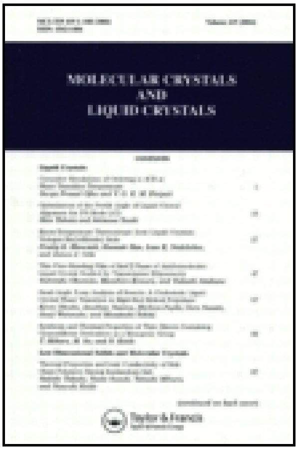

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ELECTROCHEMICAL CELLS EMPLOYING $(CH)_x$-CATHODES IN A NONAQUEOUS ELECTROLYTE

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Abstract Polyacetylene films have been used as cathodes in electrochemical cells of the type $Al/Li/LiClO_4(1...2M)$ - PC/$(CH)_x$/Pt. Their performance characteristics have been measured. The results show that these cells can be cycled 10 to 15 times at deep discharges, over 300 times at shallow discharges and over 1000 times at very light discharges. Due to the instability of the oxidized $(CH)_x$ the charge retention of the cells is poor.

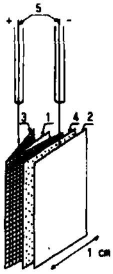
INTRODUCTION

During the last few years polyacetylene, $(CH)_x$, has been the subject of intensive studies in electrochemical applications. Scientists have been especially fascinated of its use as an electrode material in nonaqueous electrochemical cells.[1-7] In principle $(CH)_x$, oxidized with proper dopants and coupled with lithium, offers a possibility to construct a lightweight secondary battery. One can indeed estimate, that a typical Li/$(CH)_x$ cell has gravimetric and volumetric energy densities of 40...60 Wh/kg and 100 Wh/dm^3, compared with the values 20...30 Wh/kg and 80 Wh/dm^3, respectively, for a common lead acid battery.

The main problem with $(CH)_x$ as an electrode material is its poor stability. However, relatively little work describing the stability of conducting polymers has been published. There are even very optimistic opinions concerning this feature,[6] but there are also critical articles, e.g. those of Yen et al.,[8] Huq and Farrington,[9] Somoano[4] and Münstedt et al.[10] In this work we briefly discuss some of the main electrochemical characteristics of the p-doped $(CH)_x$.

EXPERIMENTAL

Polyacetylene films were synthesized by the Shirakawa method at -78 °C. Electrodes made of these films had typically the following dimensions: area 1...4 cm^2, thickness 70...150 μm, weight 4...8 mg/cm^2 and capacity 1.8...3.6 C/cm^2 (at 6 % doping level) or 0.50...1.00 mAh/cm^2. Aluminium foils used as a substrate for the Li electrode were chemically pure (99.999 %). The thickness of the foils ranged between 50 and 100 μm, corresponding to 14...27 mg/cm^2. The polypropylene separator (cf. figure 1) was 200 μm thick corresponding to 5 mg/cm^2. In some experiments the Al/Li electrode surrounded both sides of the $(CH)_x$ electrode.



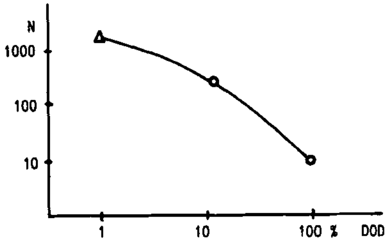


FIGURE 1 Electrode assembly. 1, $(CH)_x$ film; 2, Al/Li foil; 3, Pt grid; 4, separator; 5, Pt wires.

FIGURE 2 Cycle life vs. the depth of discharge. Circles, this work; triangle, Ref. 6.

Electrolytes were prepared from p.a. grade $LiClO_4$ and spectrophotometry grade propylene carbonate. Chemicals and electrode materials were carefully dried; water content of the solutions were analyzed to be about 50 ppm. Before using the solutions they were purified by percolation through activated alumina, which was also added to some cells. To minimize the effect of impurities in the cells, small amounts (0.5...1.0 ml) of 1.0 or 2.0 M electrolyte solutions were used. Electrodes, separators and electrolyte solutions were charged in flat glass tubings which were sealed by melting under dynamic vacuum. All manipulations were done using vacuum and dry box techniques.

Charging and discharging were mainly done galvanostatically. The initial doping was always done by starting with a low current density and increasing it gradually up to 0.5 mA/cm² . Cell voltages over 3.9 V were avoided.

RESULTS AND DISCUSSION

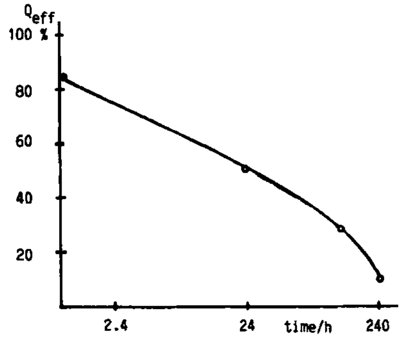
Our cyclic voltammograms conform to those measured by other research groups:[11,12] between 2.5 and 5.0 V vs. Li there are two oxidation peaks; the first one at 3.75 V represents reversible doping of $(CH)_x$ by dopant anions, the second one at 4.50 V corresponds to an irreversible reaction of $(CH)_x$ with dopant anions.

The relatively poor stability of the oxidized $(CH)_x$ can be seen from figures 2, 3 and 4. In figure 2 the cycle number N is depicted vs. the depth of discharge (DOD) when $i_{ch} = i_d = 0.5$ mA/cm² . The curve indicates that at high DODs (> 30 %) the cell performances are modest.

The discharges in figure 2 were done immediately after charging. One can achieve over 90 % qoulombic efficiences at DODs less than about 20 %. We have studied the charge retention of the cells by storing fully charged cells for various times before discharging. From figure 3, where the qoulombic efficiency (Q_{out}/Q_{in}) is drawn vs. storage time, the high tendency to self-discharge is obvious.

From figure 4 it is, on the other hand, clearly demonstrated that the performance of the cells strongly depends on the doping level and discharge rates. We find a significant decrease in Q_{eff} when going from y=0.06 to y=0.08. The stability of the $(CH)_x$ electrode can be deduced by measuring the floating current, i.e.

the current needed to keep the cell at full charge. Typical values are 15 μA/cm² and 10 μA/cm² for y=0.08 and 0.06, respectively (a background current due to the instability of the electrolyte solution has to be substracted). Short circuit currents were initially 50 to 100 mA/cm² but decreasing with increasing cycle number.



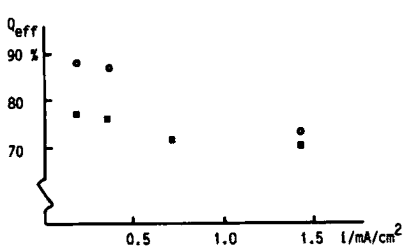


FIGURE 3 Charge retention of a Li/$(CH)_x$ cell. y=0.06 and i_d=i_{ch}=0.5 mA/cm².

FIGURE 4 Qoulombic efficiency vs. discharge current and doping level. Circles, y=0.06; squares, y=0.08.

CONCLUSIONS

We have shown that, in principle, rechargeable Li/$(CH)_x$ secondary batteries can be constructed exhibiting higher energy densities than common lead-acid batteries. However, the intrinsic instability of highly p-doped $(CH)_x$ leads to a severe reduction of the depth of discharge, charge retention and cycle life of the cells. Thus the instability of p-doped $(CH)_x$ has to be improved considerably before any large scale applications of nonaqueous Li/$(CH)_x$ batteries become feasible.

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