

Conducting Polymer-coated Electrode as a Reference/Counter Electrode in an Organic Phase and Its Application to a Two-electrode Type Thin-layer Cell for Voltammetry at the Liquid | Liquid Interface

Yumi YOSHIDA,^{*,**†} Satoshi YAMAGUCHI,^{*} and Kohji MAEDA^{*}

^{*}*Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606-8585, Japan*

^{**}*PRESTO, Japan Science and Technology Agency, Sanbancho bldg., 5-Sanbancho, Chiyoda, Tokyo 102-0075, Japan*

An indium tin oxide glass electrode coated with poly(3,4-ethylenedioxythiophene), PEDOT, PEDOT-ITOE, was proposed as an electrode workable as both a reference electrode and a counter one, a reference/counter electrode, in an organic phase and applied to a thin-layer cell of a two-electrode system for voltammetry at the liquid | liquid interface. By oxidizing the PEDOT film by 50% and doping a supporting electrolyte anion in an organic phase into the PEDOT film, a suitable depolarization was realized at the PEDOT | organic phase interface. The partially oxidized PEDOT-ITOE showed a Nernstian response to the supporting electrolyte anion concentration in the organic phase. The electrode potential was stable within ± 3 mV for 12 h, and showed a consistent value among the PEDOT-ITOE prepared under the same procedure (the error range was about 7 mV, $n = 8$).

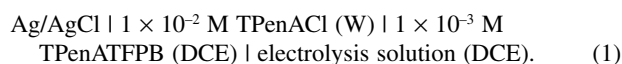
(Received December 25, 2009; Accepted January 15, 2010; Published February 10, 2010)

A conducting polymer has been indicated as a good ion-electron mediator,^{1,2} and applied to an all-solid-state ion-selective electrode, as reported in many papers.¹⁻⁸ Conducting polymer is less soluble in an organic phase, and its redox reaction is accompanied by doping-dedoping an ion. If a supporting electrolyte ion in an organic phase is doped into the polymer, the conducting polymer-coated electrode can work as a good counter electrode in the organic phase, because the reaction product of the electrode does not contaminate the organic phase. Moreover, the electrode potential in the organic phase is determined by the dopant ion, which can exchange between the polymer and the organic phase.⁹ Hence, the conducting polymer-coated electrode is applicable as a reference electrode in the organic phase. However, a conducting polymer-coated electrode has been employed as neither a reference electrode nor a counter one in voltammetry at a liquid | liquid interface. Only Amemiya's group has reported voltammetric measurements by employing a poly(3-octylthiophene)- or poly(3,4-ethylenedioxythiophene)-modified electrode covered with a PVC membrane.³⁻⁵ They applied these electrodes to a stripping analysis of heparin,³ perchlorate⁴ and hexafluoroarsenate.⁵ In these reports, the reproducibility of the electrode potential value was low.³ The interfacial potential at the conducting polymer | PVC membrane interface was not measured directly, and depolarization at the interface was unclear.

In the present work, we propose an indium tin oxide glass electrode coated with partially oxidized poly(3,4-ethylenedioxythiophene), PEDOT, PEDOT-ITOE, which is an electrode workable as both a reference electrode and a counter one, a reference/counter electrode, in an organic phase, and applied to a two-electrode thin layer cell for voltammetry at the liquid | liquid interface. Depolarization at the interface between PEDOT and

the organic phase was achieved by doping an hydrophobic anion of the supporting electrolyte, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, TFPB⁻, into the PEDOT film and directly examined by voltammetric measurements. PEDOT has a lower oxidation potential than other thiophene derivatives, and its oxidized and reduced forms are chemically stable.⁸ In addition, PEDOT was less soluble in an organic solvent than other thiophene derivative polymers, such as poly(alkylthiophene) or poly(bithiophene) when TFPB⁻ was doped in the polymer.

The PEDOT-ITOE was made by the electrodeposition of 3,4-ethylenedioxythiophene, EDOT, on a ITO glass electrode. Electrodeposition was carried out by immersing the ITO glass electrode in 1,2-dichloroethane, DCE, containing 0.1 M ($M = \text{mol dm}^{-3}$) EDOT and a supporting electrolyte of 0.1 M bis(triphenylphosphoranylidene)ammonium perchlorate, BTTPA, and by electrolyzing at an electrode potential, E , of 2.0 V vs. the tetrapentylammonium ion selective electrode, TPenA-ISE, for 20 s under an argon condition. Here, TPenA-ISE has the following composition:



The electrolytic cell for electrodeposition was a three-electrode system with a counter electrode of Pt mesh and a reference

Abbreviations

PEDOT: poly(3,4-ethylenedioxythiophene)
EDOT: 3,4-ethylenedioxythiophene
ITO: indium tin oxide
TFPB: tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate
DCE: 1,2-dichloroethane
BTTPA: bis(triphenylphosphoranylidene)ammonium
TPenA: tetrapentylammonium
TEA: tetraethylammonium

[†] To whom correspondence should be addressed.
E-mail: yyoshida@kit.jp

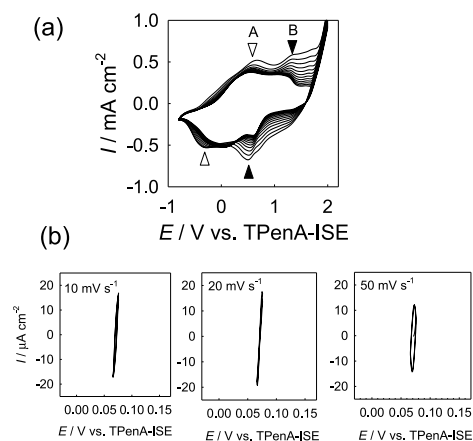


Fig. 1 Redox reaction of PEDOT film with doping and dedoping of TFPB⁻ in DCE containing 0.1 M BTTPATFPB. (a) Multiscan cyclic voltammogram of the PEDOT-ITOE in a milli ampere scale, (b) cyclic voltammograms of partially oxidized PEDOT-ITOE in a micro ampere scale.

electrode of TPenA-ISE. In the electrodeposition, the electrolysis solution was stirred with a magnetic stirrer. DCE used in all experimental procedures were purified by washing with distilled water three times and by drying with molecular sieves.

After electrodeposition of the PEDOT, the deposited PEDOT film was completely reduced at -0.1 V for 60 s in order to dedope ClO_4^- from the PEDOT film. The doping of TFPB⁻ into the PEDOT was accomplished by repeating oxidation and reduction of the PEDOT in DCE containing 0.1 M BTTPATFPB. Figure 1(a) shows a multiscan cyclic voltammogram of the PEDOT redox reaction with doping and dedoping of TFPB⁻. At the first scan, there were mainly two large waves with positive and negative current peaks (waves A and B in Fig. 1(a) in the voltammogram. A remarkable color change of the PEDOT was observed around 0.1 V of wave A. When cyclic potential scans were repeated, wave B decreased, and small blue fragments were generated from the PEDOT film. Wave B and the small blue fragments are inferred to be due to the short chain fraction in PEDOT, whose oxidized form is more soluble and has a more positive oxidation potential than the long-chain fraction. In order to remove the short-chain fraction of PEDOT, cyclic potential scans in the range of -0.8 and 1.5 V were repeated fifteen times at potential scan rate of 0.1 V s⁻¹. The surface area of ITO covered with the PEDOT film was approximately 1 cm². The solubility of PEDOT film in DCE was low, even if TFPB⁻ was doped in the film. The maximum redox capacity was chronocoulometrically determined to be $3.5 - 4.5$ mC cm⁻² by completely oxidizing at 0.6 V, and reducing all of the oxidized form at -0.4 V. The partially oxidized PEDOT-ITOE was employed as a reference/counter electrode in following electrochemical measurements. The proportion of oxidized PEDOT was chronocoulometrically adjusted to be 50% by partially reducing at -0.4 V after completely oxidizing at 0.6 V. The obtained PEDOT-ITOE was held for 12 h in DCE containing 10^{-3} M BTTPATFPB.

The E of the partially oxidized PEDOT-ITOE was measured with respect to TPenA-ISE potentiometrically by immersing in DCE containing various concentrations of BTTPATFPB. The E showed a constant value within ± 3 mV for 12 h. With a stepwise increase of the TFPB⁻ concentration in DCE, E showed a Nernstian response (slope of 54.5 mV/decade) in the TFPB⁻ concentration range of $10^{-6} - 10^{-3}$ M, as illustrated in Fig. 2.

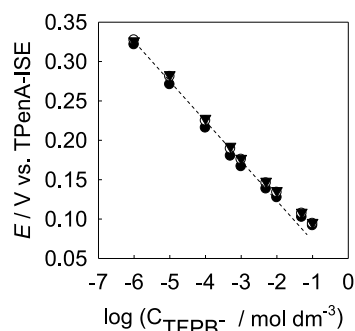
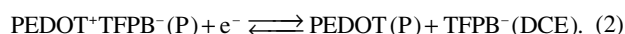


Fig. 2 Potential responses of the PEDOT-ITOE to the concentration of TFPB⁻ in DCE containing BTTPATFPB. Potentiometry was carried out from low- to high-concentration of TFPB⁻, and repeated three times by using the same PEDOT-ITOE: first (●), second (○), third (▲).

The redox reaction occurring at the PEDOT-ITOE is expressed as⁹



Here, P and DCE in parentheses indicate the polymer phase and the DCE phase, respectively. The E of the partially oxidized PEDOT-ITOE depends on the activity of TFPB⁻ in DCE and the ratio of PEDOT (P) and PEDOT⁺TFPB⁻ (P),

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{\text{PEDOT}^+\text{TFPB}^-(\text{P})}}{a_{\text{PEDOT}(\text{P})}} - \frac{RT}{F} \ln a_{\text{TFPB}^-(\text{DCE})}. \quad (3)$$

The results given in Fig. 2 demonstrate that the E of PEDOT-ITOE can be explained by Eq. (3). Potentiometric measurements were repeated three times by using the same PEDOT-ITOE. After the first series of potentiometric measurements, the PEDOT-ITOE was washed with pure DCE and used in the next series of measurements without any conditioning. As shown in Fig. 2, the E reproduced same value within ± 6 mV in repeated measurements. Eight electrodes were made by the same procedure. The E of these electrodes showed a consistent potential value, e.g., 0.162 V (95% confidence interval 0.169 to 0.155 V) in DCE containing 10^{-3} M TFPB⁻. Therefore, the PEDOT-ITOE is workable as a reference electrode in DCE. High reproducibility of the electrode potential value should be noted as being a large advantage in studies of the conducting polymer-coated electrode because the electrode potential value has been unstable, and not reproduced in previous reports.³⁻⁵ In the present work, the following points contributed to a reproducible electrode potential: (1) using a conducting polymer of low oxidation potential, such as PEDOT, (2) controlling the ratio of the oxidized form to the reduced one of the PEDOT (50%). Especially, by purification of the DCE solvent, the latter was able to be easy and stable, while the reduced form was completely oxidized without purification of the DCE solvent.

Figure 1(b) indicates voltammograms of the partially oxidized PEDOT-ITOE in DCE containing 0.1 M BTTPATFPB. Voltammograms sharply cross the zero current axis, indicating that ideal depolarization was achieved at the PEDOT | DCE interface. The E at zero current, $E_{I=0}$, was almost 0.075 V, which approximates to the midpoint potential of wave A in Fig. 1(a). With an increase of potential scan rate (≥ 50 mV s⁻¹), $E_{I=0}$ of the positive potential scan was not same as that of the negative-potential scan. The difference of $E_{I=0}$ is due to the kinetics of the PEDOT redox reaction. Therefore, at a potential

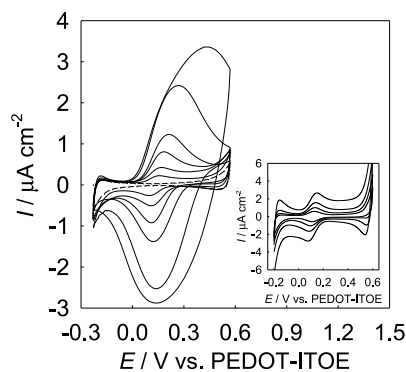


Fig. 3 Cyclic voltammograms at a liquid | liquid interface measured using a thin-layer cell in the absence (dash line) and presence (full line) of 1, 2, 5, 10, 20 and 50 $\times 10^{-5}$ M TEA in W. Scan rate is 20 mV s^{-1} . The supporting electrolyte was 0.01 M NaCl in W and 10^{-3} M BTTPATFPB in DCE. Inset: Scan-rate dependence (5, 10, 20, and 50 mV s^{-1}) of cyclic voltammograms in the presence of 2×10^{-5} M TEA.

scan rate slower than 50 mV s^{-1} , the PEDOT-ITOE reversibly worked even as a counter electrode. The influence of the current flow on E of the PEDOT-ITOE was also measured by constant-current chronopotentiometry (10 nA cm^{-2}). When a total charge of 20 $\mu\text{C cm}^{-2}$ flowed in the PEDOT-ITOE, potential shift of 5 – 15 mV appeared. Accordingly, the PEDOT-ITOE is workable as a reference/counter electrode under the following condition: the total charge amount of the current flow is $<20 \mu\text{C cm}^{-2}$ and the potential scan rate is $<50 \text{mV s}^{-1}$.

A thin-layer cell for voltammetry at the liquid | liquid interface was prepared by employing PEDOT-ITOE (Fig. S1 of Supporting Information). The cell was the two-electrode system. The thin W, which was filled in the internal square space (0.77cm^2) of a Teflon frame (thickness of 50 μm), was placed on a thin DCE layer, which was stabilized in the pores of a hydrophobic polytetrafluoroethylene membrane filter (Advantec, T300A, thickness of 75 μm), and thin W and DCE layers were put between an Ag/AgCl plate electrode and the PEDOT-ITOE. Here, the Ag/AgCl plate electrode and the PEDOT-ITOE work as reference/counter electrodes in W and DCE, respectively. The W | DCE interface was formed at the W side surface of the membrane filter with DCE, and the area of the W | DCE interface was controlled by the inner space of the Teflon frame.

Figure 3 shows cyclic voltammograms at the liquid | liquid interface obtained using the thin-layers cell. E was applied as the potential of an Ag/AgCl electrode with respect to the PEDOT-ITOE. In the absence of an objective ion, there was no peak due to the transfer of residual ClO_4^- in the PEDOT film, indicating that the dopant anion in PEDOT film was TFPB $^-$. The potential window was almost 0.8 V, which was the same as that measured by a conventional cell for voltammetry at the liquid | liquid interface. In the presence of the tetraethylammonium cation, TEA^+ , in W, positive and negative peaks for the transfer of TEA^+ were observed in the voltammogram. These peak currents were proportional to the TEA^+ concentration of 1×10^{-5} – 10×10^{-5} M. When the concentration of TEA^+ was increased to more than 2×10^{-4} M, the shape of the cyclic voltammogram became broad, and the peak potential difference increased (120 mV at 2×10^{-4} M, 300 mV at 5×10^{-4} M). These results are attributable to a potential shift of PEDOT-ITOE by current flow, because the total charge of the current flow

under high-concentration condition (e.g., almost 45 $\mu\text{C cm}^{-2}$ at 2×10^{-4} M) exceeded 20 $\mu\text{C cm}^{-2}$, which is the threshold for a workable reference/counter electrode. Thus, the thin-layer cell is usable for a low amount detection, such as $<10^{-4}$ M TEA^+ .

Inset of Fig. 3 shows the scan rate dependence of a voltammogram measured in the presence of 2×10^{-5} M TEA^+ in W. At a faster scan rate (20 to 50 mV s^{-1}), positive and negative peak currents were proportional to the square root of the scan rate. However, at a slower scan rate, of less than 10 mV s^{-1} , these peak currents were proportional not to the square root of the scan rate, but to the scan rate. With a decrease in the scan rate from 50 to 5 mV s^{-1} , the peak potential difference decreased from 62 to 10 mV. These results are capable of the following interpretation: At a faster scan rate, the transfer of TEA^+ from W to DCE was controlled by the diffusion of TEA^+ in W. However, at a slower scan rate, the thickness of the diffusion layer became the same as that of W, and most amount of TEA^+ in W transferred to DCE. Therefore, a voltammogram measured at 5 mV s^{-1} was close to a bell shape, symmetrical about a zero current axis. In fact, the total charge of the positive and the negative peaks at 5 mV s^{-1} were 8.8 and 9.2 μC , respectively, indicating that almost 80% of TEA^+ in the presence of W transferred to DCE.

In the present work, we showed that PEDOT-ITOE was a suitable electrode as a reference/counter electrode in the organic phase, and applicable to two-electrode system of voltammetry for ion transfer at the liquid | liquid interface. Advantage of PEDOT-ITOE is that the ionic product of the electrode reaction does not inhibit voltammetric measurement at the liquid | liquid interface. A PEDOT-ITOE can be synthesized easily, and has a simple configuration, which makes a micro flow electrochemical cell with a thin aqueous and organic layer technologically-feasible.

Acknowledgements

This study was supported by PRESTO from the Japan Science and Technology Agency and by a Grant-in-Aid for Scientific Research (No. 19750060) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information

The construction of a thin-layer cell and the scheme of a two-electrode type thin-layer cell are shown as (a) and (b) in Fig. S1. Figure S1 is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. N. Oyama and T. Hirokawa, *Anal. Chem.*, **1987**, *59*, 258.
2. N. Oyama, T. Ohsaka, F. Yoshimura, M. Mizunuma, S. Yamaguchi, N. Ushizawa, and T. Shimomura, *J. Macromol. Sci. Chem.*, **1988**, *A25*, 1463.
3. J. Guo and S. Amemiya, *Anal. Chem.*, **2006**, *78*, 6893.
4. Y. Kim and A. Amemiya, *Anal. Chem.*, **2008**, *80*, 6056.
5. Y. Kim, P. Rodgers, R. Ishimatsu, and S. Amemiya, *Anal. Chem.*, **2009**, *81*, 7262.
6. A. Cadogan, Z. Gao, A. Lewenstam, and A. Ivaska, *Anal. Chem.*, **1992**, *64*, 2496.
7. J. Bobacka, A. Ivaska, and A. Lewenstam, *Electroanalysis*, **2003**, *15*, 366.
8. J. Bobacka, A. Ivaska, and A. Lewenstam, *Chem. Rev.*, **2008**, *108*, 329.
9. J. Ghilane, P. Hapiot, and A. J. Bard, *Anal. Chem.*, **2006**, *78*, 6868.