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Effect of heat-treatment on the performance of PtM/C (M = Cr, Pd, Co) catalysts towards the oxygen reduction reaction in PEM fuel cell

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ABSTRACT

Effect of heat-treatment on the performance of the PtM/C (M = Cr, Pd, Co) catalysts towards the oxygen reduction reaction (ORR) in acid solution and in proton exchange membrane (PEM) fuel cell was explored. Compared with the Pt/C catalyst, the heat-treatment induced the formation of a more crystallite PtM structure and an agglomeration of Pt particles in all PtM catalysts, resulting in a decreased electrochemical surface area (ESA). Besides, the heat-treatment increased the electrical conductivity, which consequently affected the ORR activity and stability of the PtM/C catalyst. Among all prepared PtM/C catalysts, the PtCo/C catalyst exhibited the highest ORR activity, with a current density of around 392.8 mA/cm^2 (235.7 mW/cm^2) at 0.6 V under a H_2/air environment at 60 °C and ambient pressure with the ESA loss of 58.7% after 500 cycles of cyclic voltamogram (CV). Heat-treatment of this catalyst under a N_2 atmosphere slightly decreased the ORR activity by 3.41% but significantly increased the stability by ~17.2%.

1. Introduction

Currently, the commercialization of proton exchange membrane (PEM) fuel cells is limited by their high cost due to the utilization of platinum (Pt) metal and the sluggish kinetics of the ORR at the cathode side [1–3]. Thus, the Pt alloyed with other metals have been extensively explored in order to reduce the catalyst cost and to improve the ORR activity and stability [4]. The addition of a suitable second metal to Pt to form a Pt alloy (PtM) catalyst affects the electronic and geometric parameters of the Pt metal, such as the Pt-Pt interatomic distance, metal particle size and surface structure, and consequently affects the ORR activity and stability of the Pt/C catalyst [5]. The *d*-orbital coupling of two metals in the binary catalyst can significantly decrease the Gibbs free energy for the electron transfer steps in the ORR, resulting in enhanced ORR kinetics [6]. By using the periodic density functional theory (DFT) and electronic structure calculations [7], the electronic structure of the Pt surface was tuned after alloying Pt with non-noble transition metals and the overpotential for ORR was reduced due to the positive shift in the onset potential for forming OH_{ads} on the PtM catalysts relative to Pt. Both of these effects then led to an enhanced catalytic activity of the PtM alloys towards the ORR. Previously, the binary PtM catalysts have been classified, in terms of their ORR activity and tolerance to the chemical corrosion, into four categories [8] of: (*i*) highly corrosive and highly active (M = Fe, Co, V and Mn); (*ii*) corrosive and highly active (M = Zn, Cu, Mo and Ni); (*iii*) stable, but less active (M = Zr, Cr and Ta); and (*iv*) stable and active (M = W and Ti). Based on this classification, various efforts have been performed to prepare both binary catalysts (*ex.* PtCo/C [9,10], PtNi/C [9,10], PtFe/C [9], PtV/C [9], PtPd/C [11–13], PtW/C [14], PtAg/C [13,15,16], PtAu/CNT [17]) and ternary PtM catalysts (*ex.* PtAgFe/C [18], PtNiFe/C [19], PtMCo/C (M = Cr, Mn, Fe, Ni or Cu) [20], PdMoFe/C [21]) that have both sintering resistance and activity towards the ORR.

Recently, it was found that the catalyst synthesis procedure particular the heat-treatment is an important and sometimes necessary step during the catalyst synthesis for activity and stability improvement [5,22,23]. This is because a heat-treatment can change the surface- and textural properties of support. Besides, it can alter the catalyst properties such as particle size, morphology, dispersion, degree of alloying, active site formation, and stability [5]. Generally, the heat-treatment can be carried out via a traditional oven/furnace heating [24], microwave heat-treatment [25],

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plasma thermal treatment [26], and ultrasonic spray pyrolysis [27] under inert (N_2, Ar, or He) or reducing (H_2) atmosphere in the temperature range of 80–900 °C for 1–4 h [24]. For supportive material, a heat treatment of Vulcan XC-72 in NH_3 atmosphere at 1000 °C for 2 h can improve its resistance to the electrochemical oxidation in acid electrolyte [28]. As the use of this support for the Pt catalyst, the N-doped carbon nanospheres-supported Pt (Pt/HNC) exhibited a better stability than the Pt/C one during the accelerated durability test in 0.5 M H_2SO_4 solution. A heat-treatment at temperature up to 1000 °C can enhance a decrease of wall thickness, but increased weight loss and micropore volume of carbon nanotubes, which greatly the improved catalytic activity and remarkably enhanced electrochemical stability [29]. For the catalyst substance, the heat treatment of Pt/C catalyst affected insignificantly its size, nanostructure and morphology, but can improve the catalytic activity and stability in fuel cell [30–32]. A two-step reduction method followed by heat-treatment can achieve high catalytic activity for ORR and superior stability of PtCo/C catalyst because the heat-treatment changed its crystalline and lattice structure, which further enhanced the ORR activity and stability [33,34]. A relatively small different result was observed for the Pt_3Co catalysts. That is, the mass activity of the PtCo/C catalyst decreased drastically after heat-treatment because of small ESA [35]. However, for the Pt_3Cr/C catalysts, the mass activity increased even after heat-treatment due to an increase of the specific activity and a relatively small decrease of ESA. Besides, the heat-treatment can achieve a high mass activity of the $PtCo_{0.5}Cr_{0.5}$/C-900 catalyst by exhibiting specific activity and ESA value intermediate to PtCo/C-900 and PtCr/C-900 catalysts [35]. Increasing heat treatment time at 350 °C from 1 to 30 min decreased the cell performance in the high-current-density region rather than in the low-current-density region of the PTFE-bonded membrane electrode assemblies for PBI based high-temperature PEM fuel cells, due to the agglomeration of dispersed PTFE and adjacent catalyst particles [36], which resulted in an increase in mass transport resistance and concentration overpotential in the high-current-density region. The heat-treatment of the Pt_xCr/C catalyst ($x = 1–5$) under either H_2 or N_2 environments increased the degree of alloying, but decreased the ESA and led to the formation of different catalyst morphologies, which consequently affected the ORR activity and stability of the Pt_xCr/C catalyst [37]. However, the heat-treatment under N_2 atmosphere can enhance more stability of the Pt_xCr/C catalyst than in H_2 atmosphere [37]. The PtNi/C alloy catalysts prepared in a reducing atmosphere 95% Ar + 5% H_2 exhibited a high ORR activity in comparison with Pt/C catalyst [38]. This is because the Ni metal can decrease the absorption process of the oxygenated groups on Pt crystals, leading to the decrease of intermediate groups As a consequence, the ORR become easier with the mechanism of four-electron direct exchange at potential value of 1.229 V. A heat-treatment in H_2/N_2 atmosphere at 300 °C can promote the performances of PdSn-based catalysts for the ORR in the H_2/O_2 single PEM fuel cell, attributed to the alloying degree and/or to the presence of intermetallic compounds [39].

From the above literature, the best PtM catalyst, distinguished in terms of high ORR catalytic activity and stability is still contradictory and equivocal. In addition, the condition used to prepare catalysts, particular the heat-treatment, affected importantly the electronic and geometric properties of the obtained catalysts. Thus, this work was performed with two metal categories; (*i*) a low occupancy of *d*-orbitals (Co and Cr) and (*ii*) a fully occupied *d* orbitals (Pd). The effects of heat-treatment on the morphology of PtM/C catalysts, ORR activity and stability in both an acid solution and a PEM fuel cell under a H_2/air atmosphere were explored.

2. Experimental

2.1. Treatment of carbon powder and membrane

Due to the presence of organic and inorganic substances in the carbon powder and membrane after the production process, they were both treated before use. Briefly, the carbon powder (Vulcan XC72, Cabot) was treated in acid solution by dispersing the carbon powder in a 1:1 (v/v) HNO_3: H_2SO_4 solution (12 M) with constant stirring (250 rpm) for 6 h and then without stirring for 18 h [40]. The acid-treated carbon powder was harvested by vacuum filtration, rinsed with deionized water until the filtrate pH was constant. The ready-to-use treated carbon was obtained after drying in air at 110 °C for 2 h.

For the membrane treatment, a 5 cm × 5 cm membrane (Nafion 115, Electrochem, Inc.) sheet was soaked in 100 mL deionized water at 80 °C for 1 h and then immersed in 100 mL 3% (w/v) H_2O_2 (Carlo Erba) at 80 °C to eliminate the contaminated organic substances until a clear membrane was obtained. The organic-free membrane was then soaked in 100 mL of 0.5 M H_2SO_4 at 80 °C for 1 h to eliminate the contaminated inorganic substances and finally soaked again in 100 mL deionized water at 80 °C for 1 h to remove residual ions [41].

2.2. Preparation of the sublayer ink-coated gas diffusion layer

Approximately 2.668 μL of 60 wt.% polytetrafluoroethylene (Sigma-Aldrich) was mixed with 1 mL of deionized water and sonicated at room temperature for 30 min. Then, 2 mL of isopropanol (99.99%, Fisher) was added and sonicated continuously for 30 min. Subsequently, the treated carbon (section 2.1) was dispersed in this solution and sonicated at room temperature for 2–3 h. The well-mixed carbon slurry was applied onto the surface of a gas diffusion layer (GDL) (carbon cloth, Electrochem, Inc.) by the brushing method to get a sublayer ink loading of 2 mg/cm^2 and then dried at 300 °C for 1 h to obtain the ready-to-use sublayer ink-coated GDL.

2.3. Preparation of the PtM/C, catalyst-coated membrane and membrane electrode assembly

A series of PtM/C catalysts, where M is the second metal (Cr, Pd or Co) was prepared at a metal loading of 20 wt.% on the acid-treated carbon by impregnation-seeding technique [42], using $Cr(NO_3)_3 \cdot 9H_2O$ (Himedia), $PdCl_2$ (Fluka) and $CoCl_2 \cdot 6H_2O$ (Kanto) as the Cr, Pd and Co precursors, respectively. For each PtM/C catalyst, the $H_2PtCl_6 \cdot 6H_2O$ (Fluka) and the selected second metal precursor were mixed together in deionized water at a Pt: M atomic ratio of 3: 1. In the same period, the carbon slurry was also prepared by dispersing 0.1 g of acid-treated carbon in 2 mL deionized water and sonicating at 70 °C for 30 min. The pH of this slurry was adjusted to 2.0 using 6 M HCl (37 wt.%, QRëC). Next, approximately 10 vol.% of the PtM solution was mixed thoroughly with the carbon slurry under sonication at 70 °C for 30 min, and then reduced by of 20 mL of 0.2 M $NaBH_4$. The wet solid catalyst was separated from the slurry by filtration and washed with deionized water until the filtrate pH did not change and was further used as the seed catalyst. Next, the obtained seed catalyst was dispersed in 10 mL deionized water and mixed with the remaining portion of the PtM solution (~90 vol %). The obtained slurry was added slowly by 20 mL of 0.2 M $NaBH_4$ to reduce the remaining metal ions on the surface of the seed catalyst and then washed with deionized water and dried at 110 °C for 24 h to yield the ready-to-use PtM/C catalyst. For the heat-treatment catalyst (H-PtM/C), the selected PtM/C catalyst powder was heated at 900 °C for 2 h under nitrogen (N_2) gas