Enhancement of Ethanol Oxidation Reaction on Pt (PtSn)-Activated Nickel Foam Through In situ Formation of Nickel Oxy-Hydroxide Layer

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Abstract The present paper reports on a significant enhancement of ethanol oxidation reaction (EOR), investigated on Pt and PtSn-modified nickel foam electrodes, realized via in situ formation of surface nickel oxy-hydroxide layer in 0.1 M NaOH solution. In the presence of ethanol in electrolyte, adsorbed C₂H₅OH molecules (and/or its oxidation intermediates) prevent Pt (PtSn) sites from their extensive dissolution upon prolonged surface electrooxidation of Ni foam electrode. The above was elucidated through cyclic voltammetry examinations and a.c. impedance-derived charge transfer resistance parameter values. Surface topography and the presence of catalytic additives were revealed from the combined scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX) analyses.

Keywords Pt (PtSn)-modified nickel foam · Nickel oxy-hydroxide · Ethanol oxidation reaction · Electrochemical impedance spectroscopy · Cyclic voltammetry

Introduction

Electrooxidation of aliphatic alcohols (e.g. methanol and ethanol) attracts significant interest because of its potential application into energy conversion technologies, i.e. direct alcohol fuel cells (DAFCs). Ethanol is a renewable fuel, as it could be produced by fermentation of sugar-containing biomass. In

fact, in addition to being relatively non-toxic, ethanol is characterized by about 30% greater energy density than CH₃OH, its major competitor. Ethanol oxidation reaction (EOR) is a complex anodic process, which involves dissociation of pre-adsorbed ethanol molecules to produce surface-adsorbed carbon monoxide (CO_{ad}) species and further oxidation of C₂H₅OH to form (apart from numerous intermediates and by-products) two major chemicals, namely acetaldehyde and acetic acid (Pathway I: 4e[−]). In fact, most of these products might become adsorbed on the catalyst surface, and thus, quantitative cleavage of the C–C bond (in order to finally generate CO₂ Pathway II: 12e[−]) in an ethanol molecule constitutes a key technical problem [1–8].

Pathway I [7]:

- a) $\text{CH}_3\text{--CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{--COOH} + 4\text{H}^+ + 4\text{e}^-$
- b) $\text{CH}_3\text{--CH}_2\text{OH} \rightarrow \text{CH}_3\text{--CHO} + 2\text{H}^+ + 2\text{e}^-$

Pathway II [7]:

- a) $\text{CH}_3\text{--CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$
- b) $\text{CH}_3\text{--CH}_2\text{OH} + 5\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 14\text{H}^+ + 12\text{e}^-$
- c) $\text{CH}_3\text{--CH}_2\text{OH} + 5\text{H}_2\text{O} \rightarrow 2\text{CO}_3^{2-} + 16\text{H}^+ + 12\text{e}^-$

Significant facilitation of the EOR's kinetics in basic environments [4, 9–11] enabled application of non-noble and highly corrosion-resistant metals, such as different forms of nickel [12, 13]. Thus, employment of highly modifiable, large specific surface area nickel foam could be a key point in the development of low noble metal level and highly electroactive catalyst composites for alkaline direct ethanol fuel cells [14–16]. In addition, nickel foam itself could be made

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catalytic for alcohol oxidation reaction through the surface formation of extensive oxide/hydroxide layer [5, 17–19]. Nickel foams are usually produced by chemical vapour deposition (CVD), physical vapour deposition (PVD) and electrochemical or electroless deposition method with a polyurethane foam precursor [16, 20–22]. Extensive structural and electrochemical characterizations of the CVD-based nickel foam were published by Grden et al. [21] and by van Drunen et al. [22, 23].

Platinum [4, 24–28] and especially PtSn [1, 2, 27, 29–32] catalysts are well-known to exhibit superior electrocatalytic properties towards the EOR. Thus, in this contribution, Pt- and PtSn-modified Ni foam electrodes were prepared by means of spontaneous deposition methods [16, 30, 33, 34]. Such obtained catalyst materials were then subjected to in situ formation of surface nickel oxy-hydroxide layer via extended cyclic voltammetry treatments, carried out in 0.1 M NaOH solution, in the presence of 0.5 M ethanol.

Experimental

All electrochemical work was performed in a three-compartment Pyrex glass cell. The cell contained three electrodes: a Ni foam-based working electrode (WE) in a central part, a reversible Pd (0.5 mm diameter, 99.9% purity, Aldrich) hydrogen electrode (RHE: denoted as Pd/H₂) as reference and a Pt (1.0 mm diameter, 99.9998% purity, Johnson Matthey, Inc.) counter electrode (CE), both positioned in separate compartments. WEs were prepared from MTI nickel foam having the following: purity >99.99% Ni; thickness, 1.6 mm; surface density, 346 g m⁻²; porosity >95% and mass of ca. 43 mg (1.1 × 1.1 cm) per sample. The electrochemically active surface area of the MTI foam has been estimated at 19.2 cm² (548 cm² g⁻¹) in recent work from this laboratory [35]. In short, freshly cut nickel foam samples were subjected to acetone and CH₂Cl₂ wash (both for 15 min under ultrasonication), following air drying and acid etching in 2 M HCl (for 15 min at 60 °C) [36]. Spontaneous deposition of Pt was performed by dipping previously pretreated Ni foam electrodes in 0.005 M chloroplatinic acid hexahydrate: CPAH, Sigma-Aldrich (pH = 1.0, *t*_{dep.} = 60 s and *T*_{dep.} = 293 ± 1 K). On the other hand, PtSn deposition was carried out in a mixture of 0.005 M CPAH and 0.0025 M SnCl₂, anhydrous pure p.a., Chempur (pH = 1.0, *t*_{dep.} = 60 s and *T*_{dep.} = 293 ± 1 K).

Electrochemical impedance spectroscopy and cyclic voltammetry techniques were employed in this work. All measurements were performed at room temperature by means of Solartron 12,608 W Full Electrochemical System. For a.c. impedance measurements, the generator provided an output signal of 5 mV and the frequency range

was swept between 1.0×10^5 and 0.1 Hz. The instruments were controlled by ZPlot 2.9 (or Corrware 2.9) software for Windows (Scribner Associates, Inc.). Typically, three impedance measurements were conducted at each potential value, independently at two foam electrodes. Reproducibility of such-obtained results was usually about 10%. Data analysis was carried out with ZView 2.9 (Corrview 2.9) software packages, where the impedance spectra were fitted using a complex, non-linear, least squares immittance fitting program *LEVIM 6* [37]. All other experimental details, i.e. preparation of supporting electrolyte (0.5 M C₂H₅OH/Stanlab, pure, p.a. in 0.1 M NaOH/AESAR, 99.996% pellets), pretreatments applied to electrochemical cell and reference/counter electrodes, were previously described in Refs. 11, 36, 38.

Results and Discussion

SEM and EDX Characterizations of Pt- and PtSn-Modified Nickel Foam Electrodes

Figure 1a, b below shows SEM micrograph pictures and EDX patterns of MTI-manufactured, Pt-modified nickel foam (at ×10,000 magnification), taken for a fresh electrode (Fig. 1a) and after 40 cyclic voltammetry (CV) sweeps, carried out over the potential range of 0.05–2.20 V vs. RHE in 0.1 M NaOH solution (in the presence of 0.5 M ethanol, Fig. 1b). In the latter case, extended cyclic voltammetry treatment resulted in in situ formation of surface nickel oxide (oxy-hydroxide) layer, evidenced through surface roughening and increased oxygen content recorded in Fig. 1b as compared to those observed in Fig. 1a. Furthermore, Fig. 1c illustrates SEM micrograph picture (×10,000 magnification) and EDX pattern for a PtSn-activated Ni foam electrode sample, recorded after 10 CV sweeps over the potential range of 0.05–2.50 V, performed in 0.1 M NaOH, alcohol-based supporting electrolyte. The presence of Pt and Sn entities (comparatively to Pt spikes observed in EDX spectra of Fig. 1a, b) could be clearly observed in an EDX micrograph of Fig. 1c.

Furthermore, average quantities of the deposited Pt and PtSn catalysts on the nickel foam substrate were assessed on the order of 0.3 wt% by means of a weighing method (for average Ni foam electrode mass of 43 mg), whereas SEM-approximated catalysts grain size values came to 10.5 ± 3.2 and 13.3 ± 3.5 nm for the Pt and PtSn deposits, correspondingly (see Ref. 35 for details on the respective procedure). It should be stressed however that platinum distribution was rather non-uniform, where Pt grains typically formed numerous nests on the Ni foam surface (Fig. 1d), thus resulting in highly increased platinum content (derived through the EDX analysis) over that produced by the weighing (see Cyclic

Fig. 1 **a** SEM micrograph picture and EDX pattern of Pt-modified Ni foam surface (ca. 0.3 wt% Pt), taken at $\times 10,000$ magnification for a fresh electrode. **b** As in (a), but taken after 40 extended CV sweeps, carried out in 0.1 M NaOH (in the presence of 0.5 M C_2H_5OH). **c** As in (b), but taken

after 10 extended CV sweeps, performed on PtSn-modified Ni foam surface. **d** SEM micrograph picture of Pt-modified Ni foam surface showing Pt nesting effect (ca. 0.3 wt% Pt), taken at $\times 10,000$ magnification after 100 extended CV sweeps, carried out in 0.1 M NaOH

Voltammetry Behaviour of Ethanol Oxidation Reaction and Table 1). Furthermore, no estimates on the PtSn atomic ratio

and the possibility of PtSn alloying were given or discussed in this work [2, 31].

Table 1 EDX-derived (for acceleration voltage of 2.0 kV) surface elemental (Pt and O) composition for Pt-modified Ni foam samples; sample 1—unexposed to electrolyte, sample 2—after oxidation pretreatment: 100 cycles (0.05–1.90 V/RHE) in 0.1 M NaOH at a sweep rate of 200 mV s^{−1}

Element	Measurement	Sample 1	Sample 2
Pt/%	1	23.60	9.42
	2	20.00	9.51
	3	18.70	7.66
O/%	1	1.30	2.36
	2	1.10	1.96
	3	1.20	2.16

Cyclic Voltammetry Behaviour of Ethanol Oxidation Reaction

Figure 2a presents the cyclic voltammetric behaviour of ethanol electrooxidation (at 0.5 M C₂H₅OH), carried out at room temperature on surface-electrooxidized (500 CV sweeps between 0.5 and 2.0 V/Pd/H₂ at a sweep rate of 200 mV s^{−1}, see inset of Fig. 2a) Ni foam electrode in 0.1 M NaOH supporting electrolyte. Surface oxidation of ethanol is accomplished through the reaction of C₂H₅OH molecule with a β-NiOOH species, formed upon prolonged CV cycling (inset of Fig. 2a). Hence, a sharp increase of anodic oxidation current beyond the potential of ca. 1.4 V is predominantly related to an ongoing process of ethanol surface oxidation reaction (in addition to oxygen evolution reaction). The above follows with significant diminution (and anodic displacement) of β-NiOOH electroreduction charge (see broad peak A in Fig. 2a). These findings are in very good agreement with those presented by Barbosa et al. [5], Motheo et al. [17] and by Kim and Park [18]. It should be stressed however that comprehensive studies of Ni oxide growth and characterization were published in important papers by van Drunen et al. [22] and by Alsabet et al. [39–41].

On the other hand, progressive in situ formation of nickel oxy-hydroxide layer exhibited significant influence on the process of ethanol electrooxidation. The above could be clearly observed in cyclic voltammetric profiles of Fig. 2b, c, recorded on Pt- and PtSn-activated Ni foam electrode surfaces in 0.1 M NaOH (in the presence of 0.5 M C₂H₅OH), respectively. Thus, for the Pt-activated Ni foam extended cycling over the potential range of 0.05–2.10 V/Pd/H₂ caused a radical enhancement of the EOR, which is evidenced in rising of the maximum anodic current density in the voltammogram from about 0.35 A g^{−1} (for cycle no. 1) to over 1.80 A g^{−1} for the 40th cycle (by ca. ×5.2). For the PtSn-modified nickel foam electrode, the corresponding maximum anodic current density value reached about 1.75 A g^{−1}, just after completion of ten full voltammetric cycles (compare again Fig. 2b, c). It should

also be noted that upon voltammetric cycling, the peak potential value of this oxidation peak (widely assigned in literature to the formation of C₂H₅OH surface oxidation products, principally to acetaldehyde) becomes shifted to more positive potentials, reaching about 1.75 V for the Ni foam/Pt electrode (after 40 cycles) and 1.70 V for the Ni foam/PtSn after ten voltammetric cycles. Another oxidation peak that appears in the CV profiles (see Fig. 2b, c, potential range ca. 0.50–0.90 V) upon the reverse scan towards the hydrogen reversible potential is generally assigned to the process of surface oxidation of CO_{ads} species [16, 24–26].

However, it could be observed in Fig. 2d that when the nickel oxy-hydroxide layer is formed on the Pt-modified nickel foam in the presence of alcohol in electrolyte, the process of ethanol oxidation is greatly enhanced, as compared to the case, where the EOR is performed on the surface of the Pt-activated Ni foam that was pre-oxidized (100 CV sweeps at 200 mV s^{−1}) in pure 0.1 M NaOH solution. Hence, for the latter case maximum of the anodic EOR current density value was recorded on the tenth cycle and reached about 40% of that derived for the former case.

In fact, it seems that surface-electrosorbed ethanol molecules and their oxidation intermediates (primarily available on the Pt sites) are effectively blocking (and thus securing) platinum sites from being disrupted/dissolved [42, 43] during an extended cyclic voltammetry-based surface oxidation process. Table 1 shows the EDX-derived surface (Pt and O) qualitative elemental composition for electrolyte-unexposed and electrooxidized (100 cycles performed over the potential range of 0.05–1.90 V/RHE in 0.1 M NaOH, at a sweep rate of 200 mV s^{−1}) Pt-modified nickel foam sample. Hence, extended oxidation pretreatment resulted in a radical reduction of Pt content (from an average recorded value of 20.8 to 8.9%: ×2.3) along with a significant increase of oxygen presence (from 1.2 to 2.2%: ×1.8). Similar Pt catalyst ‘stabilization effect’ to that discussed for the Pt-modified Ni foam in Fig. 2d could also be argued for the PtSn-based composite foam electrode. However, the latter catalyst seems to be much more resistant towards dissolution of Pt (PtSn) entities than the former one was for disruption of Pt sites (compare Fig. 2d, e).

a.c. Impedance Characterization of EOR

The a.c. impedance spectroscopy behaviour of ethanol electrooxidation reaction (at 0.5 M C₂H₅OH) on the Pt- and PtSn-activated Ni foam electrode surfaces in 0.1 M NaOH is presented in Table 2 and Figs. 3 and 4 below. Thus, the impedance behaviour of the EOR recorded on extensively oxidized Ni foam electrode is characterized by a single, partial and distorted semicircle, exhibited in the Nyquist impedance spectra (not shown in this work). This semicircle refers to the charge transfer resistance (*R*_{ct}) of the ethanol oxidation reaction (see Table 2 and equivalent circuit in Fig. 3a). The charge

Fig. 2 **a** Cyclic voltammograms for ethanol electrooxidation on surface pre-oxidized Ni foam electrode, carried out in 0.1 M NaOH, at a sweep rate of 50 mV s⁻¹ and in the presence of 0.5 M C₂H₅OH (inset: development of nickel oxy-hydroxide layer on Ni foam electrode; 500 CV sweeps at 200 mV s⁻¹). **b** Cyclic voltammograms for simultaneous ethanol electrooxidation and formation of nickel oxy-hydroxide layer on Pt-modified Ni foam electrode, carried out in 0.1 M NaOH at a sweep rate of 50 mV s⁻¹ and in the presence of 0.5 M C₂H₅OH. **c** As in (b), but performed on PtSn-modified Ni foam electrode. **d** Cyclic

voltammograms for simultaneous ethanol electrooxidation and formation of nickel oxy-hydroxide layer on untreated Pt-modified Ni foam electrode (carried out in 0.1 M NaOH at a sweep rate of 50 mV s⁻¹ and in the presence of 0.5 M C₂H₅OH) compared with a CV profile for EOR obtained under analogous experimental conditions, but on pre-oxidized (100 CV sweeps at 200 mV s⁻¹) Ni foam/Pt electrode in pure NaOH solution; maximum anodic (EOR) current density was recorded on the 10th cycle. **e** As in (d), but performed on PtSn-modified Ni foam electrode

transfer resistance recorded at an onset of the EOR (at 1400 mV) came to 0.49 Ω g, whereas that derived at 2000 mV (most likely for a combined ethanol oxidation and oxygen evolution processes) reached 0.05 Ω g. Then, the respective double-layer capacitance (C_{dl}) parameter exhibited significant reduction from 1,011,854 μF g⁻¹ s^{0.1-1} at 1400 mV to 608,756 μF g⁻¹ s^{0.1-1} at 2000 mV, where the former one is about ×120 greater than that previously recorded for unmodified MTI nickel foam surface (see Table 2 in Ref. 36).

On the other hand, Table 2 presents the a.c. impedance-derived kinetic EOR parameters obtained for the Pt-modified (1st, 10th, 20th, 30th and 40th cycles) and the PtSn-activated (10th cycle) Ni foam electrodes. Thus, the EOR impedance behaviour is characterized by the presence of a single or two partial semicircles in the Nyquist impedance plot. A high frequency and low diameter semicircle corresponds to the process of ethanol electrooxidation (R_{ct}), whereas low frequency, large diameter semicircle most likely refers to adsorbed intermediates (see, e.g. Refs. 17, 18 for details) species (R_{Ads}),

Table 2 Resistance and capacitance parameters for electrooxidation of ethanol (at 0.5 M C₂H₅OH) on surface-oxidized, pure, Pt-modified and PtSn-activated Ni foam electrodes in 0.1 M NaOH supporting solution, obtained by finding equivalent circuits, which best fitted the recorded impedance data, as shown in Fig. 3a–c. The recorded values of dimensionless parameters φ_1 and φ_2 (for the CPE components in

Fig. 3a–c) oscillated between 0.62–0.98 and 0.74–0.89, correspondingly (impedance reproducibility usually below 10%, $\chi^2 = 9 \times 10^{-5}$ to 1×10^{-3} ; lower and upper potential values for all examined configurations refer to onset and maximum of the voltammetric current density for EOR, correspondingly)

<i>E</i> /mV	$R_{ct}/\Omega \text{ g}$	$C_{dl}/\mu\text{F g}^{-1} \text{ s}^{\varphi_1-1}$	$R_{Ads}/\Omega \text{ g}$	$C_{Ads}/\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$
Ni foam (500 cycles)				
1400	0.49 ± 0.01	1,011,854 ± 17,707	—	—
2000	0.05 ± 0.00	608,756 ± 46,874	—	—
Ni foam/Pt 1st cycle				
400	4.23 ± 0.11	313,325 ± 3888	—	—
900	0.13 ± 0.01	90,365 ± 4507	3.31 ± 0.20	108,848 ± 6231
Ni foam/Pt 10th cycle				
600	1.15 ± 0.04	223,020 ± 8807	—	—
1250	0.09 ± 0.01	108,926 ± 12,036	21.83 ± 2.98	244,511 ± 12,847
Ni foam/Pt 20th cycle				
			$R_o/\Omega \text{ g}$	L/H
700	1.11 ± 0.05	173,065 ± 11,048	0.71 ± 0.04	20.3 ± 1.5
			$R_{Ads}/\Omega \text{ g}$	$C_{Ads}/\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$
1550	0.05 ± 0.00	656,721 ± 94,725	0.11 ± 0.00	1,610,488 ± 138,297
Ni foam/Pt 30th cycle				
			$R_o/\Omega \text{ g}$	L/H
750	1.00 ± 0.05	158,148 ± 11,475	0.52 ± 0.04	14.3 ± 0.9
			$R_{Ads}/\Omega \text{ g}$	$C_{Ads}/\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$
1650	0.04 ± 0.00	578,441 ± 31,423	0.08 ± 0.00	1,381,698 ± 74,441
Ni foam/Pt 40th cycle				
			$R_o/\Omega \text{ g}$	L/H
800	1.19 ± 0.07	110,046 ± 9443	0.54 ± 0.03	9.9 ± 0.7
			$R_{Ads}/\Omega \text{ g}$	$C_{Ads}/\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$
1750	0.03 ± 0.00	552,767 ± 41,527	0.08 ± 0.01	1,102,139 ± 82,800
Ni foam/PtSn 10th cycle				
			$R_o/\Omega \text{ g}$	L/H
800	0.69 ± 0.03	218,743 ± 16,918	0.53 ± 0.03	9.7 ± 0.8
			$R_{Ads}/\Omega \text{ g}$	$C_{Ads}/\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$
1700	0.02 ± 0.00	412,152 ± 19,371	0.10 ± 0.00	1,314,236 ± 24,512

generated upon ethanol oxidation (see Table 2, equivalent circuit in Figs. 3b and 4 for details). Hence, for the Pt-activated foam, the charge transfer resistance (R_{ct}) parameter for the anodic peak current density potential exhibits significant reduction upon prolonged cycling: from 0.13 $\Omega \text{ g}$ for the first cycle to reach 0.03 $\Omega \text{ g}$ after 40 cycles (ca. $\times 4.3$). Simultaneously, the C_{dl} parameter recorded for the respective CV sweeps and potentials increased by about $\times 6.1$. On the other hand, for enhanced EOR (cycles 20 through 40), the adsorption charge transfer resistance (R_{Ads}) oscillated around 0.1 $\Omega \text{ g}$, whereas pseudocapacitance (C_{Ads}) parameter dramatically increased to the level of 1,102,139–1,610,488 $\mu\text{F g}^{-1} \text{ s}^{\varphi_2-1}$. In fact, for the potentials corresponding to the sharp anodic peak (ca. 0.50–0.85 V/Pd/H₂, Fig. 2b)

the impedance behaviour exhibited an inductive loop over the low frequency end (see the recorded inductive resistance, R_o , and inductance, L , parameters in Table 2 and Fig. 3c). This behaviour is analogous to that reported by other authors on the process of ethanol electrooxidation at composite catalyst materials [4, 31, 44]. The presence of the inductive loop (at ca. 700–800 mV/Pd/H₂) is presumably associated with the process of oxidative removal of CO_{ads} species from the catalyst surface, leading simultaneously to the release of the catalyst active sites.

In contrast, for the PtSn-modified foam electrode, the R_{ct} resistance of 0.02 $\Omega \text{ g}$ (in reference to the C_{dl} value of 412,152 $\mu\text{F g}^{-1} \text{ s}^{\varphi_1-1}$) was recorded at 1700 mV, already after ten full CV sweeps. The latter is in-line with previous findings

Fig. 3 Three equivalent circuits used for fitting the obtained a.c. impedance spectroscopy data, where R_s is solution resistance; C_{dl} is double-layer capacitance (represented as CPE: constant phase element to account for distributed capacitance); R_{ct} is charge transfer resistance parameter for electrooxidation of ethanol; C_{Ads} and R_{Ads} are pseudocapacitance (given as CPE) and resistance of adsorption intermediates, respectively; R_o and L are inductive resistance and inductance parameters, correspondingly

on the superior EOR performance of PtSn vs. Pt catalyst deposits [30, 31]. Thus, it is supposed that the Sn role in facilitation of the EOR is related to enhancement of the removal of adsorbed intermediates from the Pt sites [30].

Interestingly, in a previously mentioned paper [5], Barbosa et al. have recently studied ethanol electrooxidation (at 0.5 M C_2H_5OH) on polycrystalline Ni electrode in 1 M NaOH solution. There, a maximum value of anodic current density of 17 mA cm^{-2} was recorded at 1.55 V vs. Pd/ H_2 (compare with ca. 4 mA cm^{-2} for the Pt-modified Ni foam electrode with a surface area roughly estimated-based on the a.c. impedance-derived double-layer capacitance parameter [45, 46] at 17.9 cm^2 in this work [36]). In addition, Huang et al. [47] presented a comparison for the EOR performance of various (primarily Pt/Ni-related) catalysts and experimental conditions, where Pt-activated NiO/C composite electrode exhibited a maximum of anodic voltammetric current density of 10 mA cm^{-2} , recorded in 1 M KOH/1 M C_2H_5OH solution. On the other hand, Motheo et al. [17], Kim and Park [18] and Gupta et al. [31] provided comprehensive a.c. impedance

Fig. 4 Complex plane impedance plots for Pt- and PtSn-modified Ni foam electrodes in contact with 0.1 M NaOH, in the presence of 0.5 M C_2H_5OH , recorded at the stated potential values. The solid lines correspond to representation of the data according to the equivalent circuit shown in Fig. 3b

examinations of the EOR (under analogous experimental conditions) on surface-electrooxidized Ni electrodes and PtSn catalyst entities, correspondingly. Hence, the recorded there maximum ethanol oxidation voltammetric current densities came to about 2.5 [17] and 6 mA cm^{-2} [18]. On the other hand, minimum values of the recorded charge transfer resistance parameter for the process of ethanol oxidation reached 58.5 [17] and 42.9 Ω cm^2 [18] (compare with 204, 12.5 and 8.3 Ω cm^2 values of the R_{ct} parameter derived in this work for electrooxidized pure nickel foam and Pt-modified and PtSn-activated/in situ electrooxidized Ni foam electrodes, correspondingly).

Finally, complementary impedance study (carried out down to the frequency of 10 mHz) and cyclic voltammetry (sweep rate dependent) examinations of the EOR were conducted on electrooxidized Ni foam/Pt electrode. The impedance experiments (performed for 0.05 and 0.5 M ethanol concentrations in 0.1 M NaOH solution) showed practically no diffusion-type behaviour (not shown in this work) at all probed potential values (900–1300 and 1200–1850 mV vs. RHE for 0.05 and 0.5 M ethanol concentrations, respectively), in reference to the anodic oxidation peak observed in Fig. 2b. Similarly, no conclusions could be made about the involvement of mass transport control from examining the sweep rate characteristics of the voltammetric's maximum anodic current density peak value. In fact, for both plots [peak current density vs. sweep rate (Fig. 5a), as well as the peak current density vs. (sweep rate) $^{1/2}$ (Fig. 5b)], the deviations from linearity are similar and rather insignificant, also based on the derived R^2 parameter values.

Fig. 5 **a** Peak anodic current density value vs. sweep rate for electrooxidized, Pt-modified Ni foam electrode in contact with 0.1 M NaOH, in the presence of 0.05 and 0.5 M ethanol. **b** As in (a), but peak anodic current density value vs. square root of sweep rate

Conclusions

Extended surface area, Pt- and PtSn-modified (ca. 0.3 wt% Pt or PtSn) and electrooxidized nickel foam samples proved to possess significant catalytic properties towards ethanol oxidation in 0.1 M NaOH supporting electrolyte. Nickel surface electrooxidation (formation of surface nickel oxy-hydroxide species) for catalyst-modified Ni foam is most efficient when combined with the process of ethanol oxidation. There, surface-adsorbed ethanol molecules and their oxidation intermediates play an effective role in securing platinum (PtSn) catalyst sites from being disrupted/dissolved upon prolonged cyclic voltammetry-based surface oxidation process.

Such composite catalysts could potentially find interest from the perspective of the development of alkaline direct ethanol (alcohol) fuel cell. However, as possible formation of carbonate constitutes a major problem for these devices, the above requires that special measures be considered and undertaken, including CO₂ purging mechanism, air filtration and application of an anion-exchange membrane.

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