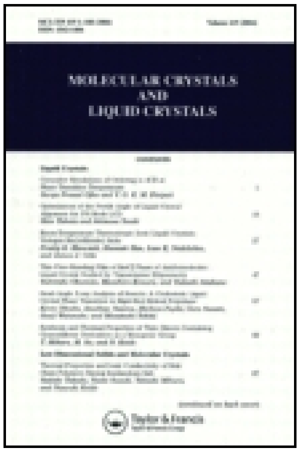

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Development of an All-Carbon Accumulator with Aqueous Electrolyte-HBF_4-Evaluation for the GIC-Positive

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A positive electrode made from natural graphite flakes and 20 wt% PP as binder was combined with a negative electrode made from carbon black and 10 wt% PTFE to yield a metal free rechargeable battery. Aqueous electrolytes with strong acids were employed to meet the requirements of the graphite intercalation compounds (GIC). Aqueous HBF_4 (c= 2-8 M) was studied in detail. The reversible formation of the GIC $C_{48}BF_4$ (2nd stage) was proved by XRD in the range c= 6-8 M. For c= 2 (4) M stage 5 (3) was found as limit. To make use of the GIC in an accumulator the electrolyte has to be cycled between 6 and 8 M upon charge and discharge. The current efficiency (reversibility) is almost 100% under these conditions. But the electrochemical equivalent for the GIC and the required electrolyte is as low as 9.4 Ah/kg, mainly due to the coinsertion of HBF_4 in the GIC.

Keywords: graphite intercalation compounds; tetrafluoroboric acid; battery; capacitor

INTRODUCTION

The highly reversible formation of GICs of the acceptor type in concentrated H_2SO_4 has been proposed as positive electrode reaction in rechargeable batteries as early as 1938[1]. Lateron, aqueous acids such as H_2SO_4, $HClO_4$, HBF_4 or H_2F_2 of medium concentrations were successfully employed[1-7]. But it is difficult to find a suitable negative electrode, which is stable under those conditions required for the GICs. The Pb/Pb^{2+}-electrode was shown to be reversible for special electrolyte compositions, and the system natural graphite/50% HF/Pb was cycled more than 3000 times[5]. A second approach led to a metal free accumulator: for the negative the solid redox couple anthraquinone(AQ)/ anthrahydroquinone(AQH_2) was employed in 8 M HBF_4[8] or 60% HF[9]. Due to irreversible side reactions at AQH_2 at low pH the cyclability is limited[10], however.

More recently a metal free secondary battery combining a GIC-positive with precompacted carbon black (c.b.) negative electrodes was described[11]. The high specific surface (> 1000 m^2/g) of c.b. is used to store electrical charge in the electrochemical double layer. The storage mechanism is physically as well as electrochemically, where pseudo capacitances are essential[12,13]. This asymmetric design of an all-carbon accumulator is superior to the well known electrochemical double layer capacitor, where two identical C- or RuO_2-electrodes are combined, cf.[14,15].

In the following, the special problem of an optimum aqueous electrolyte is discussed. 10-12 M H_2SO_4[11] and 50-60% HF[5,9] were already investigated in detail. HBF_4 is another possibility. We like to report the electrochemical behaviour of graphite in this electrolyte.

EXPERIMENTAL

For the **positive** GIC electrode a composite CPP[3] (80 wt% natural graphite flakes with 20% polypropylene) was employed. The **electrolyte** was 2-8 M HBF_4, derived from 50 wt% (8 M) HBF_4 (Fluka, purum). The cells were made of PE. Constant current cycling (CCC) with standard electrochemical equipment was used for single electrodes. Electrode potentials are stated vs. SHE and denoted as U_H.

RESULTS AND DISCUSSION

HBF_4 as an *aqueous acid* was only sporadically considered for GICs[2,7]. The slow CVs showed a current efficiency of α= 84-87 % for 3-8 M HBF_4 at 1 mV/s. Métrot et al. report the anodic intercalation of BF_4^- from a HBF_4-solution in diethylether[16], without any relevance to battery applications. The anion is subject to hydrolysis. The first slow step is the following

$$2\,BF_4^- + 2\,H_20 \rightleftarrows 2\,BF_3(OH)^- + H_2F_2 \qquad (1)$$

The equilibria involved are extremely complex[17,18]. However, only the BF_4^- itself seems to be intercalated. Its intercalation potential is nearly identical to that of HSO_4^- and much more negative with reference to that of HF_2^-, the final hydrolysis product[1-7], cf. Fig. 1.

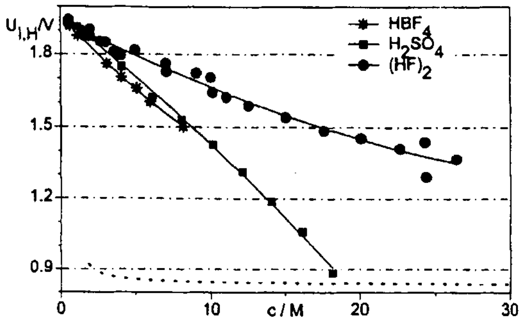

FIGURE 1 Potential of intercalation $U_{H,I}$ vs. concentration c of aqueous acids shown in the key, 2nd cyclovoltammetric cycle, 1 mV/s. Nernst behavior is represented by the dotted line.

Fig. 2 displays the influence of the electrolyte concentration on the current efficiency α for *cycling at a constant current density (CCC)*. The experiments were performed at a large excess of electrolyte. As a consequence the electrolyte concentration did not appreciably change. Clearly, α was close to 100 % at 8 and 6 M HBF_4, but α decreased at lower concentrations. The α's seem to be superior to the former finding with slow CV technique[2]. The

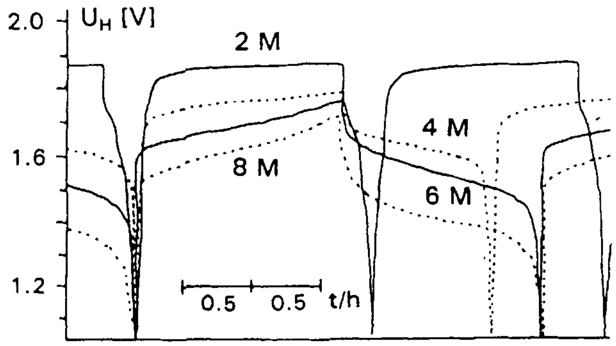

FIGURE 2 Constant Current Cycling CCC (j= ± 3 mA/cm^2) at CPP-electrodes in aqueous HBF_4 (2 - 8 M); stationary curves at cycle 15.

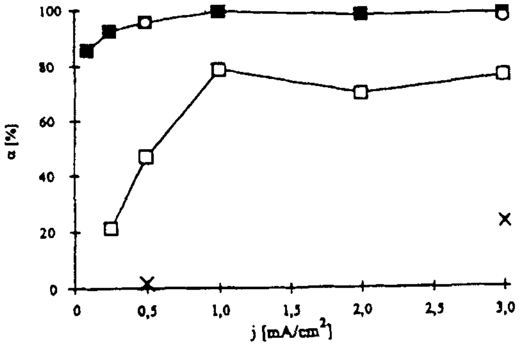

FIGURE 3 Constant Current Cycling CCC at CPP-electrodes charged with 1.5 C/cm^2 in aqueous HBF_4 of various concentrations (X) 2, (□) 4, (O) 6 and (■) 8 M; current efficiency α vs. current density j. Average values from at least 10 cycles.

current density j is another important parameter. Some decrease of α at low values of j was observed, cf. Fig. 3. But the main influence was again due to the acid concentration.

Last but not least, the *charge stoichiometry* in the solid is of great importance for the battery application. Table I compiles our results for the XRD determination[19]. The 2nd stage ($C_{48}BF_4$) can be attained in the concentration range of 8-6 M HBF_4.

TABLE I Stage no. of GICs C_xBF_4, prepared anodically from natural graphite flakes in aqueous HBF_4 (2-8 M); I_c directly from the 001 peak and calculated from peaks of higher order.

c_{HBF4} / M	I_c / pm (001 peak)	I_c / pm (calcul.)	stage no.
2	2066	2036	5
4	1488	1418	3
6	1084	1081	2
8	1081	1087	2

CONCLUSIONS

The charge transfer reaction for this positive electrode in aqueous solutions of the acid HA formulated for stage 2 GIC is

$$[C_{48}] + (1+\nu)\,HA \rightleftharpoons [C_{48}^{+}\,A^{-}\,\nu\,HA] + H^{+} + e^{-} \qquad (2)$$

The stoichiometric number ν for the coinserted solvate acid is in the order of 2. Thus, a high amount of electrolyte is consumed during charge. Due to the instability of GICs in diluted acids a minimum concentration c_{min} has to be maintained. If c_{max} is the maximum concentration and ρ the corresponding density, the mass m_{El} of the required electrolyte per molar conversion according to eqn.(2) can be calculated with eqn.(3):

$$m_{El} = \rho\,\frac{1+\nu}{c_{max} - c_{min}} \qquad (3)$$

For cycling the electrolyte between c_{max}= 8 M and c_{min}= 6 M and with ν= 2, the necessary electrolyte mass for 1 Faraday = 26.8 Ah is m_{El}= 2.12 kg, the corresponding volume is 1.5 dm^3. Compared to this high value the equivalent mass for the graphite m_C is relatively low. In spite of stage 2 and considering 20% PP as binder, m_C= 0.72 kg is found. For the sum of active mass and electrolyte the electrochemical equivalent is 9.4 Ah/kg. Similar values are reported in[9]. This very low value is mainly caused by the electrolyte. According to eqn.(3), there is no chance to decrease m_{El}, because aqueous HBF_4 is not available with concentrations above 8 M.

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