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Carbon-supported Co-phthalocyanine modified with pyridine, 2-acid pyridine and 2-methyl pyridine as novel cathode catalysts for alkaline PEM fuel cells

Ming Xu, Chao Li, Hongqiang Ren*, Lili Ding, Ke Xu, Jinju Geng

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, Jiangsu, PR China

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ABSTRACT

The catalyst materials are synthesized using carbon-supported cobalt phthalocyanine (CoPc) as the base material modified by pyridine (Py), 2-acid pyridine (AP) and 2-methyl pyridine (MP) (defined as Py-CoPc/C, AP-CoPc/C and MP-CoPc/C, respectively). The oxygen reduction reaction (ORR) catalyzed by these catalysts in alkaline solution is investigated by electrochemical methods to quantitatively understand the ORR kinetics. The results show that modification of Py, AP and MP as co-N-precursors can significantly improve the catalytic ORR activity of CoPc/C, and the activity is varied with the order of MP > AP > Py. X-ray photoelectron spectroscopic (XPS) study is conducted in order to examine the surface composition and the possible ORR active sites. The catalytic activities of these catalysts are also validated using an alkaline fuel cell performance, demonstrating these catalysts are promising for fuel cell applications.

1. Introduction

It is commonly recognized that polymer electrolyte membrane (PEM) fuel cells would become the effective powers for automotive and stationary applications due to their high energy efficiency and low/zero emissions [1]. In PEM fuel cells, the cathode oxygen reduction reaction (ORR) has been identified as the kinetically dominating reaction when compared to the anode hydrogen oxidation reaction (HOR). Due to the reaction kinetics of O_2 electroreduction is much slower than that of H_2 oxidation, a much larger cathode overpotential (or polarization) than that of HOR is normally observed, resulting in lower fuel cell performance that that expected even using electrocatalysts to accelerate the ORR process [1–4]. Currently, the feasible and practical ORR catalysts are Pt or Pt alloys-based ones. However, the high the high cost and limited availability of the Pt-based catalysts have been identified as the major barriers in PEM fuel cell commercialization [5,6]. Therefore, developing alternative ORR catalysts such as non-Pt-based or non-noble metal catalysts is the major effort in current PEM fuel cell research and development.

Actually, PEM fuel cells can be classified as two categories, one is the acidic PEM fuel cells, and the other is the alkaline PEM fuel cells. Normally, the former is more popular than the later. However, recently the alkaline PEM fuel cells research has recently attracted a noticeable attention due to their distinct advantages when operating in an alkaline environment [7–9]. One of the most advantages when compared to acidic PEM fuel cell is the fast fuel cell reaction kinetics under alkaline conditions, allowing many cost-effective catalysts to be used for cathode ORR [10]. For example, some inexpensive, non-noble metal catalysts such as transition metals, macrocyclic complexes and transition metal chelates with simple nitrogen-containing ligands can be explored for cathode oxygen reduction reaction [10–14].

Regarding non-noble metal catalysts, non-precious cobalt (Co)-based complex materials in alkaline media have been extensively explored for ORR, including Co-phthalocyanine (CoPc), cobalt-fullerene, binary Co–Fe nitrogen containing chelate, Co-polypyrrole, and other cobalt macrocycles [15–17]. Among these Co-based catalyst materials, CoPc complexes have been widely studied because of their high conjugate structure and good chemical stability [18–20]. In particular, they have demonstrated some ORR activity and stability even in their as-prepared form (the molecular form) [6,21,22]. However, the electrocatalytic activity and stability of the macrocycle catalysts are considerably lower than those of Pt-based catalysts, further improvements in both their catalytic activity and stability for ORR are definitely necessary [6]. In addition, as these nitrogen-containing ligands have complex structures, thus their high cost is not avoidable. Therefore, it is necessary to improve the performances of the catalysts by modifying with different materials including more common, simple, and

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* Corresponding author. Tel.: +86 25 89680512; fax: +86 25 89680569.
E-mail addresses: hqren@nju.edu.cn, kexu@nju.edu.cn (H. Ren).

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cost-effective nitrogen source and metal [14,15,23]. Most recently, Ding et al. [24] reported on the electrochemical performances of carbon supported CoPc catalyst (CoPc/C) modified with the first-row transition metal elements, M (where M = Fe, Co, Ni, V) as the co-added metal precursors. It was found that the 5 wt% of Fe added CoPc catalyst could give improved catalytic ORR activity both in acid and alkaline electrolytes due to the synergistic effect between co-added Fe and CoPc [24].

In this paper the possibility of constituting new electrocatalysts with the modification using N-rich ligand complexes, such as pyridine (Py), 2-acid pyridine (AP) and 2-methyl pyridine (MP) to carbon-supported cobalt phthalocyanine (defined as Py-CoPc/C, AP-CoPc/C and MP-CoPc/C, respectively) are presented. The activities of these as-prepared catalysts toward ORR were evaluated by cyclic voltammetry (CV) and linera sweep voltammetry (LSV) using a rotating disk electrode (RDE) technique. RDE theory and the kinetic parameters such as Tafel slopes were analyzed to address the possible ORR mechanisms. For fundamental understanding, X-ray photoelectron spectroscopy (XPS) was used to detect surface structure changes and shed some light on the nature of the active centers of the catalyst. At last, these catalysts were employed for the fabrication of MEAs as alternative cathode materials to Pt/C in alkaline H_2/O_2 fuel cell using Tokuyama A201 membrane. Considering that the manufacturing of the catalysts requires a simple and low cow cost mixture of Py, HP, MP and CoPc on carbon, they would be very attractive for practical applications.

2. Experimental

2.1. Materials and catalyst preparation

All carbon-supported CoPc/C catalysts modified by pyridine, 2-methyl pyridine, and 2-acid pyridine were prepared via a combined solvent-impregnation and milling procedure at room temperature. The carbon support used in this study was Vulcan XC-72R carbon black (Cabot Corporation, $S_{BET} = 236.8\ m^2\ g^{-1}$). Pyridine (Py), 2-acid pyridine (AP) and 2-methyl pyridine (MP) were all analytically pure and used as the co-added N-precursors for CoPc modifications.

In order to disperse the catalyst on the surface of Vulcan XC-72R, a mixture of CoPc and carbon black in 20 ml methanol was prepared and carefully milled in a mortar for at least 2 h, then vacuum dried at 40 °C for 1 h. During the process, a desired amount of Py, AP or MP was added to the mixture. For a convenient comparison, all catalysts were kept to be 40 wt%, i.e., 40 wt% N-CoPc catalyst + 60 wt% Vulcan XC-72 carbon, where the N (N = Py, AP or MP) and the mass ratio of N and CoPc was kept in a 50%:50%. Thus the catalysts studied in this work were designated as 220%Py–20%CoPc/C, 20%AP–20%CoPc/C and 20%MP–20%CoPc/C, respectively. For a better comparison, two baseline samples of carbon supported pure 40%CoPc and 40%Py were also prepared under the same conditions described above. All the above catalysts were all presented as initial loading, and the final loading was not ascertained.

2.2. Physical characterization

X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Kratos AXIS UltraDLD electron spectrometer to determine the surface composition with Al K X-ray anode source ($h\nu = 1486.6$ eV) at 250 W and 14.0 kV.

2.3. Electrode preparation and testing

For working electrode preparation, a pre-cleaned rotating disk electrode (RDE) (glassy carbon electrode with a diameter of 6.0 mm corresponding to a geometric surface area of 0.25 cm^2, purchased from Pine Instruments) was coated with catalyst to form the catalyst layer. The catalyst ink was prepared by ultrasonically mixing 4.0 mg catalyst with 2.0 ml of isopropyl alcohol. Then 10 μl portion of such ink was then deposited onto the glassy carbon (GC) disk electrode. After dried at room temperature, one drop of methanol/Nafion® solution (50:1 wt%) was deposited to adhere the catalyst on GC electrode. The overall loading of the catalyst was $2.8 \times 10^{-5}\ g\ cm^{-2}$ for the apparent electrode area of the GC disk (0.25 cm^2). Therefore, the current densities reported here are all using the geometric area of the carbon electrode.

RDE (Pine, 5908 Triangle Drive, Raleigh, NC) measurements were performed in a standard three compartment electrochemical cell at 25 °C. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All measured potentials were converted into the values referring to a standard hydrogen electrode (SHE). Electrochemical experiments were carried out in 0.1 M KOH solution. For ORR activity measurements, cyclic voltammetry (CV) was conducted between −0.4 and 0.8 V at 50 $mV\ s^{-1}$ in O_2-saturated 0.1 M KOH solution, and linear sweep voltammetry (LSV) was conducted between −0.35 and 0.2 V at 5 $mV\ s^{-1}$ in O_2-saturated KOH solution at various rotating speeds. The electrolyte was saturated with oxygen for at least 30 min before each ORR electrochemical measurement.

2.4. Electrode fabrication and H_2/O_2 single-cell performance measurements

For single cell testing, the membrane-electrode assemblies (MEAs) were fabricated with commercial carbon-supported Pt catalyst (Pt/C) as anode catalyst and Py-CoPc/C, AP-CoPc/C or MP-CoPc/C on cathode sides of the Tokuyama polymer membrane (A201 membrane, Tokuyama Corporation, Japan). The catalyst ink was prepared by mixing 40% Pt/C (Johnson Matthey) with a solution of 5 wt% Nafion (DuPont) and isopropanol, and then sonicated for 4 h to get a homogeneous solution, where the ratio of Pt/C catalyst to Nafion was 3:1. The catalyst ink was sprayed onto the carbon paper (Toray TGP-H-090) to deposit a catalyst layer with a Pt loading of 0.5 $mg\ cm^{-2}$ for the anode and the Py(AP, MP)-CoPc loading of 1.5 $mg\ cm^{-2}$ for the cathode. Then three drops of alkaline ionomer, Tokuyama AS-4, were loaded on the catalyst layers.

The MEA was fabricated by hot-pressing the sandwich composed of catalyzed anode and cathode carbon papers with A201 membrane in between at a pressure of 10 MPa at 70 °C for 3 min. The MEA was then assembled in a H_2/O_2 fuel cell with an active area of 4 cm^2. Pure H_2 and O_2 were supplied to enter the anode and cathode channels at a flow rate of 100 and 60 $ml\ min^{-1}$, respectively, through a humidifier maintained at 25 °C under ambient pressure. Polarization curves were obtained using a fuel cell evaluation system (GE/FC1-100).

3. Result and discussion

3.1. Electrochemical activity of CoPc/C catalyst modified with Py, AP and MP toward ORR

There has been a general agreement in the literature that heat-treatment can effectively improve the electrocatalytic activity of the macrocyclic complex catalysts such as phthalocyanine and porphyrins complexes, where the CoPc and FePc complexes are popular non-noble metal catalysts due to their reasonable activity and remarkable selectivity toward ORR in both acidic and alkaline electrolytes. On the other hand, they have also demonstrated some ORR activity and stability even in their as-prepared form, i.e., in molecular form [6,21,22]. Fig. 1 shows CV response of O_2-saturated 0.1 M KOH on three catalysts coated GCs, i.e., 20%Py–20%CoPc/C, 20%AP–20%CoPc/C and 20%MP–20%CoPc/C, respectively. For a