

Article

Efficient Oxygen Evolution Reaction Performance Achieved by Tri-Doping Modification in Prussian Blue Analogs

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Abstract

The high cost of hydrogen production is the primary factor limiting the development of the hydrogen energy industry chain. Additionally, due to the inefficiency of hydrogen production by water electrolysis technology, the development of high-performance catalysts is an effective means of producing low-cost hydrogen. In water electrolysis technology, the electrocatalytic activity of the electrode affects the kinetics of the oxygen evolution reaction (OER) and the hydrogen evolution rate. This study utilizes the liquid phase co-precipitation method to synthesize three types of Prussian blue analog (PBA) electrocatalytic materials: Fe/PBA($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$), Fe-Mn/PBA($(\text{Fe}, \text{Mn})_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$), and Fe-Mn-Co/PBA($(\text{Mn}, \text{Co}, \text{Fe})_3^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$). X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses show that Fe-Mn-Co/PBA has a smaller particle size and higher crystallinity, and its grain boundary defects provide more active sites for electrochemical reactions. The electrochemical test shows that Fe-Mn-Co/PBA exhibits the best electrochemical performance. The overpotential of the oxygen evolution reaction (OER) under 1 M alkaline electrolyte at $10/50 \text{ mA} \cdot \text{cm}^{-2}$ is 270/350 mV, with a Tafel slope of $48 \text{ mV} \cdot \text{dec}^{-1}$, and stable electrocatalytic activity is maintained at $5 \text{ mA} \cdot \text{cm}^{-2}$. All of these are attributed to the synergistic effect of Fe, Mn, and Co metal ions, grain refinement, and the generation of grain boundary defects and internal stresses.

Keywords: Prussian blue analogues; electrocatalysis; oxygen evolution reaction



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1. Introduction

Driven by the global energy crisis and environmental degradation, extensive research into sustainable clean energy sources has been initiated. Hydrogen energy, as a zero-emission energy carrier, exhibits tremendous potential to replace fossil fuels [1,2]. Nowadays, the use of photovoltaic and wind energy for water electrolysis to produce cheap hydrogen is an effective way to achieve energy conversion. Although significant progress has been made, there are still some challenges in the actual production of hydrogen production from electrolytic water: (1) insufficient active sites and poor conductivity of traditional catalysts, resulting in high overpotential and fast degradation; (2) because structural collapse or metal leaching often occurs under harsh alkaline conditions, the balance between catalytic activity and stability is still difficult to control. Therefore, how to achieve low-cost hydrogen production and develop highly active and stable OER electrocatalysts is crucial for advancing hydrogen energy technology [3,4].

In the process of electrolyzing water to produce hydrogen, water is decomposed into hydrogen and oxygen through the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), which is a promising pathway for green hydrogen production [5,6]. However, in the two semi-reactions, the OER kinetics is relatively slow and the catalytic activity is insufficient, resulting in the need for high-cost catalytic materials for hydrogen production, which greatly limits the practical application of energy conversion technology. At present, the OER performance can be improved by using substrates with high surface area, such as carbon cloth and nickel foam, to increase the loading of the catalyst, synthesizing porous electrode materials by reducing the particle size, and enhancing the inherent catalytic ability of active sites by element introduction, lattice engineering, defects, and other methods [7]. Nowadays, the source of catalysts for hydrogen evolution from electrolytic water is mainly replaced by noble metal oxides (such as IrO_2 and RuO_2), but these oxides are scarce and expensive [8]. Prussian blue analogs (PBAs), with a special metal–organic framework structure and their advantages of low cost, easy synthesis, and stable three-dimensional structure of the whole skeleton, have attracted widespread attention [9,10]. Although PBAs have advantages in structural flexibility, they still face limitations such as low inherent conductivity and limited exposure of active sites. However, recent studies have demonstrated that strategic doping of PBAs with specific metal ions (e.g., Fe, Co, and Ni) can synergistically enhance their electrocatalytic performance. This synergy often arises from concerted modifications in electronic structure and active site configuration, rather than merely additive effects of individual dopants [11]. For instance, Yu et al. [12] achieved a core–shell Ni/Co-doped PBA exhibiting excellent HER activity. They attributed the improvement primarily to the presence of Co^{3+} ions, which facilitated efficient charge transfer pathways within the structure. Similarly, Liu et al. [13] combined Fe doping with phosphorylation in Fe-based PBAs, finding that this synergistic approach effectively lowered the energy barrier for the key OH dehydrogenation step* (a critical step in OER, $4\text{OH}^- \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$), leading to significantly reduced overpotentials. This highlights how dopants can directly modulate the adsorption energetics of reaction intermediates. Li et al. [14] leveraged polymetallic doping to engineer a hollow porous PBA architecture. While the structure inherently increased active site exposure and mass transport, the synergy between the dopants was crucial in accelerating electron transfer kinetics and reducing the overall reaction activation energy, suggesting dopant interactions optimized the electronic conductivity and potentially the intrinsic activity of the sites. Fan et al. [15] further demonstrated the power of synergy in NiCoFe/PBA catalysts. Their work emphasized that the hierarchical structure, combined with the synergistic electronic effects of bimetallic selenization and Fe-induced electronic rearrangement, collectively contributed to enhanced performance. Notably, the Fe doping was proposed to induce favorable electronic structure modifications. Zhangang et al. [16] employed a lattice-matching strategy to create a core–shell Ni-Co@Fe/PBA, achieving exceptional stability. Their work suggests that the synergistic interaction between the metals, potentially through optimized interfacial charge transfer and stabilized lattice structures via lattice matching, contributed to the reduced potential energy landscape and robust stability. On this basis, we use the intrinsic redox activity of single-doped iron-based PBA to construct ternary PBA by doping Co or Mn, respectively, adjusting the local coordination environment and inducing lattice strain, so as to realize the reversible insertion and extraction of metal ions and adjust the active sites of transition metals [17]. With the gradual deepening of ternary metal doping research, the synergistic effect of multimetals based on Prussian blue also has the possibility of further improving the activity of OER.

Therefore, in this study, we aimed to synthesize trimetallic Fe-Mn-Co/PBA electrocatalysts by a simple liquid phase co-precipitation method and to systematically reveal the

internal mechanism of their enhanced OER performance. This particular combination of elements (Fe, Mn, and Co) was strategically chosen based on the promising synergistic effects reported in previous studies: the Mn doping is effective in refining the particle size and suppressing agglomeration in PBAs [18], whereas the incorporation of Co enhances the crystallinity and introduces beneficial lattice strains and specific crystalline facets [19]. Crucially, synergistic interactions between Fe and Co in PBA structures have demonstrated optimized electronic structures and accelerated reaction kinetics [20], and the potential for ternary systems (e.g., Ni-Co-Fe) to further improve performance through multimetallic synergistic interactions is increasingly recognized [21]. Our co-doping of Fe, Mn, and Co within the PBA framework will synergistically optimize the crystal morphology (e.g., obtaining smaller, more homogeneous nanoparticles), introduce controlled lattice strains/defects, and tailor the electronic structure to ultimately maximize the density and intrinsic activity of the catalytic sites. In conclusion, this work not only elucidates the electronic structure modulation mechanism of multimetal doping in PBAs, but also develops a new strategy for designing highly efficient OER catalysts through metal synergism, which is of great application value for advancing the industrialization of green hydrogen production technology.

2. Results and Discussion

2.1. Characterization of the Electrocatalysts

In this study, three kinds of samples of Fe/PBA, Fe-Mn/PBA, and Fe-Mn-Co/PBA were successfully prepared by the liquid phase co-precipitation method. The chemical reaction equations of the Prussian blue analogs deposited after the reaction and the chemical compositions of their analog compounds are shown in the Table 1 below.

Table 1. The chemical reaction equation of Prussian blue analogs and the chemical composition of the reaction products.

Sample Name	Reaction Equation	Outgrowth
Fe/PBA	$3\text{Fe}^{2+} + 2\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow \text{Fe}_3[\text{Fe}(\text{CN})_6]_2\downarrow + 6\text{K}^+ + (4-x)\text{H}_2\text{O}$	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2$
Fe-Mn/PBA	$\text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + x\text{Mn}^{2+} \rightarrow (\text{Fe}_{3-x}\text{Mn}_x)[\text{Fe}(\text{CN})_6]_2 + x\text{Fe}^{2+}$	$(\text{Fe}, \text{Mn})_3[\text{Fe}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$
Fe-Mn-Co/PBA	$x\text{Mn}^{2+} + y\text{Co}^{2+} + z\text{Fe}^{2+} + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow (\text{Mn}_x\text{Co}_y\text{Fe}_z)[\text{Fe}(\text{CN})_6]_2\downarrow + 4\text{K}^+$	$(\text{Mn}, \text{Co}, \text{Fe})_3^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_2 \cdot n\text{H}_2\text{O}$

Figure 1 shows the X-ray diffraction (XRD; Rigaku SmartLab diffractometer (Dandong Haoyuan Instrument Co., Ltd., Dandong, China); Cu-K α radiation source, $\lambda = 1.5406 \text{ \AA}$) patterns of three electrocatalysts (Fe/PBA, Fe-Mn/PBA, and Fe-Mn-Co/PBA). All three Prussian blue analogs (PBAs) showed a diffraction peak at $2\theta = 35.3^\circ$, corresponding to the (400) crystal plane. This peak is consistent with the diffraction peak of the standard Prussian blue card (PDF#01-0239) (Figure 1). Comparing Figure 1a,b, the diffraction peaks of Fe-Mn-Co/PBA have higher intensities, sharper peak shapes, and significantly reduced half-height widths (Figure 1c), indicating that Fe-Mn-Co/PBA has high purity, excellent crystallinity, and small grain size. The changes in the diffraction peak intensities reflect the changes in the specific crystal structure [22]. Due to the doping of Co ions, a diffraction peak of the (220) crystal plane emerges at a 2θ value of 24.6° . In Figure 1b,c, multiple broadened diffraction peaks occur within the range of 2θ values from 50 to 60° . Owing to the doping of Mn and Co ions and the preferred orientation of the crystal, it is beneficial to the growth of the crystal planes. The internal stress generated leads to the broadening

of the peak shapes of these crystal plane diffraction peaks and the rightward shift of the (400) crystal plane diffraction peak [23]. The diffraction peak intensity of Fe/PBA is the minimum (Figure 1a), indicating that the crystallinity of Fe/PBA is relatively low, and the proportion of the ordered crystalline phase is relatively small [24].

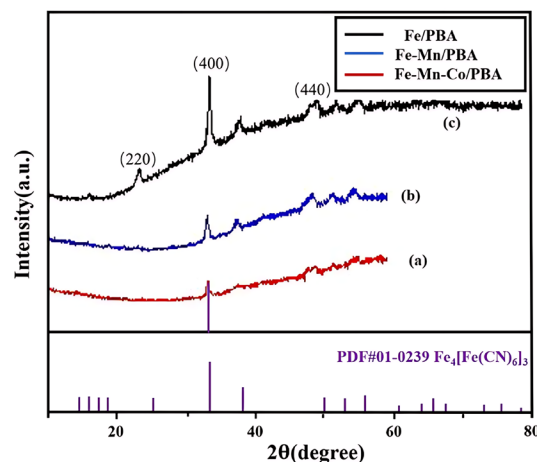


Figure 1. XRD patterns of (a) Fe/PBA, (b) Fe-Mn/PBA, and (c) Fe-Mn-Co/PBA.

Scanning electron microscopy (SEM, Beijing Zhongke Keji Co., Ltd., Beijing, China) images (Figure 2) show the morphological features of the three electrocatalysts (Fe/PBA, Fe-Mn/PBA, and Fe-Mn-Co/PBA). The internal porous structure facilitates the release of electrons and improves the alternating electron carrier, reflecting the catalytic advantages of multiple PBAs. Fe/PBA (Figure 2a) exhibits large-sized particles (>200 nm) with particle defects, which is attributed to the local supersaturation of Fe ions resulting in the limited exposure of the active sites. In contrast, the particle size of Fe-Mn/PBA (Figure 2b) remained heavily agglomerated despite the localized reduction, suggesting that the doped Mn ions inhibited the particle growth and reduced the improved activity and stability of the catalyst [25]. On the other hand, the particle size of Fe-Mn-Co/PBA (Figure 2c) was further reduced and distributed more uniformly with a smaller particle size, indicating that the introduction of Co ions further optimized the growth and distribution of the particles, which was conducive to the intercalation and de-intercalation of ions through redox reactions. The study of its spatial structure and the confirmation of the mechanism of interaction with the three ions indicate that the grain refinement of Fe-Mn-Co/PBA is an important factor leading to the broadening of the diffraction peaks, which is consistent with the results of the XRD analysis, and further confirms its advantages in the field of electrocatalysis [26].

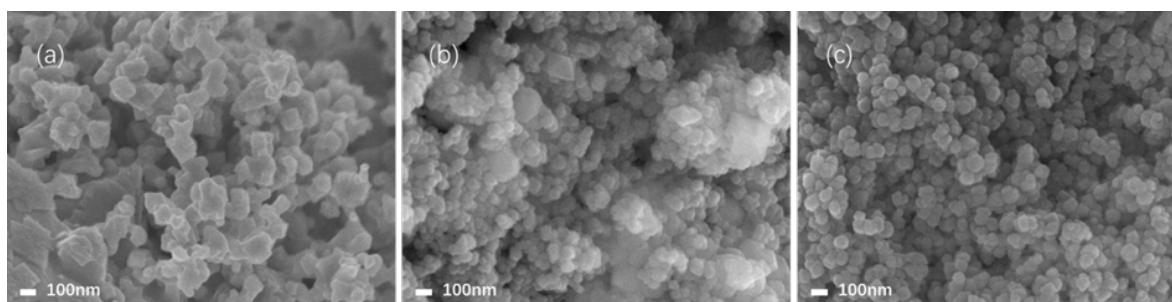


Figure 2. SEM images of (a) Fe/PBA, (b) Fe-Mn/PBA, and (c) Fe-Mn-Co/PBA.

The microstructure of the sample was characterized by High-Resolution Transmission Electron Microscopy (HRTEM), as shown in Figure 3. In Figure 3a, it can be seen that the

proportion of lattice fringes of Fe/PBA is small, and most of them are characterized by scattered irregular fringes, which indicates that most of them are amorphous structures with low crystallinity, which is consistent with the low intensity of the XRD diffraction peak [27]. The structure of Fe-Mn/PBA is mostly amorphous (Figure 3b), and the lattice stripes are visible in small regions. However, the black part in the middle of the Figure is the crystal grain, and the lattice stripes are faintly visible, indicating that the crystallinity has increased. Due to the differences in radius, charge, and other properties between doped Mn ions and Fe ions, Mn ions disturb the coordination structure around iron ions, resulting in the growth of other crystal planes of Fe-Mn/PBA. The diffraction peaks of these crystal planes can also be seen from the XRD patterns in Figure 1b. The pattern shown in Figure 3c shows visible lattice fringes of Fe-Mn-Co/PBA. The spacing between crystal planes (0.298 nm, 0.224 nm, and 0.149 nm) belongs to the (220, 400, 440) crystal planes, which is consistent with the XRD patterns (24.6° , 35.3° , and 50.3°). The lattice defects at the grain boundary are also clearly visible. Grain boundary defects promote the phase transition of Fe-Mn-Co/PBA and form crystalline phases with higher catalytic activity, thus improving the electrocatalytic performance [28]. In Figure 3d, it can be seen that there are many nanoparticles on the surface of the amplified active sites, and the size of the nanoparticles is about 80–100 nm. Nanoparticles can improve the active sites, and the synergistic effect of multiple atoms can reduce the activation energy and improve the OER of materials [29].

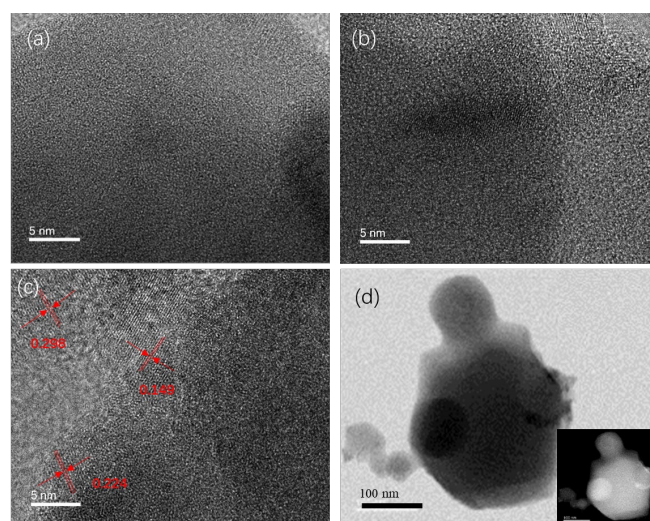


Figure 3. TEM images of (a) Fe/PBA, (b) Fe-Mn/PBA, and (c) Fe-Mn-Co/PBA, and (d) TEM image of particles with a dark and light background at high magnification.

The TEM test results of the Fe-Mn-Co/PBA sample are shown in Figure 4a. By using the scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDS) test, we can obtain the distribution ratio of elements and effectively understand their micro-catalytic effects. The STEM-EDS diagram (Figure 4b–g) indicates that the C, N, O, Fe, Mn, and Co elements of Fe-Mn-Co/PBA are evenly distributed in the structure. The weight ratios of the above elements are 29.56%, 47.44%, 21.82%, 0.21%, 0.10%, and 0.18%, respectively (Figure 4h). The proportion of C and N is relatively high, and ferrous ions are easily oxidized and combined by CN, resulting in the formation of a large number of stable iron cyanide coordination bonds, with a larger proportion of elements by weight. The iron cyanogen coordination bond has special adsorption and ion exchange properties [30], making the doped Mn and Co ions embedded in the larger hole in the center of the crystal structure cube form compounds. Therefore, there are more active sites and defects on the cube surface.

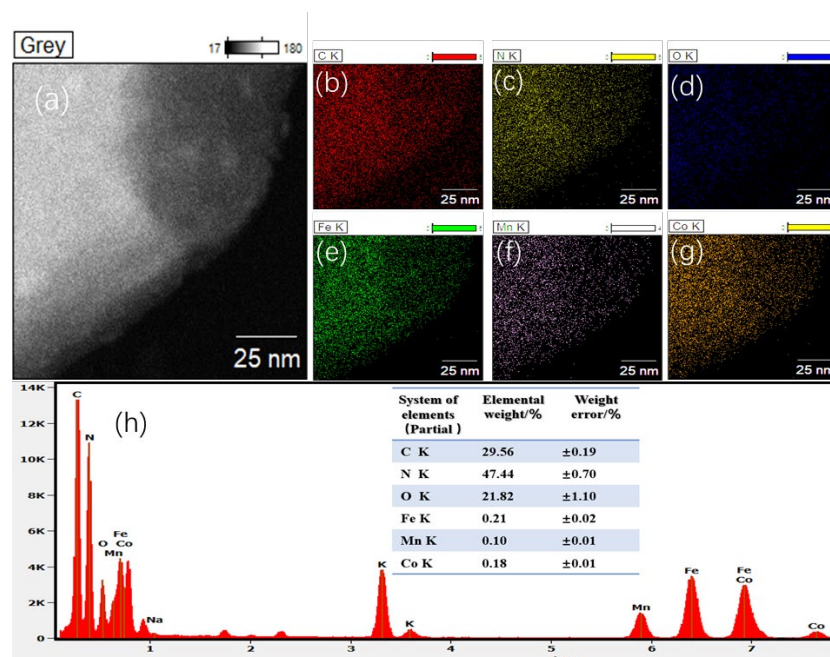


Figure 4. (a) TEM image of Fe-Mn-Co/PBA, (b–g) STEM-EDS elemental images of Fe-Mn-Co/PBA, and (h) EDS image and element content of Fe-Mn-Co/PBA.

2.2. OER Activity

In this study, the catalytic performance of the oxygen precipitation reaction (OER) was tested by linear scanning voltammetry (LSV) in a 1.0 M NaOH electrolyte system. The test system utilized a standard three-electrode configuration: a Pt sheet (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) as the counter electrode, an Ag/AgCl electrode (Gaoss Union Technology Co., Ltd., Wuhan, China) with potentials converted to the RHE scale as the reference electrode, and a rotating disk electrode (Shanghai Yidi Scientific Instrument Co., Ltd., Shanghai, China) loaded with Fe-Mn-Co/PBA catalyst as the working electrode, whose speed was precisely regulated by a Pine Research MSR-modulated rotational speed controller (Model AFMSRCE, Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). All electrochemical data were acquired by a CHI 760E electrochemical workstation (CH Instruments, Shanghai, China) with a fixed scan rate of 5 mV/s and a potential range of 1.2–1.8 V vs. RHE. As shown in Figure 5b, compared with Fe/PBA (318 mV and 490 mV) and Fe-Mn/PBA (287 mV and 375 mV), Fe-Mn-Co/PBA shows excellent overpotential of 260 mV and 350 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ and $50 \text{ mA}\cdot\text{cm}^{-2}$, respectively, indicating that the synergy between Fe, Mn, and Co metal ions results in lower actual overpotential required for current density, stronger electron transmission capacity, and promotes its oxygen precipitation effect [31,32]. The Tafel slope was derived from LSV polarization curves scanned at 5 mV/s within $\pm 0.3 \text{ V}$ of the open-circuit potential. Compared with the Tafel slope of Fe/PBA ($138 \text{ mV}\cdot\text{dec}^{-1}$) and Fe-Mn/PBA ($280 \text{ mV}\cdot\text{dec}^{-1}$), the Tafel slope of Fe-Mn-Co/PBA ($48 \text{ mV}\cdot\text{dec}^{-1}$) is smaller, indicating that the electrode reaction is more sensitive to the change in the electrode potential, the reaction rate is faster, and it is easier for the reaction to proceed, showing better oxygen evolution kinetic properties. Under alkaline conditions, through a brief quantitative comparison of Fe-Mn-Co/PBA, the superiority of the relative performance of the material is highlighted. For example, the optimized Fe-Mn-Co/PBA exhibits an overpotential of 260 mV and a Tafel slope of $48 \text{ mV}\cdot\text{dec}^{-1}$ at $10 \text{ mA}\cdot\text{cm}^{-2}$, which is highly competitive with the benchmark NiFe-LDH catalyst (263 mV and $60 \text{ mV}\cdot\text{dec}^{-1}$) and close to the performance of the noble metal RuO_2 ($250\text{--}300 \text{ mV}$ and $60\text{--}80 \text{ mV}\cdot\text{dec}^{-1}$) [33,34]. These indicators indicate that Fe-Mn-Co/PBA

has excellent oxygen evolution performance under alkaline conditions. In addition to the brief activity comparison analysis, the intrinsic catalytic efficiency is also quantified by the turnover frequency (TOF). As shown in Figure 5d, based on the active site density ($\Gamma = 2.1 \times 10^{-9} \text{ mol} \cdot \text{cm}^{-2}$, calibrated by the Cu UPD method) and catalyst mass loading ($1.50 \pm 0.05 \text{ mg} \cdot \text{cm}^{-2}$, measured by the weighing method), the turnover frequency (TOF) of Fe-Mn-Co/PBA reached 0.238 s^{-1} at $\eta = 270 \text{ mV}$ overpotential, which was significantly higher than that of the control sample (Fe/PBA: 0.020 s^{-1} ; the sample Fe-Mn/PBA: 0.015 s^{-1}), showing high catalytic activity and a fast reaction rate.

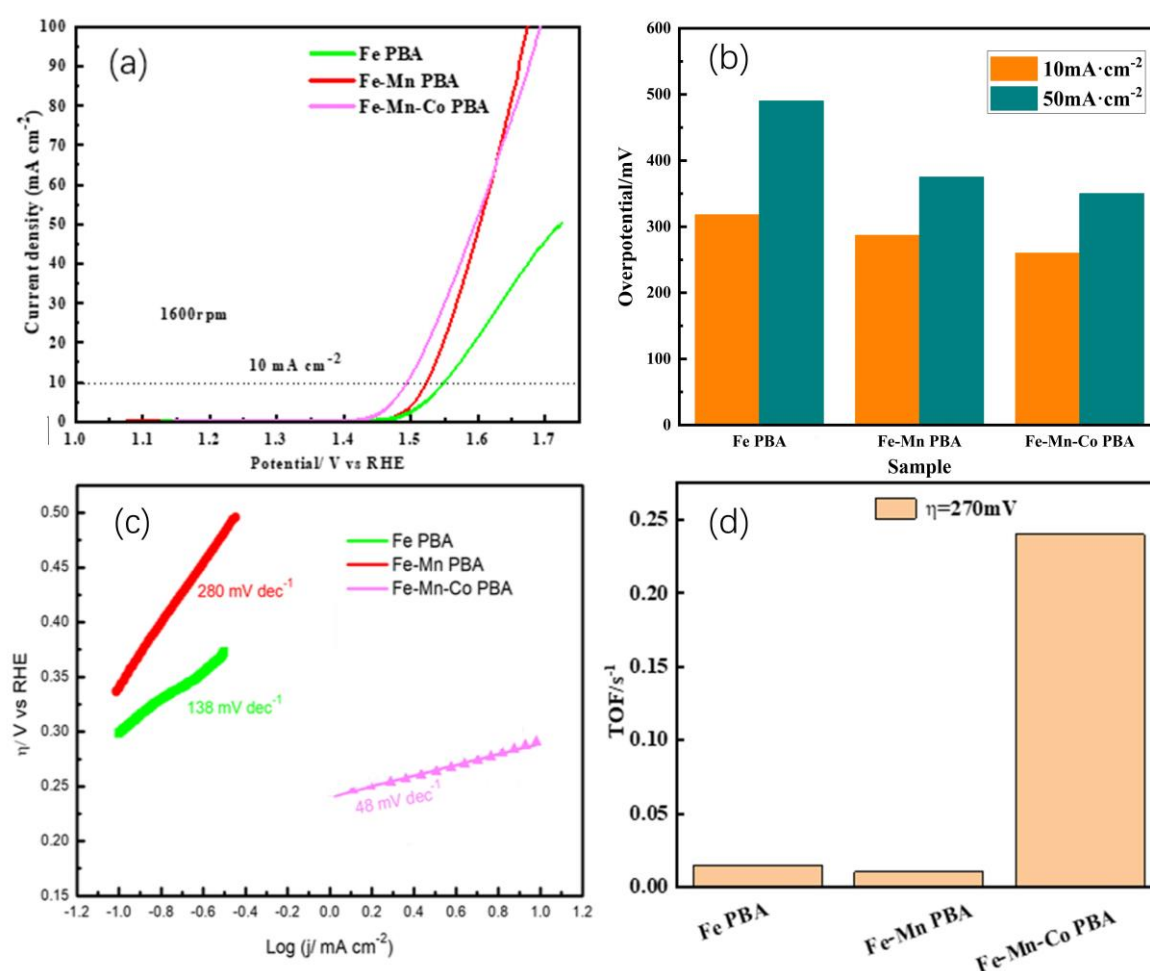


Figure 5. OER electrochemical performance testing of Fe/PBA, Fe-Mn/PBA, and Fe-Mn-Co/PBA: (a) LSV curves of three samples in 1 M NaOH at 1600 rpm; (b) corresponding overpotential of 10/50 $\text{mA} \cdot \text{cm}^{-2}$; (c) the Tafel slopes; (d) turnover frequency (TOF).

The CV test calculated the double-layer capacitance at different scan speeds, and then the electrochemical active area was calculated. Figure 6a–c show the CV curves of three samples scanned under different voltages, respectively. We then fit the CV curves to obtain the corresponding C_{dl} effect curve (Figure 6d), and calculated the slope of the straight line where the fitting scatter points are located, that is, the double-layer capacitance (C_{dl}) value of the corresponding catalyst (Fe/PBA- $7.26 \times 10^{-4} \text{ mF}$, Fe-Mn/PBA- $1.79 \times 10^{-3} \text{ mF}$, and Fe-Mn-Co/PBA- $5.24 \times 10^{-3} \text{ mF}$). According to the active point area formula, $\text{ECSA} = C_{dl}/C_s$, (where C_s is $0.040 \text{ mF} \cdot \text{cm}^{-2}$), the corresponding ECSA values of all PBA materials are $1.815 \times 10^{-2} \text{ cm}^2$, $4.475 \times 10^{-2} \text{ cm}^2$, and $1.31 \times 10^{-1} \text{ cm}^2$, respectively. It is found that the ECSA value of Fe-Mn-Co/PBA ($1.31 \times 10^{-1} \text{ cm}^2$) is significantly increased. This suggests that many grain boundary defects are generated due to the synergistic effect

of doped iron, manganese, and cobalt metal ions, resulting in more active sites and higher catalytic efficiency of Fe-Mn-Co/PBA [35].

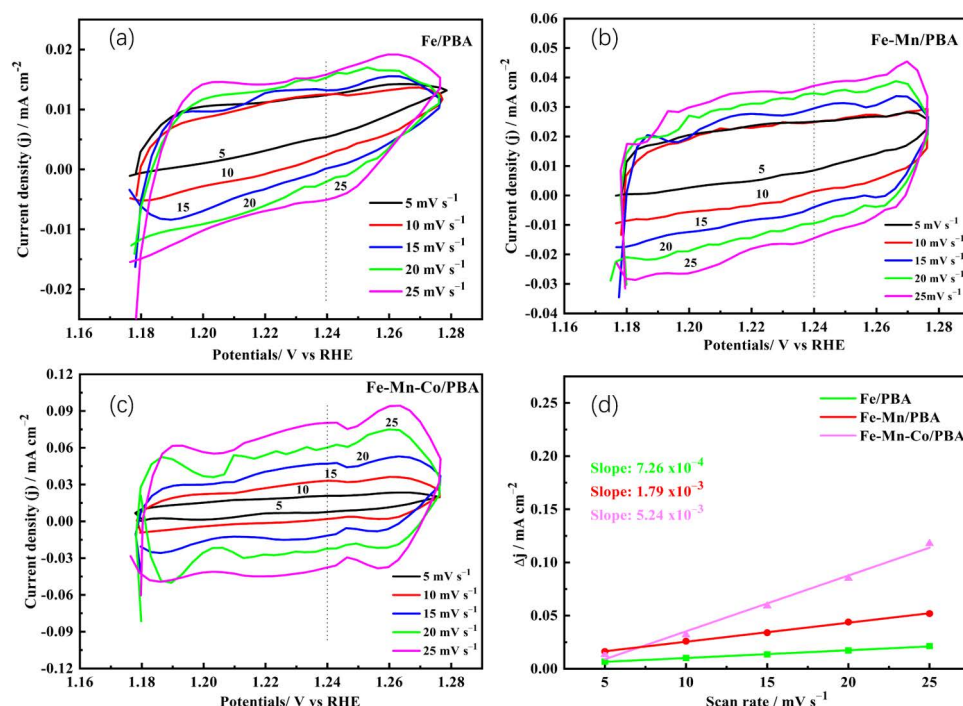


Figure 6. Cyclic voltammograms in the non-Faraday zone of different materials in 1.0 M NaOH solution at different scan rates: (a) Fe/PBA, (b) Fe-Mn/PBA, and (c) Fe-Mn-Co/PBA (scan range 1.16 V to 1.28 V, scan rate 5 mV/s to 25 mV/s at a temperature of 25 °C). (d) Calculated Cdl plots (derived from the slope of the plot of Δj versus scan rate).

For energy converter devices, in addition to electrocatalytic performance, the stability of the electrocatalyst is also a key factor [36]. Through the study of layered nanoarrays, Samanta et al. successfully prepared a multimetal-doped Ni-Co-Fe/PBA catalyst by using a layered nanosheet array, which leverages the synergistic effect of bimetallic selenium and the electronic structure rearrangement caused by Fe-based doping [37]. It shows low OER performance in terms of electrochemical performance. It was found that the surface of the catalyst may be reconstructed, resulting in a decrease in potential and the formation of an active site more conducive to the hydrogen evolution reaction, with an ultra-long durability at 10 mA·cm⁻². Wang et al. prepared Ni-Co@Fe/PBA with a core-shell structure by lattice matching principle, and prepared Ni-Co@Fe/PBA with a core-shell structure by reduction potential energy and particle deintercalation. It is worth noting that a protective film is formed on the surface of the catalyst, which can reduce the overpotential and improve the stability of the catalyst, so that the activity attenuation of OER within 24 h is only 5% [38]. The 20 h stability of this catalyst is better than most Ru-based benchmarks (such as Mo-Cu-RuO₂, which decays 86 mV at 20 h), but lower than long-lived systems such as Nb/Mn-RuO₂ (200 h). A novel and effective scheme is demonstrated in the study of various targeted applications of multi-doping. Through Fe-based doped PBA to achieve electron rearrangement and particle deintercalation, the catalyst undergoes a self-optimization process. It gradually reaches a more stable state, thus showing better stability performance. Therefore, this also improves the operation of the electrocatalyst and achieves efficient stability for Fe-Mn-Co/PBA at a current density of 5 mA·cm⁻² (Figure 7).

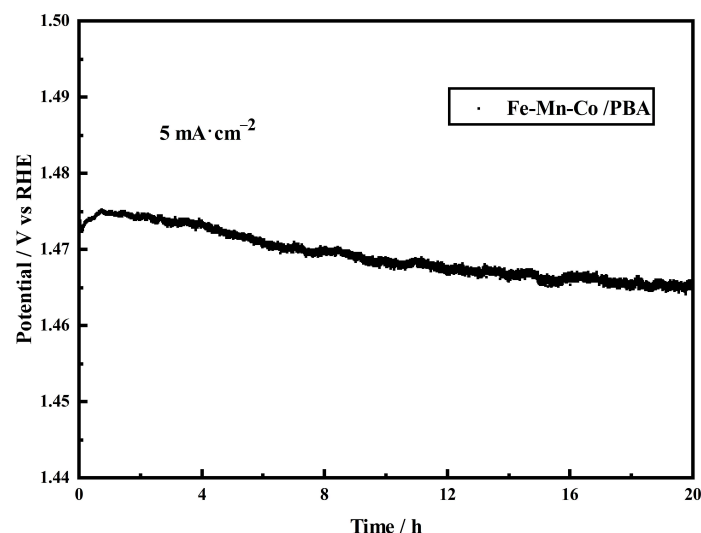


Figure 7. Stability plots of the three materials at room temperature as measured by chronopotentiometry (CH Instruments, Model 760E).

3. Materials and Methods

3.1. Preparation of Materials

In this study, a series of Prussian blue analogs (PBAs)—monometallic Fe/PBA, bimetallic Fe-Mn/PBA, and trimetallic Fe-Mn-Co/PBA—were synthesized by liquid phase co-precipitation to systematically investigate the multimetallic (Fe, Mn, and Co) doping on the OER electrocatalytic synergistic effect. The experimental parts are as follows.

The raw materials used in this experiment were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China).

The raw materials used in this experiment are all chemical reagents: trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, CAS 6132-04-3, $\geq 99.0\%$), potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$, CAS 13943-58-3, $\geq 99.0\%$), manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, CAS 7487-49-4, $\geq 99.0\%$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, CAS 7783-41-0, $\geq 99.0\%$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CAS 10045-99-8, $\geq 99.0\%$), ethanol ($\text{C}_2\text{H}_5\text{OH}$, CAS 64-17-5, $\geq 99.5\%$), and homemade deionized water. The schematic diagram of the preparation process flow of the Fe-Mn-Co/PBA sample is shown in Figure 8.

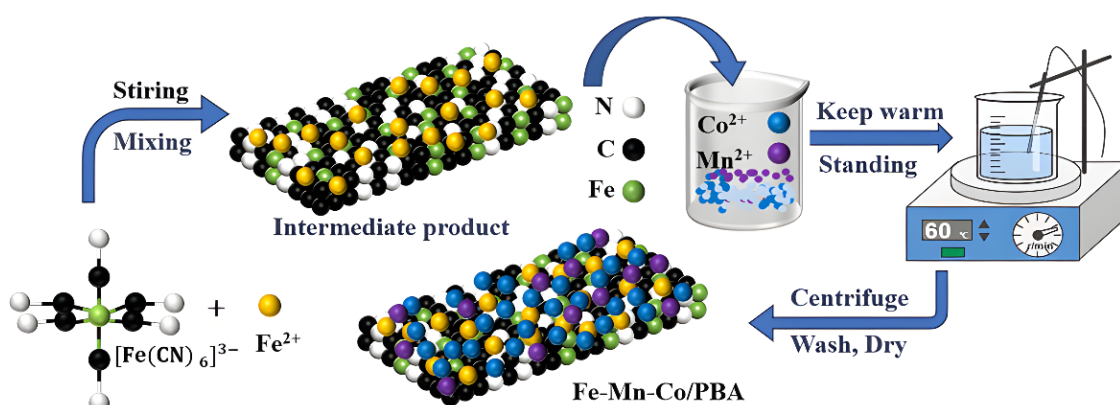


Figure 8. Schematic diagram of the preparation process of the Fe-Mn-Co/PBA sample.

In this paper, we take the preparation of Fe-Mn-Co/PBA samples as an example, and introduce the method of preparing the corresponding catalytic samples by liquid phase co-precipitation. Step 1: Dissolve 5 mmol of ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and 25 mmol of trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) in 50 mL of deionized water at

room temperature, and stir the solution with magnetic stirring (700 rpm) for 30 min until complete dissolution to form Solution A. Step 2: Dissolve 5 mmol of potassium ferricyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) in 50 mL of deionized water to form Solution B. Step 3: Mix Solution A and Solution B, and further add 5 mmol of manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and 10 mmol of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). After 30 min of magnetic stirring (700 rpm), Solution C is formed. Step 4: Allow Solution C to stand at 50 °C for 12 h. After 24 h at room temperature, a precipitate is produced. Finally, centrifugation at 7000 rpm for 10 min, washing with deionized water and anhydrous ethanol, in that order, and drying in a vacuum oven at 120 °C for 24 h yielded the desired Fe-Mn-Co/PBA sample. For comparison, the Fe/PBA sample was prepared by the same synthetic route without step 3, while the Fe-Mn/PBA sample was synthesized by the same synthetic route without the addition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in step 3.

3.2. Preparation of the Working Electrode

Preparation of working electrodes by standardized slurry coating method: Taking the Fe-Mn-Co/PBA powder sample as an example, in order to ensure the comparability of the performance tests, we used the standardized slurry coating method to make the working electrodes for the rotating disk electrode (RDE) test. The process was as follows: first, the Fe-Mn-Co/PBA powder was mixed with acetylene black conductive agent at a 1:1 mass ratio, and a solvent mixture of isopropyl alcohol/deionized water (3:1 *v/v*) containing 2 vol% Nafion solution (5 vol% of the total slurry) was added to form a homogeneous ink. The paste was dispersed in an ice bath by sonication at 150 W for 20 min to eliminate agglomerates. Substrate pretreatment was then performed as follows: using a 5 mm diameter glassy carbon electrode (GCE) as a substrate, the substrate was sequentially polished with 0.3 μm and 0.05 μm alumina pastes, and then rinsed with deionized water and N_2 blow-dried. For more precise coating, 5 μL of catalyst ink was dropped onto the GCE surface using a micropipette to achieve a controllable catalyst loading of $0.25 \text{ mg} \cdot \text{cm}^{-2}$, followed by drying at room temperature for 10 min, and then curing in a vacuum oven at 60 °C for 20 min. Finally, electrochemical testing was initiated after a non-Faraday zone pretreatment at 0.4–0.6 V vs. RHE (hydrogen adsorption zone) for 10 min.

4. Conclusions

In summary, three kinds of Prussian blue analogs (Fe/PBA, Fe-Mn/PBA, and Fe-Mn-Co/PBA) were prepared using the liquid phase co-precipitation method. XRD, SEM, and other technical methods were used to analyze their structure and morphology. Compared with Fe/PBA and Fe-Mn/PBA, Fe-Mn-Co/PBA shows a smaller particle size, larger specific surface area, and higher surface activity. Grain boundary defects provide more active sites for electrochemical reactions, thus improving the electrocatalytic activity. At the same time, Fe-Mn-Co/PBA has excellent electrochemical performance. At $10/50 \text{ mA} \cdot \text{cm}^{-2}$, the overpotential of the OER is 270/350 mV, and its Tafel slope is $48 \text{ mV} \cdot \text{dec}^{-1}$. It can maintain stable electrocatalytic activity within 20 h at $5 \text{ mA} \cdot \text{cm}^{-2}$. These are attributed to the synergistic effect of Fe, Mn, and Co metal ions, grain refinement, and the generation of grain boundary defects and internal stress. This study not only proposes a low-cost and efficient preparation of Fe-Mn-Co/PBA electrocatalytic material, but also provides reference data for high-efficiency hydrogen production by the electrolysis of water.

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