2025年臺灣國際科學展覽會
優勝作品專輯

作品編號　030033

參展科別　化學

作品名稱　Low-Cost Nickel-based Catalyst for Electrocatalytic Splitting Of Ammonia Towards Clean Hydrogen Production

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TISEF 2025 Project Report

Project Title: **Low-Cost Nickel-based Catalyst for Electrocatalytic Splitting of Ammonia Towards Clean Hydrogen Production**

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Chemistry

Section 1: Introduction

Increasing energy needs alongside the urgent issues of chemical pollution has prompted the need for developing novel green energy sources. Nitrogen-based fertilizers are of fundamental importance for the ecosystem as their usage has increased use of ,increased eight times in the last fifty years [1]. On the other hand nitrogenous fertilizers is followed by higher ammonia emissions, which are dangerous pollutants responsible for deterioration in biodiversity by means of eutrophication, acidification of soil and water, and climate change [2]. Ammonia has the2apacityy to bond with other pollutants including sulfur oxides and nitrogen oxides to create particles that cause smog, which is associated with lung disease. Ammonia also increases frost sensitivities and causes necrosis of many plant species Therefore, there is a need to properly manage the ammonia-rich nitrogen waste .[3] to decrease the environmental threat factors.

Of the possible approaches suggested for ammonia waste treatment, the ammonia electro-oxidation reaction (eAOR) has various promising features for application in the energy sector. It is economically appealing because Ammonia can serve as an excellent hydrogen carrier due to its storage capabilities and existing transport infrastructure alongside having no net carbon emissions. Apart from this, it requires 95% less of the theoretical energy [4] to perform the process. But the reaction is kinetically slow [5], which has been a research obstacle during the development of (eAOR), due to factors ofmslow reaction rate and large catalytic overpotential that this process consumes an unnecessary amount of power [6].

,Nickel-based catalysts are a promising solution to these problems, they are cheaper more stable and easier to produce than electrocatalysts for water electrolysis which makes it highly energy efficient for widespread use on the industrial scale. N films deposited on the anodic side also allow the creation of N-containing products such as (NH42SO3) and nitrates, which can be converted into fertilizers or renewed into the nitrogen cycle to make the process more environmentally friendly while enhancing the (eAOR) process [7,8]. Compared to Pt and Ir which are the most used noble metals, they are less poisoned on the potentials less than 0.65V and are more noble metals are scarce, and their cost is high for industrial ,stable [9,10]. However applications as well as the energy they waste during (eAOR) [11].

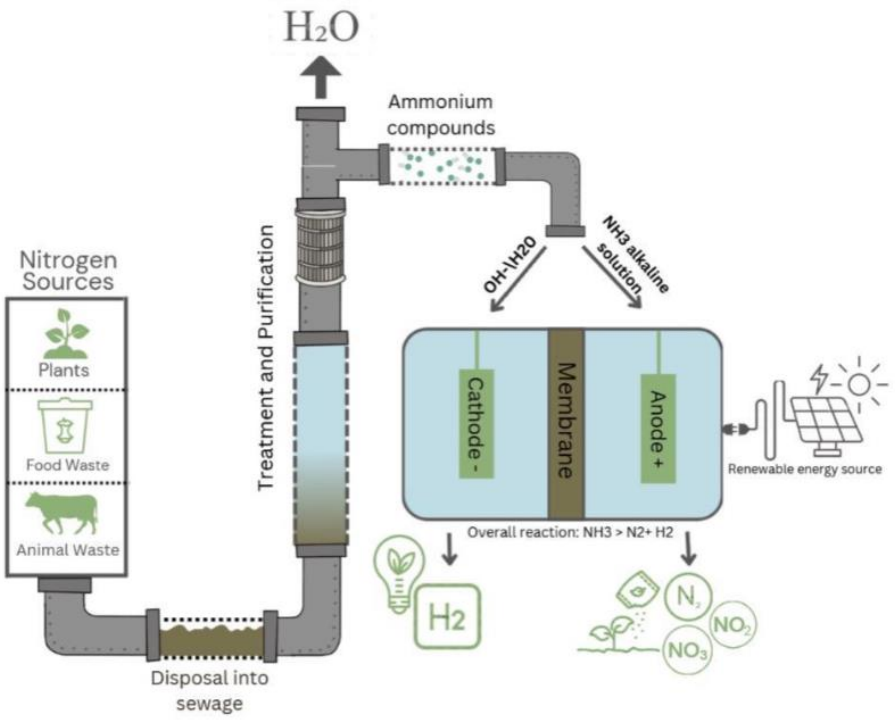

Fig 1. Schematic of industrial (eAOR)

Section 2: Literature Review

Several studies have been conducted over the last few years on the electrochemical decomposition of NH3 into N2 and H2 for wastewater management, fuel cell synthesis, and other related fields. Several electrocatalysts were developed in order such as Pt, Pd and Ir for ,to support this reaction, most notably utilizing noble metals their high activity [12] as well as experimental studies examining PtIr alloys that verified their display of higher activity but lower ammonia oxidation potential than their respective single-metal counterparts.[11] Pt species such as Pt(100) and Pt(111) have proven to be very effective and selective catalysts for ammonia oxidation, with Pt(100) allowing faster oxidation.

Yet, widespread use of noble metals as electrocatalysts is hindered by [13,14] practical limitations such as their high cost and rapid deactivation rates [15,16]. In many experimental studies have been ,comparison with similar non-noble metals conducted studying the (eAOR) capabilities of Ni-based catalysts. Ni possesses many advantages that could simplify the (eAOR) process, such as relative ease of surface modification and natural abundance [17]. DFT studies have revealed that the theoretical onset potential for Ni in (eAOR) is 0.33V vs RHE, which is comparable to Pt's 0.28V. However, it must be stated that Ni is inherently inactive when conducting (eAOR) in alkaline media, which is linked to formation of a thin NiO layer on .[8,16] electrode surface area

Potential solutions include utilization of Ni alloys for (eAOR). It is certain that introduction of specific elements can help alter Ni catalytic properties and further increase (eAOR). Cu is the most optimal candidate amongst 3D transition metals for enhancing Ni's catalytic activity [17,18]. As Ni takes on the structure of Ni(OH), many studies have been performed in order to construct NiCu double hydroxides (NiCuDH) and alter its properties to pursue further electrode optimization. NiCu alloys have proven to possess desirable qualities in terms of both onset potential and current density [19].

Other studies have pursued utilization of similar first-row transition metals as electrode dopants, and further emphasized Cu's unique properties as an (eAOR) enhancer [20]. Hailong et al [21] synthesized unique three-dimensional nanoflower-like structured Ni1Cu1Co0.5- S-T/CP electrodes for eAOR.

Electrochemical investigation showed that the Ni1Cu1Co0.5-S-T/CP electrodes demonstrated an incredibly high current density of 121.1 mA/cm2 at 1.65 V vs RHE, and excellent stability for an approximative 12 ,a low onset potential of 1.241 V hours. The produced electrode exhibited a removal rate of 98.07 % and a high N2

selectivity of 81.21 %. Kenji et al [22] have fabricated (NiCu/MnO2) electrodes via .electrodeposition method for (eAOR) that are selective to nitrogen

Compared to their single-cation counterparts, the resulting (NiCu/MnO2) electrodes exhibited a notably high catalytic activity with much lower overpotential towards (eAOR). This electrode had achieved faradaic efficiency (FE) as high as nearly 100% (97.4%) for nitrogen evolution at a constant potential of +0.6 V vs Hg/HgO. In more recent research, Jing et al [23] have reported a hydrothermal method for self-supported CuM (M = Ni, Fe, Co) loaded on carbon cloth electrodes for (eAOR).

It is important to mention the formation of nitrate products during the (eAOR) mechanism, which could be taken advantage of to make fertilizers. Relatively minimal research has been made into analyzing the kinetics of the associated reactions, however, Johnston et al. [24] has identified two separate mechanisms in their work. Specifically, homogeneous catalysis of NH3 electrooxidation via dissolved Cu2+/3+ species preferentially produced NO2− with Faradaic efficiency of 87%. Most (eAOR) catalysts that are developed to aim for generation of nitrates are restricted to non-noble based electrodes, such as Cu and Ni. In studies focusing on the environmental applications of (eAOR), Jury et al. [25] displayed that NH3-containing solutions of Na2SO4 or K2HPO4 may be electrolyzed to generate solutions of recycled PKNS and PKN fertilizers. This process leverages their Ni(OH)2's catalyst's ability to selectively oxidize ammonia to nitrate. With further catalyst optimization (via means such as surface doping), this approach holds promise for sustainable repeated electrochemical synthesis of N-fertilizers. Additionally, they have conducted experimental research to showcase that ammonia-to-nitrite oxidation proceeds instantly on NiOOH electrode surfaces, wherein the resulting nitrate is developed into fertilizers.

Section 3: Methodology

We will adapt novel low-cost synthetic strategies aiming to prepare the catalysts which are expected to improve the efficiency and selectivity of the (eAOR). On the other hand, we will interrogate the catalysts material with different structural and electrochemical techniques targeting a full understanding of how the catalyst affects .the (eAOR) efficiency and selectivity.

Preparation of proposed materials Ni(OH)2/NF based catalysts. Synthesis of the .1 Ni(OH)2/NF based catalysts was conducted by the use of the in-situ solvothermal method Figure.2. By introducing different wt. % ratios of both copper chloride, and phenyl boronic acid (PBA) as Cu, and B precursor and Di methyl formamide (DMF) .solvent

Characterization of prepared electrodes. Detailed electrochemical measurements .2 will be carried out using techniques such as cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) will be used to evaluate the electrocatalytic activity and stability of prepared Ni-based catalysts towards (eAOR). Measurements such as CV and CA can provide us with information about the electrochemical surface area and electrode stability. Ammonia - can be oxidized to many products such as N2, H2 gases, and NO_2^-, NO_3^- .ionic product

The faradic efficiency of each product either in the gas or liquid phase should be estimated to show the catalytic performance of the catalyst. This can be done by converting the molar concentrations of each product considering the number of electrons involved in the reaction. Chromatographic techniques (GC) are usually used to quantify products in gas phase. While non-gases products such as NO_2^-, and NO_3^- will be analyzed by ion chromatography (IC).

Section 4: Preliminary Results

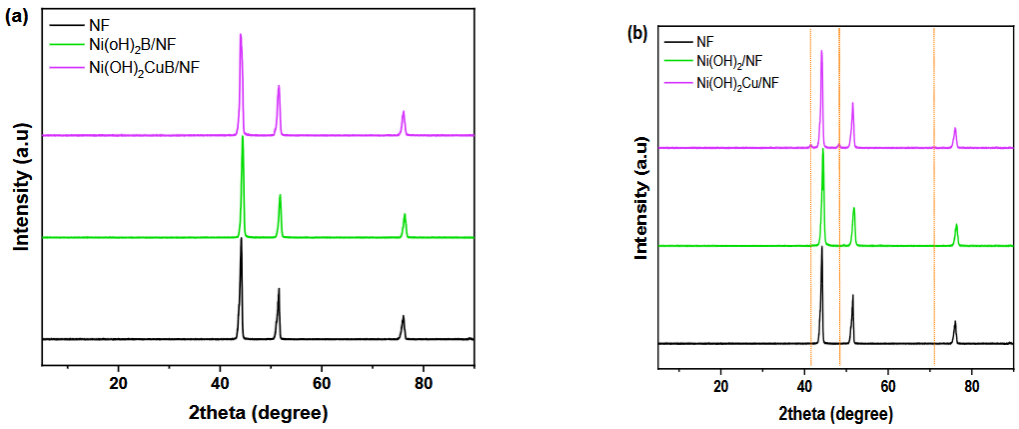

Figure 2: Characterization done via XRD of catalysts

:Structural Characterization

To identify the phase and crystal structure of the catalysts, XRD patterns of Nf, / Ni(OH) CuB/NF were performed as shown in Figure 2a, and 2b. Ni(OH)B/NF, and Cu/NF, Ni(OH)2Ni(OH).

In Figure 3a, all the catalysts have the same main diffraction peaks for crystal phase CuB/NF, and that are2B/NF, and Ni(OH)2which indicates the ,tetragonal NF amorphous nature of Ni(OH) comparable with the standard JCPDS data corresponding to the main lattice plane (111),(101).

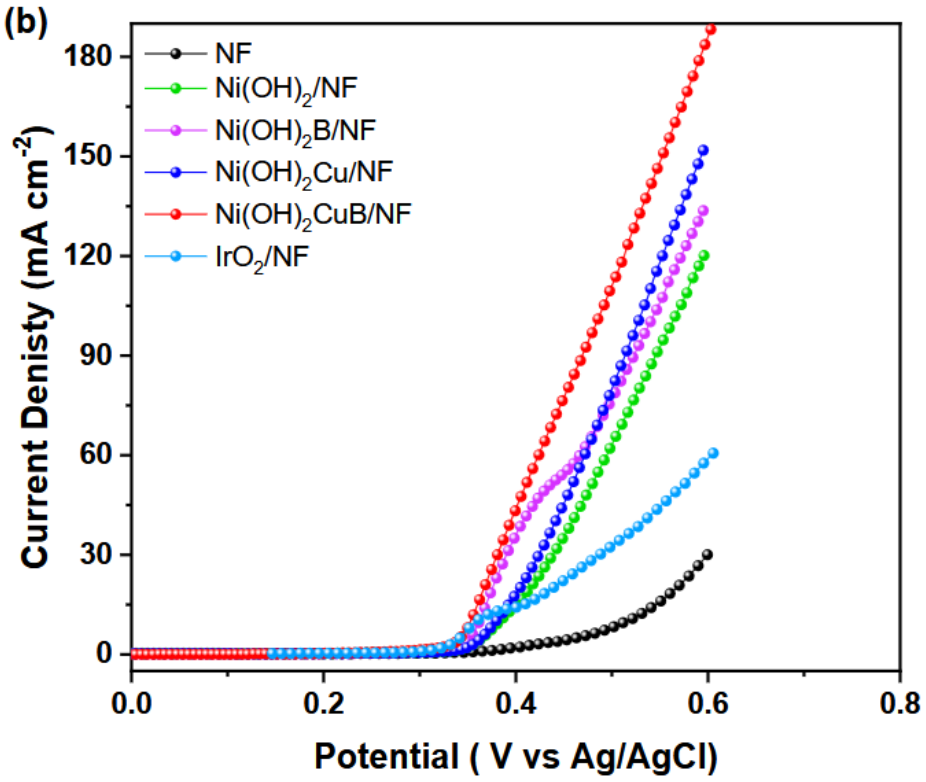

Figure 3: Electrochemical performance of catalysts

A crucial element for the catalyst assessment is its long-term (eAOR) performance durability. The CuB/NF catalysts Cu/NF, and Ni(OH)2Bi/NF, Ni(OH)2Ni(OH)/NF, term durability of Ni(OH)-long is measured by chronoamperometry at constant potential starting at 0.30 V vs. Ag/AgCl, as seen in the Figure. The current was changed by 0.05v every 2000 seconds and stayed stable for the 12000 sec electrolysis at applied potentials. Based on the measurements of the Nyquist curves for the compared with monobits the smallest semicircleCuB/NF exhi2loaded NF electrode, Ni(OH)-catalyst CuB/NF exhibits2/NF samples. Compared with other electrode materials, Ni(OH)2doped and Ni(OH) significantly higher (eAOR) activity, which is in line with the reduction of (eAOR) charge transfer.

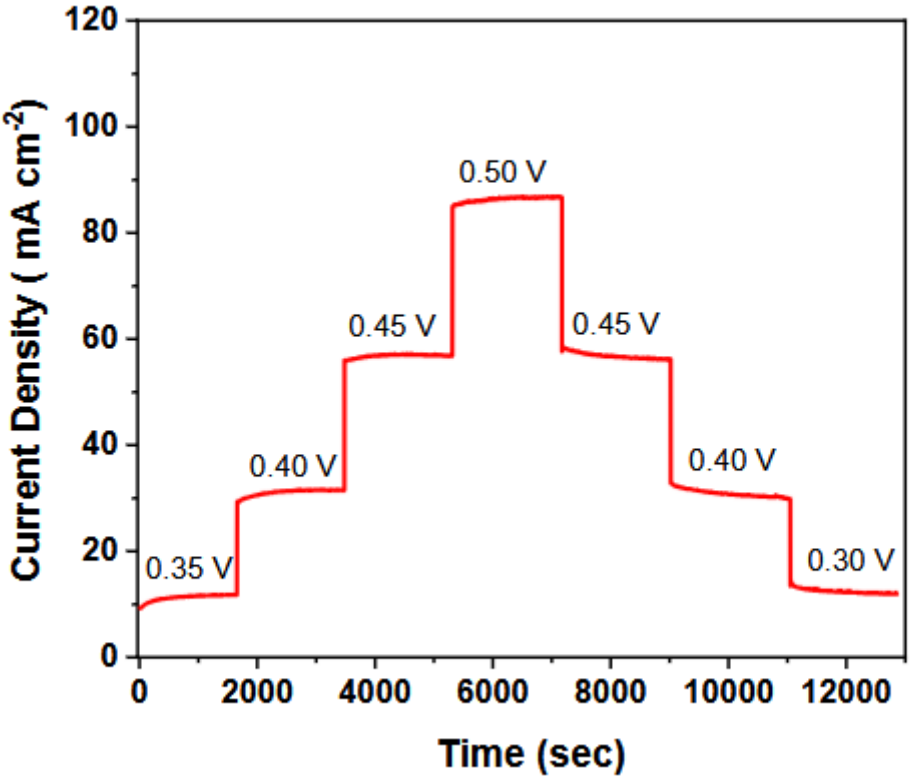

Figure 4: Chronoamperometry done of NiCub catalyst

Section 5: Results

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【評語】030033

The student has synthesized the Ni(OH)2/NF based catalysts by the use of the in-situ solvothermal method. The prepared electrodes were characterized by electrochemical measurements including cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) to evaluate the electrocatalytic activity and stability of prepared Ni-based catalysts. The faradic efficiency of each product either in the gas or liquid phase was estimated by gas chromatography (GC) or ion chromatography (IC) to evaluate the catalytic performance of the catalyst. The subject is appealing and interesting. The performance of this study is notably better than the reported literature. Thus, this work is not only promising, it can also turn into a publishable research.