Oxidation of hydroxide ions at platinum-modified zeolite electrode

Tihana M. Mudrinić, Zorica D. Mojović, Anđela S. Abu Rabi-Stanković, Ana Z. Ivanović-Šašić, Aleksandra D. Milutinović-Nikolić, Dušan M. Jovanović

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Department of Catalysis and Chemical Engineering, Belgrade, Serbia

Abstract
NaX zeolite was modified by platinum *via* impregnation/thermal decomposition technique, using Pt(II)-acetyl acetonate in acetone as an impregnating solution. The samples were characterized by scanning electron microscopy (SEM) and cyclic voltammetry methods. The mixture of modified zeolite and 10 wt.% of carbon black, in a form of thin layer, was pasted to a glassy carbon surface. With this mixture as the electrode material, oxidation of hydroxide ions was studied by cyclic voltammetry. The response of modified zeolite electrodes was compared with bare platinum electrode and platinum electrode covered with Nafion film.

Keywords: platinum-modified zeolite; hydroxide ion oxidation; cyclic voltammetry.

Available online at the Journal website: http://www.ache.org.rs/HI/

Zeolites are crystalline aluminosilicates of an ordered cavity structure, with a rather developed inner surface area, approaching several hundred square meters per gram. The cations of transition or in particular noble metals introduced in zeolite cavities within the ion exchange process may be reduced chemically to metal atoms or clusters, and such systems usually display pronounced catalytic activity in various media [1,2].

The extensive reviews and monographs [3–7] are devoted to main applications of zeolite modified electrodes (ZMEs), particularly charge and mass transport characterization, batteries, molecular sieves, electrocatalysis, and electroanalysis. Xu *et al.* [8] have investigated the oxidation of hydrazine, alcohol and hydroquinone in water solution on zeolite/carbon mixture fixed on an electronically conductive support. The electroactive species, for example methylviologen [9] or iron ion [10], have been incorporated inside the zeolite cavities in order to investigate the kinetics of redox process of the species inside the cavities. Li *et al.* [11] have investigated silver exchanges in zeolite A. Reduction of Ag^+ at different sites of the zeolite and reduction of silver clusters in the zeolite gave different peaks at cyclic voltammograms.

In this work, zeolite NaX was used as a support for platinum particles. Zeolite NaX was used in previous work to support platinum particles in order to investigate hydrogen evolution kinetics [12] as well as electrochemical water splitting [13]. Electrooxidation of phenol from acidic, alkaline and neutral solutions on

cobalt, silver or platinum nanoparticles incorporated in NaX zeolite cavities has been studied by cyclic voltammetry [14].

In this study, the reaction of hydroxide ions oxidation was investigated. Cyclic voltammograms of oxidation of hydroxide ions to oxygen have a characteristic sigmoidal diffusion-controlled wave due to the direct oxidation of OH^- to form oxygen:

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e^- \tag{1}$$

This wave is well defined only for conventional glassy carbon electrodes in non-aqueous solvents [15], while on metal electrodes, including noble metals, hydroxide oxidation is more complex due to oxides formation. A clear oxidation wave, well separated from the background discharge due to water, under the steady-state conditions on gold electrode was obtained by several groups of authors [16–19]. Defined waves were obtained in dilute as well as in concentrated solutions of strong bases [20]. The investigations [16–20] were conducted on both microdisc and conventional electrodes. The same wave was observed at platinum and nickel microdisc electrodes [5]. The oxidation wave was as well as recorded on Pt-microdisc electrode in ammonia dilute solution [21].

The wave height was found to be proportional to the concentration of hydroxide ions. The usefulness of these waves for analytical purposes depends on the nature of the employed electrode material. Until now, the golden electrode of micrometric dimension has been shown to be the most promising one for the voltammetric detection of alkalinity of aqueous solutions [16,17]. Platinum particles supported on zeolite are expected to have benefits from both nanometer size of particles and preconcentration of analyte in zeo-

lite cavities. Therefore, in this study, the Pt-based zeolite electrode behavior in diluted alkaline solution was tested in order to evaluate its possible application in the estimation of alkalinity. The aim was to consider the stability and reproducibility of the voltammetric response obtained on a Pt-modified zeolite electrode. The investigated material was applied on the electrode surface by casting of electrode coating from a suspension of zeolite particles in dissolved Nafion. Therefore, the influence of Nafion on voltammetric response was also investigated.

EXPERIMENTAL

The zeolite NaX, alternatively labeled 13X (Linde Co.) was heated up to 350 °C in order to remove adsorbed water, and subsequently cooled to room temperature in desiccator. Such sample was then wetted with diluted acetone solution of Pt(II)-acetyl acetonate. The wet sample was dried at 90 °C enabling evaporation of acetone, and further heated at 400 °C under the hydrogen atmosphere with the purpose of decomposition of acetylacetonate salt and removal of gaseous decomposition products. Degradation of acetyl acetonate salt in air atmosphere led to nanodispersed metal clusters incorporated into the zeolite cages. The impregnation/decomposition procedure [22] was repeated until the weight ratio of Pt/zeolite of 0.1 was reached. Finally, the modified zeolite changed color from white to dark gray. The sample was designated as 13XPt.

SEM Experiments for 13X and 13XPt samples were performed on a JSM-6460LV electron microscope (JEOL, Japan) operating at an accelerating voltage of 25 kV with samples previously coated with a thin film of Au. The presence of Pt in 13XPt sample was tested by Energy Dispersive X-Ray (EDX) method using INCA X-sight Oxford.

In order to use the modified zeolite as the electrode material, the zeolite sample was homogeneously dispersed in 5 wt.% Nafion solution in a mixture of isopropyl alcohol and water using ultrasonic bath. The electronic conductivity of the sample was enhanced by adding 10 wt.% of carbon black Vulcan XC72 (Cabot Corp.) into the initial suspension. A droplet of this suspension was placed on the surface of a glassy carbon rotating disc electrode. After the solvent removal by evaporation, the zeolite particles were uniformly distributed on the glassy carbon support in a form of thin layer. For electrochemical investigations in a three-electrode all glass cell, glassy carbon disc with a layer of homogeneous mixture of zeolite and 10 wt.% of carbon black, was used as a working electrode. The reference electrode was Ag/AgCl in 1 M KCl, while a platinum foil served as a counter electrode. The device used for electrochemical measurements was a 757 VA Computrace Metrohm.

The reaction of oxidation of hydroxide ions was investigated on smooth platinum electrode (Pt), platinum electrode covered with a layer of Nafion (Pt(naf)) and on platinum modified zeolite sample (13XPt). The reason for investigating a platinum electrode covered with a layer was that Nafion was used to attach zeolite sample to the surface of carbon glass electrode. The diameter of glassy carbon and platinum electrode was 2 mm.

RESULTS AND DISCUSSION

Sample characterization

The SEM micrographs of the original and platinum modified 13X zeolites are presented in Fig 1. The microphotographs were taken under the magnification of 10,000 times in order to observe the surface morphology of the samples.

The crystallite size of the various commercial zeolites depends on the synthesis conditions. The zeolite 13X used in this work was crystalline with a particle diameter in the range of 0.5–4 μm with average diameter of approximately 2 μm. From Figure 1 it can be observed that there was no significant difference in size and shape of the original and the platinum modified samples. In conjunction with electron microscopy, elemental identification of surface features was performed by qualitative EDX analysis. The EDX results varied greatly depending on the spot where analysis was performed. The obtained results for Pt content were in the range of 1–10 wt.%.

TEM Results (published elsewhere [23]) confirmed the presence of platinum particles inside zeolite cavities for 13XPt sample. Considering the most reliable data for the diameter of a Pt atom, it was concluded that the number of Pt-atoms per supercage was preferably one, rarely two or three, which might amount to not more than 3 wt.% of the platinum in the zeolite. The missing amount, supplementing the 10 wt.% of platinum in the zeolite, should exist in another form. Therefore, the sample designated as 13XPt actually had platinum particles inside zeolite cavities as well as on the outer surface of the zeolite. However, the particles located within the supercages obviously completely experienced the templating effect of the supercage dimensions.

Hydroxide ion oxidation

In order to investigate powder samples as electrode materials, they are usually applied onto an electrode surface in a form of coating. Several preparation methods for zeolite-modified electrodes have been developed [3,5]. One of the simplest methods, adopted in this work, is casting of electrode coating from a suspension of zeolite particles in dissolved polymer. Re-
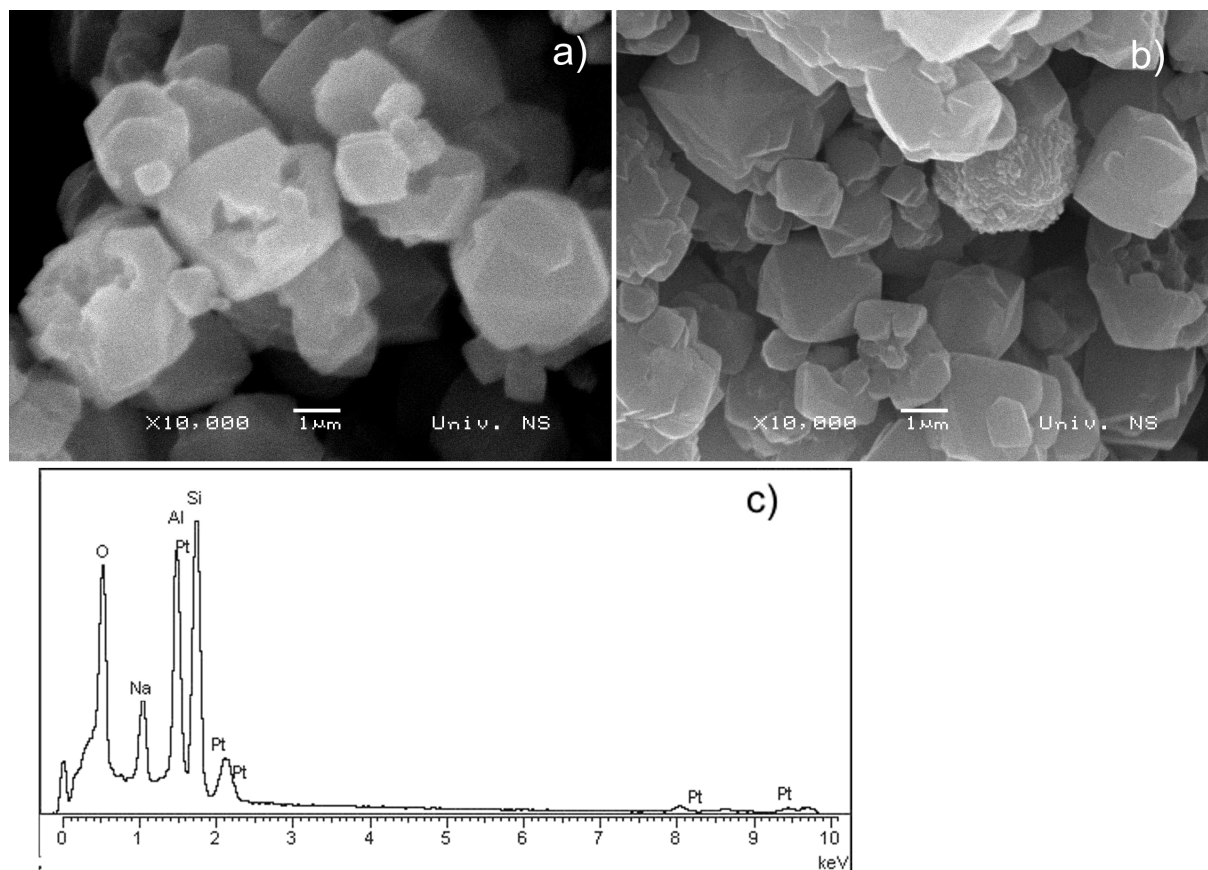
Figure 1. SEM Photograph of a) original zeolite 13X and b) platinum-modified 13X; c) EDX spectrum of 13XPt.

sults obtained in this manner might be influenced by the presence of polymer. Therefore, polymer influence on hydroxide ion oxidation should be studied prior to investigation of same reaction on zeolite material in order to be able to interpret the obtained results in appropriate way.

The polymer used in this paper is Nafion, a sulfonated tetrafluoroethylene-based fluoropolymer applied in different electrochemical systems because of its selectivity, chemical and thermal stability and high proton conductivity. The influence of Nafion presence on the kinetics of oxygen reduction [24–26] and anodic hydrogen oxidation [27,28] has been studied in detail since Nafion membranes are widely used in proton exchange membrane fuel cells. The investigations of the influence of Nafion film on the kinetics of other electrochemical reactions are quite rare [29].

Consequently, hydroxide ion oxidation was firstly investigated on the smooth platinum electrode, bare and covered with Nafion.

Smooth platinum electrode

The voltammograms recorded for a bare platinum electrode in a 1 M Na_2SO_4 solution with different concentrations of NaOH are presented in Figure 2a.

Hydrogen evolution occurs at a potential lower than −0.75 V *versus* Ag/AgCl, while oxygen evolution starts at a potential of 1.2 V. Between these two potential values, processes of OH^- adsorption, surface oxide reduction and surface oxide formation occur. Voltammograms recorded in solutions containing hydroxide ions showed an expected hydroxide ion oxidation wave at the potential above 0.75 V, followed by oxygen evolution at potentials above 1.4 V. In order to maintain the clarity of presentation, the parts of the voltammogram corresponding to the reversed, cathodic polarization direction were omitted. The hydrogen evolution potential is shifted toward lower potentials for about 200 mV in alkaline solution in comparison with the voltammogram recorded in support electrolyte.

One drop of 5 wt.% Nafion was placed on the platinum rotating disc electrode. After the evaporation of the solvent, a thin film was formed over the electrode. The same reaction has been investigated under the same conditions for the Nafion covered platinum electrode (Figure 2b).

The limiting current of hydroxide ion oxidation obtained for the Nafion covered platinum electrode was significantly lower than the current obtained for the bare electrode. In solutions with excess electrolyte, the steady-state limiting current depends on the actual
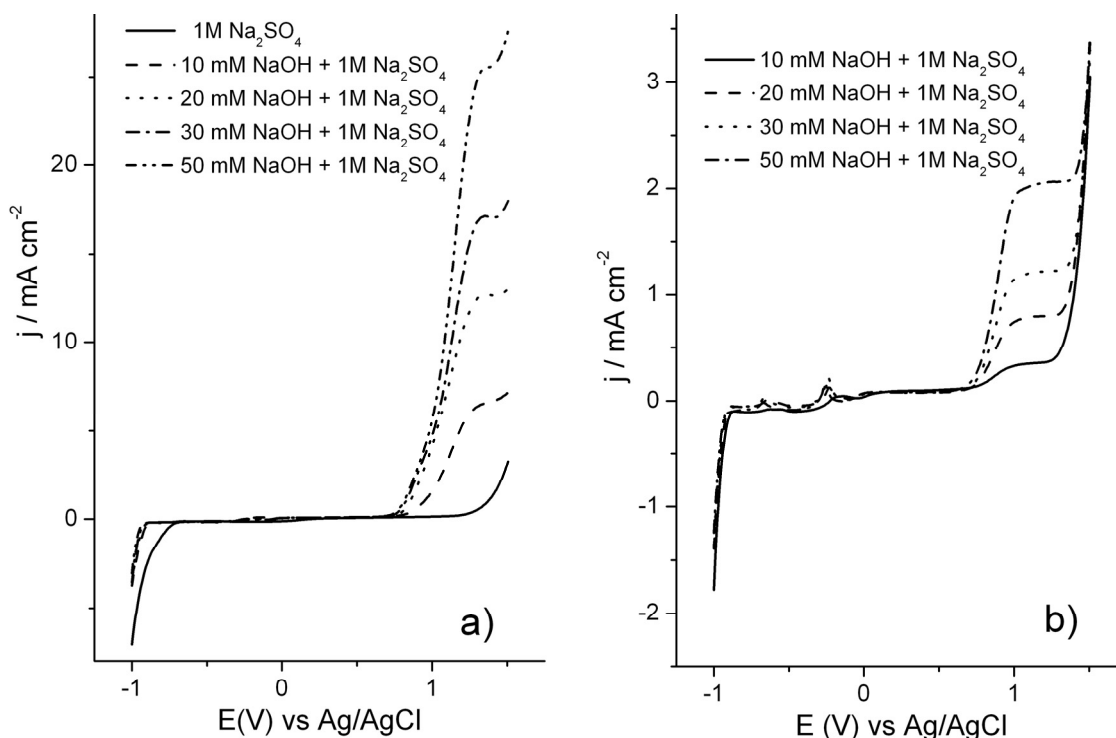
Figure 2. The voltammograms of the rotating platinum disc electrode in a 10, 20, 30 and 50 mM NaOH + 1 M Na$_2$SO$_4$ solutions, recorded at polarization rate of 50 mV s^{-1} and rotation rate of 600 rpm: a) bare platinum electrode; b) Nafion covered platinum electrode.

concentration of the supporting electrolyte, as the diffusion coefficient of the electroactive species varies with both the ionic strength and viscosity of the medium [16,17]. Since the same supporting solution was used for the both bare and Nafion covered electrode, it is obvious that the presence of Nafion on the surface of the platinum electrode caused this current drop. However, a sigmoidal wave is clearly defined for the potential range of 400 mV at the Nafion covered electrode for all used solutions, while at the bare platinum electrode plateau is no longer well defined with increase of OH$^-$ concentration. In their investigation of Cu/Bi electrode for monitoring heavy metal traces in the water Legeai and Vittori [30] noticed that presence of Nafion membrane precludes formation of bismuth hydroxide. Nafion is permselective, being more permeable to cations than anions [31]. Although Nafion is a cation-exchange membrane, anions can readily diffuse through it when it is in contact with a high ionic strength or low pH solution [32]. However, the amount of hydroxide ions in contact with platinum was lower than in case of bare platinum electrode leading to lower current.

Zeolite-modified electrode

The voltammograms obtained for the synthesized zeolite modified electrode are presented in Figure 3a. The onset potential of hydroxide ion oxidation for this electrode was 0.4 V. Instead of a plateau (as in Figure 2), a peak is obtained at the potential of 1.3 V, followed

by oxygen evolution. The presence of this peak indicates high concentration gradients. Such phenomenon is characteristic for zeolite-based electrodes. Namely, after reaching the oxidation potential, the concentration of hydroxide ions drops. Due to additional diffusion through the zeolite electrode this loss cannot be easily compensated, causing depletion of the surface electroactive substance concentration, which is expressed as a peak on the voltammogram.

In order to avoid peak shaped voltammograms, a lower polarization rate (2 mV s^{-1}) was applied. The obtained voltammograms are presented in Figure 3b.

Even at low polarization rates, peaks at the potential of 1.3 V were obtained.

Considering hydroxide ion oxidation on 13XPt it must be pointed out that zeolites have little or no affinity for anionic species due to negative charge of zeolites framework [33]. However, hydroxide ions can diffuse into zeolite which was proved by Ojani *et al.* [34] They investigated Ni(II) incorporated in zeolite. The current value due to Ni(OH)$_2$/NiOOH redox couple was very low, but during cycling it increased, which can be attributed to diffusion of hydroxide ion into zeolite and more conversion of Ni^{2+} to Ni(OH)$_2$ species couple.

Tafel analysis

Tafel plots obtained for investigated electrodes at different concentrations of hydroxide ions are presented in Figure 4. The Tafel slopes were determined in
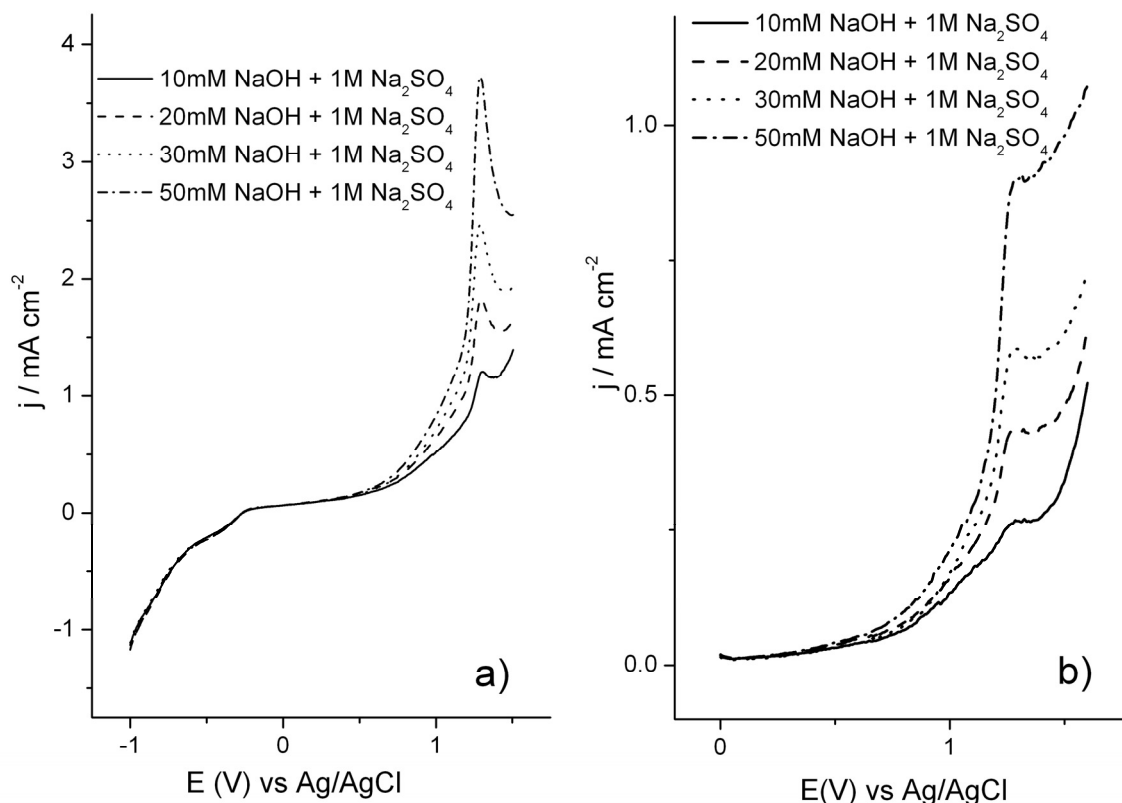
Figure 3. The voltammograms of 13XPt electrode in 10, 20, 30 and 50 mM NaOH + 1 M Na₂SO₄ solutions; a) at polarization rate of 50 mV s⁻¹ and rotation rate of 600 rpm; b) at polarization rate of 2 mVs⁻¹ and rotation rate of 600 rpm.

the potential region of 0.7–0.9 V *versus* Ag/AgCl. Tafel slopes obtained for bare platinum electrode did not vary significantly with concentration of hydroxide ions, unlike Tafel slopes obtained for Pt(naf) and 13XPt electrodes. Lasia [35] noticed that Tafel slope at porous electrodes is strongly affected by the concentration gradient. At higher concentrations, *i.e.*, when the concentration gradient is low, a "normal" Tafel slope was obtained. We have observed similar behavior for Pt(naf) and 13XPt electrodes. Namely, Tafel slopes of these electrodes approached to the normal value with the increase of hydroxide ions concentration.

The Tafel slopes obtained for 13XPt and Pt(naf) electrodes were several times higher than the Tafel slopes obtained for bare platinum electrode. These increased values are probably the consequence of hindered diffusion of hydroxide ions to the electrode surface by the presence of Nafion film or zeolite layer on the surface of the electrode.

Detection of hydroxide ions

The dependence of this wave/peak height on hydroxide ion concentration for all investigated electrodes is shown in Figure 5.

The lines given in Figure 5 represent the best fit obtained by linear regression analysis of the experimental

data. The obtained equations and corresponding correlation coefficient are as follows:

for bare platinum electrode,

$$j_p = 3.208 + 0.475c_{OH^-} \ (R = 0.9994) \tag{2}$$

for Nafion covered platinum electrode,

$$j_p = -0.017 + 0.0415c_{OH^-} \ (R = 0.9999) \tag{3}$$

for zeolite-modified electrode,

$$j_p = 0.597 + 0.062c_{OH^-} \ (R = 0.9999)$$

where current density, j_p is expressed in mA cm⁻², and concentration, c_{OH^-}, in mmol dm⁻³.

The presented experimental data are obtained for the first cycle for each measurement recorded at polarization rate of 50 mV s⁻¹ and rotation rate of 600 rpm. The wave height was not stable and reproducible for bare platinum electrode. However, Nafion covered platinum electrode and zeolite-modified electrode exhibit reproducibility during cycling if the cycling is performed with the cathodic limit at −1 V. If the cathodic limit was set at 0 V, the current of the hydroxide ion oxidation decreased with cycling, unless cathodization at −1 V for 90 s was performed before each cycle.

It is well known that at anodic polarization of platinum two types of oxides are formed: α-oxide that is formed under mild oxidizing conditions, and hydrous
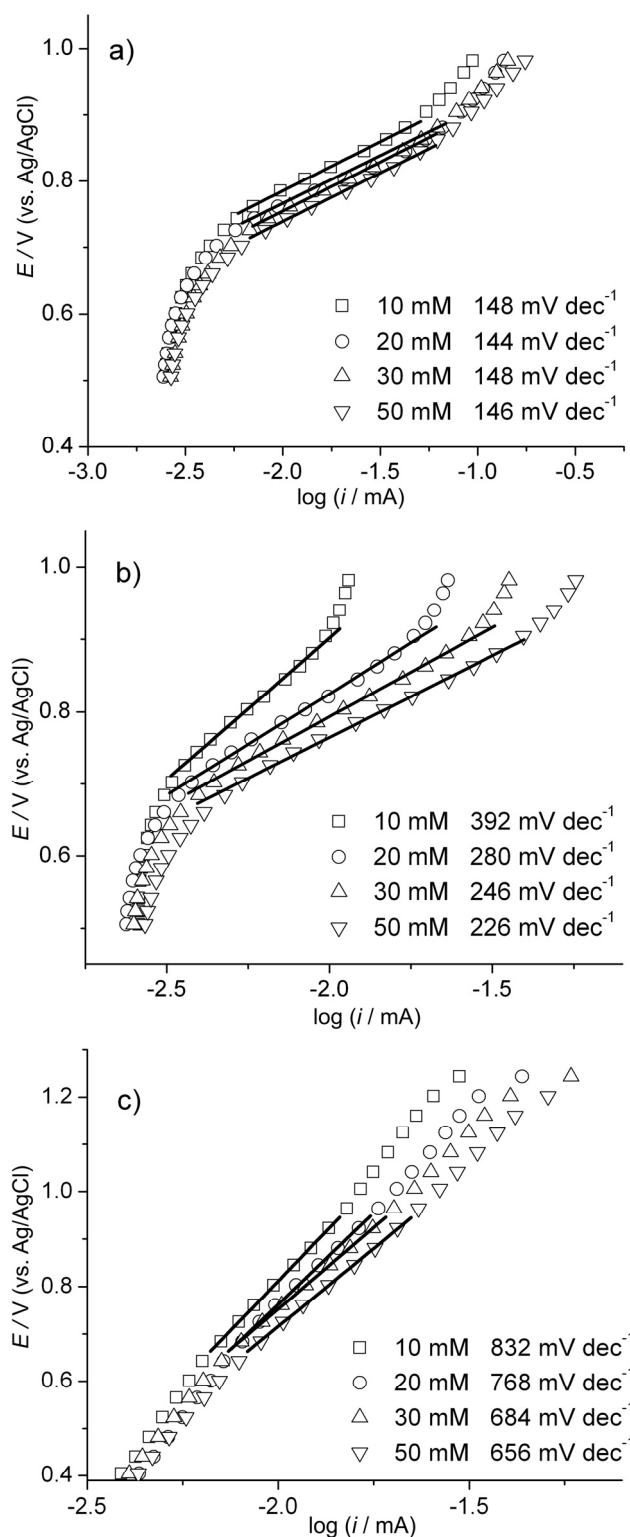
Figure 4. Tafel plots at different concentration of hydroxide ions for a) Pt, b) Pt(naf) and c) 13XPt electrode.

β-oxide film that request higher potentials to form. The formation and reduction of these oxides were previously studied in details [36–38]. The reduction of the oxide films produced at high anodic potentials has as a consequence increased surface roughness [39]. The

roughened surface can be "electrochemically annealed" to its original roughness by repeated cycling between 0.05 and 1.40 V *versus* RHE, for 12–24 h. However, if this annealing is not performed prior each cycle, the induced roughness will affect the obtained results. There-

fore, irreproducibility of current densities obtained for hydroxide ion oxidation during repeated cycling is a consequence of oxide formation/reduction in the previous cycle.
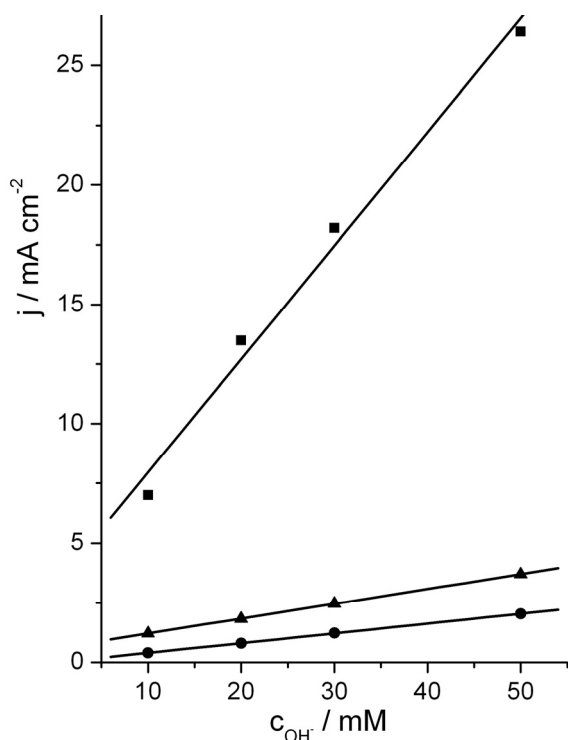

Figure 5. The dependence of limiting current density on the concentration of the hydroxide ions for bare platinum electrode (squares), nafion-covered platinum electrode (circles), 13XPt electrode (triangles).

The presence of Nafion improved data reproducebility for platinum disc electrode as well as for platinum modified zeolite electrode, enabling possible use of these electrodes for analytical purposes. Further studies should be conducted in order to investigate hydroxide ion oxidation kinetics on the Nafion covered platinum disc electrode as well as on the platinum modified zeolite electrode. The sensitivity of these electrodes should also be tested.

CONCLUSION

In this study, the electrochemical oxidation of hydroxide ion on platinum modified zeolite was studied. Impregnation/thermal decomposition technique was used in order to obtain Pt metal nanodispersion on zeolite. The influence of Nafion on hydroxide ion oxidation was tested on bare and Nafion covered platinum disc electrode. It was shown that the presence of Nafion on platinum electrode reduced hydroxide ions concentration on electrode surface resulting in decrease oxidation currents. On the other hand, the presence of Nafion improved reproducibility of both covered pla-

tinum electrode and platinum modified zeolite electrode. Therefore, the Nafion covered platinum electrode can be used to detect high concentration of hydroxide ions, while the 13XPt electrode can be used for low concentration.

In order to avoid electrode deactivation caused by oxide formation, the cathodic limit had to be set at potential of hydrogen oxidation.

REFERENCES

[1] A.M. Ferrari, K.M. Neyman, T. Belling, M. Mayer, N. Rösch, Small platinum clusters in zeolites: a density functional study of CO adsorption on electronically modified models, J. Phys. Chem., B **103** (1999) 216–226.

[2] W.A. Weber, A. Zhao, B.C. Gates, NaY zeolite-supported rhodium and iridium cluster catalysts: characterization by X-ray absorption spectroscopy during propene hydrogenation catalysis, J. Catal. **182** (1999) 13–29.

[3] A. Walcarius, Zeolite-modified electrodes in electroanalytical chemistry, Anal. Chim. Acta **384** (1999) 1–16.

[4] A. Walcarius, Zeolite-modified electrodes: Analytical applications and prospects, Electroanal. **8** (1996) 971–986.

[5] D.R. Rolison, Zeolite-modified electrodes and electrode-modified zeolites, Chem. Rev. **90** (1990) 867–878.

[6] F. Bedioui, L. Roue, E. Briot, J. Devynck, S.L. Bell, K.J Balkus Jr., Electrochemistry of chemically modified zeolites: Discussion and new trends, J. Electroanal. Chem. **373** (1994) 19–29.

[7] A. Walcarius, T. Barbaise, J. Bessiere, Factors affecting the analytical applications of zeolite-modified electrodes preconcentration of electroactive species, Anal. Chim. Acta **340** (1997) 61–76.

[8] M. Xu. W. Horsthemke, M. Schell, Comparison of zeolite-modified electrodes with a graphite electrode: Postulated enhancement of electroactivity through stabilization of intermediates, Electrochim. Acta **38** (1993) 919–925.

[9] Z. Li, C.M. Wang, L. Persaud, T.E. Mallouk, Electrochemistry of metalloporphyrins and viologens at zeolite Y-modified electrodes: evidence for electron trapping by monomolecular porphyrin layers, J. Phys. Chem. **92** (1988) 2592–2597.

[10] C. Iwakura, S. Miyazaki, H. Yoneyama, Effects of solution pH on the voltammetric behaviour of ferrous/ferric ions at zeolite-modified electrodes, J. Electroanal. Chem. **246** (1988) 63–72.

[11] J.W. Li, K. Pfanner, G. Calzaferri, Silver-zeolite-modified electrodes: an intrazeolite electron transport mechanism. J. Phys. Chem. **99** (1995) 2119–2126.

[12] S. Mentus, Z. Mojović, N. Cvjetićanin, Z. Tešić, Hydrogen evolution on zeolite supported platinum clusters, Fuel Cells **3** (2003) 15–20.

[13] S. Mentus, Z. Mojović, N. Cvjetićanin, Z. Tešić, Elecro-chemical splitting on zeolite support platinum clusters, J. New Mater. Electrochem. Syst. **7** (2004) 213–220.

[14] Z. Mojović, A. Milutinović-Nikolić, S. Mentus, D. Jova-nović, Electrochemical oxidation of phenol on metal-impregnated zeolite electrode, Chem. Eng. Technol. **32** (2009) 738–744.

[15] P.K.S. Tsang, P.Cofre, D.T. Saweyer, Electrochemical oxi-dation of hydroxide ion in acetonitrile and its facilitation by transition-metal complexes, Inorg. Chem. **26** (1987) 3604–3609.

[16] M.E. Abdelsalam, G. Denuault, M.A. Baldo, S. Daniele, Voltammetry of hydroxide ion in aqueous solutions on gold microelectrodes, J. Electroanal. Chem. **449** (1998) 5–7.

[17] M.E. Abdelsalam, G. Denuault, M.A. Baldo, C. Bragato, S. Daniele, Detection of hydroxide ions in aqueous solu-tions by steady-state voltammetry, Electroanal. **13** (2001) 289–294.

[18] S. Daniele, M.A. Baldo, C. Bragato, M.E. Abdelsalam, G. Denuault, Steady-state voltammetry for hydroxide ion oxidation in aqueous solutions in the absence of and with varying concentrations of supporting electrolyte, Anal. Chem. **71** (1999) 811–818.

[19] S. Daniele, M.A. Baldo, C. Bragato, M.E. Abdelsalam, G. Denuault, Steady-state voltammetry of hydroxide ion oxidation in aqueous solutions containing ammonia, Anal.Chem. **74** (2002) 3290–3296.

[20] D.W. Kirk, F.R. Foulkes, W.F. Graydon, The electroche-mical formation of Au(I) hydroxide on gold in aqueous potassium hydroxide, J. Electrochem. Soc. **127** (1980) 1069–1076.

[21] I. Ciani, S. Daniele, Oxidation of hydroxide ions from dilute unbuffered solutions of ammonia at platinum microdiscs surrounded by thick and thin insulating sheaths, J. Electroanal. Chem. **564** (2004) 133–140.

[22] M. Okumura, T. Tanaka, A. Ueda, M. Haruta, The reac-tivities of dimethylgold(III)β-diketone on the surface of TiO$_2$: A novel preparation method for Au catalysts, Solid State Ionics **95** (1997) 143–149.

[23] S. Mentus, Z. Mojović, V. Radmilović, The use of NaxX zeolite as a template to obtain monoatomic Pt disper-sion by impregnation with Pt(II) acetyl acetonate/ace-tone solution, J. Serb. Chem. Soc. **74** (2009) 1113–1123.

[24] J. Maruyama, M. Inaba, Z. Ogumi, Rotating ring-disk electrode study on the cathodic oxygen reduction at Nafion®-coated gold electrodes, J. Electroanal. Chem. **458** (1998) 175–182.

[25] S.K. Zecević, J.S. Wainright, M.H. Litt, S.Lj. Gojković, R.F. Savinell, Kinetics of O$_2$ reduction on a Pt electrode co-vered with a thin film of solid polymer electrolyte, J. Electrochem. Soc. **144** (1997) 2973–2982.

[26] A. Ayad, Y. Naimi, J. Bouet, J.F. Fauvarque, Oxygen re-duction on platinum electrode coated with Nafion®, J. Power Sources **130** (2004) 50–55.

[27] J. Maruyama, M. Inaba, K. Katakura, Z. Ogumi, Z. Take-hara, Influence of Nafion® film on the kinetics of anodic hydrogen oxidation, J. Electroanal. Chem. **447** (1998) 201–209.

[28] R.M.Q. Mello, E.A. Ticianelli, Kinetic study of the hyd-rogen oxidation reaction on platinum and Nafion® co-vered platinum electrodes, Electrochim. Acta **42** (1997) 1031–1039.

[29] J. Langmaier, A. Trojánek, J. Weber, Z. Samec, Kinetics of the ferric/ferrous electrode reaction on Nafion®-coated electrodes, J. Electroanal. Chem. **469** (1999) 11–17.

[30] S. Legeai, O. Vittori, A Cu/Nafion/Bi electrode for on-site monitoring of trace heavy metals in natural waters using anodic stripping voltammetry: an alternative to mer-cury-based electrodes, Anal. Chim. Acta **560** (2006) 184–−190.

[31] M. Pineri, A. Eisenberg, Structure and properties of ionomers, NATO ASI Series; Series C: Mathematical and physical science, vol.198, D. Reidel Publishing Co., Dor-drecht, 1987.

[32] K.L. Huang, T.M. Holsen, J.R. Selman, Anion partitioning in and diffusion through a Nafion membrane, Ind. Eng. Chem. Res. **42** (2003) 3620–3625.

[33] G.M. Haggerty, R.S. Bowman, Sorption of inorganic an-ions by organo-zeolites, Environ. Sci. Technol. **28** (1994) 452–458.

[34] R. Ojani, J.B. Raoof, S. Fathi, S. Alami-Valikchali, Electro-chemical behavior of Ni(II) incorporated in zeolite Y-mo-dified carbon electrode: application for electrocatalytic oxidation of methanol in alkaline solution, J. Solid. State. Electrochem. **15** (2011) 1935–1941.

[35] A. Lasia, Porous electrodes in the presence of a con-cen-tration gradient, J. Electroanal. Chem. **428** (1997) 155–−164.

[36] S.J. Xia, V.I. Birss, Hydrous oxide film growth on Pt. I. Type I *β*-oxide formation in 0.1 M H$_2$SO$_4$, Electrochim. Acta **44** (1998) 467–482.

[37] C-C. Hu, K-Y. Liu, Voltammetric investigation of platinum oxides. I. Effects of ageing on their formation/reduction behavior as well as catalytic activities for methanol oxidation, Electrochim. Acta **44** (1999) 2727–2738.

[38] C-C. Hu, K-Y. Liu, Voltammetric investigation of platinum oxides II. Effect of hydration on their reduction be-havior, Electrochim. Acta **45** (2000) 3063–3068.

[39] G.Tremiliosi-Filho, G. Jerkiewicz, B.E. Conway, Characte-rization and significance of the sequence of stages of oxide film formation at platinum generated by strong anodic polarization, Langmuir **8** (1992) 658–667.

IZVOD

OKSIDACIJA HIDROKSILNIH JONA NA ZEOLITU MODIFIKOVANOM PLATINOM

Tihana M. Mudrinić, Zorica D. Mojović, Anđela S. Abu Rabi-Stanković, Ana Z. Ivanović-Šašić, Aleksandra D. Milutinović-Nikolić, Dušan M. Jovanović

Univerzitet u Beogradu, Institut za hemiju, tehnologiju i metalurgiju, Centar za katalizu i hemijsko inženjerstvo, Beograd, Srbija

(Naučni rad)

Zeolit tipa NaX je modifikovan platinom tehnikom impregnacija/termalna degradacija. Kao impregnirajući rastvor je korišćen rastvor Pt (II) acetilacetonata u acetonu. Uzorci su okarakterisani metodama skenirajuće elektronske mikroskopije (SEM) i ciklične voltametrije. Modifikovani zeolit je homogeno dispergovan u rastvoru Nafiona (5 mas.%) u mešavini izopropil alkohola i vode pomoću ultrazvučnog kupatila. Elektronska provodljivost uzorka je poboljšana dodatkom 10 mas.% ugljenika (carbon black Vulcan XC72 (Cabot Corp.)) u suspenziju. Kap suspenzije je postavljena na površinu elektrode o staklastog ugljenika. Nakon isparavanja rastvarača na elektrodi je formiran tanak film. Oksidacija hidroksilanih jona je ispitana na ovako formiranoj elektrodi metodom ciklične voltametrije. Na osnovu SEM mikrografija moglo se uočiti da ne postoji značajna razlika u obliku i veličini čestica polaznog zeolita i zeolita modifikovanog platinum. Rezultati EDX analize su značajno varirali u zavisnosti od mesta na uzorku na kome je izvršena analiza. Sadržaj platine se kretao u intervalu 1—10 mas.%. Reakcija oksidacija hidroksilnih jona je, poređenja radi, ispitana na čistoj platinskoj elektrodi i platinskoj elektrodi pokrivenoj filmom Nafiona. Na platinskoj elektrodi, kako čistoj tako i pokrivenoj Nafionom, dobijen je očekivani sigmoidalni talas sa platoom koji odgovara graničnoj difuzionoj struji. Prisustvo Nafiona na platinskoj elektrodi dovelo je do nižih graničnih struja pri oksidaciji hidroksilnih jona. Međutim, reproduktivnost ciklovoltamograma je značajno poboljšana, a povećan je i opseg potencijala u kome se dobija jasno definisan plato. Ciklovoltamogrami zeolitske platinisane elektrode, snimljeni pri istim uslovima kao i platinska elektroda, ispoljili su pojavu pika usled velikog koncentracionog gradijenta. Tafelovi nagibi Nafionom pokrivene platinske elektrode i zeolitske platinisane elektrode pokazuju značajnu zavisnost od koncentracije hidroksilnih jona, dok Tafelovi nagibi čiste platinske elektrode nisu zavisili od koncentracije analita. Granične gustina struje pokazuje linearnu zavisnost od koncentracije hidroksilnih jona sa dobrim korelacinim faktorom, za sve tri ispitivane elektrode.

Ključne reči: Zeolit modifikovan platinom • Oksidacija hidroksilnih jona • Ciklična voltametrija