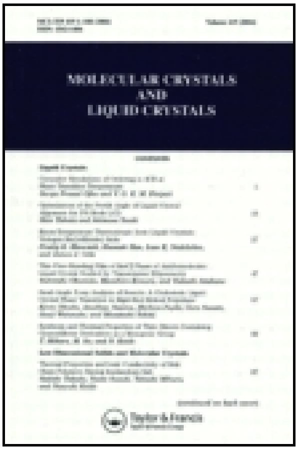

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NEW STRUCTURAL PHASES OF POLYMER BATTERY ANODE MATERIALS: ALKALI-METAL-DOPED POLYACETYLENE AND POLYPHENYLENE

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Abstract

New ordered phases of alkali-metal complexes of polyacetylene and poly(p-phenylene) have been identified by x-ray diffraction studies and by quasi-equilibrium measurements of potential vs. composition during electrochemical reduction with Li^+, Na^+, and K^+ counterions.

INTRODUCTION

Polyacetylene[1], polyphenylene[2,3] and other conjugated polymers have been considered for application in nonaqueous-electrolyte secondary batteries where they may function as either anode or cathode. We will present some important structural characteristics of polyacetylene (PA) and polyphenylene (PPP) as they relate to the potential use of these polymers as anodes. In this case, we will be concerned with partially reduced polymers for which the ion-insertion reaction may be represented by

$$[P]_x + xyC^+ \underset{-xye}{\overset{+xye}{\rightleftarrows}} [P^{-y}C_y^+]_x \quad , \qquad (1)$$

where P denotes the polymer compositional repeat unit, C^+ the inserted cation, y the fractional charge per repeat unit, and x the degree of polymerization. P is -CH- for PA and $-C_6H_4-$ for PPP.

One of the most important considerations relating to the use of electroactive polymers in batteries concerns the charge storage capacity (maximum value of y). To date, there has been a discrepancy for polyacetylene in the reported values of y obtainable with Li^+ by chemical means[4] ($y = 0.3$) and by electrochemical means[5] ($y = 0.08$). We have been able to resolve this discrepancy by performing electrochemical reductions in more cathodically stable electrolytes. Potential vs. composition curves are presented in Fig. 1 for Li^+, Na^+ and K^+ insertion in polyacetylene. We have found that the maximum value of y for Li^+ counterions in PA is $y = 0.18 \pm 0.01$. This value is supported by our

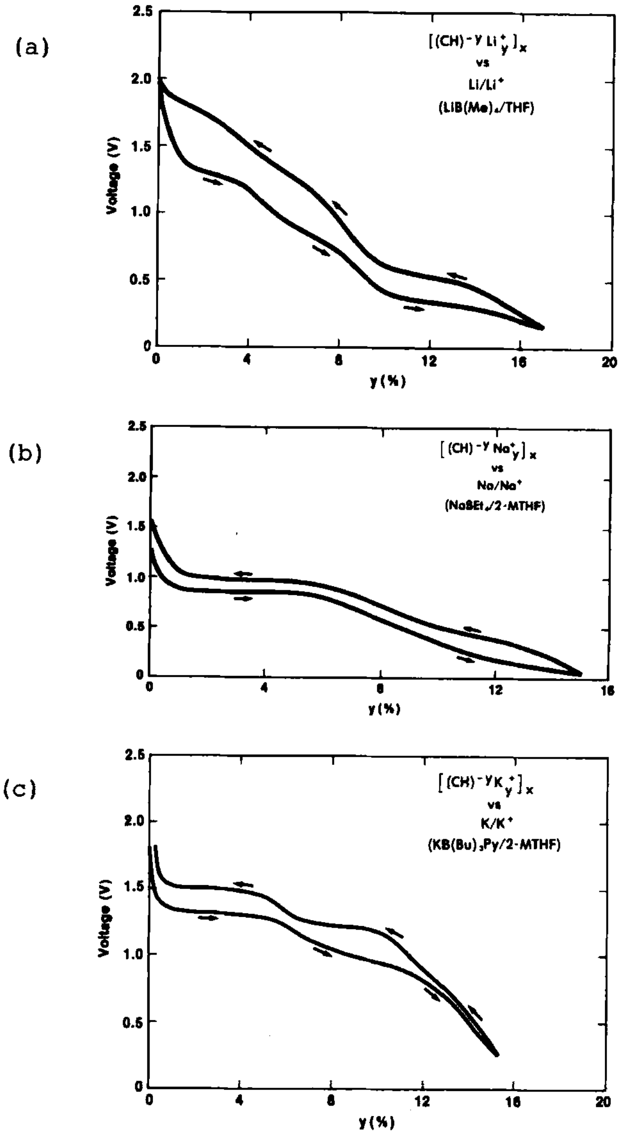


FIGURE 1 Li^+, Na^+, K^+ insertion and extraction in PA with electrolytes of lithium tetramethylborate (a), sodium tetraethylborate (b), and potassium tributyl(N-pyrrolyl)borate (c).

electrochemical data and by elemental analysis of samples chemically doped with lithium biphenyl. The remaining discrepancy with the literature[4] probably results from solvent coinsertion[6], which will raise the apparent lithium content as determined by weight increase.

POLYACETYLENE STRUCTURE

Having found a stable electrochemical system, we have been able to study the structural evolution of polyacetylene at varying degrees of reduction. As illustrated in Fig. 1, PA exhibits a series of plateaus in the voltage vs. percent reduction curves for Li^+, Na^+ and K^+. These features may reflect a maximum in the electronic density of states of the polymer, but are more likely to have a structural origin. Sharp plateaus in voltage vs. composition curves are normally indicative of multiphase structural effects as seen in the electrochemical intercalation of graphite[7], TiS_2[8] and WO_2[9].

Since PA or PPP chains are only weakly bonded to form a three-dimensional crystalline structure, considerable changes in the packing of these chains are possible during ion insertion. In the case of alkali-metal ion insertion in PA (with the exception of Li^+), a channel-like structure has been identified for chemically prepared, heavily doped material ($y \simeq 0.17$). In this structure the inserted ions are arranged in columns which are each surrounded by four polyacetylene chains[10]. The plateaus observed at low levels of reduction ($y \simeq 0.05$) are indicative of other types of ordered structures for these more dilute compositions.

Because polyacetylene complexed with potassium displays the most distinct plateaus and forms the most crystalline complexes, we have studied this material in detail. Measurements of potential vs. composition (Fig. 2) were taken with a computer controlled incremental-voltage-step technique[11]. The potential of the polymer electrode vs. a K/K^+ reference was stepped in 25 mV increments or decrements between preset voltage limits. The current after each voltage step was allowed to decay to a preset minimum corresponding to 50 $\mu A/cm^2$.

In different runs, samples were removed during K^+ insertion with y values near 6%, 12% and 16% and x-ray diffraction data were obtained. (Electrical conductivities were 170, 220, and 260 S/cm, respectively). The x-ray data, which will be more fully discussed elsewhere[12], suggest that the organization of K^+ ions in columns is preserved in the more dilute compositions. However, the spacing of ions within columns and the number of chains per column is variable.

At the highest doping levels obtained, the structure of ref. 10 is observed where the ratio of PA chains to columns of K^+ ions is 2. Meridional x-ray data suggest a separation around 3.7Å

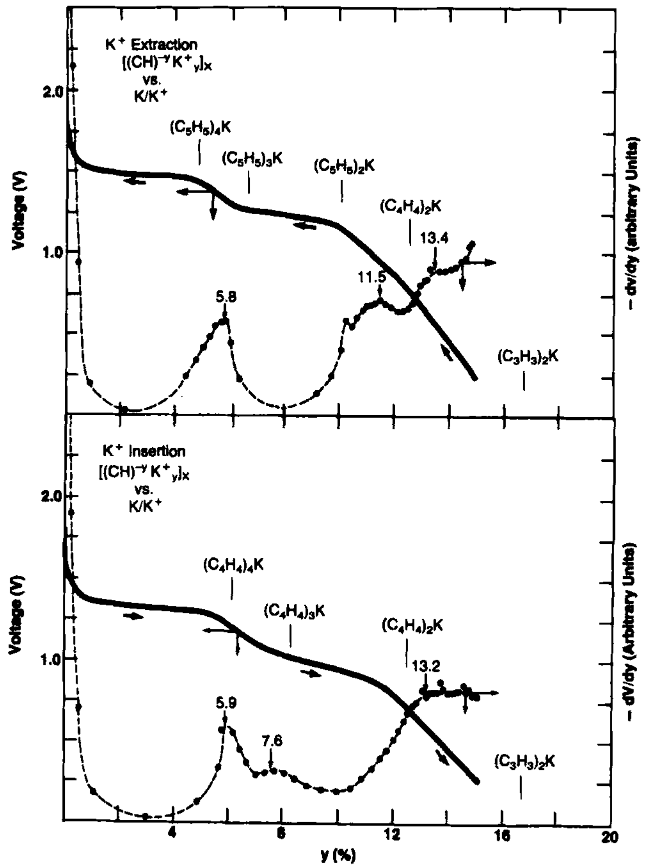


FIGURE 2 Immediate open-circuit voltage (solid curve) and its derivative (broken curve) are plotted for K^+ insertion (bottom) and extraction (top). Maxima in |dV/dy| indicate probable transition points between the growing of one phase and the next. Possible ordered compositions are also plotted according to their predicted *y* value.

between K^+ ions in a given column. Such a spacing leads to a commensurate arrangement of ions along a given polymer chain as shown in Fig. 3.

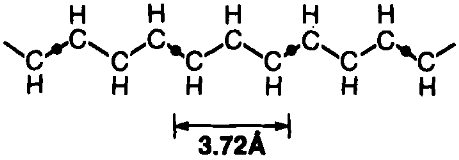
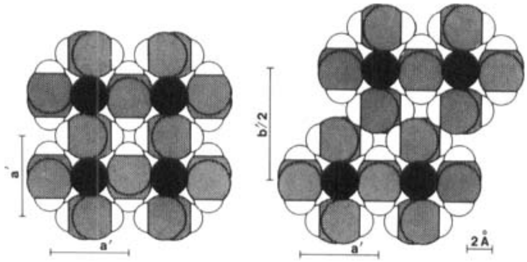


FIGURE 3 A commensurate phase identified for heavily reduced polyacetylene. Black dots show the positions of K^+ ions in a given ion column in relation to one of four neighboring PA chains.

Since there are 3 CH units per ion and 2 chains per ion column in this phase we denote this composition by $(C_3H_3)_2K$, i.e., $y = 0.167$. Various possible phases are plotted in Fig. 2 according to their particular composition. X-ray data from samples taken at the end of the first plateau ($y \simeq 6\%$) exhibit a long spacing of ca. 8.2Å which supports the "second stage" structure of Fig. 4 where there are 3 polymer chains per ion column. Other "higher stage" compounds are likely to be identified by further study since preliminary evidence suggests a longer spacing (11.7Å) for samples taken near 5% reduction. Samples taken at $y = 12\%$, 15%, or 16% all exhibit a long spacing of 6.0Å and other shorter spacings characteristic of the "first stage" structure of Fig. 4. The samples near 16% also exhibit a meridional line corresponding to a 3.72Å spacing between K^+ ions. As already mentioned, this spacing leads to a theoretical composition of 16.7% for the crystalline regions observable by x-ray diffraction. Amorphous regions of the sample may be doped to a lesser degree.

Although the exact structure of the dilute phase(s) at compositions near 6% and the details of their evolution are yet to be precisely determined, the present electrochemical evidence suggests that K^+ ion insertion in PA largely proceeds in two steps from very lightly doped polymer ($y < 0.5\%$) through an intermediate phase ($y \simeq 6\%$) to the "first stage" complex ($y \geq 12\%$). The flatness of the first plateau strongly suggests that a single intermediate phase having a composition near $y = 6\%$ is kinetically favored over other possible phases. X-ray diffraction data on "aged samples" suggest that other less kinetically favored but more thermodynamically stable phases can appear after aging times of days or weeks. The "second stage" complex in Fig. 4 appears to be one of the thermodynamically stable phases. After formation of the "first stage" complex is completed near $y = 12\%$, further evolution of this phase occurs with continued K^+ insertion. The extended tail between ca. 12% and ca. 16% which displays little hysteresis (Fig. 1c) is associated with the con-



FIRST STAGE
$(C_nH_n)_2M$

SECOND STAGE
$(C_nH_n)_3M$

FIGURE 4 Proposed "First Stage" Structure where a'(calc) = 6.04Å and a'(obs) = 5.98Å, and "Second Stage" structure where b'/2(calc) = 8.18Å and b'/2(obs) = 8.20Å. View is along the chain direction. K^+ ions (black circles) are arranged in columns.

tinuous compression of K^+ ions into already established channels. Thus, a nearly continuous evolution is seen upon ion insertion from the commensurate phase, $(C_4H_4)_2K$, to the commensurate phase, $(C_3H_3)_2K$, and likewise, upon ion extraction, the reverse evolution is seen from $(C_3H_3)_2K$ to $(C_4H_4)_2K$ and possibly to $(C_5H_5)_2K$. This filling or emptying of the channels forces successively higher or lower reduction levels for each chain and hence the voltage is much more rapidly varying than over the plateau regions where new structures are being established. The low hysteresis observed over the tail portion also supports the idea that no major structural reorganization is occurring in this range. In the region of $y < 12\%$, it is likely that the kinetic limitations in the transformation from one phase to another will cause the sequence of phases observed during insertion to be different from the sequence during extraction. Particularly, long spacings between K^+ ions in a given channel (e.g., with $(C_5H_5)_2K$) are most likely to be observed during ion extraction from an already established channel. Such different pathways on insertion and extraction are likely to cause a large part of the hysteresis observed for $y < 12\%$ (Fig. 1c).

POLY(p-PHENYLENE) STRUCTURE

We have also investigated the structural evolution of polyphenylene (P is C_6H_4 in Eq. 1) during alkali-metal ion insertion and extraction. As may be seen in Fig. 5, PPP also exhibits a series of plateaus with Li^+ and with K^+ (not shown). It appears that the limiting reduction level with PPP for the counterions Li^+, Na^+, and K^+ is 0.50 electrons per phenyl ring.

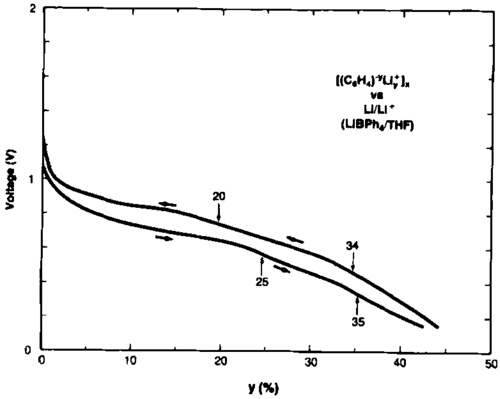


FIGURE 5 Li^+ insertion and extraction in poly(p-phenylene) using an electrolyte of lithium tetraphenylborate in THF.

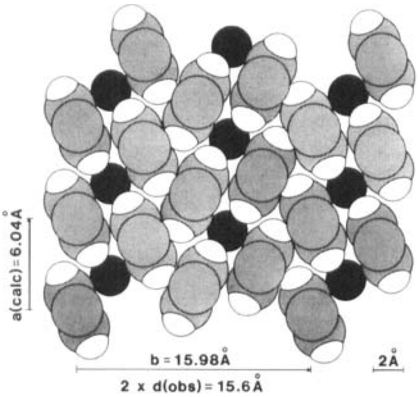


FIGURE 6 Proposed structure for PPP inserted by K^+ ions to the maximum composition, $y = 0.50$.

X-ray diffraction studies on heavily reduced PPP suggest the structure illustrated in Fig. 6, where again alkali-metal atoms are arranged in columns with each column being associated with two polyphenylene chains. If one assumes a commensurate arrangement of ions along each chain (a spacing of K^+ ions matching that of phenyl rings, 4.35Å), then a series of phases may be postulated as described in Table 1 where the number of chains per column varies from 2 to 4. The table illustrates the excellent agreement between the compositions predicted by this model and the inflexion points observed for Li^+ and K^+ insertion in PPP.

TABLE 1: Possible Commensurate Phases
For Alkali-Metal Doped Poly(p-phenylene)

	y from Theory	y from Li^+ Insertion	y from Li^+ Extraction	y from K^+ Insertion
$(C_6H_4)M$	(1.00)		Not Observed	
$(C_6H_4)_2M$	0.50	0.48	0.48	0.50
$(C_6H_4)_3M$	0.33	0.35	0.34	0.37
$(C_6H_4)_4M$	0.25	0.25	0.20	0.25

$(C_6H_4)_mM$ denotes m Polymer Chains per Channel

CONCLUSIONS

Our electrochemical and x-ray diffraction data demonstrate that alkali-metal insertion in PA and PPP proceeds at least in part via a sequence of stoichiometric phases. The discontinuous transformation from one phase to the next causes the appearance of plateaus in potential vs. composition curves obtained during ion insertion or extraction. Such a process will lead to the nucleation and growth of particular ordered phases and not to a homogeneous distribution of dopant. In other regimes where plateaus are not evident, continuous evolution of nonstoichiometric phases is suggested.

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