Research on the electrocatalytic reactions of zeolitic imidazolate frameworks (ZIFs) and their derivatives.

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Abstract:

In the present era, the world is deeply entrenched in a severe air pollution predicament. Particularly, the massive emissions of harmful gases such as greenhouse gases have imposed a heavy burden on the ecological environment. However, the cutting-edge technology of electrocatalysis holds the promise of effectively reducing these harmful emissions through specific chemical reactions, thus offering a new solution to improve air quality. This research focuses on utilizing metal-organic frameworks, especially the zeolitic imidazolate frameworks, to meticulously fabricate special catalysts. Three representative types, namely ZIF-67, ZIF-67@Ni, and ZIF-67@DCD, are selected. Through a series of complex and rigorous synthesis, characterization, and comprehensive performance tests, including linear sweep voltammetry, cyclic voltammetry, and current intensity tests, their catalytic efficiencies are thoroughly investigated. The results reveal that, due to the addition of nickel, ZIF-67@Ni exhibits outstanding catalytic activity and stability. This fully demonstrates the enormous potential of customized ZIF-based materials in enhancing electrocatalytic performance, which is expected to bring significant breakthroughs in the fields of hydrogen energy utilization and environmental remediation and open a new chapter in green development.

Keywords: catalyst, ZIF-67, zeolitic imidazolate framework, electrocatalysis

Introduction

In the current era, the impact of pollution on the environment has reached an increasingly critical level, prompting numerous scientists to explore various means to address this pressing issue. Pollution manifests in diverse forms, with gaseous pollution standing out as one of the principal categories[1,2]. This encompasses the release of greenhouse gases and toxic gases, which pose significant threats to the ecological balance and human well-being. Scientists have been actively engaged in devising and testing a multitude

of strategies, employing a wide range of materials, in an attempt to mitigate the adverse effects of greenhouse gases and gaseous pollution.

Electrocatalysis has emerged as a major approach, capable of facilitating different electrochemical reactions such as the carbon dioxide reduction reaction (CO2RR), oxygen reduction reaction (ORR), the oxygen evolution reaction (OER), and the hydrogen evolution reaction (HER) [3]. These reactions offer promising solutions for reducing our reliance on fossil fuels, curbing carbon consumption, minimizing the emission of warm gases, and enhancing energy storage capabilities, thereby effectively aligning with the ambitious goals set by the scientific community.

However, the existing materials possess certain limitations [4,5]. For instance, in the context of complex proton-coupled multi-electron reactions, slow reaction kinetics and unfavorable thermodynamics present significant challenges. Additionally, the selectivity issue that arises when a single catalyst is required to handle multiple reactions cannot be overlooked. In the pursuit of an ideal catalyst with an extended operational lifespan and minimal efficiency degradation, the pyrolysis of tunable metal-organic frameworks (MOFs) has been proposed as a viable alternative to the costly and scarcely available noble metal-based catalysts [6,7].

Recently, 3D transition metal alloys, with a particular emphasis on cobalt (Co), nickel (Ni), and iron (Fe), as well as their corresponding single-atom catalysts (SACs)[8,9], have witnessed extensive application in ORR, OER, HER, and CO2RR, paving the way for the development of multifunctional catalysts for these processes. MOFs, owing to their unique structural and compositional tunability, have the potential to incorporate these elements and composites, rendering them highly valuable subjects for in-depth investigation. Among the MOFs, zeolitic imidazolate frameworks (ZIFs) offer the distinct advantage of being adjustable to contain specific target metals in the desired proportions[10-12].

In the present study, methyl alcohol and other relevant materials are utilized to synthesize ZIF. The influence of adding various elements to ZIFs will be meticulously examined using advanced equipment. This will enable us to ascertain whether and to what extent these additives can enhance the performance characteristics of the base ZIF, providing valuable insights into the design and optimization of more efficient catalysts for environmental remediation and energy conversion applications. By delving deeper into the properties and behavior of these materials,

we hope to contribute to the development of sustainable solutions that can help combat the ever-growing threat of pollution and promote a cleaner and more sustainable future for our planet.

Materials and Methods

There are three different samples that are tested later. The samples are single ZIF-67, ZIF-67@DCD and ZIF-67@Ni. The second and third samples are the products after additions of different elements on the structure of simple ZIF-67.

ZIF-67 is synthesized by the method of co-precipitation. Firstly, dissolve 0.11 mmol of $Co(NO_3)_2$ into 45 ml of anhydrous methanol and keep stirring for 30 minutes. The solution gained now is called "solution A." Then, slowly adding 6mmol of imidazole solution ($C_3H_4N_2$) with concentration of 1mmol/15ml methanol into the metal precursor, and use automate stirrer to stir for 4 hours under room temperature. Purple turbid liquid will be formed during this process. The solid products are then collected through centrifuges. The products are rinsed by m ethanol for two times and dried in vacuum for one night. Under the condition of controlled gas flow of Ar, and temperature of 750C, black solid powder obtained by pyrolysis on former products are rinsed with 2mmol/L HCL and the rinsed by water and methanol. The rinsed solid powders are ZIF-67.

ZIF-67@DCD has similar preparation steps with ZIF-67. After making up solution A (mentioned in the former paragraph), add 0.6 mmol DCD (Dicyandiamide, C2H4N4), and wait until homogeneous solution to be formed. The afterward process of adding imidazole, centrifuging and pyrolysis is totally as same as the process of making up ZIF-67, and the amount of chemicals used does not change. By the same process, black solid powder products of ZIF-67@DCD are gained.

ZIF-67@DCD has similar preparation steps with ZIF-67@DCD. The only difference is that extra amount of 0.6mmol of Ni(NO3)2 are added into solution A. The other processes remain the same.

The solid powders are impossible to be adhered on the carbon paper of . instead, the powders will dissolve in the strong base solution, and experiments fail. Thus, we use 500ml water, 480ml isopropyl alcohol and 20ml 5% nation solution to make "solution B" that serves the function of glues, and dissolve the three samples of powders separately in solution B. The powder-added glues are applied on the surface of carbon paper. Consequently, these powders will stick on the carbon paper for experiments.

The reagents used in this experiment are listed in Table 1.1.

<div align="center">**Table 1.1 Experimental Reagents**</div>

Reagent Name	Chemical Formula	Purity	Source
5% Nafion Solution	$C_9Hf_{17}O_5S$	99.9%	Aladdin
Isopropanol	C_3H_8O	98%	Aladdin
Methanol	CH_3OH	99.9%	Aladdin
2-Methylimidazole	$C_4H_6N_2$	98%	Aladdin
Potassium Hydroxide	KOH	99.9%	Aladdin
Dinitrile Diamine	$C_2H_4N_4$	99.9%	Aladdin
Nickel nitrate hexahydrate	$Ni(NO_3)_2 \cdot 6H_2O$	99.9%	Aladdin
Cobalt Nitrate hexahydrate	$Co(NO_3)_2 \cdot 6H_2O$	99.9%	Aladdin

Results and Analysis

All the samples were subjected to testing within an electrochemical workstation. The original data were obtained by conducting and processing experiments involving linear potential sweep (LSV), cyclic voltammetry (CV), and I-t curve (current intensity over useful time). In the graphs presented, "cp" is used to denote carbon paper, which serves as the substrate onto which the samples are adhered.

Upon analyzing the LSV graph, it was noted that ZIF-67@Ni exhibited the lowest absolute voltage, approximately 1.8 V. In contrast, the pure ZIF-67 demonstrated a relatively higher absolute voltage. From this observation, it can be inferred that ZIF-67@Ni displays relatively superior performance as a catalyst. The trend of the current intensity variation further corroborates this conclusion. Looking at the CV graph, there are dips or depressions in the curve when the voltage reaches around -0.5V. Among these, the depression corresponding to ZIF-67@Ni is significantly more pronounced than those of the other samples. This indicates that a more vigorous reduction reaction is taking place at this voltage for ZIF-67@Ni compared to the other samples, thereby reinforcing the notion of its better catalytic performance.

Once it was established that ZIF-67@Ni exhibited the best catalytic performance among the tested catalysts, its stability was evaluated using the I-t graph. During the 18-hour test period, with the potential maintained at -0.8V, the current showed only minimal decay, and the curve was nearly linear. This outcome alleviates concerns regarding the instability of ZIF-67@Ni. Tests for the other samples were not carried out comprehensively, as they share similar structures and are expected to possess comparable stabilities. This assumption is based on the understanding that materials with analogous compositions and architectures often exhibit similar stability characteristics in electrochemical systems.
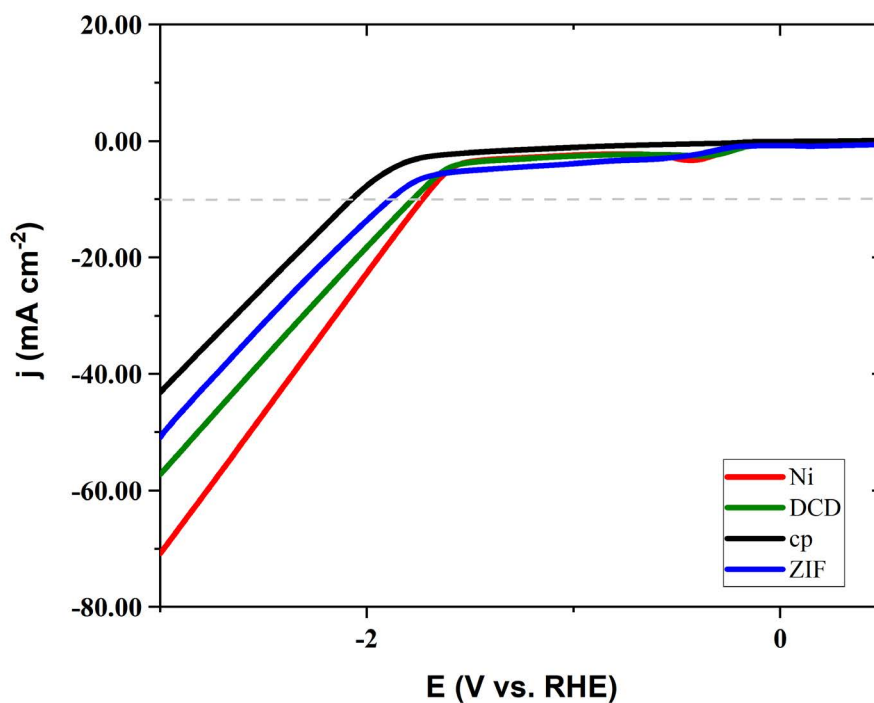
Figure 1. LSV Curve of DCD, Ni, cp and ZIF for Hydrogen Evolution in Water Electrolysis
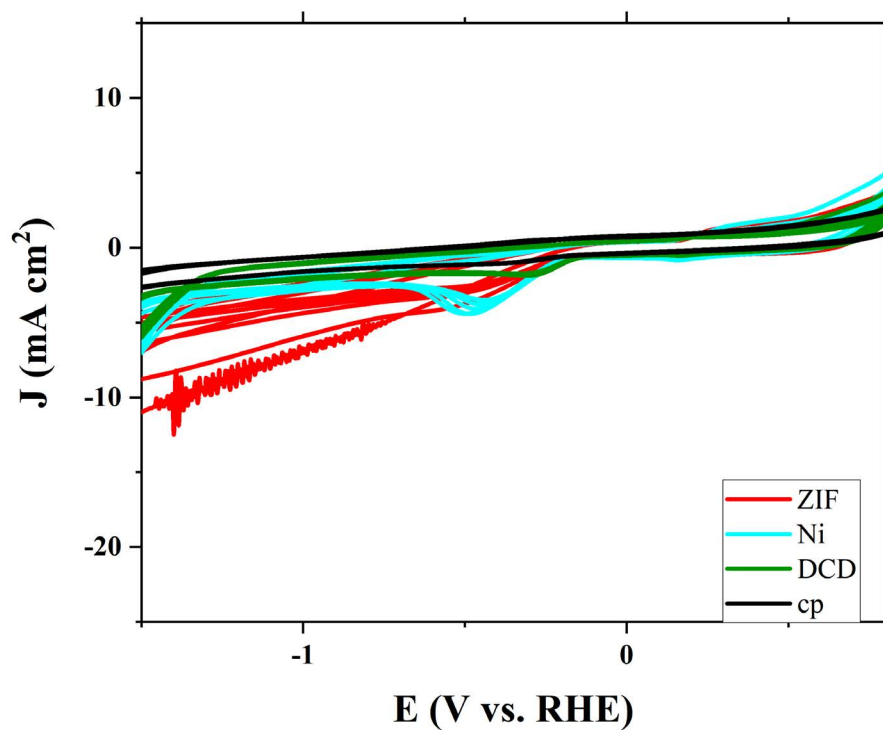

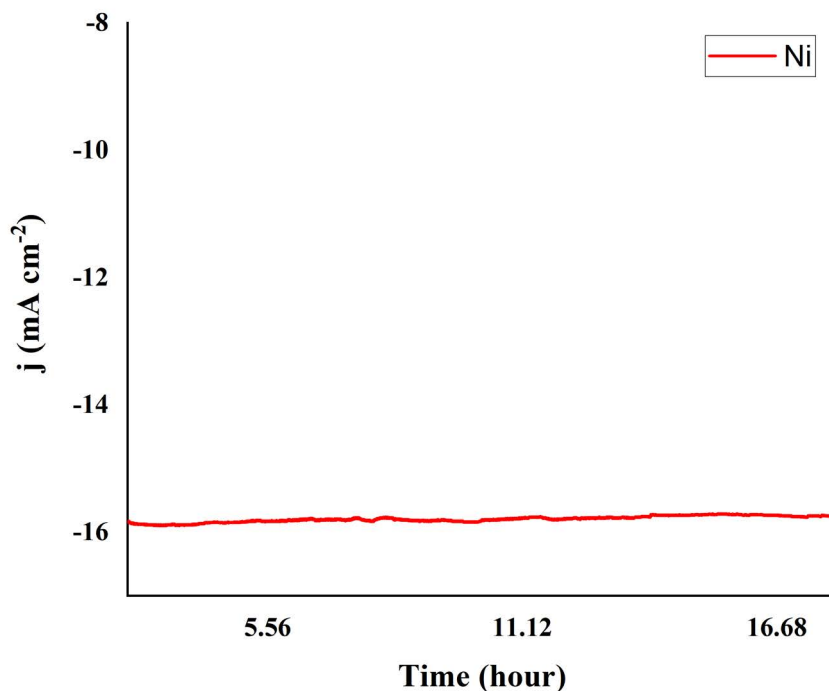**Figure 2. CV Curve of DCD, Ni, cp and ZIF for Oxygen Reduction**

Figure 3. I-t Curve of Ni in Electrochemical Reaction

Conclusion and outlook

In conclusion, the paper utilizes strategies of linear potential sweep (LSV) cyclic potential sweep (CV) and I-t curve (current intensity-useful time) to examine the stability and the effectiveness of the three different catalysts (samples of ZIF-67, ZIF-67@Ni, ZIF-67@DCD). The catalysts are all relatively stable. ZIF-67@Ni has the best performance and single ZIF-67 has the relatively worse performance, given the data analyzed previously. Thus, it is deduced that the addition of element Ni (from $Ni(NO_3)_2$) and element N (from DCD) on the structure of single DCD are both able to improve the catalyst performance in hydrogen evolution reaction (HER). This article provides elements that are capable to improve catalyst performance when adding them to catalyst structures. The conclusion can contribute to the procession of metal/hydrogen ion absorption, provide possibility of higher reaction rate. This can lead to wider usage of hydrogen energy, leading to alleviation in gaseous pollution. By absorbing targeted metals, ZIF-67@Ni can also contribute to the procession of waste water.

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