

Physical characterization of Pt-M binary electrocatalysts for water splitting

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Combinations of mono- and bimetallic compounds, oxides and composite materials, in which Pt is partly or totally replaced by cheaper elements (Cr and Mn) were synthesised. Mechanically treated Ebonex was used as a support. The synthesized catalysts were characterized by several bulk and surface analysis, such as the XRD, XPS and SEM. XRD and XPS analysis showed that Cr- and Mn- components are in amorphous and oxidized state, while Pt is predominantly in metallic state. No alloying between Pt and Cr or Mn is registered. The catalysts are electrochemically tested toward oxygen evolution reaction (OER) for water splitting in a PEM electrolytic cell using a commercial Nafion 117 as a proton conducting electrolyte. It is seen that the best catalytic activity for the OER exhibits Pt-Cr/Ebonex. It has higher efficiency at lower Pt loading relative to all other compositions, including Pt/Ebonex. The results obtained are explained with electronic interactions between the metallic components and the support, providing a synergetic effect.

Key words: PEM water splitting, Pt/Cr/Mn-Ebonex electrocatalyst, XRD, XPS, SEM

INTRODUCTION

Among the individual metals, Pt possesses the best catalytic activity toward the oxygen evolution reaction (OER) for PEM water splitting and is still the most frequently used catalyst [1, 2]. However, Pt being a noble metal is rather expensive. In addition, the world resources of this metal deplete fast, which imposes the need to search proper substitutes of Pt.

Generally, the efficiency of the electrocatalysts is determined by two major groups of factors, geometrics and electronics, and in this context there are two possibilities to enhance the activity of the pure Pt. The first one is to increase the surface area by dispersing it on a supporting the electro conductivity material with highly developed surface. The second one is to combine it with other pure metals under preliminary theoretical calculations and considerations, based on the Brewer interactive interionic bonding theory and corresponding predictions about the probability for hyper- hypo-d-electron interactions [3, 4].

The unique combination of the electrical conductivity, which approaches that of the metal, and the high corrosion resistance, which approaches that of the Ebonex ceramics (Magneli phase titanium oxides with general formula Ti_nO_{2n-1}), gives a reason to consider it as a substitute

supportive material for the anodic catalyst [5-7].

The physical characteristics of the electrocatalysts (the phase and composition of the active components, the particle size and size distribution, the morphology and crystal planes, etc.) are very important not only for understanding of the catalyst performance but also for exploring the structure-activity relationship at the electron/molecular level, and ultimately for a rational design of new catalysts [8].

In this work combinations of mono- and bimetallic compounds, oxides and composite materials in which Pt is partly or totally replaced by cheaper elements (Cr and Mn) on Ebonex as a support, were synthesised using the sol-gel method. The prepared materials were characterized by several bulk and surface analysis, such as XRD, XPS and SEM, and their structure was discussed in relation to their electrocatalytic action toward OER in PEM water splitting.

EXPERIMENTAL

Catalyst synthesis

The synthesis of the chosen composite materials consisted in direct selective grafting of platinum and other metals from acetylacetonate precursors ($M[(C_5H_7O_2)_n]_m$ or M-acac (M = Pt, Cr, Mn). Commercial Ebonex powder was used as a substrate and it was subjected to mechanical treatment in a planetary ball mill for 40 h prior to the synthesis. The metallic part in each of the catalyst was 20 wt. %, while the metal ratio was

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1:1. The preparation procedure was described in details elsewhere [3].

Physical Characterization

The phase composition, the morphology and the surface structure of the catalysts under studying were investigated by the methods of X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). XRD spectra were recorded by Philips APD15 X-ray diffractometer. The diffraction data were collected at a constant rate of $0.02 \text{ }^\circ\text{s}^{-1}$ over an angle range of $2\theta = 10 - 90$ degrees. The size of Pt crystallites was determined by Scherrer equation [8, 9]

$$D = k\lambda / \beta \cos \Theta, \quad (1)$$

where D is the average dimension of crystallites, k is the Scherrer constant in the range of 0.85–1.0 in dependence of the crystal type (usually assumed to be $k \approx 1$); λ is the X-ray wavelength, Θ is the Bragg angle, and $\beta = \sqrt{\beta_s^2 - \beta_r^2}$ is the peak broadening in radians (β_s and β_r are peak widths of the sample and standard in radians). The XPS of the samples were recorded with ESCALAB MK II (VG Scenific, England) electron spectrometer. The photoelectrons were excited with a twin anode X-ray source using Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) radiation. C 1s photoelectron line at 284.6 eV was used as a reference for calibration. The morphology of the electrocatalysts was investigated trough scanning (SEM) electron microscopy. JEOL JEM – 200 CX microscope was used in scanning regime.

Laboratory PEM cell and test procedure

The electrochemical tests were performed on membrane electrode assemblies (MEAs), using a Nafion 117 membrane as an electrolyte. The catalysts under study were investigated as electrodes for the oxygen evolution reaction (OER), while a commercial E-TEK catalyst, containing 20 % Pt on a carbon support, was used to prepare both, the hydrogen (HE) and the reference electrodes (RE). The electrodes have a complex multilayered structure, consisting of gas diffusion, backing, and catalytic layers. The preparation procedure is described in details elsewhere [10].

The performance characteristics of the prepared MEA were investigated in a self made laboratory PEM electrolytic cell [6]. It consists of two gas compartments where hydrogen and oxygen evolution take place, separated by the membrane electrode assembly under study. A reference electrode is situated in the hydrogen evolution

compartment. The catalytic activity of the prepared catalysts was studied using the techniques of cyclic voltammetry and steady state polarization at operating temperature of $20 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$. All electrochemical measurements were carried out with a commercial Galvanostat/ Potentiostat POS 2 Bank Elektronik, Germany.

RESULTS AND DISCUSSION

Physical characteristics XRD analysis

Fig. 1 and Fig. 2 present the XRD spectra of the Ebonex and the synthesized composite catalysts. The Magneli phase titanium oxide characteristics for Ebonex are registered. Only the support peaks can be seen for the Mn-Ebonex and Cr-Ebonex (Fig. 1). The absence of peaks for the Cr and Mn metallic phase means that the M-components are amorphous and most probably are in an oxidized state.

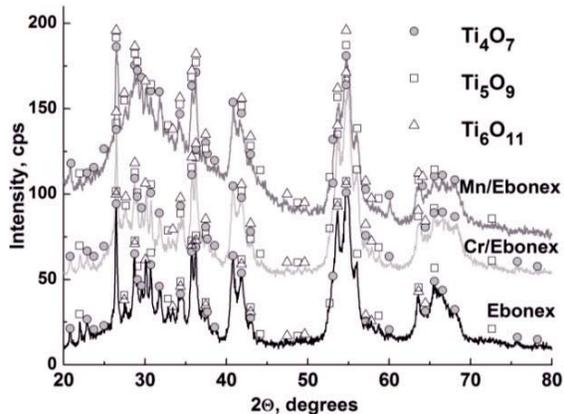


Fig. 1. XRD spectra of the Ebonex and the synthesized composite M/Ebonex (M=Mn, Cr) catalysts.

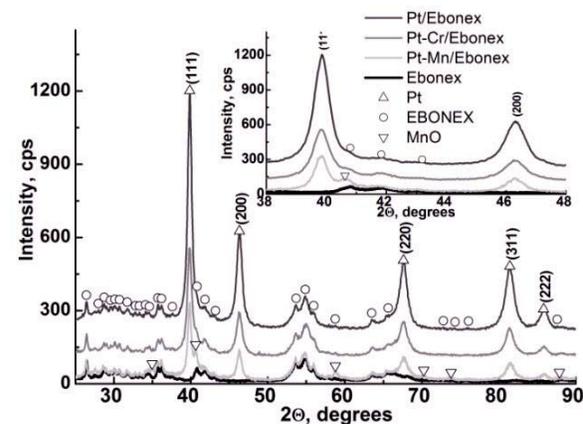


Fig. 2. XRD spectra of the composite Pt-M/Ebonex catalysts.

The appearance of MnO in the Pt-Mn/Ebonex spectrum (Fig. 2) supports this assumption. For all Pt-containing catalysts the fcc Pt peaks appear as well. There is no shift of the Pt peaks with the addition of the Cr or Mn (Fig. 2 inset), and hence there is no change in the Pt cell parameter (the deviation of the calculated values in Table 1 is within the error range). It implies that Mn and Cr are not incorporated in the Pt crystal cell. The intensity of the Pt XRD peaks of the different catalysts decreases in the order of Pt/Ebonex > Pt-Cr/Ebonex \approx Pt-Mn/Ebonex, which corresponds to the reduced Pt content in the Pt-M/Ebonex catalysts. The crystallite size is in the range between 13 and 16 nm.

Table 1. Calculated Pt cell parameters and crystallite size

Sample	Pt cell Å	Crystallite size nm	
		$D_{(111)}$	$D_{(200)}$
Pt/Ebonex	3.9195 ± 0.0004	14	11
Pt-Cr/Ebonex	3.9204 ± 0.0005	12	10
Pt-Mn/Ebonex	3.9186 ± 0.0008	16	13

SEM analysis

The SEM images of Pt/Ebonex and Pt-Cr/Ebonex are shown in Fig. 3. The Pt particles of both catalysts are uniformly distributed on the Ebonex support. In the case of Pt/Ebonex the distribution density is higher which correlates with the XRD analysis. The average particle size is of 50–60 nm, meaning that one particle is composed of 4–5 crystallites.

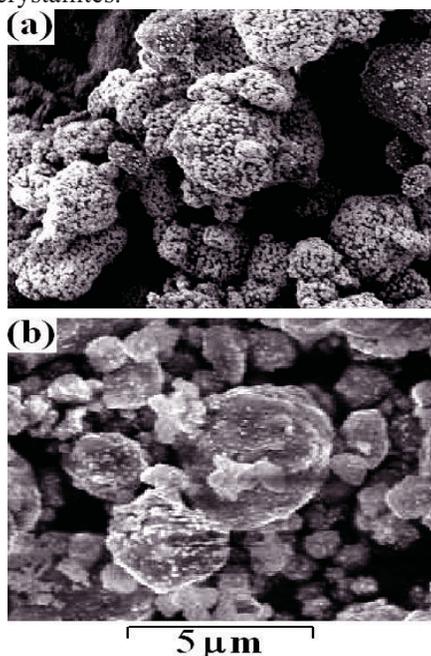


Fig. 3. SEM of the: (a) Pt/Ebonex catalyst; (b) Pt-Cr/Ebonex catalyst.

Electrochemical characteristics

The efficiency of the catalyst containing Pt, Cr and Mn is tested using the method of steady state polarisation. The anodic E/j- curves of the catalyst under study are presented in Fig. 4. The curves are recorded at the typical PEMWE operation temperature of 80°C.

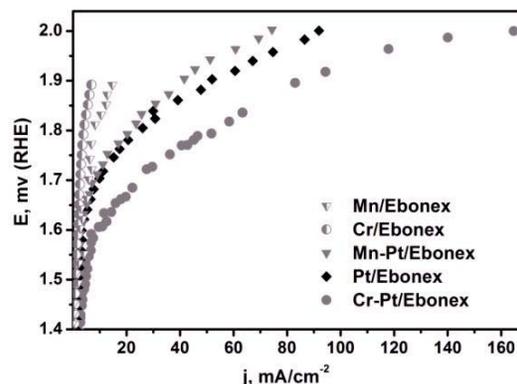


Fig. 4. Anodic E/j- curves of the catalysts recorded at 80°C.

It can be seen that the Pt free Cr/Ebonex and Mn/Ebonex do not demonstrate catalytic activity. The partial replacement of platinum with Mn does not facilitate the OER but results in improved mass activity, compared to pure Pt, while in the case of Cr substitution, the OER efficiency improves at reduced Pt loading.

Similar results, showing a positive effect of Cr and Mn inclusion on the Pt activity, have been reported by other authors for the carbon supported electrocatalysts [11–14]. The observed increase in the catalytic activity can be explained with the occurrence of hypo-hyper-d-electron interactions between both metals and the substrate. In order to verify this assumption the surface state of the prepared catalyst was studied further using XPS analysis.

The investigated catalysts show stability at high anodic potentials, which give reasons to consider Ebonex as an alternative support.

XPS analysis

XPS investigations were performed to identify the valence state of the components on the catalyst surface. Fig. 5 shows the 2p XPS spectra of Mn and Cr. These spectra confirm the supposition for the oxidized state of Mn and Cr based on the XRD data. The position of the Cr 2p_{3/2} peak at 577.0 eV as well as the spin orbital splitting of 9.7 eV correspond to Cr³⁺ (Cr₂O₃, CrOOH) [15, 16].

The Mn 2p peak is broad and covers different valence states of Mn (Fig. 5b). The peak around

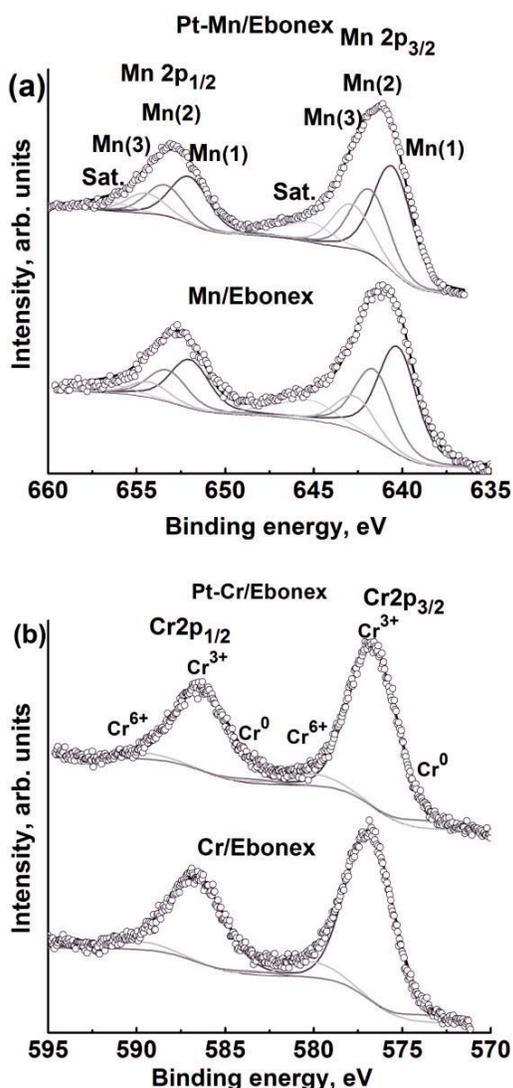


Fig. 5. 2p XPS spectra of: (a) Mn; (b) Cr.

640.0 – 640.7 eV (marked Mn(1)) in the Mn 2p_{3/2} region is attributed to Mn²⁺ cations, whereas the peaks around 641.6 eV (Mn(2)) and 642.6 eV (Mn(3)) are assigned to Mn³⁺ and Mn⁴⁺ cations respectively [17]. The formal deconvolution of the Mn 2p XPS peak into three components - Mn(1), Mn(2), and Mn(3), positioned around these values, generally implies availability of three Mn valence states. However, such a conclusion can be misleading due to the multiplet splitting nature of Mn 2p XPS spectrum for each of those three valence states with overlapping components [18], which complicates the peak interpretation. In our case, the fitting picture is close to the multiplet splitting spectrum of MnO, i.e. to Mn²⁺. The exchange splitting of the Mn 3s spectrum is more informative.

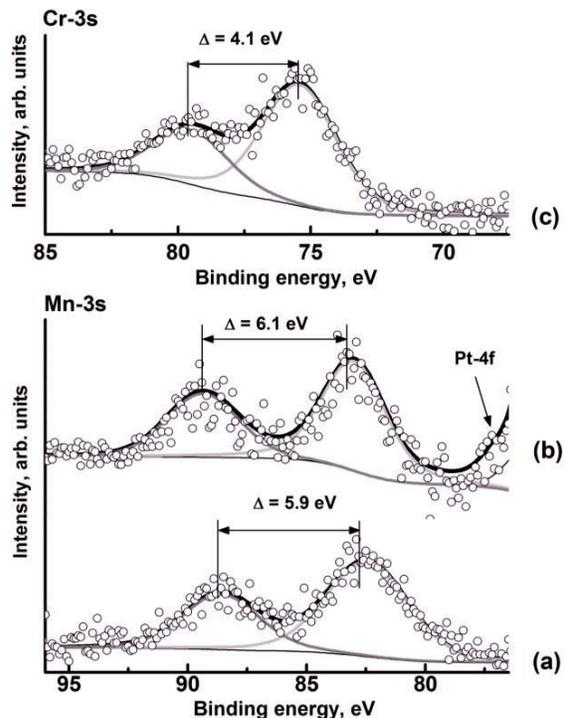


Fig. 6. 3s XPS spectra of : (a) Mn 3s of Mn/Ebonex catalyst; (b) Mn 3s of Pt-Mn/Ebonex catalyst; (c) Cr 3s of Cr/Ebonex catalyst

Fig. 6 presents the Mn 3s and Cr 3s XPS spectra which are used to establish the Mn and Cr valence states. The observed values of the exchange splitting of the 3s levels for the Mn and Cr ions are close to those found in [13] for some 3d metal oxides MO_x (M = Cr, Mn). The splitting of the 3s level is 6.2-6.5 eV for Mn²⁺, 5.5 eV for Mn³⁺, and 4.5 eV for Mn⁴⁺ [17,19], meaning that the Mn/Ebonex and Pt-Mn catalysts consist mainly of Mn²⁺ species (splitting is 5.9–6.1 eV).

The magnitudes of the Cr 3s multiplet splittings are 3.8-4.2, and 3.5 eV for Cr²⁺ (Cr₂O₃, CrOOH) and CrO₂ respectively [20]. From the value of the Cr 3s exchange splitting (4.1 eV) can be concluded that in Cr/Ebonex catalyst the Cr ions are trivalent.

The Cr 3s split spectrum of Pt-Cr /Ebonex catalyst overlaps with the Pt 4f line and for that reason it is presented together with the others Pt 4f spectra in Fig. 7.

The Pt 4f XPS spectra can be deconvoluted into 3 doublets corresponding to Pt⁰ (~71.2 eV), Pt²⁺ (~72.5 eV), and Pt⁴⁺ (~75.0 eV). For Pt-Cr/Ebonex catalyst Cr 3s exchange splitting line is introduced in addition (Fig. 7b). As it can be seen, platinum presents mainly in metallic form. The second component indicates a surface oxidation of Pt which is higher in the case of Pt-Cr/Ebonex

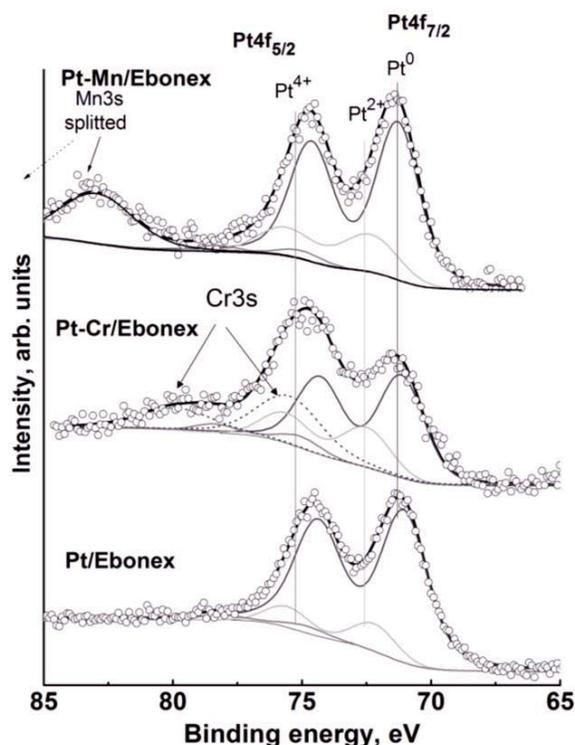


Fig. 7. Pt4f XPS spectra of Pt-M/Ebonex catalysts.

catalyst. We assume that besides $\text{Pt}(\text{OH})_2$ formation [21], mixed Pt-O-Me (Me = Ti, Mn, Cr) bonds appear. These two oxide types are responsible for the hypo-hyper interaction, and it can explain the higher electrochemical activity of the Pt-Cr/Ebonex catalyst.

CONCLUSIONS

The synthesized composite Pt-M (M = Cr, Mn) nanomaterials on Ebonex support were investigated as OER catalysts for PEM water splitting. Physical analysis showed that Cr- and Mn- components are in amorphous and oxidized state, while Pt is predominantly in a metallic state. No alloying between Pt and Cr/Mn is registered. The results from the electrochemical experiments demonstrate superior catalytic activity of the Pt-Cr/Ebonex compared with the Pt-Mn/Ebonex and the Pt/Ebonex catalysts.

This effect is explained with the occurrence of hypo-hyper-d-electron effects between both, the metals and the substrate, proven by XPS analysis.

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**ФИЗИЧНО ОХАРАКТЕРИЗИРАНЕ НА Pt-M ДВУКОМПОНЕНТНИ
ЕЛЕКТРОКАТАЛИЗАТОРИ ЗА РАЗЛАГАНЕ НА ВОДА**

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(Резюме)

Синтезирани са комбинации от моно- и биметални смеси, оксиди и композитни материали, в които Pt е частично или изцяло заменена с по-евтини елементи (Cr и Mn). Като носител е използван механохимично третиран Ebonex. Синтезираните катализатори са охарактеризирани с обемни и повърхностни методи, като XRD, XPS и SEM. XRD и XPS анализите показват, че Cr- и Mn-компоненти са в аморфно и окислено състояние, докато Pt е предимно в метално състояние. Не е регистрирано сплавяване между Pt и Cr или Mn. Катализаторите са електрохимически изпитани по отношение на реакцията на отделяне на кислород при разлагане на водата в ПЕМ електролизна клетка. Като протонпроводящ електролит е използван търговският продукт Nafion 117. Установено е, че най-добра каталитична активност показва Pt-Cr/Ebonex, който проявява по-висока ефективност при по-ниски натоварвания на Pt в сравнение с всички други композиции, включително Pt/Ebonex. Получените резултати могат да се обяснят с електронни взаимодействия между металните частици и носителя, осигуряващи синергичен ефект.