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THE CYCLE LIFE OF P-DOPED POLYACETYLENE ELECTRODES

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Abstract The cycle life of a PA electrode doped to 9 mole % is very poor. This early capacity decay is attributed to crosslinking reactions between PA chains.

ELECTROCHEMICAL EXPERIMENTS

Figure 1a shows cyclovoltammetric curves of a PA electrode between the OCV (2,5 V vs Li/Li^+) and the decomposition voltage of the electrolyte (0,5m $LiClO_4$ - PC at about 5,2 V) as a function of different scan rates. Besides the decomposition of the electrolyte two main reactions (peaks) are observed. The integrals of these cyclovoltammetric curves (Figure 1b) show 9 % doping under the first peak independent of the scan rate, while the integrals under the second peak slightly depend on the scan rate.

As shown in Figure 2a - 2c a variation of the dopant (ClO_4^- or AsF_6^-) does not effect the "first peak characteristics" (cyclovoltammetric curves, degree of doping and change in conductivity) while the "second peak characteristics" strongly depend on the dopant. Here it is obvious that the electronic conductivity decreases when the second reaction becomes more and more important.

Especially the last observation leads to the assumption that the reversibility of oxidized PA is restricted to the "first peak reaction" with 9 % doping. As shown in Figure 3 this assumption is correct because a significant cathodic peak is obtained exclusively if PA is scanned over the first peak only.

As shown in Figure 4 the cycle life of the reversible range is very poor. The capacity (anodic charge) is halved within 12 cycles. This effect again is independent from the dopant.

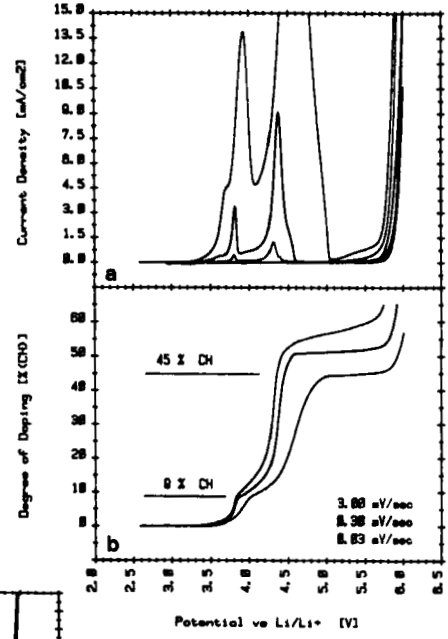

FIGURE 1
Cyclovoltammetric curves and their calculated integrals obtained with different scan rates of the cell Li/0.5 m $LiClO_4$-PC/PA

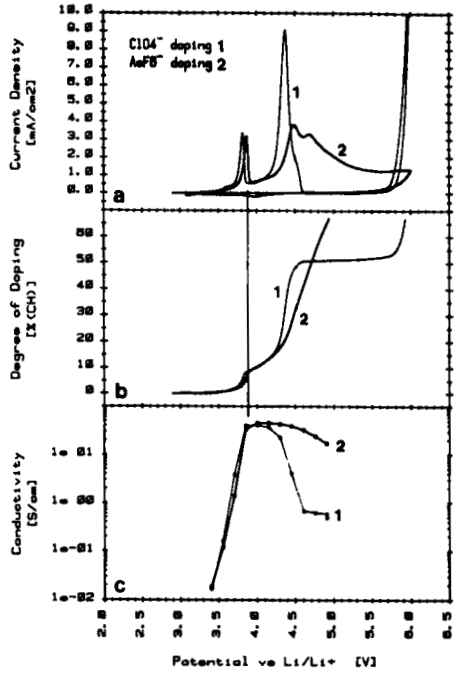

FIGURE 2
Cyclovoltammetric curves, their integrals and the electronic conductivity of the polymer obtained with different dopants

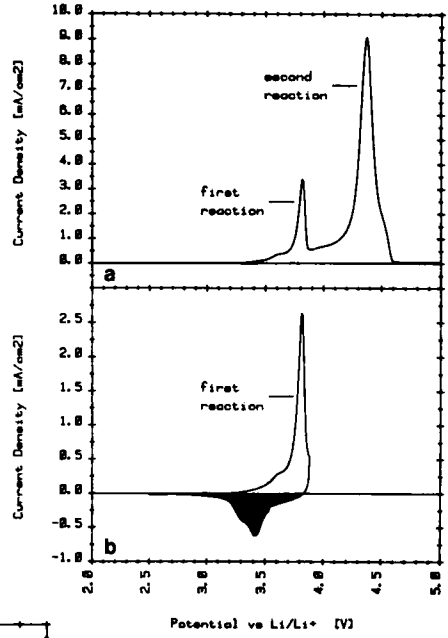

FIGURE 3
Cyclovoltammetric curves (0.3 mV/sec) of the cell Li/0.5m $LiClO_4$-PC/PA

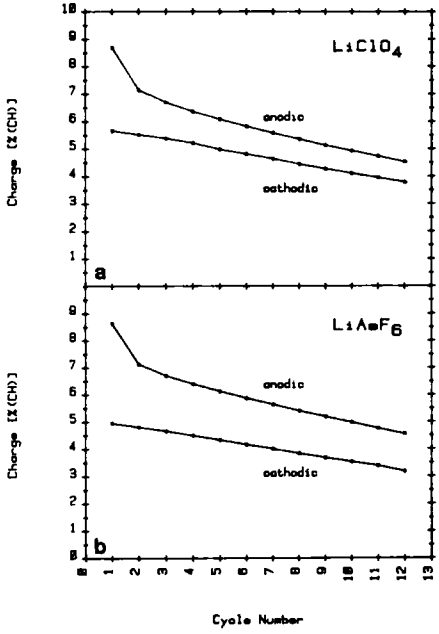

FIGURE 4
Anodic and cathodic charges as a function of cyclovoltammetric cycles

ANALYTICAL RESULTS

The poor cycle life of an PA electrode doped to 9 mole % can be attributed to two different aspects

1. to reactions of the oxidized PA with the solvent
2. to crosslinking effects within the polymer itself.

Reactions with the solvent

After 12 cycles within the range of 0 to 9 mole % a lot of ether bonds are detectable in the polymer (ESCA and "Zeisel's Method"). In addition the content of water, protons, propandiole and propionaldehyde increases in the electrolyte.

Crosslinking effects

Within 10 cycles nearly 50 % of the sp^2 centers change to sp^3 centers as shown by ATR spectroscopy (Figure 5). This effect will explain the observed decreasing capacity of the PA electrode (Figure 4) even quantitatively.

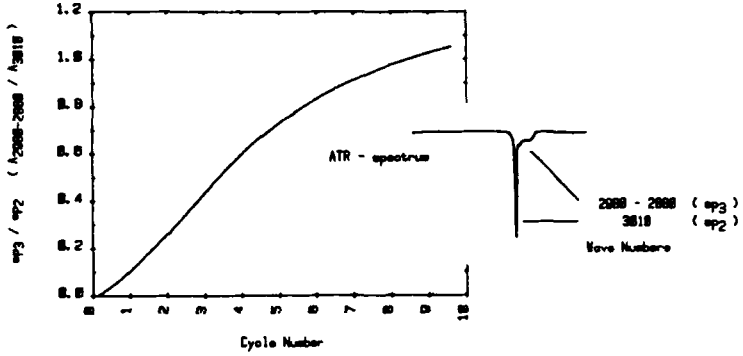

FIGURE 5 The ratio of sp^3 to sp^2 centers measured by ATR spectroscopy as a function of the cycle number

A major fraction of the formed sp^3 centers can be attributed to crosslinking effects (2 + 3 cycloaddition detected by the method of "Pyrolysis-GC"), while a minor fraction only has to be attributed to the etherbonds formed by the reaction with the electrolyte.