Modification of Polyaniline Films with Heteropolyanions: Electrocatalytic Reduction of Oxygen and Protons

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The first functionalization of polyaniline films, using acid forms of heteropolyanions as electrolytes, is reported; the modified electrodes thus obtained are employed in electrocatalytic reduction of oxygen and protons.

Electrochemical polymerization of organic molecules is of great interest in the modification of electrode surfaces.[1] Electrically conductive polymers, such as polypyrrole, polythiophene, and polyaniline are useful as conductive matrices to immobilize molecules which exhibit specific properties at the surface of an electrode. There are two principal methods for the immobilization of the active sites in such polymers. (i) The use of a soluble salt containing anionically charged active molecules for the electrochemical synthesis. The ions of the salt are the electrolyte and the anion will be the doping agent of the polymer.[2] (ii) The covalent linkage of a specific molecule to the starting monomer. The latter procedure has been applied in the case of polypyrrole[3] and polythiophene,[4] but is difficult to apply to polyaniline, because of the high reactivity of the amino group of the aniline ring. The use of method (i) is also difficult with polyaniline because its polymerization requires a relatively strong, non-nucleophilic, acidic medium. Incorporation of multi-charged anionic species into poly(N,N-dialkyl substituted aniline) films has been demonstrated by Ohsaka *et al*[5] by the cycling of a polyaniline film already prepared in the usual acid solution. In this communication we report the first example of polyaniline functionalization, using the acidic forms of heteropolyanions (HPA) as electrolytes. The modified electrode obtained was employed in the electrocatalytic reduction of oxygen and protons.

The Keggin-type acids of HPAs were used: 12-tungstophosphoric acid $H_3[PW_{12}O_{40}]$, 12-tungstosilicic acid $H_4[SiW_{12}O_{40}]$, and 12-molybdophosphoric acid $H_3[PMo_{12}O_{40}]$, (all Fluka). Such acids possess interesting catalytic properties which are extremely valuable for a large number of chemical[6] and photochemical[7] reactions. The corresponding anions can exchange several electrons, and at the same time are strong Brönsted acids. The acids of HPAs are highly soluble and fairly stable in water and organic solvents. Because of the poor solubility of HPA–aniline salts in water, all syntheses were performed in acetonitrile which has not previously been reported as a solvent for aniline electropolymerization. We have observed that acetonitrile solutions of classical mineral acids (HCl, $HClO_4$, *etc.*) give
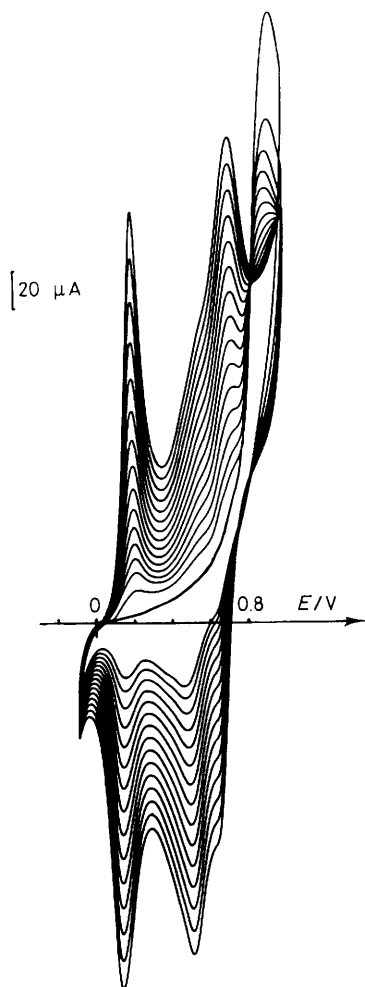
Figure 1. Successive cyclic voltammograms at 10 mV s^{-1} on a GC electrode ($S = 0.07$ cm^2) of an acetonitrile solution containing 0.01 M aniline and 0.1 M $[SiW_{12}O_{40}]^{4-}$.
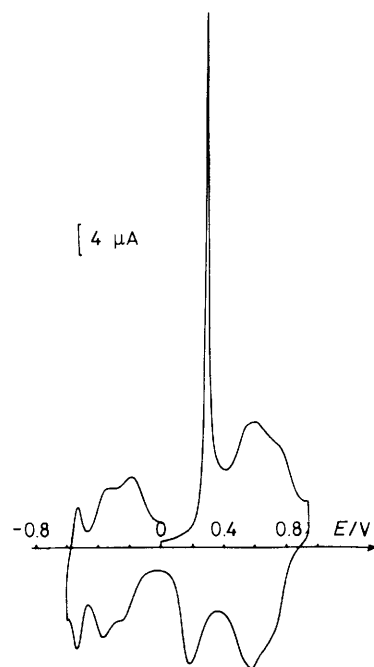
Figure 2. Cyclic voltammograms at 100 mV s^{-1} of a GC electrode modified with a polyaniline film doped with $[SiW_{12}O_{40}]^{4-}$ in H_2SO_4, pH = 0. The film was prepared by electrolysis at 1 V, by passing 3 mC through the solution as in Figure 1.
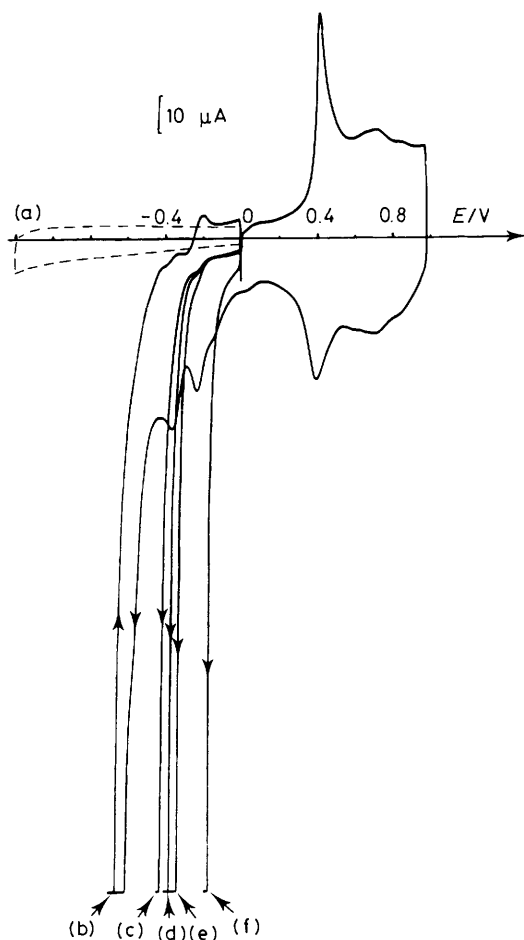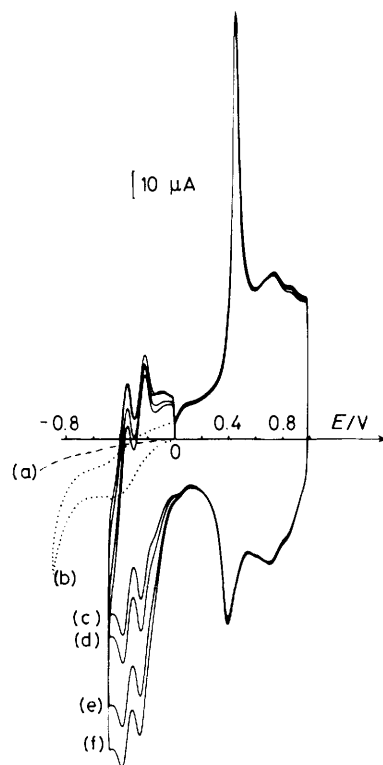
Figure 3. Cyclic voltammograms at 50 mV s^{-1} in a solution of HClO$_4$ in acetonitrile (0.5 M deaerated solution): (a) on naked GC; (b) first scan and (c) second scan on modified electrode as in Figure 2. After activation of the modified electrode by polarization at -1.5 V for (d) 1 min and (e) 30 min; and (f) at -2 V for 5 min.

Figure 4. Cyclic voltammograms at 50 mV s^{-1} in a solution of HClO$_4$ in acetonitrile (0.5 M). (a) On naked GC in deaerated solution. (b) After introduction with stirring of 15 cm^3 of air. (c) In deaerated solution on a modified electrode obtained by electrolysis, passing 5 mC at 1 V through the solution as in Figure 1. After successive introduction of (d) 5, (e) 10, and (f) 15 cm^3 of air.

poor yields. Using acetonitrile we obtained good electroactive polyaniline thin films. However, it was not possible to obtain thick handleable films on which to perform elemental analyses as we have done with polypyrrole and polythiophene containing HPAs.[8]

Figure 1 shows typical voltammograms obtained by scanning electropolymerization from -0.15 to $+1.0$ V on a glassy carbon (GC) electrode ($S = 0.07$ cm^2) of an aniline solution (0.01 M) in acetonitrile containing H$_4$[SiW$_{12}$O$_{40}$] (0.1 M), the curves obtained are very similar to those obtained with H$_3$[PW$_{12}$O$_{40}$]. The regular growth of the polyaniline deposit is evident from the continuous increase of three distinct redox systems, which appear as oxidation at $+0.2$, $+0.6$ (sh), and $+0.7$ V (vs. Ag/10^{-2} M Ag$^+$). These values are close to those observed for polyaniline in aqueous solution.[9]

The polymer film displays the same electrochemical properties when formed either by potential sweep or controlled-potential electrolysis. The polyaniline deposit adhered strongly to the supporting carbon electrode, but some coloured soluble oligomeric products were seen near the electrode during the electrodeposition process, indicating a nonquantitative polymerization, as observed in other media.[9]

After washing and transferring the modified polyaniline–HPA electrode to a deaereated 1 M aq. H$_2$SO$_4$ solution, it was established by cyclic voltammetry (c.v.)
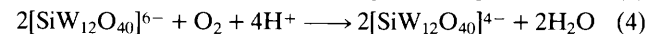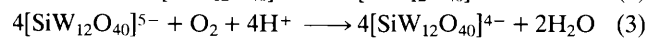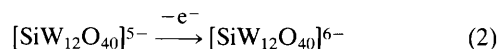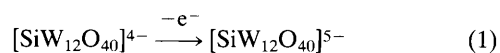
(Figure 2), that the HPA molecules were immobilized in the polymer and did not exchange with sulphate anions. Well-defined peaks corresponding to the reduction and oxidation of HPA are observed. The current peaks are stable during continuous cycling between -0.6 and $+1$ V (vs. Ag/10^{-2} M Ag$^+$) in aqueous solution. More cathodic switching potentials lead to irreversible modifications of immobilized HPA, as seen in homogeneous HPA solution.[10]

In a recent series of papers,[11] Keita and Nadjo have described a procedure for the activation of GC electrode surfaces by potentiostatic cathodic treatment in the presence of aq. [SiW$_{12}$O$_{40}$]$^{4-}$, which produces a very thin coating of unknown structure, containing heteropolyanions with electrocatalytic properties. We have observed similar results starting from a catalytic material as a volumetric dispersion of HPA in the polyaniline film.

Figure 3 shows the voltammograms at 50 mV s^{-1} of a perchloric acid solution (0.5 M) in acetonitrile (a) on naked GC and (b–f) on polyaniline–HPA modified GC electrodes after successive activation obtained by cathodic polarisation of the electrode. It is found that the reduction of protons in the solution is as efficient as with a pure platinum electrode.

It has also been found that HPA catalyses oxygen reduction.[12] Figure 4 shows the c.v. curves for O$_2$ reduction on two types of electrodes: (b) on a naked GC electrode, and (c—f) on a polyaniline-modified GC electrode doped with [SiW$_{12}$O$_{40}$]$^{4-}$; with the introduction of successive amounts of air, the cathodic current of the reduction systems of the [SiW$_{12}$O$_{40}$]$^{4-}$ anion denotes catalytic phenomena. By comparison with the naked GC electrode, the reduction peaks

give an anodic shift for the catalytic reduction of oxygen of 300 to 350 mV. Similar behaviour was observed in the case of the immobilized $[PW_{12}O_{40}]^{3-}$ anion. Such results can be explained by EC and EEC catalytic regeneration mechanisms (equations 1—4).

$$[SiW_{12}O_{40}]^{4-} \xrightarrow{-e^-} [SiW_{12}O_{40}]^{5-} \quad (1)$$

$$[SiW_{12}O_{40}]^{5-} \xrightarrow{-e^-} [SiW_{12}O_{40}]^{6-} \quad (2)$$

$$4[SiW_{12}O_{40}]^{5-} + O_2 + 4H^+ \longrightarrow 4[SiW_{12}O_{40}]^{4-} + 2H_2O \quad (3)$$

$$2[SiW_{12}O_{40}]^{6-} + O_2 + 4H^+ \longrightarrow 2[SiW_{12}O_{40}]^{4-} + 2H_2O \quad (4)$$

This single step electrochemical method should be extendable to other isopoly and heteropoly oxometalates,[10] yielding various modified electrodes.

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