Research Article

MOF-Based Co and Mn Embedded in Nitrogen-Doped Microporous Carbon as an Efficient Catalyst for Oxygen Reduction Reaction in Anion Exchange Membrane Fuel Cell

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Abstract

Developing a low-price, high catalytic activity, and strong durability electrocatalyst for alkaline oxygen reduction reaction (ORR) is significantly important for anion exchange membrane fuel cell (AEMFC). Herein, Co and Mn salts were added into ZIF-8 to obtain CoMn-ZIF-Ac-2. Co and Mn embedded in nitrogen-doped microporous carbon (CoMn-N-C-Ac-2-Ts, Ts = 700, 800, 900, and 1000°C) were obtained by carbonizing CoMn-ZIF-Ac-2 at various temperature. The influence of various pyrolysis temperature and molar ratios between Co and Mn toward ORR catalytic activity was researched. For CoMn-N-C-Ac-2-Ts, CoMn-N-C-Ac-2-800 had the highest ORR catalytic activity with the half-wave potential of 0.875 V in 0.1 M KOH, only 5 mV lower than that of 20 wt % Pt/C. Besides, high 4e⁻ selectivity, excellent stability (retaining 100% for 20 h at 0.6 V vs. RHE), and methanol tolerance are also exhibited. In addition, CoMn-N-C-Ac-2-800 exhibited better ORR activity than Mn-N-C-Ac-800 and Co-N-C-Ac-800, which was attributed to more Co-N₄, more Mn III species, and higher surface area. Moreover, the AEMFC based on the CoMn-N-C-Ac-2-800 cathode catalyst obtained a maximal power density of 291 mW·cm⁻², which was 78% of the P_max achieved with 20 wt % Pt/C (375 mW·cm⁻²). The highest ORR performance for CoMn-N-C-Ac-2-800 was contributed by the highest defect degree, the most amounts of Co/Mn-N₄ active site, the maximum BET surface area, and micropore structure.

1. Introduction

A large number of fossil fuel resources are broadly applied to the industrial development, leading to environmental pollution. Therefore, more renewable energy sources should be exploited to replace fossil fuels and meet environmental requirement [1]. Among others, polymer electrolyte membrane fuel cells are an ideal portable power source on account of low operating temperature, low emission, and rapid startup [2]. Compared with the proton exchange membrane fuel cells (PEMFCs), anion exchange membrane fuel cells (AEMFCs) provide a milder operating environment [3, 4], allowing more variety of materials to be applied for the catalysts, membranes, and bipolar plates [5], because of high-pH environment. Therefore, AEMFCs are more likely to decrease or eliminate platinum group metal (PGM) requirements [6–8], whose high price limits the commercial applications of polymer electrolyte membrane fuel cells.

Currently, the highly active and stable nonnoble metal catalysts for alkaline ORR have been widely studied to decrease the cost of the AEMFCs. Among the studied nonnoble metal catalysts, transition metals and nitrogen-doped carbon (M-N-C, M: Fe, Co, Mn, Ni, etc.) catalysts have received great attention because of their good catalytic activity, ideal stability, and cost-effective scalable synthesis [9–20]. Previous researches have reported that the electrocatalytic performance of the M-N-C catalysts follows the order of Fe > Co > Mn > Ni in alkaline electrolytes [21–23]. Compared with other M-N-C catalysts, Fe-N-C displayed
the best ORR electrocatalytic performance toward alkaline ORR. However, Fe-based catalysts are liable to produce Fe\(^{3+}\) or Fe\(^{3+}\), which react with the formed H\(_2\)O\(_2\) to generate hydroxyl and hydroperoxyl radical species (Fenton reactions) [24, 25]. These radical species produced by the Fenton reaction will damage the AEMFC ionomer and membrane, leading to fast performance degradation and cell failure. Therefore, Co-N-C is considered as good M-N-C catalysts to achieve durable and inexpensive AEMFCs [26, 27].

In the meantime, Mn-based catalysts also display preferable ORR electrocatalytic activity due to having a controllable surface valence and having a high valence [28, 29]. Hence, this is a good way to make a catalyst with ideal ORR catalytic activity by combining the advantages of Co-based and Mn-based catalysts. In addition, metal organic frameworks (MOFs) were known as the promising precursors to prepare porous transition metals and nitrogen-doped carbon, because of their large surfaces, high nitrogen contents, and huge diversity [30–32]. Particularly, zeolitic imidazolate frameworks (ZIFs) are widely applied for synthesizing M-N-C catalysts. Wei et al. [33] pyrolysed Mn-doped ZIF-67 to synthesize Mn/Co-N-C and exhibited the half-wave potential of 0.80 V in 0.1 M KOH. Chao et al. [34] carbonized Co-doped ZIF-8 (Mn) to produce MnCo-N-C and displayed the half-wave potential of 0.80 V in 0.1 HClO\(_4\). Chen et al. [32] calcined MnO\(_2\) hollow nanowires@ZIF-67 to generate highly porous MnO@Co-N/C and showed the half-wave potential of 0.83 V in 0.1 M KOH. Park et al. [35] first produce a precursor (MnCo-Mil) by mixing Co and Mn salts with 2-methylimidazole in N-methyl-2-pyrrolidone (NMP). MnCo-NCF was synthesized by pyromolyzing MnCo-Mil and exhibited the half-wave potential of 0.843 V in 0.1 M KOH. Furthermore, Huang et al. [36] calcined MznZIF-67 precipitate to produce Mn-incorporated Co\(_3\)O\(_4\) catalysts (Mn/Co-450) and displayed the half-wave potential of 0.78 V in 0.1 M KOH. However, those approaches suffer from complex preparation process and lower ORR performance than commercial Pt/C catalyst.

Herein, we put forward a simple one-step pyrolysis method to obtain Co and Mn embedded in nitrogen-doped microporous carbon (CoMn-N-C-Ac-2-Ts). Co and Mn salts were added into ZIF-8 and pyrolysis at various temperatures (700, 800, 900, and 1000°C). Assessed by a novel ORR catalyst, CoMn-N-C-Ac-2-800 displayed the highest half-wave potential of 0.875 V in 0.1 M KOH, only 5 mV lower than 20 wt % Pt/C. It also had higher 4e\(^{-}\) selectivity, more notable durability, and methanol tolerance than 20 wt % Pt/C. In addition, it exhibited better ORR electrocatalytic activity than Co-N-C-Ac-800 and Mn-N-C-Ac-800, which was attributed to more Co-N\(_4\) more Mn\(^{II}\) species, and higher surface area. When applied for AEMFCs, the CoMn-N-C-Ac-2-800-based AEMFC showed a maximal power density of 291 mW cm\(^{-2}\), which was 78% of the \(P_{\text{max}}\) achieved with 20 wt % Pt/C (375 mW cm\(^{-2}\)). The highest defect degree, the most amounts of Co/Mn-N\(_4\) active site, the maximum BET surface area, and micropore structure are responsible for the excellent ORR performance in AEMFCs.

### 2. Experimental Section

#### 2.1. Materials.

Zn(NO\(_3\))\(_2\)-6H\(_2\)O, Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O, Mn(CH\(_3\)COO)\(_2\), 2-methylimidazole, and isopropyl alcohol were purchased from Aladdin. Methanol was purchased from China National Pharmaceutical Group Corp. Potassium hydroxide (95%) and N-propanol were obtained from Macklin. Ethyl alcohol was purchased from Damao Chemical Reagents. The Nafion solution (5 wt %) was purchased from Dupont. The ultrapure water (18.2 M\(\Omega\) cm) was produced from a Millipore Elix water system.

#### 2.2. Synthesis of Catalysts.

1. 1.993 g Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O (8 mmol), 0.692 g Mn(CH\(_3\)COO)\(_2\) (4 mmol), and 3.570 g Zn(NO\(_3\))\(_2\)-6H\(_2\)O (12 mmol) were added into 300 mL methanol and were ultrasonically dissolved for 15 min, which was marked as solution A. 3.941 g 2-methylimidazole (48 mmol) was put into 300 mL methanol and was stirred for 15 min, which was marked as solution B. After that, solution B was added into solution A and was stirred for 30 min. After stirring, the mixed solution was put into a blast air oven at 60°C for 24 h. Co- and Mn-codoped ZIF-8 (CoMn-ZIF-Ac-2) was acquired by centrifugation, washing in anhydrous ethanol for two times and drying at 80°C for 12 h. According to Table 1, Mn-ZIF-Ac was prepared without Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O, CoMn-ZIF-Ac-0.5 was prepared with 4 mmol Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O and 8 mmol Mn(CH\(_3\)COO)\(_2\), CoMn-ZIF-Ac-1 was prepared with 6 mmol Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O and 6 mmol Mn(CH\(_3\)COO)\(_2\), CoMn-ZIF-Ac-5 was prepared with 10 mmol Co(CH\(_3\)COO)\(_2\)-4H\(_2\)O and 2 mmol Mn(CH\(_3\)COO)\(_2\), and Co-ZIF-Ac was prepared without Mn(CH\(_3\)COO)\(_2\), Mn-ZIF-Ac, CoMn-ZIF-Ac-0.5, CoMn-ZIF-Ac-1, CoMn-ZIF-Ac-2, CoMn-ZIF-Ac-5, and Co-ZIF-Ac were pyrolyzed at 800°C for 3 h (ramping rate of 5°C/min) under an Ar atmosphere.

2. 2.3. Physical Characterization.

The morphology of the prepared samples and precursors was observed by the field-emission scanning electron microscope (FE-SEM, JSM-6360, JSM-7800F, and JEOL) and transmission electron microscope (TEM, JEM-2000, and JEOL). These samples were recognized by X-ray diffraction (XRD, Empyrean-100, Panaco, Almelo, Netherlands). The graphitization and defect degree of the prepared samples were obtained by Raman Spectrometer (Raman, Nano Wizard Ultra Speed &in Via, Waltham, MA, USA) with a laser wavelength of 532 nm. The X-ray photoelectron spectroscopy (XPS) was tested on ESCALAB 250Xi (Thermo Fisher, Waltham, MA, USA). The BET specific surface area and pore size distribution were measured by N\(_2\) adsorption-desorption measurement (autosorb iQ\(_3\), Quantachrome). The Co and Mn contents of the prepared samples were acquired by inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer, NexION 300D, Santa Clara, CA, USA).
24. Electrochemical Characterization. All electrochemical tests were operated on Electrochemical Station (Model 730D) by a standard three-electrode configuration. A three-electrode configuration was used with a working electrode, counter electrode, and reference electrode. The working electrode was 5 mm glassy carbon rotating disk electrode (RDE, 0.1963 cm²) or 5.61 mm rotating ring-disk electrode (RRDE, 0.2472 cm²). The counter electrode and reference electrode were a Pt foil and an Ag/AgCl (saturated KCl). All potentials in 0.1 M KOH were calibrated to the reference electrode were a Pt foil and an Ag/AgCl (saturated KCl). All potentials in 0.1 M KOH were calibrated to the reversible hydrogen electrode (RHE) potential by the Nernst equation ($E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.962\, \text{V}$). 5 mg of catalyst, 50 μL of 5 wt % Nafion solution, and 1 mL isopropyl alcohol were mixed to acquire the catalyst inks, and the inks were ultrasonically blended for more than 30 min. Next, 16 μL or 20 μL of the dispersed ink was pipetted onto the rotating disk electrode or rotating ring-disk electrode surface, respectively. The loadings of the prepared catalysts were 0.388 mg·cm⁻². Besides, the mass loading of 20 wt % Pt/C was 20 μg·cm⁻². Cyclic voltammetry (CV) curves were obtained in 0.1 M O₂-saturated KOH with a scan rate of 50 mV s⁻¹. Linear sweep voltammetry (LSV) curves were acquired in 0.1 M O₂-saturated KOH, and the background currents were obtained in N₂-saturated 0.1 M N₂-saturated KOH between 0 and 1.2 V (vs. RHE) with a rotating speed of 1600 rpm and a scan rate of 10 mV·s⁻¹. The ORR current was obtained after subtracting the background current.

For RRDEs, the electron transfer number ($n$) and the hydrogen peroxide yield ($\% \text{H}_2\text{O}_2$) were determined by

$$\% \text{H}_2\text{O}_2 = \frac{200I_r}{N[I_d] + I_r}, \quad (1)$$

$$n = 4 - 2 \times \frac{\% \text{H}_2\text{O}_2}{100}. \quad (2)$$

Here, $N$ is the current collection efficiency of the RRDE (0.37), the $I_d$ is the disk current, and the $I_r$ is the ring current. For the accelerated durability test (ADT), the electrodes were measured between 0.6 and 1.0 V for 10000 cycles in 0.1 M O₂-saturated KOH with a scan rate of 100 mV·s⁻¹. Besides, ORR polarization curves were obtained in 0.1 M KOH at 10000 cycles to acquire the performance degradation of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C. The durability was evaluated by chronoapermometric test at 0.6 V vs. RHE for 20 h. The methanol tolerance capacity was measured by appending 5 vol% methanol into 0.1 M KOH at 0.8 vs. RHE.

2.5. MEA Preparation and AEMFC Test. The membrane electrode assembly (MEA) was prepared by gas diffusion layer (GDL) and catalyst-coated membranes (CCM). The GDL was obtained from Sunrise Power Co., Ltd., which was employed on both anode and cathode side. In detail, carbon paper (Toray TGP-H-060) was hydrophobically handled by PTFE and sprayed with carbon powder. The carbon powder loadings and PTFE in the GDL were 1.0 mg·cm⁻² and 40 wt %, respectively. When trifluoroacetic acid and trifluoromethanesulfonic acid were used as catalysts, N-methyl-4-piperidone reacted with p-terphenyl to produce a linear polymer. QAPPT was synthesized after the linear polymer reacted with CH₃I in DMSO/NMP mixed solution at 70°C [37]. 0.667 g QAPPT was dissolved into 13.33 mL DMSO and 17.78 mL ethyl alcohol. Then, the mixed solution was dried on a glass plate to obtain the 10 × 10 cm² QAPPT membrane. The CCM was fabricated by a hand spray method. The catalyst ink was prepared by ultrasonic dispersion of catalysts, N-propanol, and ionomer (N-methylpiperidine-p-tribiphenyl (QAPPT)) for 1 h, which was sprayed on a QAPPT anion exchange membrane with a 4 cm² active area (the QAPPT membrane was prepared in-house). The anode catalyst was 60 wt % Pt-Ru/C with the Pt-Ru loading of 0.4 mg·cm⁻²·cm⁻². The cathode catalyst was CoMn-N-C-Ac-2-800 with a loading of 1.5, 2.0, and 2.5 mg·cm⁻². Furthermore, the cathode catalyst might also be 20 wt % Pt/C with a loading of 0.2 mg·cm⁻²·cm⁻². Then, the CCM was soaked in 2 M KOH solution for 24 h before use. The AEMFC test was operated at 80°C on a standard fuel cell test system (850e) with 100% RH of H₂ and O₂ at a flow rate of 1 L·min⁻¹. For polarization curve measurement. Backpressure of 1 bar was used. Electrochemical impedance spectroscopy (EIS) tests were operated at 200 mA·cm⁻². An amplitude of 5% was used to the single cell, and the frequency varied from 10 kHz to 0.1 Hz. In addition, the 850e was produced by Scribner Associates Incorporated.

3. Results and Discussion

3.1. Synthesis and Morphology Characterization of the Catalysts. The Co-Mn dual metals embedded in N-doped microporous carbon (CoMn-N-C-Ac-2-800) was synthesized by a one-step pyrolysis as showed in Figure 1. At first, a series of precursors were prepared by the first procedure, and the FE-SEM images of Mn-ZIF-Ac, CoMn-ZIF-Ac-0.5, CoMn-ZIF-Ac-1, CoMn-ZIF-Ac-2, CoMn-ZIF-Ac-5, and Co-ZIF-Ac were exhibited in Figure 2(a) and Figure S1. With the increasing of cobalt content, the particle diameter of the precursors increased slightly. This result indicated that Co doping promoted the growth of Mn-ZIF-Ac particles. After the pyrolysis at 800°C, the Co and Mn contents of the catalysts are shown at Table S1. The Co contents of the synthesis catalysts augmented and the Mn contents decreased accompanying with the increasing of
Figure 1: Schematic illustration of the preparation process of CoMn-N-C-Ac-2-800.

Figure 2: FE-SEM images of (a) CoMn-ZIF-Ac-2 and (b) CoMn-N-C-Ac-2-800, (c) TEM images of CoMn-N-C-Ac-2-800, (d) HRTEM images of CoMn-N-C-Ac-2-800, and (e) HAADF-STEM image and elemental mapping images of CoMn-N-C-Ac-2-800.
the added Co content, but CoMn-N-C-Ac-2-800 had the highest Co content. However, there was little difference in the ORR activity among CoMn-N-C-Ac-0.5-800, CoMn-N-C-Ac-1-800, CoMn-N-C-Ac-2-800, and CoMn-N-C-Ac-5-800. Therefore, we only researched Mn-N-C-Ac-800, CoMn-N-C-Ac-2-800, and Co-N-C-Ac-800, and the TEM images of them are shown in Figure 2(c) and Figure S2. More Co metal nanoparticles were found from the TEM image of Co-N-C-Ac-800 than that of CoMn-N-C-Ac-2-800. In addition, there was no Mn metal nanoparticle at Mn-N-C-Ac-800, which was consistent with the XRD results (Figure S4a). This result suggested that Mn existed in the form of Mn-N4.

In addition, the pyrolysis temperatures were researched. The FE-SEM and TEM images of CoMn-N-C-Ac-2-700, CoMn-N-C-Ac-2-800, CoMn-N-C-Ac-2-900, and CoMn-N-C-Ac-2-1000 are shown in Figures 2(b) and 2(c) and Figure S3. The morphology of CoMn-N-C-Ac-700 was regular rhombic dodecahedron. When the pyrolysis temperature was 800°C, the surface of the catalyst began to sag and formed a regular pore structure, which would improve the mass transfer efficiency inside the catalyst. However, when the pyrolysis temperature was raised, the morphology became distorted and the agglomeration of Co nanoparticles increased, which would reduce the porosity of the catalysts. Furthermore, according to ICP-AES (Table S2), the Co and Mn contents increased with the rise of calcination temperature, which could be attributed to the pyrolysis of carbon. Nevertheless, CoMn-N-C-Ac-2-800 had higher Co and Mn content. Therefore, the optimum pyrolysis temperature could be 800°C.

From the HRTEM images of CoMn-N-C-Ac-2-800 (Figure 2(d)), the lattice fringe spacings of 0.203 and 0.351 nm were well matched with the crystal planes of Co (111) and C (002), which were consistent with XRD characterization in Figure 3(a). Furthermore, the high-angle annular dark field scanning TEM (HAADF-STEM) image and element mapping images (Figure 2(e)) of CoMn-N-C-Ac-2-800 revealed that Co, Mn, N, and C were evenly distributed on the catalyst and Mn was scattered among Co, which indicated that the central Mn-N4 and CoN4 could exist according to the structure of Figure 1.

3.2. Structure Characterization of the Catalysts. X-ray diffraction (XRD) was employed to measure the crystal planes of CoMn-N-C-Ac-2-Ts, Co-N-C-Ac-800, and Mn-N-C-Ac-800 (Figure 3(a) and Figure S4a). All catalysts showed the graphitic carbon (002) characteristic peak at 2θ = 26.2°. Apart from Mn-N-C-Ac-800, CoMn-N-C-Ac-2-Ts and Co-N-C-Ac-800 exhibited Co characteristic peaks at 2θ = 44.2°, 51.5°, and 75.9° in line with the crystal planes of (111), (200), and (220) (PDF#15-0806), which was consistent with the TEM results (Figures 2(c) and 2(d) and Figures S2 and S3). For CoMn-N-C-Ac-2-Ts, the (111), (200), and (220) Co peaks were clearly enhanced with the improvement of calcination temperature. The results suggested that Co nanoparticles increased with the precursors pyrolyzed at higher temperatures. Furthermore, the Co peaks of Co-N-C-Ac-800 were stronger than CoMn-N-C-Ac-2-800, which also indicated that Co-N-C-Ac-800 had more Co nanoparticles than CoMn-N-C-Ac-2-800. This result also suggested that the central Mn-N4 could promote the transformation of Co nanoparticles into CoN4.

Raman spectra of CoMn-N-C-Ac-2-Ts, Co-N-C-Ac-800, and Mn-N-C-Ac-800 were conducted to examine the defective structure and graphitization degree (Figure 3(b) and Figure S4b). These samples exhibited two distinct peaks, which centred around 1345 cm⁻¹ (D band: disordered carbon) and 1580 cm⁻¹ (G band: ordered sp²-graphitic carbon), respectively [38]. And the IG/ID value (intensity ratio) presented the defect sites and the graphitic extent [39]. For CoMn-N-C-Ac-2-Ts, their IG/ID values were 1.16 (CoMn-N-C-Ac-2-700), 1.01 (CoMn-N-C-Ac-2-800), 1.05 (CoMn-N-C-Ac-2-900), and 1.15 (CoMn-N-C-Ac-2-800), respectively. The defect degree of CoMn-N-C-Ac-2-800 was the highest in all samples. In addition, the defects were additional active sites, so CoMn-N-C-Ac-800 could have the highest catalytic activity. By contrast, the IG/ID value for both Co-N-C-Ac-800 and Mn-N-C-Ac-800 was 1.03, which is higher than the one for CoMn-N-C-Ac-2-800. This result indicated that CoMn-N-C-Ac-2-800 could have the higher catalytic activity than Co-N-C-Ac-800 and Mn-N-C-Ac-800. Therefore, the optimum pyrolysis temperature was 800°C, and the synthesis catalyst had the higher catalytic activity than the contrast samples.

N₂ adsorption-desorption isotherms and the corresponding pore size distribution patterns were employed to evaluate the pore properties of CoMn-N-C-Ac-2-Ts (Figures 3(c) and 3(d)). As contrast, Mn-N-C-Ac-800 and Co-N-C-Ac-800 were measured by the same method (Figure S5). Pore size distribution curves were acquired by the DFT method. A clear type-IV plot with a hysteresis loop is presented in all samples, suggesting the generation of microporous structures (Figure 3(c) and Figure S5a). Microporous structures were critically important in hosting active site for ORR [40]. Textural properties (surface area, micropore volume, total pore volume, and average pore size) of all samples are exhibited in Table 2, and the BET surface areas were obtained by the BET method. CoMn-N-C-Ac-2-800 exhibited higher BET surface area (888 m²·g⁻¹), micropore volume (0.29 cm³·g⁻¹), and total pore volume (0.67 cm³·g⁻¹) than those of CoMn-N-C-Ac-2-700 (601 m²·g⁻¹, 0.21 cm³·g⁻¹, and 0.32 cm³·g⁻¹), CoMn-N-C-Ac-2-900 (885 m²·g⁻¹, 0.29 cm³·g⁻¹, and 0.64 cm³·g⁻¹), and CoMn-N-C-Ac-2-1000 (529 m²·g⁻¹, 0.14 cm³·g⁻¹, and 0.58 cm³·g⁻¹). This result was attributed to incomplete pyrolysis at 700°C and structure shrinkage and pore collapse at higher temperatures of 900 and 1000°C. In the pore size distribution (Figure 3(d)), CoMn-N-C-Ac-2-900 and CoMn-N-C-Ac-2-1000 exhibited obvious peak at around 5.1 nm, whereas CoMn-N-C-Ac-700 and CoMn-N-C-Ac-800 displayed clear peak at around 0.8 and 1.1 nm, respectively. This result indicated that CoMn-N-C-Ac-2-800 had more micropores than other CoMn-codoped materials. Besides, the surface area and total pore volume of CoMn-N-C-Ac-2-800 were higher than those of Mn-N-C-Ac-800 (730 m²·g⁻¹ and 0.51 cm³·g⁻¹) and Co-N-C-Ac-800 (751 m²·g⁻¹ and 0.49 cm³·g⁻¹), which indicated that Co and Mn codoping
Figure 3: (a) XRD patterns, (b) Raman spectra, (c) N₂ adsorption-desorption isotherm, and (d) the corresponding pore size distribution curve of CoMn-N-C-Ac-2-Ts.

Table 2: BET surface areas, pore volume distribution, and average sizes of Mn-N-C-Ac-800, Co-N-C-Ac-800, and CoMn-N-C-Ac-2-Ts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>Micropore volume (cm³·g⁻¹)</th>
<th>Total pore volume (cm³·g⁻¹)</th>
<th>Average pore size (nm)</th>
</tr>
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<tr>
<td>Mn-N-C-Ac-800</td>
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<td>0.51</td>
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<tr>
<td>Co-N-C-Ac-800</td>
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</table>
nitrogen carbon could improve the surface area and micropore structure.

X-ray photoelectron spectroscopy (XPS) was measured to probe the chemical element types and the chemical valence on the surface of CoMn-N-C-Ac-2-Ts, Co-N-C-Ac-800, and Mn-N-C-Ac-800 catalysts (Figure 4 and Figure S6). As exhibited in Figure 4(a) and Figure S6a, the survey spectra of CoMn-N-C-Ac-2-700 and CoMn-N-C-Ac-2-800 presented the coexistence of C, N, O, Mn, Co, and Zn elements. When the calcination temperature improved, the Zn element disappeared, which could be attributed to the evaporation of Zn at high temperatures. Furthermore, Co-N-C-Ac-800 contained C, N, O, Co, and Zn elements, and Mn-N-C-Ac-800 contained C, N, O, Mn, and Zn elements in the survey spectra. As displayed in Figure 4(b) and Figure S6b, the Co 2p_{3/2} spectrum revealed three peak positions at binding energies of around 780.4, 781.6, and 783.0 eV, corresponding to the characteristic peaks of Co II, Mn II, Mn III, displayed in Figure S6e, the high-resolution Mn 2p spectrum site (Figure S6d), which indicated that CoMn bimetal pyrolysis temperature for ORR. Furthermore, CoMn-N-C-Ac-2-800 presented the coexistence of C, N, O, Mn, Co, and Zn elements. When the calcination temperature improved, the Zn element disappeared, which could be attributed to the evaporation of Zn at high temperatures. Furthermore, Co-N-C-Ac-800 contained C, N, O, Co, and Zn elements, and Mn-N-C-Ac-800 contained C, N, O, Mn, and Zn elements in the survey spectra. As displayed in Figure 4(b) and Figure S6b, the Co 2p_{3/2} spectrum revealed three peak positions at binding energies of around 780.4, 781.6, and 783.0 eV, corresponding to the characteristic peaks of Co, Co-Ox, and Co-N 4 [27], respectively. The Co metal could act as the active center of catalytic oxygen reduction reaction (ORR), but the available surface area for O 2 was not large, and most Co atoms inside were not directly associated with O 2 to promote oxygen reduction reaction. Co-Ox was another possible active center of the cathode catalyst. However, the Co-O bonding might not enter into the carbonaceous network structure and constitute dangling, individual oxides in the carbon matrix, such as CoO or CoOx. Co-N 4 exhibited as the single-atom center in catalysts, which was the best active center for ORR when it was used as cathode of the AEMFC. For CoMn-N-C-Ac-2-Ts, CoMn-N-C-Ac-2-800 had the highest Co-N 4 content, which indicated that 800°C could be the optimum pyrolysis temperature for ORR. Furthermore, CoMn-N-C-Ac-2-800 contained more Co-N 4 and less Co than Co-N-C-Ac-800. This result suggested that the central Mn-N 4 might promote the conversion of Co to CoN 4. As presented in Figure 4(c) and Figure S6c, the N 1s spectrum of CoMn-N-C-Ac-2-Ts, Co-N-C-Ac-800, and Mn-N-C-Ac-800 displayed five peaks around 398.4, 399.0, 399.8, 400.8, and 401.4 eV, aligning with the characteristic peaks of pyridinic N (Py-N), Co/Mn-N 4, pyrrolic N (Pyr-N), graphic N (G-like), and oxidized N (Py-N-O) [41–43], respectively. The Co/Mn-N 4 structures were identified as the most possible active sites for Co/Mn-based nitrogen-doped carbon catalysts. For CoMn-N-C-Ac-2-Ts (Figure 4(d)), CoMn-N-C-Ac-2-800 exhibited the highest Co/Mn-N 4 amounts (26.8%), which would result in the best ORR activity. In comparison with Co-N-C-Ac-800 (19.2%) and Mn-N-C-Ac-800 (19.2%), CoMn-N-C-Ac-2-800 still obtained the most amounts of Co/Mn-N 4 active site (Figure S6d), which indicated that CoMn bimetal codoping would improve electrocatalytic activity. As displayed in Figure S6e, the high-resolution Mn 2p spectrum exhibited three pairs of characteristic peaks of Mn II, Mn III, and Mn IV that were positioned at 638.4 and 649.9 eV, 641.5 and 652.4 eV, and 646.1 and 654.7 eV [33, 44, 45]. It was reported that Mn III species were beneficial for the ORR activity, because the change of the E g orbit number in the Mn III species reduced oxygen adsorption and facilitated the exchange of hydroxy groups. CoMn-N-C-Ac-2-800 possessed more Mn III species than Mn-N-C-Ac-800, which suggested that CoMn-N-C-Ac-2-800 could display higher ORR performance than Mn-N-C-Ac-800.

3.3. ORR Performances of the Catalysts. The rotating-disk electrode (RDE) measurement was further employed to evaluate the catalytic activity of the prepared samples. The electrochemical performances of Co-N-C-Ac-800, Mn-N-C-Ac-800, CoMn-N-C-Ac-x-800 s, and CoMn-N-C-Ac-2-Ts were first evaluated by cyclic voltammetry (CV) in 0.1 M KOH. The curves of all catalysts showed well-defined cathodic peaks corresponding to oxygen reduction in O2-saturated electrolyte, which indicated the electrocatalytic activity toward ORR (Figures 5(a) and 5(b)). Remarkably, the peak potential of CoMn-N-C-Ac-2-800 at 0.792 V versus reversible hydrogen electrode (RHE) was the most positive among all samples (Table S3), which suggested superior ORR catalytic activity of all prepared samples [46]. Then, the onset potential (E onset) and the half-wave potential (E 1/2) of these catalysts were exhibited in Table S4. Firstly, the polarization curves of Co-N-C-Ac-800, Mn-N-C-Ac-800, CoMn-N-C-Ac-x-800 s, and 20 wt % Pt/C are presented in Figure 5(c). For CoMn-N-C-Ac-x-800 s, there was little difference in their catalytic activity, but CoMn-N-C-Ac-2-800 showed the higher onset potential (1.00 V) and half-wave potential (0.875 V) than others. This result might be due to the low Mn doping content. In addition, Mn only promoted the transformation of Co nanoparticles into CoN 4, but small changes in Mn content did not influence the ORR activity of catalysts. However, CoMn-N-C-Ac-2-800 had the highest Co content, which led to the best catalytic activity. Therefore, CoMn-ZIF-Ac-2 was chosen as precursor to research the pyrolysis temperatures. The influences of the calcination temperatures on the ORR performance are evaluated and exhibited in Figure 5(d). As the calcination temperature increased (T from 700°C to 800°C), E onset and E 1/2 of CoMn-N-C-Ac-2-800 reached the maximum (1.00 and 0.875 V), which was due to the highest defect degree, the most Co-N 4 content, and the largest porosity. However, the ORR performances of CoMn-N-C-Ac-2-900 and CoMn-N-C-Ac-2-1000 decreased with the further enhancement of pyrolysis temperature, since higher temperature leads to more Co nanoparticle agglomerations and structural distortion with fewer defects and lower porosity. Furthermore, CoMn-N-C-Ac-2-800 exhibited higher onset and half-wave potentials than Co-N-C-Ac-800 (0.96 and 0.835 V) and Mn-N-C-Ac-800 (0.87 and 0.765 V) and only 5 mV lower half-wave potential than 20 wt % Pt/C (Figure 5(a)). This result suggested that the synergistic effect between Co-N 4 and Mn-N 4 led to better catalytic performance of codoped CoMn-N-C-Ac-2-800 than Co-N-C-Ac-800 and Mn-N-C-Ac-800. Besides, the central Mn-N 4 promotes the transformation of Co nanoparticles into CoN 4.
Meanwhile, the as-prepared CoMn-N-C-Ac-2-800 catalyst presented the high ORR activity comparable to other published catalyst (Table S5). The RRDE polarization curves of CoMn-N-C-Ac-2-800 and 20 wt % Pt/C are presented at Figure 5(e). CoMn-N-C-Ac-2-800 acquired a hydrogen peroxide yield (% H₂O₂) of below 1% and the electron transfer number (n) of 3.98-3.99 (Figure 5(f)), which were higher than those of 20 wt % Pt/C (3.90-3.98, below 5%). This result also proved the dominant 4e⁻ reduction pathway of CoMn-N-C-Ac-2-800.

3.4. The Stability of the Catalysts. The accelerated durability test (ADT) was used to assess the durability of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C. Figures 6(a),
Figure 5: Continued.
which was attributed to more Co-N₄ and less Co nanoparticles in CoMn-N-C-Ac-800 than that in Co-N-C-Ac-800. In addition, the Pt nanoparticles suffered from serious degradation due to agglomeration, dissolution, and Ostwald ripening [47]. In order to evaluate the possibility of its use in direct methanol fuel cells (DMFCs), chronoamperometric responses of CoMn-N-C-Ac-2-800 and 20 wt % Pt/C accompanied by adding 5 vol.% methanol into 0.1 M KOH solution are used in Figure 6(f). Compared with the significant change of chronoamperometric response curves of 20 wt % Pt/C, the relatively flat curve of CoMn-N-C-Ac-2-800 indicated a better ability to tolerate methanol. This result laid the foundation to apply CoMn-N-C-Ac in DMFCs.

6(b), and 6(c) exhibited the ORR polarization curves of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C before and after being cycled between 0.6 and 1.0 V vs. RHE for 10000 cycles in 0.1 M O₂ saturated KOH with a scan rate of 100 mV s⁻¹. They revealed that the half-wave potentials of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C have decayed 20 mV, 25 mV, and 45 mV, respectively (Figure 6(d)). This consequence indicated that the CoMn-N-C-Ac-2-800 displayed the better durability than Co-N-C-Ac-800 and 20 wt % Pt/C. The chronoamperometric curves were measured to assess the stability of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C in 0.1 M KOH (Figure 6(e)). After 20 h at 0.6 V vs. RHE, the relative current of CoMn-N-C-Ac-2-800 was up to 100%, which was much better than those of Co-N-C-Ac-800 (92.48%) and 20 wt % Pt/C (69.39%). These results revealed that CoMn-N-C-Ac-2-800 exhibited the better durability than Co-N-C-Ac-800 and 20 wt % Pt/C, which was attributed to more Co-N₄ and less Co nanoparticles in CoMn-N-C-Ac-2-800 than that in Co-N-C-Ac-800. In addition, the Pt nanoparticles suffered from serious degradation due to agglomeration, dissolution, and Ostwald ripening [47]. In order to evaluate the possibility of its use in direct methanol fuel cells (DMFCs), chronoamperometric responses of CoMn-N-C-Ac-2-800 and 20 wt % Pt/C accompanied by adding 5 vol.% methanol into 0.1 M KOH solution are used in Figure 6(f). Compared with the significant change of chronoamperometric response curves of 20 wt % Pt/C, the relatively flat curve of CoMn-N-C-Ac-2-800 indicated a better ability to tolerate methanol. This result laid the foundation to apply CoMn-N-C-Ac in DMFCs.

3.5. Alkaline Anion Exchange Membrane Fuel Cell (AEMFC) Performances. According to the ORR studies in 0.1 M KOH, the CoMn-N-C-Ac-2-800 catalyst with different loadings was chosen for evaluating the AEMFC (Figure 7). As contrast, the result for 20 wt % Pt/C was also exhibited. The $P_{\text{max}}$ values presented that the CoMn-N-C-Ac-2-800 with the loading of 2.0 mg cm⁻² exhibited the highest power density (291 mW cm⁻² at 601 mA cm⁻² and 80°C), which was 78% of the $P_{\text{max}}$ achieved with 20 wt % Pt/C (375 mW cm⁻²). When the loadings of CoMn-N-C-Ac-2-800 decreased to 1.5 mg cm⁻², less active sites led to worse performance (213 mW cm⁻²), because the cathode catalyst content was low. After the loading increased to 2.5 mg cm⁻², the maximal power density decreased to 141 mW cm⁻². This result was similar to previous reports [48]. To further clarify the degradation behavior under different cathode catalyst loadings, electrochemical impedance spectroscopy (EIS) characterization was used to determine the three types of polarization loss by measuring the ohmic, charge transfer resistance, and mass transfer resistance, respectively [49] (Figure 7(b)). The EIS test was performed under 200 mA cm⁻², and EIS fitting results (Table 3) displayed that after the loading was increased to 2.5 mg cm⁻², the mass transfer resistance increased by 1.180 Ω cm⁻², but the charge transfer resistance and ohmic resistance hardly changed. Clearly, thicker catalytic layer increased mass transport distances, leading to the larger mass transfer resistance, so the single cell performance decayed. In addition, a comparison of AEMFC results of other nonprecious metal catalysts from recently published articles is shown in Table S6, and CoMn-N-C-Ac-2-800 exhibited comparable peak power density.
Figure 6: The RDE polarization curves of (a) CoMn-N-C-Ac-2-800, (b) Co-N-C-Ac-800, and (c) 20 wt % Pt/C before and after 10000 CV cycles (between 0.6 and 1.0 V vs. RHE) with a rotating speed of 1600 rpm and the scan rate of 10 mV s$^{-1}$. (d) Comparison of the corresponding onset potentials and half-wave potentials before and after ADT measured on CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C. (e) Chronoamperometric response curves of CoMn-N-C-Ac-2-800, Co-N-C-Ac-800, and 20 wt % Pt/C at 0.6 V vs. RHE at 400 rpm in 0.1 M O$_2$-saturated KOH. (f) Chronoamperometric response curves of CoMn-N-C-Ac-2-800 and 20 wt % Pt/C after adding 5 vol % methanol at 200 s at 1600 rpm in 0.1 M O$_2$-saturated KOH at 0.8 vs. RHE.
4. Conclusions

In summary, manganese- and cobalt-codoped nitrogen microporous carbon complex (CoMn-N-C-Ac-2-Ts) was synthesized by adding Co and Mn salts into ZIF-8 and pyrolyzing at various temperatures (700, 800, 900, and 1000 °C). The Co/Mn molar ratio had little impact on ORR performance of CoMn-N-C-Ac-x-800s, but CoMn-N-C-Ac-2-800 exhibited slightly better catalytic activity than others. Furthermore, pyrolysis temperatures greatly affected the ORR activity of CoMn-N-C-2-Ts. 800 °C was determined as the optimal calcination temperature. CoMn-N-C-Ac-2-800 presented the half-wave potential of 0.875 V in 0.1 M KOH, only 5 mV lower than 20 wt % Pt/C. Meantime, it also showed high 4e⁻ selectivity, excellent stability (retaining 100% for 20 h at 0.6 V vs. RHE), and methanol tolerance. This result was due to the highest defect degree, the most Co-Mn-N_4 amounts, the maximum BET surface area, and micropore structure. In addition, the Co- and Mn-codoped nitrogen microporous carbon catalyst (CoMn-N-C-Ac-2-800) presented better ORR performance than single-metal-doped Mn-N-C-Ac-800 and Co-N-C-Ac-800, which was ascribed to more Co-N_4, more Mn^III species, and higher surface area. Most excitingly, when employed in cathode of the AEMFC, the CoMn-N-C-Ac-2-800-based AEMFC exhibited the maximal power density of 291 mW·cm⁻², which was 78% of the P_{max} achieved with 20 wt % Pt/C (375 mW·cm⁻²). This work also offers a simple method to synthesize other MOF-based bimetal or trimetal N-doped carbon catalysts for storage devices and clean energy conversion.

Data Availability

The underlying data supporting the results of our study can be obtained by requesting the author.

Conflicts of Interest

The authors declare no competing financial interests.

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Supplementary Materials

Figure S1: FE-SEM images of (a) Mn-ZIF-Ac, (b) CoMn-ZIF-Ac-0.5, (c) CoMn-ZIF-Ac-1, (d) CoMn-ZIF-Ac-5, and (e) Co-ZIF-Ac. Figure S2: TEM images of (a) Co-N-C-Ac-800 and (b) Mn-N-C-Ac-800. Figure S3: FE-SEM images and TEM images of (a, b) CoMn-N-C-Ac-2-700, (c, d) CoMn-N-C-Ac-2-900, and (e, f) CoMn-N-C-Ac-2-1000. Figure S4: (a) XRD patterns and (b) Raman spectra of Mn-N-C-Ac-800, Co-N-C-Ac-800, and CoMn-N-C-Ac-2-800.
Figure S5: (a) N₂ adsorption-desorption isotherm and (b) the corresponding pore size distribution curve of Mn-N-C-Ac-800, Co-N-C-Ac-800, and CoMn-N-N-C-Ac-2-800. Figure S6: (a) XPS survey spectra, (b) XPS spectra of Co3/2, (c) XPS spectra of N 1 s, (d) contents of pyridinic N, Co/Mn-N4, pyrrolic N, graphitic N, and oxidized N, and (e) XPS spectra in Co-N-C-Ac-800, Mn-N-C-Ac-800, and CoMn-N-C-Ac-2-800. Table S1: the Co and Mn contents in the reactants and products of Mn-N-C-Ac-800, CoMn-N-C-Ac-x-800 s, and Co-N-C-Ac-800 characterized by ICP-AES. Table S2: the Co and Mn contents of CoMn-N-C-Ac-2-Ts characterized by ICP-AES. Table S3: the CV peak potential of Mn-N-C-Ac-800, Co-N-C-Ac-800, and CoMn-N-C-Ac-2-800. Table S4: the onset potential and half-wave potential of Mn-N-C-Ac-800, Co-N-C-Ac-800, CoMn-N-C-Ac-800 s, CoMn-N-C-Ac-2-Ts, and 20 wt % Pt/C. Table S5: comparison of the ORR performance of CoMn-N-C-Ac-2-800 with the recently published nonnoble metal catalysts (0.1 M KOH at 1600 rpm). Table S6: comparison of AEMFC performances using different NPMC cathode catalysts. (Supplementary Materials)

References


