

A modified lithium–iodine battery

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(Received October 4, 1990; in revised form July 26, 1991)

Abstract

The present paper deals with the problem of coating the lithium anode for the lithium–iodine battery. It has been found that addition of anthracene to the commonly used poly(2-vinylpyridine) (P2VP) as coating material produces a positive effect on the discharge behavior of the battery. To interpret this influence modeling reactions outside the battery were carried out. As result it has been stated that at first lithium anthracene adducts are formed which react with P2VP to yield higher molecular products by coupling via the pyridine rings.

Introduction

As early as the 70s it was stated that pre-coating of the lithium anode by poly(2-vinylpyridine) (P2VP) within the processing of the lithium–iodine battery plays a dominant role for a favourable discharge behavior, which is most important for application as a pacemaker battery [1, 2]. Since then, work has been carried out to find an explanation for this positive effect [3–9]. As a result it has been shown that the LiI layer growing up during the discharge process does not form a compact crystalline coat on the anode, but has a distorted porous micro-structure, and the inner resistivity remains nearly constant for a long discharge period. However, the mechanism of the theoretically possible interaction between the anode metal and P2VP has not been taken into account.

It is known that the heterogeneous interaction between pyridine and alkali metals results in addition compounds which are unstable and couple in the C4 position of the ring. Pyridine rings are a component of the P2VP polymer, being fixed at the chain via the C2 position, but unsubstituted in position C4. Therefore, these pyridine rings should react with alkali metals in the same way to yield analogous reaction products. This procedure should result in a change of the chain structure to a network one. But it is also generally known that such a polymer analogous reaction may occur much more slowly, especially in the absence of any solvent, between the solid P2VP layer and the lithium metal on the anode surface in a solid state reaction. It was, therefore, necessary to find a component which could facilitate the transfer of lithium atoms from the anode surface to the polymer P2VP molecules. Such a component could be an aromatic, anthracene for instance, able to form addition compounds with alkali metals, especially in the presence of coordinating solvents such as tetrahydrofuran (THF).

Thus, for proving such an effect, batteries with mixtures of P2VP and anthracene as coating materials were tested. Furthermore, modeling reactions outside the battery were performed to support the conclusions drawn from the battery performance.

Experimental

For the coating experiments the following battery arrangement was chosen:

col/Li/coating/BuUrI + I₂/col

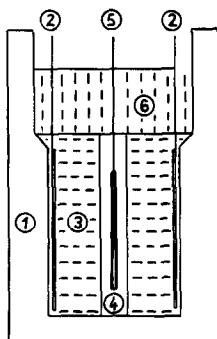
collector (col): stainless steel

anode: Li + coating material

cathode: n-butyltrotropinium iodide (BuUrI) + iodine

Instead of the commercially used charge transfer complex P2PV/I₂ as cathode material, a mixture of n-butyltrotropinium iodide (BuUrI) and iodine, which form a polyiodide *in situ*, has been proved to be most suitable for laboratory experiments [10–13]. The polyiodide is a liquid and so it can easily be poured into the battery case. This material shows a sufficiently high conductivity of approximately 10⁻² S/cm at room temperature to use it as a cathode. The iodine serves as a supply to reproduce the polyiodide in a equilibrium reaction during the discharge process. The battery design is shown in Fig. 1; the case is made of polyester resin. The preparation of the component parts and their mounting will be described in detail elsewhere. The coating procedure of the lithium anode was done in a glove-box under an argon atmosphere by dipping it into a solution of 1 g P2VP in 10 ml THF saturated with anthracene (0.34 g/10 ml THF), followed by evaporation of the solvent (THF). The reaction of the lithium metal with anthracene starts immediately covering the anode with a blue layer consisting of a lithium anthracene adduct (see below). The anode surface prepared in such a way is highly sensitive to air and moisture. After evaporating the solvent for 2 h the anode was mounted into the battery case, followed by loading with the cathode material and hermetically sealing with polyester resin.

The charge characteristics of the batteries were then determined (plot of voltage versus discharge time). For this purpose the batteries were discharged by applying a continuous load of 140 kΩ at 37 °C, and in definite time intervals the cell voltage (*U*) was measured, in each case under different constant loads, the resistivity being infinite (open circuit), 140, 5 and 1 kΩ, respectively.



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|---------------------|-------------------|
| ① battery case | ④ lithium anode |
| ② cathode collector | ⑤ anode collector |
| ③ cathode material | ⑥ hermetic seal |

Fig. 1. Battery design.

Results of battery testing

As in the present paper a different cathode material was used compared to the literature, it was first necessary to compare the batteries with lithium anodes coated by the conventional P2VP layer and those without any coating. The discharge curves are compared in Fig. 2. It can be seen that voltage decline with time is higher in the case of uncoated anodes, due to the well-known fact that the increase of cell impedance for coated anodes is lower than that for cells with uncoated anodes. This means that, in principle, any coating is advantageous. In a previous paper [10] it was shown that other coating materials such as PEO, PEO/LiI, BuUrI/LiI can also be used, but P2VP has proved the most effective up to now.

In Fig. 3 the discharge behavior of batteries with P2PV anode coating and those with a mixture of P2VP and anthracene as coating material is compared. In all cases studied up to now the addition of anthracene [14, 15] brings about a positive effect concerning the discharge behavior, the discharge curves being more flat. On the one hand, the maximum voltage is reached very quickly, without storing the battery for long, on the other hand, the load voltages are remarkably higher, which is clearly represented by measuring points when applying loads of 5 and 1 k Ω .

The positive influence of anthracene addition on the discharge behavior has also been observed in the case of other cathodic materials such as polyiodides bonded to functional groups in exchange resins [16–18].

Modeling reactions

To interpret the positive influence of anthracene addition to the coating material, modeling reactions outside the battery were carried out. From the literature it has been known for a long time that lithium and anthracene (atc), as well as other alkali metals, react in two steps to form addition compounds (eqns. (1) and (2)).

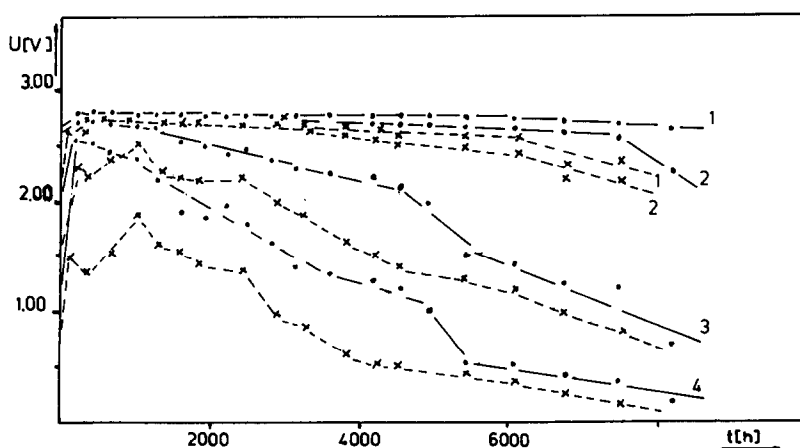


Fig. 2. Discharge curves: continuous line, P2VP coated anode; dotted line, without any coating. 1: Open circuit, 2: measured under 140 k Ω load, 3: under 5 k Ω load, 4: under 1 k Ω load.

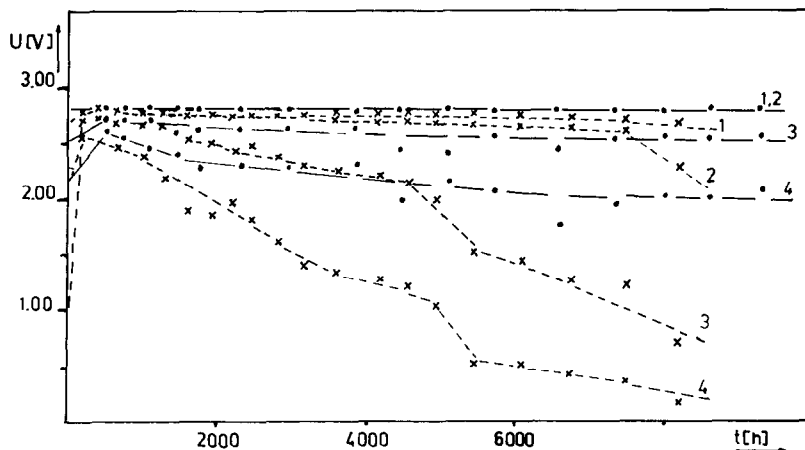
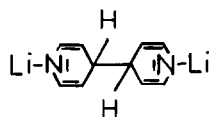
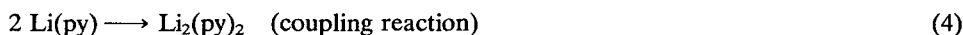


Fig. 3. Discharge curves: dotted line, P2VP coated anode; continuous line, P2VP+anthracene coated anode. Numeration, see Fig. 2.

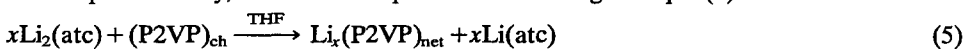


Some time ago we isolated the diadducts of anthracene with lithium, sodium and potassium as solid compounds from their solutions by crystallization [19–21]. Adduct formation is much favoured by using solvating ethers as the solvent, therefore, tetrahydrofuran (THF) was used to prepare solutions for coating the lithium anodes. As in the literature P2VP is usually applied as the coating material, being a polymer consisting of chains at which pyridine groups are attached, the reaction between pyridine (py) and dilithium anthracene, $\text{Li}_2(\text{atc})$, was studied in detail [22–24]. It can, therefore, be stated that not only lithium metal reacts with pyridine, but the dilithium anthracene adduct also reacts in a similar way (eqns. (3) and (4)).



In the case of pure pyridine such coupling products have been isolated [23, 24]. As a consequence, the pyridine rings attached to the P2VP chain should react in the same way, i.e. in the first step, the P2VP chains become polyradical anions, the negative charge being localized on the pyridine rings, which are, in principle, unstable. Therefore, in the second step, the negatively charged pyridine rings will couple in position C4 of the ring to build up a higher molecular network structure, shown schematically in Fig. 4. To differentiate the chain and network structures from each other in the formulae, the corresponding structures are designated by the symbols $(\text{P2VP})_{\text{ch}}$ and $(\text{P2VP})_{\text{net}}$, respectively, which are structural units of the polymer compounds.

Experimentally, we obtained products according to eqn. (5).



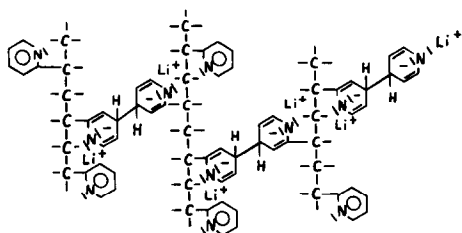


Fig. 4. Structure model for $\text{Li}_x(\text{P2VP})_{\text{net}}$.

The composition of the products depends on the reaction conditions, e.g. the manner of pouring together the starting components and the ratio of their amounts. The value of x approaches a limit of $x=1$, related to the structural unit. Values lower than 1 can actually be expected in so far as not each pyridine ring will add a lithium atom and couple for sterical reasons. This problem is still under investigation at this time.

There are several arguments for suggesting a higher molecular network structure. First, the analogy of substituted and unsubstituted pyridine rings for this reaction is widely known from the literature [22]. Furthermore, on hydrolysis of $\text{Li}_x(\text{P2VP})_{\text{net}}$ by water or alcohol followed by air oxidation, higher molecular products are formed having different properties compared to the starting P2VP compound.

In analogy to the unsubstituted pyridine the direct formation of the product $\text{Li}_x(\text{P2VP})_{\text{net}}$ from the components lithium and P2VP is also possible, but the reaction occurs very slowly, because it is a heterogeneous one and, moreover, the resulting solution becomes more and more viscous. This effect can clearly be observed if a solution of P2VP in THF is allowed to react with pieces of metallic lithium under inert conditions and intensive shaking of the reaction vessel. The solution becomes syrup-like with time as a consequence of a further polymerization process, i.e. the conversion of the starting chain structure of P2VP to a network structure as discussed above. So the reaction will be incomplete, even after long reaction times.

Discussion

We suggest that all the reactions described above also occur in the battery, already starting during the coating process. It seems appropriate to distinguish between reactions occurring during preparation and storing, and those taking place during the discharge process. All possible processes are schematically demonstrated in Fig. 5.

In the presence of anthracene, with P2PV as the coating material in THF, the following steps may occur on the surface of the lithium anode during preparation and storage.

(1) Formation of the mono- and diadduct of anthracene with lithium according to eqns. (1) and (2) takes place. During the coating process under inert conditions an immediate coloring of the lithium surface can be observed, becoming dark blue on account of the formation of alkali metal anthracene adducts.

(2) The lithium adduct $\text{Li}_2(\text{atc})$ is assumed to transfer lithium atoms, that means lithium ions and electrons, to the pyridine rings bonded at the P2PV chains in the manner of a polymer analogous reaction according to eqn. (5). As a consequence the pyridine rings of one chain couple with those of a different chain to build up a higher molecular network structure (see Fig. 4), at least to a certain extent, for it must be

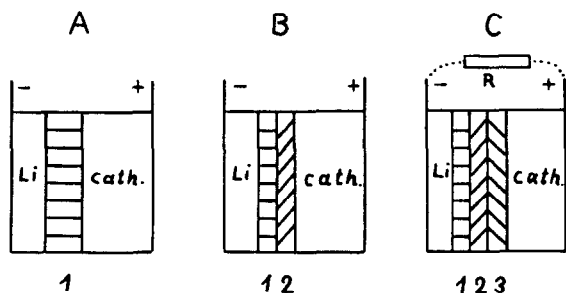


Fig. 5. Supposed state of battery after different times (schematically): A, after manufacturing; B, after storing; C, during discharge process.

Designation layers: Li, lithium anode; cath., cathodic material; layer 1, $\text{Li}_x(\text{P2VO})_{\text{net}}$; layer 2, $\text{P2VP} + \text{LiI}$; layer 3, cathodic material + LiI .

taken into account that sterical hindrance between the chains is highly probable. So, not all pyridine rings attached to the chain will be able to couple in contrast to the free pyridine radical anions.

(3) The layer of $\text{Li}_x(\text{P2PV})_{\text{net}}$ formed according to eqn. (5) will react with iodine from the cathode side as a self-discharge process expressed by eqn. (6).



But this reaction will certainly decline after a short time, stopped by the thin layer of LiI which will be deposited within the remaining polymer P2VP layer. This LiI layer formed *in situ* is a necessary one as it acts as the solid electrolyte of the battery system, but, on the other hand, its formation in a crystalline compact form would widely limit the battery performance due to the relatively low mobility of the lithium ions, if it should continue during the discharge process. These limitations will partly be compensated for by structural peculiarities which arise from the formation of a polymer electrolyte consisting of LiI and the polymer P2PV as discussed below.

By reaction (eqn. (6)) the network structure of $\text{Li}_x(\text{P2PV})_{\text{net}}$ will be destroyed in a small region, because the bonds between the pyridine rings can be split, as was proved by a model reaction in the case of pure pyridine [24] but this thin layer will not negatively influence the overall conductivity. To prove this we studied the conductivity of different mixtures of P2VP and LiI . As a consequence, while pure P2VP is an isolator, the conductance of mixtures of both components goes through a plateau in a wide range of concentrations, showing nearly the same values as for pure LiI (see Fig. 6).

The $\text{Li}(\text{atc})$ species formed in the primary stage may be regarded as a carrier to transfer lithium atoms from the anode to the P2VP chains (see eqns. (1), (2), (5)). Small amounts of THF omitted here will play a decisive role. By this process the network structure in the form of the compound $\text{Li}_x(\text{P2VP})_{\text{net}}$ is built up, the formation of which we assume to be the most important step. The lithium ions located within the network structure (see eqn. (5)) are assumed to be more mobile than within the chain structure, and therewith, will show a higher conductivity.

If pure P2VP is used as the coating material, without any anthracene addition, only an extremely thin layer of $\text{Li}_x(\text{P2VP})_{\text{net}}$ on the metal surface can be expected, because the direct formation from the components as a solid state reaction should be very slow (see above). Only those pyridine rings located next to the metal surface will be able to react with lithium and couple in the way described above.

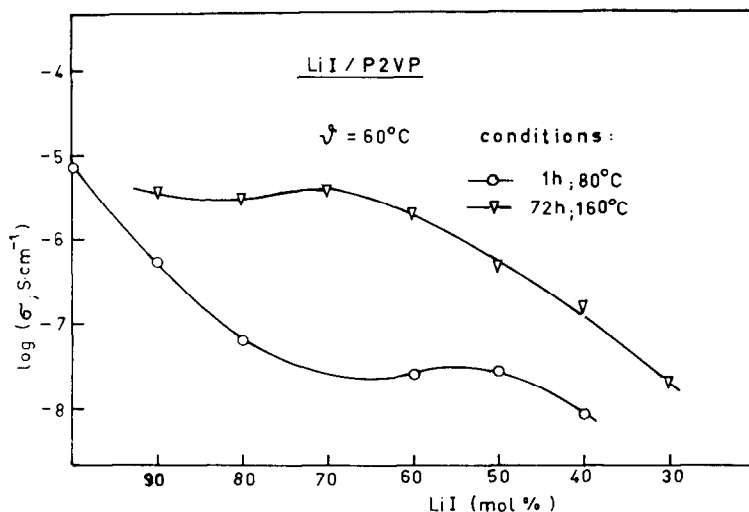
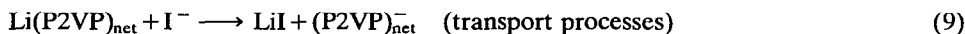


Fig. 6. Conductivity of mixture of P2VP and LiI dependent on LiI concentration and annealing conditions.

Let us now consider the discharge process itself. The lithium ions migrate through the solid electrolyte layer, passing the anion units of the network structure, $(P2VP)_{net}^-$, as well as the anthracenide ions, $(atc)^-$, to combine with the iodide ions formed on the cathode side (eqns. (7)–(10)).



LiI formed according to eqn. (9) will not separate in a closed form, but will be partly embedded in the network structure, and so form a strongly distorted and porous structure, having an evidently decreased resistance. When the coating layer is saturated with LiI, this will disappear into the cathode material as described in the literature (see 'Introduction') without raising the inner resistance of the battery significantly. The probable amorphous network structure of P2VP gives rise to a sufficiently high bulk conductivity for lithium ions as well as to a strong low electronic conductivity. This behavior results in a low cell impedance of the battery for a rather long discharge period and an extremely low self-discharge rate.

Conclusions

The present studies lead not only to an improved lithium/iodine battery, but also give a more profound insight into the possible processes as regards the manufacture, storage and discharge behavior of the battery. Moreover, an attempt is made to explain why only P2VP has attained such a great importance as a coating material and, likewise, as the basic component in the commercial lithium/iodine battery. Using this information it will be possible to develop more effective coating materials.

Acknowledgements

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

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