

## ELECTRIC FIELD ENHANCED DIFFUSION IN POLYACETYLENE

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Résumé - Nous avons développé une théorie qui montre comment une batterie peut délivrer une forte puissance et des densités de courant élevées malgré la diffusion lente et la faible conductivité ionique du polyacétylène. Un voltage appliqué ou une résistance externe fait passer un courant et génère un champ électrique important dans les fibrilles. Ce phénomène se produit uniquement quand la longueur d'écrantage électronique est du même ordre de grandeur que le rayon des fibrilles. Ce champ augmente d'une façon importante le taux de transport ionique.

Abstract - A theory is developed which shows how high power and current densities can be generated by a  $(\text{CH})_x$  battery cell despite the slow diffusion and low conductivity characteristic of ionic motion in polyacetylene. The presence of a small driving potential (or a load) causes current to flow and generates a large electric field in the fibrils when the electronic screening length is of the order of a fibril radius. This field dramatically increases the ion transport rate.

Recent measurements of the free diffusion of ions into  $(\text{CH})_x$  fibrils in electrochemical cells reveal diffusion constants of  $D \approx 4 \times 10^{-18} \text{ cm}^2/\text{sec}$ . /1,2/. On the same cells, however, high short circuit currents and high power densities are obtained /3-6/. An explanation of this apparent contradiction is the subject of this paper.

The observed enhanced ion transport may be due to the large electric field present in the  $(\text{CH})_x$  fibrils under current carrying conditions /7/. For example, after a voltage step,  $\Delta V$ , current flows and an electric field exists;  $E \sim \Delta V/r_0$  where  $r_0$  is the radius of a fibril. This field, present as long as the electronic screening length in the anisotropic conductor is comparable to or greater than the radius of a fibril, will literally drive the ions into (or out of) the fibrils leading to significant enhancement of the ion transport rate.

Under conditions of current flow, a second term must be added to the first integral of the diffusion equation:  $\vec{J}_I = -D_0 \vec{\nabla} c + \bar{\sigma}_I \vec{E}/e$   
 Using the Maxwell equation ( $\vec{\nabla} \cdot \vec{E} = 4\pi e(c_I - c_e)$ ) and the continuity equation ( $\vec{\nabla} \cdot \vec{J}_I = \partial c_I / \partial t$ ) yields a forced transport equation

$$\frac{\partial c_I}{\partial t} = -D_0 \nabla^2 c_I + 4\pi \bar{\sigma}_I (c_I - c_e)$$

Then, using Ohm's law and the empirical relation for  $V_{OC}$  vs.  $Q$  found for polyacetylene ( $V_{OC} = A \pm Bv^\gamma C_I^\gamma$ ) we obtain an equation with the form of a free diffusion equation with an enhanced decay rate

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{4\pi \bar{\sigma}_I}{edR_i} \tau \left[ (A - V_{ext}) \left( \frac{B}{A - V_{OC}} \right)^\gamma - B \left( \frac{B}{A - V_{OC}} \right)^\gamma - 1 \right]$$

In the above equation,  $v$  is the volume of the  $(CH)_x$  electrode,  $R_i$  is the measured internal resistance of the cell and  $d$  is the number density of  $(CH)$  units.

The solution to this equation predicts an increase in ionic transport rates by a factor  $\sim 10^3$  to values in general agreement with the experimental results.

We conclude that the fibrillar morphology of  $(CH)_x$  is critically important to the potential use of this polymer as a battery electrode in two ways:

- 1) the fibrils provide a microgrid such that ions from the electrolyte need to traverse distances no greater than about 100Å
- 2) the small diameter of the fibrils provides an enhancement of the local electric field (during charging and discharging) which increases the ionic transport rate by several orders of magnitude over that obtained from free diffusion.

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