



Short communication

Planar polyphthalocyanine cobalt absorbed on carbon black as stable electrocatalysts for direct methanol fuel cell

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ABSTRACT

In this work, a novel catalyst is prepared by dispersing planar polyphthalocyanine cobalt (PPcCo) synthesized by polymerizing cobalt (II)-4,4',4'',4'''-phthalocyanine tetracarboxylic acid (TcPcCo) using a high surface area carbon powder (Vulcan XC 72), and then heat-treated in argon (Ar) atmosphere. The polymer and PPcCo/C catalysts are characterized systematically by a variety of methods, such as ultraviolet–visible (UV–vis) spectrophotometer, Fourier transform infrared spectrometer (FT-IR), thermogravimetric analysis (TGA), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM). Results show that the PPcCo obtained is stable below 600 °C. The active site of PPcCo/C is CoN₄ in phthalocyanine ring, and the PPcCo is dispersed homogeneously on the surface of XC 72. Electrochemical properties and electrochemical stability of the catalysts in 0.5 mol L⁻¹ H₂SO₄ are evaluated by RDE measurements. The initial potential for O₂ reduction in O₂-saturated H₂SO₄ is 0.81 V and it catalyzed O₂ reduction mainly through a four-electron process. Almost no performance degradation is observed over continuous cyclic voltammetry (CV) at 10,000 cycles (4 days). Polarization curves obtained by linear sweep voltammetry (LSV) at 200 cycles also show no change. PPcCo/C catalysts display significant electrocatalytic performance for O₂ reduction, tolerance towards methanol, and long-term stability.

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1. Introduction

Direct methanol fuel cells (DMFCs) are considered as a promising technology for future sustainable electricity generation. However, two major difficulties persistently hinder their commercialization: high material cost and limited durability. High costs are mainly due to the expensive catalysts and membrane materials necessary for its production [1]. Since the 1960s, transitional metal macrocycles (TMM), which include cobalt (Co) phthalocyanine species, have been actively studied as a promising alternative to platinum-based catalysts [2]. Even so, the stability and volumetric specific activity of TMM catalysts still require further improvement. Later research revealed that pyrolyzed TMM catalysts are more active and stable than their unpyrolyzed analogues, and many studies were performed on the heat treatment of TMM [3–5]. The catalysts used were usually pyrolyzed at high temperatures (>700 °C), resulting in the formation of MeN₂/C and MeN₄/C [6,7]. Pyrolyzing mixtures of metallic salt, organic precursor, and ammonia in an inert atmosphere produces similar results [8–11]. However, the structure of these catalysts has not been defined well enough for true quantitative studies [12]. In an acidic medium,

these catalysts show poor stability due to the loss of either a bare inorganic metal or an inorganic metal in partially enclosed catalysts [13]. The search for a more active and stable TMM catalyst has thus become an important topic in this area.

The polyphthalocyanine cobalt molecule is a planar conjugated system made up of delocalized aromatic π -electrons with a delocalized energy lower than its monomer. PPcCo/C catalysts made by dispersing PPcCo on high surface area carbon (Vulcan XC72) electrodes are expected to show high electrocatalytic activity and stability, as well as good selectivity via a four-electron transfer mechanism.

In this study, we prepared a new kind of PPcCo catalyst supported on carbon to be used as a methanol-tolerant for DMFCs. This catalyst is synthesized by polymerizing TcPcCo. The resulting PPcCo and PPcCo/C were characterized systematically using UV–vis, FT-IR, TG, XRD, XPS, and TEM. Their electrocatalytic properties were also investigated using RDE measurements. Results indicate that the synthesized catalysts presented sufficient activity, tolerance towards methanol, and long-term electrocatalytic performance for oxygen reduction reaction (ORR) catalysts in acidic medium.

2. Experimental

2.1. Preparation of PPcCo

The synthesis of cobalt (II)-4,4',4'',4'''-phthalocyanine tetracarboxylic acid (TcPcCo) is based on previously reported procedures

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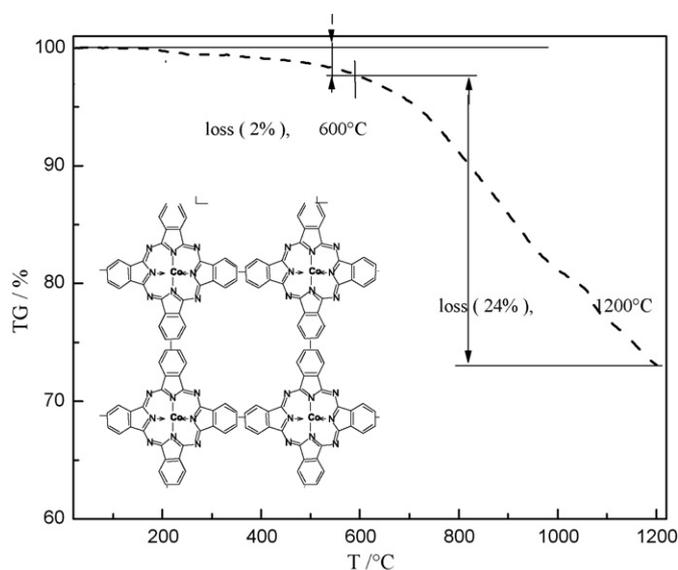


Fig. 1. Thermogravimetric analysis and the structure of PPcCo. Inset is the structure of PPcCo.

[14]. Finely ground cobalt(II)-4,4',4''-phthalocyanine tetracarboxylic acid was placed in a porcelain boat, which was then put into a homemade reactor and purged with Ar gas by repeated evacuation and refill. The boat was heated to 400 °C in a current of Ar and maintained at this temperature for 2 h. The structure of PPcCo is shown in Fig. 1 inset.

2.2. UV-vis and IR analyses

UV-vis spectra were recorded on a Lambda 35 Perkin Elmer spectrophotometer. IR spectra were recorded on a Nicolet 5700 spectrophotometer.

2.3. Thermogravimetric analysis

TGA data were obtained using STA-409 Netsch under Ar atmosphere with a flow rate of 30 mL min⁻¹ and heating rate of 10 °C min⁻¹. The sample size was 10 mg.

2.4. Preparation of PPcCo/C

PPcCo was adsorbed onto XC72 according to the following procedure: a total of 0.5 g of the precursor was dispersed with 0.5 g of XC 72 in 40 mL of DMSO. The dispersion was stirred under reflux and heated for 24 h. Then, it was dried at 75 °C in air for 12 h. Finally, the precipitate was ground into a fine powder and subsequently heat-treated in Ar at temperatures of 400 and 600 °C.

Samples of catalysts with mass ratios of 1:1.5 and 1.5:1 for PPcCo/XC72 were also prepared.

2.5. Bulk and surface analyses

Surface analyses of PPcCo/C catalysts were characterized by XPS on a PHI-5300 ESCA spectrometer. The structure of the catalyst was determined via XRD on D8Advance, Bruker. The morphological parameters of the electrocatalyst particles were observed via TEM using Tecnai G2 F20.

2.6. Electrochemical measurements and stability test

The catalysts were evaluated using the rotating disk electrode technique (RDE). A total of 16 mg of finely ground catalyst were

ultrasonically mixed for 1 h with 200 μL ultra-pure water and 30 μL 5 wt% solution of Nafion (Aldrich). Then, 6 μL ink was pipetted and spread onto a glassy carbon disk, which was then used as the rotating electrode. The film was dried in air at 75 °C. RDE measurements were performed in a three-electrode cell; a platinum filament was used as counter electrode and Hg/Hg₂SO₄ as reference electrode. All potentials reported in this paper, refer to that of the reversible hydrogen electrode (RHE). The surface area of the working electrode was 0.1075 cm². Electrochemical measurements were carried out in 0.5 mol L⁻¹ H₂SO₄ solution saturated with O₂ or Ar under quasi-stationary conditions at 20 °C with sweep rate 5 mV s⁻¹. The rotation rate varied from 500 to 2500 rpm. Long-time stability experiments were carried out for PPcCo/C catalysts using continuous and repeated cyclic voltammetry, linear sweep voltammetry (LSV), and chronoamperometry with the electrode rotation rate was fixed at 1500 rpm. Cyclic voltammograms (CV) were obtained after 30 min of equilibration between consecutive cycles.

3. Results and discussion

3.1. UV-vis and IR analyses

The UV-vis absorption spectra of PPcCo and TcPcCo exhibited the characteristics Q and B bands. PPcCo showed absorptions at 315 and 779 nm, while TcPcCo showed absorptions at 302 and 774 nm. The absorption bands of PPcCo appeared at higher wavelengths compared to the parent phthalocyanine.

The IR spectra of PPcCo exhibited a decrease in absorption peaks corresponding to the carboxylic acid groups is taken as the occurrence of polymerization reaction [15]. Phthalocyanine skeletal absorption bands were observed in the polymeric materials, indicating the presence of phthalocyanine structures. IR spectra further revealed that the planar polyphthalocyanine cobalt (PPcCo) was synthesized.

3.2. Thermogravimetric analysis

Thermogravimetric analysis result is presented in Fig. 1. As shown in the figure, PPcCo was heated from room temperature to 1200 °C in an Ar atmosphere, during which two relatively stable weight losses were observed during heat-treatment. The first weight loss (2%) was observed at temperature range of room temperature to 600 °C, which can be ascribed to the evaporation of small amount of residual water. The second weight loss (24%), from 600 to 1200 °C, indicates the destruction of phthalocyanine rings. This observation provides indirect evidence that the active center of PPcCo/C catalysts is Co-N₄ in the phthalocyanine ring.

3.3. Bulk and surface analyses

An XRD study of PPcCo/C was performed beyond the 2θ range from 3° to 60°. No diffraction peaks were seen in the XRD spectra, indicating that PPcCo is amorphous in nature.

To determine the active center of the synthesized catalyst, we investigated the interactions between Co and macrocycles via XPS analysis of PPcCo/C (400 °C, 1:1). Fig. 2(a)–(c) shows Co 2p, nitrogen (N) 1s, and C 1s regions of typical XPS spectra. The spectra were identified according to XPS functional group data reported in the literature [16,17]. According to Co 2p XPS data (Fig. 2(a)), binding energy bands appear at 780 and 796 eV, corresponding to Co(II) and Co(III), respectively. The Co atom is located at the ligand environment of the nitrogen-enriched structure of the phthalocyanine ring. The main peak (at 398.84 eV) of the N1s spectra (Fig. 2(b)) can be ascribed to the two chemically nonequivalent N atoms (four central N atoms and four aza N atoms) [18]. The latter

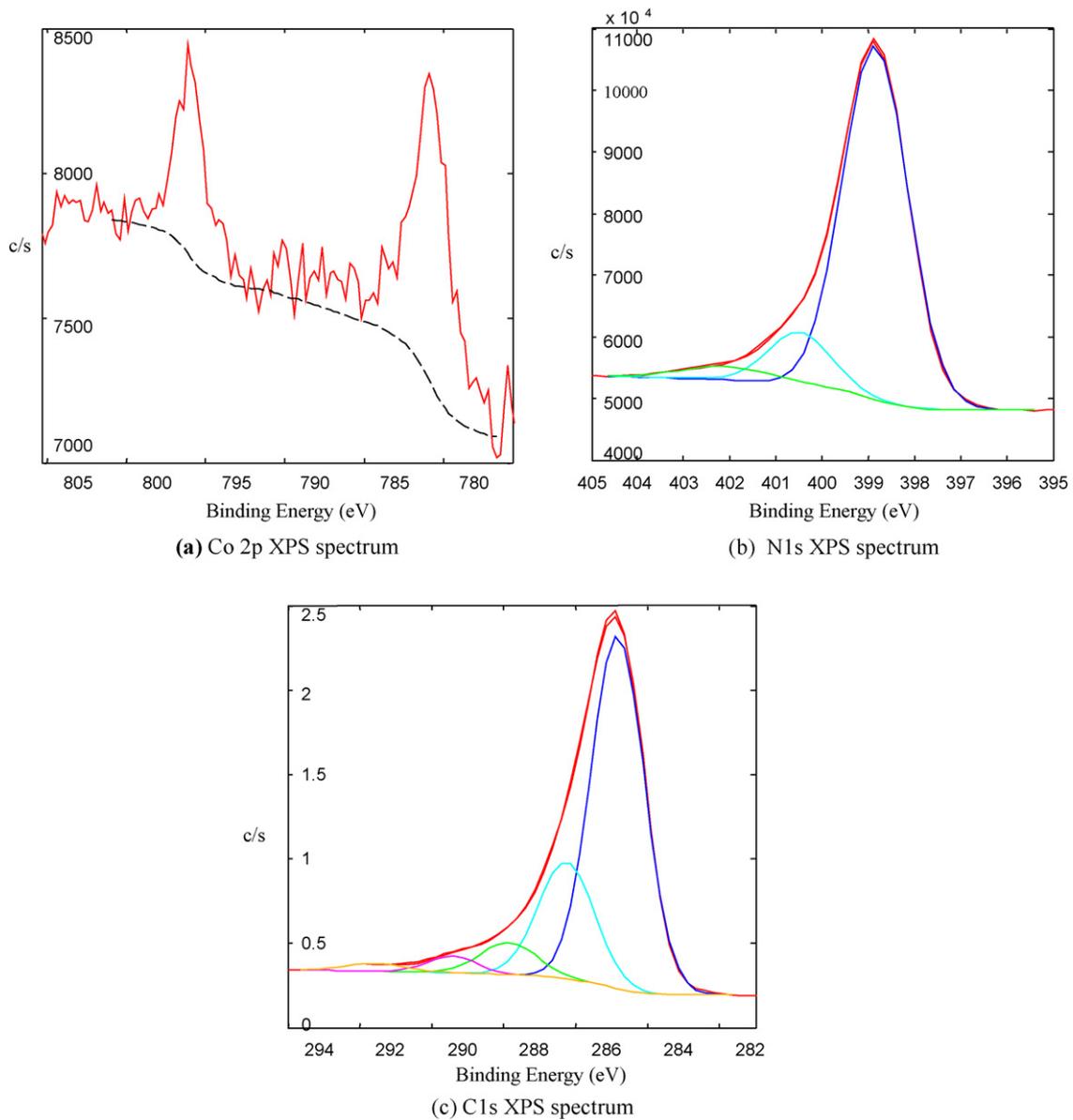


Fig. 2. XPS spectra of PPcCo/C. (a) Co 2p XPS spectrum; (b) N1s XPS spectrum; (c) C 1s XPS spectrum.

peak (at 398.84 eV) can be attributed to a shake-up satellite [19]. The C 1s spectra (Fig. 2(c)) were fitted with bands at 284.8, 286.26, 287.86, and 289.43 eV, which were attributed to aromatic C–C bonds, N–C=N, C=O, and C=C bonds [20]. A shake-up satellite appeared at 291.59 eV. The XPS spectra suggest that the phthalocyanine ring was not destroyed in the catalysts, further confirming that the active center of the ring is Co–N₄ in the phthalocyanine ring. The morphology of PPcCo/C observed by TEM is depicted in Fig. 3. The black particle, PPcCo, is deposited on large particles of XC 72, indicating dispersion of PPcCo on XC 72.

3.4. Kinetic parameters obtained through the Koutecky–Levich approach

The kinetic parameters of the O₂ reduction reaction on PPcCo were investigated using a rotating disk electrode coated with PPcCo/C in O₂-saturated 0.5 mol L⁻¹ H₂SO₄. The resulting polarization curves and Koutecky–Levich plots are presented in Fig. 4.

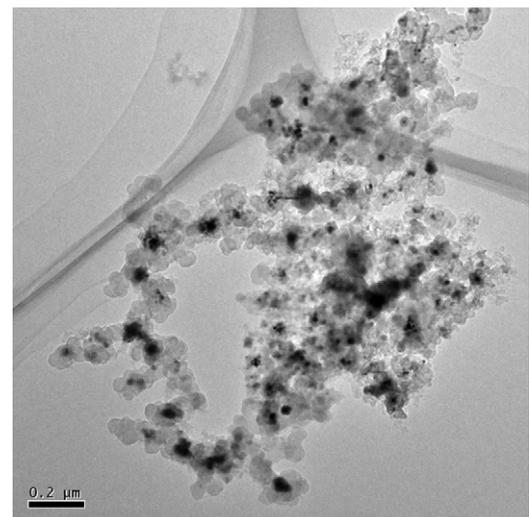


Fig. 3. TEM micrograph of PPcCo/C.

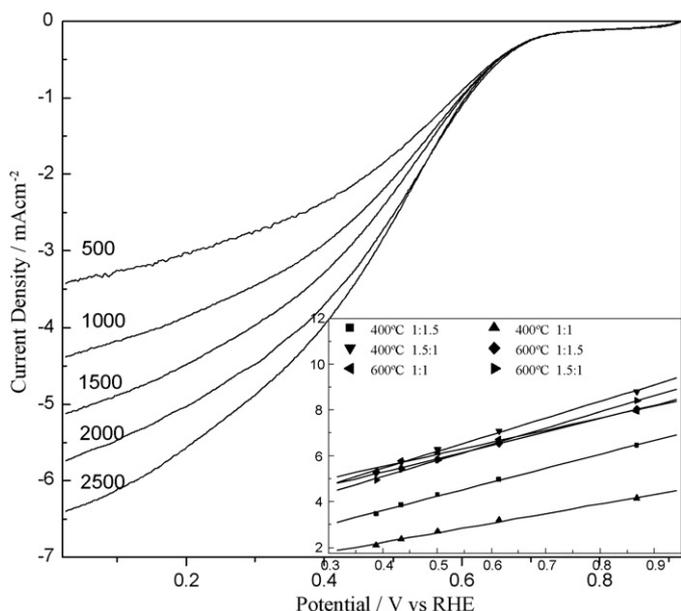


Fig. 4. Polarization curves at different rotation rates ω recorded at a PPcCo/C electrode in O_2 -saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ($T = 20^\circ\text{C}$, $v = 5 \text{ mV s}^{-1}$). Inset right: Koutecky–Levich plots of different weight ratio of PPcCo/C catalysts heat-treated at different temperature.

RDE current (I) is related to the diffusion-limited current (i_{diff}) and the kinetic current (i_{kin}), according to the Koutecky–Levich equation. Limiting currents presented in Fig. 4 were plotted against the square root of the rotation rate, as shown in Fig. 4 inset (right), depicting a linear relationship. The straight line complies with the Koutecky–Levich equation [21], which can be written as follows:

$$\frac{1}{I} = \frac{1}{IK} + \frac{1}{Id} = \frac{1}{IK} + \frac{1}{B\omega^{1/2}} \quad (1)$$

$$I_d = c0.62nFAcO_2\omega^{1/2}DO_2^{2/3}\gamma^{-1/6} \quad (2)$$

$$I_K = 10^3 nFAK\tau \quad (3)$$

In these equations, F is Faraday's constant, B is K–L slope, A is electrode area, n is number of electrons involved in ORR, CO_2 is oxygen concentration, ω is electrode rotation speed, K is global rate of the reaction, and τ is surface concentration. Using a bulk O_2 solubility of $1.1 \times 10^{-6} \text{ mol cm}^{-3}$, diffusion coefficient (DO_2) of $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and a kinematics viscosity (γ) of $0.01 \text{ cm}^2 \text{ s}^{-1}$ in H_2SO_4 solution were obtained [18]. By combining Eqs. (1)–(3), and by using the slopes from Fig. 4 (right inset), the number of electrons transferred was obtained. Results for the overall electron transfer number n and the onset potential obtained for PPcCo/C are listed in Table 1. The number of electrons transferred in different catalysts is around 3.7, indicating that PPcCo/C catalyzes O_2 reduction mainly through a four-electron process in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ [22]. The best catalyst, based on Table 1, was obtained by heat treatment at 400°C under weight ratio 1:1 for PPcCo/C.

Table 1
Dependence of the activity of catalysts for ORR at a rotating disc electrode on their composition and heat-treating temperature.

Temperature	Ratio (PPcCo/C)	n	Onset potential (V)
400 °C	1:1.5	3.6	0.76
	1:1	3.7	0.81
	1.5:1	3.5	0.78
600 °C	1:1.5	3.4	0.75
	1:1	3.6	0.76
	1.5:1	3.2	0.77

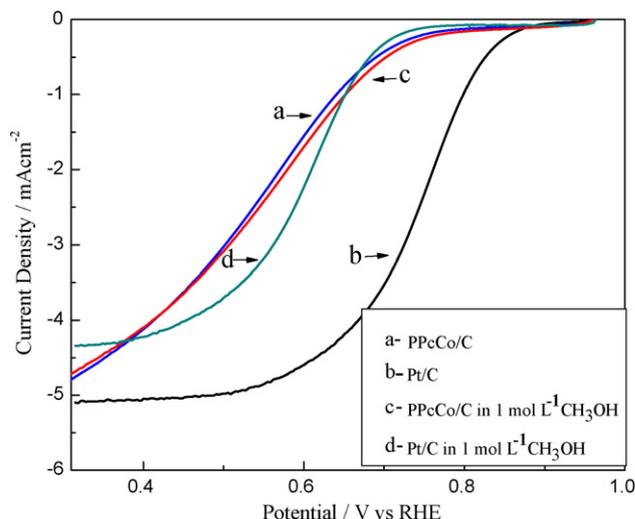


Fig. 5. Polarization curves at rotation rates fixed at 1500 rpm recorded on PPcCo/C and Pt/C electrode in the presence and absence of 1.0 mol L^{-1} methanol O_2 -saturated $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ($T = 20^\circ\text{C}$, $v = 5 \text{ mV s}^{-1}$).

3.5. Methanol tolerance of PPcCo/C catalysts

The methanol tolerance test result is shown in Fig. 5. In the absence of methanol, the onset of the O_2 reduction curve at the PPcCo-based electrode starts at a higher overpotential than at a platinum-based electrode, which is close to 0.81 V vs. RHE for the former and 0.94 V vs. RHE for the latter. In the presence of methanol, the polarization curve obtained on the PPcCo/C electrode was not affected by the presence of 1.0 mol L^{-1} methanol in the electrolyte, indicating that the PPcCo/C catalyst is completely insensitive toward methanol. In contrast, for the platinum-based electrode, the presence of 1.0 mol L^{-1} methanol in the electrolyte led to a shift of the onset of O_2 reduction to a lower potential of about 0.2 V . Under these conditions, the onset of the O_2 reduction curve was potentially 0.08 V higher on a PPcCo/C-based electrode than on a Pt/C-based electrode. This insensitivity enables PPcCo to be used as an alternative to platinum for ORR in methanol-containing media.

3.6. Stability of the PPcCo catalyst

Monomer metallophthalocyanine (MPC) catalysts are known to present decreases in their catalytic activity for ORR during cycling or long-term measurements [21]. This loss in oxygen reduction activity may be attributed to either the desorption of MPC from the electrode, or the destruction of the macrocycle and demetallation of phthalocyanine under electrochemical conditions in O_2 -saturated acidic media.

In order to investigate if the degradation results from demetallation of PPcCo, stability experiments were carried out using CV and LSV methods in O_2 -saturated H_2SO_4 . Cyclic voltammograms are exhibited in Fig. 6. As illustrated, no electrocatalytic activity loss was observed after cyclic voltammetry scanning at 10,000 cycles (4 days). This is similar to results from previous studies that do not show any performance loss or catalyst degradation after more than 150 cycles [22]. Fig. 7 shows the chronoamperometry curve recorded at 0.5 V vs. RHE. It was found that performance deterioration was not as severe as earlier indicated by previous literature (i.e., the oxygen reduction current is about 65% lower after 3 h than at the beginning of the measurements) [23]. Fig. 8 presents the polarization curves for the O_2 reduction on a PPcCo/C rotating disc electrode. As illustrated, the O_2 reduction current shows almost no change from cycle 1 to cycle 200, compared to the results

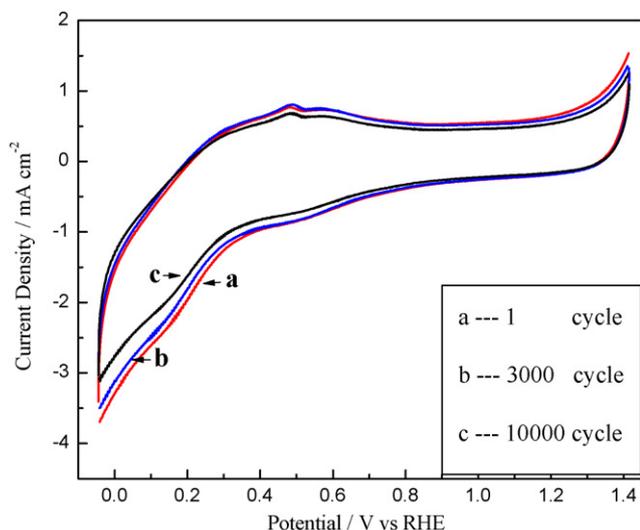


Fig. 6. Study of the electrode stability: cyclic voltammograms for oxygen reduction on a PPcCo/C rotating disk electrode recorded at 1500 rpm in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte ($T = 20\text{ }^{\circ}\text{C}$, $\nu = 5\text{ mV s}^{-1}$).

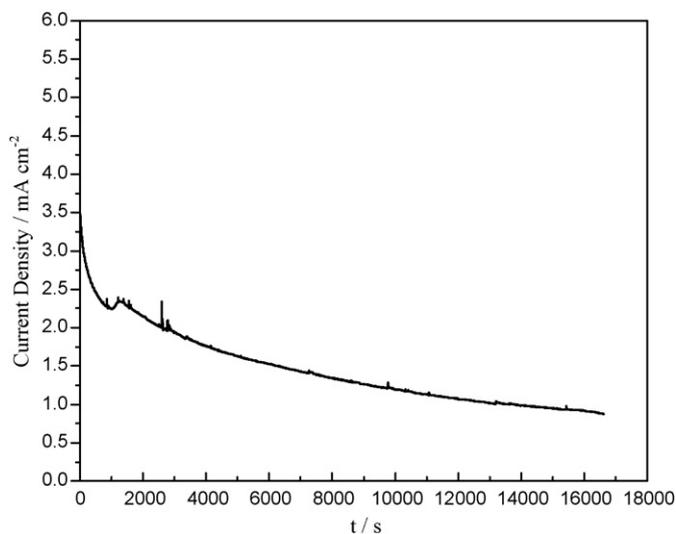


Fig. 7. Chronoamperometric curve (i/t) of the ORR in 0.5 mol L⁻¹ H₂SO₄ O₂-saturated electrolyte on a PPcCo/C electrode at $E = 0.5\text{ V}$ vs. RHE.

obtained by Baranton et al. [24], who found that the catalytic activity of PPcCo/C electrodes experiences a drastic decrease from cycle 1 to cycle 11. Two aspects contribute to the significant stability of PPcCo/C. First, its molecule is a planar conjugated system made up of delocalized aromatic π -electrons with delocalized energy lower than the monomer; therefore, the PPcCo/C catalyst is stable. Second, the bonding force between PPcCo and XC 72 is strong, primarily owing to PPcCo that was activated by heat treatment after adsorption onto XC 72; this step makes PPcCo resistant to desorption.

4. Conclusion

PPcCo catalysts were prepared and their electrocatalytic activities for O₂ reduction were determined. Based on XPS analysis and TG data, the active site of PPcCo/C catalysts is composed of Co-N₄ in the phthalocyanine ring. In O₂-saturated H₂SO₄, the onset potential of PPcCo/C catalysts for O₂ reduction is 0.81 V. PPcCo/C catalyzes O₂ reduction mainly through a four-electron process in 0.5 mol L⁻¹ H₂SO₄, and PPcCo/C catalysts generally offered as good catalytic activity for ORR as Pt/C in the presence of 1 mol L⁻¹ methanol. Our

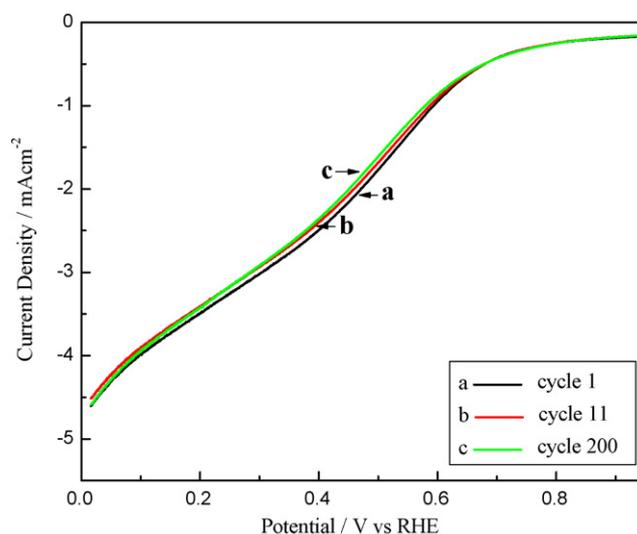


Fig. 8. Study of the electrode stability: first 200 cycles polarization curves for the oxygen reduction on a PPcCo/C rotating disk electrode recorded at 1500 rpm in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte ($T = 20\text{ }^{\circ}\text{C}$, $\nu = 5\text{ mV s}^{-1}$).

findings suggest that PPcCo/C is a promising catalytic material due to its sufficient activity, tolerance towards methanol, and long-term electrocatalytic performance in acidic medium.

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