

Spontaneous Chemical Charging and Discharging of Polyacetylene

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A spontaneous discharge process for doped polyacetylene in electrolytic solutions has been identified which will limit the reversibility of this and similar conductive polymers when used as electrode materials.

Numerous studies^{1,2} have shown that polyacetylene (PA) may be oxidized or reduced with Lewis acids and bases to produce electrically conductive material. Nigrey, *et al.*^{3,4} have shown

that PA may also be doped (and undoped) electrochemically, and have proposed that an 'organic battery' could be made from the doped material. In the electrochemical process, the

charge balancing anions (p-doping), or cations (n-doping), enter the PA upon charging, and at equilibrium the electrochemical potential of the charging ion is equal in the electrolytic solution and in PA. The degree of reversibility and the kinetics of charging and discharging will control the battery performance, and will determine its practicality.

In the course of our study of the chemical and electrochemical charging and discharging of polyacetylene, a spontaneous discharge process was observed which is the subject of this communication. The discharge reaction occurred when a chemically doped material, described below, was immersed in an electrolytic solution containing ions which are reversible with those in the charged material. The spontaneous discharge will prevent this and other similar systems from being utilized in polyacetylene batteries.

Films of PA, made by the Shirakawa technique,^{5,6} were exposed to I₂ saturated 1,2-dimethoxyethane (DME) in an inert helium atmosphere. DME was purified by distillation from a biphenyl-lithium solution. The doped material was rinsed with pure DME to remove excess of I₂ and dried *in vacuo*. Four-point d.c. conductivity measurements under ambient conditions in a dry box showed the PA to be highly conductive (about 10 Ω⁻¹ cm⁻¹). Immersion of the charged samples in a LiI-DME solution gave a deep yellow coloured solution after several minutes, indicative of the formation of I₃⁻. The polyacetylene samples were again rinsed with DME and dried. The conductivity of the PA material was found to be lower by more than eight orders of magnitude (σ < 10⁻⁸ Ω⁻¹ cm⁻¹), indicating spontaneous discharge of I₂ doped PA in LiI-DME.

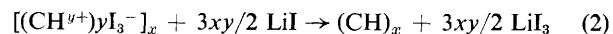
Experiments were performed in order to investigate the electrochemical doping of PA from a LiI-DME solution. Sufficient current was passed to have doped the polyacetylene sample to several mol %. The electrolytic solution turned yellow during the charging. The sample was removed, rinsed in DME, and dried *in vacuo*. Conductivity measurements showed the material to be insulating (σ < 10⁻⁹ Ω⁻¹ cm⁻¹), approaching the conductivity of the undoped original material. The results indicate that there is no net electrochemical doping in this system. The spontaneous discharge process is probably responsible for the low coulombic

efficiency for electrochemical charging on LiI reported in the literature.³

The charging (doping) reaction is shown in equation (1).



Upon exposure of the doped material from equation (1) to LiI-DME, spontaneous discharge was observed [equation (2)]. Reaction (2) will approach an equilibrium such that a



net doping level will remain in PA, but our results indicate that this level will be quite low and that the equilibrium lies far to the right.

Since the spontaneous discharge process described here is also found for electrochemically p-doped PA in LiI, this system will not be suitable for battery applications. Similar limitations will apply to any system where the product of the doping reaction remains in the matrix, and leaches out with spontaneous discharge upon exposure to an electrolyte solution. Transition metal oxidants, *e.g.* FeCl₃,¹ may be such examples.

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