

# Heat-treatment effects on oxygen evolution reaction of nickel-cobalt layered double hydroxide

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**Abstract** Alkaline oxygen evolution reaction (OER) electrocatalysts have been widely studied for improving the efficiency and green hydrogen production through electrochemical water splitting. Transition metal-based electrocatalysts have emerged as promising materials that can significantly reduce the hydrogen production costs. Among the available electrocatalysts, transition metal-based layered double hydroxides (LDHs) have demonstrated outstanding OER performance owing to the abundant active sites and favorable adsorption-desorption energies for OER intermediates. Currently, cobalt doped nickel LDHs (NiCo LDHs) are regarded as the benchmark electrocatalyst for alkaline OER, primarily owing to the physicochemical synergetic effects between Ni and Co. We report effects of heat-treatment of the as-grown NiCo LDH on electrocatalytic activities in a temperature range from 250 to 400°C. Electrocatalytic OER properties were analysed by linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). The heat-treatment temperature was found to play a crucial role in catalytic activity. The optimum heat-treatment temperature was discussed with respect to their OER performance.

**Key words** Electrocatalysis, Water splitting, OER, NiCo LDH, Heat-treatment

## 1. Introduction

Hydrogen (H<sub>2</sub>) has been intensively studied as one of the most prospective alternative energies to the unsustainable fossil fuels in perspective of the formidable energy and environmental issues [1]. One reasonable approach to generating hydrogen is electrocatalytic water splitting involving two processes, which are hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). The HER and OER have caught worldwide attention during the past few decades [2,3]. Despite the remarkable electrocatalytic performance of noble metal based materials (e.g., Ir, Pt, or Ru) for HER and OER, the large scale utilization of these catalysts is economically hampered by their low abundance and high cost [4,5]. Therefore, it is of paramount significance to pursue innovative catalyst with low in price and high efficiency for hydrogen production.

Nanostructured materials based on first-row transition metal have been widely studied as prominent electrocatalysts for HER and OER with layered hydroxides [6], complex oxides [7] or metal chalcogenides [8-10]. Among them, layered double hydroxides (LDHs) have drawn

much interests due to their flexible configuration and tunable composition [11,12]. Recently, tremendous efforts have been made for LDH (especially NiCo LDH) serving as desirable OER or HER catalysts in water oxidation due to their layered structure, low in price and ease of scale-up [13,14]. However, the relatively poor conductivity and incompletely exposed active site of LDHs are detrimental to the electron transfer and ultimately affect the electrocatalytic performance [15]. It has been well established that hybridizing LDHs with conductive supports (such as Cu foam, Ti mesh and Ni foam, etc) provides a reliable strategy to significantly enhance the electrical conductivity [16,17].

When served as supports, nickel foam (NF) has several distinguished advantages: (1) the three-dimensional (3D) microporous structure of NF offers a large area for accommodating the catalyst, resulting in the high loading amount and abundant exposure of the catalytically active sites. (2) The 3D interconnected skeletons of NF with high conductivity and excellent mechanical strength provide continuous highways for electron transport, significantly improving the electron transfer efficiency [18, 19]. (3) The NF decorated with active component may be directly applicable as a self-supported electrode without binder for electrochemical measurements. Moreover, the binder-free NF based working electrode can effec-

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tively prevent the aggregation and peeling off active sites, reducing the contact resistance and exhibiting remarkably durability [20].

Motivated by the above-mentioned considerations, we believe that the NiCo LDH could display the excellent OER performance. Absolutely, there have been many reports on the growth and electrocatalytic properties of NiCo LDHs [21-23]. However, heat-treatment effects in low temperature on OER properties for the grown NiCo LDHs have not been reported yet. In this study, we show that low-temperature heat-treatment for NiCo LDHs can be a promising strategy for increasing electrocatalytic strength for alkaline OER. Encouraged by the above discussion, we introduced heat-treatment process in a temperature range from 250 to 400°C after a simple solvothermal growing process, and optimum heat-treatment condition was discussed on the electrocatalytic OER performance.

## 2. Experimental

### 2.1. Synthesis of NiCo LDH and its heat-treatment

NiCo LDHs were grown on NFs by a simple hydrothermal method [24]. NFs were treated with acetone and then with 3 M HCl solution for 10 min using an ultrasonication cleaner. The cleaned NFs were then dried overnight. All chemicals were purchased from Junsei Chemical and used directly without further purification. For the synthesis of NiCo LDH, the as-prepared NFs were immersed in 20 mL of deionized (DI) water. Further, 1.00 mg of Co (II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ) was dissolved in the solution at room temperature. Sonication was performed 10 min to completely dissolve the Co precursor in the solution. The resulting solutions were moved to autoclave with Teflon-lining and hydrothermally reacted at 160°C for 5 h. After several washes with deionized water, the NiCo LDH samples were dried in a vacuum chamber at 90°C for 10 h. The NiCo LDHs grown on NFs were heat-treated at 250, 300, 350 and 400°C for 1 h in air to investigate effects on electrocatalytic properties. The heat-treated NiCo LDH samples are designated as HT-250, HT-300, HT-350 and HT-400, respectively.

### 2.2. Characterizations

Surface morphology of the NiCo LDHs and HT samples were observed by field-emission scanning electron

microscopy (FE-SEM) equipped with energy-dispersive X-ray (EDX) spectrometry. Crystal structure evolution performed by heat-treatment were analyzed using X-ray diffraction (XRD) with Cu-K $\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 kV and 30 mA. The electrochemical properties of the NiCo LDHs and heat-treated samples were analyzed using a three-electrode electrochemical cell controlled by an electrochemical workstation (Autolab PGSTAT; Metrohm) in 1 M KOH solution. NFs with pristine NiCo LDH and heat-treated NFs were used directly as the working electrode. The electrolyte was purged for about 10 min with oxygen ( $\text{O}_2$ ) gas before measurement. A graphite rod and  $\text{Hg}|\text{Hg}_2\text{SO}_4$  were used as the counter and reference electrodes, respectively. Linear sweep voltammetry (LSV) was performed at a scan rate of 0.5 mV/s in the range from 1.23 to 1.9 V. The applied potentials were calibrated against the reversible hydrogen electrode (RHE), and all polarization curves were iR-compensated. Electrochemical impedance spectroscopy (EIS) analyses were conducted over the frequency range from 0.1 to 100 kHz. A sinusoidal voltage with amplitude of 5 mV was applied during EIS measurements.

## 3. Results and Discussion

NiCo LDH microcrystal was grown on NF via hydrothermal reaction at 160°C for 5 h. Typical XRD analysis confirmed the formation of the NiCo LDH grown on NF as shown in Fig. 1(a). XRD patterns for the heat-treated samples are shown in Fig. 1(b-e). The strong diffraction peaks near 44° and 51° could be assigned to Ni

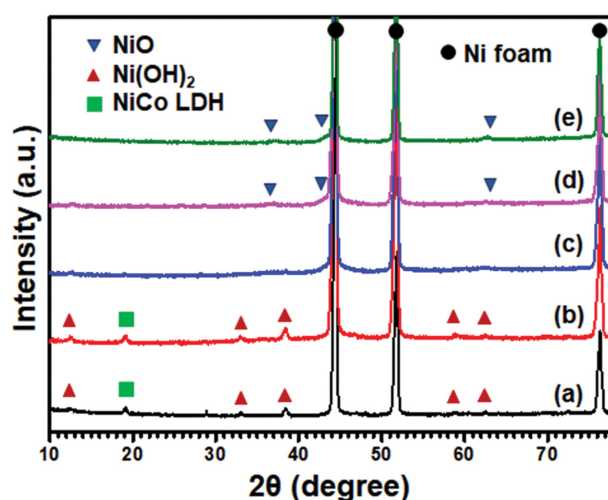


Fig. 1. XRD patterns of the (a) as-grown NiCo LDH, (b) HT-250, (c) HT-300, (d) HT-350, and (e) HT-400 samples.

metal in the NF substrate. The XRD patterns revealed the crystal structure and phase purity of the NiCo LDH crystal grown on NF. Except for the peaks from the NF substrate, all other detectable diffraction peaks at low  $2\theta$  angles could be indexed to the hydroxalite-like LDH phase (PDF 00-014-0525). Prominent diffraction peaks for the layered nickel cobalt hydroxide were observed from  $12^\circ$ ,  $33^\circ$ ,  $38^\circ$ ,  $58^\circ$  and  $62^\circ$ . Notably, secondary phase related to  $\text{Ni(OH)}_2$  was observed at  $19^\circ$  in the XRD pattern of the as-grown NiCo LDH sample. Figure 1(b) indicates that crystallinity of the HT-250 sample is increased compared to the as-grown sample. However, Fig. 1(c-e) shows the diffraction peaks for the NiCo LDH or  $\text{Ni(OH)}_2$  disappeared and NiO peaks are prominent. Therefore, it is confirmed that the NiCo LDH structure is transformed to NiO crystal structure by heat-treatment above  $300^\circ\text{C}$ .

Figure 2 shows highly magnified FE-SEM images for the (a) as-grown NiCo LDH and heat-treated samples at (b)  $300^\circ\text{C}$ , (c)  $350^\circ\text{C}$  and (d)  $400^\circ\text{C}$  for 1 h. Figure 1(a) represents that large-scale highly interconnected and aligned microplate structure vertically grow on the skeletons of the NF with uniform morphology and dense loading, forming an ordered and 3D network with a highly open and interstitial structure. Homogeneous microplate structure on the 3D macroporous NF was clearly observed. For the heat-treated samples, it is confirmed that crystal

morphology is not changed but crystal size increased with heat-treatment. For the HT-250 sample, crystal morphology and crystal size was similar to the as-grown sample.

The electrocatalytic activities of the NiCo LDH as-grown and heat-treated samples were tested in alkaline media (1 M KOH aqueous solution) using a three-electrode system. Linear sweep voltammetry (LSV) was performed at a scan rate of  $0.5\text{ mV/s}$  on the samples. NF substrates were directly used as working electrodes, while a rotating disk electrode (RDE) was employed for testing powder samples such as  $\text{RuO}_2$ . To remove the bubbles generated during measurement, the RDE was continuously rotated at  $2,000\text{ rpm}$ . All measured potentials were  $iR$ -compensated and were then referenced to the reversible hydrogen electrode (RHE). Notably, heat-treated samples exhibited poorer catalytic activity for water oxidation compared to as-grown sample.

The HT-250 sample exhibited similar catalytic activity. The overpotential ( $\eta$ ) required to transmit a current density of  $10\text{ mA/cm}^2$  ( $\eta^{10}$ ) is conventionally used as a standard to compare electrocatalytic OER performance. Figure 3 shows LSV curves with a scan rate of  $0.5\text{ mV/s}$  for electrocatalytic OER properties of the as-grown NiCo LDH and heat-treated samples. The  $\eta^{10}$  substantially increased when heat-treatment temperature is higher than  $250^\circ\text{C}$ . The as-grown NiCo LDH sample

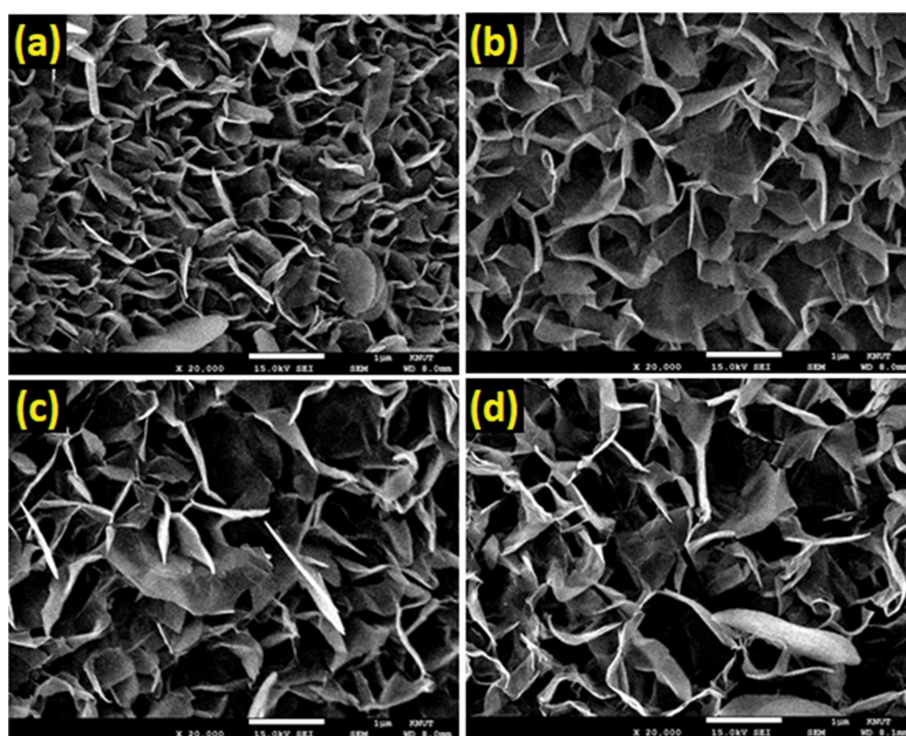


Fig. 2. Highly magnified FE-SEM images for the (a) as-grown NiCo LDH, (b) HT-300, (c) HT-350 and (d) HT-400 samples.

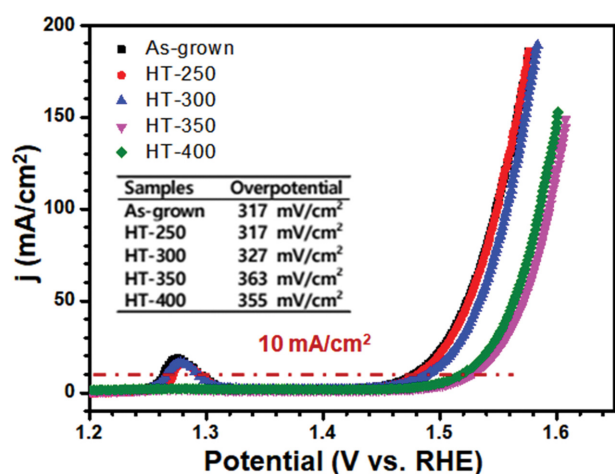


Fig. 3. LSV curves at a scan rate of 0.5 mV/s for electrocatalytic OER properties of the as-grown NiCo LDH and heat-treated samples.

required an  $\eta^{10}$  of 317 mV, while  $\eta^{10}$  for HT-300 and HT-400 were about 327 and 355 mV as shown in Fig. 3. This indicated that NiO phase grown by heat-treatment was not beneficial for practical electrolysis applications as shown in Fig. 1.

Tafel plots of the samples were derived from the measured LSV curves based on the Tafel equation ( $\eta = b \times \log(j) + a$ ), where  $\eta$  is the overpotential,  $j$  is the current density, and  $b$  is the Tafel slope. Tafel slopes of as-grown NiCo LDH and heat-treated samples were calculated and represented in Fig. 4. The measured Tafel slopes of the as-grown NiCo LDH sample was 30.78 mV/dec. Tafel slope value of HT-250 sample was 28.81 mV/dec, which is lower than that of as-grown sample. However, heat-treatment over 300°C increased Tafel slope value. This means that the heat-treatment at 250°C exhibits the smallest Tafel slope compared to as-grown

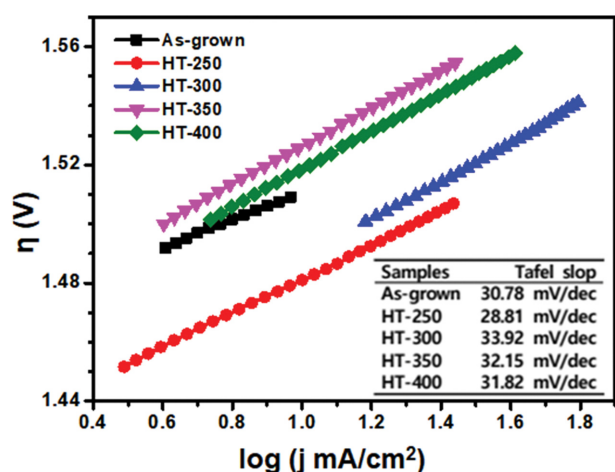


Fig. 4. Tafel slopes of the as-grown NiCo LDH and heat-treated samples derived from the measured LSV curves.

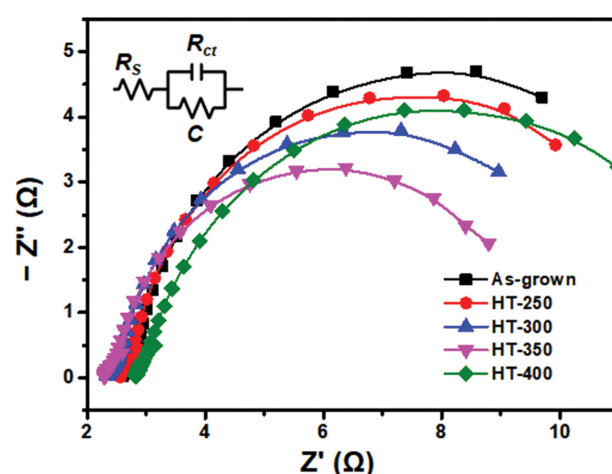


Fig. 5. EIS data of the of the as-grown NiCo LDH and heat-treated samples.

sample, highlighting the potential use of heat-treatment of NiCo LDH sample at 250°C for industrial electrolyzer because a smaller Tafel slope is desirable to reduce power losses [25].

Charge transfer resistance ( $R_{ct}$ ) between electrocatalysts and electrolytes can be obtained from the semicircle diameter in the high-frequency region of a Nyquist plot ( $Z'$  vs.  $-Z''$ ) measured by electrochemical impedance spectroscopy (EIS). Here, the smaller diameter generally represents the lower  $R_{ct}$ . Figure 5 represents the EIS data of the samples, where heat-treated samples showed a obviously lower value of  $R_{ct}$  than that of the as-grown sample in a temperature range from 250 to 350°C. Notably, HT-350 sample exhibited a minimum  $R_{ct}$ , implying the significant role of heat-treatment for facilitating charge transfer from the catalyst surface to the adsorbed chemical reactants. Further increasing heat-treatment temperature (HT-400) increased its charge transfer resistance, which may be related to poorly grown NiO nanosheets on the nickel foam substrate, which is same result with LSV curve and Tafel slope.

#### 4. Summary

In summary, heat-treatment effect of NiCo LDH on electrocatalytic activities in a temperature range from 250 to 400°C was studied. The XRD pattern indicate that diffraction peaks for the NiCo LDH or Ni(OH)<sub>2</sub> disappeared and NiO peaks are prominent when heat-treatment temperature rise up to 300°C. Crystal morphology didn't change but crystal size increased with heat-treatment above 300°C. The overpotential ( $\eta^{10}$ ) substantially

increased when heat-treatment temperature is higher than 300°C. The as-grown NiCo LDH sample required an  $\eta^{10}$  of 317 mV, while  $\eta^{10}$  for HT-300 and HT-400 were about 327 and 355 mV, which indicated that NiO phase grown by heat-treatment was not beneficial for practical electrolysis applications. The heat-treatment at 250°C exhibited the smallest Tafel slope compared to as-grown sample, highlighting the potential use of heat-treatment at 250°C of NiCo LDH sample for industrial electrolyzer.

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