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L. Shacklette, R. Elsenbaumer, R. Baughman. ELECTROCHEMICAL CELLS EMPLOYING POLY-ACETYLENE AND POLY(p-PHENYLENE) AS ACTIVE MATERIALS. Journal de Physique Colloques, 1983, 44 (C3), pp.C3-559-C3-565. 10.1051/jphyscol:19833111 . jpa-00222621

HAL Id: jpa-00222621

<https://hal.science/jpa-00222621>

Submitted on 4 Feb 2008

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ELECTROCHEMICAL CELLS EMPLOYING POLYACETYLENE AND POLY(p-PHENYLENE)
AS ACTIVE MATERIALS

L.W. Shacklette, R.L. Elsenbaumer and R.H. Baughman

Allied Corporation, Corporate Research Center, Morristown, New Jersey 07960, U.S.A.

Résumé - Le comportement électrochimique du polyacétylène et du poly(p-phénylène) est discuté en fonction de la structure de bande et de la structure cristalline.

Abstract - The electrochemical behavior of polyacetylene and poly(p-phenylene) is discussed in terms of band-structure and crystal structure.

I - INTRODUCTION

Polyacetylene¹ (PA) and poly(p-phenylene)² (PPP) are conjugated polymers which can be either oxidized or reduced electrochemically. This process results in the formation of a highly conducting complex between the reduced or oxidized polymer and the appropriate counter ion from the electrolyte. The electrochemical reaction which occurs in a cell containing PA or PPP electrodes involves the removal or addition of electrons through the external circuit and the insertion of ions from the electrolyte into the polymer lattice. Therefore, polyacetylene and polyphenylene function in an electrochemical cell as ion-insertion electrodes and may be compared with other well-studied systems which exhibit similar behavior, e.g. layered transition-metal dichalcogenides,³ rutile-related transition-metal dioxides,⁴ and graphite.⁵ The polymer lattice is generally expanded and reorganized in order to accommodate inserted counter ions. Since PA or PPP chains are only weakly bonded into a three-dimensional crystalline structure, considerable changes in that structure are possible during ion insertion. One expects that the particular structure of the complex will depend on stoichiometry (i.e. doping percent) and on ion size and shape. In some cases the solvent from the electrolyte may also be inserted along with the ions. Due to strain energy effects, it is expected that the counter ions will tend to aggregate, that is, that a minimum local concentration of ions will be required to obtain rapid insertion kinetics and that the ions will not be homogeneously distributed within the polymer lattice.

II - BEHAVIOR OF OXIDIZED POLYMERS

We have constructed cells with oxidized polymer cathodes and lithium anodes. Data obtained for poly(p-phenylene) is presented in Fig. 1. The electrolyte employed in this case was 1M LiAsF₆ in sulfolane, which was found to give superior stability toward the oxidized polymer. The percentage doping per phenyl ring was determined by

the amount of charge extracted during discharge to 3.0V. The crosses on the curve represent the open-circuit voltage obtained after a six-hour wait before discharge (the circles after a 3-day wait). The coulombic efficiency for all points represented by crosses were greater than 80 %.

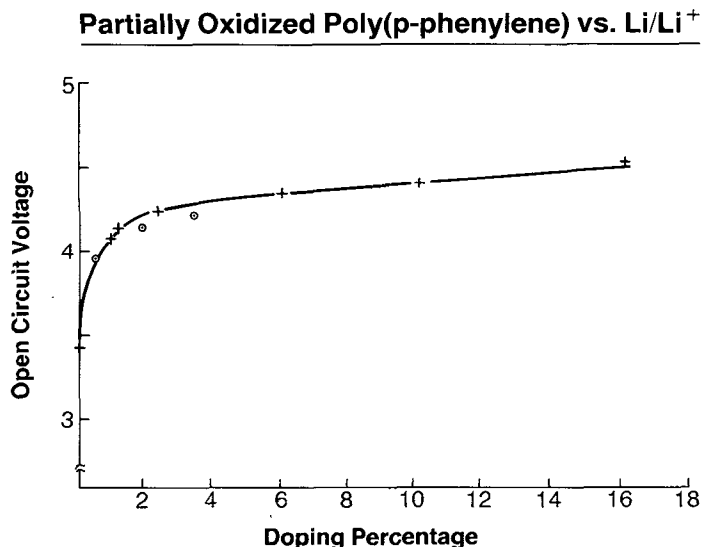


Fig. 1 Open-circuit voltage vs. oxidation level per phenyl ring for PPP

The maximum doping percentage per phenyl ring (16%) depicted in Fig. 1 represents the highest reversible oxidation level achieved to date with PPP. This maximum percentage implies a composition $[(\text{C}_6\text{H}_4)^{+0.16}(\text{AsF}_6^-)_{0.16}]_x$. After cycling through 32 deep cycles, elemental analysis of the PPP electrode was obtained after charging to an expected oxidation level of 15% based on the number of coulombs passed. The analysis gave $\text{C}_{6.00} \text{H}_{4.00} (\text{AsF}_5.2)_{0.15}$ with 4.6% of the sample weight unaccounted for. The low fluorine to arsenic ratio might be explained by simple measurement error, or by the presence of various arsenic oxides or oxyfluorides, produced perhaps by reaction of the dopant with air, water, or the solvent. The theoretically correct carbon to hydrogen ratio suggests that the polymer itself is not degraded during cycling.

The charge/discharge behavior of trans polyacetylene is shown in Fig. 2. These curves were taken at a current density of $50 \mu\text{A}/\text{cm}^2$. The coulombic efficiency in this case was 80%. Rapid charge and discharge ($1 \text{mA}/\text{cm}^2$) generally gave efficiencies of 90% or better.

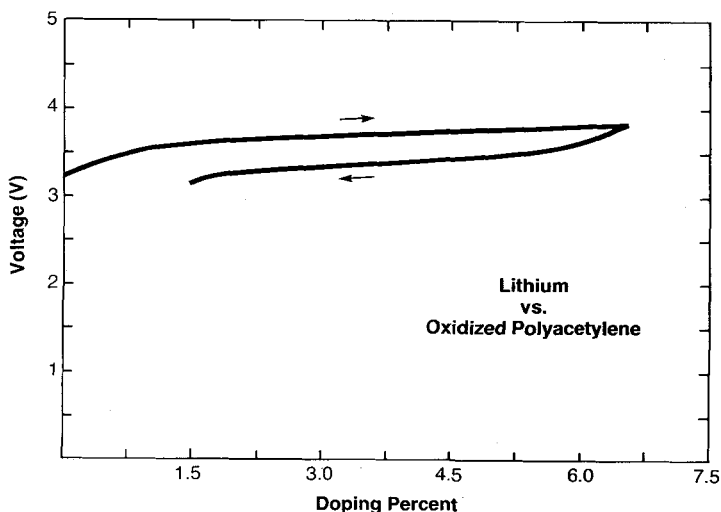


Fig. 2 Voltage vs. oxidation level per CH unit for PA.

III - BEHAVIOR OF REDUCED POLYMERS

We have also assembled cells composed of alkali-metal anodes reduced polymer cathodes, and an electrolyte of the appropriate alkali-metal salt in tetrahydrofuran, THF.

Voltage as a function of charge is presented in Fig. 3 for lithium-doped PA vs. Li/Li^+ and Fig. 4 for sodium-doped PA vs. Na/Na^+ . These curves were obtained by stepping the voltage in small increments and waiting for the current to decay to a small value ($10 \mu\text{A}/\text{cm}^2$). The curves are theoretically equivalent to those that would be obtained for a constant current discharge at $10 \mu\text{A}/\text{cm}^2$ (or considering the polymer weights, 1.25 mA/g for Li and 2 mA/g for Na). Even though the effective charge/discharge rates for the curves in Figs. 3 and 4 are very low, an appreciable hysteresis is evident (especially in the case of the Li-doped sample). One may also note that there is evidence for a distinct plateau in the case of both the sodium-doped and the lithium-doped sample. The voltage and doping range covered by the plateau are very similar for the two types of dopants (assuming Li/Li^+ is 0.35 V negative of Na/Na^+).

Poly(p-phenylene) can also be reduced in a $\text{LiClO}_4/\text{THF}$ electrolyte. As can be seen from Fig. 5, the reduction of PPP takes place at a generally lower voltage vs. Li/Li^+ than the reduction of PA (Fig. 3). The reduction occurs primarily along a plateau extending from about 0.9 V to 0.6 V . More important for the potential use of PPP as an anode, is the fact that essentially all the lithium is put in or taken out at potentials below 1 V (as compared to 1.9 V for PA, as seen in Fig. 3). The observed hysteresis at a current density of $40 \mu\text{A}/\text{cm}^2$ (0.8 mA/g) is also comparatively low.

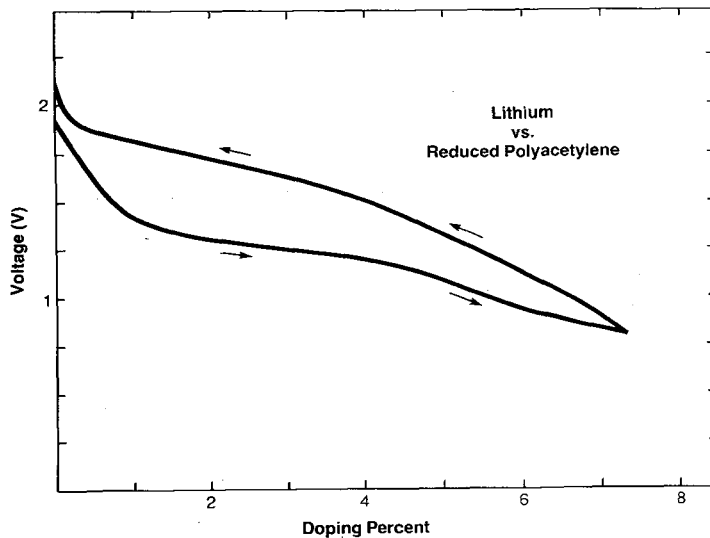


Fig. 3 Voltage vs reduction level per CH unit for reduced PA with Li^+ counter ions

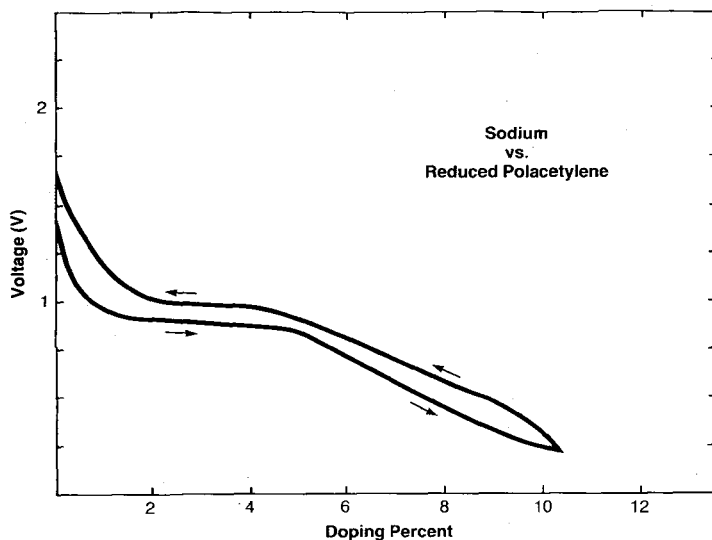


Fig. 4 Voltage vs reduction level per CH unit for reduced PA with Na^+ counter ions

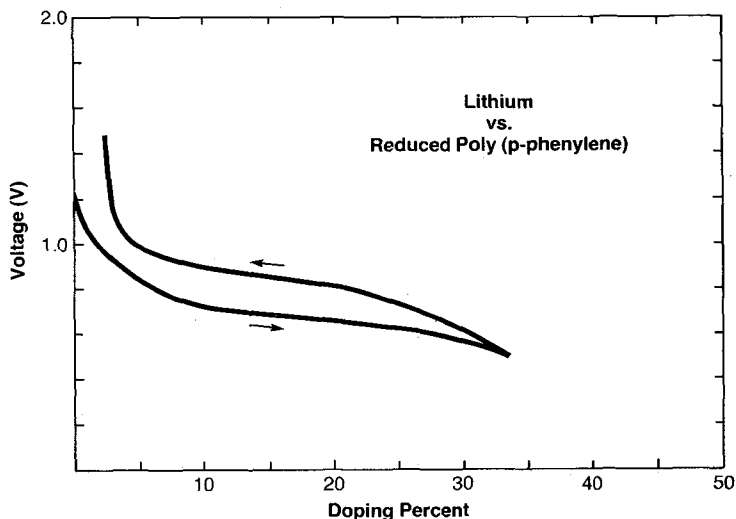


Fig. 5 Voltage vs. reduction level per phenyl ring for PPP.

IV - DISCUSSION

It is obvious from the data presented for emf vs. capacity that there is much similarity in the electrochemical behavior of polyacetylene and polyphenylene. Furthermore the appearance of plateaus suggests that the mechanisms behind the observed behavior is complex.

The variation in voltage at low doping levels may be fit by a logarithmic expression reminiscent of the Nernst Equation. However, the observed voltage varies much more rapidly than would be predicted by the Nernst Equation alone. This result is not surprising since the Nernst equation assumes a fixed thermodynamic potential for the electrochemical reaction. This assumption is invalid since the polymers are expected to have an array of reduction or oxidation potentials as successive electrons are transferred to or from a given chain. From a solid-state point of view, this array of reduction or oxidation potentials will directly result from the shift in chemical potential caused by the filling and shifting of the polymer conduction band (reduction) or the emptying and shifting of the valence band (oxidation). The movement of the chemical potential (μ) will be controlled by the behavior of the density of states ($N(E)$) near the band edge. In a rigid band in the degenerate limit the variation of the chemical potential will be controlled by the following relation:

$$\int_0^{\mu} N(E) dE \propto \text{Doping Percent}$$

The voltage of the cell (V) is naturally related to the chemical potential through Faraday's constant, $V = -\mu/F$. For a one-dimensional polymer in a disordered three-dimensional lattice, the density of states is expected to peak near the band edge and to tail into the gap because of the disorder. Since the voltage will vary slowly when the density of states is at a maximum and more rapidly elsewhere, a weak plateau-like behavior in the voltage vs doping level can result. Also one expects that the onset of reduction and oxidation will occur just before the band edges. This latter idea is well supported by the data in TABLE 1 which shows the close correlation between band gaps inferred from optical and electrochemical data.

Table 1: Comparison of Electrochemical and Optical Data

	<u>Oxidation</u>	<u>Reduction</u>	<u>Optical Absorption</u>		
	Onset of p-Doping	Onset of n-Doping	Onset Gap	Edge	Peak
Polyacetylene:	3.20	1.90	1.30V	1.4eV	1.9eV
Polyphenylene:	3.70	1.15	2.55	2.8	3.35

We have so far neglected effects brought on by structural changes induced by electron transfer and by the physical insertion of ions into the polymer lattice. These effects are expected to be important, especially at high doping levels. The fact that the polymer lattice must be expanded and reorganized in order to accommodate the inserted counter ions implies that a minimum local concentration of ions will be required before insertion will be enthalpically favorable. However, low levels of reduction or oxidation of the polymer will still be possible without ion insertion since the dimension of the polymer fibrils (both PA and PPP) are comparable with the depth of the expected space charge layer. In this limit, doping levels will be small since the available surface area ($\sim 50 \text{ m}^2/\text{g}$ for PA and PPP) will accommodate no more than about 0.003 ions per carbon atom in the bulk. A more important consequence of the necessary structural change is that once ions are inserted they will tend not to be homogeneously distributed. The occurrence of distinct phases is a likely possibility. In fact, the observation of sharp plateaus in Figs. 3 and 4, is indicative of multiphase behavior as seen in the electrochemical intercalation of graphite^{5,6}, TiS_2 ,³ and WO_2 .⁴ Recent x-ray measurements on iodine-doped polyacetylene have demonstrated the possibility of the formation of distinct dilute phases in this material as well.⁷ The sharper plateaus observed with sodium doping may stem from the fact that this complex is crystalline while the Li complex is amorphous. Structural measurements on the alkali-metal complexes of PA have shown that only Li (among Li, Na, K, Rb, Cs) fails to form a tetragonal channel complex.⁸ The difference in hysteresis may also relate to the difference in structure which will affect diffusion rates within the polymer. In addition, it has been reported⁹ that lithium-doped polyacetylene co-intercalates THF to a higher degree than does sodium-doped PA. The inclusion of solvent will undoubtedly further affect crystallinity, diffusion rates, and hysteresis.

CONCLUSION

Polyacetylene and poly(p-phenylene) can both be reversibly oxidized and reduced. The electrochemical behavior of these materials at low doping levels can be successfully related to the one-dimensional band structure which characterizes the pristine polymers. At higher doping levels more complex behavior is observed which is indicative (most clearly in the case of sodium doping) of separation into distinct dilute and concentrated phases.

References

1. D. MacInnes, Jr., M.A. Druy, P.J. Nigrey, D.P. Nairns, A.G. MacDiarmid, and A.J. Heeger, J. Chem. Soc., Chem. Comm. (1981), 317.
2. L.W. Shacklette, R.L. Elsenbaumer, R.R. Chance, J.M. Sowa, D.M. Ivory, G.G. Miller, and R.H. Baughman, J. Chem. Soc., Chem. Comm. (1982), 361.
3. M.S. Whittingham, Prog. Solid St. Chem. 12 (1978), 41, and references therein.
4. D.W. Murphy, F.J. Disalvo, J.N. Carides, and J.V. Waszczak, Mater. Res. Bull 13 (1978), 1395.
5. M. Armand and P. Touzain, Mater. Sci. and Eng. 31 (1977), 319, and references therein.
6. J.O. Besenhard and H.P. Fritz, Electroanal. Chem. and Interfacial Electrochem. 53 (1974), 329.
7. R.H. Baughman, N.S. Murthy, G.G. Miller, and L.W. Shacklette, to be published.
8. R.H. Baughman, N.S. Murthy, and G.G. Miller, J. Chem. Phys., to be published.
9. B. Francois and C. Mathis, Abstract (Internal Conference on the Physics and Chemistry of Conducting Polymers, Les Arcs, France, 1982).