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Supporting Information

Polyanilines with Pendant Amino Groups as Electrochemically Active Copolymers at Neutral pH

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XPS of PABA copolymers

The XPS core regions of C1s and O1s were very similar in the different films studied. As an example, spectra of extreme compositions (PABA and PANI) are presented in **Fig. SI 1** and **SI 2**. In these figures, black lines are the experimental background subtracted spectra, grey lines are the components used for fitting and red lines are the results of the fitting. The C1s core spectrum level can be deconvoluted into 4 components (**Fig. SI 1** and **Table SI 1**). The component corrected to 285 eV is due to CH/CC from aromatic backbone and aliphatic contaminants and probably also due to uncharged CN.^[1] The following component in energy has been assigned to C bound to charged nitrogen (CN⁺/C=N⁺).^[2] The other minor components at higher energy can be assigned to C bound to O, due to overoxidation of some units and contamination.^[2,3] Finally, the oxygen signal (O1s) appears at about 232.5 eV and can be fitted to two components (232.0 and 233.3 eV, fwhm=2.1 eV) (**Fig. SI 2**).^[1] The presence of oxygen can be attributed to contamination,^[3] overoxidation^[2] or water tightly bound to amine groups as previously reported.^[4]

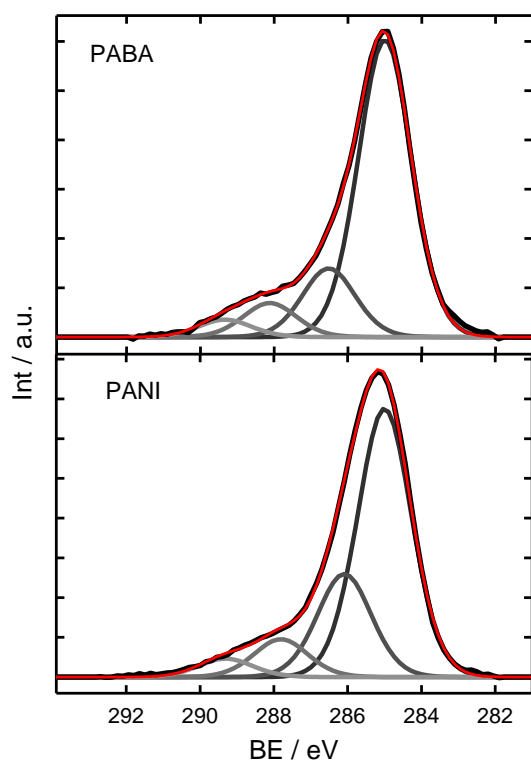


Figure SI 1. C1s XPS spectra of PABA and PANI films. Components are detailed in **Table SI 1**

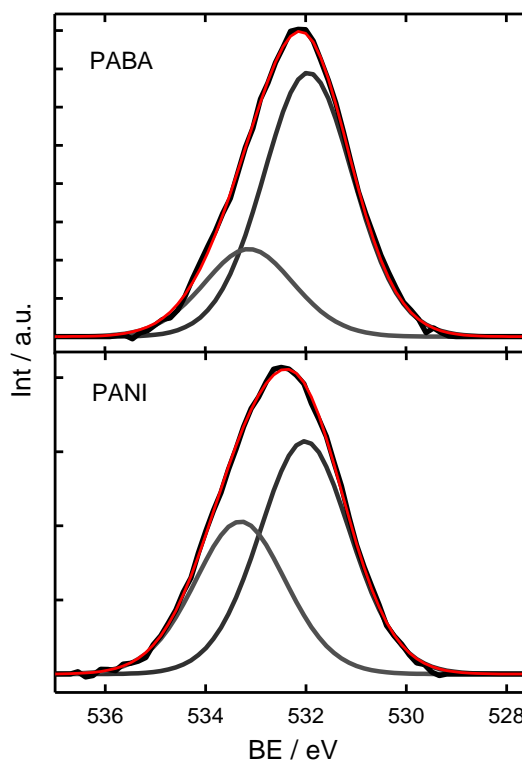


Figure SI 2. O1s XPS spectra of PABA and PANI films.

Table SI 1. C1s core components used for fitting of PANI and PABA contributions (fwhm=1.7 eV).

	C1s	CH/CC/CN	CN+/C=N+	CO/C=O	COO
PANI	BE / eV	285.0	286.1	287.8	289.3
	%	62.7	24.1	8.9	4.3
PABA	BE / eV	285.0	286.5	288.1	289.3
	%	71.2	16.5	8.1	4.2

Ascorbic Acid Oxidation

Fig. SI 3 shows the voltammograms of the oxidation of ascorbic acid (AA) on polymer modified electrodes at neutral pH. The nature of the copolymer affects both the peak position (electrocatalysis) and the peak current. Voltammograms of an unmodified electrode are also presented in this figure for comparison. The electrocatalytic effect is more important in the case of PABA 0.7. **Fig. SI 4 to 6** show the performance of a PABA 0.7 modified electrode at intermediate (1 mM) and high (10 mM) concentrations of AA.

In a simplified model, AA oxidation can be thought as represented by **Scheme SI 1**. According to this scheme, the AA reaches the surface of the film by diffusion (1). In contact with the film, electrons are transferred to the polymer (2) as AA is oxidized to dehydroascorbic acid (DHA); and finally electrons reach the metal by travelling along the film (3). More detailed models can be found elsewhere.^[5,6]

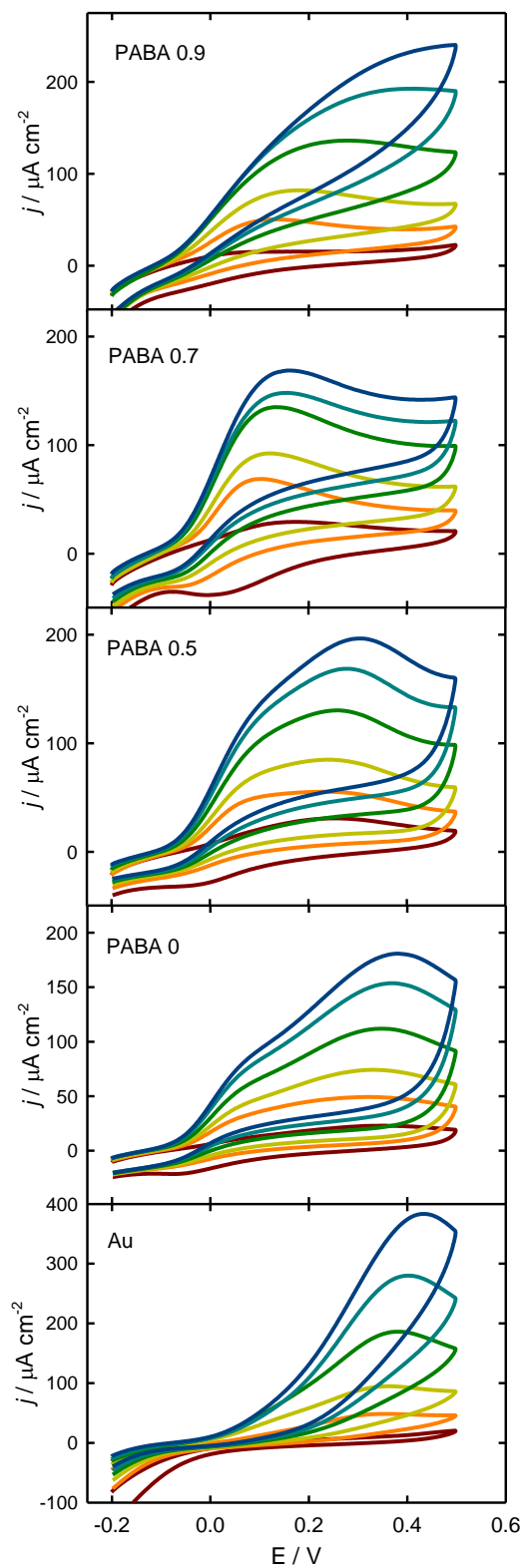
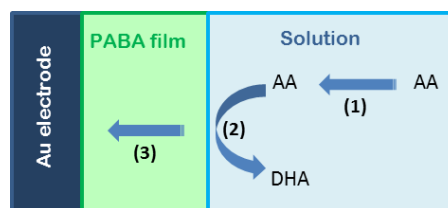


Figure SI 3. CV response of modified electrodes in ascorbic acid solutions of increasing concentration (0, 0.5, 1, 2, 3 and 4 mM) in 10mM pH 7 phosphate buffer. $v = 10 \text{ mV s}^{-1}$.



Scheme SI 1. Simplified steps of ascorbic acid (AA) oxidation on a polymer modified electrode.

For some given experimental conditions, one of the these proposed steps can be slower than the others and then becoming rate limiting step (current limiting). When the concentration of the diffusing species in solution is low enough, the rate limiting step is (1) and voltammograms show the typical dependence of diffusion-controlled irreversible electrochemical reactions.^[7] As concentration of the diffusing redox species increases, the step (1) becomes faster and other steps becomes rate-limiting. The voltammograms show no peak but a limiting value of current.

For polymer film modified electrodes, the peak current does reach a plateau for increasing AA concentrations (**Fig. 11 (a)**), which means that charge transport within the films (3) becomes current-limiting at high concentrations of the diffusing species. On the contrary, no plateau is found in the unmodified electrode in the same range of concentrations (**Fig. 11 (a)**). However, on the polymer films the electrooxidation takes place at lower potentials (**Fig. 11 (b)**). As said before, this indicates that there is some electrocatalysis by the polymer films. The transition from diffusion-controlled to limited by charge transport within the film as AA concentration increases can be also found when varying the sweep rate. At intermediate AA concentrations (1 mM), the voltammetric response behaves as diffusion-limited at low sweep rates, but it becomes limited by the transport within the film as the sweep rate increases (**Fig. SI 4**). On the other hand, at high AA concentrations (10 mM), diffusion is fast enough and current is limited by step (3) even at low sweep rates (**Fig. SI 5**).

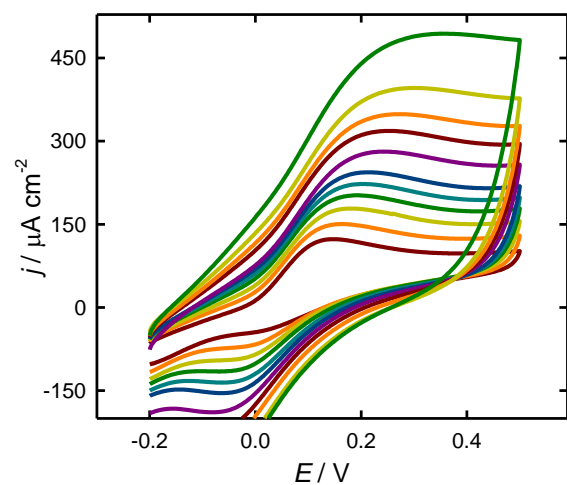


Figure SI 4. Voltammograms of a PABA 0.7 film modified electrode at different sweep rates (0.01 to 0.2 V s⁻¹). [AA] = 1mM in 10mM pH 7 phosphate buffer.

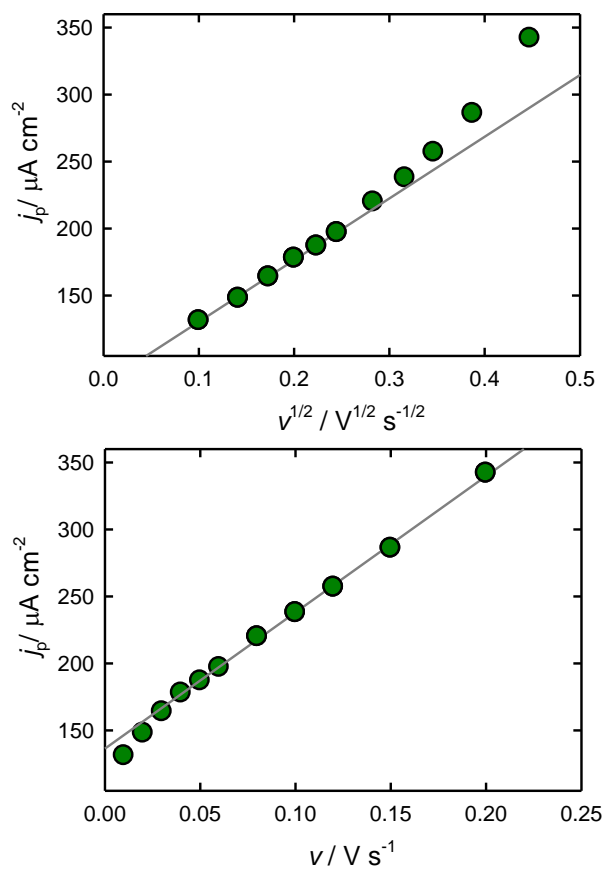


Figure SI 5. Peak current density of AA oxidation of PABA 0.7 modified electrodes for different sweep rates. [AA] = 1mM in 10mM pH 7 phosphate buffer.

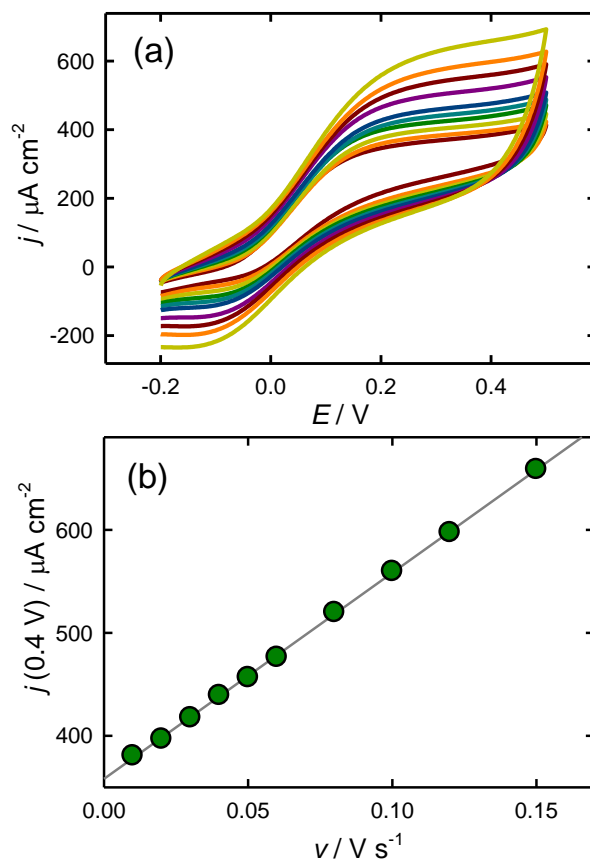


Figure SI 6. (a) Voltammograms of a PABA 0.7 film modified electrode in at different sweep rate (0.01 to 0.15 Vs^{-1}); $[\text{AA}] = 10\text{mM}$ in 10mM pH 7 phosphate buffer. **(b)** Current density at 0.4 V as a function of the sweep rate.

For intermediate AA concentration, the peak current depends linearly on the square root of the sweep rate for low sweep rates (**Fig. SI 5**, top). This behavior indicates that current is limited by diffusion of the electroactive species in solution (semi-infinite diffusion) ^[7]. As sweep rate increases, charge transport within the films becomes a slow step and the peak current depends linearly on the sweep rate (**Fig. SI 5**, bottom), as it is expected for a thin film (finite) charge transport ^[7]. At high electroactive species concentrations in solution, diffusion is not limiting even at low sweep rates, no peak is observed and current depends linearly on the sweep rate (**Fig. SI 6**) indicating that transport within the film is the limiting step of the global electron transport.

References

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