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COMPOSITES OF CONDUCTING POLYMERS: POLYACETYLENE - POLYPYRROLE

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Abstract: Pyrrole can be electrochemically polymerised onto polyacetylene anodes. The morphology of the resulting conducting composites depends on the initial doping state (e.g. conductivity) of the polyacetylene. The air and water stability of the conducting composites is excellent compared to doped polyacetylene. Both components conduct the current.

SYNTHESIS

Pyrrole can be electropolymerised onto polyacetylene (pac) anodes¹ under conditions that are usual for polypyrrole (ppl) synthesis² (e.g. acetonitrile solution, 0.1 M supporting electrolyte (NBu_4BF_4 , NBu_4ClO_4), 0.1 M pyrrole, +1.0 V vs SCE, room temperature).

Doped as well as undoped pac-films can be used as anode.

The progress of the polymerization can be easily monitored by observing the dull black layer of ppl. During electrolysis a red colour develops in the solution near the anode.

For undoped pac-films the polymerization starts at the current supporting wire after a short induction period and proceeds then slowly along the film (almost identically on both of its sides). With doped films as anode the polymerization starts over the whole surface of the film immediately after application of the voltage.

MORPHOLOGY

The morphology of the composites is depending on the initial doping state (e.g. conductivity) of the pac-anode.

Undoped pac as anode gives a sandwich like composite (type A) see fig. 1, whereas doped pac-films give composites (type B) with the same porous structure as the starting pac.

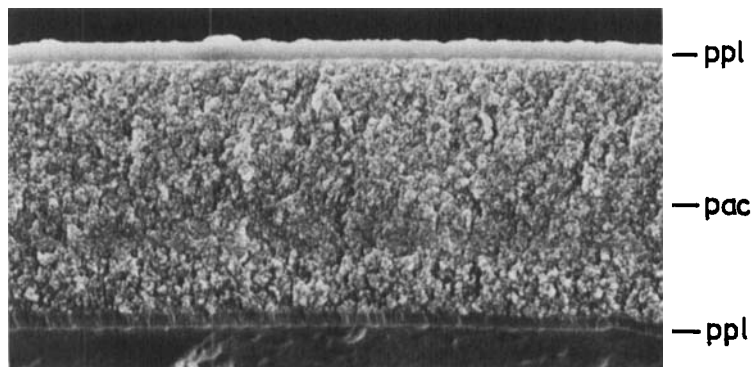


FIGURE 1: Microphotograph of the cross-section through a type A composite. Magnification ca 500 x.

PROPERTIES

The polypyrrole layer of type A composites adhere very strongly to the polyacetylene. It does not peel of on scratching.

The mechanical properties of type B composites resemble those of highly doped pac.

Both kinds of composite have electrical conductivities in the range $20 - 40 \Omega^{-1} \text{cm}^{-1}$.

Their stability in air and water is excellent compared to doped polyacetylene (see figs. 2, 3).

Their e.s.r. spectra are apparently identical and consist only of a single very intense and narrow Lorentzian shaped line:

$$g = 2.0027, \Delta H^{\text{PP}} = 0.2 - 0.4 \text{ G.}$$

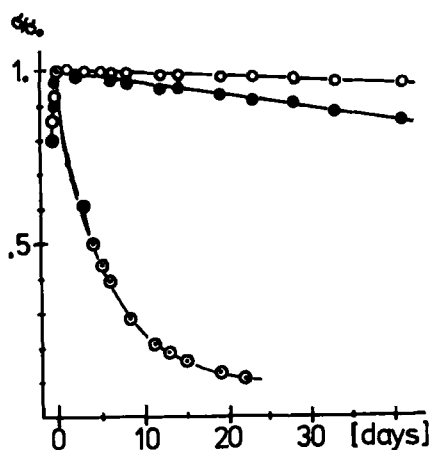


FIGURE 2: Relative electrical conductivity vs time (days) of air exposure of conducting polymer films. The composites show first an increase of conductivity on air exposure. Their conductivity is scaled against the maximum conductivity taken as σ_0 .

● composite type A, ○ composite type B, ⊙ doped pac (InCl_4^-)

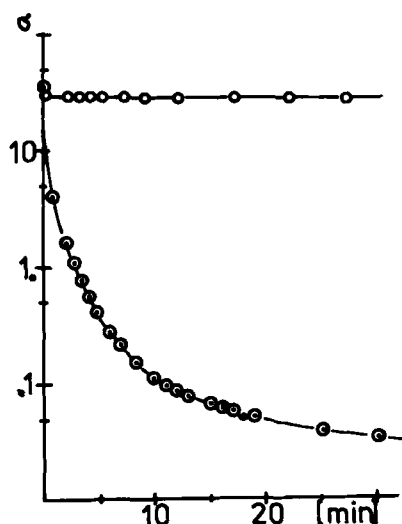


FIGURE 3: Electrical conductivity (S/cm) vs time of insertion into water of conducting polymers:

EDXA - RESULTS

EDXA-analyses of cross-sections of the composite films revealed that the interior pac-film is doped.

For type A composites (fig. 4) exist a concentration gradient from the highly doped outside to the lesser doped inside of the film. For type B composites is the dopant concentration almost constant through the whole film.

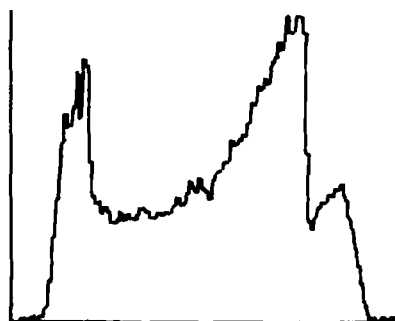


FIGURE 4: Chlorine profile through a perchlorate doped type A composite.

COMPENSATION WITH AMMONIA

Doped pac is much more sensitive to ammonia than ppl.³ Therefore, the conductivity along and through the film was measured for both kinds of composite both before and after 3 hrs of exposure to vapours from a concentrated ammonia solution.

Conductivity of the B type diminished in both directions by a factor of 30. In comparison, conductivity of the A type diminished by factors of 17 and 4600, along and through the film, respectively. These data indicate that both components support the current in the composites. In addition, our results show promise for the possible application of compensated A-type composites as capacitors.

A piece of film 7 x 4 x 0.1 mm was measured at 1 kHz to have a capacity of 30 pF and a dielectricity constant of $\epsilon = 12$ for the compensated polyacetylene.

CONCLUSIONS

Based on the S.E.M. microphotographs, together with the EDXA analysis and the results of the compensation experiments, we deduced the following:

- Polyacetylene as well as polypyrrole support the current in the composites.
- In type A composites, polypyrrole formed only on the outer surface of the pac-film.
- In type B composites, each individual pac-fiber is coated with a thin ppl layer throughout the entire film.

Cyclovoltammograms show that both composites are electroactive. This electroactivity, combined with the composites' environmental stability make them excellent candidates for use as electrodes.

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