Electrochemical Dissolution and Redeposition of Electropolymerized Polyindole Film

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An electropolymerized polyindole film was solubilized into a dichloromethane solution by its electrochemical reduction, and the electrochemical reoxidation of the soluble species produced the film again on the electrode surface. These dissolution and redeposition behavior were investigated by using cyclic voltammetry, UV–vis, NMR, FT-IR, and MALDI-TOFMS measurements.

Electropolymerized conducting polymer films have been the subject of intense research due to their fundamental interest and large variety of applications.[1] However, conventional electropolymerized films exhibit a negligible solubility in any solvent and non-fusibility in a temperature range below the decomposition temperature, making it difficult to process them. If we control their dissolution into a solution, their partial etching can be made possible, leading to the preparation of patterned conducting polymer films, and therefore, a contribution to digital fabrication technology.[2] Additionally, if the redeposition process is also feasible, information displays based on the dissolution (erasing) and redeposition (writing) may be constructed. However, as far as we know, no such material and system have been reported. In this letter, we describe the first finding of the electrochemical dissolution and redeposition of a conducting polymer film.

We have chosen polyindole (PInd) as the conducting polymer material since PInd and its derivatives are regarded as intriguing and promising materials with possible applications in electrochromic displays,[3] Schottky diode,[4] secondary batteries,[5] anticorrosion coatings,[6] etc. PInd films were prepared on an indium-tin-oxide-coated glass (ITO) or a Pt plate by the electrooxidation of indole (10 mM) in dichloromethane containing tetrabutylammonium perchlorate (TBAP, 0.1 M) at +1.2 V vs. a saturated calomel electrode (SCE) in a two-compartment-type cell equipped with a Pt plate cathode under a nitrogen atmosphere, the typical amount of electricity passed through the electrode, Q, being $500\,\mathrm{mC\,cm^{-2}}$.[7]

The repeated cyclic voltammograms of the PInd film measured in a dichloromethane/TBAP (0.1 M) system in the potential range of −1.3 to +0.6 V vs. SCE showed anomalous voltammetric responses. The first potential sweep exhibited reduction waves at ca. 0 and −0.9 V.[7] The former wave can be assigned to the dedoping of $\mathrm{ClO_4}^-$ in the PInd film.[8] The latter wave was accompanied by the dissolution of the film in the solution and the color of the solution changed from colorless to green. As a result of this dissolution of the film, no current was observed after the second redox cycling. Additional finding is the redeposition behavior of the soluble species. The sample solution of the soluble species was prepared by the electroreductive dissolutions of 6 fresh samples of the PInd films in a dichloromethane/TBAP (0.1 M) system followed by the concentration of the solution to one-sixth of its original volume. The soluble species exhibited steep current rise at ca. +1.2 V during the potential sweep toward the anodic direction which was accompanied by the formation of a film on the ITO electrode. Figure 1 shows the spectroscopic demonstration of the above electrochemical behavior of the PInd film on the ITO. The UV–vis absorption exhibited by the as-grown PInd film [curve (a)] completely disappeared on the controlled-potential electroreduction of the film at −1.2 V [curve (b)], demonstrating the complete dissolution of the film by its electroreduction. The reoxidation of the resultant soluble species [curve (c)] produced a film again on the ITO which showed no solubility in $\mathrm{CH_2Cl_2}$. Its spectrum [curve (d)] is slightly different in shape from that of the as-grown PInd film [curve (a)], being most likely due to the difference in the film morphology.[7]

MALDI-TOF mass analyses were performed to find out the origin of the dissolution and redeposition behavior. No matrix

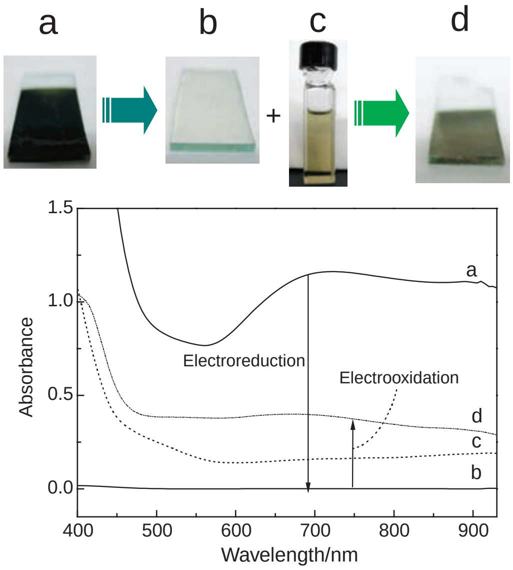

Figure 1. UV–vis absorption spectra of the PInd film on the ITO (prepared at $Q = 500\,\mathrm{mC\,cm^{-2}}$) (a), the ITO substrate electrode obtained after the electroreduction of the PInd film at −1.2 V ($Q = 60\,\mathrm{mC\,cm^{-2}}$) (b), the film prepared by the electrooxidation of the soluble species (+1.4 V, $100\,\mathrm{mC\,cm^{-2}}$) generated during the electro-reduction (d), and the soluble species (c). Solution (c) was obtained by electroreduction ($Q = 60\,\mathrm{mC\,cm^{-2}}$) of the PInd film ($15 \times 20\,\mathrm{mm^2}$). Film (d) was prepared using a solution obtained by electroreduction (−1.2 V, $Q = 360\,\mathrm{mC\,cm^{-2}}$) of 6 fresh samples of the PInd film.

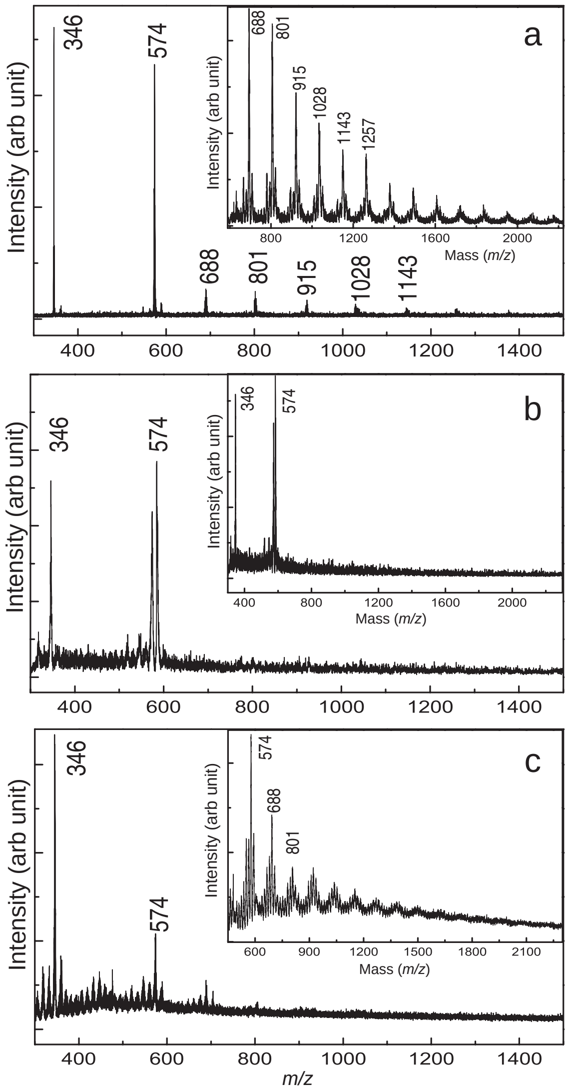

Figure 2. MALDI-TOFMS spectra of the PInd film (a), the soluble species (b), and the redeposited film (c). The insets show the spectra in which the abscissa is enlarged.

was used. Figure 2 shows the mass spectra for the PInd film (a), the soluble species (b), and the redeposited film (c). The largest peak situated at *m/z* 346 in the spectrum (a) is consistent with the cyclic indole trimer[9] (see Figure 3a). The other signals were observed at *m/z* 574, 688, 801, 915, 1028, 1143, and 1257 with intervals of 113–115, which is the molecular weight of repeating unit.

These results agrees with the view that the PInd consists of cyclic indole trimer and linear oligomers of larger size (pentamer to undecamer) and that the linear oligomers are in the intermediate states between diimine (Figure 3b) and enediamine (Figure 3c). The contribution of the diimine form to the formation of the PInd film is consistent with the electropolymerization model proposed by Talbi et al.[10] On the other hand, only two signals are exhibited by the soluble species at *m/z* 346 and 574 (Figure 2b), which can be assigned to the cyclic indole trimer and the pentamer, respectively. This finding indicates that higher molar mass oligomers (6–11 repetitive units) in the PInd film are cleaved and rearranged into the pentamer and the cyclic trimer by their electroreduction. In addition, the easy dissolution of these species in dichloromethane implies that these species are trapped in the insoluble matrix of higher molar mass oligomers (hexamer to undecamer) in the initial PInd film. A comparison of the ^{1}H NMR spectrum[7] of the soluble species with the reported spectrum for the PInd[11] confirmed that no decomposition of the indole unit occurs during the electroreductive dissolution. The mass spectra for the redeposited film (Figure 2c) show the signals corresponding to higher molar mass oligomers (hexamer to undecamer) besides the pentamer and the cyclic trimer. This finding indicates that the electrooxidation of the soluble species, i.e., the indole pentamer and/or the cyclic trimer, produces the insoluble oligomers of larger size to form the film on the electrode surface. A comparison of the FT-IR spectrum of the redeposited film[7] with that of the initial PInd film confirmed again that no destruction of the indole unit occurs during the electrooxidative redeposition.

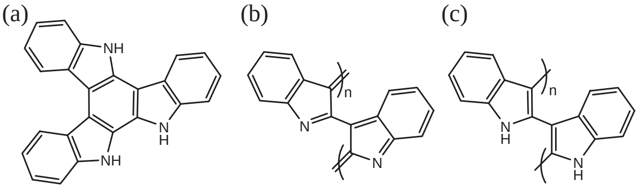

Figure 3. Structures of the cyclic indole trimer (a), and diimine (b) and enediamine moieties (c) in the PInd film.

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