

PtCoNi Alloy Towards Efficient Oxygen Reduction Reaction

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Abstract: A ternary alloy catalyst, CoNi-Pt/C-600, was prepared using a simple polyol method and thermal annealing treatment, and its oxygen reduction reaction (ORR) performance in acidic medium was studied. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) were used to characterize the structure and morphology of the catalyst particles. These techniques provided information on the structure and morphology of the catalyst. Electrochemical testing was conducted to evaluate the ORR activity and stability of the catalyst. CoNi-Pt/C-600 was compared with JM Pt/C. The results showed that the mass activity (MA) of CoNi-Pt/C-600 was 1.87 times higher than that of JM Pt/C (CoNi-Pt/C-600: 174.02 mA/mg_{Pt}, JM Pt/C: 93.22 mA/mg_{Pt}). The specific activity (SA) of CoNi-Pt/C-600 was 3.60 times higher than that of JM Pt/C (CoNi-Pt/C-600: 0.6537 mA/m²_{Pt}, JM Pt/C: 0.1814 mA/m²_{Pt}). This indicates that CoNi-Pt/C-600 exhibits better ORR activity. Furthermore, durability testing demonstrated the superior electrocatalytic performance of CoNi-Pt/C-600. In conclusion, this study successfully prepared a ternary alloy catalyst, CoNi-Pt/C-600, with excellent ORR activity and stability. This research provides valuable reference for the development of efficient catalysts for the oxygen reduction reaction.

1 Introduction

Hydrogen energy, as an efficient and clean renewable energy source, has attracted significant research attention in recent years¹. Fuel cells are the primary application of hydrogen energy technology, as they offer high energy conversion efficiency by directly converting the chemical energy of fuel into electricity. Proton exchange membrane fuel cells (PEMFCs) are widely regarded as one of the most efficient fuel cell technologies due to their mature membrane preparation techniques and ability to start quickly at low temperatures². However, the commercialization of PEMFCs is hindered by the use of catalysts. Without catalysts, the oxidation-reduction reactions at the anode and cathode of fuel cells, especially the oxygen reduction reaction (ORR) at the cathode, would proceed very slowly. The most widely used catalyst in PEMFCs is platinum (Pt) catalyst^{3,4}, which is expensive and scarce, limiting its development. However, since no better catalyst than Pt has been found in the short term, it is necessary to consider modifying Pt catalysts from the perspective of catalyst utilization to improve their efficiency.

To simultaneously reduce the Pt loading and enhance the ORR catalytic performance, researchers have proposed the formation of multi-component Pt-based metal catalysts by alloying Pt with transition metals such as copper, iron, nickel, cobalt, etc⁵⁻⁸. Studies have shown that introducing transition metals into the Pt lattice can

change the surface electronic structure of the alloy metal particles in the catalyst, further adjusting the bonding energy of reaction intermediates on the surface, thereby improving the catalytic activity of ORR⁹. Lokanathan¹⁰ et al. prepared an ordered Pt₂CoNi ternary alloy nanoparticle catalyst, which modified the electronic structure to optimize the Pt-O bonding energy, exhibiting excellent stability and activity for ORR in acidic medium, with a mass activity (MA) five times higher than that of commercial Pt/C. Additionally, the crystal structure of Pt-based catalysts can be tuned by high-temperature annealing treatment, transforming their atomic disorder structure into an ordered structure with a higher degree of alloying, thereby exposing more active Pt sites and facilitating the smooth progress of the ORR^{11,12}. Wang¹³ et al. investigated the influence of the structural changes of PtNiCo catalysts after heat treatment on the ORR activity and stability, and found that the heat-treated PtNiCo catalyst exhibited significantly better electrocatalytic performance than commercial Pt/C, with an MA approximately four times higher.

In this study, we prepared a ternary metal alloy catalyst, CoNi-Pt/C, by doping Co and Ni using a polyol method. The introduction of transition metals into Pt/C catalysts was explored to investigate their effect on the electronic structure of Pt/C catalysts. The electrochemical performance of the Pt-based alloy catalysts before and after high-temperature annealing treatment was compared to examine the role of crystal structure modulation in the ORR.

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Based on the above content, we prepared the CoNi-Pt/C ternary metal alloy catalyst using ethylene glycol as a reducing agent and polyvinylpyrrolidone (PVP) as a structure-directing agent. The catalyst was synthesized by reducing a mixture of cobalt hexahydrate nitrate, nickel hexahydrate nitrate, chloroplatinic acid, and carbon carrier, followed by high-temperature annealing of the ground CoNi-Pt/C. The resulting CoNi-Pt/C-600 exhibited an MA of 174.02 mA/mg_{Pt} and an SA of 0.6537 mA/m²_{Pt}, surpassing the commercial JM Pt/C catalyst (MA: 93.22 mA/mg_{Pt}, SA: 0.1814 mA/m²_{Pt}).

2 Experimental section

2.1 Materials

Polyvinylpyrrolidone (PVP, (C₆H₉NO)_n) was provided by Maclyn Company. Co(NO₃)₂·6H₂O was purchased from Shanghai Zhongqin Chemical Reagent Co., Ltd. Ni(NO₃)₂·6H₂O, H₂PtCl₆, carbon black, and ethylene glycol were provided by China National Pharmaceutical Group Chemical Reagent Co., Ltd. The equipment used includes an ultrasonic instrument, centrifuge, tubular furnace, and oil bath.

2.2 Preparation of carbon-based Co-Ni alloy Pt electrochemical catalysts

To synthesize CoNi-Pt/C, the following steps were carried out:

Preparation of materials: Add 20 mg of PVP, 20 mg of carbon carrier, 1.62 mg of cobalt hexahydrate nitrate, 1.62 mg of nickel hexahydrate nitrate, and 1.15 mL of chloroplatinic acid (with a theoretical molar ratio of Co:Ni:Pt of 1:1:4, and a Pt loading of 17.4%) to 20 mL of ethylene glycol. Sonicate the mixture for 30 minutes.

Heating and stirring: Transfer the solution to an oil bath and heat it while stirring. Raise the temperature to 130°C and maintain it for 3 hours. Allow the reaction mixture to cool naturally to room temperature.

Centrifugation and washing: Centrifuge the reaction mixture and collect the black precipitate. Wash the precipitate three times with deionized water and ethanol.

Drying: Dry the collected black precipitate at 60°C for 12 hours to obtain CoNi/Pt-C.

For comparison, Pt-C was prepared without the involvement of cobalt hexahydrate nitrate and nickel hexahydrate nitrate. This synthesis method allows for the preparation of CoNi-Pt/C catalyst with the desired composition, and by excluding cobalt and nickel, Pt-C catalyst can be obtained.

We conducted a heat annealing treatment on the obtained CoNi-Pt/C catalyst to promote the surface structural rearrangement of the catalyst, aiming to form a Pt layer surface that can expose more active sites and enhance the electrocatalytic performance. For this purpose, the CoNi-Pt/C catalyst was placed in a tubular furnace and annealed under a N₂ atmosphere for thirty minutes. We tried three different annealing temperatures: 600 °C, 700 °C, and 800 °C. The resulting samples were labeled as CoNi-Pt/C-600, CoNi-Pt/C-700, and CoNi-Pt/C-800.

The Pt/C catalyst annealed at 600 °C was labeled as Pt/C-600.

2.3 Physical characterization

TEM images were obtained using a JEM-2100 electron microscope at an accelerating voltage of 200 kV. High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images, energy-dispersive X-ray spectroscopy (EDS), and elemental mapping were acquired using a 300 kV Titan microscope equipped with a probe aberration corrector. X-ray diffraction (XRD) analysis of the lattice structure was performed using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) with a scanning rate of 8°/min within the 2 θ range of 30° to 90°.

2.4 Electrochemical measurements

The electrochemical performance of the sample was evaluated on an electrochemical workstation using a three-electrode setup with a rotating disk electrode (RDE) to test the performance of the oxygen reduction reaction (ORR). A glassy carbon electrode was used as the working electrode for loading the prepared electrocatalyst. The working electrode was prepared by dispersing 3 mg of electrocatalyst powder in a mixture solution of 2.7 mL ethanol, 0.3 mL water, and 18 μ L Nafion through ultrasonic dispersion. Cyclic voltammetry (CV) curves were recorded at a scan rate of 50 mV/s to calculate the electrochemically active surface area (ECSA) of the electrocatalyst. Furthermore, linear sweep voltammetry (LSV) analysis of the ORR activity of the electrocatalyst was conducted at a scan rate of 10 mV/s and 1600 rpm under O₂-saturated 0.1 M HClO₄ solution at 25 °C, obtaining LSV curves. The durability of the electrocatalyst was evaluated through chronoamperometry (CA) testing. The test conditions involved a 0.1 M N₂-saturated HClO₄ solution, a cyclic potential scan range of 0.6-1.0 V, a scan rate of 500 mV/s, and 5000 cycles.

3 Results and discussion

3.1 Synthesis and Characterization of Electrocatalysts

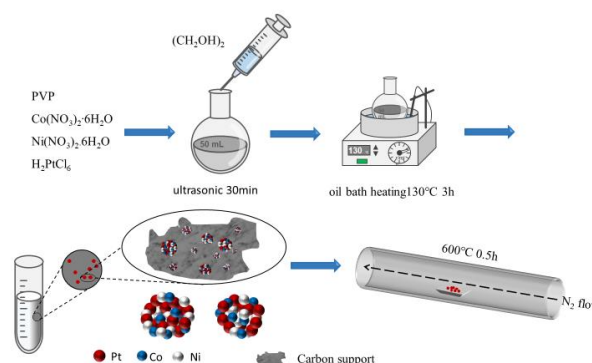


Figure 1 The preparation of CoNi-Pt/C-600

CoNi-Pt/C is synthesized using ethylene glycol as the reducing agent and PVP as the surfactant. Carbon support, nickel hexahydrate nitrate, cobalt hexahydrate nitrate, and chloroplatinic acid are mixed together and sonicated. The mixture is then heated at 130 °C for 3 hours, cooled to room temperature, and centrifuged. After three washes with pure water and ethanol, the CoNi-Pt/C catalyst is dried. To improve the electrochemical performance by enhancing the aggregation of the metal support, the CoNi-

Pt/C catalyst is further calcined at 600 °C in a tube furnace for half an hour. The resulting catalyst powder is named CoNi-Pt/C-600. Figure 1 illustrates the specific synthesis steps.

For the as-synthesized CoNi-Pt/C catalyst before heat treatment, its TEM image is shown in Figure 2a with an average size of 2.63 nm. As seen from Figure 2b, the alloy particles are evenly distributed on the carbon support, indicating that the catalyst has a good morphology.

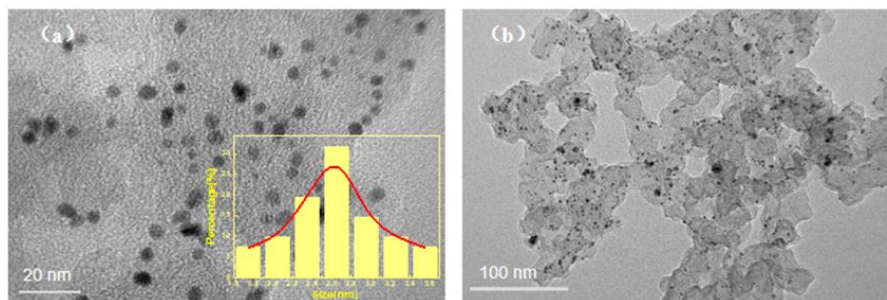


Figure 2 (a) The TEM image and size distribution histogram of the catalyst before heat treatment, (b) The TEM image of CoNi-Pt/C

After further heat treatment, the CoNi-Pt/C catalyst was calcined at 600 °C for half an hour. The resulting catalyst powder was named CoNi-Pt/C-600, and its HAADF-STEM image is shown in Figure 3a. The analysis suggests that the average size of CoNi-Pt/C-600 is 4.80 nm. Compared to the as-synthesized CoNi-Pt/C, the particle size of the catalyst has increased. The HAADF-

STEM image and corresponding elemental mapping illustrate that the metal particles of Co, Ni, and Pt are evenly distributed within CoNi-Pt/C (Figure 3b). Furthermore, clear lattice fringes spaced at 0.224 nm can be observed, which corresponds to the Pt ¹⁴ crystal plane (Figure 3c).

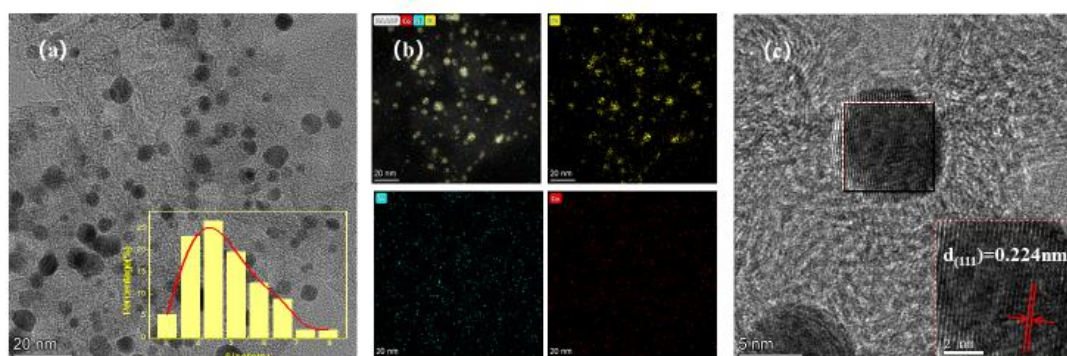


Figure 3 (a) The TEM image obtained after heat treatment with its size distribution histogram, (b) The HAADF-STEM image and the corresponding elemental mapping, (c) The high-resolution HAADF-STEM image with aberration correction is shown, where the red highlighted regions indicate the lattice spacing of CoNi-Pt/C-600 (111).

The crystal structures of CoNi-Pt/C, Pt/C-600, CoNi-Pt/C-600, CoNi-Pt/C-700, and CoNi-Pt/C-800 electrocatalysts were studied using XRD analysis. As shown in the figure, four characteristic peaks corresponding to the (111), (200), (220), and (311) crystal planes of FCC structure were observed. Compared to Pt/C-600, the Pt (111) peak of CoNi-Pt/C-600 shifted towards higher 2θ angles. This could be attributed to the formation of an alloy between Co, Ni, and Pt. The smaller atomic radii of Co and Ni entering the lattice of Pt results in lattice contraction, causing the diffraction peak to shift towards higher 2θ angles. After thermal annealing, the

diffraction peaks corresponding to Pt crystal planes became sharper, indicating a higher degree of crystallization and surface restructuring, which favors the exposure of more active Pt sites. With increasing annealing temperature, the diffraction peaks of all crystal planes became sharper and narrower due to particle aggregation and increased atomic radii. The main peak positions were located between Pt (111) and Ni (111) or Pt (111) and Co (111), indicating that thermal annealing enhanced the degree of alloying, which effectively improves the ORR performance of the Pt-based catalyst.

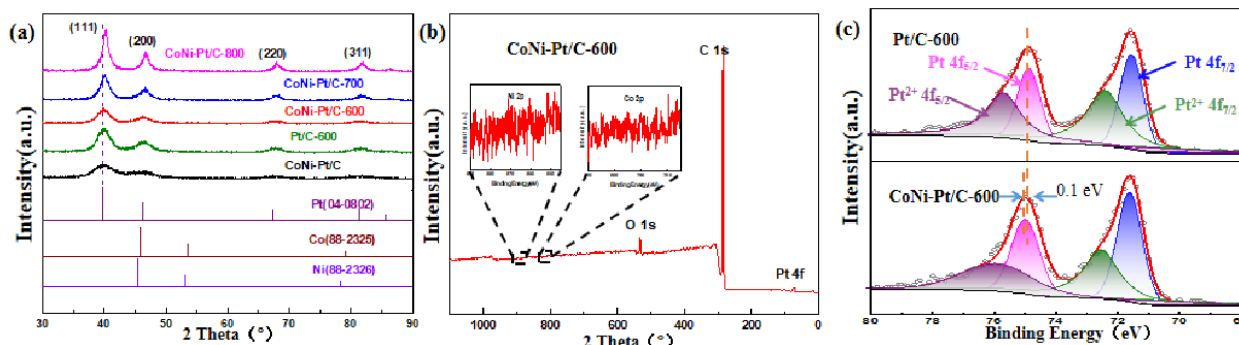


Figure 4 (a) XRD spectra of CoNi-Pt/C-600 and the prepared catalyst, (b) XPS full spectrum of CoNi-Pt/C-600, (c) High-resolution Pt 4f spectra of CoNi-Pt/C-600 and JM Pt/C electrocatalyst.

The electronic structure and surface composition of CoNi-Pt/C-600 were analyzed using XPS. Figure 4 shows the XPS spectrum of the catalyst, revealing the coexistence of Co, Ni, Pt, and C elements. However, due to the lower content of Co and Ni, their peak intensities are weaker. In the high-resolution spectrum, the Pt 4f spectrum of CoNi-Pt/C-600 exhibits two sets of doublet peaks, corresponding to metallic Pt peaks at 75.0 eV and 71.6 eV, and oxidized Pt peaks at 76.0 eV and 72.5 eV. Compared to Pt/C-600, the Pt 4f peak of CoNi-Pt/C-600 shifted by 0.1 eV. This shift could be attributed to the alteration of electronic structure and crystal contraction effects caused by the alloying of Pt with Co and Ni, further confirming the conclusions from the XRD analysis. According to XPS analysis, the surface atomic ratio of Co, Ni, and Pt in the CoNi-Pt/C-600 catalyst is 0.46:0.38:1.

3.2 The effect of the metal components in synthetic catalysts on the catalytic activity of ORR (oxygen reduction reaction)

The electrochemical performance of the catalyst was determined using a three-electrode system in 0.1M HClO₄. Figure 5a shows the CV curves of CoNi-Pt/C-600, CoNi-Pt/C-700, CoNi-Pt/C-800, and JM Pt/C in N₂-saturated HClO₄. The ECSA was calculated from the hydrogen reduction peak, and the ECSA values for CoNi-Pt/C-600, CoNi-Pt/C-700, CoNi-Pt/C-800, and JM Pt/C were 26.62 m²/g_{Pt}, 26.23 m²/g_{Pt}, 25.24 m²/g_{Pt}, and 51.49 m²/g_{Pt}, respectively. It can be seen that the difference in ECSA values between the catalysts with different heat treatment temperatures is small, indicating that the starting performance of the catalyst is not significantly affected by the heat treatment temperature. The ORR performance of CoNi-Pt/C-600 was found to be better than that of JM Pt/C, as shown by the oxygen reduction peak in the CV curve (Figure 5a). To demonstrate the good ORR performance of CoNi-Pt/C-600, we tested the LSV curves of CoNi-Pt/C-600 and JM Pt/C in O₂-saturated HClO₄ (Figure 5b).

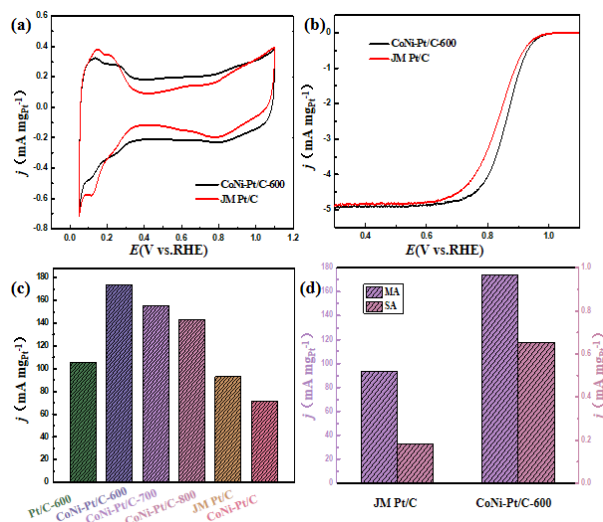


Figure 5 (a) The CV curves of JM Pt/C and CoNi-Pt/C-600 in N₂-saturated 0.1 M HClO₄ at a scan rate of 50 mV/s, (b) The LSV curves of JM Pt/C and CoNi-Pt/C-600 in O₂-saturated 0.1 M HClO₄ at 1600 rpm with a scan rate of 10 mV/s, (c) A comparison of the mass activity (MA) between CoNi-Pt/C-600 and the prepared catalyst, (d) A comparison of the MA and surface area (SA) between JM Pt/C and CoNi-Pt/C-600.

The half-wave potentials of CoNi-Pt/C-600 catalyst were measured to be 0.860 V, significantly higher than the 0.835 V (vs. RHE) of the JM Pt/C catalyst. Despite different annealing temperatures (Figure 5c), CoNi-Pt/C-600 still exhibited the highest half-wave potential, while the half-wave potentials of CoNi-Pt/C-700 and CoNi-Pt/C-800 were similar but still higher than that of JM Pt/C. This indicates that annealing treatment is advantageous for improving the ORR performance of CoNi-Pt/C, with 600°C being the optimal annealing temperature. Although the surface atomic composition of annealed CoNi-Pt/C is slightly inferior to that of JM Pt/C, their ORR electrocatalytic activity is higher than that of JM Pt/C, suggesting that annealed alloy catalysts possess better surface activity. Therefore, based on the Koutecky-Levich (K-L) equation, we calculated the dynamic current at 0.9 V and used this to determine the specific activity (SA) and mass activity (MA) of the catalyst.

The mass activities of CoNi-Pt/C-600, CoNi-Pt/C-700, and CoNi-Pt/C-800 are 174.02 mA/mg_{Pt}, 155.60 mA/mg_{Pt}, and 43.42 mA/mg_{Pt}, respectively, while JM Pt/C is only 93.22 mA/mg_{Pt}. It can be seen that the mass activity (MA)

of CoNi-Pt/C-600 is 1.87 times that of JM Pt/C. Furthermore, based on the previously calculated effective surface area (ECSA) values, we determined the corresponding specific activity (SA). The specific activity of CoNi-Pt/C-600 is $0.6537 \text{ mA/m}^2_{\text{Pt}}$, which is 3.60 times that of JM Pt/C ($0.1814 \text{ mA/m}^2_{\text{Pt}}$) (Figure 5c). It can be inferred that the increase in MA and SA is likely due to the optimization of the catalyst's electronic structure and crystal geometry after annealing treatment.

Based on the data obtained from the above tests, it can be concluded that the CoNi-Pt/C-600 catalyst treated at 600°C for 0.5 hours exhibits the highest electrocatalytic activity. Therefore, we conducted further durability tests on CoNi-Pt/C-600 and JM Pt/C, as durability is an important indicator for evaluating the catalytic performance of electrocatalysts.

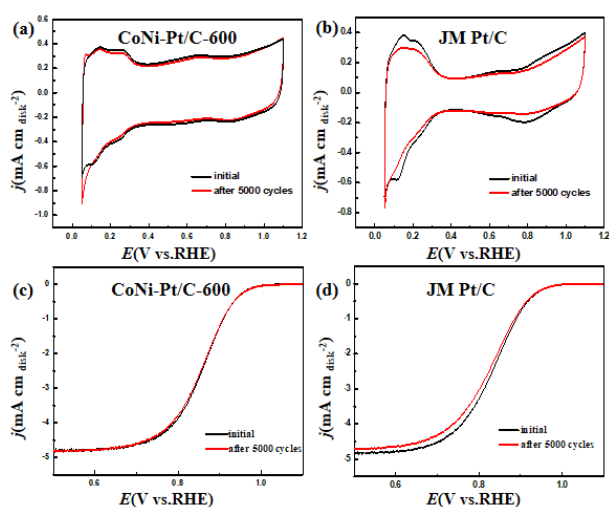


Figure 6 (a) CV curves of CoNi-Pt/C-600 before and after durability testing, (b) CV curves of JM-Pt/C before and after durability testing, (c) LSV curves of CoNi-Pt/C-600 before and after durability testing, (d) LSV curves of JM-Pt/C before and after durability testing.

The CV curves (Figure 6a, b) and LSV curves (Figure 6c, d) of CoNi-Pt/C-600 and JM Pt/C before and after the durability test are shown in the figures. For JM Pt/C, after 5000 cycles of durability testing, the CV curves exhibited a significant contraction, and the ORR polarization curves shifted towards lower potentials. The half-wave potential decreased by 7 mV after 5000 cycles. In contrast, CoNi-Pt/C-600 showed almost no decrease in half-wave potential after 5000 cycles, and the CV curves did not exhibit a noticeable contraction trend. This indicates that the electrocatalytic activity of CoNi-Pt/C-600 remained almost unchanged.

Comparing the ORR curves of CoNi-Pt/C-600 and JM Pt/C before and after durability testing, it was found that the half-wave potential of JM Pt/C was initially 25 mV lower than that of CoNi-Pt/C-600. After durability testing, the difference increased to 28.5 mV. These data indicate that CoNi-Pt/C-600 exhibits better ORR activity and superior durability compared to JM Pt/C.

4 Conclusion

We synthesized a ternary Pt-based alloy catalyst, CoNi-Pt/C-600, which displayed outstanding electrocatalytic performance in acidic solutions following a heat treatment at 600°C . X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM) analyses confirmed the presence of Pt, Co, and Ni metals in the catalyst particles. Electrochemical testing revealed that the MA and SA values of the catalyst were 1.87 and 3.60 times higher than those of JM Pt/C, respectively. Additionally, after undergoing durability testing, the electrochemical performance of JM Pt/C significantly deteriorated, while CoNi-Pt/C-600 maintained its relatively stable performance, which was further supported by TEM images. These findings clearly demonstrate that CoNi-Pt/C-600 outperforms JM Pt/C as a superior catalyst. This study highlights the ability to fabricate three-metal alloy catalysts with improved oxygen reduction reaction (ORR) activity and stability through the manipulation of the catalyst particles' electronic and crystal structures. It provides a reliable pathway for the advancement of electrocatalyst development.

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