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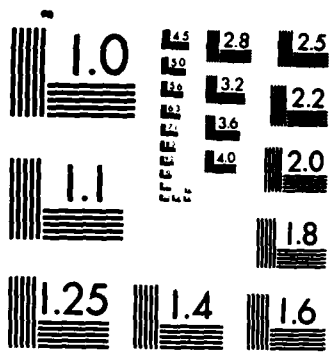
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Electrochemical Properties of Conducting,  
Nitrogen-Bearing Iodinated Polymers

Final Report

Seymour Aronson and Henry Teoh

November 30, 1985

U. S. Army Research Office  
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Brooklyn College of the City University of N.Y.

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The primary objective of this investigation was to determine the feasibility of using conducting, iodinated polymers as cathode materials for high energy-density, high power-density electrochemical cells with lithium as the anode. A complementary objective was to study the electrical and thermodynamic properties of these iodinated polymers.

#### Summary of Important Results

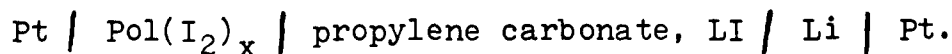
The following nitrogen-bearing, conjugated polymers were either prepared in our laboratory or were purchased: 2-polyvinylpyridine, cyclized polyacrylonitrile, aniline black, paracyanogen, polyquinoxaline and polybenzimidazole. Only the first three polymers exhibited high electrical conductivity when reacted with iodine. Additional work was done on these polymers.

The electrical and thermodynamic properties of iodinated 2-polyvinylpyridine and cyclized polyacrylonitrile were investigated. The results are described in a paper accepted for publication in the journal Polymer (preprint in Appendix I). The primary conclusion of this study is that both polymers bond iodine in a manner similar to the polycyclic aromatic hydrocarbons, pyrene and perylene. The bonding is very weak and only a small amount of charge transfer occurs between the polymer and iodine molecules. The interaction between iodine and these polymers is probably much different than in iodine-doped polyacetylene.

The electrical and thermodynamic properties of aniline black-iodine compositions have also been studied. The bonding between iodine and aniline black is very weak as in the case of the other two polymers. The electrical conductivity of aniline black-iodine samples appears to be significantly dependent on the detailed experimental procedures of the preparation of the aniline black.

An investigation of the nature of the conduction mechanism in the iodinated polymers has been partially completed. Voltage measurements have been performed on electrochemical cells of the type  $\text{Ag} \mid \text{AgI} \mid \text{Pol}(\text{I}_2)_x \mid \text{Pol}(\text{I}_2)_y \mid \text{AgI} \mid \text{Ag}$ . The results indicate that the conductivity in the aniline black- $\text{I}_2$  2-polyvinylpyridine- $\text{I}_2$  and cyclized polyacrylonitrile- $\text{I}_2$  complexes is more than 90% electronic. Polarization phenomena have been observed which indicate that, under certain conditions, ion separation may greatly effect the movement of electrons in the complexes. A paper on this subject is being prepared for publication. An abstract of a talk given at the Electrochemical Society Meeting in May, 1985 is in Appendix II.

Short-term evaluations (up to 24 hours) of the discharge characteristics of electrochemical cells using polymer- $\text{I}_2$  cathodes in the form of pressed pellets have been performed. The cells were of the type



The cells had open circuit voltages greater than 3 volts and discharged in a satisfactory manner during the time periods employed. The tests were discontinued because the problem of high iodine solubility in propylene carbonate could not be overcome. Iodine is very soluble in almost all organic solvents. This high solubility is detrimental in two ways. It depletes the polymer of its iodine content and subjects the lithium to direct iodination. Attempts to overcome these problems by employing other solvents and by inserting a protective barrier between the iodine and the lithium were not successful.

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### Publications

S. Aronson, S. Wilensky, K. Jawitz, and H. Teoh, "Electrochemical Properties of Complexes of Iodine with Cyclized Polyacrylonitrile and 2-Polyvinylpyridine" (in press, the journal POLYMER).

H. Teoh and S. Aronson, "Ionic Conductivity in PVP-I<sub>2</sub> Systems", presented at the Electrochemical Society Meeting, May 12, 1985, (Abstract in J. Electrochem. Soc., March, 1985, page 132c).

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### Appendices

Appendix I. Preprint of paper to be published in the journal POLYMER

Appendix II. Abstract of talk presented at the Electrochemical Society Meeting, May, 1985.



# Electrochemical properties of complexes of iodine with cyclized poly(acrylonitrile) and 2-poly(vinylpyridine)

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Electrochemical and conductivity measurements have been performed on the iodine complexes of cyclized poly(acrylonitrile) and 2-poly(vinylpyridine). The thermodynamic activity of iodine as a function of iodine content was determined using cells of the type  $\text{polymer(I}_2\text{)}_x|\text{AgI}|\text{Ag}$ . The results indicate that chemical bonding between iodine and polymer is relatively weak. The conductivity data show a strong dependence of conductivity on the iodine content of the complex.

(Keywords: iodine: complexes: poly(acrylonitrile); poly(vinylpyridine); conductivity: free energies)

## INTRODUCTION

2-Poly(vinylpyridine) (2-PVP) and cyclized poly(acrylonitrile) (CPAN) react with iodine to form conducting polymers<sup>1-4</sup>. Interest in 2-PVP-I<sub>2</sub> has been strong over the past decade because of its utilization as a component in electrochemical power sources for heart pacemakers. Considerably less attention has been paid to CPAN-I<sub>2</sub>. A similar feature of the structure of CPAN and 2-PVP is that nitrogen atoms form part of an alternating system of double and single bonds (see *Figure 1*). In the case of 2-PVP, however, the alternation occurs only in the individual hexagonal rings.

Phase equilibria work has been performed on the 2-PVP-I<sub>2</sub> system which indicates that the phase diagram is complex<sup>4</sup>. Brennen and Untereker<sup>3</sup> have reported some iodine vapour pressure and electrochemical measurements on 2-PVP-I<sub>2</sub> as a function of iodine concentration. There is, nevertheless, little information available on the thermodynamic activity of iodine in the complexes. In this study, we present electrochemical data on solid-state cells of the type  $\text{polymer(I}_2\text{)}_x|\text{AgI}|\text{Ag}$  and electrical conductivity data on the iodinated polymers.

## EXPERIMENTAL

The chemicals pyrene (Py), perylene (Pe), PAN and 2-PVP were obtained, in the highest commercial grades available, from Aldrich Chemical Co. of Milwaukee, Wisconsin. PAN was heated in a sealed, evacuated Pyrex tube for 7 days at 180°C and was subsequently heated in a pumping vacuum at 250°C for 6 h. This material we designate as CPAN-1. A portion of the CPAN-1 was further heated in a pumping vacuum at 350°C for 3 h and is designated as CPAN-2. Elemental analysis was performed on CPAN-1 and CPAN-2 samples by Schwarzkopf Microanalytical Laboratory of Woodside,

New York. The compositions of CPAN-1 and CPAN-2 were found to be C<sub>3</sub>H<sub>3</sub>N<sub>0.97</sub> and C<sub>3</sub>H<sub>2.44</sub>N<sub>0.90</sub> respectively. I.r. spectra of CPAN-1 and CPAN-2 showed the absorption peaks corresponding to cyclized PAN<sup>1</sup>. The peaks for CPAN-2 were generally broader. We conclude from the data that CPAN-1 and CPAN-2 are primarily cyclized PAN. CPAN-2 has been degraded somewhat by the higher temperatures resulting in a loss of nitrogen and hydrogen.

Preliminary information on the uptake of iodine by CPAN-1, CPAN-2 and 2-PVP was obtained by enclosing samples of each in evacuated tubes with iodine at 90°C for 48 h. The polymer and iodine were in contact only through the vapour phase. The amount of iodine absorbed (moles I<sub>2</sub>/moles repeating polymer unit), as measured by the weight increase, was 0.9-1.0 for CPAN-1, 1.0-1.1 for CPAN-2 and 2.20-2.40 for 2-PVP.

Designated compositions of Pe-I<sub>2</sub>, Py-I<sub>2</sub>, CPAN-1-I<sub>2</sub> and CPAN-2-I<sub>2</sub> were prepared by mixing weighed amounts of iodine and organic substance and heating in sealed, evacuated tubes for 48 h at 90°C. In the case of 2-PVP-I<sub>2</sub>, the iodine-polymer mixtures were annealed either at 50°C for 4 days, 70°C for 3 days, 90°C for 2 days or 150°C for 1 day.

For the electrochemical measurements, a sample of powdered iodine or iodinated hydrocarbon or polymer was mixed with graphite and was pressed into a pellet using a Parr pellet press. The graphite served as an inert, electrically conducting medium. The electrochemical cells were assembled in two parts. A layer of silver iodide powder was pressed on top of a layer of silver powder. The iodinated polymer or hydrocarbon pellet was placed on top of the Ag-AgI pellet and the two pellets were compressed by springs between pieces of platinum foil attached to platinum leads. Emf measurements at room temperature were made using a Keithley 602 electronic voltmeter. Readings on a sample were continued until a

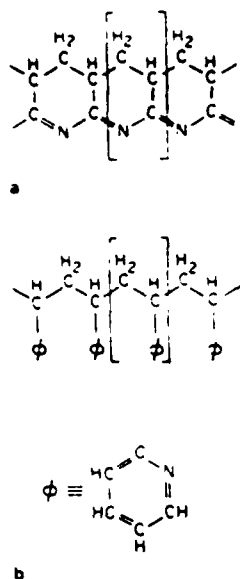


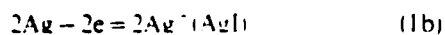
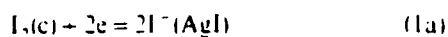
Figure 1 Structures of (a) cyclized polyacrylonitrile (CPAN) (b) 2-poly(vinylpyridine) (2-PVP)

steady reading ( $\pm 0.5$  mV) was obtained for a half-hour. Measurements with varying amounts of graphite mixed with the organic component confirmed that the voltage was independent of graphite content within wide limits. The reproducibility of voltage readings, taking into account day to day voltage changes on the same sample and variations from sample to sample of the same composition prepared separately was generally within  $\pm 10$  mV.

The electrical conductivity of the iodinated polymers was measured by using a four probe van der Pauw method<sup>6-8</sup> on pressed pellets. Sample pellets, 13 mm in diameter and about 1 mm in thickness, were formed by compressing the material in an evacuable die with a Carver press. Pellet thickness was determined by means of a micrometer. Current to the sample was supplied by a Power Design Model 5020 constant voltage source. Output d.c. voltage was detected by a Keithley Model 191 Digital Multimeter linked to a Fluke Model 2240B Datalogger. Electrical contacts were made by using copper electrodes in earlier work and was subsequently replaced with platinum contacts. Measured sample resistance was independent of the types of contacts used and was also verified for ohmic behaviour. The electrical conductivity of the iodinated polymers was measured at room temperature.

## RESULTS AND DISCUSSION

*E.m.f.* data were obtained on electrochemical cells of the type  $I_2(c)|AgI|Ag$  at room temperature.  $I_2(c)$  represents either pure  $I_2$  or iodine complexed in varying amounts with the polycyclic hydrocarbons, Py and Pe, or with CPAN-1, CPAN-2 or 2-PVP. We assume electrochemical reversibility and the following electrode reactions



The overall cell reaction is



On the basis of standard thermodynamic relationships it follows that

$$\bar{G}_{I_2}(c) - \bar{G}_{I_2}^* = -nF(\varepsilon^* - \varepsilon) = RT \ln(a_{I_2}/a_{I_2}^*) \quad (2)$$

The difference of the two terms on the left is the relative partial molar free energy of iodine i.e. the difference between the partial molar free energy of iodine in the complex and in pure, solid iodine:  $n$  is the number of electrons transferred,  $2$ ;  $F$  is Faraday's Number;  $\varepsilon^*$  and  $\varepsilon$  are the *e.m.f.*'s of the cell with pure iodine and complexed iodine respectively;  $a_{I_2}$  and  $a_{I_2}^*$  are the thermodynamic activities of iodine in the complex and in pure iodine, respectively.

*E.m.f.* data obtained on the various samples are shown in Figures 2 and 3. In Figure 2, data on CPAN-1- $I_2$  and 2-PVP- $I_2$  are compared to data on Py- $I_2$  and Pe- $I_2$ . It is interesting to note that breaks in the curves for CPAN-1- $I_2$  and 2-PVP- $I_2$  occur at the approximate compositions CPAN-1( $I_2$ )<sub>1.0</sub> and 2-PVP( $I_2$ )<sub>2.3</sub>. These compositions correspond to the maximum uptake of iodine from the vapour, noted above. One may conclude that the thermodynamic activity of iodine at these compositions approaches that of pure, solid iodine.

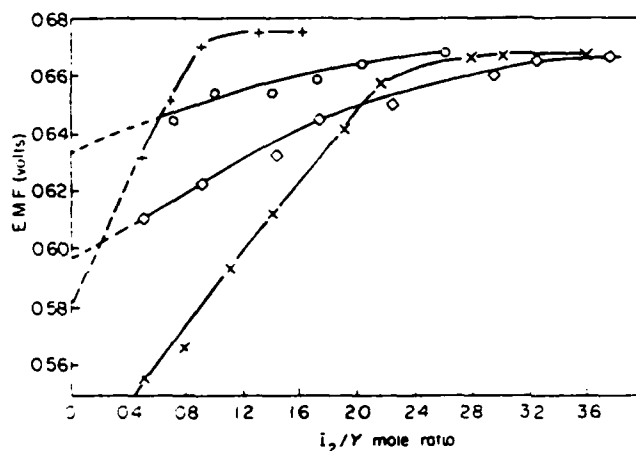


Figure 2 Variation of cell voltage with iodine content: (+), Y  $\equiv$  CPAN-1 repeat unit; (x), Y  $\equiv$  2-PVP repeat unit, 90 C anneal; (O), Y  $\equiv$  Py; ( $\diamond$ ), Y  $\equiv$  Pe

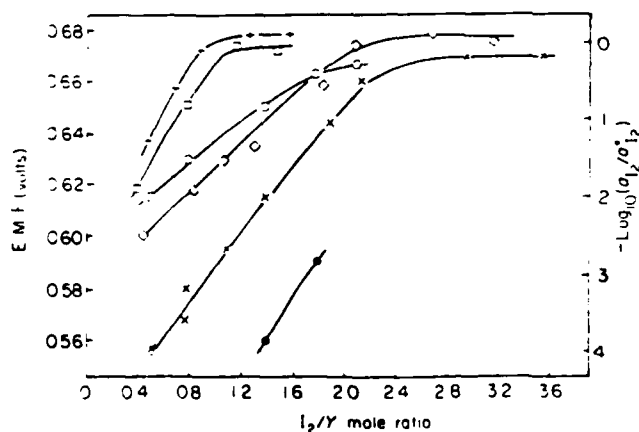


Figure 3 Variation of cell voltage with iodine content: (+), Y  $\equiv$  CPAN-1 repeat unit, 30 C anneal; ( $\square$ ), Y  $\equiv$  CPAN-2 repeat unit, 70 C anneal; (O), Y  $\equiv$  2-PVP repeat unit, 70 C anneal; ( $\diamond$ ), Y  $\equiv$  2-PVP repeat unit, 90 C anneal; ( $\bullet$ ), Y  $\equiv$  2-PVP repeat unit, 150 C anneal

Free energies of formation of the complexes per mole of  $I_2$ ,  $\Delta G$ , were calculated by numerical integration of the expression<sup>9</sup>

$$\Delta G = \left( \frac{1 - X'_1}{X X'_2} \right) \int_0^{X_1} \frac{\bar{G}_1 - G_{I_2}^*}{(1 - X_1)^2} dX \quad (3)$$

$X_1$  is the mole fraction of iodine complexed with the organic substance;  $X'_1$  is the mole fraction of iodine at the composition where the thermodynamic activity of iodine approaches that of pure iodine. Since the integration must start at  $X_1 = 0$ , the data in Figure 2 were extrapolated to a mole ratio of iodine to organic species of 0.

$X'_1$  values for CPAN-1- $I_2$  and 2-PVP- $I_2$  were selected to correspond to iodine to organic species mole ratios of 1.0 and 2.3 respectively. Mole ratios of 2.0 and 2.9 were selected for Py- $I_2$  and Pe- $I_2$ , respectively, because other studies<sup>10</sup> have shown that these ratios correspond to the maximum uptake of iodine in these systems.

Free energies of formation were calculated by applying Equation (3) to the data in Figure 2. The results are given in Table 1. Free energy values for Py( $I_2$ )<sub>2.0</sub> and Pe( $I_2$ )<sub>2.9</sub> calculated from iodine vapour pressure measurements<sup>10</sup> are listed for comparison. The values for AgI, Py( $I_2$ )<sub>2</sub> and Pe( $I_2$ )<sub>2.9</sub> obtained by the *e.m.f.* method are reasonably close to the values obtained by the other methods. This supports the validity of the *e.m.f.* method used here. The free energies of formation of all the complexes are relatively low indicating that the bonding between iodine and the organic species is weak.

*E.m.f.* data for different samples of CPAN- $I_2$  and 2-PVP- $I_2$  are shown in Figure 3. The data on CPAN-1 and CPAN-2 are very similar. In the case of 2-PVP- $I_2$ , increasing the annealing temperature results in a decrease in iodine activity. Samples annealed at a temperature of 150°C could not be measured above a mole ratio of 1.8 because the material was too viscous to use. The *e.m.f.* values for 2-PVP- $I_2$  samples annealed at 50°C, 70°C and 90°C approach that of pure iodine at a mole ratio of about 2.3. The *e.m.f.* data on 2-PVP- $I_2$  do not show correspondence to the phase diagram of Phillips and Untereker<sup>4</sup>. This may be attributed to the complex nature of the phase diagram and the possibility that phase changes may not be completely reversible in this temperature range.

Electrical conductivity data for CPAN- $I_2$  and 2-PVP- $I_2$  samples at room temperature are shown in Figures 4 and 5, respectively. It is observed that the CPAN- $I_2$  and 2-PVP- $I_2$  curves reach plateaus at mole ratios of about 1.0 and 2.3, respectively. These ratios correspond to the compositions at which the thermodynamic activities of

Table 1 Comparison of free energies of formation of iodine complexes

Reaction	- $\Delta G$ (kcal/mole $I_2$ )	
	<i>E.m.f.</i> method*	Other methods
Ag + 0.5 $I_2$ = AgI	30.9	31.70 <sup>b</sup>
Py + 2 $I_2$ = Py( $I_2$ ) <sub>2.0</sub>	0.8	0.2 <sup>c</sup>
Pe + 2.9 $I_2$ = Pe( $I_2$ ) <sub>2.9</sub>	1.5	0.9 <sup>c</sup>
CPAN-1 + $I_2$ = CPAN-1( $I_2$ ) <sub>1.0</sub>	2.0	
2-PVP + 2.3 $I_2$ = 2-PVP( $I_2$ ) <sub>2.3</sub>	3.2	

\* Estimated limits of error,  $\pm 1.0$  kcal/mole  $I_2$ .

<sup>b</sup> Handbook of Chemistry and Physics, 1981, p D-75

<sup>c</sup> From ref. 7, estimated limits of error,  $\pm 0.5$  kcal/mole  $I_2$ .

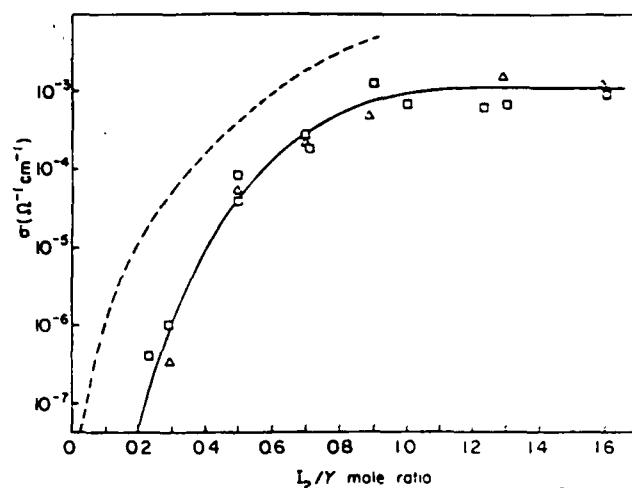


Figure 4 Variation of conductivity with iodine content: (□), Y ≡ CPAN-2 repeat unit; (---), data of N. R. Lerner (ref. 1).

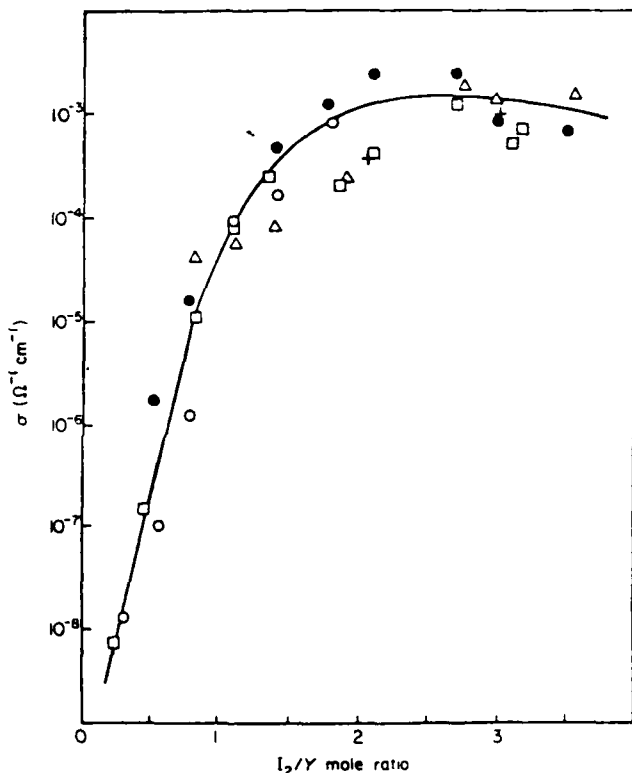


Figure 5 Variation of conductivity with iodine content: (●) ≡ 2-PVP repeat unit; (●), 50°C anneal; (□), 70°C anneal; (Δ), 90°C anneal; (○), 150°C anneal; (+), data of Phillips and Untereker (ref. 4).

iodine approach that of pure iodine. The implication in the case of CPAN- $I_2$  is that free iodine is present above a mole ratio of 1. The significance of the plateau is less clear in the case of 2-PVP- $I_2$  since the phase diagram is complex. Lerner measured the electrical conductivity of CPAN- $I_2$  samples in the form of fibres, rather than pressed pellets. His conductivity values are seen in Figure 4 to be somewhat higher than ours. The conductivity values of Untereker *et al.* (Figure 5), obtained on 2-PVP- $I_2$  samples at mole ratios above 2 are in the same range as our values.

The nature of the CPAN- $I_2$  and 2-PVP- $I_2$  systems seem to be considerably different from polymeric systems such as polyacetylene- $I_2$ . CPAN and 2-PVP are able to absorb significantly more iodine and attain electrical

conductivities several orders of magnitude lower than polyacetylene. Unlike polyacetylene, CPAN-I<sub>2</sub> and 2-PVP-I<sub>2</sub> are stable in air for long periods of time. The electrical conduction mechanism in CPAN-I<sub>2</sub> and 2-PVP-I<sub>2</sub> may be much different from that in polyacetylene-I<sub>2</sub>. The electronic and ionic contributions to conductivity in CPAN-I<sub>2</sub> and 2-PVP-I<sub>2</sub> are currently under investigation.

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IONIC CONDUCTIVITY IN  
POLYVINYLPIRIDINE-IODINE SYSTEMS.\*

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The performance of the lithium battery is greatly improved by complexing the iodine with polyvinylpyridine (PVP) or by coating the lithium anode with the polymer. As the cell discharges, lithium iodide is formed, increasing the cell resistance. Treating the cell with PVP, either as the anode coating material or complexed with iodine as the cathode material, reduces the cell resistance, resulting in improved discharge characteristics (1). The exact mechanism of this improved cell performance is not well understood.

Our approach to a better understanding of how the polymer improves the cell performance is to investigate the charge transport of iodine complexed with PVP. The polymer itself and the iodine are not electrically conductive, but as the iodine reacts with the PVP, the complex attains a conductivity on the order of  $10^{-3}$   $\text{ohm}^{-1} \text{cm}^{-1}$  (2). Based on the positive temperature dependence of conductivity of PVP and iodine systems, Brenner and Untereker (2) indicated that electrical transport in the  $\text{I}_2/\text{PVP}$  systems is primarily ionic in nature, the charge carrying species being polyiodide ions such as  $\text{I}_3^-$ . However, other workers suggest that the conductivity is principally electronic in nature (3). The role of ionic conductivity in the cathode material may play an important role in the discharge process.

Using a four probe technique, the DC conductivity of  $\text{I}_2/\text{PVP}$  systems was studied. The conductivity increases from  $10^{-9}$   $\text{ohm}^{-1} \text{cm}^{-1}$  for low  $\text{I}_2$  concentrations to  $10^{-3}$   $\text{ohm}^{-1} \text{cm}^{-1}$ , an increase of six orders of magnitude with a conductivity maximum occurring at about three moles of iodine per mole of pyridine. This is in agreement with previously reported data (4).

In this work, the current was measured as a function of time. As shown in Figure 1, the current decays exponentially when connected to constant voltage electrodes. This decay curve suggests polarization between the two probes and thus indicates ionic conduction. Reversing the polarity, the current increases to a maximum, indicating reverse polarization, and then decays asymptotically, demonstrating polarization in the opposite direction. This behavior is again observed in subsequent reversals of polarity.

Assuming exponential decay of the current, the time constant may be used as a quantitative measure of the characteristics of the ionic component of the electrical conductivity of the cathode material. A better understanding of the ionic characteristics may establish optimum conditions for cell performance in such solid electrolyte battery systems.

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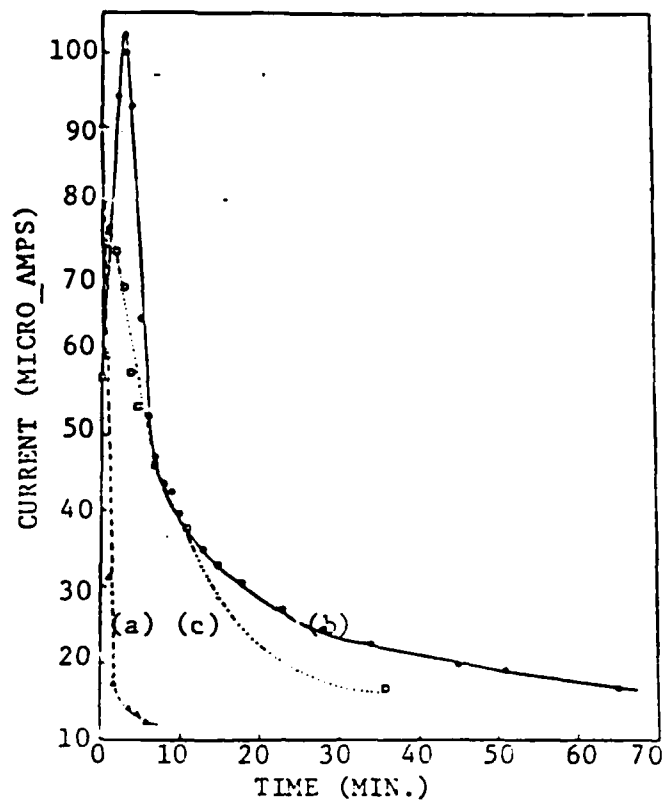


Figure 1. Current Growth and decay in  $I_2$ /PVP Complexes. Curve (a) represents dc current in one direction, (b) current in reverse polarity, and (c) current in original direction.

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