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Article (Special Issue of the 17th Chinese National Youth Conference on Catalysis (17th CNYCC))

An alternate aqueous phase synthesis of the Pt₃Co/C catalyst towards efficient oxygen reduction reaction

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ARTICLE INFO

Article history:

Received 22 January 2019

Accepted 28 February 2019

Published 5 December 2019

Keywords:

ORR electrocatalyst

Pt-Co alloy

Aqueous phase synthesis

Dimethylamine borane

Structure and property

ABSTRACT

Carbon supported Pt-Co alloys are among the most promising electrocatalysts towards oxygen reduction reaction (ORR) for the application in low temperature fuel cells and beyond, thus their facile and green synthesis is highly demanded. Herein we initially report an alternate aqueous phase one-pot synthesis of such catalysts (containing nominally ca. 20 wt.% Pt) based on dimethylamine borane (DMAB) reduction. The as-obtained electrocatalyst (denoted as Pt₃Co/C-DMAB) is compared with the ones obtained by NaBH₄ and N₂H₄·H₂O reduction (denoted as Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O, respectively) as well as a commercial Pt/C, in terms of the structure and electrocatalytic property. It turns out that Pt₃Co/C-DMAB exhibits the highest ORR performance among all the tested samples in an O₂-saturated 0.1 mol/L HClO₄, with the mass activity (specific activity) ca. 4 (6) times as large as that for Pt/C. After 10000 cycles of the accelerated degradation test, the half-wave potential for ORR on Pt₃Co/C-DMAB decreases only by 4 mV, in contrast to 24 mV for that on Pt/C. Pt₃Co/C-NaBH₄ or Pt₃Co/C-N₂H₄·H₂O shows a specific activity comparable to that for Pt₃Co/C-DMAB, but a mass activity similar to that for Pt/C. ICP-AES, TEM, XRD and XPS characterizations indicate that Pt₃Co nanoparticles are well-dispersed and alloyed with a mean particle size of ca. 3.4 ± 0.4 nm, contributing to the prominent electrocatalytic performance of Pt₃Co/C-DMAB. This simple aqueous synthetic route may provide an alternate opportunity for developing efficient practical electrocatalysts for ORR.

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1. Introduction

The commercialization of proton exchange membrane fuel cells (PEMFCs) is largely hindered by high cost and low abundance of Pt [1], as well as insufficient kinetics [2] for oxygen reduction reaction (ORR) on Pt-containing catalysts. Despite numerous efforts so far to develop a variety of ORR catalysts

[2–10], Pt-M (3d metals) alloy catalysts appear to be the most attractive catalysts for practical applications with improved catalytic activity and stability and lowered Pt usage compared to the monometallic Pt ones. Pt-M alloys show an appropriately lowered Pt *d*-band center due to the charge transfer [11] from M to Pt and the lattice contraction of Pt [12], thus providing a suitable binding energy (BE) for O-containing intermediate

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This work was supported by the National Basic Research Program of China (973 Program, 2015CB932303), the National Natural Science Foundation of China (NSFC) (21733004 and 21473039), and the International Cooperation Program of Shanghai Science and Technology Committee (STCSM) (17520711200).

DOI: S1872-2067(19)63338-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 12, December 2019

species [13]. In fact, carbon supported Pt-Co alloy nanoparticles have been used as the ORR catalysts for PEMFCs to drive commercial electric vehicles, consistent with the suggestion that this bimetallic alloy is located near the peak position [14,15] in the predicted Sabatier volcano-plot of ORR activity versus BE of oxygen species.

Currently, several typical methods are employed to synthesize carbon supported Pt-Co alloy nanocatalysts, namely organic solvothermal (or modified nanocapsule) [4,6,13,16–20], polyol reduction [21–24], water-in-oil microemulsion (or reverse micelle) [25–27], impregnation-reduction [28–31] and aqueous phase [32–36] syntheses. The organic solvothermal synthesis can yield homogeneous Pt-bimetallic alloy nanocatalysts but normally involves non-environmentally friendly organic solvents, capping agents and additives as well as costly Pt(acac)₂ and Co(acac)₂ precursors. Polyol reduction synthesis of carbon supported Pt-Co nanoparticles using ethylene glycol as the solvent and reductant is a good addition to the organic solvothermal method considering relatively easy removal of polyol with water, but a high-temperature post-annealing is often required [21] and the resulting Co composition is typically lower than the desired [23]. Microemulsion synthesis is favorable for controlling nanoparticle sizes through tuning the size of aqueous micelles in oil phase by varying the ratio of water to surfactant [25,26]. However, random encapsulation of the precursors into reverse aqueous micelles may cause notable compositional inhomogeneity among the resulting metallic nanoparticles. Furthermore, time-consuming post-cleaning procedures are required for both organic solvothermal and microemulsion syntheses, to remove as much as possible the organic residues on metal and carbon surfaces. The impregnation-reduction method [28–31] involves the impregnation of carbon black in a Pt and Co salt solution followed by high-temperature calcination in a H₂ atmosphere. The sintering of PtCo nanoparticles may compromise the mass activity for ORR despite a high specific activity arising from an ordered structure.

The aqueous phase synthesis is here referred to the use of water as the only solvent for the precursors, complexing agents and reductants in one-pot synthesis without introducing strong surfactants. Aqueous phase synthesis of carbon supported PtCo alloy nanocatalysts is environmentally friendly and economical, but underdeveloped. The most challenging issue for this method is to attain well-dispersed Pt-Co nanoparticles on carbon black support with desired Pt/Co ratio, good alloying degree and reasonably small but narrowly distributed nanoparticle size. NaBH₄ is a widely used reducing agent [37] in this method, able to yield monometallic Pt catalysts [38] with a mean nanoparticle size of ca. 3–4 nm. Nevertheless, the extension to the synthesis of Pt-M bimetallic alloy catalysts normally leads to metallic particle sizes larger than 6 nm [32,33] with rather poor dispersion and low alloying degree probably owing to its excessive reducing power. Although subsequent annealing of the as-prepared Pt-Co/C catalysts at 500 °C in mixed N₂ and H₂ atmosphere was reported to increase the alloying degree, the particle size increased from 6 to 10 nm [33], limiting the enhanced mass activity of the resulting catalysts. Addition of eth-

anol in water may help to decrease the particle size, but lose the control over the desired stoichiometry of the Pt-Co alloy [34,35]. N₂H₄·H₂O is another reductant often used in aqueous phase synthesis of Pt-Co/C [36], nonetheless, similar concerns persist on particle size, dispersion and alloying degree. Thus, it is of great interest to develop the aqueous phase synthesis by seeking a mild but sufficiently strong reducing agent for the synthesis of Pt-Co/C catalyst.

Dimethylamine borane (DMAB) was a widely used and water soluble reductant in chemical deposition of metal films in microelectronics manufacture, with a reducing power relatively weaker than that of NaBH₄ and N₂H₄·H₂O [39]. It had not been used for preparing electrocatalyst until we reported the synthesis of carbon supported B-doped Pd catalyst (Pd-B/C) in 2009 [40]. This catalyst was found to be efficient for formic acid oxidation reaction, hydrogen production from formic acid-formate solution [41], oxygen reduction reaction [42,43] and carbon dioxide reduction [44]. Recently, DMAB was applied to the synthesis of carbon supported Pt-Ni alloy catalyst with B-doping [45], yielding 3 times enhancement in mass activity towards ORR as compared to the commercial Pt/C. It is thus enticing to explore the feasibility of using DMAB in the aqueous phase synthesis of carbon supported Pt-Co alloy nanoparticles, in order to address the challenge mentioned above as well as to extend DMAB to be a common reductant for preparing practical catalysts.

In this work, DMAB is initially examined as the reducing agent in aqueous phase synthesis of Pt₃Co/C, Pt₂Co/C and Pt₄Co/C. For comparison, NaBH₄ and N₂H₄·H₂O are also tested respectively as the reductants to synthesize Pt₃Co/C in aqueous phase synthesis. The ORR activity and stability are evaluated on the three kinds of Pt₃Co/C catalysts and the state of art commercial Pt/C, and their structure and property correlation is briefly discussed.

2. Experimental

2.1. Preparation of catalysts

20 wt.% Pt/C was purchased from Johnson Matthey Company. Pt₃Co/C-DMAB with 20 wt.% Pt was synthesized in an aqueous phase using DMAB as the reductant [40,45]. Briefly, 125 mg of H₃BO₃, 60 mg of NH₄Cl, 0.18 ml of 1 g/25 ml CoSO₄·7H₂O and 3.192 ml of 1 g/100 ml K₂PtCl₄ were mixed and dissolved in 20 ml of Milli-Q water. The N₂-deaerated solution was stirred vigorously, and NH₃·H₂O was added dropwise to adjust the solution pH to 10. The solution was kept stirring until it turned dark green. Then, 58.5 mg of Vulcan XC-72 carbon was added into the solution. After sonication for 30 min, the mixture was kept in an ice-water bath and vigorously stirring for 1 h. Next, 10 ml of 0.1 mol/L DMAB was added dropwise into the suspension by a peristaltic pump at a rate of 0.5 ml min⁻¹. The suspension was kept stirring in the ice-water bath for another 4 h to ensure the complete reduction of Pt(II) and Co(II) species. After that, the slurry was stirred at 30 °C for 8 h. The powder was filtered out of the suspension, and rinsed with 0.1 mol/L CH₃COOH and copious amount of ultrapure

water. The as-obtained catalyst was dried in a vacuum oven at 70 °C for 8 h.

NaBH₄ and N₂H₄·H₂O were used as the reducing agent for preparing the Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O catalysts, respectively, with otherwise same procedures used for preparing Pt₃Co/C-DMAB. And all the alloy catalysts were heated at 240 °C in N₂ atmosphere for 2 h to increase the alloy degree, prior to the following measurements.

2.2. Catalyst characterizations

The metal loadings and the atomic ratios of Pt-based catalysts were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo Fisher iCAP 7400 spectrometer. Before the measurement, a catalyst was heated in aqua regia to dissolve the metals. Then, the solution was separated from the carbon black by filtration. The morphology and size distributions of the catalysts were characterized by transmission electron microscopy (TEM) using a Tecnai G2 F20 S-Twin microscope. The crystalline structures of the Pt-based nanoparticles were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance with Cu K_α radiation. The metallic electron structures of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi with Al K_α radiation and the C 1s peak at 284.6 eV was used as the reference for calibrating binding energies.

2.3. Electrochemical measurement

The electrochemical measurement was carried out on a CHI 760E electrochemical workstation. The catalyst ink was prepared by mixing and sonicating 2 mg of a Pt₃Co/C sample, 0.8 ml of water, 0.2 ml of isopropanol and 20 μl of 5 wt.% Nafion to form a rather uniform suspension ink. 10 μl of the ink was evenly casted on a glassy carbon rotating disk electrode (GC-RDE, 5 mm diameter) via a micropipette. Then, the ink was dried under an isopropanol gas atmosphere. The Pt loading was set to be ca. 20 μg cm⁻² on each electrode. The catalyst layer-coated GC-RDE served as the working electrode, a reversible hydrogen electrode (RHE) and a Pt sheet electrode were used as the reference and counter electrodes, respectively, in a three-compartment cell. All the electrochemical measurements were performed with 80% iR drop compensation. All the potentials reported in this work are relative to RHE unless specified otherwise.

Potential cycling was run in an Ar-saturated 0.1 mol/L HClO₄ between 0.02 and 1.20 V at a scan rate of 50 mV s⁻¹ until stable cyclic voltammograms (CVs) were obtained. The ORR polarization curves were recorded in an O₂-saturated 0.1 mol L⁻¹ HClO₄ solution at 10 mV s⁻¹ from 0.02 to 1.05 V. In anodic CO stripping voltammetry, the working electrode was first kept at 0.15 V while bubbling CO into the solution for 15 min to allow CO preadsorption, followed by bubbling N₂ for 45 min to remove the dissolved CO, and anodic CO stripping curves were recorded from 0.02 to 1.20 V at 10 mV s⁻¹. Accelerated degradation tests (ADTs) were conducted in an air-contained 0.1 mol/L HClO₄ with the potential cycling from 0.60 to 1.05 V at

50 mV s⁻¹ for 10000 cycles.

3. Results and discussion

3.1. physicochemical characterization

Fig. 1 shows the typical TEM micrographs of Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-DMAB and Pt₃Co/C-N₂H₄·H₂O. For the Pt₃Co/C-DMAB catalyst, metallic nanoparticles are rather uniformly dispersed on carbon black with a mean size of 3.4 ± 0.4 nm, slightly larger than the commercial Pt/C nanoparticles (3.0 ± 0.6 nm). Significant agglomeration of alloy nanoparticles occurs for Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O, with typical sizes of agglomerates reaching 15.9 and 50.0 nm, respectively. The agglomeration lowers the utilization of Pt, as will be demonstrated later. Notably, poor size and dispersion control over the Pt-Co alloy nanoparticles on carbon support could be attributed to excessive reducing power of N₂H₄·H₂O or NaBH₄ in the aqueous phase synthesis.

ICP-AES analysis shows that the Pt weight percentages of Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB are 19.6 wt.%, 18.0 wt.%, 15.8 wt.% and 19.1 wt.%, respectively, while the Pt/Co atomic ratios of Pt₃Co/C-DMAB, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-NaBH₄ catalysts were 3.0, 3.1 and 2.9, respectively. It is clear that DMAB enables the Pt and Co precursors to be completely reduced with a desired Pt weight percentage and a preset Pt/Co atomic ratio, which is otherwise hard to attain by means of aqueous phase synthesis without strong organic surfactants [32,33]. Unlike our previous DMAB-based synthesis of Pt₃Ni/C-DMAB in which Pt₃Ni nanoalloy was doped with 6–7 at.% B [45], negligible B-doping is found (< 2 at.%) for Pt₃Co nanoalloy.

XRD patterns of Pt/C, Pt₃Co/C-DMAB, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-NaBH₄ catalysts are shown in Fig. 2. The diffraction peaks around 39.8°, 46.3° and 67.5° observed for Pt/C are characteristic of Pt face-centered cubic (111), (200) and (220) planes. Neither separated Co nor ordered Pt₃Co features can be identified in the XRD patterns [21,28,29], indicating that the synthesized Pt₃Co nanoparticles largely compose of alloy phase. The characteristic diffraction peaks of Pt₃Co nanoparticles shift to higher values compared to those of Pt, in agreement with a smaller atomic size of Co in the alloy lattice. The lattice shrinkage was reported to enhance the intrinsic electrocatalytic activity of Pt towards ORR [12,13].

In order to semi-quantitatively evaluate the alloying degree, let us assume the same dependence of the lattice parameter on Co content for supported and unsupported Pt-Co alloys, the Co atomic fraction of carbon supported Pt-Co nanoparticles, x_{Co} , can be evaluated according to Vegard's law, i.e.,

$$x_{\text{Co}} = \frac{(a_0 - a)}{k} \quad (1)$$

where a_0 is the lattice parameter of the carbon supported Pt (JM), i.e., 0.3927 nm obtained from the above XRD analysis, and $k = 0.0368$ nm is a constant, obtained from the lattice parameters of unsupported Pt (0.3923 nm) and Pt₃Co alloy (0.3831 nm), assuming a linear dependence of lattice parameter on Co atomic fraction [34]. From the XRD analysis, α is 0.3890, 0.3886

Fig. 1. Transmission electron microscopy (TEM) images and corresponding histograms of Pt/C (a, b, c), Pt₃Co/C-DMAB (d, e, f), Pt₃Co/C-NaBH₄ (g, i) and Pt₃Co/C-N₂H₄·H₂O (h).

and 0.3863 nm for Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB, respectively. For fully alloying, $x_{\text{Co}} = 0.25$. The calculated x_{Co} is 0.17, 0.10 and 0.11 for Pt₃Co/C-DMAB, Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O, respectively. In other words, the Co alloying degree for Pt₃Co/C-DMAB reaches about 69%, significantly higher than that for Pt₃Co/C-NaBH₄ (ca. 40%) and for Pt₃Co/C-N₂H₄·H₂O (ca. 44%). To form a bimetallic alloy with a higher alloying degree, thermodynamically, the reduction potentials of the two precursor metal ions should be made closer; kinetically, a relatively slower nucleation and growth rate allows for a better mixing of metallic atoms, alleviating the formation of monometal phases. Since the redox potentials for [PtCl₄]²⁻/Pt and Co²⁺/Co differ a lot (0.76 and -0.28 vs. SHE, respectively), NH₃·H₂O was added to form Pt(II) and Co(II) complex ions to narrow the reduction potential gap for the two metals. Moreover, a lower reduction rate was achieved by using a milder but sufficiently strong reducing agent, like DMAB in this work. In a recent publication regarding the organic phase synthesis of Pt-Co alloy using NaBH₄ and N₂H₄, the authors also reported a relatively higher alloying degree with the milder reductant N₂H₄ [46].

Fig. 2. X-ray diffraction (XRD) patterns of Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O, Pt₃Co/C-DMAB and Pt/C. The labelled XRD features correspond to (111), (200) and (220) planes of the face-centered cubic Pt (wine dash lines, PDF #87-0646) and Co (blue dot lines, PDF #15-0806), respectively. The XRD pattern for Pt/C is adapted from a previous report [45].

As Scherrer's equation suggests, the nanoparticle size is negatively correlated with the bandwidth at half height of a diffraction peak. This indeed applies well to the Pt₃Co/C-NaBH₄ catalyst. Nevertheless, the bandwidths are more or less close to each other for the Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB catalysts, suggesting that the large agglomerates seen from the TEM images are likely composed of loosely aggregated finer alloy nanoparticles.

XPS was applied to investigate the modification of electronic property of Pt by Co alloying. The Pt core level XPS spectra for the Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB samples are shown in Fig. 3. By deconvoluting the Pt 4f_{7/2} and Pt 4f_{5/2} doublets in the Pt 4f region XPS spectra, the presence of Pt⁰, Pt²⁺ and Pt⁴⁺ components can be revealed. As listed in Table 1, the Pt⁰ 4f_{7/2} peaks are located at 71.7, 71.5, 71.4 and 71.3 eV for Pt₃Co/C-DMAB, Pt₃Co/C-N₂H₄·H₂O, Pt₃Co/C-NaBH₄ and Pt/C, respectively. Compared to that of Pt/C, the Pt⁰ 4f_{7/2} peak for Pt₃Co/C shifts to a higher value. It was reported that the Pt *d*-band center shifts in the same direction as the Pt core level does, suggesting a downshift of the Pt *d*-band with reference to the Fermi level [11]. Our XPS results and related explanation are in agreement with those by Watanabe's group [11]. The appropriate downshift of Pt *d*-band center contributes to a modest weakening of adsorption strength of O-containing species, which may significantly enhance the ORR activity on Pt sites [11–15]. In fact, according to

Fig. 3. Pt core level region X-ray photoelectron spectroscopy (XPS) spectra for Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB. XPS spectrum for Pt/C is adapted from a previous report [45].

Table 1

Binding energies and corresponding percentages of Pt⁰ deconvoluted from Pt 4f_{7/2} XPS spectra for Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB.

Catalyst	Core level	Species	Binding energy (eV)	Percentage (%)
Pt/C (JM)	Pt 4f _{7/2}	Pt ⁰	71.3	46
Pt ₃ Co/C-NaBH ₄	Pt 4f _{7/2}	Pt ⁰	71.4	55
Pt ₃ Co/C-N ₂ H ₄ ·H ₂ O	Pt 4f _{7/2}	Pt ⁰	71.5	64
Pt ₃ Co/C-DMAB	Pt 4f _{7/2}	Pt ⁰	71.7	64

the theoretical prediction, nearly optimal binding energy occurs on Pt₃Co alloy, compared to that on other Pt-M bimetallic alloys [14,15]. Also noted is that the Pt⁰ component in each Pt₃Co/C catalyst is appreciably higher than that in Pt/C, consistent with a weakened adsorption of O-containing species on the former.

3.2. Electrochemical performance

Pt₂Co/C, Pt₃Co/C and Pt₄Co/C using DMAB-based aqueous phase method were first synthesized and screened for ORR. The results shown in Fig. S1 (see Supporting Information) indicate that under the otherwise same conditions Pt₃Co/C exhibits the highest mass and specific activities among the three, in harmony with previous reports [13,19]. Next, we focus on the comparison of the Pt₃Co/C catalysts synthesized in aqueous phase using different reducing agents. Fig. 4(a) shows the cyclic voltammograms (CVs) for Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB catalyst layers in an Ar-saturated 0.1 mol L⁻¹ HClO₄. All the catalysts exhibit hydrogen adsorption-desorption and oxide reduction features typical of Pt [21], suggesting the presence of Pt-rich skin layers over the Pt₃Co nanoparticles, and the core and shell-like structure may promote the ORR [21,28]. Pt₃Co/C-DMAB shows a slightly smaller cathodic current as compared to Pt/C in the above two potential regions. In contrast, both Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-NaBH₄ show much smaller cathodic currents due to the larger nanoparticles (or agglomerates) as detected by TEM. Given the same Pt loading, larger nanoparticles expose smaller electrochemical active areas, decreasing the Pt mass utilization. The Pt-O reduction peak shifts positively on the three Pt₃Co/C catalysts with respect to that on Pt/C, corroborating again that the binding strength of O-containing species on Pt sites is weakened due to the Co alloying. A bit more negative Pt-O reduction peak on Pt₃Co/C-DMAB than that on Pt₃Co/C-NaBH₄ or Pt₃Co/C-N₂H₄·H₂O may be assigned to slightly stronger adsorption of O-containing species on smaller Pt₃Co nanoparticles [6], in line with the above TEM observation.

The electrochemical surface area (ECSA) of each catalyst was evaluated by measuring the anodic stripping charge of pre-adsorbed CO monolayer according to the following equation,

$$\text{ECSA} = \frac{Q_{\text{CO}}}{Q_0 m_{\text{Pt}}} \quad (2)$$

where Q_0 is the theoretical charge for oxidizing a CO monolayer (420 $\mu\text{C cm}^{-2}$), m_{Pt} is the Pt loading on the glassy carbon electrode, and Q_{CO} is the charge of stripping a CO monolayer on

Fig. 4. (a) Cyclic voltammograms (CVs) for the Pt/C, Pt₃Co/C-DMAB, Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O catalysts measured in an Ar-saturated 0.1 mol L⁻¹ HClO₄ at 50 mV s⁻¹; (b) Anodic CO stripping voltammograms in an Ar-saturated 0.1 mol L⁻¹ HClO₄ at 10 mV s⁻¹.

Pt-Co nanoparticles. The ECSAs on Pt/C, Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O and Pt₃Co/C-DMAB are estimated to be ca. 79, 16, 14 and 51 m² g⁻¹ (Fig. 4(b)). The onset and peak potentials shift negatively on the three Pt₃Co/C catalysts compared to those on Pt/C, attributable at least partly to relatively weaker adsorption of CO on Pt-rich skin due to a lowered *d*-band center.

Positive-going linear sweep voltammograms (LSVs) for different catalyst layers were measured in an O₂-saturated 0.1 mol L⁻¹ HClO₄ solution at 10 mV s⁻¹ and 1600 r min⁻¹. All the ORR curves in Fig. 5(a) are presented with background correction. Pt₃Co/C-DMAB displays excellent activity with the half-wave potential shifted positively by 36 mV, as compared to Pt/C (Fig. 5(a)), while Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O show more or less the same half-wave potential as that on Pt/C. To analyze the ORR activities of all the catalysts, the kinetic currents at 0.90 V vs RHE are calculated by applying the Koutecky-Levich equation,

$$\frac{1}{-i} = \frac{1}{-i_k} + \frac{1}{-i_d} = \frac{1}{-i_k} + \frac{1}{0.62nFAD^{3/4}\nu^{-1/4}C_{O_2}\omega^{1/2}} \quad (3)$$

where *i_k* is the kinetic current, *i_d* the limiting diffusion current, *i* the measured current, *F* the Faraday constant (96500 C mol⁻¹), *n* the number of electrons transferred per O₂ molecule, *A* the

geometric area of the rotating disk electrode (0.196 cm²), *D* the diffusion coefficient of O₂ (1.93 × 10⁻⁵ cm² s⁻¹), *ν* the dynamic viscosity of the electrolyte (0.01 cm² s⁻¹), *C_{O2}* the saturated concentration of O₂ in 0.1 mol L⁻¹ HClO₄ (1.22 × 10⁻⁶ mol cm⁻³), and *ω* the angular velocity of the rotating disk electrode (rad s⁻¹).

The mass activity (MA) and specific activity (SA) are calculated by normalizing the kinetic current to the actual Pt mass loaded on GC electrode and the ECSA, respectively. The MAs and SAs of Pt₃Co/C-NaBH₄, Pt₃Co/C-N₂H₄·H₂O, Pt₃Co/C-DMAB and Pt/C are shown in Fig. 5(b). Several parameters related to the ORR properties of these catalysts are listed in Table 2. For Pt₃Co/C-DMAB, the MA is 0.85 A mg⁻¹_{Pt} at 0.90 V, 4 times as high as that on Pt/C while the SA is 1.67 mA cm⁻²_{Pt}, that is 6 times as high as that on Pt/C. Meanwhile, the MA for Pt₃Co/C-NaBH₄ or Pt₃Co/C-N₂H₄·H₂O is close to that for Pt/C; however, the former two catalysts exhibit an SA value similar to that for Pt₃Co/C-DMAB, which is 5–6 times as high as that for Pt/C. The high SA (the intrinsic activity) on a Pt₃Co/C catalyst can be assigned to the lattice compression and charge-transfer by Co alloying. Nevertheless, based on the above TEM and XRD results, the low MA for Pt₃Co/C-NaBH₄ or Pt₃Co/C-N₂H₄·H₂O should arise from poor dispersion or even aggregation of Pt₃Co nanoparticles on carbon black given that the order of reducing

Fig. 5. (a) Linear sweep voltammograms (LSVs) for Pt/C, Pt₃Co/C-DMAB, Pt₃Co/C-NaBH₄ and Pt₃Co/C-N₂H₄·H₂O measured in an O₂-saturated 0.1 mol L⁻¹ HClO₄ at 10 mV s⁻¹ with a rotating rate of 1600 r min⁻¹; (b) Pt mass and specific activities at 0.90 V.

Table 2
ORR parameters and ECSAs in 0.1 mol L⁻¹ HClO₄ for different catalysts.

Catalyst	ECSA _{CO} (m ² g ⁻¹)	E _{1/2} (mV)	MA (A mg ⁻¹ Pt)	SA (mA cm ⁻² Pt)
Pt/C (JM)	79	889	0.21	0.27
Pt ₃ Co/C-NaBH ₄	16	892	0.24	1.50
Pt ₃ Co/C-DMAB	51	925	0.85	1.67
Pt ₃ Co/C-N ₂ H ₄ ·H ₂ O	14	884	0.21	1.50

power decreases in the sequence of NaBH₄, N₂H₄·H₂O and DMAB [39]. In fact, the onset oxidation potentials of NaBH₄, N₂H₄·H₂O and DMAB are -1.18, -0.94 and -0.83 V (vs. SCE) at Co, respectively, while at Pt the corresponding values are -0.98, -0.80 and -0.63 V (vs. SCE). In other words, DMAB served as a mild but sufficiently strong reductant in our aqueous phase synthesis, responsible for the balanced control over the size, dispersion, weight percentage and alloying degree of resulted Pt₃Co nanoparticles on carbon support. As such, this ensures a reliable comparison of the catalyst performance for ORR on Pt₃Co/C-DMAB and Pt/C.

To evaluate the stability of the catalysts, accelerated degradation test (ADT) was carried out by scanning potential from

Table 3
ORR parameters and ECSAs in 0.1 mol L⁻¹ HClO₄ after 10000 cycles.

Catalyst	ECSA _{CO} (m ² g ⁻¹)	E _{1/2} (mV)	MA (A mg ⁻¹ Pt)	SA (mA cm ⁻² Pt)
Pt/C JM	52	865	0.11	0.21
Pt ₃ Co/C-NaBH ₄	17	882	0.19	1.12
Pt ₃ Co/C-DMAB	38	921	0.64	1.68

0.6 to 1.05 V at 50 mV s⁻¹ for 10000 cycles in air-contained 0.1 mol L⁻¹ HClO₄ solution. Owing to severe agglomeration of metallic nanoparticles, the Pt₃Co/C-N₂H₄·H₂O catalyst was not used for this test. As shown in Fig. 6, the half-wave potential (E_{1/2}) for Pt₃Co/C-DMAB decreased only by 4 mV after the ADT compared to 10 mV for Pt₃Co/C-NaBH₄ and 24 mV for Pt/C. In addition, Pt₃Co/C-DMAB maintains an MA of 0.64 A mg⁻¹Pt after the ADT (see Table 3), while Pt₃Co/C-NaBH₄ and Pt/C yield 0.19 and 0.11 A mg⁻¹Pt, respectively. Moreover, Pt₃Co/C-NaBH₄ and Pt/C suffer losses of 25% and 22% (Fig. 7) for their SA values, respectively, while the SA for Pt₃Co/C-DMAB increased by 0.6%.

It can be anticipated that partial dissolution and redeposition of metal species occur during the ADT. As a result, metallic nanoparticles tend to grow due to the so-called Ostwald effect, accompanied inevitably with decreasing ECSA and MA. Pt₃Co/C-NaBH₄ possesses initially larger Pt₃Co nanoparticles with a lower alloying degree, and vice versus for Pt₃Co/C-DMAB. Lower alloying degree suggests leaching more Co, and smaller nanoparticles tend to aggregate more readily during the ADT. Presumably, these two effects may account for the different changes of their SA and MA values after the two catalysts are subjected to repetitive potential cycling. This issue shall be further addressed in a subsequent study. Nevertheless, the MA retained for Pt₃Co/C-DMAB is still 3 (5) times more than that for Pt₃Co/C-NaBH₄ (Pt/C). Notably, the formation of an intermetallic phase after post annealing treatment at 700 °C may help to stabilize the mass activity of Pt₃Co/C-700 despite a relatively lower value [21].

Briefly, besides the harmonic electronic effect, the rather uniform size, good dispersion and alloying degree of Pt₃Co nanoparticles should contribute to the superb overall performance of the Pt₃Co/C-DMAB catalyst.

Fig. 6. LSVs for Pt/C, Pt₃Co/C-NaBH₄ and Pt₃Co/C-DMAB at 10 mV s⁻¹ in an O₂-saturated 0.1 mol L⁻¹ HClO₄ before and after 10000 potential cycles. Disk rotating rate: 1600 r min⁻¹. The inset shows the comparison of CVs before and after ADT. The upper panel is adapted from a previous report [45].

Fig. 7. MAs and SAs for ORR on Pt/C, Pt₃Co/C-NaBH₄ and Pt₃Co/C-DMAB before and after ADT as well as the corresponding degradation percentages.

4. Conclusions

Carbon supported Pt-Co nanoalloys are very promising practical catalysts towards ORR in the cathode of PEMFCs and beyond. Aqueous phase synthesis of Pt-Co/C is a green and economical method, but is extremely difficult to provide a balanced control over the desired size, dispersion, composition and alloying degree. To address this challenge, in this work we have examined DMAB as a new reductant in aqueous phase synthesis to replace traditional NaBH_4 or $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ by comparative study. Owing to its milder but sufficiently strong reducing power, DMAB produces relatively small and well-dispersed Pt_3Co nanoparticles with the desired Pt and Co compositions and a higher alloying degree. $\text{Pt}_3\text{Co}/\text{C}$ -DMAB yields the highest overall ORR performance in an O_2 -saturated $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ among all the catalysts tested including Pt/C , $\text{Pt}_3\text{Co}/\text{C}$ - NaBH_4 , $\text{Pt}_3\text{Co}/\text{C}$ - $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and $\text{Pt}_3\text{Co}/\text{C}$ -DMAB in terms of mass activity and specific activity. The present study presents an alternate route to the aqueous phase synthesis of carbon supported Pt-based alloy catalysts in one pot, promising for scale-up fabrication and application to future PEMFCs.

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Graphical Abstract

Chin. J. Catal., 2019, 40: 1895–1903 doi: S1872-2067(19)63338-3

An alternate aqueous phase synthesis of the $\text{Pt}_3\text{Co}/\text{C}$ catalyst towards efficient oxygen reduction reaction

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$\text{Pt}_3\text{Co}/\text{C}$ with well-controlled size, dispersion and alloying degree was obtained using aqueous phase synthesis with DMAB being the reductant, exhibiting excellent electrocatalytic activity and durability for ORR.

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高效氧气还原催化剂Pt₃Co/C的水相法新合成

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摘要: 碳载型Pt-Co合金催化剂是一种针对低温燃料电池最实用的阴极氧还原(ORR)催化剂, 因此很有必要发展一种简易、环保的合成方法。目前碳载型Pt-Co合金催化剂的合成方法主要包括有机溶剂热法、多元醇还原法、反向微乳液法、浸渍还原法和水相法。其中, 有机溶剂热法虽然能较好地实现含Pt双金属纳米合金催化剂的合成, 但该方法所用的有机溶剂和封端剂会引起环境污染, 同时Pt(acac)₃和Co(acac)₃前驱体成本较高。多元醇还原法采用乙二醇作为溶剂和还原剂, 多元醇溶于水、较易去除是该方法的优点, 但该方法难以获得制定剂量比的PtCo合金, 且后续需较高温度退火以提高合金度。反向微乳液法能较好地控制颗粒粒径, 但金属纳米颗粒组成的均一性较难达成。同时, 有机溶剂热法与反向微乳液法均面临去除有机物步骤繁琐且耗时长的问題。浸渍还原法需在H₂气氛下高温煅烧含Pt和Co盐浸渍液的碳黑, 虽可形成PtCo有序化合金结构, 但易导致PtCo纳米颗粒的烧结, 限制催化剂的质量比活性。水相合成法采用水作为前驱体和络合剂的唯一溶剂, 并基于水溶性还原剂一锅法合成, 无需强表面活性剂。虽然水相合成法是一种环境友好、成本低廉的合成方法, 但其最大挑战是难以按投料金属比合成分散性良好、粒径较小及合金化程度高的PtCo纳米颗粒, 因此需要进一步的发展。本研究首次报道了以一种非经典的二甲基胺硼烷(DMAB)还原剂为基础的水相一锅法合成碳载型PtCo催化剂(Pt含量约为20 wt.%)的方法。重点合成了具有最优原子比的Pt₃Co/C-DMAB催化剂, 并与采用NaBH₄或N₂H₄·H₂O合成的催化剂Pt₃Co/C-NaBH₄和Pt₃Co/C-N₂H₄·H₂O以及商业化催化剂Pt/C在结构和电催化性能方面进行了对比研究。结果表明, Pt₃Co/C-DMAB在O₂饱和的0.1 mol L⁻¹ HClO₄溶液中表现出最好的电催化ORR性能, 质量比活性与面积比活性分别是商业化Pt/C的4倍和6倍。Pt₃Co/C-DMAB在含氧的0.1 mol/L HClO₄溶液中, 在0.60和1.05 V(vs. RHE)区间经历了10000圈的电位扫描后, ORR半波电位仅降低了4 mV, 而商业化Pt/C催化剂在该条件下半波电位降低了24 mV。Pt₃Co/C-NaBH₄和Pt₃Co/C-N₂H₄·H₂O虽然在面积比活性上与Pt₃Co/C-DMAB相近, 但前二者的质量比活性与商业化Pt/C的相近。ICP-AES、TEM、XRD和XPS等表征方法表明, 除了PtCo合金有利的电子效应外, Pt₃Co/C-DMAB上Pt₃Co纳米粒子良好的分散性、较小的平均粒径(约3.4 ± 0.4 nm)和较高的合金度是该催化剂对ORR表现出色性能的成因。这种环保简便的水相合成法将为开发实用型ORR催化剂提供新途径。

关键词: 氧还原电催化剂; 铂钴合金; 水相合成; 二甲基胺硼烷; 结构与性能

收稿日期: 2019-01-02. 接受日期: 2019-02-28. 出版日期: 2019-12-05.

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基金来源: 国家重点基础研究发展计划(2015CB932303); 国家自然科学基金(21733004, 21473039); 上海市“科技创新行动计划”政府间国际科技合作项目(17520711200).

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