Electrocatalytic Oxidation of Sodium Borohydride on a Nanoporous Ni/Zn-Ni Electrode

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Abstract: A Ni-Zn binary metal coating was electrochemically deposited on a copper electrode that was coated with nickel (bottom layer). This was then etched in concentrated alkaline solution (30 wt% NaOH) to produce a nanoporous Ni electrocatalytic surface for borohydride electro-oxidation in alkaline solution. The bulk and surface compositions of the coating before and after alkaline leaching were determined by atomic absorption spectroscopy and energy dispersive X-ray analysis. The surface morphology was investigated by scanning electron microscopy. The characterization showed that the leached Ni/Zn-Ni coating has a nanoporous structure. Electrocatalytic activity for borohydride electro-oxidation was assessed by cyclic voltammetry and electrochemical impedance spectroscopy. The improved activity of the electrode was related to the removal of corrosion products and the formation of nanopores and cracks during alkaline leaching. Cyclic voltammetry studies confirmed that the alkaline leaching process improved the activity of the Ni/Zn-Ni coating in comparison to that of a smooth Ni deposit, and it gave an anodic peak current density that was 21 times higher.

Key words: leached Ni/Zn-Ni coating; electrochemical deposition; nanoporous; borohydride electro-oxidation; electrochemical impedance spectroscopy

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Recent studies using an alkaline medium [1,2] and the development of hydroxyl ion conducting membranes [3–7] have increased the interest in alkaline fuel cells (AFCs) [8–10], but the right fuel for these systems is still a key problem. Pure hydrogen or hydrogen-rich gases give high efficiency, but their production, storage, and distribution would constraint a large scale development [11,12]. The electro-oxidation of formic acid [13], methanol [14], ethanol [15], and other alcohols and polyols in AFCs have only achieved a few tens of mW/cm² as the best cell performance [8–10]. This relatively low cell performance is partly because the oxidation of alcohols and other liquid organic fuels is difficult to catalyze, even in an alkaline medium. Sodium borohydride, which is safe, non-toxic, chemically stable, and easy to transport in its dry state, is an attractive hydrogen source for fuel cells [16]. The direct borohydride fuel cell (DBFC) as a direct liquid fuel cell with a high energy density, which is 9296 Wh/kg for NaBH₄, has attracted more interest recently [17,18]. The DBFC was first proposed in the early 1960s by Indig and Snyder [19], and Jasinski [20]. The electrochemical reactions in a DBFC employing oxygen as the oxidant are as follows.

The electrocatalyst is a key component in the DBFC. Different metals have been studied as the anode catalyst, including Pt [21–24], Au [21,22,25–28], Ag [29–32], Os [33,34], Ni [18,22,30], Pd, and Cu [22]. Pt and Ni are more attractive than the other metals and have been proposed as the anode catalyst for DBFC by many researchers. In recent years, the interest in DBFC has been revived, as evidenced by the appearance of a number of papers on the DBFC [35–37]. Most of these works have focused on testing model DBFCs with different catalysts and different cell and/or electrode structures [35,36]. As catalysis is a surface effect, the catalyst needs to have the highest possible surface area. Active carbon materials are a common choice for supporting electrocatalyst particles because of their large surface areas, high electrical conductivities, and nanoporous structures [38–42]. In this study, nanoporous nickel electrodes prepared by the leaching of Zn was studied. It showed that the caustic leaching of Zn was accompanied by volume loss that led to the formation of nanopores and cracks, which yielded a highly porous catalytic surface suitable for the

electro-oxidation of borohydride in alkaline solution.

1 Experimental

1.1 Preparation

The copper electrodes were cut and mounted in polyester while leaving a surface area of 1 cm² for electrochemical measurements. Electrical connection was provided by a copper wire. Before electrodeposition, the electrode surface was polished with emery paper (up to 2500 grit size), then washed with distilled water, thoroughly degreased in 30 wt% NaOH solution for 5 min, washed again with distilled water, dipped into 10 wt% H₂SO₄ solution for 1 min followed by a rinse with distilled water and then immediately immersed in the bath solution. The plating baths and conditions used for the different Ni coatings were: (a) for the smooth Ni coating, these were 330 g/L NiSO₄·6H₂O + 45 g/L NiCl₂·6H₂O + 37 g/L H₃BO₃ (Watts bath) at pH = 4.0–4.5, 50 °C, and 50 mA/cm² for 40 min, and (b) for the Ni/Zn-Ni coating, the co-deposition of Zn-Ni was done on the surface of smooth Ni using a bath that was the same as in (a) plus 20 g/L ZnCl₂ at the beginning of the deposition, and the electrolysis time was 30 min at pH = 4.0–4.5, 50 °C and a current density of 50 mA/cm². The surface of the Cu was coated with Ni and Ni (bottom layer)/Zn-Ni (top layer), respectively, so that smooth Ni and Ni/Zn-Ni electrodes were obtained. After deposition and rinsing with distilled water, the Ni/Zn-Ni electrode was immersed in 30 wt% NaOH solution at room temperature for 48 h to get the zinc metal to dissolve to obtain a more porous electrode. After the leaching, the working electrode was held at 100 mA/cm² cathodic current density in 1 mol/L KOH solution for 30 min to reduce the oxide film on the electrode surface and remove corrosion products from the pores of the coating and to obtain a reproducible electrode [43].

1.2 Characterization

The bulk composition of the coatings and the loadings on the smooth nickel and Ni/Zn-Ni electrodes before and after leaching were determined by atomic absorption spectroscopy (AAS, NovAA 400-Analytikjena). The surface compositions of the coatings before and after leaching were determined by energy dispersive X-ray (EDX) analysis. Scanning electron microscopy (SEM) images were taken using a Philips Model XL30 instrument.

1.3 Electrochemical test

The electrochemical studies were carried out in a conventional electrochemical cell. All the solutions were purged

with purified nitrogen for 10 min before the measurement. A standard three-electrode cell arrangement was used in all experiments. A platinum sheet with a geometric area of about 20 cm² was used as the counter electrode. All potentials were measured with respect to a commercial saturated calomel electrode (SCE). The catalytic activity of the electrodes was measured by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The electrochemical experiments were carried out using a Princeton Applied Research, EG&G PARSTAT 2263 Advanced Electrochemical system ran by the PowerSuite software. The r.m.s amplitude of the modulation potential for the EIS measurements was 10 mV. The frequency range was 100 kHz to 10 mHz. All the chemicals were analytical grade and used as received. For each experiment, a freshly prepared electrode and solution were used.

2 Results and discussion

2.1 Characterization results

The bulk composition and metal loading of the electrodes were characterized by AAS of a solution obtained by the complete dissolution of the deposits in diluted HNO₃ solution. The percentage metal ratios determined are given in Table 1. The chemical composition analysis by AAS revealed that the dezincification process left a surface rich in nickel. The Zn content was decreased from 32.05 wt% to 2.29 wt% after the selective dissolution. The AAS analysis for the smooth nickel coating was 26.00 mg/cm². The loading amounts of Ni and Zn on the Ni/Zn-Ni electrode before leaching were 27.40 and 12.92 mg/cm², respectively, while after leaching, the loadings of Ni and Zn were 21.38 and 0.50 mg/cm², respectively. The surface compositions of the deposit before and after leaching were analyzed by EDX analysis. The results are shown in Table 1. The Ni content of the bulk composition (AAS) was higher than that of the surface (EDX) and the Zn content of the bulk composition was lower than that of the surface. These results suggested that the Ni/Zn-Ni deposit did not have a homogenous chemical composition and the chemical composition of the deposit changed as the film got thicker. The AAS and EDX analysis results revealed that the large amounts of Zn dissolved from the deposit led to pore and crack formation,

Table 1 Bulk composition (determined by AAS) and surface composition (determined by EDX) of the coated deposits before and after leaching

Leaching	Bulk composition (wt%)		Surface composition (wt%)	
	Ni	Zn	Ni	Zn
Before	67.95	32.05	15.42	84.58
After	97.71	2.29	59.51	40.49

Fig. 1. SEM images of smooth nickel surface (a) and Ni/Zn-Ni surface before (b) and after (c) treatment with 30% NaOH solution.

which yielded a highly porous surface suitable for borohydride electro-oxidation.

The SEM images in Fig. 1 showed significant differences in the morphology of the two different coatings. The smooth Ni electrode showed a relatively homogeneous surface with little roughness, which can be considered a quasi-two dimensional surface (Fig. 1(a)). The SEM images of the Ni/Zn-Ni electrode before and after leaching are shown in Fig. 1(b) and 1(c), respectively. The deposit had a porous structure before leaching. Moreover, the porosity of surface was increased and more cracks and nanopores appeared after the leaching of Zn from the deposit, which gave a high surface area for borohydride electro-oxidation (Fig. 1(c)).

2.2 Cyclic voltammetry

Figure 2 shows the CV voltammograms of the smooth nickel electrode and nanoporous Ni/Zn-Ni electrode in 1 mol/L NaOH solution recorded at a potential sweep rate of 10 mV/s. During the anodic sweep, both electrodes exhibited only one anodic peak at 0.38 and 0.49 V, respectively. In the reverse sweep, only one cathodic peak was detected, which was assigned to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox process. Com-

Fig. 2. Cyclic voltammograms of the smooth nickel electrode and leached Ni/Zn-Ni electrode in 1 mol/L NaOH solution at a potential sweep rate of 10 mV/s.

pared to the smooth nickel electrode, the current density on the nanoporous Ni/Zn-Ni electrode was higher (45.5 mA/cm^2), which can be attributed to the increase in surface area and changes in surface features.

Figure 3 shows the cyclic voltammograms of the electro-oxidation of borohydride on the nanoporous Ni/Zn-Ni electrode in the absence and presence of borohydride in 1 mol/L NaOH solution. An increase in the anodic peak current for peak a_1 followed by the appearance of a new peak (a_2) at a more positive potential (0.635 V vs. SCE) were the main effects observed on the addition of 0.02 mol/L borohydride to the electrolyte. The a_1 peak became ill-defined and was hard to distinguish in the presence of borohydride. Moreover, E_{pa2} was higher than E_{pa1} , which indicated that the active species needed for borohydride oxidation were mainly generated at a higher anodic potential. The appearance of the new anodic peak (a_2) led to the conclusion that borohydride oxidation took place after the oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH [44,45]. The $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox couple acts as a catalyst for the oxidation of borohydride in basic solutions. Therefore, for the Ni/Zn-Ni electrode, peak a_1 was due to the $\alpha\text{-Ni}(\text{OH})_2/\text{NiOOH}$ redox couple and peak a_2 was assigned to the electro-oxidation of borohydride.

Fig. 3. Cyclic voltammograms of leached Ni/Zn-Ni electrode in the absence and the presence of 0.02 mol/L borohydride in 1 mol/L NaOH solution at a potential sweep rate of 10 mV/s.

The electro-catalytic activity of the leached Ni/Zn-Ni electrode for borohydride oxidation was evaluated by cyclic voltammetry and compared to that of the smooth nickel electrode. Figure 4 shows that the current density of the Ni/Zn-Ni electrode was much higher than that of the smooth nickel electrode. For example, at the potential of peak a_2 , the Ni/Zn-Ni electrode showed a current density of 125.8 mA/cm², which was nearly 21 times higher than that of the smooth nickel electrode (6.0 mA/cm²). In addition, Fig. 4 shows that the onset oxidation potential of the α -Ni(OH)₂/NiOOH redox couple on the leached Ni/Zn-Ni electrode was lower than that with the smooth nickel electrode. Generally, the leached Ni/Zn-Ni electrode showed significantly higher electro-catalytic activity for borohydride oxidation. The higher activity of the leached Ni/Zn-Ni electrode was due to the high surface area that was formed after the selective dissolution of Zn from the surface, as substantiated by the SEM images (Fig. 1(c)).

Fig. 4. CVs of smooth nickel electrode and leached Ni/Zn-Ni electrode in 0.02 mol/L borohydride and 1 mol/L NaOH solution at a potential sweep rate of 10 mV/s.

Table 2 presents a comparison of the peak current (i_p) during borohydride oxidation on the leached Ni/Ni-Zn electrode with those of different electrodes in the literatures [46–51]. It is evident from Table 2 that the peak current density of the leached Ni/Ni-Zn electrode was higher than those of the other different electrodes. In other word, among

these electrodes, the leached Ni/Ni-Zn electrode has the best electro-catalytic activity for borohydride electro-oxidation in alkaline medium. The enhanced electro-catalytic activity of the Ni/Zn-Ni electrode can be attributed to the increase in surface area.

The influence of the scan rate on the CV behavior of the leached Ni/Zn-Ni electrode in 1 mol/L NaOH/0.02 mol/L borohydride is shown in Fig. 5. This shows the CVs of the leached Ni/Zn-Ni electrode from -0.90 to 0.85 V at different potential sweep rates from 1 to 20 mV/s in 1 mol/L NaOH + 0.02 mol/L borohydride solution. As the scan rate increased, the anodic peak potential was shifted to more positive values and the cathodic peak potential was shifted in a slightly negative direction.

Fig. 5. Cyclic voltammograms obtained in 1 mol/L NaOH + 0.02 mol/L borohydride for the leached Ni/Zn-Ni electrode at various scan rates.

The plot of the CV peak currents I_{pa} against the square root of the voltage scan rate ($v^{1/2}$) gave a linear relationship ($R^2 = 0.9955$, Fig. 6). In semi-infinite diffusion-controlled cyclic voltammetry in liquid electrolytes, I_{pa} against $v^{1/2}$ gives a linear relationship for a kinetically simple redox reaction. Thus, the linear relationship between I_{pa} and $v^{1/2}$ demonstrated that the electrochemical reaction of the formation NiOOH from Ni(OH)₂ was a diffusion-controlled process.

Table 2 Composition of the peak current density (i_p) during the oxidation of NaBH₄ on leached Ni/Ni-Zn electrode and different electrodes

Electrode	Medium	Scan rate (mV/s)	i_p /(mA/cm ²)	Ref.
Ni deposited carbon fiber	0.8 mmol/L NaBH ₄ + 2 mol/L KOH	50	56.0	[46]
Nickel	0.05 mol/L NaBH ₄ + 1 mol/L NaOH	10	4.0	[47]
Ni/C	0.2 mol/L NaBH ₄ + 2 mol/L NaOH	50	18.0	[48]
Ni ₃₇ -Pt ₃ /C	0.2 mol/L NaBH ₄ + 2 mol/L NaOH	50	26.0	[48]
Ag	0.001 mol/L NaBH ₄ + 0.1 mol/L NaOH	100	2.5	[49]
Au	0.00125 mol/L NaBH ₄ + 0.2 mol/L KOH	100	0.4	[50]
Nanoporous gold wire array	0.02 mol/L NaBH ₄ + 1 mol/L NaOH	10	73.6	[51]
Leached Ni/Zn-Ni	0.02 mol/L NaBH ₄ + 1 mol/L NaOH	10	125.8	this work

Fig. 6. Plot of anodic current density versus $v^{1/2}$ in 1 mol/L NaOH + 0.02 mol/L borohydride for the leached Ni/Zn-Ni electrode.

Figure 7 shows typical CVs of the Ni/Zn-Ni electrode from -0.90 to 0.85 V at the scan rate of 5 mV/s in 1 mol/L NaOH solution as the concentration of borohydride was changed from 0.02 to 0.06 mol/L. As the borohydride concentration was increased, the current density of the anodic peak a_2 increased. This further indicated that the anodic peak a_2 was due to the electrooxidation of borohydride. It seems from Fig. 7 that only one anodic peak a_2 appeared in the presence of borohydride. This was because the current density of the anodic peak a_2 was so large that the anodic peak a_1 became ill-defined.

Fig. 7. Cyclic voltammograms of the leached Ni/Zn-Ni electrode from -0.90 to 0.85 V at the scan rate of 5 mV/s in 1 mol/L NaOH solution with the various concentrations of borohydride.

According to Aytac et al. [46], the electrochemical oxidation of $NaBH_4$ at Ni electrodes is

Active $NiOOH$ formed during the positive potential scan is consumed by reaction (6). Subsequently, the $Ni(OH)_2$

formed in reaction (6) is oxidized to $NiOOH$ during the anodic potential sweep. This results in an increase in oxidation current in the presence of $NaBH_4$.

Generally, the total anodic reaction of BH_4^- on the Ni electrode can be expressed as [18]

At the Ni/Zn-Ni electrode, the oxidation of $NaBH_4$ gave a typical electro-catalytic response. The anodic current in the positive sweep was proportional to the amounts of $NaBH_4$ (Fig. 8) and an increase in the amounts of $NaBH_4$ caused a linear enhancement of the anodic current. So, there was electro-oxidation of $NaBH_4$ on the Ni/Zn-Ni electrode. It can be seen from Fig. 8 that the current density I_{pa} was linearly proportional to the concentration of borohydride. The linear dependence of I_{pa} on borohydride concentrations indicated that the Ni/Zn-Ni electrode may be used as an amperometric sensor for borohydride detection.

Fig. 8. Anodic current density versus borohydride concentration for the leached Ni/Zn-Ni electrode.

2.3 Electrochemical impedance spectroscopy results

Figure 9 presents the equivalent circuits and Nyquist diagrams of the smooth nickel and leached Ni/Zn-Ni electrodes recorded at the potential of 0.38 V vs. SCE, both in the absence of borohydride in 1 mol/L NaOH solution. In order to fit the impedance spectra obtained for the Ni/Zn-Ni electrodes, a two constant phase element (CPE's) serial model was applied (shown in the inset of the Nyquist diagram in Fig. 9). This consisted of the solution resistance, R_s , in series with two parallel $Z_{CPE}-R$ elements (2CPE model) [52,53]. This was used for the analysis of the EIS results of the electro-oxidation of $NaBH_4$ at Ni/Zn-Ni electrodes. The Z_{CPE} was defined by two parameters, T and Φ , in the equation for the impedance [54]:

$$Z_{CPE} = 1/T(j\omega)^\Phi \quad (8)$$

where CPE is the constant phase element, T is the capacitance parameter, and Φ is the phase shift which can be explained by the degree of surface inhomogeneity. In this

Fig. 9. Equivalent circuits and Nyquist diagrams of the smooth nickel and leached Ni/Zn-Ni electrodes in 1 mol/L NaOH solution at the potential 0.38 V vs. SCE.

model, the high frequency time constant, which is independent of the potential and is described by R_p and CPE_p connected in parallel, indicated electrode porosity, while the potential dependent time constant gave the kinetics of the electro-oxidation of borohydride (R_{ct} and CPE_{dl} connected in parallel). The capacitance parameter T_{dl} gave the average double layer capacitance C_{dl} by the relationship

$$C_{dl} = \{T_{dl}/[(R_s + R_p)^{-1} + R_{ct}^{-1}]^{(1-\Phi)}\}^{1/\Phi} \quad (9)$$

where Φ represents a factor of homogeneity [53]. In the case of the smooth nickel electrode, the capacitance parameter T_{dl} was related to the average double layer capacitance C_{dl} by a slightly different relationship [53]:

$$C_{dl} = \{T_{dl}/[R_s^{-1} + R_{ct}^{-1}]^{(1-\Phi)}\}^{1/\Phi} \quad (10)$$

Because its Nyquist diagrams exhibited only one semi-circle. The equivalent circuit includes the CPE in parallel with the charge transfer resistance R_{ct} (shown in the inset of the Nyquist diagram in Fig. 9). The values of the charge transfer resistance, double layer capacitance, total surface area, and roughness factor for the two electrodes are presented in Table 3. The capacitance, C_{dl} , determined for the Ni/Zn-Ni electrode was two orders of magnitude larger than that for the smooth nickel. Taking the average double layer capacitance (C_{dl}) of a smooth metal surface as $20 \mu\text{F}/\text{cm}^2$ [55,56], the total surface area was calculated as $A_{\text{real}} = C_{dl}/20 (\text{cm}^2)$ [57]. The roughness factor, the total-to-geometrical surface area ratio, was calculated as $R_f = A_{\text{real}}/A_{\text{geometric}}$. It can be seen from Table 3 that the smooth Ni electrode had the lower total surface area and roughness factor, while the Ni/Zn-Ni electrode had the higher total surface area and

roughness (also compare with Fig. 1). This was the reason why the catalytic activity of the Ni/Zn-Ni electrode was higher.

Figure 10 shows the equivalent circuit and Nyquist plots of the impedance of the Ni/Zn-Ni electrode for borohydride electro-oxidation at different potentials in 1 mol/L NaOH + 0.02 mol/L borohydride solution. The Nyquist plots in Fig. 10 also showed the porosity of the electrode surfaces. Typi-

Fig. 10. Equivalent circuits and experimental Nyquist diagrams as a function of applied potential for borohydride electro-oxidation on the leached Ni/Zn-Ni electrode in 1 mol/L NaOH + 0.02 mol/L borohydride aqueous solutions for potential between 0.275 and 0.375 V vs. SCE (a), potential between 0.4 and 0.5 V vs. SCE (b), and potential between 0.525 and 0.675 V vs. SCE (c).

Table 3 Double layer capacitance, surface area, and surface roughness calculated from the EIS data of Fig. 9

Electrode	$R_s/$ ($\Omega \cdot \text{cm}^2$)	$T_p/$ ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^\Phi$)	$R_p/$ ($\Omega \cdot \text{cm}^2$)	Φ_p	$T_{dl}/$ ($\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{s}^\Phi$)	$R_{ct}/$ ($\Omega \cdot \text{cm}^2$)	Φ_{dl}	$C_{dl}/$ ($\mu\text{F}/\text{cm}^2$)	$A_{\text{real}}/$ cm^2	R_f
Smooth Ni	4.66	—	—	—	0.0003405	2090.0	0.860	119.2	5.959	5.959
Porous Ni/Zn-Ni	4.06	0.15	26.85	0.69	0.0068580	103.5	0.914	5785.0	289.250	289.250

Table 4 Equivalent circuit parameters of electro-oxidation of 0.02 mol/L borohydride on the leached Ni/Zn-Ni electrode in 1 mol/L NaOH solution obtained from Fig. 10

E/V	$R_s/(\Omega\cdot\text{cm}^2)$	$T_p/(\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^{\Phi_p})$	$R_p/(\Omega\cdot\text{cm}^2)$	Φ_p	$T_{dl}/(\Omega^{-1}\cdot\text{cm}^{-2}\cdot\text{s}^{\Phi_{dl}})$	$R_{ct}/(\Omega\cdot\text{cm}^2)$	Φ_{dl}	$C_{dl}/(\mu\text{F}/\text{cm}^2)$	Error (%)
0.275	0.93	0.7210	0.5608	0.825	0.3340	135.800	0.836	290704.12	1.58
0.300	1.54	0.6640	6.8200	0.701	0.4500	108.700	1.000	450000.00	1.44
0.325	1.38	4.5420	4.9000	0.317	1.1820	52.660	0.970	1253225.74	2.35
0.350	1.47	3.3300	6.2300	0.182	0.6248	37.340	0.969	653073.75	1.57
0.375	1.41	1.9900	1.6700	0.560	1.8690	21.520	1.000	1869000.00	4.65
0.400	1.45	0.7203	1.1780	0.998	1.1750	21.090	1.000	1175000.00	4.85
0.425	1.50	2.1300	0.8700	0.306	0.5780	13.860	1.000	578000.00	2.73
0.450	1.48	1.1320	0.3660	0.348	0.5270	5.920	1.000	527000.00	2.84
0.475	1.52	0.7860	0.2520	0.452	0.4880	3.230	1.000	488000.00	1.88
0.500	1.51	1.1280	0.3140	0.385	0.5010	2.080	1.000	501000.00	0.90
0.525	1.53	0.8560	0.1860	0.401	0.5617	0.980	0.955	534623.85	0.70
0.550	1.52	0.7690	0.1720	0.558	0.5142	0.939	0.839	238790.59	1.40
0.575	1.55	0.6320	0.1380	0.444	0.5056	0.686	0.926	452091.20	0.53
0.600	1.56	0.1510	0.0780	0.688	0.4622	0.649	0.880	421604.31	0.51
0.625	1.56	0.1608	0.0730	0.694	0.4650	0.564	0.873	366587.88	0.50
0.650	1.57	0.0375	0.0460	0.942	0.4614	0.531	0.835	330365.33	0.60
0.675	1.57	0.0730	0.0520	0.812	0.4806	0.423	0.828	328977.97	0.60

cally, Nyquist plots of nanoporous electrodes show either a line with a slope of 45° or a semicircle at high frequencies followed by a semicircle at low frequencies [58,59]. The two constant phase element (2CPE) model of Chen and Lasia [60] can be used to explain the impedance results of the Ni/Zn-Ni electrode. The impedance data from borohydride electro-oxidation on the Ni/Zn-Ni electrode were interpreted using the equivalent electric circuit for nanoporous electrodes [60] in the inset of the Nyquist diagrams in Figs. 9 and 10. The charge transfer resistance decrease with increasing potential indicated a faster reaction at higher potentials. In the potential below 0.375 V vs. SCE, large depressed capacitive semicircles were observed (Fig. 10(a)), which indicated a slow rate of borohydride electro-oxidation. In the potential between 0.4 and 0.5 V (Fig. 10(b)), the semicircle diameters decreased sharply with increasing potential. In Fig. 10, the impedance data at 0.275–0.500 V were higher than those at 0.525–0.675 V because the borohydride electro-oxidation reaction commenced at potentials higher than 0.5 V. These observations were consistent with the CV results.

Table 4 shows the values of the equivalent circuit elements obtained by fitting the experimental results. In the whole overpotential range, the very low resistance R_p and values of the CPE_p exponent Φ_p can be explained by pore resistance and diffusion in the pores of the deposit [61]. However, the CPE_{dl} exponent Φ_{dl} values were much closer to 1. Also the mean error was smaller than 5%, indicating a good fit of the experimental data. Generally, the presence of borohydride speeds up the oxidation of $\text{Ni}(\text{OH})_2$ to NiOOH because of the removal of NiOOH by borohydride, showing

a significantly higher catalytic activity of the Ni/Zn-Ni electrode for borohydride oxidation.

3 Conclusions

A smooth nickel electro-catalyst and a Ni/Zn-Ni electro-catalyst were prepared by electrodeposition. A high surface area nickel electrocatalyst was successfully prepared by an electrodeposition methodology that used the selective removal of Zn. SEM results showed that the alkaline leaching process produced a highly porous catalytic surface that was suitable for the electro-oxidation of borohydride. Cyclic voltammetric measurements and electrochemical impedance spectroscopy showed that the Ni/Zn-Ni electrode was an efficient catalyst for the electro-oxidation of borohydride in an alkaline medium, and its electro-catalytic activity for borohydride oxidation was higher than that of the smooth nickel electrode. During the anodic potential sweep, the electro-oxidation of borohydride resulted in the formation of NiOOH on the electrode surface and this was then catalyzed by NiOOH .

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