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NiA and NiX zeolites as bifunctional electrocatalysts for water splitting in alkaline media

Jadranka Milikić^{a,1}, Milica Vasić^{a,1}, Luís Amaral^b, Nikola Cvjetičanin^a, Dragana Jugović^c, Radmila Hercigonja^a, Biljana Šljukić^{a,*}

^a Faculty of Physical Chemistry, University of Belgrade, Studentski Trg 12–16, 11158 Belgrade, Serbia

^b Center of Physics and Engineering of Advanced Materials (CeFEMA), Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisbon, Portugal

^c Institute of Technical Sciences of SASA, Knez Mihailova 35/IV, Belgrade, Serbia

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ABSTRACT

NiA and NiX zeolites were prepared and characterised using XRD, FTIR and SEM, and subsequently tested as electrodes for hydrogen (HER) and oxygen (OER) evolution reactions in alkaline media. Linear sweep voltammetry and chronoamperometry techniques showed that NiA has higher catalytic activity for these two reactions, as evidenced by higher current densities, which can be correlated with a higher weight fraction of Ni in this electrocatalyst than in the NiX and with its higher conductivity. HER and OER kinetic parameters, including Tafel slope, exchange current density and apparent activation energy were evaluated. Electrochemical impedance spectroscopy analysis yielded values of the resistance of the solution, charge transfer and mass transfer, as well as double layer capacitance and pseudo-capacitance of the working electrode, at different potentials and temperatures. Unlike the HER, during which the mass transfer resistance of the adsorbed intermediate is dominant in the case of NiA, the OER impedance response is controlled by the charge transfer process itself at the potentials of interest for these process. The overall resistance related to the HER is lower for NiA than for NiX.

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Introduction

Alkaline water electrolysis (Eq. (1)) is considered as a simple and clean method for hydrogen (and oxygen) production [1,2]. Still, this process is not thermodynamically favourable, requiring high quantity of energy for water molecule splitting [3]. Namely, oxygen evolution reaction (OER) (Eq. (2))

proceeding at the anode and hydrogen evolution reaction (HER) (Eq. (3)) proceeding at the cathode require large overpotential to proceed at reasonable rates [4,5]. These further results in high cost of alkaline water electrolysis process and high cost of produced hydrogen [6,7]. Therefore, it is necessary to design electrocatalysts with high activity for these two reactions, along with good electrical conductivity, large active

* Corresponding author.

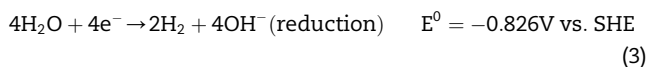
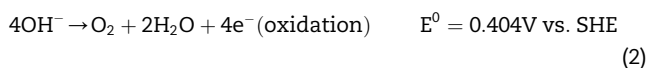
E-mail address: biljka@ffh.bg.ac.rs (B. Šljukić).

¹ Equally contributed.

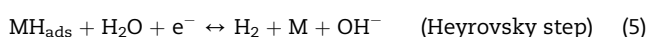
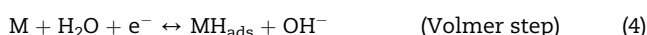
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surface area, electrochemical stability and selectivity, high corrosion resistance, and low cost [5,8–11].



In alkaline solutions, HER on a metallic electrode follows one of the two possible mechanisms – Volmer–Heyrovsky (Eqs. 4 and 5) or Volmer–Tafel (Eqs. 4 and 6) mechanism [12]:



where MH_{ads} is a hydrogen atom adsorbed on the electrode surface. The strength of the MH_{ads} bond determines the HER rate, with the best electrocatalysts exhibiting intermediate MH_{ads} bond strength values [13,14]. High catalytic activity towards HER is a characteristic of noble metals such as platinum, but their practical application is limited by their low abundance and high price [15,16]. On the other hand, nickel (Ni) is a promising electrode material for large-scale application since it has relatively low price and has shown good activity for HER [17–19]. Recently, attention has been directed towards improvement of HER activity of Ni-based electrocatalysts, including Ni alloying with other metals [20–24], non-metals or rare earth elements [25–29], fabrication in the form of foam [30] or nanostructured Ni composites [31–34], etc. The latest research is focused on Ni-sulphides (NiS , NiS_2 and Ni_3S_2) [35], phosphides (Ni_2P and Ni_5P_4) [36], nitrides (Ni_2N and Ni_3N) [37–39] and selenides [40] that have been shown to possess excellent activity for HER, with high current densities at low overpotentials (10 mA cm^{-2} at the overpotentials ranging from 49 to 474 mV) [16].

The best electrocatalytic response towards OER is achieved for nanocomposites of precious metals, ruthenium and iridium, as they show the lowest OER overpotential, but they suffer from low stability in alkaline media [16,41]. Ni and its alloys exhibit lower electrocatalytic activity for OER, but they have long time stability in highly alkaline media (typically, concentrated KOH) and they are corrosion resistant [42–47]. OER on transition metal electrodes occurs at surface already covered by oxide layer. Namely, it has been observed that, during OER on Ni surface, NiO is firstly formed and then it is electrochemically oxidized to Ni_2O_3 [41]. Thus, Ni-based electrodes have a rest potential of oxide couple (Ni/NiO or $\text{NiO}/\text{Ni}_2\text{O}_3$) close to the equilibrium potential of the OER. Again, Ni sulphides (FeNiS_2) [48], phosphides (Ni_2P , $\text{Ni-Fe}_x\text{P}$ and $(\text{Ni}_{0.87}\text{Fe}_{0.13})_2\text{P-Ni}$) [32,49], nitrides ($\text{Ni}_3\text{N}/\text{Ni}$) [50] and selenides (Ni_3Se_2 and $\text{Ni}_x\text{Fe}_{1-x}\text{Se}_2$) [51,52], deliver high current density at low overpotentials.

Zeolites are recently finding application in electrochemistry area, in electroanalysis [53,54], as well as in

electrochemical energy conversion and storage [55–59]. Thus, Pt–, Pd– and Ni-ion exchanged zeolites were tested as anode electrocatalysts in fuel cells for oxidation of fuels such as alcohols and borohydride [57,59–63]. These zeolites were also tested for HER [55] and OER [64]. There are more than 40 natural and 200 synthetic forms of zeolites [65,66] with basic structure made by three-dimensional combination of tetrahedral $(\text{AlO}_4)^{5-}$ and $(\text{SiO}_4)^{4-}$ units [66]. The negative charge of these anionic groups is balanced by a positive ion (Na^{+1} , Ag^{+1} , Ni^{2+} , Mn^{2+} , Pt^{2+} , Pd^{2+} , etc.). The use of zeolites has a number of advantages, with some of them being good mechanical, thermal and chemical stability, and large surface areas [53,67].

In this work, two types of Ni^{2+} cation-exchanged zeolites, NiA and NiX, with different Si/Al ratios, were prepared. Subsequently, oxygen and hydrogen evolution reactions were studied at these two Ni zeolites in highly alkaline media by cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA).

Experimental

Syntheses and characterisation of Ni zeolite materials

Ni^{2+} cation-exchanged forms of NaX (Union Carbide) and NaA (BDH) zeolites used in this work were obtained by conventional ion-exchange procedure [54]. The composition of two zeolites was determined by chemical analysis so that NiX and NiA zeolites are represented by the formula $\text{Na}_{23}\text{Ni}_{32}(\text{AlO}_2)_{87}(\text{SiO}_2)_{105}$ and $\text{Ni}_6(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}$, respectively. The Ni zeolite samples were characterised by X-ray powder diffraction (XRPD), Fourier-transformed infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. X-ray diffraction data were collected on a Philips PW 1050 diffractometer with $\text{Cu-K}\alpha_{1,2}$ radiation (Ni filter) at room temperature. Measurements were done in 2θ range of $5\text{--}80^\circ$ with a scanning step width of 0.05° and time of 3 s per step. FTIR spectra of the powdered samples, dispersed in KBr and compressed into pellets, were recorded in $4000\text{--}400 \text{ cm}^{-1}$ range at 64 scans per spectrum at 2 cm^{-1} resolution using Avatar 370FT-IR Spectrometer (Thermo Nicolet). The morphology of the zeolites was investigated using a JEOL JSM 7001F scanning electron microscope.

Electrical conductivity measurements were done using Precision LCR Meter (LCR-6100) at the frequency of 1 kHz. Conductivity was measured directly in the die (with hard plastic interior and steel exterior) at 125 kPa.

Preparation of the working electrodes

In order to prepare catalytic inks, a mixture of zeolite (NiA or NiX, 4 mg) and Vulcan carbon black (1 mg) was dispersed in 125 μL of polyvinylidene fluoride (PVDF) solution (2 wt% PVDF in N-methyl-2-pyrrolidone) and homogenised in an ultrasonic bath for 30 min. Subsequently, 10 μL of the ink was deposited onto glassy carbon substrates, and then dried at 110°C overnight to make the working electrodes.

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