



A New Design Strategy for Developing Bi-Functional Catalysts for Zinc–Air Batteries

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2020-2021

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P 0 0 3 1 C 1 6 0 1 4 1

Abstract

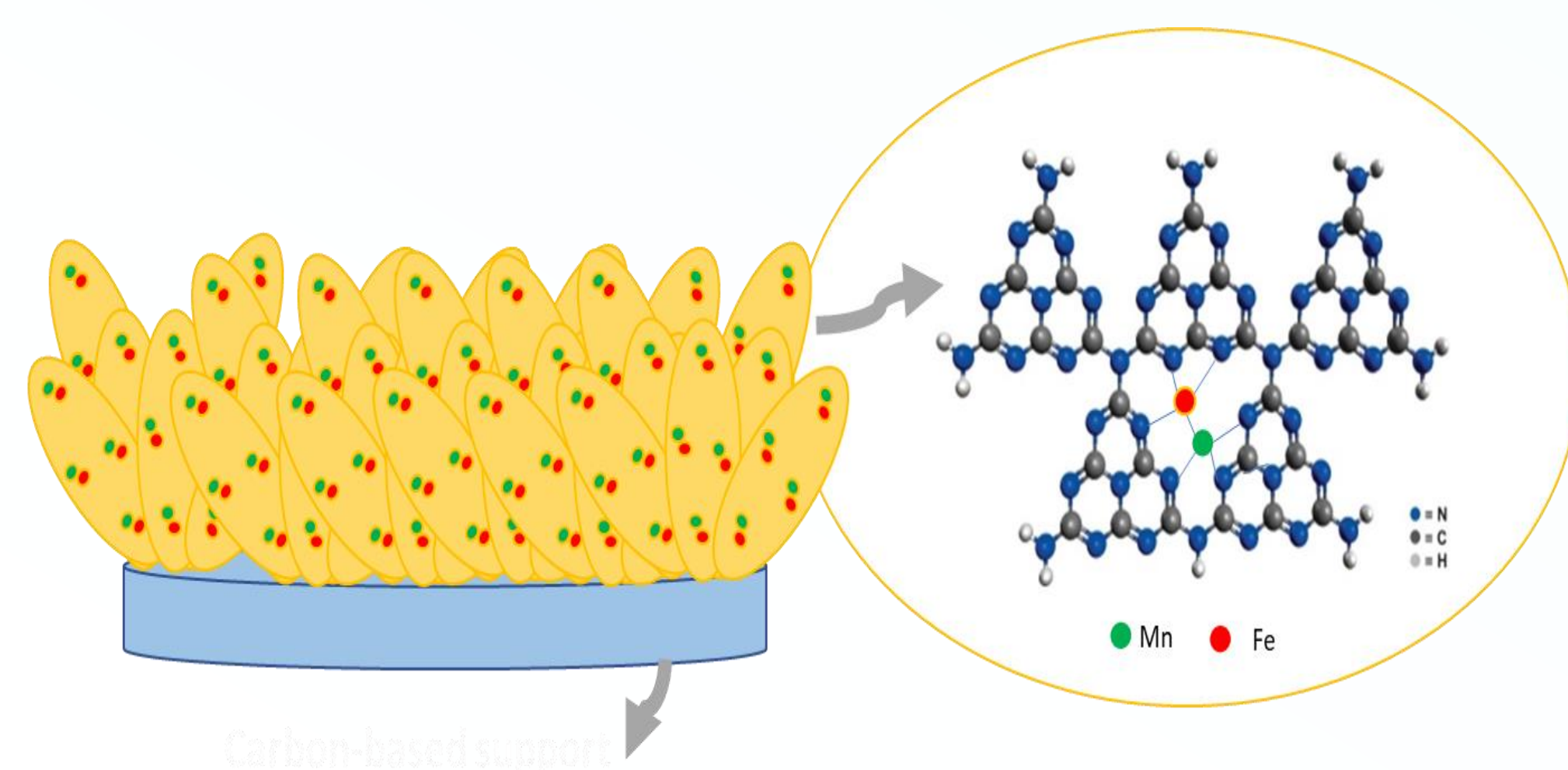
Zinc-air batteries are a great alternative to replace lithium batteries, but they require an electrocatalyst for better ORR kinetics. In this work, we proposed a new synthesis strategy for a bifunctional electrocatalyst based on Fe-Mn co-doped carbon nitride supported on carbon nanofibers (CF-CN-Fe-Mn). Cyclic Voltammetry (CV) electrochemical measurements were performed in alkaline medium (pH = 13.5), using a VersaSTAT 4 Potentiostat Galvanostat station. The CF-CN-Fe-Mn catalyst did not demonstrate a higher electrocatalytic activity ($E_{\text{onset}} = 1.2260 \text{ V}$, $E_{1/2} = 1.5549 \text{ V}$) compared to the platinum on activated carbon, 10%Pt (Pt/C) standard ($E_{\text{onset}} = 1.2526 \text{ V}$, $E_{1/2} = 1.5555 \text{ V}$). The presence of iron oxide (Fe_3O_4), noted from X-Ray Diffraction (XRD), indicates that the synthesis of the catalyst was not done as intended. Thus, the proposed synthesis method requires improvements.

Introduction

Lithium batteries have gained a dominant position in the battery market for electronic devices. However, these batteries present a problem due to their flammability and potential source of hazardous metal pollutants in the environment. In consequence of the dangers that lithium batteries pose, it is of great importance to find alternatives. Zinc-air batteries (ZABs) are a promising alternative, with their low cost, large theoretical energy density, and safety. Despite their advantages, the cathode of the battery has sluggish oxidation-reduction reaction (ORR) kinetics (Sarkar et al., 2020). To solve this, in this investigation, the aim is to prepare a potentially highly active electrocatalyst based on dual transition-metals (Fe and Mn) with attached carbon nitride nanostructures grown into carbon nanostructures.

Objectives

Fabricate and characterize a novel electrocatalytic nanomaterial for Zn-air batteries, based on Fe-Mn co-doped carbon nitride supported on carbon nanofibers.



Methodology

Catalyst Ink Preparation

Five different samples of catalyst were prepared: (1) carbon nanofibers (CF), (2) carbon nanofibers + melamine (CF-CN), (3) carbon nanofibers + melamine + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (CF-CN-Fe), (4) carbon nanofibers + melamine + $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (CF-CN-Mn), and (5) carbon nanofibers + melamine + $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ + $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (CF-CN-Fe-Mn). For this process, three salt solutions were prepared. The first one was prepared by mixing 2.2 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 60.0 mL of water. The second solution was prepared with 1.64 g of manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) in 60.0 mL of water. The third solution was prepared with 1.1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.818 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in 60.0 mL of water. For the catalyst preparation, 1.5 g of melamine and 1.5 g of carbon nanofibers were dissolved in 80.0 mL of water, while being heated at 100 °C and constant stirring, until it was completely dried. For samples 3, 4 and 5, the designated salt solution was added to the fibers. After this, the solution was dried once more at 100 °C. The dried mixture was calcinated at 550 °C. The resultant catalyst was characterized by X-Ray Diffraction (XRD).

Electrochemical Measurements

Catalyst suspensions were prepared by mixing 6 mg of the catalyst material with 1500 μL of ethanol and 600 μL of Nafion. This tincture was sonicated for 20 minutes. Another tincture with platinum on activated carbon, 10%Pt (Pt/C) was also prepared. Fluorine doped tin oxide (FTO) glass with an area of 1 mm^2 was loaded with 10 μL of catalyst suspension. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) electrochemical measurements were performed using a VersaSTAT 4 Potentiostat Galvanostat station. All electrochemical tests were done at room temperature in 0.1 M KOH which was saturated first in N_2 and then in O_2 for 20 minutes each. All the experiments were performed in Ag/AgCl (3 M KCl) reference electrode. The potentials were converted to standard reversible hydrogen electrode (RHE) potential by:

$$E_{\text{RHE}}(\text{V}) = E_{\text{Ag/AgCl}}(\text{in V}) + (0.058 \times \text{pH}) + 0.210 \text{ V}$$

Analysis and Results

To study the ORR electrocatalytic activity, electrochemical performances were done in alkaline (pH = 13.5) medium. The onset potential (E_{onset}) and the half-wave potential ($E_{1/2}$) values were retrieved from the CV data. These values, shown in Figure 1d, determine the electrocatalytic activity of the catalyst. Although the CF-CN-Fe-Mn catalyst demonstrated higher potential values, compared to the other catalyst samples, it did not obtain a higher value than Pt/C. This means that the designed catalyst did not demonstrate a higher electrocatalytic activity than the standard. Furthermore, when comparing the CV for CF-CN-Fe-Mn in N_2 saturated KOH with O_2 saturated KOH, as shown on Figure 1c, there is no noticeable difference between the two. These results were not expected since the catalyst should have exhibited a more intense response in the O_2 saturated medium. In Figure 1a, the XRD for the CF-CN-Fe-Mn catalyst is demonstrated. The peaks at $2\theta = 45^\circ, 65^\circ$ and 82° are attributed to metallic iron. Comparing the XRD pattern to the one presented in the work by Ali et al. (2013), the intense peaks at approximately $2\theta = 33^\circ, 35^\circ, 41^\circ, 49^\circ, 54^\circ, 63^\circ, 64^\circ$ and 72° are characteristic of iron oxide (Fe_3O_4). The presence of this compound indicates that the iron species are not all chemically coordinated to the carbon nitride host (Wang et al., 2009). This indicates that the synthesis of the catalyst was not done as intended.

Data

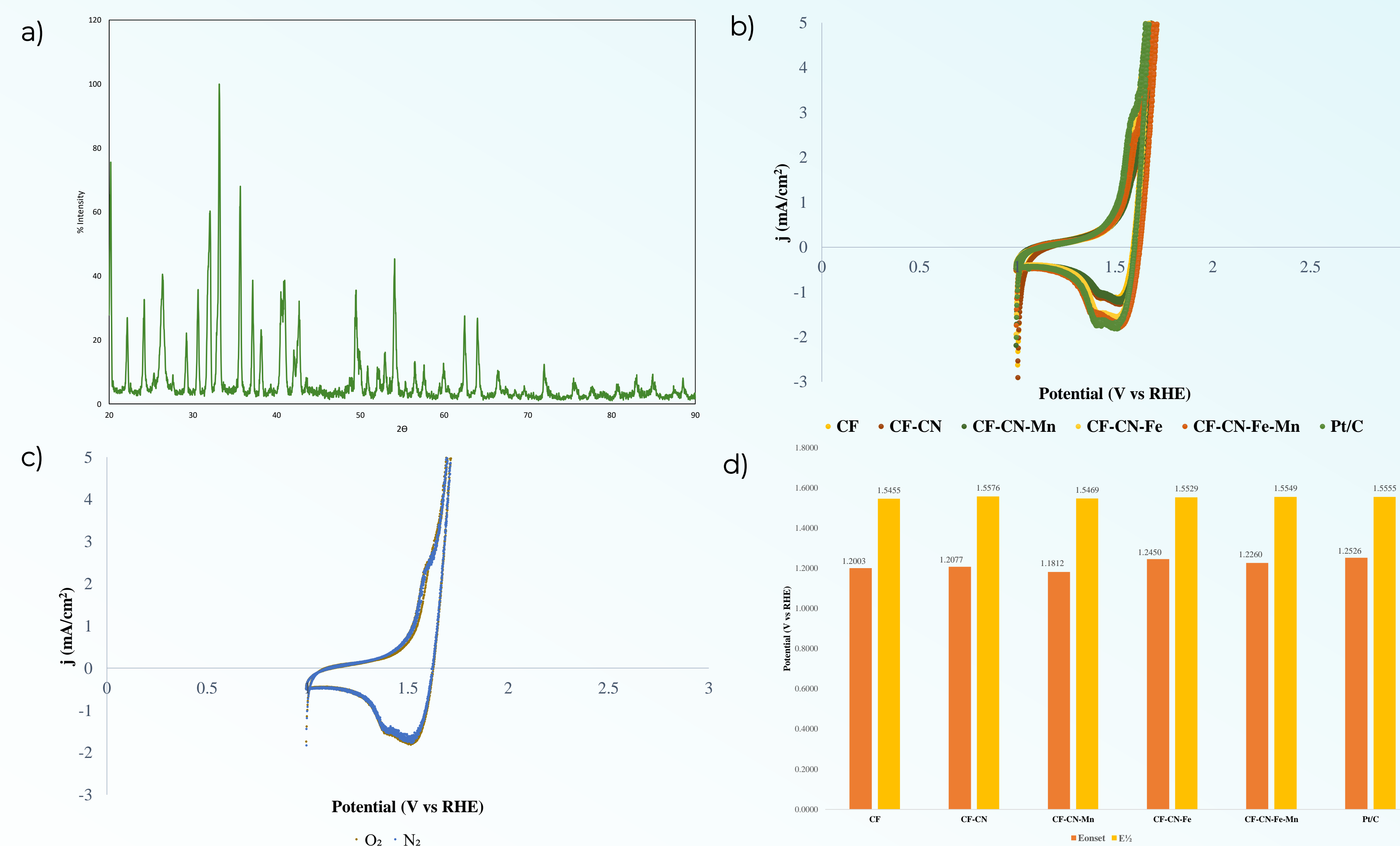


Figure 1: (a) XRD for CF-CN-Fe-Mn catalyst (b) CV response in O_2 saturated 0.1 M KOH solution for different catalyst samples and commercial Pt; scan rate 10 mV s^{-1} (c) CV response for CF-CN-Fe-Mn catalyst in N_2 saturated 0.1 M KOH and O_2 saturated 0.1 M KOH (d) Comparison plot of E_{onset} and $E_{1/2}$ for all catalyst samples and Pt/C.

Conclusion and Recommendations

In conclusion, the designed catalyst did not perform as expected. In this case, according to the XRD, the catalyst did not coordinate to the carbon nitride host, which is crucial for the electrocatalytic activity. For future work, a better method of synthesis is needed. Furthermore, electrochemical measurements should be performed with a rotating disk electrode (RDE) to obtain more accurate results.

References

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