

A Novel Polyviologen Electrode Fabricated by Electrochemical Crosslinking

Hsien-Chang Chang, Masatoshi Osawa, Tomokazu Matsue* and Isamu Uchida

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Sendai 980, Japan

A polyviologen modified electrode was fabricated by electrochemical crosslinking of a viologen oligomer in the presence of glutaraldehyde; the electrode showed excellent capabilities for preconcentration of anionic redox compounds and for adsorption of diaphorase.

Redox polymer-modified electrodes¹ are currently the subject of extensive investigation. These electrodes are, in general, fabricated by dip- or spin-coating of redox polymers dissolved in appropriate solvents followed by drying. Recently, electropolymerization has been used for the modification. Since the polymerization proceeds only at the electrode surfaces, it is particularly suitable for the modification of area-defined electrodes such as micro and array electrodes.^{2,3} The polymerization is usually conducted in non-aqueous media, which sometimes causes problems in modifying hydrophilic redox moieties. Here, we present a novel method for preparation of polyviologen (PV) modified electrodes based on the electrochemical crosslinking reaction of a water-soluble viologen oligomer. This modified electrode possesses a satisfactory stability in successive redox cycles.

The viologen (= 4,4'-bipyridinium) oligomer⁴ **1**, and glutaraldehyde (GA) were dissolved in a deaerated 50 mmol dm⁻³ 2-aminoethanol (AEA) or tris(hydroxymethyl)aminoethane (Tris) aqueous solution (pH 7.0); concentrations of **1** and GA were 0.25% w/v and 0.75% v/v, respectively. The PV modified electrode was prepared by controlled potential electrolysis at -1.0 V vs. standard calomel electrode (SCE). A PV membrane (thickness, ca. 0.1 μm) was formed on the glassy carbon disk electrode (diameter, 3 mm), when 7.1 × 10⁻² C cm⁻² of charge was passed. We have investigated the electrolysis under a variety of conditions and found the following. (i) The presence of GA in solution is essential. (ii) The pH of the solution should be in the 6-8 range. (iii) PV membranes are formed in the presence of amino compounds having alcoholic or carboxylic group, such as AEA, Tris, or glycine. (iv) The electrolysis potential should correspond to the second reduction of **1**.

ESCA of the PV membrane showed two nitrogen 1s peaks at 402.3 and 400.1 eV. The peak at 402.3 eV is attributed to pyridinium nitrogen and the peak at 400.1 eV to nitrogen

originating from the amino compound added to the polymerization solution. FTIR spectroscopy demonstrated the presence of pyridinium and C-O-C units; however, peaks for N-H, C=O and O-H were not observed. GA is known to form an oligomer **2** by aldol condensation. From the experimental and spectroscopic results, we speculate that reaction of the oligomer with AEA stabilizes the oligomer, as shown in Scheme 1. The unreacted aldehyde or imine groups would react with the enamine form of the two-electron reduced viologen unit, resulting in crosslinking to form an insoluble PV membrane at the electrode surface.

The cyclic voltammogram (CV) for the first redox wave of the PV membrane at the electrode surface is extremely stable (Fig. 1a). No obvious decrease in the peak height was observed after 100 successive scans. The peak current is proportional to the scan rate for scan rates of less than 100 mV s⁻¹. The total charge for the reduction peak indicated that the surface concentration of the viologen unit was 1.3 × 10⁻⁸ mol cm⁻² (volumetric concentration, 1.3 mol dm⁻³). The apparent diffusion coefficient was determined by the potential step method and found to be ca. 5.5 × 10⁻⁹ cm² s⁻¹, which is somewhat larger than that for a viologen-based polysiloxane.³

This PV modified electrode possesses an excellent preconcentration capability for anions, such as Fe(CN)₆⁴⁻ and Mo(CN)₈⁴⁻. The CV, observed in the presence of 0.05 mmol dm⁻³ Fe(CN)₆⁴⁻ in solution, shows a surface redox wave for preconcentrated Fe(CN)₆⁴⁻³⁻ at ca. 0.15 V (Fig. 1b). The peak height increases with the concentration of

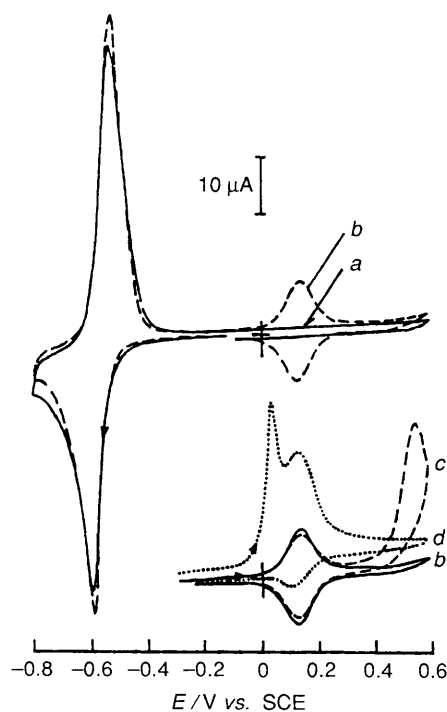
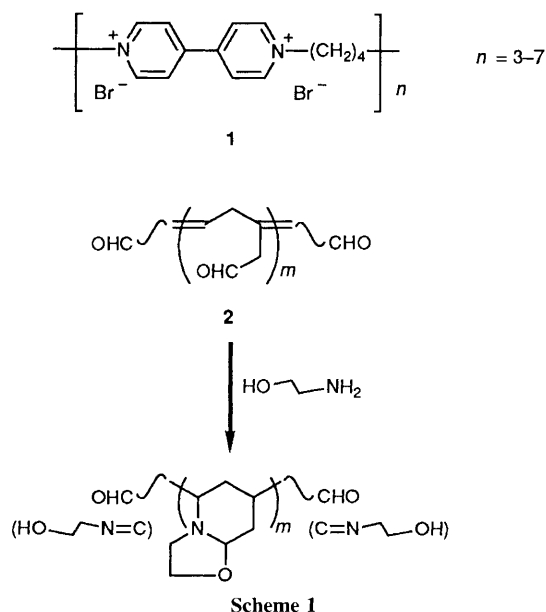


Fig. 1 Cyclic voltammograms at a PV electrode. (a): no addition. (b): with 15 μmol dm⁻³ K₄Fe(CN)₆ in solution. (c): With 15 μmol dm⁻³ K₄Fe(CN)₆ and 1 mmol dm⁻³ NADH in solution. (d): at diaphorase-adsorbed PV electrode, other conditions as (c).

$\text{Fe}(\text{CN})_6^{4-}$ in solution, but tends to saturate when the concentration is $>0.02 \text{ mol dm}^{-3}$. The apparent partition coefficient between the membrane and solution is more than 10^5 . The saturated concentration for $\text{Fe}(\text{CN})_6^{4-}$ in the membrane was found to be 1.2 mol dm^{-3} . This unusually high loading level compared to the concentration of the viologen unit (1.3 mol dm^{-3}) suggests that protonated amine in the crosslinking part contributes to the preconcentration capability of the membrane.

We found that the PV membrane strongly absorbs diaphorase (Dp, EC 1.6.99.—, from *Bacillus stearthermophilus*), a flavoenzyme catalysing the oxidation of NADH by electron acceptors.^{5,6} Therefore, we have investigated the electrocatalytic oxidation of NADH at the PV modified electrode with adsorbed Dp and preconcentrated $\text{Fe}(\text{CN})_6^{4-}$ as the electron-transfer mediator. The PV modified electrode with adsorbed Dp was prepared by soaking it in Dp solution for 30 min followed by ultrasonic cleaning. Without adsorbed Dp, the CV shows a direct oxidation peak for NADH at ca. 0.6 V, in addition to the peaks for preconcentrated $\text{Fe}(\text{CN})_6^{4-}$ (Fig. 1c). The adsorption of Dp on the PV electrode results in a drastic change in the CV behaviour (Fig. 1d) i.e., (i) an increase in the oxidation peak for $\text{Fe}(\text{CN})_6^{4-}$, (ii) appearance

of a sharp prepeak, and (iii) disappearance of the direct oxidation peak for NADH. The above phenomena indicate that the adsorbed Dp effectively catalyses the electron-transfer from NADH^{5,6} to the electrogenerated $\text{Fe}(\text{CN})_6^{3-}$ in the PV film. The CV behaviour showed no obvious change after repeated measurements for at least one week.

We are indebted to Dr K. Ogasawara for useful discussions.

Received, 14th January 1991; Com. 1/00188D

References

- 1 R. W. Murray, in *Electroanalytical Chemistry*, ed. A. J. Bard, Dekker, New York and Basel, vol. 13, 1984, pp. 191–368.
- 2 L. Coche and J.-C. Moutet, *J. Electroanal. Chem.*, 1987, **224**, 111.
- 3 C.-F. Shu and M. S. Wrighton, in *Electrochemical Surface Science*, ed. M. P. Soriaga, ACS Symposium Series 378, American Chemical Society, Washington DC, 1988, ch. 28.
- 4 A. Factor and G. E. Heinsohn, *Polymer Lett.*, 1971, **9**, 289.
- 5 T. Matsue, H. Yamada, H.-C. Chang, I. Uchida, K. Nagata and K. Tomita, *Biochim. Biophys. Acta*, 1990, **1038**, 29.
- 6 T. Matsue, H. Yamada, H.-C. Chang and I. Uchida, *Bioelectrochem. Bioenerg.*, 1990, **24**, 347.