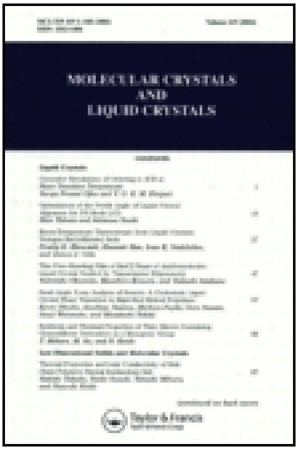

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GRAPHITE INTERCALATION COMPOUNDS AS POSITIVES IN RECHARGEABLE METALFREE BATTERIES

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Abstract Two essentially metalfree rechargeable batteries are described, containing graphite salts as a positive. The one has a blend of anthraquinone / carbon black to form the negative and an aqueous electrolyte (8 M HBF_4). The other is a nonaqueous system (0.2 M $LiClO_4$ in propylenecarbonate) and makes use of an electrodeposited polypyrrole layer on carbon black filled polypropylene. Results of cycling these prototypes of a secondary battery at current densities of 3 and 0.5 mA cm^{-2}, respectivily, are reported in detail.

1. INTRODUCTION

Graphite can be regarded as an alternative host lattice with respect to the many inorganic solid compounds,[1] which are presently proposed for rechargeable batteries. These are of permanent interest as an important component in modern energy technologies. Graphite is a widely available and low cost material with no environmental impacts. Donor (D)- as well as the otherwise rather rare acceptor (A)-type GIC's are known for a long time. They were already combined with inorganic counterelectrodes, e.g. $Li^+C_6^-/MnO_2$ [2,3] or $Pb/C_{24}^+HSO_4^-$.[4]

For the first time, two combinations of GIC as a positive with organic materials at the negative, anthraquinone and polypyrrole, respectively, are reported in sections 3 and 4. Essentially metalfree batteries are realized, with many attractive features, as reviewed elsewhere.[5]

2. EXPERIMENTAL

Electrolytes were prepared from 50 % HBF_4 (Fluka, purum) and distilled H_2O and from $LiClO_4$ (Riedel-de Haen, 99%) and propylenecarbonate PC (Fluka, purum >99%), distilled at 94-95 °C, 15 mm Hg. The cycling experiments were performed at 20 °C under Ar in a stagnant electrolyte. Current densities in the order of 1 mA cm^{-2} were used and switched by a AMEL bigalvanostat Model 545, eventually in combination with a timer Indigel, IDE 546. Metal free base electrodes "RPP" (current collectors) were fabricated from carbon black (Corax L from Degussa) filled polypropylene. The positive active material was a composite electrode "CPP", made of 80 wt% natural graphite (Normalflocke, Kropfmühl) and 20 wt% polypropylene.[6] Anthraquinone AQ (Fluka, purum >99%) as the one negative was mixed with 30 wt% carbon black to yield a blend AQ/CB with optimum conductivity and active mass utilization after compression to a pellet.[7] A 100 μm polypyrrole (PPy)-layer was electrodeposited onto RPP at 4 mA cm^{-2} from a bromide catalyzed electrolyte to yield the alternative negative.

3. CYCLIC BEHAVIOUR OF THE AQ/CPP-BATTERY

8 M aqueous HBF_4 is used as electrolyte. The overall reaction is given by:

$$2\,C_{48} + AQ + 6\,HBF_4 \underset{\text{disch.}}{\overset{\text{ch.}}{\rightleftharpoons}} 2\,[C_{48}^{+}BF_4^{-}\cdot 2\,HBF_4] + AQH_2 \qquad (1)$$

A large amount of electrolyte is involved in the cyclic process. Theoretical o.c.v. is $U_0 = 1.5$ V, but only the second stage of the GIC can be attained. On the other hand 10 M H_2SO_4 in acetic acid was found to allow for the formation of the first stage (C_{24}), but voltage drops to $U_0 = 0.95$ V. Thus the theoretical energy density of this system is 37.1 Wh kg^{-1}, but for (1) it is higher, 42.6 Wh kg^{-1}, cf.[5] and the literature cited therein.

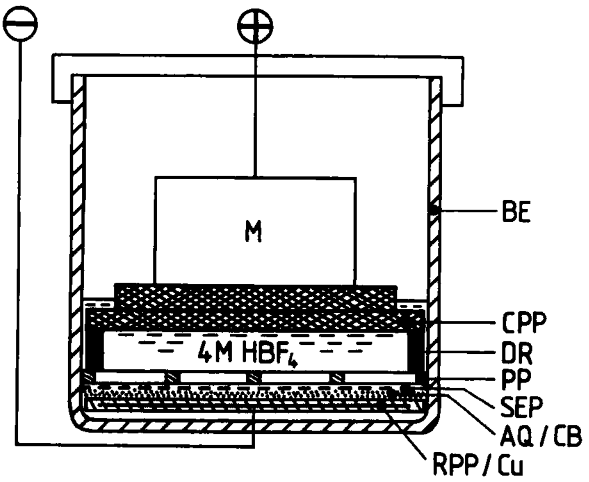

FIGURE 1 Experimental battery cell. BE, polyethylene beaker; SEP, separator; DR, distance ring, h= 1 cm; PP, backing plate.

Fig. 1 displays the experimental metalfree battery cell with horizontal electrodes, A= 44 cm^2. The metal mass M and the 0.1 mm Cu-inlet in RPP/Cu as end contacts can be omitted in compact bipolar cell designs. 0.03 g cm^{-2} 70% AQ/CB-blend[7] was spread on the negative RPP. Thus one has a coverage of 10^{-4} mole AQ cm^{-2} or 19.3 C cm^{-2}. At the positive, a penetration depth of 0.8 mm can be expected, assuming a sharp concentration profile. The conversion of a 10 mm electrolyte layer becomes 15%, but both only in the case of full charge. Thus the cell is limited by the negative.

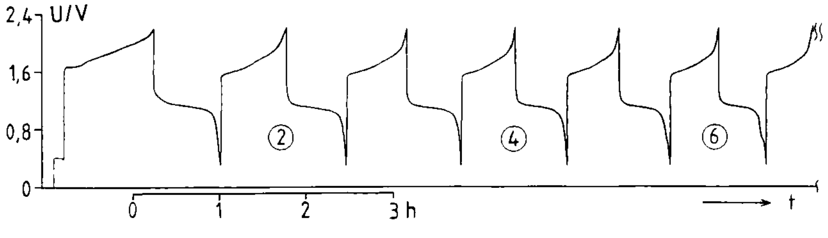

FIGURE 2 Cycling profiles of the AQ/GIC-cell in 8 M HBF_4, 3 mA cm^{-2}.

A typical galvanostatic cycling curve is shown in Figure 2. Cycling began with both active materials in the pristine state. At a current density of 3 mA cm^{-2}, the cell is charged up to 2.2 Volts, and it is discharged down to 0.3 Volts. In the course of the first charge, a charge of $Q_{c,1}$= 11.3 C cm^{-2}, corresponding to 58.7% of the theoretical redox capacity Q_{th}= 19.3 C cm^{-2}, mentioned above, is found. First discharge redox capacity is $Q_{d,1}$= 44.1% of the theory. Upon further cycling, some decay is observed. At the 5th cycle, $Q_{d,5}$ has decreased to 32.3% of Q_{th}. Current efficiency is near 100%, beginning with the 5th cycle. It should be mentioned, that the electrolyte, 8 M HBF_4, must be considered as a compromise. The graphite forms yet GIC in a reversible manner with good current efficiency.[8,9] The anthrahydroquinone AQH_2 does not yet undergo this very fast disproportionation to anthrone and AQ, which is observed in 85% H_2SO_4, cf.[5,10] and the literature cited therein.

4. CYCLIC BEHAVIOUR OF THE POLYPYRROLE/CPP BATTERY

0.2 M $LiClO_4$ in PC is employed as the electrolyte. Eq.(2) shows the overall reaction:

$$C_{24} + [\text{-Py}_3^+\text{-} \cdot ClO_4^- \cdot \nu\, S] \underset{\text{disch.}}{\overset{\text{ch.}}{\rightleftharpoons}} [C_{24}^+ClO_4^- \cdot \nu'\, S] + \text{-Py}_3\text{-} + (\nu\text{-}\nu')\, S \quad (2)$$

The coinsertion of solvent molecules S, which is well known [11,12], is considered with different stoichiometries ν. Besides this marginal effect, no net conversion of the electrolyte takes place in this system. With U_0= 1.7 V and a degree of insertion y= 33% for polypyrrole, $E_{s,th}$ becomes 82.7 Wh kg^{-1}. Graphite attains the first stage, but the electrolyte compatibility is improved in the sequence MeCN (acetonitrile) < PC < sulfolane. Unfortunately, some anodic PC-decomposition remains, cf.[3,5] and the literature cited therein. The cyclic behaviour of the 100 μm thick layer polypyrrole electrode is improved in the order opposite to that. Thus PC was chosen as a compromise. A thin layer cell with vertical electrodes was employed. The cross section was 5.93 cm^2. Electrolyte layer thickness was minimum (d= 1 mm) due to the nonconsumption of the salt.

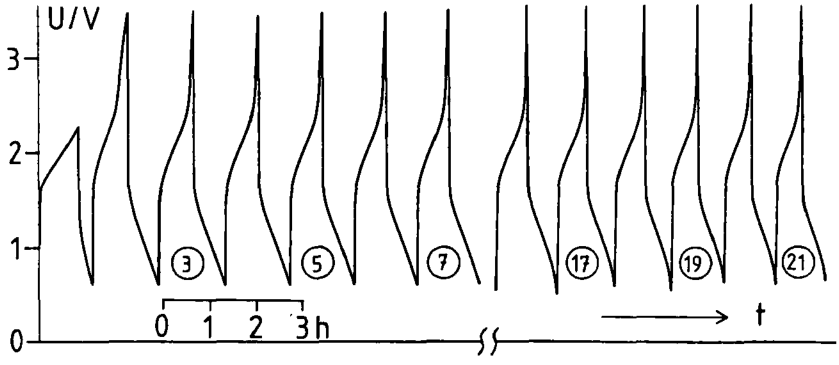

FIGURE 3 Cycling profiles of the PPy/GIC-cell in 0.2 M $LiClO_4$/PC, 0.5 mA cm^{-2}.

Cycling of the cell began with a first charge, cf. Equation (2), for the PPy is synthesized in the doped form. The charge was deliberately limited to 1.5 C cm^{-2}, corresponding to 31% of the whole PPy redox capacity. The 3 mm thick CPP plate was only charged to a degree of 1.0% (with respect to C_{24}). As shown in Fig.3, steady state cycles with about α= 85% current efficiency can be obtained. The deficit is caused by anodic side reactions with the solvent molecules at the positive. The corresponding current/voltage curves must be relatively flat, for at higher current densities, α rises to about

90%. The discharge voltage is found to vary in the region 1.6....0.8 V, as expected from a combination of two acceptor electrodes. Clearly, an anion shuttle mechanism is operative. Starting with the 22nd cycle (Z= 22), the capacity Q_0 decays after $Q_{22+Z} = \alpha^{Z} Q_0$ due to the exhaustion of the initial PPy capacity. Improvements are possible through higher μ and α at the negative and a higher selectivity at the positive.

5. CONCLUSIONS

We have demonstrated for the first time the feasability of metalfree rechargeable batteries with GIC-electrodes (A-type) as a positive. The natural graphite positive with an appropriate binder[13] exhibit an excellent stability upon cycling in both electrolytes. TABLE 1 summarizes the three principal types of electrode combinations. For organic host lattices an equivalent weight of m_e= 200 g F^{-1} is assumed, for inorganic 100 g F^{-1}. 1 M $LiClO_4$ is used as a typical electrolyte. The net reactions are written, beginning with the negative (index 1). The upper arrow is for charging. Clearly, the D/D-system is optimum, but the A/A-type (e.g. PPy/GIC) is not much inferior. A strong negative effect, however, is due to the stoichiometric conversion of the electrolyte in case of A/D-type (e.g. AQ/GIC). Moreover, the lighter host lattices and the higher voltages (3.0 V vs. 1.5 V) for inorganic D/D-systems lead to a theoretical energy density higher by a factor of nearly 4. However, this must be relativized again in favor to the organic systems, for plastic

TABLE 1 Relative electrochemical equivalents m_e for batteries with inorganic or organic host lattices W, cf. text. 100 corresponds to 400 g F^{-1} for organic and 200 g F^{-1} for inorganic systems. The electrolyte (1 M $LiClO_4$) is assumed to have a density of 1.

Type	Net Reaction	Relative m_e	
		Organic	Inorganic
D/D	$W_1 + W_2^-Li^+ \rightleftharpoons W_1^-Li^+ + W_2$	100	100
A/A1)	$W_1^+A^- + W_2 \rightleftharpoons W_1 + W_2^+A^-$	123	145
D/A2)	$W_1 + W_2 + LiA \rightleftharpoons W_1^-Li^+ + W_2^+A^-$	344	580

1) cf. PPy/GIC 2) cf. AQ/GIC

technologies can be easier applied. Thus there is hope to utilize a higher degree of the relative low theoretical energy densities quoted in the previous sections.

A problem of principal importance, however, must be considered in connection to irreversible side reactions at the positive electrode. These are due to the nucleophilic attack of H_2O to the radical cationic centers, if aqueous acids of medium concentrations are employed. Previous experience with 60% HF[4] demonstrates, that even then long term cycling is feasible. Current efficiencies on cycling of CPP single electrodes in 2, 4, 6 and 8 M HBF_4 at 3 mA cm^{-2} are found to be α- 34, 76, 98 and 99%, respectively. For the aprotic PC-electrolyte, current efficiencies at 0.5 mA cm^{-2} were determined at single electrodes to be α- 94%. This is higher than the 85% according to Fig. 3. In this case, anodic oxidation of the organic solvent molecules is the main side reaction, which dominates even more at MnO_2 etc. in spite of the more negative potentials.[2,3] Improvements of selectivity of the positive GIC electrode is necessary for future work.

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