

## CONDUCTIVE POLYMERS: NEW TOOLS AND MATERIALS FOR ELECTROCHEMISTRY

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Polymers have come into widespread use as a result of their mechanical and insulating properties. However, two new classes of macromolecular materials possessing either ionic (polyethers) or electronic (polyacetylene) conductivities emerged almost simultaneously six years ago [1, 2].

Polyacetylene, with its conjugated double bonds must be considered as an amphoteric redox material acting as a reservoir (valence band) or a sink (conduction band) of delocalized electrons. Thus,  $(\text{CH})_n$  behaves mainly like graphite, forming "n" type insertion derivatives, as  $(\text{Li}_y\text{CH})_n$  ( $y \approx 4$ ), and "p" type as  $(\text{CH}(\text{ClO}_4)_z)_n$  ( $z \approx 12$ ). The narrower energy bands of polyacetylene reduce the gap between "n" and "p" insertion potentials as compared to the more stable graphite; still, as shown in Fig. 1, these potentials, especially for oxidation, lie close to the stability limit of most organic solvents, while solvent co-intercalation is observed upon "n" reduction.

Staging is observed as in graphite, but the diffusion of the intercalant molecules in polyacetylene was found to be surprisingly slow:  $D \approx 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ , well below that of usual intercalation structures (Fig. 2). This drawback is usually compensated for by the felt-like fibrillar structure of  $(\text{CH})_n$  films, reducing the diffusion length when the materials are soaked with a liquid electrolyte, but at the expense of the effective electrochemical capacity, already mediocre as compared with inorganic host structures (Fig. 1).

Polyether electrolytes, the other class of electroactive polymers, are a macromolecular extrapolation of coordination chemistry. In this case, the heteroatoms (O) in the polymer backbone act as localized electron donors (no stable acceptor polymer is yet known), similarly to aprotic liquids. Since 1978, a complete electrochemical screening of complexes of this type has been undertaken to assess their usefulness as electrolytes. The wide electrochemical stability window of polyethers is at least comparable to that of aprotic solvents (THF, PC), as shown in Fig. 1; besides, no co-intercalation phenomenon occurs with 1 or 2D host structures.

A recent NMR investigation [3] of these complexes has shown, unambiguously, that only the amorphous part of the polymer is responsible for the conductivity; as no motion could be detected in the crystalline parts, the diffusion in this phase is probably as slow as in  $(\text{CH})_n$ . Such behavior probably reflects the encapsulation of guest molecules by the parallel polymer

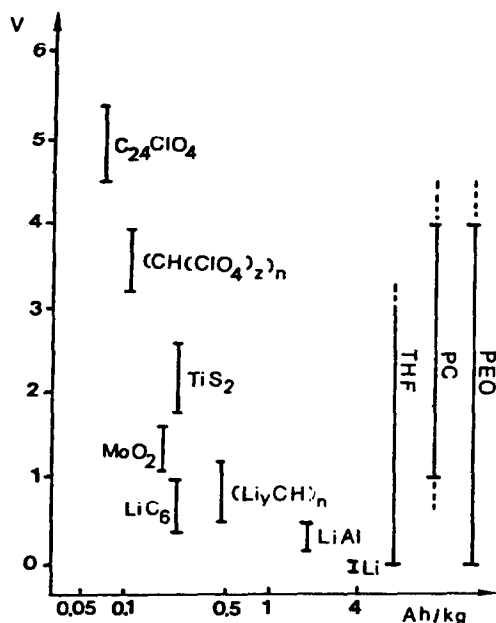


Fig. 1. Insertion potentials of electrode materials vs. capacity and stability domain of electrolytes.

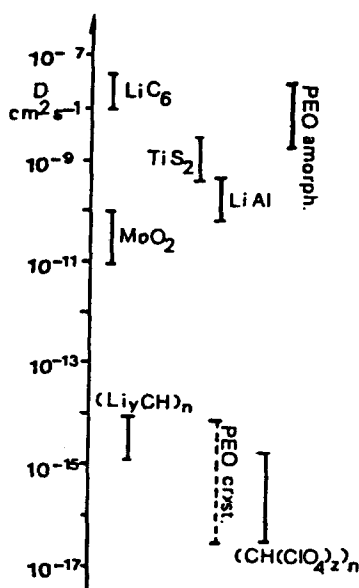


Fig. 2. Diffusion coefficients for electrode materials and PEO electrolytes.

strands. As a consequence of the liquid-like motion, both anions and cations are mobile with  $t^+ \approx 0.6$  for non-crosslinked electrolytes.

From these considerations, the most promising all-solid-state cells combine "classical" electrode materials such as  $\text{TiS}_2$ ,  $\text{V}_6\text{O}_{13}$  and Li or LiAl, whose specific capacities exceed those of  $(\text{CH})_n$ , and a PEO-based electrolyte in the amorphous state at 70 - 120 °C. In such cases, the diffusion rates are comparable for the electrolyte and the electrode (Fig. 2). Calculations for a thin-film cell (200  $\mu\text{m}$  with 30 - 40  $\mu\text{m}$  electrolyte) show that the practical energy density will be only a factor of 3 lower than the theoretical values allowing energy densities beyond 100 W h/kg. The kinetics at rates useful for EV traction ( $C/4$ ) will mainly be limited by the mobility of the anion. Performances of actual cells are given elsewhere at this conference.

## References

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