

## Electrochemical Doping of Poly-(*p*-phenylene) with Application to Organic Batteries

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The first examples of electrochemical doping of poly-(*p*-phenylene) to form n- and p-type complexes with counter ions such as  $\text{Li}^+$  and  $\text{AsF}_6^-$  are reported; polyphenylene can be used as the electroactive material in rechargeable battery electrodes.

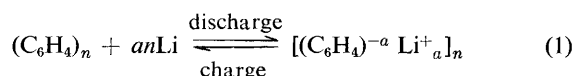
Polyacetylene has been recently reported to function as an electroactive material in rechargeable battery anodes and cathodes.<sup>1</sup> The electrochemical reactions in the battery involve the 'doping' and 'undoping' of polyacetylene, a process which controls the electrical conductivity in this conducting polymer system. We have now demonstrated that poly-(*p*-phenylene), which has been shown previously to form conductive derivatives upon exposure to a variety of chemical dopants,<sup>2,3</sup> can also be electrochemically doped to form n-type or p-type complexes with such counter ions as  $\text{Li}^+$  and  $\text{AsF}_6^-$ , respectively. These doped materials can be employed as rechargeable battery electrodes, either together as anode and cathode or in conjunction with other electrodes such as lithium metal.

Poly-(*p*-phenylene) was synthesized as a loose brown powder<sup>2-4</sup> of high surface area (about 50 m<sup>2</sup>/g). This powder was compressed to form pellets for use as electrodes. In contrast with polyacetylene prepared by the Shirakawa method,<sup>5</sup> which has appreciable conductivity due to acceptor impurities, poly-(*p*-phenylene) prepared by the Kovacic method<sup>4</sup> is a good insulator before doping ( $\sigma \leq 10^{-12}$  S/cm). In fact the conductivity is so low that electrochemical doping of the pristine polymer is very difficult. Therefore in order to impart an initial conductivity greater than about  $10^{-6}$  S/cm, polyphenylene pellets were lightly doped by brief exposure to dopants such as  $\text{AsF}_5$ ,  $\text{NOBF}_4$ , or lithium naphthalide. After this 'predoping', the polymer electrode can be electrochemically doped.

For acceptor doping, the polymer electrode is maintained at a positive potential with respect to a platinum counter electrode in an electrochemical cell. For example, doping with  $\text{PF}_6^-$  can be accomplished from a 0.5 M solution of tetraethylammonium hexafluorophosphate in rigorously dried propylene carbonate. Conductivities of 50 S/cm have been obtained in this manner with the dopant,  $\text{PF}_6^-$ .

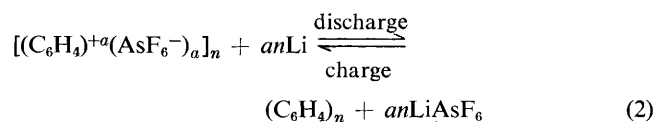
Donor doping with lithium can be carried out by employing a counter electrode of lithium in a 0.5 M solution of

lithium perchlorate in tetrahydrofuran. This configuration is itself a battery and the doping will proceed spontaneously when electrons are allowed to flow from the lithium to the polymer through an external circuit. The doping process corresponds to the discharge of the battery as shown in

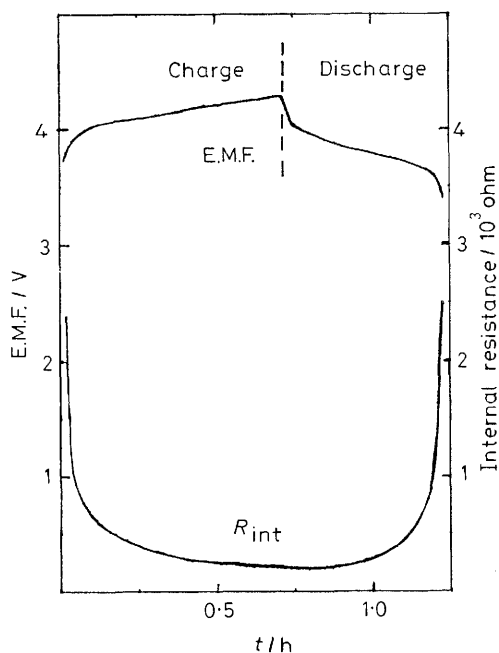


equation (1). Here the stoichiometry (*a*) given for discharge may vary uniformly from 0 to 0.5. In our preliminary experiments we have investigated discharge levels up to *a* = 0.15. This battery has a rather low open circuit voltage with a discharge characteristic extending from *ca.* 0.9 to *ca.* 0.4 V. The major portion of the discharge plateau lies between 0.6 and 0.4 V.

A much higher voltage battery can be obtained by combining an acceptor-doped polyphenylene cathode with a lithium anode in an electrolyte composed of 1 M  $\text{LiAsF}_6$  in propylene carbonate. Lithium-aluminium alloy anodes may also be used to obtain more efficient cycling at the expense of a 0.35 V drop in cell voltage.<sup>6</sup> In both cases, the cell reaction follows equation (2) where we have observed electrochemical



doping levels up to *a* = 0.10. During charge, the polyphenylene is oxidized and the  $\text{AsF}_6^-$  anions from the electrolyte enter the polymer to provide counter ions for the positively charged polymeric cation. During discharge these ions diffuse back into the electrolyte. Batteries using the salts  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ , and  $\text{LiAsF}_6$  have been constructed. Each displays approximately the same open circuit voltage (OCV) vs.



**Figure 1.** Charge-discharge characteristics of an electrochemical cell composed of a lithium-aluminum anode and a poly-(*p*-phenylene) cathode with 0.5 M LiPF<sub>6</sub> in propylene carbonate. Charge and discharge between  $a = 0$  and  $a = 0.03$  were performed with a constant current equivalent to 0.5 mA/cm<sup>2</sup> for the polymer electrode. The coulombic efficiency over this cycle was equal to 90%.

lithium, 4.4 V, for a charge level corresponding to  $a = 0.10$ . This OCV is about 0.7 V higher than that of the corresponding polyacetylene battery,<sup>1</sup> a result which is consistent with the difference in ionization potentials for the two

undoped polymers.<sup>7</sup> Current densities for the polyphenylene electrode as high as 40 mA/cm<sup>2</sup> have been observed under maximum power transfer conditions. Charge and discharge characteristics of a battery employing a lithium-aluminum alloy anode and a polyphenylene cathode are shown in Figure 1.

Batteries with alkali-metal doped polyphenylene as an anode and acceptor-doped polyphenylene as a cathode have also been constructed. In this case an open circuit voltage of *ca.* 3.3 V was observed. However, these preliminary experiments employed an electrolyte containing propylene carbonate in which the polymer anode showed poor stability. Although the question of solvent compatibility requires further investigation, batteries employing poly-(*p*-phenylene) electrodes show great promise, since doped polyphenylene exhibits many of the attributes of the ideal electrode: high electronic conductivity, high ionic mobility, insolubility, structural integrity, and high voltage.

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