



Electrocatalytic Activity of Carbon Paste Electrode Modified with Porphyrin and SWCNT for Oxygen Reduction Reaction

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A carbon paste modified electrode (CPME) with 5,10,15,20-tetraphenylporphyrinato cobalt(II) (CoTPP) and single walled carbon nanotube (SWCNT) was prepared by simple, rapid and effective method. Its electrochemical catalytic behaviour for oxygen was investigated in oxygen-saturated 0.1 mol/L $\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$ buffer solution (PBS) (pH 7). By using rotating disk electrode, the analysis was carried out that oxygen reduction on CP/CoTPP/SWCNT in 0.1 mol/L PBS (pH 7) is through two-electron pathway and the possible catalytic mechanism was discussed. The CPME was very stable and exhibited high tolerance to methanol. It is suggested that CoTPP and SWCNT modified carbon paste modified will offer a possibility of developing a sensitive method for the determination of dissolved oxygen.

Keywords: Carbon paste modified electrode, Oxygen reduction, Porphyrin, SWCNT.

INTRODUCTION

As is well known, oxygen reduction reaction (ORR) is very important for many fields, such as fuel cells, biosensors, etc. Since Jasinski found cobalt phthalocyanine was active to oxygen reduction reaction in 1964¹, metalloporphyrins have been widely considered as one of the most promising alternatives to Pt because of lower costs compared to noble metals and high tolerance to methanol²⁻⁵. Usually, working electrode are modified with electroactive substances by covalent bonding⁶, adsorption⁷⁻⁹ or electrodeposition¹⁰⁻¹⁵. Unfortunately, the modified electrodes prepared by these method are not stable. The basic reason was that the chemical bond linking porphyrin and electrode surface was fragile, which caused porphyrin leaching from the electrode surface. Moreover, the preparation procedures seem rather complicated and period is very long.

Kuwana and French¹⁶ incorporated an electro-active substance into a carbon paste matrix, *i.e.* CPME. Comparing with traditional preparation methods, CPME has a lot of advantages, such as low cost, wide potential windows, ease of preparation and renewal and convenient modification¹⁷. Especially, in recent decades, CPME has been used widely for oxygen reduction reaction^{18,19}.

Carbon nanotube (CNT) is cylinder composed solely of carbon atoms and has unique one-dimensional geometric structure. Due to its excellent properties, such as high electric conductivity, large accessible surface area and excellent

chemical stability, using CNT to oxygen reduction reaction has been a hotspot in the field of nanotechnology^{20,21}.

In this work, we report the carbon paste electrode modified with CoTPP and SWCNT (denoted by CP/CoTPP/SWCNT). We studied the electrocatalytic activity of CP/CoTPP/SWCNT for oxygen reduction reaction using cyclic voltammetry and rotating disk electrode techniques, then researched the tolerance to methanol and stability. We also discussed the catalytic mechanism and made brief analysis on the feasibility of the application of CP/CoTPP/SWCNT.

EXPERIMENTAL

5,10,15,20-Tetraphenylporphyrin (TPP) was synthesized by Adler method²². CoTPP was synthesized according to previously described procedures²³. SWCNT (purity $\geq 95\%$) was purchased from Beijing Nachen S&T Ltd., Graphite powder (purity $> 99.5\%$, $30\ \mu\text{m} \leq d \leq 100\ \mu\text{m}$) and paraffin oil were purchased from Shanghai Colloid Chemical Engineering Co.Ltd., China. All other chemicals were of analytical grade and used as received. PBS was made up using double distilled water ($17.9\ \text{M}\Omega\text{-cm}$). High purity oxygen (99.99%) was bubbled through the electrolyte for 20 min to obtain an oxygen-saturated solution.

Preparation of the modified electrode: CoTPP (2.45 mg), activated graphite powder (0.315 g) and SWCNT (0.035 g) are dissolved in 25 mL dichloromethane. The mixture was stirred by ultrasonic till all the solvent was completely

evaporated and dried for 24 h at room temperature. Then added paraffin oil (0.15 g) inside and finish whipped the ingredients into a smooth paste. A portion of the paste was packed into the end of a Teflon tube (about 2.5 mm i.d., 3 mm depth). Electrical contact was made by forcing a copper rod with the same diameter down into the Teflon and up to the back of the composite. The prepared CPME was polished with weighting paper and pretreated by applying the anodic potential of 1.6 V for 1 min in 0.1 mol/L PBS (pH 7) prior to measurement. A bare carbon paste electrode (CP) and only CoTPP modified carbon paste electrode (CP/CoTPP) were also prepared in the similar way for comparison.

Electrochemical experiments were performed using Metrohm Autolab (PGSAT32) electrochemistry workstation, coupled with a three-electrode system. The working electrode was CPME. A Pt wire and an Ag/AgCl (saturated KCl) electrode were used as counter electrode (CE) and reference electrode (RE), respectively. A digital pH-25C precision pH/mV meter from Shanghai Kangyi Apparatus Co. Ltd, China was applied for the preparation of 0.1 mol/L PBS (pH 7.0). All measurements were carried out at room temperature (20 ± 2 °C).

RESULTS AND DISCUSSION

Electrocatalytic property: Fig. 1 shows the CVs for CP, CP/CoTPP, CP/CoTPP/SWCNT in the potential range between 0 and -1 V, using oxygen-saturated 0.1 mol/L PBS as the supporting electrolyte and with a scan rate (v) of 50 mV s^{-1} . As shown in Fig. 1, there is an irreversible cathodic peak at an initial potential $E_{pc} = -0.25 \text{ V}$ (Fig. 1b), which is higher than that observed on CP, at -0.3 V (Fig. 1a). This is because CoTPP is evidently active to ORR. On CP/CoTPP/SWCNT, a significant enhancement of the initial potential is observed at -0.15 V (Fig. 1c). The results clearly indicate that catalytic activity of CoTPP for ORR can be improved by using SWCNT. The reason is that SWCNT can be stabilized with CoTPP by π - π stacking and participate in the electron transfer process²⁴.

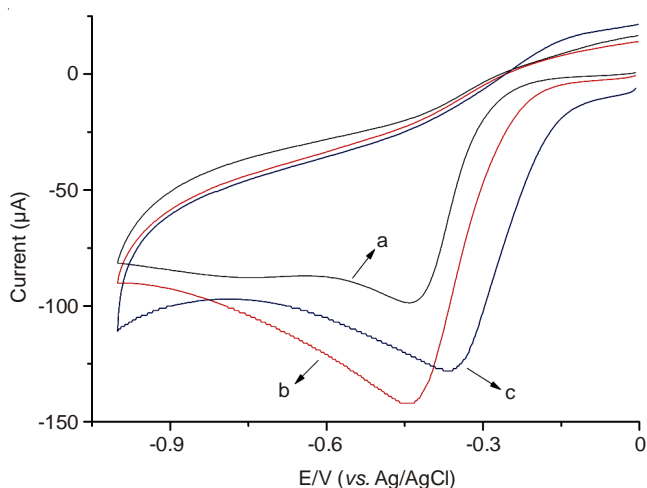


Fig. 1. CVs of CP (a) and CP/CoTPP (b) and CP/CoTPP/SWCNT (c) in O_2 -saturated 0.1 mol/L PBS (scan rate: 50 mV/s)

Electrochemical behaviour: To investigate the electrochemical behaviour of CPME, CV experiments of the CP/CoTPP/SWCNT were carried out in oxygen-saturated 0.1 mol/L

PBS (pH 7) at different scan rates. In Fig. 2, the ORR peak current (I_{pc}) increased and peak potentials moved to the negative direction with the increasing of scan rate (v). From the inset it can be seen that I_{pc} linearly vary with the square root of scan rate ($v^{1/2}$). This behaviour demonstrated that the ORR on CP/CoTPP/SWCNT is a diffusion-controlled process, which follows the formula:

$$I_{pc}/(\mu\text{A}) = -0.360 + 59.5 v^{1/2}/(\text{V s}^{-1})^{1/2} (R^2 = 0.998)$$

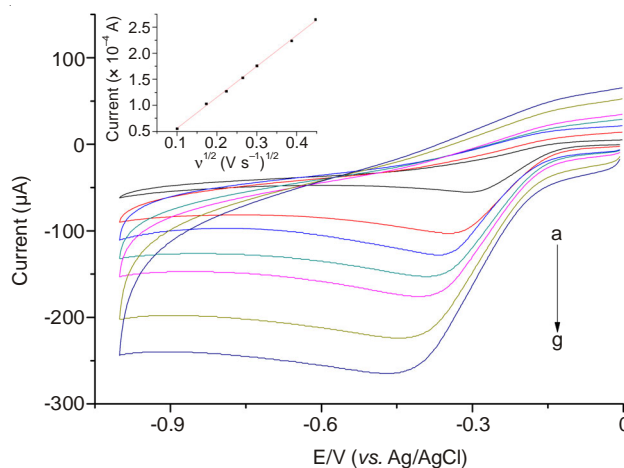


Fig. 2. CVs of the CP/CoTPP/SWCNT at different scan rates (10, 30, 50, 70, 90, 150, 200 mV s^{-1} , from a to g) in O_2 -saturated 0.1 mol/L PBS; Insert: plot of the cathodic peak currents vs. the square root of scan rate

To further research diffusion kinetics of oxygen reduction and obtain the number of electrons, the polarization curves of CP/CoTPP/SWCNT at different rotation speeds of the disk electrode in O_2 -saturated 0.1 mol/L PBS were shown in Fig. 3. The Koutechy-Levich plot was obtained with Levich equation, *i.e.* the reciprocal of the limiting currents (I_{lim}^{-1}) was plotted against the reciprocal of the square root of the rotation rate ($\omega^{-1/2}$). Four-electron and two-electron process were also calculated for comparison. From the insert, linearity between I_{lim}^{-1} and $\omega^{-1/2}$ is excellent ($R^2 = 0.997$). The Levich equation are as follows:

$$I_{lim}^{-1} = I_K^{-1} + I_d^{-1} \quad I_d = 0.62nFD^{2/3} \cdot v^{-1/6} \cdot \omega^{-1/2} \cdot c^B$$

where F is Faraday constant (96500 C), D is the diffusion coefficient ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) of oxygen in 0.1 mol/L PBS, v is the kinematic viscosity of solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$) and C^B is the saturated concentration ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$) of oxygen in 0.1 M PBS. The number of transferred electrons was calculated to be 2.7, which indicated that oxygen reduction on CP/CoTPP/SWCNT in 0.1 mol/L PBS is through two-electron pathway.

Methanol tolerance: For direct methanol fuel cell (DMFC), methanol tolerance is very important. Fig. 4 shows the CVs of CP/CoTPP/SWCNT electrode in oxygen-saturated 0.1 M PBS and 0.1 mol/L PBS + 0.5 mol/L CH_3OH . Through comparison the two curves, it can be seen that there was no significant differences on onset potential but a slight increase on reduction current. Evidence suggested that CP/CoTPP/SWCNT is good at the methanol tolerance. This is because the addition of methanol enhanced hydrophilicity of the electrode surface and increased the contact of catalyst with oxygen²⁵.

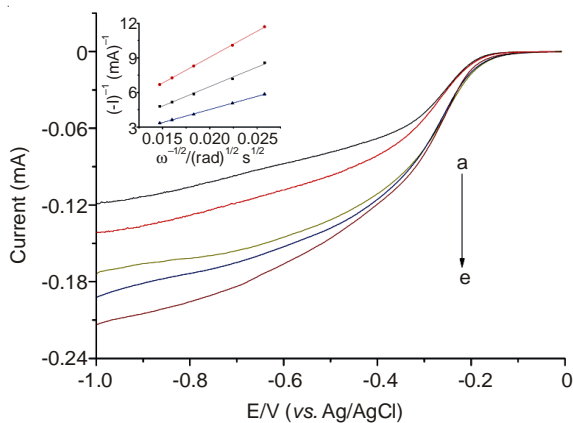


Fig. 3. Polarisation curves of CP/CoTPP/SWCNT at different rotation rates ω (1500, 2000, 3000, 3900, 4600 rad/s, from a to e) in O_2 -saturated 0.1 mol/L PBS (scan rate: 5 mV/s); Insert: Koutecky-Levich plots at -0.95 V

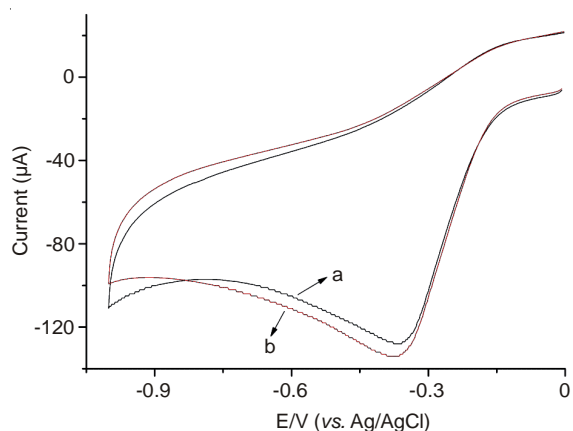


Fig. 4. CVs of CP/CoTPP/SWCNT in O_2 -saturated 0.1 mol/L PBS + 0.5 mol/L CH_3OH (a) and 0.1 mol/L PBS (b) (scan rate: 50 mV/s)

Electrocatalytic stability: Another important aspect that must be emphasized is the stability. To explore the long-term stability of the CP/CoTPP/SWCNT, the potential was continuously cycled 500 times between 0 V and -1 V in oxygen-saturated 0.1 mol/L PBS. Fig. 5 shows the CV traces of the 1st and 500th cycles. It is noticed that the ORR peak potential and current hardly any change, which suggests that CP/CoTPP/SWCNT exhibits good stability in PBS.

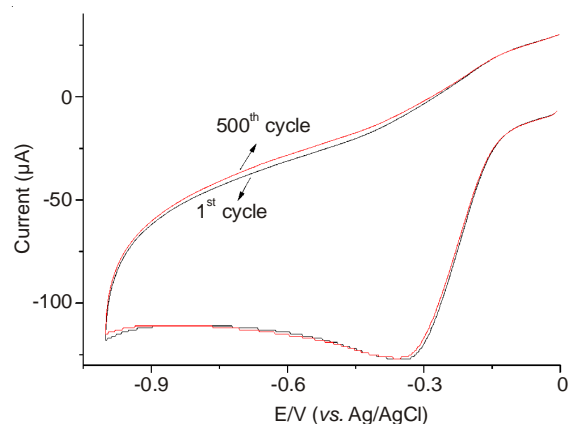


Fig. 5. CVs for the ORR at the CP/CoTPP/SWCNT on the 1st and 500th cycles of the continuous potentiodynamic sweep in O_2 -saturated 0.1 mol/L PBS (scan rate: 50 mV/s)

Conclusion

In this work, we have prepared CoTPP and SWCNT modified carbon paste electrode using a simple and rapid method. Compared with CP or CP/CoTPP, CP/CoTPP/SWCNT shows higher catalytic activity for ORR. As catalyst, CP/CoTPP/SWCNT shows high sensitivity, good stability, tolerance to methanol and so on. The Koutecky-Levich plots suggest a two-electron pathway in oxygen-saturated 0.1 mol/L PBS (pH 7).

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