Ni–CeO₂ composite cathode material for hydrogen evolution reaction in alkaline electrolyte

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In this work, nickel-based electrodes were prepared using composite electrodeposition technique in a nickel sulphamate bath containing suspended micro- or nano-sized CeO₂ particles. The prepared Ni–CeO₂ composite electrodes exhibit an enhanced high catalytic activity toward hydrogen evolution reaction (HER) in alkaline solutions. X-ray diffraction patterns indicated that the CeO₂ particles have been successfully incorporated into the Ni matrix and altered the texture coefficient (TC) of the Ni layer. The morphology of the obtained coatings was characterized by Scanning Electron Microscopy, and the CeO₂ content was determined by coupled energy dispersive X-ray spectrometry. The thermal stability of the composite electrodes was analyzed by thermogravimetric and differential scanning calorimetry, showing a good thermal stability. The catalytic activity of the composite electrodes for HER was measured by steady-state polarization and electrochemical impedance spectroscopy techniques in 1.0 M NaOH solution at room temperature. The exchange current density of HER on the Ni–CeO₂ composite electrodes was much higher than that on Ni electrode. EIS results suggested that a synergetic effect on HER may exist between CeO₂ particles and Ni matrix. Compared to nano-CeO₂, the micro-CeO₂ derived composite electrodes showed higher electrochemical activity. The possible correlation among particle size, content and catalytic activity is discussed.

1. Introduction

Hydrogen has been widely considered as a clean fuel, thank to substantial development of fuel cell technologies [1–3]. Compared to fossil fuel, the hydrogen combustion product is only water, offering many environmental benefits. Also, hydrogen has wide applications such as petroleum refining, ammonia production, metal refining and fuel cell field [4–8]. Generally, hydrogen can be produced from natural gas reforming and gasification of coal and petroleum coke. However, both of the methods using fossil fuel cause significant environment issues [4]. Alternatively, hydrogen production through water electrolysis is thought to be a sustainable method enabling to use renewable energy sources [4,9,10]. In this process, electrode materials play an important role to improve the energy conversion efficiency and reduce cost. Thus, substantial investigations on the hydrogen evolution reaction (HER) are focused on the development of the electrode materials to increase the electro-catalytic activity, and reduce hydrogen evolution over-potentials [11,12].

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In principle, the electrode materials with low over-potential towards the HER should possess two characteristics, i.e., intrinsic catalytic activity and high surface area [13–17]. It is well-known that nickel and Ni-based alloys exhibit good electro-catalytic activity for HER and sufficient corrosion resistance in alkaline solution [18]. The HER on Ni-based alloys such as Ni–P [19,20], Ni–Co [21,22], Ni–Mo [13,23] and Ni–S [24,25] have been studied in different electrolyte. Importantly, compared to its alloys, the Ni-based composite materials containing active solid particles have been received more and more attention as new electro-catalytic candidates, such as Ni–MoO2, Ni–MoO3 [26,27], Ni–Mo powder [16], Ni– rare earth (RE) compounds [18] and Ni–polyaniline [9] composite electrodes. The incorporated particles can decrease Ni grain size and result in a high electrode specific surface area. On the other hand, based on Brewer-Engel theory, Ni can exhibit a synergistic effect with the enclosed composite particles [26]. Thus, these composite Ni electrodes usually show a high activity, compared to Ni. Among the possible solid particles, rare earth compounds are the most promising due to their unique properties in hydrogen storages [28–30]. However, Ni–RE composite electrode has not been fully investigated yet, especially their structure–property correlation in HER.

Ni/CoO catalysts were prepared via co-precipitation or combustion synthesis for steam reforming [31,32]. In this work, Ni–CoO composite coatings are prepared by composite electrodeposition technique from a nickel plating solution containing suspended CoO2 particles. The CoO2 particles can be incorporated in the nickel coating during the electrodeposition. The embedded CoO2 particles are found significantly affect the morphology and the preferred orientation of the Ni crystals in the Ni-based composite electrodes. Two types of CoO2 particle were employed in the composite electrode preparation. One is in micrometer scale, and the other is in nanoscale. The effect of the CoO2 particle size and concentration on the electrochemical activity of these Ni–CeO2 electrodes for the hydrogen evolution reaction were systematically investigated.

2. Experimental

2.1. Synthesis of Ni–CeO2 composite films

Ni–CeO2 composite electrodes were electrodeposited on 10 × 10 cm² mild steel plates. The mild steel substrates were first mechanically polished with various grades of sandpaper (up to 600 grit) and degreased for 1 min with 20 wt.% NaOH at 353 K, followed by a treatment in 10 wt.% HCl. Finally, an anodic oxidation in 10 wt.% H2SO4 was conducted at a current density of 10 A dm⁻² for 1 min, which is to remove the possible oxide films on the substrates. The Ni–CeO2 samples were prepared by electrodeposition from electrolyte containing 350 g dm⁻³ Ni(NH2SO3)2, 4H2O, 10 g dm⁻³ NiCl2·6H2O, and 30 g dm⁻³ NH4Cl with various content of micro-CeO2 (5–7 µm) or nano-CeO2 (20–30 nm) particles. The composite electrodeposition was performed at a current density of 3 A dm⁻² for 1 h at 323 K with a magnetic stirring at 600 rpm.

The obtained composite coatings from micro- or nanosized CeO2 are denoted as M-1, M-2 and M-3, or N-1, N-2 and N-3, respectively, when CeO2 concentration of 5 g/L, 15 g/L and 25 g/L were used in the electrolyte.

2.2. Structural and morphological characterization

All thermogravimetric and differential scanning calorimetry (TG/DSC) experiments were carried out in a STA449F3 (NETSCH, Germany) simultaneous DSC-TGA apparatus. Prior to the test, the system was purged using argon for 30 min. The analysis were performed under argon flow, at a 10 °C min⁻¹ ramp increasing temperature from 25 °C to 800 °C.

The crystalline structure of the Ni–CeO2 coatings were determined by X-ray diffraction (XRD) using Cu Kα (λ = 0.154 nm) radiation in a Bruker D8 series diffractometer with a 2θ = 20–90° measuring interval at 2° min⁻¹. The morphology of the samples was studied using scanning electron microscopy (SEM) on FEI Quanta 200F equipment operating at 20 kV acceleration voltage. The coating composition was analyzed from quantitative energy dispersive X-ray spectrometry (EDX) coupled with the SEM.

X-rays photoelectron spectroscopy (XPS) experiments were carried out in a K-Alpha electron spectrometer (ThermoFisher Scientific Company, USA) using AlKa (1486.6 eV) radiation source. The binding energy (BE) was calibrated by setting the C1s transition at 284.8 eV.

2.3. Polarization characteristics of Ni–CeO2 samples

All the electrochemical tests were carried out using the CHI 660 electrochemical workstation (CH Instrument, USA) in a standard three-electrode electrochemical cell in 1.0 M NaOH solution at room temperature. A Pt foil and Hg/HgO/OH⁻ electrode (in 1.0 M NaOH) were used as the counter and reference electrodes, respectively.

Prior to steady-state polarization records, electrodes were first used for hydrogen evolution at a constant current density of 50 mA cm⁻² for 1 h. In the case of HER investigation, this procedure is to establish stable conditions for HER and to avoid dissolution of oxygen into the electrolyte [11,33].

Steady-state polarization curves were recorded at the scan rate of 5 mV s⁻¹. In order to correct the polarization data from IR drop effects, the uncompensated solution resistance values were calculated from the electrochemical impedance spectroscopy (EIS) measurements. The EIS measurements were performed in the frequency region of 10 K–0.01 Hz with a voltage excitation amplitude of 5 mV at 298 K. The real (Z’) and imaginary (Z”) components of electrochemical impedance spectra in the Nyquist plot were analyzed using the complex nonlinear least squares (CNLS) fitting program to simulate the equivalent resistances and capacitances.

3. Results and discussion

3.1. TG/DSC analysis

It was reported that Ni and RE can form the Ni–RE–O compounds, thereby facilitating HER activity [18,34]. In this work, in order to determine whether Ni and CeO2 can form the
Ni–Ce–O compound, TG/DSC tests were carried out in an Ar atmosphere as shown in Fig. 1. In order to avoid the oxygen interference during the tests, the samples were prepared in an argon filled glove box. It can be seen that Ni film is stable in the temperature ranging from 200 °C to 800 °C (Fig. 1a). The similar phenomenon is observed with the M-2 and N-2 composite coatings, as depicted in Fig. 1b and c, respectively. However, there is no obvious reaction occurring between micro-CeO₂ or nano-CeO₂ particles and Ni layer during the studied temperature range. No obvious endothermic behavior peak can be associated with the reaction between micro-CeO₂ or nano-CeO₂ particles and Ni layer. These results indicate that both the micro- and nano-sized CeO₂ based composite coatings have a good thermal stability.

3.2. Structural characterization

Phase composition and structure of the Ni and Ni-based composite electrodes were determined by XRD patterns. The results confirm that all the diffraction peaks can be well indexed to Ni (JCPDF No. 65–2865) and the CeO₂ phase incorporated into Ni matrix. Usually, as for the Ni layer deposited from nickel sulphamate bath, (200) diffraction peak is the preferred orientation. However, the addition of 15 g L⁻¹ micro-CeO₂ results in a change of the preferred orientation from (200) to (111) diffraction peak (Fig. 2b). The similar preferred diffraction peaks are also observed with the nano-CeO₂ composite layer prepared from the same CeO₂ content (Fig. 2c).

In order to elucidate the effect of CeO₂ on structure and preferred orientation of the deposited Ni, the texture coefficient (TC) [35] is used, which is defined as:

$$TC = \frac{I_{HKL}}{I_{qHKL}} / \frac{1}{n} \sum_{i=1}^{n} \frac{I_{HKL}}{I_{qHKL}}$$

where, $I_{HKL}$ and $I_{qHKL}$ are the diffraction intensity of the crystal plane (hkl) in the deposited and standard samples, respectively. $n$ is the number of reflection faces in the diffraction pattern. If the texture coefficient is greater than 1.0, a preferred orientation occurs.

The calculated results are listed in Table 1. Regardless of the size of the CeO₂ particles, a significant decrease in the preferred orientation (200) is observed, especially for the M-2 composite coating. The addition of CeO₂ particles also lead to slight increase in the (111), (311) and (222) TC value. The textural organization of the deposited coatings can be attributed to the existence or formation of different chemical species adsorbed at the metal–electrolyte interface during the cathodic electrodeposition process, thereby affecting the growth of crystalline planes of Ni metal. On the other hand, it was found that, during the Ni deposition, the Ni layer texture can be also affected by atomic hydrogen, molecular hydrogen and nickel hydroxide [36,37]. In this work, the addition of CeO₂ may also change the quantity and status of these intermediates at the surface, thus altering the TC values of Ni layer. The trends of the different sized CeO₂ particles affecting the Ni layer texture are found to be similar, although the micro-CeO₂ particles have a stronger influence on Ni (220) relative to the nanosized particles.

3.3. SEM and XPS analyses

SEM images of the Ni, M-2 and N-2 electrodes are compared in Fig. 3. It can be seen that the Ni film appears a typical block shape. The morphology of Ni–CeO₂ composite coatings is

![Fig. 1 – TG/DSC of (a) Ni, (b) M-2 and (c) N-2 electrodes.](image)
different to that of the Ni deposit. The uniform distribution of the CeO₂ particles in the Ni–CeO₂ coating is also discernible in SEM micrographs.

The microstructure of the pure Ni electrode consists of dendritic grains and eutectic, with non-uniform the grain size distribution. The largest one is estimated to be as large as 4 μm. However, when micro or nano CeO₂ particles are incorporated into Ni matrix, for example in the M-2 and N-2 layers, the grain size in the composite is much finer than the observed in Ni layer. The fining effect of CeO₂ on grain can be explained [38]. At first, CeO₂ particle can improve the tendency on forming more grains, and the number of crystal nuclei will, therefore, increase, leading to smaller and more uniform grain. In addition, the large CeO₂ particles are subject to be distributed mostly over the grain boundary[38,39], and results in finer grains. Fig. 3b and c show that CeO₂ is well distributed in the whole coating. The uniform distribution can relieve the internal stress and purify the boundaries of grains and phases in the coating.

The composition of the coatings was analyzed using EDX and compared with the concentration of CeO₂ particles in the electrodeposition electrolyte. The values are collected in Table 2. No matter the CeO₂ particle size is at micro- or nanoscale, the content of co-deposition CeO₂ particles increases with their amount in the solution. Importantly, a significant enhancement of the CeO₂ content in composite coating compared to its concentration in solution was found for all of cases. It was also found that the micro CeO₂ is easier to deposit into Ni layer relative to the nano-CeO₂. The faster rate of increasing CeO₂ in composite coating with particle concentration in the solution is observed with the micro-CeO₂ particle, compared to nano-particles. This experimental finding is consistent with others’ conclusion that the reduction of particle size results in a decrease of composite particle content in metallic matrix [40]. Thus, the size of particle plays an important role in the composite electrodeposition process and affects the resulting chemical and physical properties.

In both cases, with increasing the concentration of the CeO₂ particles up to 25 g/L, the composite particles content in coating still is increasing without reaching saturation [38,41].

Fig. 4 are Ni 2p3/2 and Ce 3d5/2 spectra for the M-2 and N-2 composite electrodes. Two major peak are identified in Fig. 4a and c, corresponding two different valence states of Ni. The
first peak at binding energy (BE) of 852.68 eV is attributable to Ni$^0$ metal, and the second peak at 856 eV is correspond to Ni$^{2+}$ (NiO) valence state [42]. In addition, a small peak at 859.4 eV is attributed to a Ni satellite peak [43].

In the case of Ce 3d$_{5/2}$ shown in Fig. 4b and d, only one BE peak can be seen at 882.2 eV, which is attributed to a Ce$^{4+}$ (CeO$_2$) [42]. This result shows that there is no change in the valence state of the CeO$_2$ during the electrodeposition process. Through integrating the peak areas, the Ni$^0$/Ni$^{2+}$ ratio can be calculated. The Ni$^0$/Ni$^{2+}$ ratio value in the M-2 composite electrode is 0.52, and the value in the N-2 composite electrode is 0.53. This result means the Ni oxidation at surface for thee composite electrode is independent of particle size.

3.4. Linear polarization

The steady-state linear polarization curves for HER recorded in 1.0 M NaOH on selected micro- and nano-CeO$_2$ particles based Ni–CeO$_2$ composite electrodes are shown in Fig. 5a and Fig. 5b, respectively. The polarization curve of a pure Ni electrode is also enclosed for a comparison.

In order to compare the electro-catalytic activity on different electrodes, the cathodic polarization curves were replotted (The plots were corrected for $iR_s$ drop, solution resistance $R_s$ was determined by the EIS method). A typical Tafel region was displayed, which can be described using the Tafel equation as following.

$$
\eta_c = -\frac{2.3RT}{anF}\log j_0 + \frac{2.3RT}{anF}\log j
$$

$$
\eta_c = a + b \log j
$$

Here $\eta_c$ is the cathode over potential, $R$ is the ideal gas constant, and $T$ is the absolute temperature, $a$, $n$ and $F$ are the charge-transfer coefficient, number of electrons exchanged and the Faraday constant, respectively. The $j_0$ is the apparent exchange current density, which can represent the HER catalytic activity of the electrodes [9,16,17].

The calculated kinetic parameters of HER on these composite electrodes are listed in Table 3. Evidently, a significant increase in $j_0$ is observed with the Ni–CeO$_2$ composite electrodes compared to the Ni coating. For example, the $j_0$ value obtained with the M-1 and M-2 electrode is almost 29 and 72 times higher than that with the nickel electrode, respectively. Further increasing the micro-CeO$_2$ concentration on M-3 lead to a drop of $j_0$, compared to M-2, but the value is still 42 times higher than that with the Ni electrode. This is
due to that too much CeO₂ particles embedded in the composite electrode may affect the \( H_{ads} \) desorption process, and decrease the \( j_0 \) value. In the case of the nanosized CeO₂ based composite electrode, the \( j_0 \) values measured with the composite electrode N-1 and N-2 are very close, around 32 times higher than that of the Ni electrode. Similar to the micro-CeO₂ composite electrodes, the \( j_0 \) value of composite electrode N-3 is decreased, relative to N-1 and N-2 electrodes.

Fig. 4 – XPS of the M-2 and N-2 composite electrodes: (a) Ni 2p\(_{3/2}\) in M-2, (b) Ce 3d\(_{5/2}\) in M-2 (c) Ni 2p\(_{3/2}\) in N-2 (d) Ce 3d\(_{5/2}\) in N-2.

Fig. 5 – Steady-state polarization curves for the HER in 1.0 M NaOH at 298 K on the (a) micro-CeO₂ and (b) nano-CeO₂ based composite electrodes; Ni electrode is included in each case for a comparison.
Table 3 Electrocatalysis parameters of the HER obtained from the polarization curves recorded in 1.0 M NaOH solution at 298 K.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>b/mV dec⁻¹</th>
<th>j₀/µA cm⁻²</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>131</td>
<td>1.12</td>
<td>0.44</td>
</tr>
<tr>
<td>M-1</td>
<td>158</td>
<td>32.42</td>
<td>0.37</td>
</tr>
<tr>
<td>M-2</td>
<td>157</td>
<td>80.71</td>
<td>0.37</td>
</tr>
<tr>
<td>M-3</td>
<td>141</td>
<td>47.40</td>
<td>0.41</td>
</tr>
<tr>
<td>N-1</td>
<td>164</td>
<td>35.38</td>
<td>0.35</td>
</tr>
<tr>
<td>N-2</td>
<td>165</td>
<td>36.95</td>
<td>0.35</td>
</tr>
<tr>
<td>N-3</td>
<td>163</td>
<td>29.85</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Tafel slope b is an important parameter and can provide insight into the HER mechanism on the studied electrodes. The measured slope values for these HER electrodes are listed in Table 3. The Ni electrode exhibits a slope around 121 mV dec⁻¹. However, the presence of the CeO₂ particles in the Ni matrix results in an increase in the Tafel slope value. For example, slope for the N-2 composite electrode is 165 mV dec⁻¹. This phenomenon that the electrode containing solid metal oxides shows a high Tafel slope value is in good agreement with other research [9,16].

According to the Tafel equation, b = 2.3RT/(αF), the charge-transfer coefficient α which indicated the rate-determining step (RDS) can be calculated [16].

The electrochemical HER mechanism model in alkaline solutions was proposed through following three reactions:

\[ \text{H}_2\text{O} + \text{M} + \text{e}^- \leftrightarrow \text{MH}_{\text{ads}} + \text{OH}^- \]  
Volmer reaction (4)

\[ \text{MH}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{H}_2 + \text{M} + \text{OH}^- \]  
Heyrovsky reaction (5)

\[ \text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} \leftrightarrow \text{H}_2 + 2\text{M} \]  
Tafel reaction (6)

When the charge-transfer coefficient is 0.5, the RDS is the Volmer reaction or the Volmer reaction coupled with one of other two reactions [14,17,18,44]. As listed in Table 3, the charge-transfer coefficients are all close to 0.5. Thus, the RDS of HER on the studied composite electrodes may be the Volmer reaction or the Volmer reaction coupled with one of other two reactions [45]. The low electron conductivity of the CeO₂ particles will slightly reduce the charge-transfer coefficient value of the composite electrodes.

### 3.5 Electrochemical impedance spectroscopy

In order to investigate the interfacial properties and electrocatalysis kinetics of the HER on micro-CeO₂ and nano-CeO₂ composite electrodes, impedance measurements were further carried out at a wide frequency range (10K−0.01 Hz). The classic complex plane Nyquist plots were obtained on the composite electrodes and Ni electrodes at cathode overpotential of 250 mV, as shown in Fig. 6. In order to analyze the value of each circuit element in the impedance spectroscopy, the measured data were simulated using nonlinear-least-square fitting analysis (NLS) software. The electrical circuit model selected to investigate the HER electrochemical process was shown in Fig. 7, which was similar to elsewhere proposed [46]. In the equivalent circuit, Rₐ is the solution resistance. Rₑ is the electrochemical charge transfer resistance. CPE1 is associated with the double layer capacitance (Cdl). Rₑ is related to the resistance of the adsorbed intermediate H₄ads, and CPE2 is the constant phase element of the pseudo-capacitance [14,18,46,47].

Due to the solid electrodes dispersion effect, the double layer capacitance Cdl is substituted by a constant phase element (CPE). Its impedance is given by \( Z_{\text{CPE}} = R_{\text{ct}}/(1 + jωτ)^α \). In the equation, \( ω \) is the angular frequency in rad/s of the ac voltage, and \( α \) corresponds to the depression angle 90(1-\( α \)) of the semicircle. \( T \) is a constant which is related to the double layer capacitance, Cdl, of the electrodes [14,18].

\[
T = C_{\text{dl}}(R_{\text{ct}}^{-1} + R_{\text{ct}}^{-1})^{-1 - α}
\]  

(7)

The values of the electrochemical parameters simulated from the analysis of impedance spectra are reported in Table 4. The overall electrochemical reaction resistance values (\( R_{\text{ct}} + R_{\text{p}} \)) decreases obviously with the size of CeO₂ particles embedded in the Ni electrode. The electrochemical charge transfer resistance (\( R_{\text{ct}} \)) values of the Ni and composite electrodes from different CeO₂ concentration electrolytes are compared in Fig. 8. The \( R_{\text{ct}} \) values decreased from 437.20 Ω cm⁻² to 0.85 Ω cm⁻², when the micro-CeO₂ concentration in solution was increased to 15 g L⁻¹. Compared to the micro-CeO₂ composite electrodes, the \( R_{\text{ct}} \) value corresponding to nano-CeO₂ concentration of 5 g L⁻¹ is significantly reduced to 0.75 Ω cm⁻², 583 times lower than that of Ni coating. As mentioned above, \( R_{\text{p}} \) is related to the resistance of the adsorbed intermediate H₄ads. The \( R_{\text{p}} \) values measured with these composite electrodes are all smaller than that with the Ni electrode. Importantly, the \( R_{\text{p}} \) values were found decreased first, and then increased as a function of concentration of micro-CeO₂ in the electrodeposition electrolyte. The similar trend was also observed on the nano-CeO₂ composite coatings. In terms of the overall electrochemical reaction resistance (\( R_{\text{ct}} + R_{\text{p}} \)), the value measured with M-2 is the lowest (69.14 Ω cm⁻²) among all of studied electrodes. Likewise, the N-2 electrode also presents the highest electro-catalytic activity among three studied nano-CeO₂ composite electrodes. Thus, the size dependence suggests that optimization of CeO₂ particle size is critical to improve the hydrogen evolution performance on the Ni−CeO₂ composite electrodes. It was proposed that the CeO₂ particles are active for HER, and increase the number of active sites for H₄ads [26].

These comparisons in terms of the overall electrochemical reaction resistance further attest that the co-deposition of the CeO₂ particles can accelerate the HER process in Ni electrodes. The HER activity on M-2 and N-2 composite electrodes are the highest among the studied composite electrodes using micro- and nano-scale particles, respectively. The content of co-deposition CeO₂ particles in M-2 coating was found two times more than that in N-2 coating. Given two orders of magnitude difference in particle diameters between nano-CeO₂ and micro-CeO₂ particles, the number of the active sites for H₄ads and surface cover degree of the CeO₂ particles on the nano-CeO₂ composite electrodes should be larger than those on the micro-CeO₂ composite electrodes. In principle, increased active sites for H₄ads can accelerate the Volmer
reaction, leading to a lower $R_{ct}$ in HER. However, excess CeO$_2$ particle sites also influence the desorption process of $H_{ads}$. Also too much CeO$_2$ embedded in the Ni matrix can decrease the electronic conductivity of the composite electrode. Therefore, the optimal concentration of the CeO$_2$ particles is in a moderate range regarding the maximum HER catalysis activity on the composite electrodes.

The values of double layer capacitance $C_{dl}$ calculated from different electrodes were listed in Table 4. Compare to the Ni electrode, the double layer capacitance of micro-CeO$_2$
composite electrodes is slightly increased with the embedded CeO₂ particles. However, on the contrary, incorporation of nano-CeO₂ particles into Ni leads to a reduction of double layer capacitance. Although surface area of composite electrodes increases with CeO₂ addition, the double layer capacitance values are still depended on the thickness of double layer. The large amount of H ads adsorbed on the nano-CeO₂ particles may enlarge the thickness of double layer [9], resulting in a decreased \( C_{dl} \) value.

The Volmer reaction in HER requires a filled d orbital at the metal surface for the discharge reaction. As metal Ni has 8 d orbital electrons, hydrogen ions can be reduced at the Ni surface. Ce has only 1 d orbital electron, which has several half-filled and empty d orbitals. An adsorptive bond can be formed between Ce and H. So a possible synergetic effect between the CeO₂ particles and Ni matrix can enhance the migration of the reduced H atoms from Ni surface to CeO₂, and this effect can lead more available Ni sites for further dissociation of water molecules [17,23,48,49]. As a result, much improved higher electro-catalytic activity can be obtained on the Ni–CeO₂ composite electrodes, relative to Ni.

With an appropriate CeO₂ content in the Ni matrix, the \( j_0 \) value of the composite electrode is increased, and the overall electrochemical reaction resistance can be decreased. However, excess CeO₂ particles embedded into Ni would hinder the \( H_{ads} \) desorption on the composite electrodes, resulting in a decrease of catalytic activity. In addition, a large number of Ce-Hₐds formed at the composite electrodes surface will enhance the thickness of the double layer, which would make the double layer capacitance values decreased. These experimental results suggested that the CeO₂ particles can reduce the crystalline grain size of Ni in the composite coating, and raise the surface area. However, the formation of Ce-Hₐds will increase the thickness of the double layer. Compared to the micro-CeO₂ composite electrodes, nano-CeO₂ composite electrodes contain more CeO₂ activity sites, which make the double layer capacitance values decreased obviously.

### 3.6. Electrochemical activity under electrolysis

According to the steady-state linear polarization and EIS measurement results, the optimal addition of the CeO₂ particles in the Ni coating can increase the HER activity. Durability of the developed Ni–CeO₂ composite electrode was further studied in a continuous electrolysis experiment. The morphology changes on the Ni and composite electrodes before and after the HER reaction were also investigated.

Fig. 9 shows the HER overpotential of the Ni, M-2 and N-2 electrodes in 1.0 mol/L NaOH solution at 298 K under a current density of 400 mA cm⁻² for 48 h. It can be seen that the HER overpotential on the M-2 composite electrode is the lowest among the three electrodes. This result is in agreement with the above electrochemical kinetic analysis. In addition, SEM images of the Ni, M-2 and N-2 electrodes after electrolysis are shown in Fig. 10. Compared with before electrolysis experiment in Fig. 3, slight alkaline corrosion can be seen in the electrode surface. But the surface of all three electrodes still keeps smooth and dense. The composition of the M-2 and N-2 composite electrodes after electrolysis was also determined by

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
<th>N-1</th>
<th>N-2</th>
<th>N-3</th>
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<tr>
<td>( R_s (\Omega \text{ cm}^{-2}) )</td>
<td>5.70</td>
<td>4.93</td>
<td>4.49</td>
<td>4.55</td>
<td>4.55</td>
<td>4.68</td>
<td>4.52</td>
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<td>( R_{ct} (\Omega \text{ cm}^{-2}) )</td>
<td>437.20</td>
<td>4.45</td>
<td>2.53</td>
<td>0.75</td>
<td>0.79</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>( R_p (\Omega \text{ cm}^{-2}) )</td>
<td>1754.00</td>
<td>182.60</td>
<td>68.29</td>
<td>249.30</td>
<td>253.70</td>
<td>190.70</td>
<td>496.30</td>
</tr>
<tr>
<td>( C_{dl} (10^{-5} \text{ F cm}^{-2}) )</td>
<td>7.09</td>
<td>11.80</td>
<td>7.56</td>
<td>10.80</td>
<td>0.89</td>
<td>1.48</td>
<td>2.08</td>
</tr>
</tbody>
</table>
EDX. After electrolysis, the CeO$_2$ content of the M-2 composite electrode is 6.67 at.%, and the CeO$_2$ content of the N-2 composite electrode is 3.89 at.%. Compare with results before electrolysis in Table 2, slightly decreased CeO$_2$ particles may be due to a combined effect involved H$_2$ scouring and alkaline corrosion through the electrolysis process. Importantly, the measured HER overpotential remains stable during the durability test for each electrode, suggesting that the remaining CeO$_2$ particles in Ni matrix are able to maintain a high HER activity.

4. Conclusions

In this work, highly active Ni–CeO$_2$ composite electrodes for the HER were prepared through co-deposition of micro- or nano-sized CeO$_2$ particles with Ni during electrodeposition. The influences of CeO$_2$ particles with different sizes on the morphology and crystalline structure of Ni matrix, as well as resulting electro-catalytic activity in hydrogen evolution were systematically investigated. The presence of CeO$_2$ in the Ni matrix can significantly increase the HER exchange current density, and reduce the electrochemical reaction resistance. The electro-catalytic activity of the micro-CeO$_2$ composite electrode is higher than that of the nano-CeO$_2$ composite electrode. The highest electro-catalytic activity for the HER was achieved on the composite electrode prepared from an optimal micro-CeO$_2$ concentration at a middle range. The observed promotional roles of incorporated CeO$_2$ is ascribed to possible synergetic effects between CeO$_2$ particles and the Ni matrix, leading to a facilitation of H$_{ad}$ migration from the Ni to CeO$_2$ particles.
REFERENCES


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