Interfacial Polymerization of Aniline

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Chemical oxidation of aniline at the liquid/liquid interface of two immiscible solvents results in the growth of an electroactive polymer membrane that exhibits redox behaviour similar to conventional electrodeposited polyaniline.

Although conducting polymers are most often considered in electrochemical applications such as secondary batteries and electrostatic shielding devices, there is already great interest in exploiting their high ion selectivity for use in gas-separation membranes.[1] Liang and Martin[2] have prepared such membranes based on polypyrrole while Andersen *et al.*[3] have produced polyaniline-based membranes which exhibit remarkable selectivity ratios. Therefore, we were interested in growing polyaniline (PANI) to form membrane-type films directly.

It is well known that polyaniline can be prepared by a number of methods including chemical oxidation,[4] electrodeposition,[5] enzymatic polymerization[6] and vapour deposition.[7] Chemical methods result in unoriented films and other methods typically require a supporting substrate. The two-phase polymerization of benzene has been reported.[8] Shimidzu *et al.*[9] have also noted that another conducting polymer, polypyrrole, can be formed at a vapour/liquid interface. Additionally, polypyrrole has been grown inside microtubules to form free-standing films.[10]

Novel interfacial chemical oxidation was performed in a small test tube (id 1.2 cm) containing three immiscible liquids (Fig. 1). The lowest section contained 10 ml of a 0.2 mol l^{-1} aniline–0.01 mol l^{-1} sodium dodecyl sulfate (SDS)–CCl_4 solution, while the middle layer was composed of 2 ml of 0.009 mol l^{-1} ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] in 1 mol l^{-1} HCl solution. The upper layer contained 5 ml of toluene which slowly solubilizes both the $(NH_4)_2S_2O_8$ and the HCl thereby quenching the reaction. Furthermore, it acts as liquid barrier to prevent evaporation of the oxidizing solution. Slowly, the aniline molecules migrate into the water solution, their transport being controlled by temperature, the viscosity of the solution and the large micelle.

A dark blue–black colour signalling aniline polymerization appeared at the water/CCl_4 interface quickly. As the polymer was not soluble in any of the three solvents, it was easily collected by filtering and rinsing. Then a glass slide was placed under the film and the liquid phase was allowed to evaporate.

Electrochemical polymerization for comparison samples as well as electrochemical characterization were accomplished using a three-electrode cell consisting of a saturated calomel electrode (SCE) as a reference electrode and a Pt foil counter-electrode. The working electrode, as well as the support for microscopy, was conducting indium tin oxide (ITO) glass. Potentiostatic control was maintained using a PAR model 273 potentiostat. SEM investigation was performed using Cambridge model 360 scanning electron microscope.

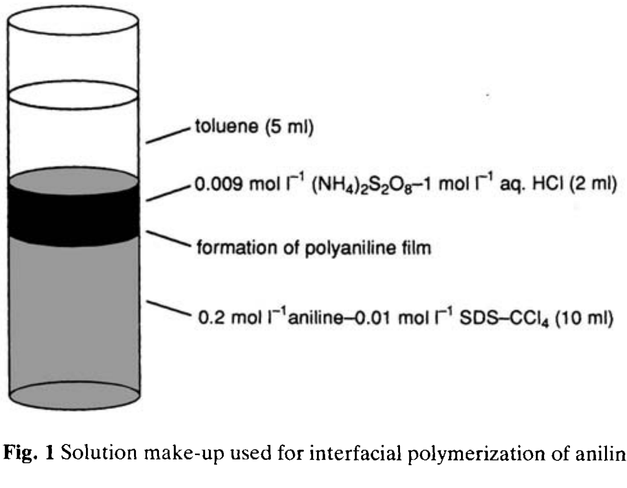

Fig. 1 Solution make-up used for interfacial polymerization of aniline

Many strategies for modifying the macrostructure of polyaniline have been presented in the literature. Both chemical[11] and physical[12] modifiers have resulted in polymer morphologies which are markedly different from the fibrillar surface revealed following the conventional polymerization of an aniline monomer solution in the absence of such additives.[13] Certain modifications have, furthermore, been accompanied by accelerated polymerization[14] or improvements in physical properties such as porosity[15] or substrate adhesion.[16]

In particular, it has already been shown that large quantities ($\geq$0.025 mol l^{-1}) of a micellar material introduced in the aniline monomer solution can greatly affect the polymer's morphology, producing a globular macrostructure.[12] When SDS is present at lower concentrations (*e.g.* 0.01 mol l^{-1}), the resulting PANI maintains its conventional fibrillar morphology. Still at this concentration, the surfactant is well above its c.m.c. of *ca.* 8.0×10^{-4} mol l^{-1} and the most of the SDS can be assumed to have formed micelles. These structures are then capable of encapsulting a group of aniline molecules which increases the local monomer concentration near the liquid/liquid interface.

By maintaining this high local concentration, one can ensure that the aniline molecules will remain near the interface following oxidation rather than dispersing into the oxiding solution. Therefore, polymerization occurs preferentially at this single immiscible electrolyte interface. The lack of any noticeable polymer product in either liquid phase supports this hypothesis.

Electron micrographs (Fig. 2) show quite conclusively that the morphology of PANI has been greatly modified by interfacial polymerization. The resulting macrostructure appears as a network of randomly oriented tubular forms. Under higher magnification [Fig. 2(*b*)], the presence of small nucleation clusters can be seen on the surface of the existing polymer macrostructure. On the contrary, normal chemical preparation of polyaniline leads to a fibrous surface similar to that shown following electrodeposition.[13]

When interfacial PANI is subject to potentiostatic cycling, reversible redox behaviour is clearly observed (see Fig. 3). Similar to electrodeposited PANI, a strong reduction peak is observed near 100 mV while the corresponding oxidation peak is centred at *ca.* 400 mV. This peak separation, much larger than suggested by the Nernstian equation for single electron transfer, indicates that charge transfer is diffusion limited. Furthermore, the film has a coulombic efficiency of *ca.* 45%, as determined by integrating the current during oxidation and the successive reduction.

Interfacial polymerization has also been achieved using lower reaction temperatures (*e.g.* 5 °C) and substituting H_2O_2 as the oxidizing agent. However, several days may be needed before a noticeable polymer is produced. Furthermore, hydrogen peroxide is more readily soluble in CCl_4 than is $(NH_4)_2S_2O_8$ so that a slight darkening of the monomer solution was observed. The aqueous phase nonetheless remains colourless.

This note presents a novel method for producing electroactive polyaniline films at a liquid/liquid interface. Additional

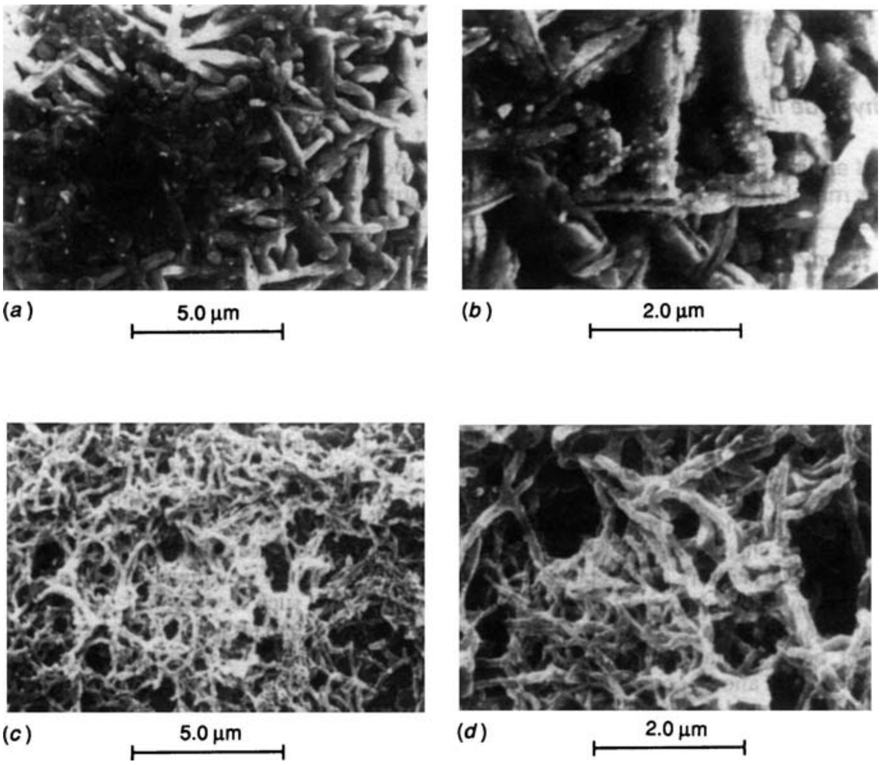

Fig. 2 SEM images of PANI samples obtained by; (*a*), (*b*) interfacial polymerization and (*c*), (*d*) conventional electropotential cycling, at two different magnifications. In each case, substrate was a 1 cm^2 conducting ITO glass plate.

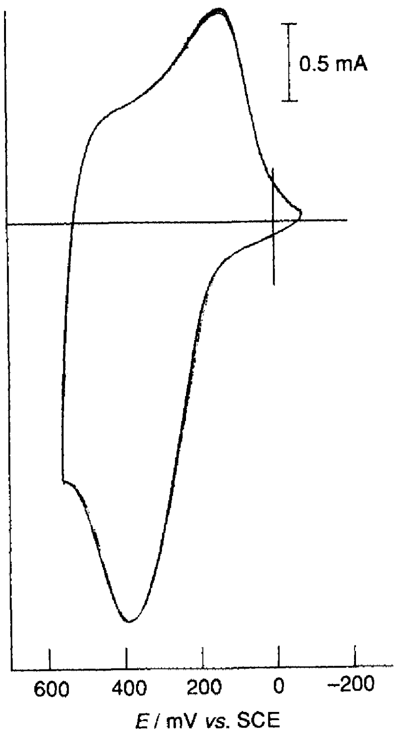

Fig. 3 Characteristic cyclic voltammogram of interfacial PANI film where the potential was varied between −50 and 550 mV at a scan rate of 10 mV s^{-1}

work will be required to evaluate their performance as permselective membranes for gas or ion separation applications. Furthermore, as such membranes must be flexible and yet sturdy free-standing films, efforts must be directed towards improving their mechanical integrity.

This research was sponsored by the Swiss Federal Office of Eduction and Science (BBW). The constant interest and support of Professor Michael Grätzel is also noted.

Received, 21st September, 1993; Com. 3/05681C

References

1 M. Fabrizio, F. Furlanetto, G. Mengoli, M. M. Musiani and F. Paolucci, *J. Electroanal. Chem.*, 1992, **323**, 197.
2 W. Liang and C. R. Martin, *Chem. Mater.*, 1991, **3**, 390.
3 M. R. Anderson, B. R. Mattes, H. Reiss and R. B. Kaner, *Science*, 1991, **252**, 1412.
4 A. Pron, F. Genoud, C. Menardo and M. Nechtschein, *Synth. Met.*, 1988, **24**, 193.
5 A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, 1980, **111**, 397.
6 M. Aizawa, L. Wang, H. Shinohara and Y. Ikariyama, *J. Biotechnol*, 1990, **14**, 301.
7 K. Uvdal, M. Lödlund, P. Dannetun, L. Bertilsson, S. Stafström, W. R. Salanek, A. G. MacDiarmid, A. Ray, M. Scherr, T. Hjertberg and A. J. Epstein, *Synth. Met.*, 1989, **29**, E451.
8 L. M. Goldenberg, S. Aeiyach and P. C. Lacaze, *J. Electroanal. Chem.*, 1992, **327**, 173.
9 T. Shimidzu, A. Ohtani, T. Iyoda and K. Honda, *J. Chem. Soc., Chem. Commun.*, 1986, 1414.
10 C. G. J. Koopal, B. Eijsma and R. J. M. Nolte, *Synth. Met.*, 1993, **57**, 3689.
11 C. Mailhé-Randolph and J. Desilvestro, *J. Electroanal. Chem.*, 1989, **262**, 289.
12 J. C. Michaelson, A. J. McEvoy and N. Kuramoto, *React. Polym.*, 1992, **17**, 197.
13 J. C. Michaelson, A. J. McEvoy and N. Kuramoto, *J. Electroanal. Chem.*, 1990, **287**, 191.
14 Y. Wei, G.-W. Jang, K. F. Hsueh, R. Hariharan, S. A. Patel, C.-C. Chan and C. Whitecar, *Polym. Mater. Sci. Eng.*, 1989, **61**, 905.
15 J. Desilvestro and W. Scheifele, *J. Mater. Chem.*, 1993, **3**, 263.
16 C. Mailhé-Randolph and A. J. McEvoy, *Ber. Bunsenges. Phys. Chem.*, 1989, **93**, 905.