

Preparation of nickel manganese oxide modified ni foam for anode catalyst direct urea fuel cell

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Abstract. Renewable energy is known as environmentally friendly, such as fuel cells. Nickel is regarded as one of the most promising transition metals to be applied as an electrocatalyst in fuel cell application due to its high catalytic activity. However, the modification of nickel is required to decrease its overpotential. In the present study, the NiMn₂O₄/Ni-foam was prepared for an anode catalyst in the direct urea fuel cell. The NiMn₂O₄/Ni-foam was synthesized through the hydrothermal method at 180°C for 24 h using Mn(NO₃)₂·6H₂O and Ni(NO₃)₂·6H₂O solutions as the precursors in the presence of urea. During the reaction, Ni foam was placed in the solution to undergo the reaction inside the porous of the Ni-foam. Cyclic voltammetry of the prepared NiMn₂O₄/Ni-foam electrode in a 2 M KOH solution and 0.33 M urea showed good maximum current density at 206 mA cm⁻². Furthermore, the prepared electrode was examined in a direct urea fuel cell with a solution containing 2 M KOH and 0.33 M urea in the anode chamber and a solution containing 2 M H₂O₂ and 2 M H₂SO₄ in the anode chamber. A power density of 0.304 mW cm⁻² was achieved, indicating the prepared electrode is promising to be developed for a catalyst in a direct urea fuel cell.

1 Introduction

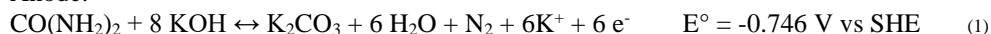
The fuel cell is a renewable energy source that attracts the attention of researchers because it holds several advantages, such as environmentally friendly, less production of carbon emissions, and less noise. The fuel cell converts chemical energy into electrical energy [1]. The system was operated by using hydrogen-rich chemical compounds such as methanol, ethanol, and urea [2]. Urea is one of the promising fuel sources because it is non-toxic, stable, non-flammable, and easy to obtain [2], [3]. However, urea has a notable disadvantage as a fuel source due to the low power density produced. Thus, a catalyst is needed to increase the urea power density and to achieve a higher performance to the fuel cell system.

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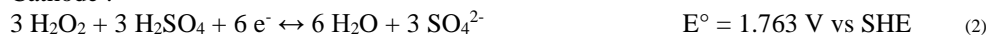
Nickel is a transition metal that has been widely utilized as an electrocatalyst in a fuel cell system due to its high activity [4], [5]. However, nickel has a disadvantage due to its high overpotential in electro-oxidation of urea, which can reduce the performance of the fuel cell [6]. The modification of nickel is required to reduce the overpotential and to increase the overall effectiveness of the fuel cell.

It was reported that modification of nickel with manganese oxide succeeded in reducing the urea oxidation potential [2]. In the present study, nickel manganese oxide was modified in nickel foam (Ni-foam). Ni-foam has a high surface area and good mass transfer property because it has a porous structure. Several studies described the modification of the composition of nickel nanowire prepared by the electrodeposition method [2], showing high urea oxidation activity and high stability. Fuel cells with urea raw material are composed of electro-oxidation urea in the anode and electro-reduction oxidants such as oxygen, air, or hydrogen peroxide in the cathode. Overall the reactions that occur in this fuel cell are as follows [7]:

Anode:



Cathode :



Overall:



$$E^\circ_{\text{cell}} = 2.509 \text{ V} \quad (3)$$

In this research, a catalyst to increase the power density of urea fuel cell was created by depositing nickel manganese oxide in the nickel foam porous.

2 Material and Method

2.1 Materials

Ethanol and acetone were retrieved from Daejung, while $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from Alfa Aesar. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, urea, and H_2O_2 were purchased from Sigma-Aldrich. Finally, KOH and H_2SO_4 were purchased from Samchun Chemicals and Merck, respectively.

2.2 Synthesis of the electrode

First, the 1 x 1 cm size nickel foam was sonicated in acetone, ethanol, and deionized water consecutively for 30 min each. Separately, 2.5 mmol $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.5 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 7.5 mmol urea were dissolved in 30 mL of distilled water. The solution was stirred with a magnetic stirrer for 30 min at 45°C (until homogeneous). The nickel foam and homogeneous solution were transferred into the autoclave and heated in the furnace at 180°C for 24 h. The samples were then annealed at 400°C for 2 h in Ar atmosphere and named as $\text{NiMn}_2\text{O}_4/\text{NF}$.

2.3 Characterizations of the prepared electrode

The X-ray diffraction (XRD) measurement was carried out by using a D/Max2500V/PC (Rigaku). Morphologies and the element distribution were investigated by field emission scanning electron microscope (SEM, JEOL JEM-7210F) equipped with an energy-dispersive X-ray spectrum (EDS) analyzer.

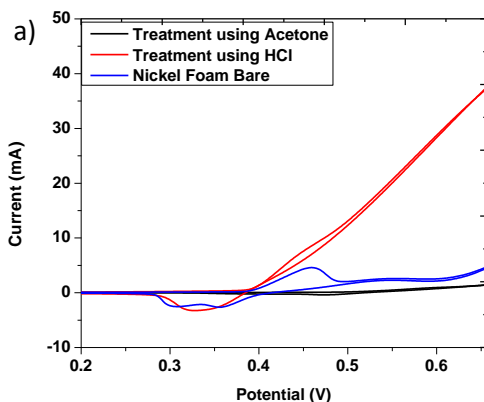
2.4 Electrochemical measurements

The prepared NiMn₂O₄/NF, an Hg/HgO system, and a Pt spiral were used as the working electrode, reference electrode, and counter electrode, respectively. Electrochemistry of the electrode was studied by using cyclic voltammetry technique in 2 M aqueous KOH solutions with and without 0.33 M urea in a potential range 0.064 V - 0.669 V and a scan rate of 100 mVs⁻¹. Meanwhile, the application for fuel cell was examined using chronoamperometry and chronopotentiometry for one hour in 2 M aqueous KOH solutions and 0.33 M urea with N₂ gas in the anode and 2 M H₂O₂ and 2 M H₂SO₄ in the cathode.

3 Results and discussion

3.1 Pretreatment of nickel foam

Prior to modification, the nickel foam pretreatment was carried out to clean Ni foam from other compounds present in nickel foam, such as sulfides and oxides [8]. The absence of impurities in the nickel foam was expected to produce clean Ni-foam as a template for nickel manganese oxide to grow. Various pretreatment methods were carried out using HCl and acetone. Electrochemical studies were carried out at a scan rate of 20 mV/s in a 2 M KOH solution with a potential current at -0.064-0.669 V. Treatment with acetone provides better results compared to a treatment with HCl, as indicated by the absence of peak oxidation and reduction as shown in **Fig. 1a**.



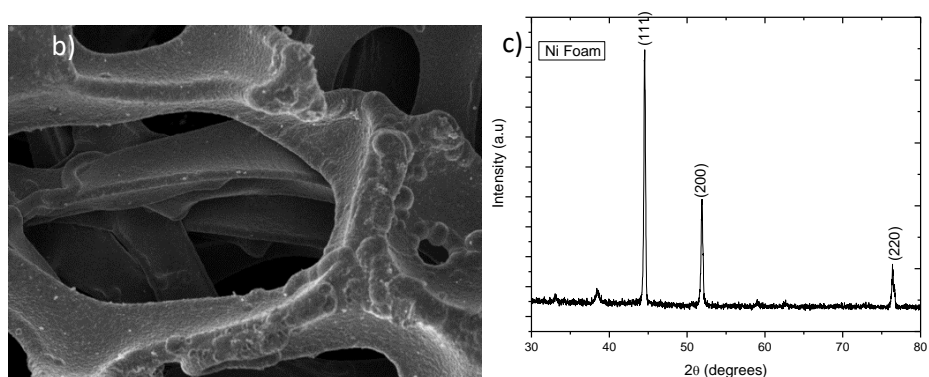


Fig. 1. (a) Cyclic voltammetry of Ni foam treated by various methods together with (b) related SEM image and (b) XRD spectrum of the cleaned Ni foam

The SEM result of the cleaned nickel foam (**Fig. 1b**) confirmed that the nickel foam has three dimensions structure with many pores and a rough surface. The physical properties produced in this study were very similar to those reported by [9]. Further characterization with XRD (**Fig. 1c**) shows that nickel foam observed three diffraction peaks of 2θ , namely 44.5° , 51.9° , and 76.4° on the index (111), (200), and (220), which corresponded to the reference diffraction values of PDF # 04-0850 [9].

3.2 Synthesis and characterization of Nickel Manganese Oxide

SEM characterization was carried out to observe the morphological information of synthesized nickel manganese oxide. **Fig. 2(a)** shows that the examples of synthesized NiMn_2O_4 particles were similar to the NiMn_2O_4 structure reported by [10] with the structure form as a bipyramidal (octahedral) nanoplate of around 100 nm sizes. Further characterization with XRD **Fig. 2(a)** shows diffraction peaks 2θ at 33.60° , 35.78° , 36.71° , 43.63° , 56.33° , 57.82° , 60.72° , and 74.08° which are corresponded to the index (220), (311), (222), (400), (422), (511), (440) and (622), respectively. Comparison of all peaks with NiMn_2O_4 (JCPDS 71-0852) [10], indicating that NiMn_2O_4 has been successfully formed.

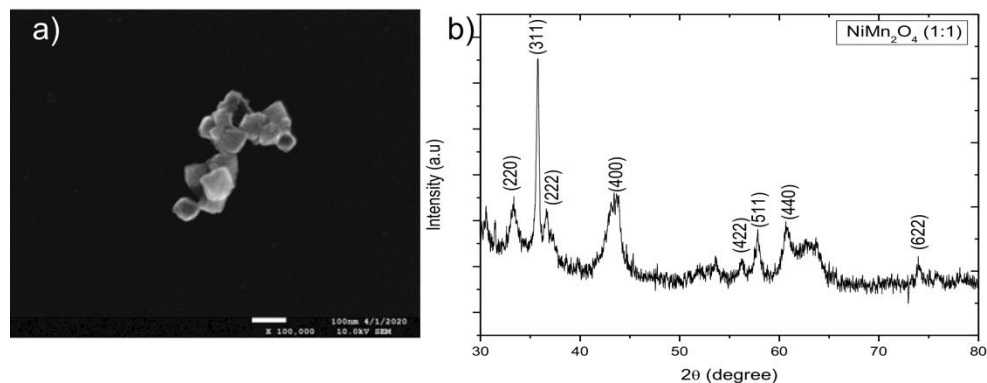


Fig. 2. (a) SEM Image of free crystal of NiMn_2O_4 with its XRD spectrum shown in (b)

3.3 Synthesis of NiMn₂O₄-modified nickel foam and its application

Fig. 3a show the photographs of nickel foams before (left) and after (right) the modification with nickel manganese oxide. It can be seen that after the hydrothermal and calcination stages, the color of nickel foam was changed from silver to darker tone, indicating that NiMn₂O₄ has been deposited on Ni-foam. Similar conditions have also been explained by Sun et al. [11].

SEM characterizations carried out to investigate the morphology and element composition of nickel manganese oxide particles that have been deposited on Ni-foam shows nickel manganese oxide was successfully deposited on the Ni-foam as well (**Fig. 3b and 3c**). The SEM image in **Fig. 3b** shows the nickel manganese oxide form as groups of plate particles with a size between 1-10 μm , while further magnification (**Fig. 3c**) shows that the groups containing nanoplates with bipyramidal or octahedral structure with the size between 100-10 μm . It seems that agglomeration was occurred during the nickel manganese oxide formation inside the nickel foam porous. Meanwhile, EDS characterization showed that elemental distributions of nickel, manganese, and oxygen observed high nickel concentrations due to the use of nickel foam as the support. The percent of weight (wt) for Ni, Mn, O of 85%, 0.2%, and 14.8%, respectively, were observed.

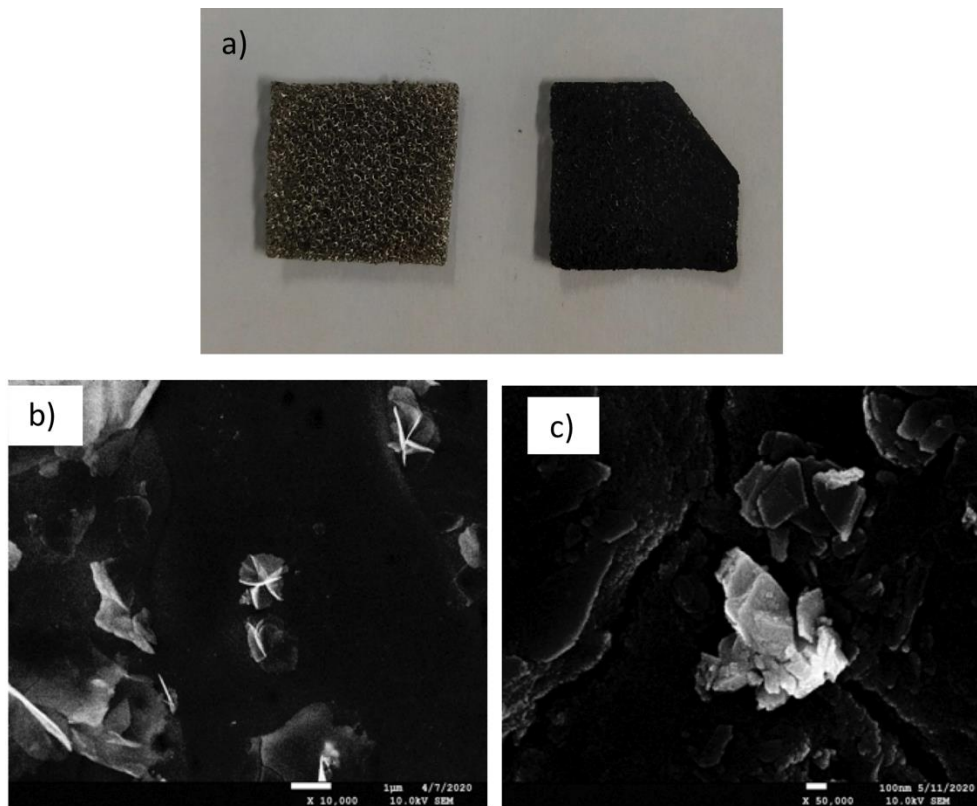


Fig. 3 (a) Photograph of nickel foam before (left) and after (right) modification with NiMn₂O₄ with SEM characterizations of the modified nickel form with (b) 10,000 and (c) 50,000 times of magnifications

Cyclic voltammograms (CV) of the prepared electrode in 2 M KOH is shown in **Fig. 4**. The CV shows the oxidation and reduction reactions of the modified nickel foam. The oxidation peak was observed between the potential area of +0.40 and 0.43 V (vs. SCE), while the reduction peak was in the potential region between +0.29 and +0.34 V (vs. SCE). The oxidation peak was proposed due to the oxidation of Ni²⁺ to Ni³⁺, whereas the reduction peak was from Ni³⁺ reduction to Ni²⁺ [1], [12]. In the CV, peak widening was also observed, indicated that the NiMn₂O₄/Ni-foam electrode has a higher active side than Ni-foam. In the presence of urea, the oxidation peak shifted to the potential more than 0.6 M. The increase of the potential also enhanced the current responses, reaction in the CV result. This indicated that manganese oxide could influence the nickel oxidation-reduction reactions in the urea solution. Based on the CV result, the maximum current density of NiMn₂O₄/Ni-foam in the presence of in 2 M KOH and 0.33 M urea solution was observed at 206.453 mA cm⁻².

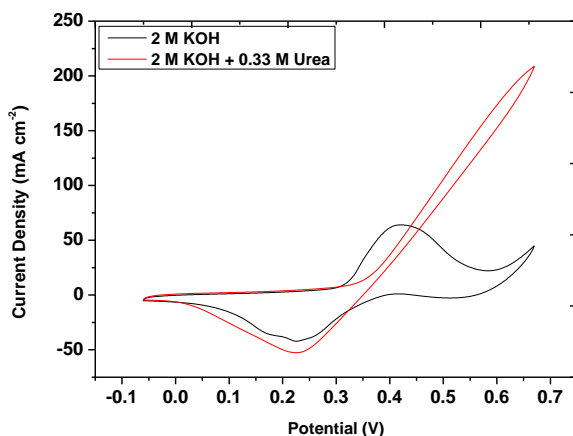


Fig. 4. CV NiMn₂O₄/Nickel Foam in 2 M KOH with and without the presence of 0.33 M urea

The urea fuel cell application test was carried out using a solution containing 2.0 M KOH and 0.33 M urea in the anode chamber and a solution containing 2.0 M H₂O₂ and 2.0 M H₂SO₄ in the cathode chamber. The measurements were performed using chronoamperometry and chronopotentiometry each for one hour to identify the produced power density. A fairly good average power density at 0.304 mW/cm² was achieved. Accordingly, although it can be concluded that the NiMn₂O₄/Ni-foam electrode can be applied as a catalyst for fuel cell application, some improvement is required, including the optimum size of the modified particles as well as its distribution inside the nickel foam porous.

4 Conclusion

Nickel manganese oxide was successfully deposited in the porous of nickel foam using the hydrothermal method as proven by EDS-XRD characterization. The SEM image affirmed that the plate structure of NiMn₂O₄ nanoparticles was bipyramidal (octahedral)-like. NiMn₂O₄/Ni-foam provides a fairly good performance as an anode catalyst in direct urea fuel cells with the resulting power density of 0.304 mW cm⁻². Further research is needed to optimize the prepared material for the fuel cell catalyst.

Acknowledgments

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