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ELECTROCHEMICAL OXIDATION AND REDUCTION OF POLYPARAPHENYLENE

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Résumé - Nous avons oxydé et réduit par électrochimie du poly paraphénylène (P.P.P.) synthétisé sous forme de poudre (1) à partir du benzène. Grâce à la porosité de l'électrode de polymère, celui-ci put être oxydé et réduit très facilement malgré sa grande résistivité initiale. Nous avons observé de forts courants de décharge, mais une efficacité coulombique limitée. La différence entre les potentiels de début d'oxydation et de réduction, de l'ordre de 2.8 V, est plus faible que celle rapportée jusqu'ici (2).

Abstract - We have studied the electrochemical oxidation and reduction of poly paraphenylene (P.P.P.) synthesized in powder form from benzene (1). Although initially insulating, the polymer could be oxidized or reduced very easily due to a good porosity of the material. High discharge currents could be obtained, but with a limited coulombic efficiency. The difference between the onset voltages of oxidation and reduction is about 2.8 V, that is a lower value than that previously reported (2).

I - EXPERIMENTAL

P.P.P. has been prepared following the procedure described by Kovacic et al. (1), which gives a brown powder.

Compact sealed cells were made as described in the literature for (CH)x (3), except that the polymer electrode was made as follows: P.P.P. was first annealed at 400°C before being pressed on a platinum mesh with a pressure over 10^9 Pa. To anneal the powder is believed to crosslink it (4) and to preserve a large specific area through compaction.

A listing of the cell constituents and of the open circuit voltages measured just after sealing is given below:

<table>
<thead>
<tr>
<th>ID</th>
<th>Solvent</th>
<th>Salt</th>
<th>PPP weight</th>
<th>Electrode area</th>
<th>V_oc</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>P.C.</td>
<td>LiClO4</td>
<td>7 mg</td>
<td>0.55 cm²</td>
<td>3.47 V</td>
</tr>
<tr>
<td>B</td>
<td>P.C.</td>
<td>LiPF6</td>
<td>17 mg</td>
<td>1.33 cm²</td>
<td>3.20 V</td>
</tr>
<tr>
<td>C</td>
<td>T.H.F.</td>
<td>LiClO4</td>
<td>7 mg</td>
<td>0.65 cm²</td>
<td>2.85 V</td>
</tr>
</tbody>
</table>

II - RESULTS - DISCUSSION

a/ Doping initiation

Although completely insulating (5), undoped P.P.P. could be electrochemically doped with fairly high current densities (up to 0.3 mA/cm²) without remarkable potential.
overshoot: $V_{\text{initial}} < 4.4 \text{ V}$ for cells A and B, P type doping, and $V_{\text{initial}} > 0.94$ for cell C, N type doping.

b/ N type doping - cell C

The reduction of P.P.P. occurs through the reaction:

$$xe^- + (C_6H_4)_x + xy \text{ Li}^+ \rightarrow [(C_6H_4)^{-y} \text{ Li}^{+y}]_x$$

Figure 1 shows the $V$ versus $Q$ curve recorded during an N type doping-dedoping cycle.

![Graph](image)

Figure 1 - P.P.P. N type doping. A: $I = 1.5 \text{ mA/cm}^2$. B: $I = 0.75 \text{ mA/cm}^2$. C: $V = 2 \text{ V}$ for 12 hrs. The charge is labelled in doping level percent $C_6H_4$.

The reduction appears to be effective below 1 V. The coulombic efficiency for the whole cycle reaches 90%.

c/ P type doping

We performed both constant current doping cycles, simulating battery operation, on cells A and B, and quasi equilibrium studies on cell B.

P type doping would occur through:

$$(C_6H_4)_x + xy \text{ ClO}_4^- \rightarrow [(C_6H_4)^{+y} \text{ (ClO}_4)_y^{-y}]_x + xy e^-$$

Figure 2 shows typical large current cycles between 0 and 10% doping levels. Oxidation begins above 4.2 V, and the voltage rises towards 4.5 V at 10% doping.
Quasi equilibrium studies of P type doping were made on cell B. Doping consisted of 500 sec. periods with a charging current of 10 mA/cm² in alternance with periods of 1000 sec. in open circuit conditions. Undoping used the same conditions, but with opposite current, and a larger recovery time (30 to 90 mn). The doping levels were between 0 and 1 %.

The results are summarized in figure 3. The important results are:

- Onset of oxidation at about 3.8 V, instead of 4.4 V previously reported (2), reducing the difference between ionization potential and electronic affinity to 2.8 V.
- Coulombic efficiency near 100 %. The cell voltage did neither exceed 4.2 V and the leakage current due to the electrolyte degradation was negligible.

An hysteresis is observed in the \( V_{oc} \) curve, which might come from:

- Kinetic effect which leads to underestimate the doping level on doping, and to overestimate it when undoping, the polymer just in contact with the platinum mesh being first undoped, with an associated increase in the internal cell resistance.
- Entropic effect associated with intercalation stages, rather unlikely below 1 % doping level.
- Electrons being taken from the valence band and reinjected at a lower potential in a polaron band formed in the gap while doping (7).
III - CONCLUSION

Electrochemical cells of the type Li/LiA/(C₆H₄)ₓ A = PF₆, ClO₄ have been made and have shown good N and P type doping abilities due to the large specific area of the polymer electrode.

High oxidation voltage and large short circuit discharge currents are the promising features of Polyparaphenylene for battery application although new electrolytes should be employed in order to improve the reversibility of oxidation.

Quasi equilibrium p type doping studies showed a good reversibility associated with an oxidation voltage starting at about 3.8 V versus Li. The difference with the reduction starting voltage is 2.8 V, and scales with the forbidden energy gap of P.P.P. We report elsewhere (8) that the onset of the $\pi \rightarrow \pi^*$ optical absorption in the U.V. range is around 2.8 ev.

REFERENCES

(1) KOVACIC P., KYRIAKIS A., J. Am. Chem. Soc. 85(1963)454


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