

## Unique Nafion-Os(bpy)<sub>3</sub><sup>2+</sup> Modified Electrodes

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**Abstract:** It was newly found that the electrodes modified by applying ethanol solutions of Nafion containing Os(bpy)<sub>3</sub><sup>2+</sup> onto the substrate electrode (the one-step method) show two pairs of stable redox peaks of Os(bpy)<sub>3</sub><sup>2+/3+</sup> on cyclic voltammogram near 0.54V and 0.25V, respectively. These modified electrodes can effectively mediate and catalyze the first and second steps of nitrite reduction in acidic media in the potential region 0-0.9V when the loading in the coating ( $X = \Gamma(\text{Os}^{2+}) / \Gamma(\text{SO}_3^-)$ ) and pH in solution are below 0.17 and 4, respectively. When X is between 0.33 and 0.17, only the current peak near 0.54V appears regardless of solution pH and only the first step of NO<sub>2</sub><sup>-</sup> reduction is catalyzed. Thus the modified electrode provides a very useful flexibility that one can control the reaction pathway and catalytic activity of nitrite reduction by simply changing the concentration of the mediator in the coating.

**Keywords:** Chemically modified electrodes, nitrite reduction, electro-catalysis, sensors.

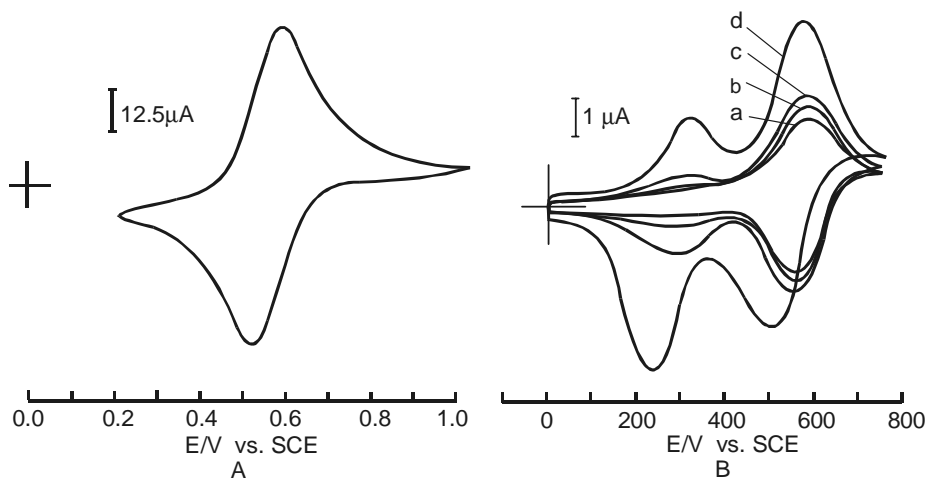
The electrodes modified with a Nafion film containing redox centers (mediators) form an attractive group of chemically modified electrodes because of their flexibility in electrocatalysis and other interesting properties. In most cases reported in the literature, a recast Nafion film was first coated on the substrate electrode and the electrode was then dipped in a solution of the mediator to be studied (the two step method). Anson and coworkers<sup>1,2</sup> reported striking effects of the mediator concentration in the coating and the hydration extent of the coating before dipping on the cyclic voltammetry (CV) of the modified electrodes. They found that besides the pair of normal stable redox current peaks another pair of unstable redox current peaks might occur, depending on the loading level and the hydration condition. However, they did not report the catalytic properties of these modified electrodes. The modified electrode may also be prepared using one-step method, *i.e.*, by applying a Nafion solution containing the mediator to the substrate electrode to complete the modification in a single step. This communication reports a new finding that the one-step prepared Nafion-Os(bpy)<sub>3</sub><sup>2+</sup> electrodes show unique CV behaviors and high catalytic activity for nitrite reduction in acidic solutions, a valuable property for developing nitrite sensors badly needed in biological and environmental applications<sup>3</sup>. This work shows that it is possible to control the pathway of a catalyzed reaction by simply changing the mediator concentration in the modification layer.

The substrate electrode used in this work was a glassy carbon disk electrode of 4mm in diameter (GCDE). In one-step modification, a diluted Nafion 1100 (Aldrich)

solution (2.5%) containing controlled concentration of  $\text{Os}(\text{bpy})_3^{2+}$  was applied to the GCDE surface to form the modification film. Electrochemical measurements were conducted at  $25^\circ\text{C}$  and a saturated calomel electrode (SCE) was used as the reference electrode. All solutions were prepared with analytical reagents and doubly distilled water. Acidic solutions of  $\text{NaNO}_2$  were freshly prepared prior to use.

We here present two typical cases where the loading in the coating,  $X = \Gamma(\text{Os}^{2+}) / \Gamma(\text{SO}_3^-)$ , are 0.33 and 0.05, respectively. The case  $X=0.33$  corresponds to the highest stable (also called saturated) concentration of the mediator in Nafion. **Figure 1** shows their CV curves in 0.05 M  $\text{H}_2\text{SO}_4$ . For the case  $X=0.33$  (**Figure 1A**), only a single pair of  $\text{Os}(\text{bpy})_3^{2+/3+}$  redox peaks appeared near 0.54V in the potential region 0-0.9V and the CV was independent of pH in the region pH 1-7. In contrast, for the case  $X=0.05$  (**Figure 1B**), besides the pair of peaks seen in **Figure 1A**, a new pair of redox peaks grew up near 0.25 V with decreasing pH. The new redox current decayed with time till reaching a stable value that accounted for about 40% of its initial value. The conditions for the new redox current peaks to occur are roughly  $X \leq 0.17$  and  $\text{pH} \leq 4$ .

**Figure 1** Cyclic voltammograms of the modified electrodes in 0.05 M  $\text{H}_2\text{SO}_4$ ; scan rate  $100 \text{ MV s}^{-1}$ . A,  $X=0.33$ ,  $\Gamma_{\text{Os}}$ :  $7.5 \times 10^{-8} \text{ mol cm}^{-2}$ . B,  $X=0.05$ ,  $\Gamma_{\text{Os}}$ :  $2.25 \times 10^{-8} \text{ mol cm}^{-2}$ . a) pH=7, b) pH=4, c) pH=3, d) pH=1.

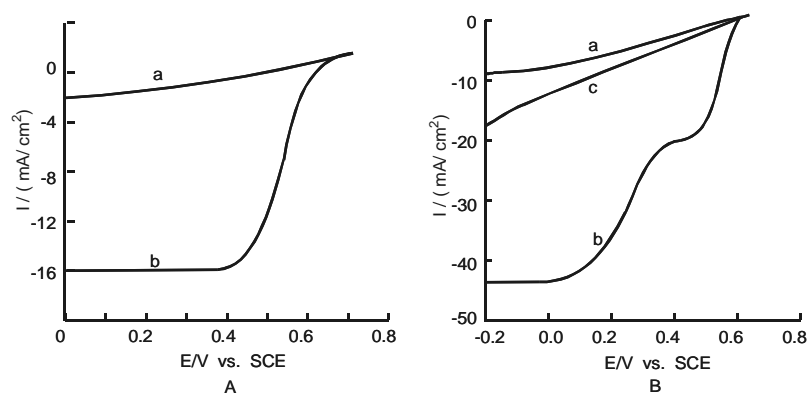


The catalytic activity of above mentioned two typical electrodes for nitrite reduction in acidic solutions also exhibited significant differences. **Figure 2** shows the polarization curves of nitrite reduction for  $X=0.33$  and  $X=0.05$ , respectively. The curves for bare electrodes are also shown for comparison.

It is generally thought<sup>4</sup> that the limiting current of nitrite reduction on bare glassy carbon electrode is controlled by a preceding chemical reaction to produce the electroactive species  $\text{NO}^+$  in acid solutions,  $\text{HNO}_2 + \text{H}^+ \rightleftharpoons \text{NO}^+ + \text{H}_2\text{O}$  (the chemical-electrochemical mechanism, CE). This made the limiting currents in **Figure 2** about two orders of magnitude lower than the diffusion limiting current for the bare GCDEs. (The difference between the currents in **Figure 2A** and **2B** for the bare GCDEs

is due to different roughness factors of the two GCDEs.) Besides, the charge transfer step at GCDE appeared to be highly irreversible. In the presence of the modification film, the reduction of nitrite was markedly enhanced. However, for the above mentioned two typical cases, the enhancements were quite different. For  $X=0.33$ , there is only a single current plateau in region 0.0-0.9V with a half-wave potential 0.54 V, about 0.3V more positive than that for the bare electrode, indicating much improved reversibility of the charge transfer step. The half-wave potential was close to the redox potential of Os(bpy)<sub>3</sub><sup>2+/3+</sup> (**Figure 1A**), implying a mediation mechanism  $\text{Os}(\text{bpy})_3^{2+} + \text{NO}^+ \rightarrow \text{NO} + \text{Os}(\text{bpy})_3^{3+}$ . Besides the catalysis by Os(bpy)<sub>3</sub><sup>2+</sup>, the Nafion film itself also showed some contribution to the current enhancement (curve c in **Figure 2B**) probably due to an enrichment of NO<sup>+</sup> in Nafion coating. The apparent partition coefficient of NO<sup>+</sup> (the ratio of NO<sup>+</sup> concentration in the coating to the NO<sub>2</sub><sup>-</sup> concentration in solution) measured by UV-VIS technology is 2.8<sup>5</sup>. The enriching mechanism has been proposed<sup>5</sup>.

**Figure 2** Steady state polarization curves for NO<sub>2</sub><sup>-</sup> reduction in 0.05 M H<sub>2</sub>SO<sub>4</sub> + 5 × 10<sup>-3</sup> M NaNO<sub>2</sub> at 500 rpm. A, (a) bare GCDE.; (b) the modified GCDE( $X=0.33$ ), Coating thickness 2 $\mu\text{m}$ ,  $\Gamma_{\text{Os}}$ : 7.5 × 10<sup>-8</sup> mol cm<sup>-2</sup>. B, (a) bare GCDE; (b) the modified GCDE ( $X=0.05$ ), coating thickness 4 $\mu\text{m}$ ,  $\Gamma_{\text{Os}}$ : 2.25 × 10<sup>-8</sup> mol cm<sup>-2</sup>; (c) pure Nafion coated GCDE.



For the modified electrode at  $X=0.05$  (**Figure 2B**), a second current plateau appeared with a half-wave potential around 0.25V, which is close to the second redox potential of Os(bpy)<sub>3</sub><sup>2+/3+</sup> (see **Figure 1B**) and is about 0.7V more positive than that for bare GCDE. The height of the second plateau is about twice the first one, most probably indicating a second electron transfer through the mediation reaction  $2\text{NO} + \text{Os}(\text{bpy})_3^{2+} + 2\text{H}^+ \rightarrow \text{N}_2\text{O} + \text{Os}(\text{bpy})_3^{3+} + \text{H}_2\text{O}$ <sup>6</sup>.

The two pairs of peaks in **Figure 1B** imply the presence of two different kinds of sites (known as the hydrophobic interfacial region and the hydrophilic ionic cluster) for the incorporated mediators in the Nafion film containing lower concentration of Os(bpy)<sub>3</sub><sup>2+</sup>.

However, because  $\text{Os}(\text{bpy})_3^{2+}$  has a large hydrophobic shell, when its concentration in the coating is sufficiently large ( $X=0.33$ ), each  $\text{Os}(\text{bpy})_3^{2+}$  ion may become surrounded by the hydrophobic shells of neighboring complex ions. This situation makes the ions in the hydrophilic clusters “feel” as if they were in the hydrophobic interfacial region. This may explain why only a single pair of redox current peaks was seen for  $X=0.33$ . Moreover, when the mediator concentration changed, not only the reduction current density but also the number of electrons involved in nitrite reduction was changed. These findings show that the modified electrodes provide much flexibility in tailoring the catalytic properties of the modified electrode. Obviously, it is possible to regulate the catalytic activity and the pathway of the catalyzed reaction by simply changing the concentration of the mediator in the Nafion film.

Above mentioned analysis was supported by preliminary FTIR and *in-situ* UV-VIS experiments. Significant spectral differences between  $X=0.33$  and  $X=0.05$  were found.

The spectroscopic characterizations and works to improve the electrode stability and to develop the modified electrodes into nitrite sensors are in progress and will be reported elsewhere.

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