Redox Behavior of Sulphonated Polyaniline in Iron (III) Environment

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Introduction

Monitoring of the electrochemical response of polyaniline (PANI) derivatives in aqueous solution containing metal ions has been an interesting subject for investigation. Studies have been directed toward applications such as electrodes for batteries, electroless plating [2] and sensors [1]. The probable inter-conversion between amine and imine in the PANI backbone is associated with metal ions-amine/imine interactions. These PANI-metal ions type interactions are enhanced by the presence of a functional group attached on the benzene ring such as hydroxyl [1]. However, to our knowledge, the effect of the sulphonic acid group in influencing the amine/imine-metal ion interactions has not been explored so far. Most reports are concentrated on the PANI-metal ion interactions in either dilute acidic [1] or neutral environment [3]. The PANI-metal ion interactions in concentrated acidic medium remain unexplored. In this report, the redox behavior of electrochemically deposited sulphonated polyaniline (SPAN) on platinum electrode immersed in $FeCl_3$/1M HCl solutions was followed by electrochemical method in the process of establishing the role of sulphonic acid group in influencing the amine/imine-Fe^{3+} ion interactions.

Discussion

The redox pairs located at $E_{1/2}$ = 0.49V (ΔE= 0.12 V) for SPAN (Fig 1), show clear increase in peak current values with increasing concentration of $FeCl_3$. Hence, the redox pair is ascribed to represent the redox reaction which occurs on the conducting polymer modified electrode:

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^{-}$$

The Fe^{2+} ion is expected to be produced from the oxidation of the amine sites in the SPAN/PANI.

The linearity of peak current values for Fe^{3+}/Fe^{2+} redox process in SPAN and PANI films implies that the diffusion of Fe cations in these films depends on $FeCl_3$ concentration. Further information about the transport of the iron cations in SPAN or PANI films was obtained through the cyclic voltammetry performed at different scan rates. The dependence of scan rate on the peak current for the redox pair, Fe^{2+}/Fe^{3+} were found to be different. This was ascertained by performing experiments with 5mM $FeCl_3$/1M HCl and 10mM $FeCl_3$/1M HCl solutions. For the former case, the peak current values linearly increase with the scan rate (Fig 2, inset), revealing the occurrence of typical surface bound electron transfer reaction in the film. For the later case, the peak current values vary linearly with the square root of the scan rate (not shown), indicating the diffusion controlled reaction. However, for the PANI film kept in wide $FeCl_3$ concentration ranges (1mM to 10mM), the diffusion-controlled process was dominant. These results suggest that the presence of sulphonic acid group in the backbone of SPAN promotes capturing of Fe^{3+} ion into the backbone units of polymer.

References

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Acknowledgement~The financial support of National Science Council of Taiwan through NSC90-2811-E-006-001 is gratefully acknowledged.

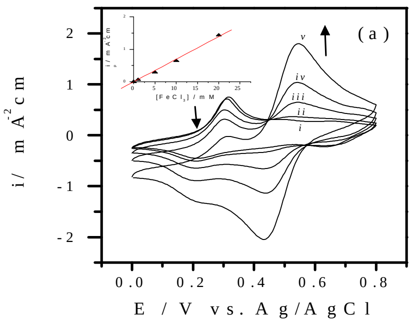

Fig. 2. SPAN immersed in different concentrations of $FeCl_3$/1M HCl.

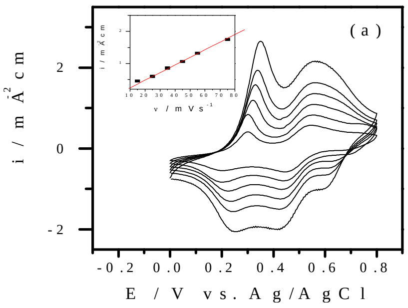

Fig. 3. Cyclic voltammogram of SPAN recorded at different scan rates. [$FeCl_3$] = 5mM