

Neutral red as electron transfer mediator: enhanced electrocatalytic activity of platinum catalyst for methanol electro-oxidation

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Abstract Organic molecule neutral red (NR), as electron transfer mediator, was introduced in the anodic electrocatalyst system for methanol oxidation and the resulting electrode was investigated by cyclic voltammetry, polarization method, and electrochemical impedance spectroscopy. For the same loading mass of platinum catalyst, 1.25 times larger exchange current density, 1.83 times higher specific activity, and better long-term cycle stability can be obtained at Pt/NR/graphite electrode, as compared to the electrode without NR. These results indicate that neutral red plays an important role on the enhanced electrocatalytic activity of platinum catalyst for methanol oxidation.

Keywords Electron transfer mediator · Neutral red · Platinum · Methanol oxidation

Introduction

Direct methanol fuel cells (DMFCs) have good potential for transportation applications and portable power sources. However, the electro-oxidation of methanol is very complex; the low catalytic activity of the anodic electrocatalyst is still a key problem for DMFCs. A great deal of efforts is recently

focused on the improvement of the catalytic activity of the anodic electrocatalyst. Among these efforts, an interesting one is that metal macrocyclic compounds (such as electropolymerized Ru(II) porphyrins [1]) are used as the second catalysts to improve the electrocatalytic activity of Pt catalyst.

On the other hand, electron transfer mediators, as a shuttle to transfer electron between the redox center of the electrode active materials and the surface of the electrode, are often used in analytical chemistry. Various metal complexes (such as ferrocene and its derivatives [2], Ru complexes [3, 4], Os complexes [5, 6]), conducting polymers (such as polyaniline and polypyrrole [7, 8]), conducting salts (such as tetrathiafulvalene- or *N*-methylphenaziniumtetracyanoquinodimethane [9], and phenazine methosulphate [10, 11]), and organic dyes [such as methylene blue [12], thionine [13–15], and neutral red (NR) [16]] have been investigated as electron transfer mediators in developing new electrochemical biosensors. Moreover, more and more electron transfer mediators have been reported in different research fields. Aryl-substituted *N*-hydroxyphthalimides were used as mediators in the laccase-catalyzed oxidation of lignin model compounds and delignification of wood pulp [17]. As an electron transfer mediator, the efficiency of dihydroxylation of alkenes was improved by cocatalysts VO(acac)₂ or MeR-eO₃+*N*-methylmorpholine system [18]. An increasing attention is particularly addressed on biological fuel cells with electron transfer mediators. An osmium-complex-linked polymer has been reported as an electron transfer mediator of glucose oxidase [19, 20]. Pyrroloquinoline quinon [20] and vitamin K3 derivative (such as 2-amino-3-carboxy-1,4-naphthoquinone [21] and 2-methyl-1,4-naphthoquinone [22]) were also recently investigated as electron transfer mediator in biological fuel cells.

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In this paper, neutral red was introduced as an electron transfer mediator and Pt nanoparticles were selected as a model of anodic electrocatalyst. The electrocatalytic activity of Pt/NR/graphite electrode for methanol oxidation has been investigated in detail. Compared with the electrode without NR, Pt/NR/graphite electrode has a better electrocatalytic performance for methanol electro-oxidation.

Experimental

Chemicals and instruments

A graphite substrate (6.0 mm in width, 11.8 mm in length, and 3.2 mm in height) was used as the working electrode. The apparent surface area of the working electrode is 0.71 cm^2 . A platinum foil served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. A CHI660A electrochemical workstation (CH Instruments) was employed for the electrochemical deposition of Pt nanoparticles and electrochemical studies of the electrodes. All chemicals were of analytical grade. All experiments were carried out at ambient temperature. All the potentials were referred to SCE. Freshly double-distilled water was used throughout.

The micrographs of Pt/graphite and Pt/NR/graphite electrodes were investigated by scanning electron microscopy (SEM, JSM 5600 LV, operating at 20 kV).

Preparation of Pt/NR/graphite electrode and electrochemical studies

Before catalyst deposition, the graphite electrode was pretreated in 30 wt% HNO_3 aqueous solution for 2 h. To further increase the electrochemical activity of graphite electrode in water solution, the electrode was cycled in the potential range of -0.15 – 1.3 V at a sweep rate of 50 mV/s in $0.1 \text{ M H}_2\text{SO}_4$ aqueous solution for 60 cycles. Then, $100 \mu\text{l}$ of 10^{-4} M neutral red aqueous solution was added on the surface of the activated graphite electrode by microsyringe. After drying under infrared lamp, Pt nanoparticles were electrodeposited on the surface of the NR-modified graphite electrode by potential-step deposition method from N_2 -saturated $1.5 \text{ mM H}_2\text{PtCl}_6$ aqueous solution. The potential jumped from 0.5 to -0.15 V (SCE) with a pulse width of 0.001 s which was carried out successively until a predetermined Pt deposition charge (Q_{dep}) had been reached. After cleaning with double-distilled water, the Pt/NR/graphite electrode was covered with $10 \mu\text{l}$ of 0.05% Nafion ethanol solution.

The electrochemical properties of the Pt/NR/graphite electrode for methanol oxidation were investigated in 1 M

$\text{CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$ aqueous solutions by cyclic voltammetry (CV), polarization method, and electrochemical impedance analysis. For comparison, Pt/graphite electrode without NR was prepared by the same procedure and the corresponding electrochemical performance was also investigated.

Results and discussion

The micrograph of the Pt/NR/graphite electrode

The micrograph of the Pt/NR/graphite electrode has been investigated by SEM and the corresponding result is presented in Fig. 1a. From Fig. 1a, Pt nanoparticles with a diameter of about 60 – 100 nm are electrodeposited uniformly on the surface of the NR/graphite electrode. For comparison, the SEM image of the Pt/graphite electrode of similar deposition charge with Pt has also been shown in Fig. 1b. From Fig. 1b, a similar result can be observed and the diameter of Pt nanoparticles is about 50 – 100 nm . This

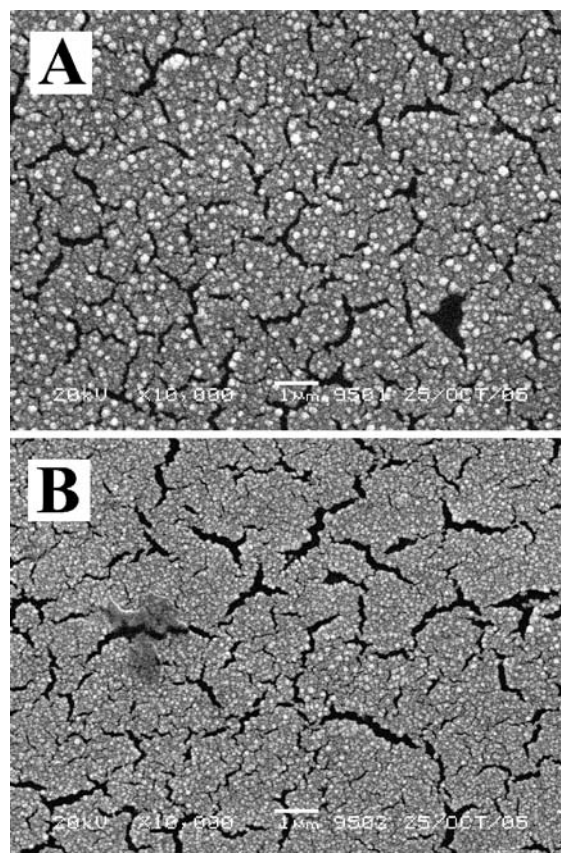


Fig. 1 SEM images of **a** Pt/NR/graphite (Pt deposition charge, $2.74 \mu\text{C cm}^{-2}$) and **b** Pt/graphite electrodes (Pt deposition charge, $2.46 \mu\text{C cm}^{-2}$). Both electrodes were covered with $10 \mu\text{l}$ of 0.05% Nafion ethanol solution

may imply that the electrodeposition of platinum nanoparticles is not obviously disturbed by the presence of neutral red.

Cyclic voltammograms of Pt/NR/graphite electrode

The electrochemical properties of graphite, NR/graphite, Pt/graphite, and Pt/NR/graphite electrodes have been investigated by cyclic voltammetry and the typical cyclic voltammograms are shown in Fig. 2. From Fig. 2a, a pair of redox peaks at about 0.35 V (vs SCE) can be observed for the NR/graphite and graphite electrodes in 1 M CH₃OH+0.1 M H₂SO₄ aqueous solutions. This may be correlated with the redox behavior of the carboxylic acid groups (such as –COOH and –OH) after the graphite electrode was activated in acid aqueous solution. The current density of the electrode is also increased by the presence of neutral red. No current peaks of methanol oxidation can be seen in Fig. 2a, which indicates that both neutral red and graphite substrate have no

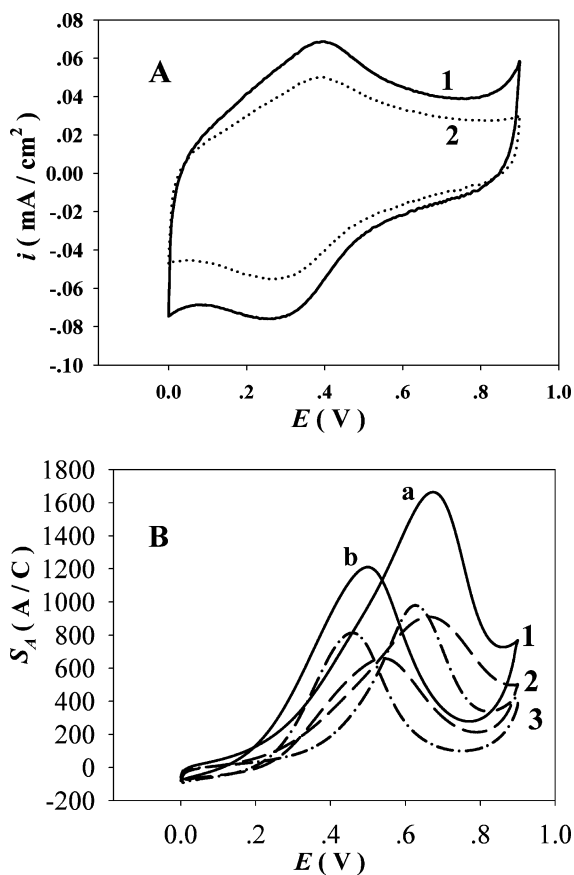


Fig. 2 Cyclic voltammograms of various electrodes in 1 M CH₃OH + 0.1 M H₂SO₄ aqueous solutions. **a** NR/graphite (curve 1) and graphite (curve 2) electrodes. **b** Pt/NR/graphite (curve 1, Pt deposition charge, 2.74 $\mu\text{C cm}^{-2}$), Pt/graphite (curve 2, Pt deposition charge, 2.46 $\mu\text{C cm}^{-2}$), and NR/Pt/graphite (curve 3, Pt deposition charge, 3.33 $\mu\text{C cm}^{-2}$) electrodes. Scan rate, 50 mV s⁻¹

electrocatalytic activity for methanol oxidation. From Fig. 2b, two oxidation peaks, which are related to the oxidation of methanol and the corresponding intermediates produced during the methanol oxidation, can be obviously observed at 0.67 and 0.50 V, respectively. The characteristics of CV curves and the corresponding peak potentials (E_p) are in agreement with other works [23]. It can also be obtained that the feature of curve 1 is similar to that of curve 2. This implies that the nature of the methanol oxidation is not disturbed by the presence of NR. However, the electrocatalytic activity of Pt electrocatalyst is enhanced greatly by NR. The oxidation current of methanol at Pt/NR/graphite electrode is much higher than that at Pt/graphite electrode. On the other hand, the specific activity (S_A) defined by peak current density per unit of catalyst deposition charge is introduced and calculated by the following equation [24]:

$$S_A = 1,000i_{pa}/Q \quad (1)$$

where i_{pa} (mA cm⁻²) is the peak current density obtained from forward CV scan (peak a), and Q ($\mu\text{C cm}^{-2}$) is the deposition charge of Pt catalyst. The specific activity of Pt/NR/graphite electrode is 1,665.2 AC⁻¹ and about 1.83 times as high as that of Pt/graphite electrode ($S_A=910.1$ AC⁻¹). This may be attributed to the presence of NR, an electron transfer mediator.

In addition, a control experiment has been carried out. According to the same procedure used in the preparation of Pt/NR/graphite electrode, the NR/Pt/graphite electrode (NR was applied after Pt deposition) was prepared. The electrochemical properties of the NR/Pt/graphite electrode have been investigated and the corresponding cyclic voltammogram is also shown in Fig. 2b. It can be observed that the electrocatalytic activity of the NR/Pt/graphite electrode is lower than that of the Pt/NR/graphite electrode. This may suggest that NR provides a good connection between catalyst and support material in the Pt/NR/graphite electrode.

Tafel plots of Pt/NR/graphite electrode for methanol oxidation

To further investigate the effect of NR on the electrocatalytic activity of Pt catalyst, the exchange current density (i_0) of methanol oxidation at different electrodes was investigated. Polarization studies for Pt/NR/graphite and Pt/graphite electrodes have been carried out and the typical Tafel curves are shown in Fig. 3. According to the Tafel equation [25], the values of i_0 for Pt/NR/graphite and Pt/graphite electrodes are calculated. The i_0 value of the Pt/NR/graphite electrode is 25.18 $\mu\text{A cm}^{-2}$ and about 1.25 times as high as that of Pt/graphite electrode ($i_0=20.19$ $\mu\text{A cm}^{-2}$). It indicates that the existence of NR accelerates significantly the process of methanol electro-oxidation. On the other hand, the open-circuit potential is

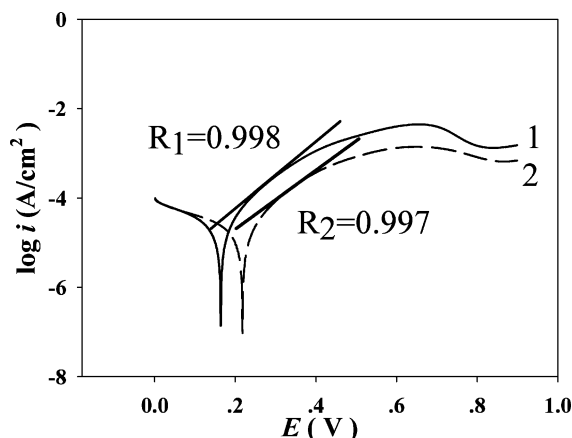


Fig. 3 Tafel plots of Pt/NR/graphite (curve 1) and Pt/graphite (curve 2) electrodes in 1 M CH₃OH + 0.1 M H₂SO₄ aqueous solutions. Scan rate, 10 mV s⁻¹

also decreased obviously from 0.218 to 0.164 V, which implies that the electro-oxidation of methanol at Pt/NR/graphite electrode is easier than that at Pt/graphite electrode due to the assistance of NR.

Electrochemical impedance spectroscopy of Pt/NR/graphite electrode

A typical electrochemical impedance spectrum presented in the form of a Nyquist plot (Z_{im} vs Z_{re}) includes a semicircle region lying on the Z_{re} -axis observed at higher frequencies corresponding to the electron-transfer-limited process, followed by a linear part at lower frequencies representing the diffusion-limited electron-transfer process. The electron-transfer kinetics and diffusion characteristics can usually be extracted from the spectra. The semicircle diameter equals to the electron-transfer resistance, R_{ct} , which is controlled by the surface modification of the electrode. The existence of NR on the graphite electrode surface is expected to enhance the interfacial electron-transfer kinetics and decreases the electron-transfer resistance.

Figure 4 shows the electrochemical impedance spectra presented as Nyquist plots (Z_{im} vs Z_{re}) of the Pt/NR/graphite and Pt/graphite electrodes recorded in an aqueous solution of 1 M CH₃OH + 0.1 M H₂SO₄. As shown in Fig. 4, the electron-transfer resistance (R_{ct} , the diameters of semicircles) between the methanol molecules and electrode surface decreases after the introduction of NR. The values of R_{ct} on Pt/NR/graphite and Pt/graphite electrodes are 19.3 and 22.2 Ω , respectively. This also implies that the electro-oxidation of methanol molecules is enhanced by the presence of NR, which is used as an electron transfer mediator.

Effect of temperature on the electrocatalytic properties of Pt/NR/graphite electrode

For methanol electro-oxidation, it is well known that the apparent activation energy can be calculated according to the Arrhenius equation:

$$i_p = k \exp\left(-\frac{W}{RT}\right) \quad (2)$$

where i_p is the peak current density, k is a constant, R is gas constant, and W is the Arrhenius activation energy. For the electrode modified with a definite catalyst, Eq. (2) can be rewritten as follows:

$$\ln SA = -\frac{W}{R} \frac{1}{T} + C \quad (3)$$

where C is a constant. A plot of $\ln S_A$ vs $\frac{1}{T}$ would yield a straight line with a slope of $-\frac{W}{R}$ [26].

To obtain the apparent activation energy for methanol oxidation at Pt/graphite and Pt/NR/graphite electrodes, the effects of temperature (T) were also investigated. In view of the practical operating condition for fuel cells, the temperature range was selected from 293 to 333 K. The corresponding results are shown in Fig. 5. For both Pt/graphite and Pt/NR/graphite electrodes, the linear relationship between $\ln S_A$ and $\frac{1}{T}$ can be observed (Fig. 5). According to Fig. 5, the apparent activation energies of methanol electro-oxidation can be calculated. For peak a, the apparent activation energies at Pt/graphite and Pt/NR/graphite electrodes are 31.41 and 27.70 kJ mol⁻¹, respectively. A similar result can also be observed for peak b (41.87 kJ mol⁻¹ for Pt/graphite electrode and 33.22 kJ mol⁻¹ for Pt/NR/graphite electrode). The apparent activation energy of methanol electro-oxidation decreases due to the presence of neutral red. These imply further that the electrocatalytic activity of Pt catalyst is

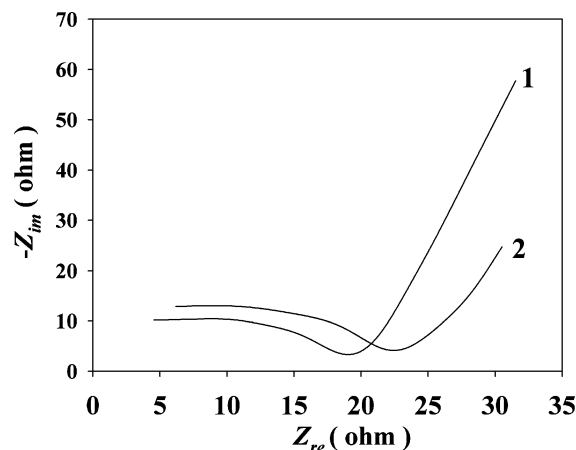


Fig. 4 Electrochemical impedance spectra of Pt/NR/graphite (curve 1) and Pt/graphite (curve 2) electrodes in 1 M CH₃OH + 0.1 M H₂SO₄ aqueous solutions. Initial potential, 0 V; amplitude, 5 mV

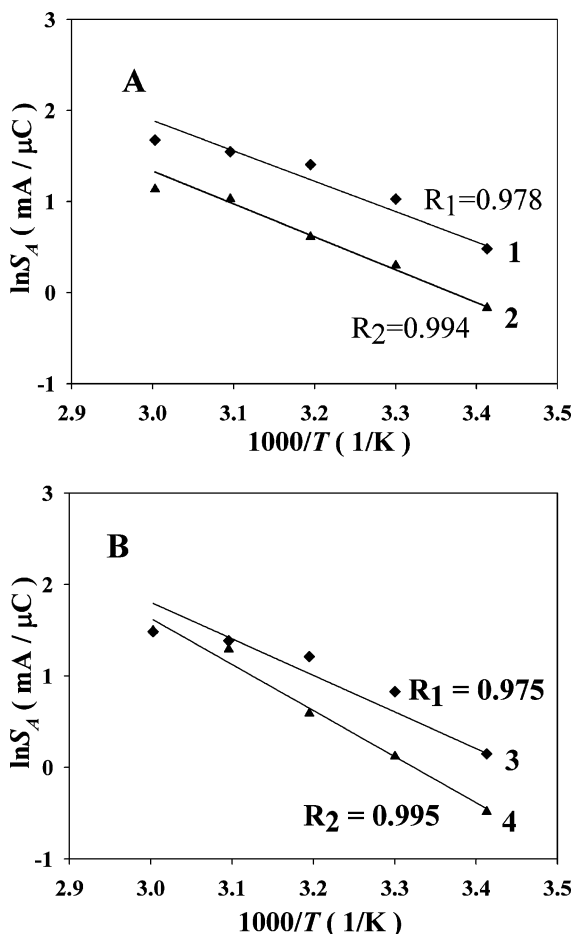


Fig. 5 Arrhenius plots of methanol electro-oxidation at Pt/graphite (curves 2 and 4) and Pt/NR/graphite (curves 1 and 3) electrodes for peaks a (plot A) and b (plot B). Solutions, 1 M CH₃OH + 0.1 M H₂SO₄ aqueous solutions; scan rate of CV, 50 mV s⁻¹

enhanced as a result of the neutral red being an electron transfer mediator.

Based on the above results, the possible mechanism of neutral red as an electron transfer mediator promoting electro-oxidation of methanol at platinum catalysts is illustrated in Fig. 6. Neutral red is immobilized on the graphite electrode by electrostatic adsorption and π-π stacking interaction and as a shuttle to enhance the electron transfer between Pt and electrode.

Long-term cycle stability of Pt/NR/graphite electrode

The long-term cycle stability of Pt/NR/graphite electrode has been investigated in 1 M CH₃OH+0.1 M H₂SO₄ aqueous solution by cyclic voltammetry and the corresponding results are shown in Fig. 7. When the potential is cycled continuously for 500 cycles, 9.03% loss of the peak current density obtained at the forward scan

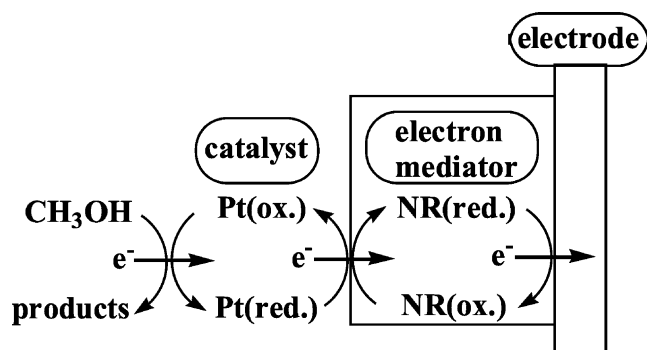


Fig. 6 Schematic diagram of the electron transfer process between Pt and electrode via NR

(*i*_{pa}) can be observed for Pt/NR/graphite electrode. However, for Pt/graphite electrode, a large decrease (50%) can be observed. The reasons for the decrease of *i*_p may be as follows: accumulation of poisonous species (such as CO_{ads}) on the surface of the Pt particles [27], methanol consumption during the successive scans, and change of the surface structure of the Pt catalyst. The results from Fig. 7 imply that the presence of NR is very helpful for the improvement of the long-term cycle stability of Pt catalyst during the electro-oxidation process of methanol.

After 500 cycles, the electrodes were stored in double-distilled water for 24 h, and then the electrocatalytic properties of the electrodes for methanol oxidation are investigated again in fresh methanol solution. The peak current density of the Pt/NR/graphite electrode still remains at 91.17% value of *i*_{pa(1)} (the peak current density for peak a at the first cycle). However, for Pt/graphite electrode, only 69.31% value of *i*_{pa(1)} remains.

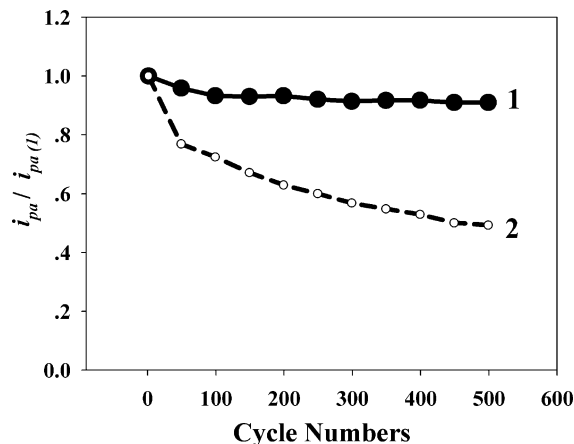


Fig. 7 Long-term cycle stability of Pt/NR/graphite (curve 1) and of Pt/graphite (curve 2) electrodes in 1 M CH₃OH + 0.1 M H₂SO₄ aqueous solutions at 50 mV s⁻¹. *i*_{pa}, the peak current density for peak a; *i*_{pa(1)}, the peak current density for peak a at the first cycle

Conclusion

Neutral red, as an electron transfer mediator, is introduced in the anodic electrocatalyst system for methanol oxidation. The electrochemical performance of the Pt/NR/graphite electrode has been investigated by cyclic voltammetry, polarization method, and electrochemical impedance spectroscopy. Good electrochemical performance (higher electrocatalytic activity and good long-term cycle stability) is achieved by the presence of NR. The corresponding results imply that the electron transfer mediators may provide a new way to improve the electrochemical performance of the electrodes in fuel cells.

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