Modulating Ni/Ce Ratio in Ni\textsubscript{y}Ce\textsubscript{100−y}O\textsubscript{x} Electrocatalysts for Enhanced Water Oxidation

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Abstract: Oxygen evolution reaction (OER) is the key reaction for water splitting, which is used for hydrogen production. Oxygen vacancy engineering is an effective method to tune the OER performance, but the direct relationship between the concentration of oxygen vacancy and OER activity is not well understood. Herein, a series of Ni\textsubscript{y}Ce\textsubscript{100−y}O\textsubscript{x} with different concentration of oxygen vacancies were successfully synthesized. The larger concentration of oxygen vacancies in Ni\textsubscript{75}Ce\textsubscript{25}O\textsubscript{x} and Ni\textsubscript{100−y}Ce\textsubscript{y}O\textsubscript{x} result in their lower Tafel slopes, small mass-transfer resistance, and larger electrochemical surface areas of the catalysts, which account for the higher OER activities for these two catalysts. Moreover, with a fixed current density of 10 mA/cm\textsuperscript{2}, the potential remains stable at 1.57 V for more than 100 h, indicating the long-term stability of the Ni\textsubscript{75}Ce\textsubscript{25}O\textsubscript{x} catalyst.

Keywords: oxygen evolution reaction (OER); Ni\textsubscript{y}Ce\textsubscript{100−y}O\textsubscript{x}; oxygen vacancies

1. Introduction

Hydrogen is considered as one of the clean energy to replace the traditional fossil fuel to solve the environmental and energy problem. Electrocatalytic water splitting is an effective way to produce hydrogen with high purity from intermittent renewable energy (i.e., wind and solar energy). Two half reactions including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are at cathode and anode, respectively. The four-electron transfer steps of OER lead to the large sluggish kinetics, resulting in a high overpotential for water splitting [1–7]. An OER catalyst with high activity is of critical importance to reduce the overpotential so that a small bias voltage can be used and thus increase the efficiency of the OER process.

The OER activity of a catalyst can be enhanced by introducing defects, especially oxygen vacancies [8–11]. The local electron density distribution will be changed and the oxygen vacancy itself can be the OER active sites. Wang et al. [12] treated Co\textsubscript{3}O\textsubscript{4} nanosheets by Ar-plasma to get rich oxygen vacancies. The specific activity of the Co\textsubscript{3}O\textsubscript{4} nanosheets with oxygen vacancies was 10 times higher than that of the pristine Co\textsubscript{3}O\textsubscript{4}. Ceria is a nonstoichiometric material and the oxygen vacancies are easily formed due to the shift between Ce\textsuperscript{3+} and Ce\textsuperscript{4+} [13–17]. The oxygen vacancies in Ce-containing catalysts such as CeO\textsubscript{2}/Co\textsubscript{3}O\textsubscript{4} accelerated the electron transfer, resulting in good OER activity [9]. In our previous work, oxygen vacancies in NiCeO\textsubscript{x} catalyst were proved to be the active sites for water oxidation [10]. However, the direct correlation between the concentration of oxygen vacancies and OER activity has not been identified yet.

In this work, a series of Ni\textsubscript{y}Ce\textsubscript{100−y}O\textsubscript{x} with different Ni/Ce ratio were synthesized on NF (nickel foam)/NiO substrate with simple dip-coating and annealing methods. The
surface NiO obtained from the oxidation of NF can prohibit the diffusion of Ni atoms to the deposited Ni₉Ce₁₀₀−₉O₃, so that the Ni/Ce ratio is not modified. Oxygen vacancy defects are formed successfully in all the NF/NiO/Ni₉Ce₁₀₀−₉O₃ (simply referred to as Ni₉Ce₁₀₀−₉O₃) catalysts. The concentration of oxygen vacancy defects for Ni₇₅Ce₂₅O₃ and Ni₅₀Ce₅₀O₃ catalysts are larger than other Ni₉Ce₁₀₀−₉O₃ catalysts, resulting in a similar larger electrochemically active surface area and the same lower Tafel slope of 66 mV/decade. The overpotential to achieve a current density of 10 mA/cm² for the Ni₇₅Ce₂₅O₃ and Ni₅₀Ce₅₀O₃ catalysts are 338 mV and 341 mV, respectively. It is noted that these overpotentials are lower than other Ni₉Ce₁₀₀−₉O₃ catalysts. With a fixed current density of 10 mA/cm², the Ni₇₅Ce₂₅O₃ catalyst exhibits an ultra-high stability of over 100 h.

2. Materials and Methods

2.1. Sample Synthesis

The synthesis of NF/NiO/Ni₉Ce₁₀₀−₉O₃ catalysts. The first step was to prepare the NF/NiO substrate. A 10 × 15 mm² Nickel Foam (NF, >99.99%, MTI Corporation, Richmond, CA, USA) substrate with a thickness of 0.08 mm was firstly cleaned by acetone (99%, Wako) in an ultrasonic bath for 5 min. Then the NF was rinsed by deionized water three times. Subsequently, the NF was dried in air and annealed for 2 h with a heating rate of 2 °C/min at 400 °C in a muffle furnace to obtain NF/NiO substrate. The second step is to prepare the nickel and cerium mixed precursor solution. The precursor solution was prepared by dissolving 0.3 M citric acid and 0.15 M metal ions in 20 mL ethanol. The molar ratio of Ni and Ce ions were 95:5, 90:10, 75:25, 50:50, 25:75, and 10:90 for the catalysts of Ni₉Ce₅₀O₃, Ni₅₀Ce₅₀O₃, Ni₇₅Ce₂₅O₃, Ni₅₀Ce₇₅O₃, Ni₂₅Ce₇₅O₃, and Ni₁₀Ce₉₀O₃, respectively. Ce(NO₃)₃·6H₂O offers the Ce ions and Ni(NO₃)₂·6H₂O offers the Ni ions. The final step is the preparation of NF/NiO/Ni₉Ce₁₀₀−₉O₃ catalysts, hereafter simply referred to as the Ni₉Ce₁₀₀−₉O₃. The prepared precursor solution was deposited onto NF/NiO by dip coating and then annealed in the same manner as the NF/NiO substrate.

2.2. Structural Characterization

A field emission Scanning electron microscope (SEM, JEOL JSM 7600 FA) was used for the measurements of SEM. A diffractometer (Rigaku Co. Ltd., SmartLab, Japan) with Cu Kα radiation (dwelling time = 2 s, incident angle = 0.5°, step size = 0.02°, λ = 1.541 Å) was used for the collecting of grazing incidence X-ray diffraction data. A Renishaw inVia Raman Microscope system was used to acquire the Raman spectra at room temperature (25 °C). A ×100 objective and a 532 nm excitation laser were used. A PHI 5000 VersaProbe (ULVAC-PHI) with an Al Kα X-ray source (1486.6 eV) was used to obtain the X-ray photoelectron spectroscopy (XPS). The pass energies of 117.4 eV and 23.5 eV were used for the electron analyzer to analyze the wide scans and narrow scans, respectively.

2.3. Electrochemical Measurements

A cylindrical glass cell with a standard three-electrode configuration was used for the electrochemical measurements. A Pt wire and a Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The working electrode was Ni₉Ce₁₀₀−₉O₃ electrode. A potentiostat (Princeton Applied Research, VersaSTAT 4) was used to perform the electrochemical measurements. The potentials were calibrated against the RHE according to the following equation: \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \ \text{pH} + E_0^{\text{Ag/AgCl}} \), where \( E_{\text{Ag/AgCl}} \) is the potential difference measured between the Ag/AgCl electrode and the working electrode, \( E_0^{\text{Ag/AgCl}} \) (0.1976 V at 25 °C) is the standard electrode potential for an Ag/AgCl electrode, pH is the pH of the electrolyte solution, and \( E_{\text{RHE}} \) is the calibrated potential. The electrolytes used were saturated with oxygen before and during the OER experiments.

The polarization curves were collected through linear sweep voltammetry (LSV), and the scan rate was 10 mV/s. Controlled-current water electrolysis was performed using a
chronopotentiometric technique [16]. The solution resistance $R_\text{s}$ (~2 Ω), determined using the electrochemical impedance spectroscopy (EIS) technique [16], was used to correct the $iR$ drop across the solution. Unless otherwise stated, all given potentials are vs. RHE and corrected for the $iR$ drop across the electrolyte. Tafel plots obtained from the steady-state polarization curves with a scan rate of 1 mV/s. Cyclic voltammetry (CV) was used to determine the electrochemical capacitance of the samples presented in this paper [18]. The potential was swept in a range from 0.05 V above the open-circuit potential (OCP) to 0.05V below the OCP in a static solution with five different scan rates: 0.005, 0.01, 0.025, 0.05 and 0.1 V s$^{-1}$. The working electrode was held for 10 s at each end of the potential sweep before continuing to the next sweep. All experiments were performed at room temperature.

3. Results and Discussion

The surface morphology information of the NF/NiO and Ni$_x$Ce$_{100-y}$O$_x$ samples was analyzed by SEM, and the images are shown in Figure 1. Holes with sizes varying from several nanometers to a few hundred nanometers were observed on the surface of NF/NiO. NF/NiO sample was prepared by annealing Ni substrate in the muffle furnace for 2 h with the elevating rate of 2 °C/min, and these holes were from the Ni foam substrate. The surface of NF/NiO consisted of small nanocrystals, as shown in Figure 1b. The Ni$_x$Ce$_{100-y}$O$_x$ samples were synthesized by depositing nickel and cerium mixed precursor solutions with different Ni/Ce ratios on NF/NiO and then annealing the samples in air. The deposited layer covers the surface of NF/NiO nanocrystals for the Ni$_x$Ce$_{100-y}$O$_x$ catalysts are indeed composed of Ni and Ce mixed oxides. The curve fitting results of Ce 3d 3/2 for Ni$_x$Ce$_{100-y}$O$_x$ samples was determined using Grazing incidence XRD measurements were performed to examine the crystal structure of the Ni$_x$Ce$_{100-y}$O$_x$ samples, and the results are shown in Figure 2a. Only Ni and NiO related peaks were found and no CeO$_2$ related peaks were detected for Ni$_x$Ce$_{100-y}$O$_x$ samples. It indicates that Ni and Ce mixed uniformly in the top layer and formed an amorphous structure. The surface element information of the Ni$_x$Ce$_{100-y}$O$_x$ samples was further analyzed by XPS. As shown in Figure 2b, Ce 3d peaks of CeO$_2$ and Ni 2p peaks of NiO were observed and indicates that the deposited layers of Ni$_x$Ce$_{100-y}$O$_x$ catalysts are indeed composed of Ni and Ce mixed oxides. The curve fitting results of Ce 3d$3/2$ for Ni$_x$Ce$_{100-y}$O$_x$ samples are shown in Figure 2c. The peak areas of Ce 3d$3/2$ for Ni$_{50}$Ce$_{50}$O$_x$, Ni$_{75}$Ce$_{25}$O$_x$, Ni$_{50}$Ce$_{50}$O$_x$, Ni$_{25}$Ce$_{75}$O$_x$ and Ni$_{10}$Ce$_{90}$O$_x$ samples are 31.7, 55.7, 206.2, 433.0 and 603.3. For Ni$_x$Ce$_{100-y}$O$_x$ samples, the peak areas of Ce 3d$3/2$ are in proportion with

![Figure 1. SEM images of NF/NiO (a,b) and Ni$_{95}$Ce$_{5}$O$_x$ (c,d) samples.](image-url)
the Ce content, and the higher Ce content will lead to larger peak areas of Ce 3d$_{3/2}$. The sequence of the peak areas of Ce 3d$_{3/2}$ of Ni$_y$Ce$_{100-y}$O$_x$ samples are in accordance with the Ce content in these samples (Table S1). This indicates that the designed Ni/Ce ratios remain constant for the synthesized Ni$_y$Ce$_{100-y}$O$_x$ samples.

![Figure 2. (a) X-ray diffraction patterns and (b,c) XPS spectra of Ni$_y$Ce$_{100-y}$O$_x$ samples.](image)

Two Raman peaks of 224 cm$^{-1}$ and 563 cm$^{-1}$ were observed for Ni$_{75}$Ce$_{25}$O$_x$, Ni$_{50}$Ce$_{50}$O$_x$, Ni$_{25}$Ce$_{75}$O$_x$, and Ni$_{10}$Ce$_{90}$O$_x$ samples, as shown in Figure 3a. For Ni$_{90}$Ce$_{10}$O$_x$ and Ni$_{90}$Ce$_{10}$O$_x$ samples, only the peak of 563 cm$^{-1}$ was observed. Crystalline CeO$_2$ is known to have a strong F$_{2g}$ Raman peak at 464 cm$^{-1}$ related to its fluorite structure [19]. The presence of ions with the oxidation states lower than Ce$^{4+}$ in the CeO$_2$ has been shown to induce a Raman band, known as the D band, from 500 to 700 cm$^{-1}$ [19–21]. This band is associated with the presence of oxygen vacancy defects created in the non-stoichiometric CeO$_{2-y}$ by the 3+ coordinated ions. In addition to the introduction of the D band, the F$_{2g}$ band will be weakened and becomes asymmetric and broad [22]. In the Raman spectra of the Ni$_y$Ce$_{100-y}$O$_x$ samples, there is no F$_{2g}$ band, which suggests that there is no crystalline CeO$_2$ with a fluorite structure in these samples [23]. The broad peak at 563 cm$^{-1}$ (D band) indicates the formation of oxygen vacancy defects. The oxygen vacancy defects should be related to the presence of Ce$^{3+}$ because of the incorporation of Ni into CeO$_2$, as suggested by the literature [19,20,23]. Furthermore, the amorphous structure of Ni$_y$Ce$_{100-y}$O$_x$ contributes to the broadness of the peak [22,23]. According to the areas of this peak among different Ni$_y$Ce$_{100-y}$O$_x$ samples, we can roughly estimate the concentration of oxygen vacancy defects in these catalysts. The peak areas of the D band have been calculated and summarized in Table S2. The peak areas of 563 cm$^{-1}$ for Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{90}$Ce$_{10}$O$_x$ samples are similar and larger than those of other Ni$_y$Ce$_{100-y}$O$_x$ samples, suggesting that these two catalysts own larger concentration of oxygen vacancy defects. The peak at 224 cm$^{-1}$ is related to Ce-OH vibrations which are resulted from surface defects. Different types of hydroxyl groups generated by the dissociation of surface adsorbed water and doubly bridging hydroxyl groups on reduced cerium oxide are detected in the Raman spectra [24].
The overpotentials of the catalysts for the current density of 10 mA/cm² are listed in Table 1. The Ni₁₀Ce₉₀Oₓ catalysts were shown in Figure 4b and Table 1. The Tafel slopes of the Ni₇₅Ce₂₅Oₓ catalysts were 338 mV and 341 mV to obtain the current density of 10 mA/cm², which were lower than that of other samples. The Tafel slope results of NiₓCe₁₀₀−ₓOₓ catalysts were shown in Figure 4b and Table 1. The Tafel slopes of the Ni₇₅Ce₂₅Oₓ and Ni₅₀Ce₅₀Oₓ catalysts (66 mV/decade) were close to that of Ni₉₀Ce₁₀Oₓ, Ni₅₀Ce₁₀Oₓ, and Ni₂₅Ce₇₅Oₓ catalysts (68 mV/decade), and were lower than that of the Ni₁₀Ce₉₀Oₓ catalyst (73 mV/decade). An electrocatalyst with a low Tafel slope will have a small kinetic barrier for electron and mass transfer [2,5]. This indicates that the transfer barriers of electron and mass in the Ni₇₅Ce₂₅Oₓ and Ni₅₀Ce₅₀Oₓ catalysts are slightly improved.

The double-layer capacitance can be used to estimate the electrochemically active surface area (ECSA) of each sample. In order to know the double-layer capacitance, we first obtained CV curves of the capacitance current in the non-Faradaic voltage region (a 0.1 V potential range centered on the OCP) for several different scan rates (Figure 5). The rate of change in the current at OCP with respect to the scan rate corresponds to the double-layer capacitance [18]. For this reason, the current at OCP was plotted against the scan rate for the NiₓCe₁₀₀−ₓOₓ catalysts, and a line of best fit was fitted for each catalyst’s data set, as shown in Figure 4c. The double layer capacitance was 12.3 mF, 14.5 mF, 20.6 mF, 19.5 mF, 10.7 mF, and 7.1 mF for the Ni₉₅Ce₅Oₓ, Ni₉₀Ce₁₀Oₓ, Ni₇₅Ce₂₅Oₓ, Ni₅₀Ce₅₀Oₓ, Ni₄₅Ce₴₅Oₓ, and Ni₃₀Ce₹₀Oₓ, respectively.

XPS was carried out on NiₓCe₁₀₀−ₓOₓ samples to further analyze the oxygen vacancy defects. The Ce 3d peaks of CeO₂ were observed for NiₓCe₁₀₀−ₓOₓ samples, as shown in Figure 3b. The Ce 3d band is composed of ten individual peaks, that are labeled on Figure 3b as v, v′, v″, u, u′, u‴, v‴, u‴, v‴, and u‴‴. The v, v′, v″, u, u′, and u‴ peaks represent the 3d¹⁰⁴f⁴ state of Ce⁴⁺, and the v‴, u‴, u‴‴, and u‴‴‴ peaks represent the 3d¹⁰⁴f⁰ state of Ce³⁺ [13,25]. The intensities of these peaks increased with the increasing Ce content in NiₓCe₁₀₀−ₓOₓ samples. The concentration of Ce³⁺ and Ce⁴⁺ can be estimated according to the relative areas of the corresponding peaks. The major valence state of Ce was 4+, Ce³⁺ were also detected for NiₓCe₁₀₀−ₓOₓ samples. It is commonly known that the oxygen vacancy defects will be formed with the appearance of Ce³⁺ to maintain electrostatic balance according to Equation (1):

$$4\text{Ce}^{4+} + \text{O}_2^− \rightarrow 4\text{Ce}^{4+} + 2\text{e}^- / \square + 0.5\text{O}_2 \rightarrow 2\text{Ce}^{4+} + 2\text{Ce}^{3+} + \square + 0.5\text{O}_2$$

 Equation (1)

□ represents the empty position by the removal of O²⁻ from the lattice (i.e., oxygen vacancy defect). It suggests that the oxygen vacancy defects formed for the NiₓCe₁₀₀−ₓOₓ samples, which is consistent with the Raman results.

To test the electrochemical performance of NiₓCe₁₀₀−ₓOₓ catalysts, the polarization curves of these catalysts (Figure 4a) were obtained using Linear Sweep Voltammetry (LSV). The overpotentials of the catalysts for the current density of 10 mA/cm² are listed in Table 1. The Ni₁₀Ce₹₀Oₓ catalyst showed the lowest current density for the applied potentials and had the largest overpotential of 363 mV for the current density of 10 mA/cm². The overpotentials for the Ni₇₅Ce₂₅Oₓ and Ni₅₀Ce₅₀Oₓ catalysts were 338 mV and 341 mV to obtain the current density of 10 mA/cm², which were lower than that of other samples. The Tafel slope results of NiₓCe₁₀₀−ₓOₓ catalysts were shown in Figure 4b and Table 1. The Tafel slopes of the Ni₇₅Ce₂₅Oₓ and Ni₅₀Ce₅₀Oₓ catalysts (66 mV/decade) were close to that of Ni₉₀Ce₁₀Oₓ, Ni₅₀Ce₁₀Oₓ, and Ni₂₅Ce₇₅Oₓ catalysts (68 mV/decade), and were lower than that of the Ni₁₀Ce₉₀Oₓ catalyst (73 mV/decade). An electrocatalyst with a low Tafel slope will have a small kinetic barrier for electron and mass transfer [2,5]. This indicates that the transfer barriers of electron and mass in the Ni₇₅Ce₂₅Oₓ and Ni₅₀Ce₅₀Oₓ catalysts are slightly improved.

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Figure 3. (a) Raman spectra and (b) XPS spectra of NiₓCe₁₀₀−ₓOₓ samples. The peak labeled a in the XPS spectra is ascribed to the Ni 2p peak.
Table 1. Electrochemically active surface area (ECSA), Tafel slope, mass-transfer resistance ($R_{CT}$) and the overpotential ($\eta$) for the current density of 10 mA/cm$^2$ for each catalyst investigated in 1 M KOH.

| Catalyst          | ECSA/cm$^2$ | Tafel Slope  | $R_{CT}$ | $\eta$ for 10 mA/cm$^2$ |
|-------------------|-------------|--------------|----------|-------------------------|
| Ni$_{25}$Ce$_{75}$O$_x$ | 307.5 cm$^2$ | 68 mV/decade | 18.2 $\Omega$ | 351 mV |
| Ni$_{50}$Ce$_{50}$O$_x$ | 362.5 cm$^2$ | 68 mV/decade | 12.6 $\Omega$ | 350 mV |
| Ni$_{75}$Ce$_{25}$O$_x$ | 515 cm$^2$  | 66 mV/decade | 9.9 $\Omega$  | 338 mV |
| Ni$_{90}$Ce$_{10}$O$_x$ | 487.5 cm$^2$ | 66 mV/decade | 7.5 $\Omega$  | 341 mV |
| Ni$_{95}$Ce$_{5}$O$_x$ | 267.5 cm$^2$ | 68 mV/decade | 21 $\Omega$  | 356 mV |
| Ni$_{10}$Ce$_{90}$O$_x$ | 177.5 cm$^2$ | 73 mV/decade | 31.8 $\Omega$ | 363 mV |

Ni$_{25}$Ce$_{75}$O$_x$, and Ni$_{10}$Ce$_{90}$O$_x$ samples, respectively. The ECSA can be calculated according to the formula ECSA = $C_{DL}$/$C_s$, where a specific capacitance of $C_s = 0.040$ mF cm$^{-2}$ was used in this work [18]. The calculated ECSA values for the Ni$_y$Ce$_{100-y}$O$_x$ catalysts as well as other relevant electrochemistry parameters are summarized in Table 1. The ECSAs of the Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts are similar and larger than that of other Ni$_y$Ce$_{100-y}$O$_x$ catalysts. This is consistent with the observed current densities, as a larger ECSA means a sample has more active sites and therefore can catalyze more reactions at once and sustain a large current.

Figure 4. (a) Polarization curves of the NF/NiO substrate and Ni$_y$Ce$_{100-y}$O$_x$ catalysts for the OER with a scan rate of 10 mV/s. (b) Tafel plots obtained from the steady–state polarization curves with a scan rate of 1 mV/s. (c) Current density at OCP vs. CV scan rate for Ni$_y$Ce$_{100-y}$O$_x$ samples. The slope of current density at OCP vs. scan rate stands for the double–layer capacitance. (d) Nyquist plots of Ni$_y$Ce$_{100-y}$O$_x$ samples obtained at 1.55 V vs. RHE. The inset is the electrical equivalent circuit.
The charge transfer resistance ($R_{CT}$) of the Ni$_x$Ce$_{100-x}$O$_x$ catalysts were obtained from their Nyquist plots, as shown in Figure 4d. As shown in Table 1, the $R_{CT}$ of the Ni$_y$Ce$_{100-y}$O$_x$ catalysts decreased firstly and then increased with the increasing Ce content in the catalysts, and the Ni$_{50}$Ce$_{50}$O$_x$ catalyst had the lowest $R_{CT}$ of 7.5 Ω at an applied bias of 1.55 V vs. RHE. The Ni$_{75}$Ce$_{25}$O$_x$ catalyst also showed a low $R_{CT}$ of 9.9 Ω. However, the $R_{CT}$ of the Ni$_{10}$Ce$_{90}$O$_x$ (31.8 Ω) catalyst was much higher than other Ni$_y$Ce$_{100-y}$O$_x$ catalysts. The small mass-transfer resistance of the Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts stands for their favorable OER kinetics.

For the Ce-based catalysts, the oxygen mobility can be promoted by the generated oxygen vacancy defects, resulting an improved ionic conductivity [10]. Also, the oxygen vacancy defects can be act as the OER active sites to catalyze the water oxidation reaction [17]. Therefore, the larger concentration of oxygen vacancy defects results in the lower Tafel slopes, small mass-transfer resistance, and larger ECSAs of the Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts, which account for the higher OER activities for these two catalysts.

Controlled-current water electrolysis (Figure 6) was done to test the long-term performance and stability of the Ni$_{75}$Ce$_{25}$O$_x$ catalyst. With a fixed current density of 10 mA/cm$^2$,
the potential remained stable at 1.57 V vs. RHE for more than 100 h. This indicates that the Ni$_{75}$Ce$_{25}$O$_x$ catalyst is very stable during long-term water electrolysis.

![Potential trace of the Ni$_{75}$Ce$_{25}$O$_x$ sample](Figure 6)

Figure 6. Potential trace of the Ni$_{75}$Ce$_{25}$O$_x$ sample obtained by fixing the current density for electrolysis at 10 mA/cm$^2$. The electrolyte was 1 M KOH (pH $\approx$ 14).

4. Conclusions

In summary, a series of NF/NiO/Ni$_x$Ce$_{100-y}$O$_x$ catalysts were synthesized through the simple dip-coating and annealing methods. The oxygen vacancy defects are formed successfully in all the Ni$_x$Ce$_{100-y}$O$_x$ catalysts, and the concentration of oxygen vacancy defects for Ni$_{75}$Ce$_{25}$O$_x$, Ni$_{50}$Ce$_{50}$O$_x$, and Ni$_{10}$Ce$_{90}$O$_x$ catalysts are larger than other Ni$_x$Ce$_{100-y}$O$_x$ catalysts. This results in the larger electrochemically active surface areas for Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts because of the abundant active sites offered by the defects. The rich oxygen vacancy defects also improve the ionic conductivity so that a lower Tafel slope of 66 mV/decade is obtained for Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts. The improved ionic conductivity also results in the small mass-transfer resistance of Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalysts, which is favorable for their OER kinetics. Therefore, the Ni$_{75}$Ce$_{25}$O$_x$ and Ni$_{50}$Ce$_{50}$O$_x$ catalyst exhibit higher OER activity than other Ni$_x$Ce$_{100-y}$O$_x$ catalysts with the overpotential of 338 mV and 341 mV for the current density of 10 mA/cm$^2$. With a fixed current density of 10 mA/cm$^2$, the potential remains stable at 1.57 V for more than 100 h, indicating the long-term stability of the Ni$_{75}$Ce$_{25}$O$_x$ catalyst.

Supplementary Materials: The following are available online at https://www.mdpi.com/2079-4991/11/2/437/s1, Figure S1: SEM images of Ni$_9$Ce$_{10}$O$_x$, Ni$_{10}$Ce$_{90}$O$_x$, Ni$_{50}$Ce$_{50}$O$_x$, Ni$_{25}$Ce$_{75}$O$_x$, and Ni$_{10}$Ce$_{90}$O$_x$ catalysts, Table S1: Atomic ratios of Ce, Ni and O in Ni$_x$Ce$_{100-y}$O$_x$ catalysts derived from XPS results, Table S2: Raman peak areas at 563 cm$^{-1}$ of Ni$_x$Ce$_{100-y}$O$_x$ catalysts.

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