

Platinum dissolution and ethanol oxidation reaction on Pt-activated nickel foam in sodium hydroxide solution

Bogusław Pierozynski*, Tomasz Mikolajczyk

University of Warmia and Mazury in Olsztyn, Department of Chemistry, Faculty of Environmental Management and Agriculture, Plac Lodzki 4, 10-727 Olsztyn, Poland

*Corresponding author: e-mail: boguslaw.pierozynski@uwm.edu.pl

Electrochemical oxidation of ethanol becomes an important process of modern electrochemistry, due to its potential application into direct ethanol fuel cell technology. As rates of ethanol oxidation reaction (EOR) are significantly enhanced in alkaline media, employment of highly corrosion resistant under alkaline conditions, but non-noble metals becomes of superior practical importance. This communication article reports on the process of anodic dissolution of platinum, which is investigated on Pt activated, electrooxidized nickel foam electrodes, employed for ethanol oxidation reaction in 0.1 M sodium hydroxide solution. The above was revealed through the application of cyclic voltammetry and combined SEM/EDX (scanning electron microscopy and energy dispersive x-ray) spectroscopy examinations.

Keywords: Pt-activated nickel foam, ethanol oxidation reaction, Pt-dissolution.

INTRODUCTION

The catalytic process of ethanol electro-oxidation brings significant attention, due to its potential application into energy conversion technologies, i.e. direct ethanol fuel cell (DEFC)^{1,2}. As kinetics of ethanol oxidation reaction (EOR) are radically enhanced in basic environments, application of non-noble, but highly stable metals under alkaline conditions (e.g. 3d nickel structures) becomes of significant importance from a technological point of view^{3–5}. Furthermore, nickel could specifically be catalysed towards the EOR through the surface formation of extended oxide/hydroxide layer^{2, 6–8} supplemented by electro(chemical) deposition of nanoparticles of noble metals, such as Pt^{3, 9–11}.

Phenomena of anodic oxidation and dissolution of platinum in acidic and alkaline media have recently been studied in works by Topalov et al.¹² and Cherevko et al.¹³, and earlier by Zolfaghari and Conway¹⁴. In this communication, we report on anodic dissolution of platinum occurred upon extended electrooxidation of Pt-modified nickel foam electrodes in 0.1 M NaOH solution, in relation to ethanol oxidation reaction.

EXPERIMENTAL

Working electrodes were prepared from MTI nickel foam samples in several stages. Starting from acetone wash (15 min + ultrasonication) of freshly cut foam samples, the process involved air drying and acid etching in 2 M HCl (15 min at 60°C). Then, Pt-modified Ni foam composite electrodes were produced through spontaneous deposition of platinum, carried-out in 0.005 M chloroplatinic acid hexahydrate: CPAH. Atmospheric oxygen was removed from solution before each electrochemical experiment through bubbling with high-purity argon (Ar 6.0 grade, Linde). Furthermore, the argon gas flow was kept above the solution upon all electrochemical measurements. All additional details on the preparation of electrodes (reference and counter), electrochemical cell and electrolyte solutions employed for the purpose of this work were comprehensively discussed in recent works from this laboratory (see Refs. 15 and 16). Combined

electrochemical (cyclic voltammetry) and spectroscopic (SEM/EDX) examinations were employed in this work. All electrochemical measurements were performed at room temperature by means of Solartron 12,608 W Full Electrochemical System (with employment of *Corrware/Corrview 2.9* software packages), whereas spectroscopic characterization of Pt-based Ni foam samples was conducted by means of JEOL JSM-7600 F/X-Max SDD Oxford Inca 250 integrated SEM/EDX unit (see details in Ref. 16).

RESULTS AND DISCUSSION

Figures 1a and 1b below show cyclic voltammograms for electrooxidation of Pt-modified Ni foam electrode (carried-out in 0.1 M NaOH) and ethanol electrooxidation performed on such pre-treated foam electrodes in the presence of 0.5 M C₂H₅OH in 0.1 M NaOH supporting electrolyte, correspondingly. Hence, a major, broad cathodic feature (peak A) that is observed in Figure 1a corresponds to the reduction of Ni(II) oxidation products, generated upon continuous cycling over the potential exceeding 1.5 V/RHE¹⁷. Then, when such-pretreated Pt-activated Ni foam electrodes are exposed to the process of ethanol oxidation (see Fig. 1b), it is clear that the EOR behaviour is significantly dependent on the employed electrode pre-treatment procedure. In other words, superior facilitation of the EOR was obtained when the surface pre-treatment involved 100 voltammetric cycles conducted at a sweep-rate of 200 mV s⁻¹ over the potential range 0.05–1.90 V vs. RHE. Conversely, the least favourable EOR behaviour was recorded on the nickel foam electrode prepared under most severe experimental conditions, i.e. with employment of 500 CV sweeps at a scan-rate of 500 mV s⁻¹ (see Fig. 1b again).

It is well-known that extended surface-electrooxidation of nickel^{2, 6–8} enhances its EOR catalytic properties. However, platinum was found to undergo significant dissolution over the potential range characteristic of oxide formation and oxygen evolution reaction^{12, 13}, where Pt oxidation and dissolution onsets in 0.05 M NaOH solu-

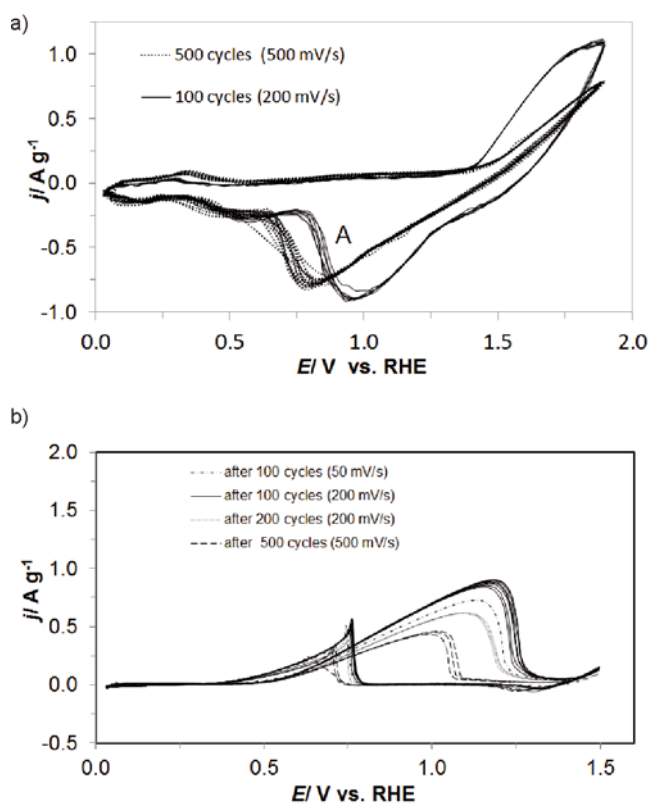


Figure 1. a) Examples of cyclic voltammograms for electrooxidation of Pt-modified Ni foam electrode, carried-out in 0.1 M NaOH (number of performed cycles and sweep-rates indicated); b) Cyclic voltammograms for ethanol electrooxidation carried-out in 0.1 M NaOH in the presence of 0.5 M C_2H_5OH on pre-electrooxidized (in 0.1 M NaOH solution) Pt-modified Ni foam electrodes (employed sweep-rate: $50\ mV\ s^{-1}$)

tion already commence¹³ around the potential values of 0.75 and 1.00 V vs. RHE, correspondingly.

In this communication, the process of surface oxidation along with a Pt dissolution effect could clearly be observed in Figures 2 and 3, and Table 1 below. Thus, Figures 2a and 2b present SEM micrograph picture and EDX pattern of Pt-modified nickel foam electrode (at $100,000\times$ magnification), electrooxidized under moderate conditions (100 voltammetric cycles over the potential range 0.05–1.90 V/RHE in 0.1 M NaOH at a sweep-rate of $50\ mV\ s^{-1}$). Then, imposition of an extensive surface oxidation treatment on the Pt-modified Ni foam sample (500 cycles over the potential range 0.05–1.90 V in 0.1 M NaOH at a sweep-rate of $500\ mV\ s^{-1}$) qualitatively

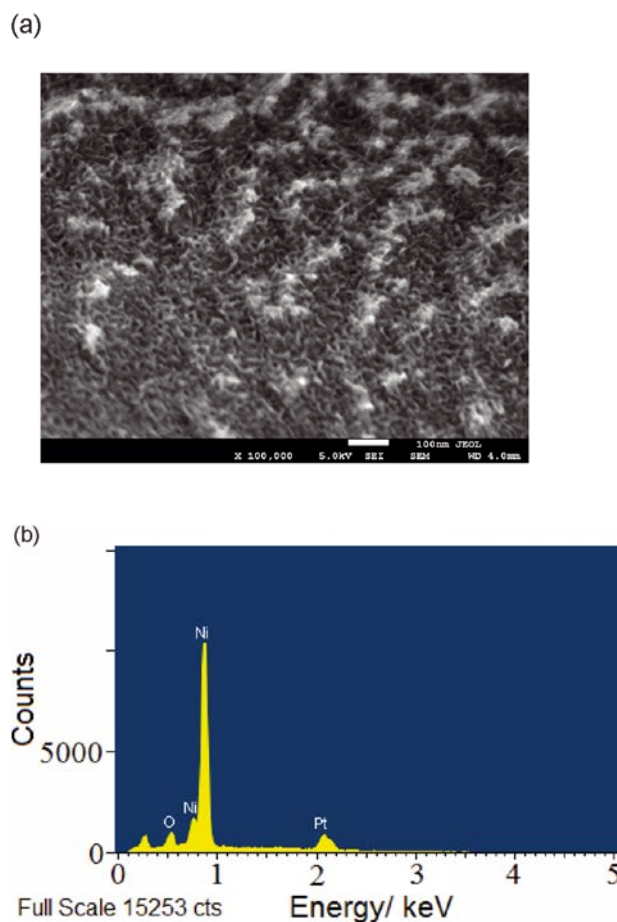


Figure 2. a) SEM micrograph picture of surface electrooxidized (100 cycles over the potential range 0.05–1.90 V/RHE in 0.1 M NaOH at a sweep-rate of $50\ mV\ s^{-1}$) Pt-modified Ni foam electrode (ca. 0.2 wt.% Pt), taken at $100,000\times$ magnification with an acceleration voltage of 5.0 kV; b) As above, but EDX spectrum

resulted in significant surface roughening (see Figure 3a) along with an increase of oxygen level and depletion of platinum intensity in the EDX spectrum (compare Fig. 2b with Fig. 3b). These results could strongly be supported by the EDX-derived numerical data shown in Table 1. In short, it could qualitatively be concluded that more extensive surface oxidation treatments result in a substantial loss of deposited Pt particles along with increased oxygen level (specifically, compare the results obtained for Sample 1 with those of Sample 3 and Sample 4 in Table 1).

Table 1. EDX-derived surface composition for electrooxidized Pt-modified Ni foam samples

Element	Measurement	Sample 1	Sample 2	Sample 3	Sample 4
Pt/ %	1	18.59	9.42	4.95	4.56
	2	19.09	9.51	8.85	5.23
	3	13.74	7.66	7.88	3.67
Ni/ %	1	79.25	88.21	92.01	90.58
	2	78.71	88.53	88.19	89.40
	3	83.80	90.19	85.25	92.42
O/ %	1	2.16	2.36	3.04	4.85
	2	2.21	1.96	2.96	5.37
	3	2.46	2.16	6.87	3.91

Sample 1: 100 cycles, 0.05–1.90 V/RHE, $50\ mV\ s^{-1}$

Sample 2: 100 cycles, 0.05–1.90 V/RHE, $200\ mV\ s^{-1}$

Sample 3: 200 cycles, 0.05–1.90 V/RHE, $200\ mV\ s^{-1}$

Sample 4: 500 cycles, 0.05–1.90 V/RHE, $500\ mV\ s^{-1}$

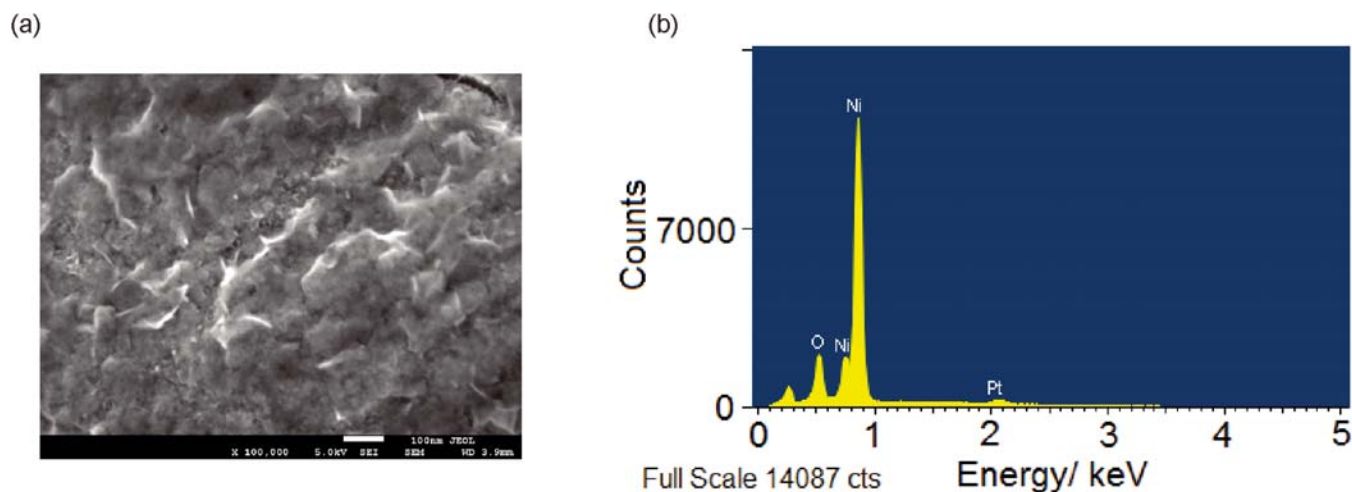


Figure 3. a) SEM micrograph picture of surface electrooxidized (500 cycles over the potential range 0.05–1.90 V/RHE in 0.1 M NaOH at a sweep-rate of 500 mV s⁻¹) Pt-modified Ni foam electrode (ca. 0.2 wt.% Pt), taken at 100.000 × magnification with an acceleration voltage of 5 kV; b) As above, but EDX spectrum

CONCLUSION

Pt-modified (ca. 0.2 wt. % Pt), electrooxidized nickel foam electrodes are catalytic towards ethanol oxidation in 0.1 M NaOH supporting electrolyte. Although formation of nickel oxide/hydroxide layer is essential for nickel to exhibit catalytic properties towards ethanol electrooxidation, extended surface oxidation of Pt-activated Ni foam leads to simultaneous Pt oxidation and dissolution phenomena. Therefore, fabrication of Pt-modified, inherently EOR active nickel foam anode requires that a special optimization procedure be employed with respect to the process of voltammetric development of surface oxides.

In fact, the latter would mean effective securing of Pt sites from their dissolution upon oxide formation, which could be achieved e.g. by preferential *in situ* surface reversible adsorption of some organic molecule(s). This aspect will be studied in detail in another work, with an intention to produce electroactive, Pt-modified Ni foam electrode, for general use in electrocatalysis.

LITERATURE CITED

1. Song, S.Q., Zhou, W.J., Zhou, Z.H., Jiang, L.H., Sun, G.Q., Xin, Q., Leontidis, V., Kontou, S. & Tsiakaras, P. (2005). Direct ethanol PEM fuel cells: The case of platinum based anodes. *Int. J. Hydrogen Energy* 30, 995–1001. DOI: 10.1016/j.ijhydene.2004.11.006.
2. Barbosa, A.F.B., Oliveira, V.L., van Drunen, J. & Tremiliosi-Filho, G. (2015). Ethanol electro-oxidation reaction using a polycrystalline nickel electrode in alkaline media: Temperature influence and reaction mechanism. *J. Electroanal. Chem.* 746, 31–38. DOI: 10.1016/j.jelechem.2015.03.024.
3. Pierozynski, B. (2012). On the Ethanol electrooxidation reaction on catalytic surfaces of Pt in 0.1 M NaOH. *Int. J. Electrochem. Sci.* 7, 4261–4271.
4. Dutta, A., Mahapatra, S.S. & Datta, J. (2011). High performance PtPdAu nano-catalyst for ethanol oxidation in alkaline media for fuel cell applications. *Int. J. Hydrogen Energy* 36, 14898–14906. DOI: 10.1016/j.ijhydene.2011.02.101.
5. Dominguez-Crespo, M.A., Torres-Huerta, A.M., Brachetti-Sibaja, B. & Flores-Vela, A. (2011). Electrochemical performance of Ni-RE (RE = rare earth) as electrode material for hydrogen evolution reaction in alkaline medium. *Int. J. Hydrogen Energy* 36, 135–151. DOI: 10.1016/j.ijhydene.2010.09.064.
6. Motheo, A.J., Machado, S.A.S., Rabelo, F.J.B. & Santos Jr., J.R. (1994). Electrochemical study of ethanol oxidation on

nickel in alkaline media. *J. Braz. Chem. Soc.* 5, 161–165. DOI: 10.5935/0103-5053.19940028.

7. Kim, J.W. & Park, S.M. (2005). Electrochemical oxidation of ethanol at nickel hydroxide electrodes in alkaline media studied by electrochemical impedance spectroscopy. *J. Korean Electrochem. Soc.* 8, 117–124. DOI: 10.5229/JKES.2005.8.3.117.

8. van Drunen, J., Napporn, T.W., Kokoh, B. & Jerkiewicz, G. (2014). Electrochemical oxidation of isopropanol using a nickel foam electrode. *J. Electroanal. Chem.* 716, 120–128. DOI: 10.1016/j.jelechem.2013.08.003.

9. Gomes, J.F., Busson, B., Tadjeddine, A. & Tremiliosi-Filho, G. (2008). Ethanol electro-oxidation over Pt(h k l): Comparative study on the reaction intermediates probed by FTIR and SFG spectroscopies. *Electrochim. Acta* 53, 6899–6905. DOI: 10.1016/j.electacta.2008.01.054.

10. Abd-El-Latif, A.A., Mostafa, E., Huxter, S., Attard, G. & Baltruschat, H. (2010). Electrooxidation of ethanol at polycrystalline and platinum stepped single crystals: A study by differential electrochemical mass spectrometry. *Electrochim. Acta* 55, 7951–7960. DOI: 10.1016/j.electacta.2010.04.008.

11. Pierozynski, B. (2012). Kinetic aspects of ethanol electrooxidation on catalytic surfaces of Pt in 0.5 M H₂SO₄. *Int. J. Electrochem. Sci.* 7, 3327–3338.

12. Topalov, A.A., Cherevko, S., Zeradjanin, A.R., Meier, J.C., Katsounaros, I. & Mayrhofer, K.J.J. (2014). Towards a comprehensive understanding of platinum dissolution in acidic media. *Chem. Sci.* 5, 631–638. DOI: 10.1039/C3SC52411F.

13. Cherevko, S., Zeradjanin, A.R., Keeley, G.P. & Mayrhofer, K.J.J. (2014). A comparative study on gold and platinum dissolution in acidic and alkaline media. *J. Electrochem. Soc.* 161(12), H822–H830. DOI: 10.1149/2.0881412jes.

14. Zolfaghari, A. & Conway, B.E. (2000) Electroless deposition of Pt at a Pd electrode by reaction with sorbed H in Pd/H. *J. Electroanal. Chem.* 488, 151–153. DOI: 10.1016/S0022-0728(00)00161-3.

15. Pierozynski, B., Mikolajczyk, T. & Turemko, M. (2015). On the temperature performance of ethanol oxidation reaction at palladium-activated nickel foam. *Electrocatalysis* 6, 173–178. DOI: 10.1007/s12678-014-0231-0.

16. Pierozynski, B. & Mikolajczyk, T. (2016). Cathodic evolution of hydrogen on platinum-modified nickel foam catalyst. *Electrocatalysis* 7, 121–126. DOI: 10.1007/s12678-015-0290-x.

17. Grdeń, M. & Czerwiński, A. (2008). EQCM studies on Pd-Ni alloy oxidation in basic solution. *J. Solid State Electrochem.* 12, 375–385. DOI: 10.1007/s10008-007-0452-8.