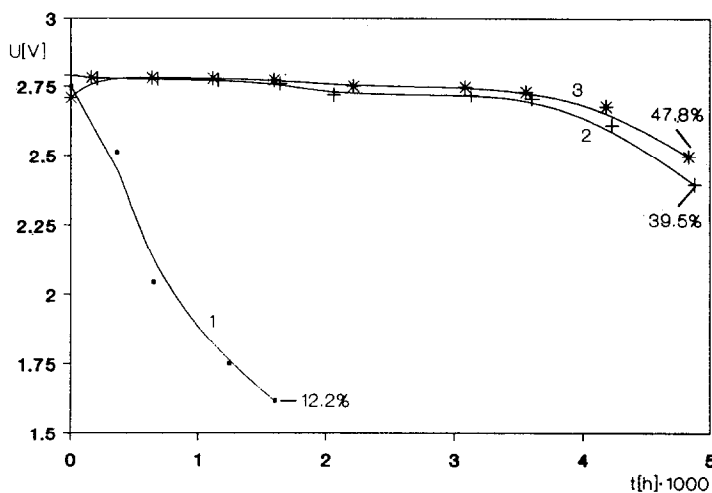


Fig. 3. Discharge characteristics of Li-I<sub>2</sub> batteries, polyiodide as cathode material. Continuous and measuring load: 140 k $\Omega$ , temperature: 25 °C. Values noted at different points of the curves, capacity used according to the time on the  $t$ -axis: (1) without coating layer, (2) coating layer: P2VP, (3) coating layer: P2VP/anthracene.

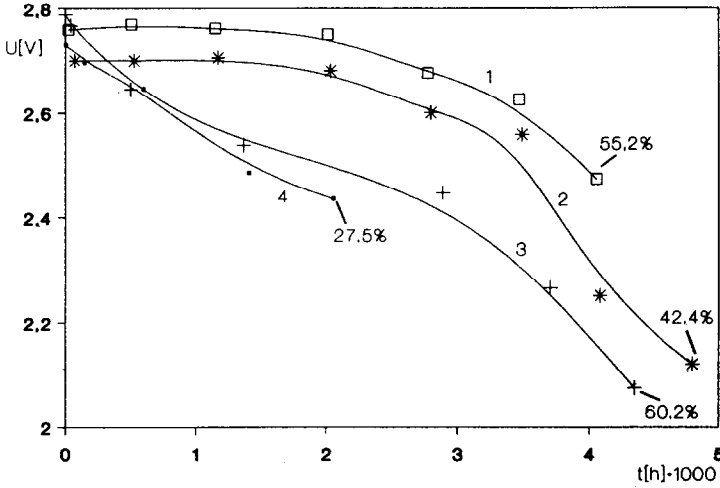


Fig. 4. Discharge characteristics of Li-I<sub>2</sub> batteries, polyiodide as cathode material. Continuous and measuring load: 140 kΩ; (1) coating layer: P2VP/anthracene, 80 °C; (2) coating layer: P2VP/anthracene, 130 °C; (3) coating layer: P2VP, 80 °C; (4) coating layer: P2VP, 130 °C.

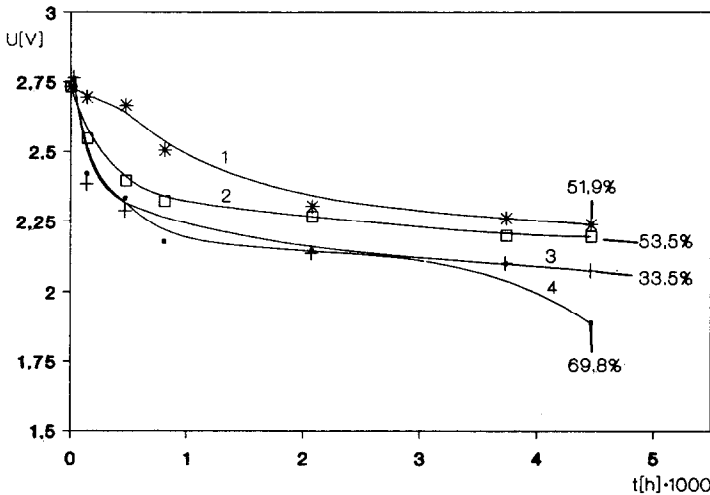


Fig. 5. Discharge characteristics of Li-I<sub>2</sub> batteries at lower temperatures, polyiodide as cathode material. Continuous and measuring load: 140 kΩ; (1) coating layer: P2VP, +1 °C; (2) coating layer: P2VP/anthracene, +1 °C; (3) coating layer: P2VP, -20 °C; (4) coating layer: P2VP/anthracene, -20 °C.

better, but after longer discharge times the discharge curves of batteries, whose anodes were coated with pure P2VP, show more stable and higher voltage levels.

#### *Polybromide and bromine on charcoal as cathode materials*

The lithium-bromine solid electrolyte battery has been known in principle, but little research has been done in this field, the results of which are mainly in patents, cited in refs. 5 and 6.

In analogy to the batteries with Poly-I as cathode material, polybromides bonded to polymers (Poly-Br) were used. In Fig. 6, batteries with different anode-coating layers for the anode are compared. As expected, batteries without anode coatings are not very successful; the voltage is very low, even from the start of the discharge (curve 1). Furthermore, a great difference between the P2VP coating and the P2VP/anthracene coating can be observed (curves 2 and 3). Only in the last case (curve 3) is the theoretical open voltage of 3.5 V nearly reached for the first 1000 h of the discharge period, while in the first case (curve 2) the load voltage only reaches 2.5 V. So it can be concluded that (i) the positive influence of anthracene addition to P2VP is, in the case of the bromine battery, much more effective than in the case of the iodine battery, and (ii) that anthracene addition plays a dominant role to make the bromine battery work to some degree.

Nevertheless, the course of the whole discharge process remains less advantageously compared to the iodine battery. For studies at lower temperatures, cathode materials consisting of bromine in charcoal (Ch/Br) were used. From Fig. 7 the discharge characteristics of batteries with a different anode coating, P2VP and P2VP/anthracene, can be seen. Regarding the corrosive behaviour of bromine, it was surprising that the lithium-bromine battery has relatively good stability, working at ambient temperature as well as at lower temperatures. In general, the discharge characteristics recorded at low temperatures (0 °C, -20 °C) were better than those at ambient temperature. We believe that this behaviour is caused by lower self-discharge rates at low temperatures as a consequence of lower bromine pressures. A comparison of curves 3 and 4 shows that the P2VP/anthracene-coated anode gives a more continuous discharge behaviour up to about 8000 h, while in the case of the P2VP-coated anode some time is necessary to build up a voltage of about 3 V, and this value falls abruptly after a relatively short discharge time of 3000 h. In all cases, the discharge time of the batteries seems to be limited, not only by an increased internal resistance, but also by irreversible processes occurring simultaneously with the discharge process.

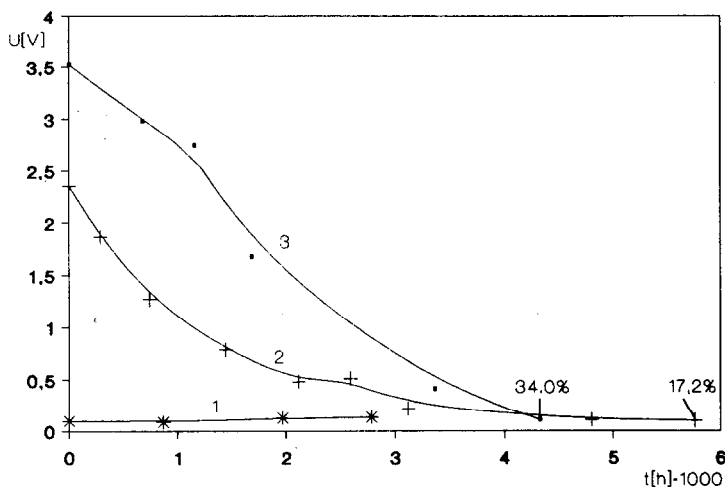


Fig. 6. Discharge characteristics of Li-Br<sub>2</sub> batteries, polybromide as cathode material. Continuous and measuring load: 140 k $\Omega$ , temperature: 25 °C; (1) without coating layer; (2) coating layer: P2VP; (3) coating layer: P2VP/anthracene.

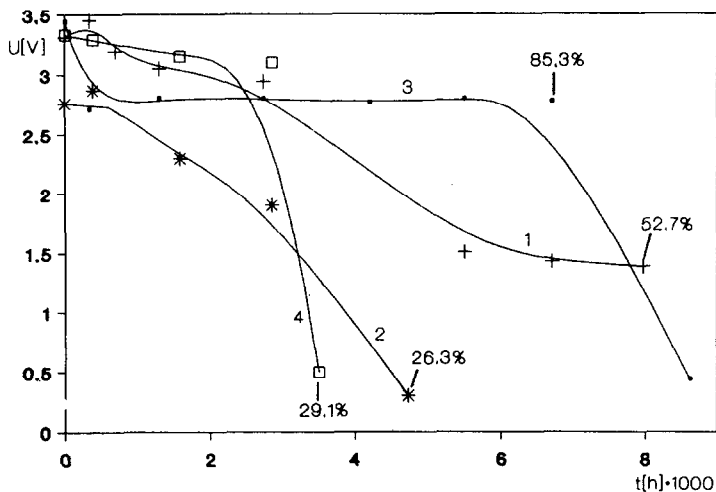


Fig. 7. Discharge characteristics of Li-Br<sub>2</sub> batteries at 0 °C and -20 °C, charcoal/bromine as cathode material. Continuous and measuring load: 140 kΩ; (1) coating layer: P2VP/anthracene, 0 °C; (2) coating layer: P2VP, 0 °C; (3) coating layer: P2VP/anthracene, -20 °C; (4) coating layer: P2VP, -20 °C.

The positive influence of the addition of anthracene to P2VP for coating the anode can be understood as outlined in ref. 1, i.e., addition compounds of lithium and anthracene are initially formed, transfer-lithium atoms to the polymer P2VP being able to form addition compounds for its part. By this process, the linear structure of P2VP is thought to change to an amorphous phase with a network structure having a higher conductance for lithium ions.

## Conclusions

The present paper shows that anode coating of lithium-halogen batteries is in all cases necessary to achieve an improved discharge process. The addition of anthracene to P2VP, commonly used in heart pacemaker batteries, gives an improvement to the discharge behaviour, independently of the kind of the cathode material used.

## Acknowledgement

This work was supported by the 'Fond der Chemischen Industrie' and 'Deutsche Forschungsgemeinschaft'.

## References

- 1 K. Lühder, P. Lobitz, M. Wehlan, A. Reiche and H. Füllbier, *J. Power Sources*, 37 (1992) 355.
- 2 L. Schmidt, *Thesis*, University of Greifswald, Germany, 1990.

- 3 A. Schnittke, *Thesis*, University of Greifswald, Germany, 1992.
- 4 A. Schnittke, H. Stegemann, H. Füllbier and J. Gabrusenoks, *J. Raman. Spectrosc.*, 22 (1991) 627.
- 5 M. Barak (ed.), *Electrochemical Power Sources, Primary and Secondary Batteries*, Peter Peregrinus LTD, Institution of Electrical Engineers, Burgess Hill, UK, 1980, p. 478.
- 6 J.-P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York/London, 1983, p. 437.