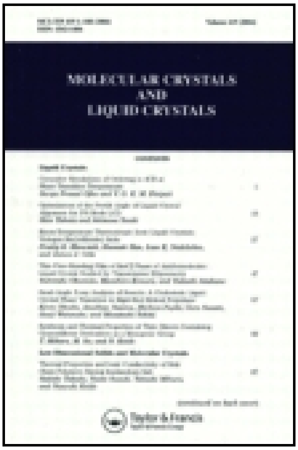

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Electrochemical Study Of Substituted Polyparaphenylene Derivatives In Aqueous And Organic Medium

H. Bidar [b] , C. Fabre [b] , E. M. Genies [a] & A. A. Syed [a]
[a] Lab. Electro. Org. Anal., LA CNRS n° 321, Lab. de Chimie Dept. Rech. Fond., CENG, 85X, F. 38041, Grenoble, Cedex
[b] Lab. d'Electro. Reson. Magn., Univ., Clermont II, BP 45, 63170, Aubiere, France

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ELECTROCHEMICAL STUDY OF SUBSTITUTED POLYPARAPHENYLENE DERIVATIVES IN AQUEOUS AND ORGANIC MEDIUM

H. Bidar*, C. Fabre*, E.M. Genies and A.A. Syed
Lab. Electro. Org. Anal., LA CNRS n° 321, Lab. de Chimie
Dept. Rech. Fond., CENG, 85X, F. 38041 GRENOBLE CEDEX
and * Lab. d'Electro. Reson. Magn., Univ., Clermont II,
BP 45, 63170 AUBIERE, France

INTRODUCTION

In recent years, organic conducting polymers have made concrete inroads in the field of battery materials. In the present communication we report, the synthesis and oxidation potentials of poly-p-phenylene (PPP), polymethylphenylene (PPPmethyl), polypropylphenylene (PPPpropyl), polysulphophenylene ($PPPSO_3H$), polychlorophenylene (PPPCl), polynitrophenylene ($PPPNO_2$) and polyaminophenylene ($PPPNH_2$). A mixture of polyvinylidene fluoride (PVF) and acetylenic carbon was used as conducting adhesive to study electrochemical properties of PPP and derivatives in acetonitrile containing 0.2 M $LiClO_4$ and aqueous sulphuric acid media. We discuss the effects of the substituent groups on PPP and possibilities of its use as a battery material in the light of EPR, conductivity and electrochemical results.

SYNTHESIS

PPP was prepared by the reaction of benzene with anhydrous aluminium chloride and cupric chloride as described by Kovacic et al (1). PPPmethyl was synthesized using anhydrous alumininum chloride, copper chloride and toluene in CS_2 medium (2). The other derivatives of PPP were obtained from the parent compound PPP, upon reaction with appropriate reagents (3-5). The elemental analysis data compares well with the results of Kovacic et al. Evidence for the structure is supported by conventional U.V., I.R., N.M.R. and E.P.R. spectroscopic data. All the polymers synthesized are almost insoluble in commonly known solvents except PPPpropyl which is soluble in THF.

Use of PVF and acetylenic carbon

By weight, PVF (M.W. 455 000), acetylenic carbon and PPP (or derivative) in the ratio of 1:2:2 were mixed well. One or two drops of DMSO was added to make a paste of the mixture. It was thin layered on a clean platinum electrode. The solvant was evaporated in a vacuum decicator for about 15 minutes. The modified electrode was transferred to a cell containing acetonitrile (or sulphuric acid) solution. Cyclic voltammogram were recorded (Fig. 1 and 3). Ag/Ag^+ $10^{-2}M$ ($Hg/Hg_2Cl_2/0.5M$ H_2SO_4) and platinum wire were employed as reference and counter electrodes respectively.

PPPpropyl in acetonitrile solution

Beckman platinum button type electrode (0.2 cm^2) was placed upside down in a vacuum decicator, over which two drops of 1% PPPpropyl in THF solution was placed and the solvent was evaporated using a pump. This leaves a thin film of the PPPpropyl on the platinum plate. The electrode was transferred to a cell containing acetonitrile and lithium perchlorate solution and cyclic voltammogram was recorded and is presented in Fig. 4.

Reversible intercalation of anions

In acetonitrile solution containing $LiClO_4$ and sulphuric acid media following reaction seems to be more probable :

$$PPP + nClO_4^- \rightleftarrows PPP^{n+}(ClO_4)_n^- + ne^-$$

$$PPP + nHSO_4^- + 2nH_2SO_4 \rightleftarrows PPP^{n+}(HSO_4^-,\ 2H_2SO_4)_n + ne^-$$

Figure 1 and 2 demonstrates the reversible intercalation of ClO_4^- and HSO_4^- anion in PPP ; fig. 3 and 4 shows the reversible intercalation of ClO_4^- anion in PPPannealed and PPPpropyl.

Redox potentials

From the values of E_{pa} and E_{pc} obtained from cyclic voltammogram two redox potentials E_1 and E_2 are determined as follows : a) $E_1 = E_{pa} + E_{pc}/2$ and b) E_2 is the intercept of the line joining E_{pa} and E_{pc} with the X-axis. These potentials should not be considered as standard potential. However, these values permit the establishment of a comparison among different compounds. The results are presented in the Table.

Influence of the substituent groups on PPP

The results presented in the Table demonstrates that when the substituent is a saturated group, for example methyl, propyl, or a group with electron pairs such as -Cl or $-NH_2$, linked to an unsaturated system, the E_{pa} value is smaller than that of PPP ; higher values are observed with the electron withdrawing groups such as $-NO_2$ or $-SO_3H$. This is complementary to the results that the substituents responsible for decreasing the ionisation energy reduces the oxidation potential.

PPP as a battery material

The assymetric EPR curve and the conductivity measurements of PPP doped electrochemically in sulphuric acid medium demonstrates that the material is a conductor and stable in air. Priliminary studies of charge/discharge curve in several acidic medium using counter electrode give promising results concerning stability and massic energy.

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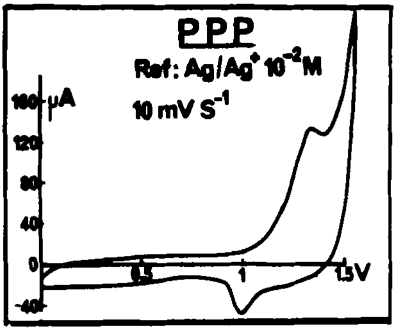

Fig 1. Cyclic voltammogram of PPP in CH_3CN-0.2M $LiClO_4$ using PVF + C paste on 0.2 sq. cm Pt electrode.

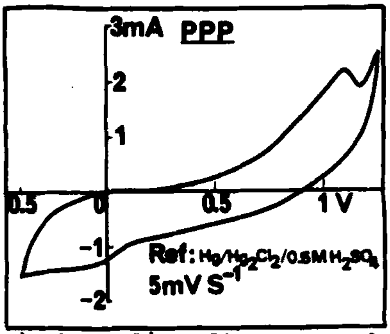

Fig 2. Cyclic voltammogram of PPP bar of 2 x 2 x 5 mm in 18 M sulphuric acid.

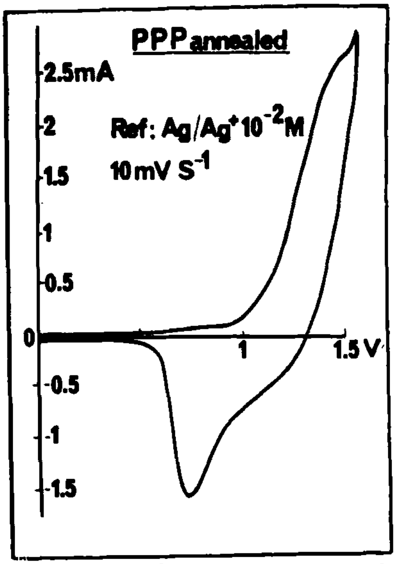

Fig 3. Cyclic voltammogram of PPPannealed using PVF + C in CH_3CN - 0.2 M $LiClO_4$ on 0.2 cm^2 pt. electrode.

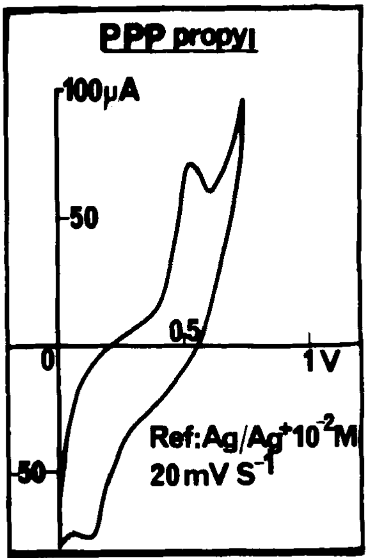

Fig 4. Cyclic voltammogram PPPpropyl film in CH_3CN - 0.2 M $LiClO_4$ on 0.2 sq. cm Pt electrode.

Name of the compound	PVF + acetylenic carbon								Bar of 2 x 2 x 5 mm			
	H_2SO_4 (9M)				CH_3CN - 0.2M $LiClO_4$				H_2SO_4 18M			
	E_1/V	E_2/V	i_{pa}/mA	i_{pc}/mA	E_1/V	E_2/V	i_{pa}/mA	i_{pc}/mA	E_1/V	E_2/V	i_{pa}/mA	i_{pc}/mA
PPP	0.45	0.40	4.6	-3.6	1.16	1.10	0.30	-0.09	0.50	0.40	66.00	-16.00
PPPannealed	0.50	0.54	22.7	-6.5	1.07	1.00	11.0	-7.40	0.50	0.47	22.70	- 6.50
PPPmethyl	0.55	0.52	0.02	-0.15	0.35	0.28	0.16	-0.05	a	a	0.20	a
PPPpropyl	0.20	0.16	0.10	-0.17	0.10	0.16	0.35	-0.35	a	a	0.06	a
$PPPSO_3H$	0.65	0.61	0.02	-0.04	a	a	a	a	0.72	0.63	2.80	-5.80
PPPCl	0.45	0.41	0.21	-0.16	a	a	a	a	a	a	0.05	a
$PPPNO_2$	0.63	0.56	0.16	-0.10	a	a	a	a	a	a	0.11	a
$PPPNH_2$	0.28	0.24	0.78	-0.65	a	a	a	a	a	a	0.01	a

The above values are obtained from cyclic voltammograms scanned at a rate of 10 mV S^{-1} employing PVF + C and 5 mV S^{-1} using a bar.

a : cyclic voltammogram is difficult to interpret