Facile electrochemical synthesis of transition metal (oxy)hydroxide as oxygen evolution electrocatalyst

Young Kyeong Kim,[a] **Jin Hyun Kim,**[a] **Jae Sung Lee**[b,*]

[a] *School of Energy Engineering, Ulsan national Institute of Science and Technology (UNIST),Ulsan 44919, Republic of Korea*

[b] *School of Energy and chemical Engineering, Ulsan national Institute of Science and Technology (UNIST),Ulsan 44919, Republic of Korea*

**Corresponding author: +82-54-27- 1599, jlee1234@unist.ac.kr*

Abstract: The electrolysis of water to produce hydrogen is an attractive approach to store renewable energy. Oxygen evolution reaction (OER) is the core reaction in these systems. But its sluggish dynamics results large overpotential. Therefore, the development of an ideal catalyst for OER is one of the main challenge. Here, we develop a novel electrochemical deposition method to make mixed transition metal (oxy)hydroxide electrocatalyst on Nickel Foam (NF). Amongst prepared electrodes, $NiFeO_xH_y/NF$ shows the highest activity in the alkaline solution, revealing current densities of 10mA/cm^2 at overpotentials of 167mV. We expect that this electrochemical approach can be applied in industry.

Keywords: Oxygen evolution reaction, Electrocatalyst, electrolysis of water.

1. Introduction (11-point boldface)

For several decades, renewable energy has been studied intensively due to increasing energy demand and impending environmental issues. Developing sustainable, fossil fuel-free pathways to produce chemical fuels is one of the solution to reduce carbon dioxide emissions and provide sustainable energy. One prospective technology is electrochemical conversion of the thermodynamically inert chemicals (e.g., H_2O and CO_2) into higher-value chemical fuels (e.g., H_2, CH_3OH and C_2H_5OH, etc.) using renewable energy sources.[1] Oxygen evolution reaction (OER) takes a key role in all these energy conversion systems. However, OER is restrained by high kinetic barriers and the instability of the electrode materials. Thus, an efficient electrocatalyst is required for overcoming these problems. Noble metal based materials such as IrO_2 and RuO_2 are benchmark OER catalysts because of their high stability and activity towards OER. However, these precious metals are not suitable for industrial scale application owing to their high price and scarcity. Hence, considerable efforts have been devoted to developing alternative materials with better OER activity. Ni, Fe and Co based (oxy)hydroxide are remarkable candidates for OER due to their comparable activity and stability as well as their affordable price. In early studies, most of the transition metal based electrocatalysts were fabricated by thermal treatment or electrodeposition on conductive substrates. However, these techniques are sensitive to many process parameters. In addition, these methods are not compatible for large scale synthesis due to their complicated procedures. Herein, we developed a fast and facile electrochemical deposition method to fabricate transition metal (oxy)hydroxide (MO_xH_y, M = combination of Ni, Fe and Co) electrocatalysts. In this method, amorphous MO_xH_y was deposited on the conducting substrates. This synthesis easily combined transition metals in an aqueous precursor solution state. The optimized sample is $NiFeO_xH_y$, with a 9:1 volume ratio of $Ni(NO_3)_2$ and $Fe(NO_3)_3$ solutions, prepared on NF substrate. This NiFe 9:1/NF is used as an oxygen electrode with high current density and low overpotential

2. Experimental

Metal nitrate was deposited on conductive substrates of fluorine doped tin oxide (FTO) and NF from an aqueous transition metal nitrate solution by the drop casting method. The metal nitrate was dried in air briefly and dipped in alkaline solution. OH^- from the alkaline solution leaded to precipitation of MO_xH_y. The entire process was completed in 3 minutes without annealing. The synthesized MO_xH_y/FTO and MO_xH_y/NF was used as an electrocatalyst for OER (Fig. 1).

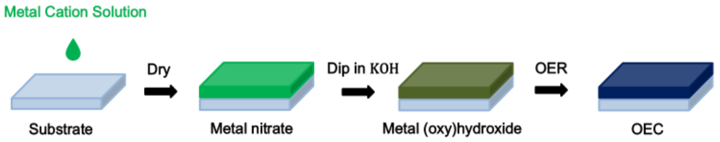

Figure 1. Schematic diagram of novel electrochemical deposition method of the transition metal (oxy)hydroxide (MO_xH_y).

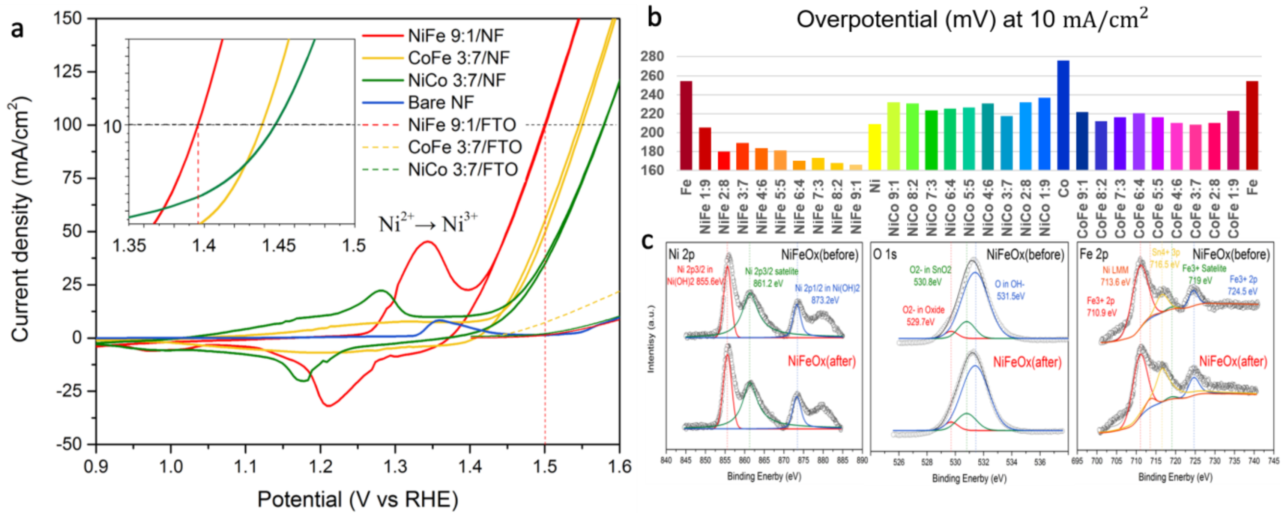

Figure 2. (a) Cyclic voltammetry curve of each compositions best sample. (b) Overpotential of thirty different ratios of MO_xH_y/NF at 10mA/cm^2. (c) XPS spectra of the MO_xH_y before and after electrochemical reaction.

3. Results and discussion

Surface elemental analysis was carried out using x-ray photoelectron spectroscopy (XPS). Fig. 2c are XPS spectra of $NiFeO_xH_y$/FTO, which showed the highest activity. In the O 1s spectra, peaks are located at 529.7 eV (M-O) and 531.5 eV (M-OH). Ni 2p XPS spectra display peaks located at 855.6 eV and 873.2 eV, corresponding to the 2p levels of Ni^{2+} and Fe peaks were observed at 710.9 eV and 724.5 eV, indicating that the oxidation state of Fe is Fe^{3+}. The OER activity of MO_xH_y/NF in alkaline solution was evaluated in 1 M KOH using a standard three electrode system. The overpotential of thirty different combinations of MO_xH_y/NF for achieving current density of 10 mA/cm^2 is observed in Fig. 2b. For solar-driven fuel production techniques, a solar to hydrogen efficiency (STH) of 10 % is considered as a benchmarking value. This efficiency is equivalent to a current density of 10 mA/cm^2, which is a figure of merit in evaluating practical solar fuel production systems. Comprehensive investigation of the OER at current densities reaching 10 mA/cm^2 is important to address electrochemical performances in relevant conditions to the practical applications. So far, 3-dimensinoal NiFe/NF electrode reported by Lu and Zhao showed the highest activity, delivering 10 mA/cm^2 at an overpotential of 215 mV.[2] Among prepared MO_xH_y/NF, NiFe 9:1/NF had the smallest overpotential, representing only 167 mV overpotential at 10 mA/cm^2, which was lower than that of the best NiFe/NF electrode reported previously. In Fig. 2a, the electrocatalytic performances of each composition's best MO_xH_y/NF and their MO_xH_y/FTO are compared with bare NF substrate. The oxidation peak detected before catalytic reaction was formed due to a change in the Ni oxidation state. Reverse direction measurement, excluding this oxidation peak, precisely exhibits the voltage at 10 mA/cm^2 (Fig. 2a inset). In comparison with bare NF substrate, NiFe 9:1/NF showed significant improvement, suggesting the high activity originates from $NiFeO_xH_y$ electrocatalyst. Moreover, the OER performances of the MO_xH_y/NF was superior to MO_xH_y/FTO. Compare with FTO, NF has 3D interconnected porous structure, offering a high surface area, good electrical conductivity and good structural stability. These factors led to high activity of MO_xH_y/NF.

4. Conclusions

In summary, we developed an effective and fast electrochemical synthesis method using transition metals. Amorphous MO_xH_y (M = combination of Ni, Fe and Co) was directly deposited on the conducting substrates through this synthesis. The obtained $NiFeO_xH_y$/NF displayed excellent catalytic activity. In alkaline electrolytes, 100 mA/cm^2 was obtained at 1.5 V vs RHE (270 mV overpotential). $NiFeO_xH_y$/NF fabricated by this noble electrochemical method is promising oxygen electrode for electrochemical energy conversion systems. we expect that this result helps to design a better catalyst and process for relevant industry

References

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