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Electrochemical Behavior of Platinized Ebonex® Electrodes

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Electrochemical properties of platinized Ebonex® electrodes have been studied. It was shown that the temperature of preparation affects the catalytic activity through the surface area and the chemical composition. Ebonex®/Pt-electrodes were found to be n-type semiconductors. Increase in treatment temperature leads to thermal diffusion of Pt deep into Ebonex® and results in shift of flatband potential to positive values and decrease in donor concentrations. The pPeak of reduction of Pt phase oxides on the cathodic branch of voltammograms characterizes the amount of electrochemically active platinum on Ebonex®-surface and could be correlated with electrocatalytic activity of thermally treated Ebonex®/Pt-electrodes.

Keywords: Ebonex®, Ebonex®/Pt, electrocatalytic activity, semiconductor properties.

1. INTRODUCTION

Exploitation of the exceptional electrocatalytic activity of precious metals is hampered by the high cost and in view of practical applications in electrocatalysis it is mandatory to use electrode materials consisting of the smallest amount possible of the active metal particles coated on different supports. On the one hand, Pt is one of the most widely used electroactive material, on the other hand, the choice of the proper supports is of paramount importance. Carbon materials has been generally used as support for catalysts due to the availability of materials with different characteristics hydrophobicity/hydrophilicity, large accessible surface area, as well as high electrical conductivity. However, carbon supports are known to be unstable toward corrosion and this will eventually result in an instability of the platinum (Pt) catalyst due to particle of even agglomeration and even to their detachment from the support. This obviously can lead to dramatic losses in the electrodes performance.

In order to overcome the mentioned problems, there is presently a big focus on the development of alternative catalyst supports to replace carbon. According to several literature reports, boron doped diamond (BDD) appears to be a potential candidate [1] due to its high corrosion resistance to chemicals and stability in a wide potential window. However, it is commonly observed that the stability of metal overlayers on BDD can be critical due to mechanical loss of particles by reason of their poor interaction with the surface [2].

Titanium has long been known to be a practical support for electrochemically active materials [3], including conductive oxides (DSA electrodes) and precious metals. In particular, platinized Ti has commercial applications although it is often remarked that the pretreatment of the support is rather critical. A common cause for electrode failure is the detachment of particles during operative conditions. In this respect, it is interesting that heat treatment produces intermetallic Pt–Ti compounds on the surface which reduces the process of delamination of platinum and considerably extends electrode lifetime [4].

In recent years much effort is being put into the study of ceramic conductive support materials [5] which are potentially able to interact strongly with coated catalysts. This interactive effect is known as SMSI (strong metal-support interaction) has been extensively investigated [6,7].

The field of metal oxide supports is growing rapidly and particularly materials based on reduced titanium oxides have received much attention owing to their chemical stability in a wide pH range [5]. Among these, a mixture of Magneli phases (titanium “sub-oxides” having the general formula Ti_nO_{2n-1}, where n=4–10) has become commercially available under the Ebonex® trade name [8–13].

Ebonex® electrodes are characterized by a high conductivity and good service life [14,15]. Generally, the electrochemical stability in a wide potential range is considered to be satisfactory [16] with regards to corrosion although the material has been reported to undergo appreciable composition changes when used both as an anode or a cathode [17]. Specifically, Ebonex® electrodes have been found to lose activity due to over oxidation leading to a more stoichiometric, less conductive surface layer [18]. Interestingly, the anode activity could be maintained through periodic reversal of polarity.

Magneli phases materials are seemingly more commonly used as supports for active electrocatalysts among which platinum and other noble metals are often the preferred choice since they exhibit unique catalytic activity. It is generally established that deposition of the thin platinum layer on Ebonex® results in a conspicuous gain in electrocatalytic activity [19–24], which has been in part ascribed to synergetic effects arising from interactions of the coated nanoparticles with Ebonex® [25,26].

The question of the electrochemical stability of metal/ Ebonex® composites has been addressed in a number of publications [17,18,27,28]. On the other hand, taking into account that the preparation of several supported electrocatalysts involves thermal treatment, the choice of support materials requires information on thermal stability. There is no detailed information on the thermal stability of Ebonex® aside from a general indication that it becomes oxidized above 400°C [27]. In the present work we present some aspects of the electrochemical behavior Ebonex® treated at different temperatures. In particular we pay particular attention to Pt/ Ebonex® since it is considered that the behavior of the Pt overlayer is a good probe for monitoring changes of properties as a function of temperature, as in analogous studies on Pt/Ti electrodes [4].

2. EXPERIMENTAL

Prior to electrodeposition the Ebonex® was prepared as follows: (i) the surface was prepared mechanically by moist abrasive paper; (ii) after rinsing it was chemically etched in a solution containing HCl (0.5 M), CH_3COOH (0.1 M), NaF (0.02 M) at 50^{o}C for 60 min; (iii) the surface was washed and ultrasonically treated in water to remove remains of etchant from the Ebonex® pores.

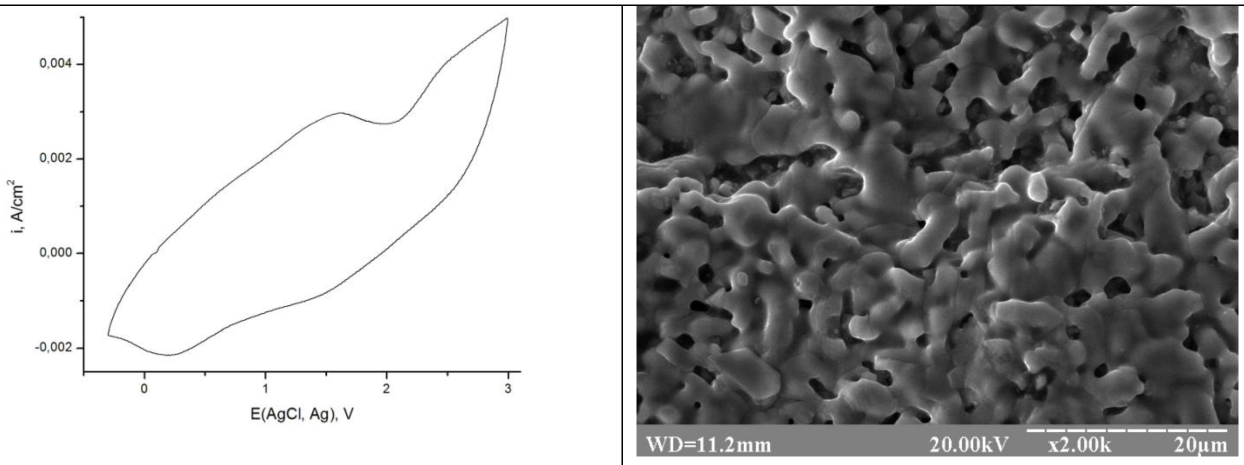
After that platinum was electrodeposited at 70^{o}C and cathodic current density 30 mA/cm^2 from the electrolyte: K_2PtCl_6 - 25.004 g/L; $NaNO_2$ - 100 g/L; solution of NH_3 (ρ=0.915 g/cm^3) - 20 mL. The coating thickness was about 4 μm (~8 mg Pt per cm^2). Thin platinum coatings with good adhesion to substrate were obtained at these conditions.

Some of Ebonex®/Pt-electrodes were thermally treated in the air using tube furnace at 230, 310 or 410ºC for 1 h and 2 h (in one experiment 4 h).

Electrochemical measurements were carried out in 1 M $HClO_4$ with GAMRY Potentiostat/Galvanostat/ZRA Reference 3000 in three-electrode cell with Pt auxiliary electrode and Ag/AgCl reference electrode.

For the photoelectrochemical measurements, the illumination source was a mercury medium pressure lamp (Helios Italquartz) equipped with cut-off filters.

3. RESULTS AND DISCUSSION



a

b

Figure 1. Cyclic voltammogram for the Ebonex®-electrode (100 mV/s) in 1 M $HClO_4$ (a) and its SEM micrograph (b).

Cyclic voltammograms of clean Ebonex®-electrodes show significant charging current (Fig. 1a) as a result of porosity (Fig. 1b). In agreement with literature, Ebonex® is characterized by high polarizability, with low activity towards reactions of oxygen/hydrogen evolution except at relatively high potentials.

As expected, electrodeposition of platinum on Ebonex® results in polarizability decrease and increase in electrocatalytic activity of electrode (Fig. 2, curve 1). Charging currents are still significant due to the contribution of the porous support and surface roughness. The cathodic branch of the curve shows the typical peak of platinum oxides reduction. Upon scan reversal, the curve features the anodic hydrogen desorption peak at -0.05 V, a current plateau corresponding to platinum phase oxides formation is observed at 1.0–1.4 V and finally the current grows exponentially as oxygen evolution ($E \geq 1.4$ V) takes place. It is important to note that some difference in CV for bulk Pt and Ebonex®/ Pt is observed. We suggest that it is effect of interaction between the substrate and coating with partial redistribution of electrons (from platinum to titanium oxide) changing physicochemical surface properties such as adsorption.

Thermal treatment of Pt/Ebonex® at 410^{0}C results in significant changes in electrochemical behavior (Fig. 2, curve 2) due to possible interaction of platinum with air and titanium oxides resulting in formation of a new phase in system Ti-Pt-O. The shift of platinum oxides reduction peak to negative potentials is added evidence of phase oxides stability increase after thermal treatment. The hydrogen desorption peak is not observed. Significant decrease in oxygen evolution current, its overvoltage increase and current lessening of platinum oxides reduction peak are also noteworthy. The reason of that must be thermal diffusion of platinum deep into porous Ebonex® and its surface redistribution due to higher metal mobility accompanied with chemical interaction between Pt and titanium oxides, formation of new phase and complete or partial Pt incapsulation [6, 29,30].

Table 1. XRD data for Ebonex®

Electrode	Phase composition	Parameters of elementary cell, Å		
		a / α	b / β	c / γ
Ebonex®	Ti_6O_{11}	5.554 / 89.81	7.128 / 79.78	9.715 / 71.51
Ebonex® 410°C, 1 h	Ti_5O_9	5.565 / 69.81	7.112 / 75.01	8.483 / 71.55
	Ti_6O_{11}	5.548 / 89.77	7.122 / 79.76	9.712 / 71.51
	TiO_2 hollandite	10.178		2.981
	TiO_2 rutile	4.595		2.950
Ebonex® 410°C, 4 h	Ti_6O_{11}	5.540 / 89.85	7.141 / 79.87	9.731 / 71.70
	TiO_2 hollandite	10.261		2.870
	TiO_2 rutile	4.603		2.966

Our suggestion is supported by preliminary results (Table 1) of an ongoing full XRD investigation. It appears that the phase composition of Ebonex® dramatically changes with temperature and time of treatment due to interaction of air oxygen with titanium suboxide oxides leading to an increase of the O/Ti stoichiometric ratio up to TiO_2 formation. Specifically, treatment of Ebonex® at

410^0C leads formation of TiO_2 as hollandite and rutile, and a new phase of system Ti-Pt-O appears (2θ (°) / d (Å): 17.70 / 6.292; 26.60 / 4.208; 30.63 / 3.665 and 35.59 / 3.168 – maximum intensity (Table 1).

Insights into the effects of thermal treatment can be gained through qualitative and quantitative examination of the reduction of platinum oxides formed at potentials of oxygen evolution. In general, this process is subscribed by the reaction:

$$PtO_x + 2xH^+ + 2x\ e^- \rightarrow Pt + xH_2O \quad (1).$$

It is reasonably assumed that the peak of Pt phase oxides reduction characterizes the amount of electrochemically active platinum on Ebonex® and can therefore be correlated with the electrocatalytic activity. For these experiments, electrodes were first polarized anodically in 1 M $HClO_4$ at 100 mA/cm^2 during 120 s, then a cathodic sweep was initiated at a potential scan rate of 100 mV/s. From the results shown in Fig. 3a one can see that reduction platinum oxides on non-thermally treated Pt/Ebonex® features higher currents and a more negative peak potential compared to bulk Pt in analogous conditions. The larger peak and charging currents are due to the larger accessible area of Pt/Ebonex® while the shift of the peak potential to less positive potentials can be ascribed to the above mentioned interaction of Pt with Ebonex®.

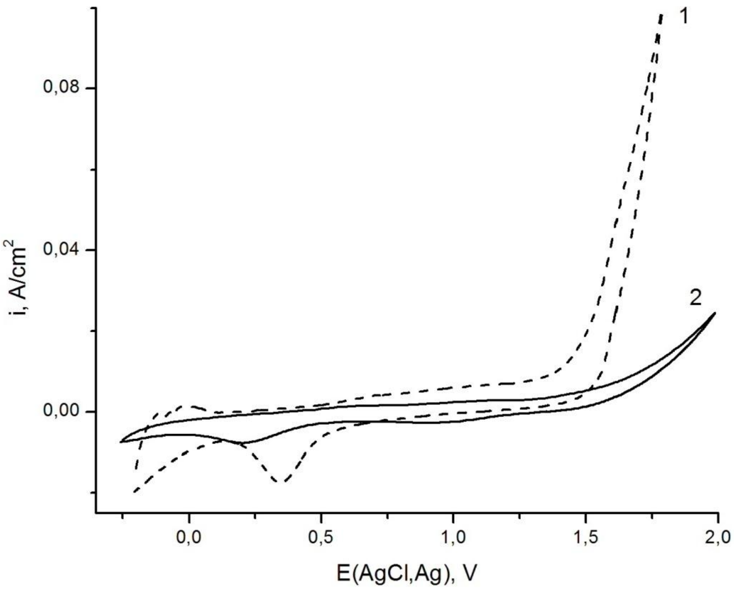


Figure 2. Cyclic voltammograms (100 mV/s) in 1 M $HClO_4$ for the Ebonex®/Pt-electrodes, obtained without thermal treatment (1) and thermally treated at 410^0C (2).

Interesting phenomena can be observed for Pt/Ebonex® electrodes treated at different temperatures. Thus thermal treatment at 230 ^{0}C leads to significant increase of both the peak current of oxide reduction and of the background charging current (cf. curve 2 in Fig. 3b, and curve 1 Fig. 3a). The data apparently reflect an increase of the active area likely due to a rearrangements of the porous structure of the substrate. At the same time, the peak of oxide reduction slightly shifts to more positive potentials. The increase of the peak current seems to indicate that the interaction Pt-Ebonex decreases so that Pt can move along the surface. This could give rise to either better dispersion, as the results seem to indicate. These phenomena continue as the treatment temperature is raised to 310^0C, adding that peak potential of oxide reduction shifts toward the value observed for bulk Pt, possibly by reason of particle coalescence forming aggregates.

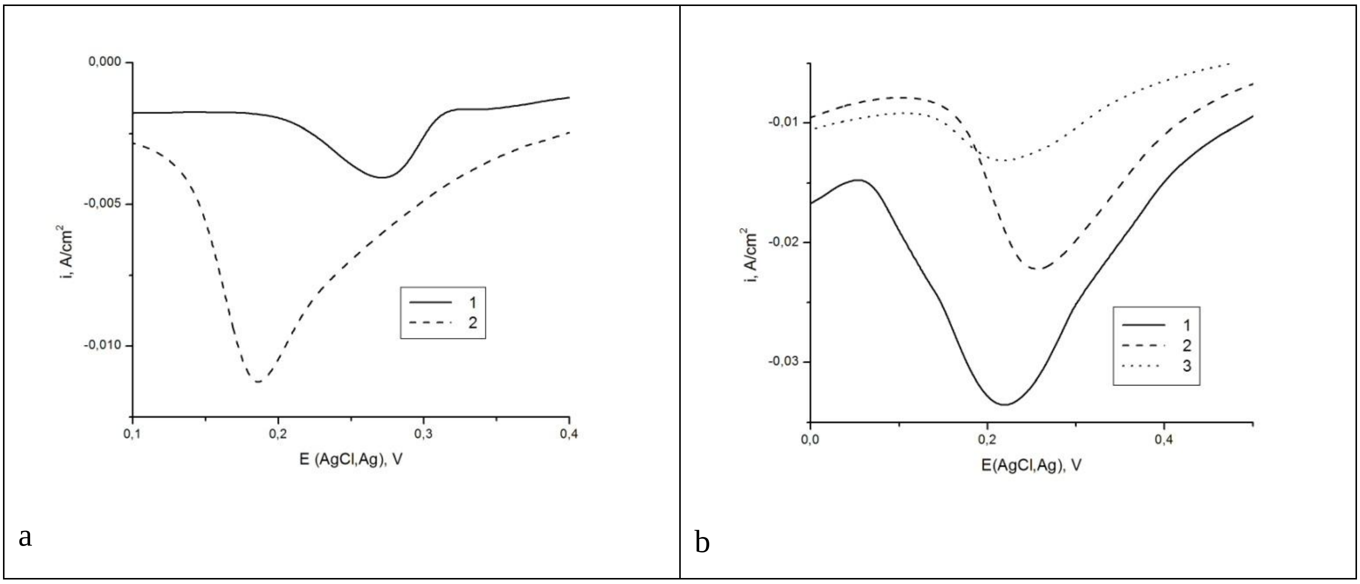
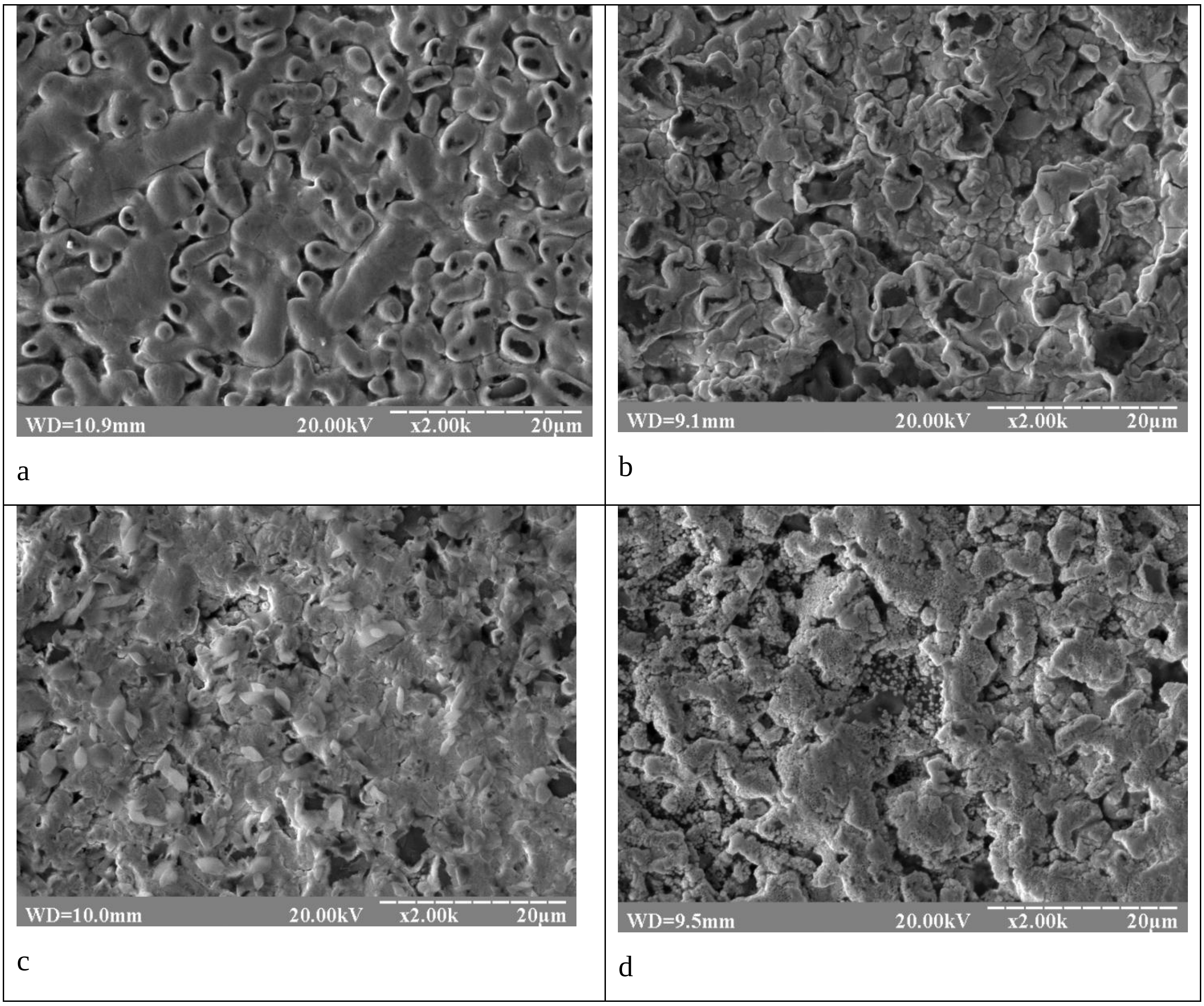


Figure 3. Inversion voltammograms (100 mV/s) in 1 M $HClO_4$ for electrodes obtained without thermal treatment (a): 1 – Pt; 2 – Ebonex®/Pt; and thermally treated Ebonex®/Pt electrodes (b): 1 – 230; 2 – 310; 3 – 410 ^{0}C.

Finally, thermal treatment of Pt/Ebonex® at 410^0C results in a shift of the peak potential again in the negative direction, and the peak current decreases conspicuously. In parallel, it was observed that the background charging current drops, at variance with the above discussed data recorded at intermediates temperatures.

Scanning electron micrographs for Ebonex®/Pt-electrodes represented at Fig. 4 are in agreement with data obtained from voltammetry. As prepared platinum coatings are smooth and reproduce the morphology of Ebonex® (Fig. 4a). Thermal treatment of electrode at 230^0C leads rearrangement of both the Pt overlayer and the porous substrate (Fig. 4b). Increase in temperature of treatment to 310^0C intensifies diffusion process and seemingly promotes Pt islands formation (Fig. 4c) and an apparent loss of surface porosity. A more severe change of the surface structure is noted Fig. 4d which illustrates to the case of Pt/ Ebonex® treated at 410^0C. Sub-surface domains of small parlicles are clearly seen. Loss of surface area due to sintering is possible [31] for thermal treatment above 400°C, but it seems plausible that oxidation of Ebonex (*vide infra*) to a more stoichiometric material with lower conductivity decreases the capacitance and contact with Pt. Effects on the electrochemical behavior a discussed in the following.

Polarization curves for Pt/Ebonex® electrodes in 1 M $HClO_4$ (potential scan rate – 5 mV/s) are shown at Fig. 5. Oxygen overvoltage rises with temperature and duration of electrode treatment. In all cases, polarization curves represented in semilogarithmic scale are linear and characterized by significant slope (>0.294 V).



a

b

c

d

Figure 4. SEM micrographs for Ebonex®/Pt, obtained without thermal treatment (a) and thermally treated at 230 (b), 310 (c) and 410 ^{0}C (d).

This denotes an increased semiconductive component and/or porosity effects. Impedance measurements were then carried out in order to investigate the semiconducting properties of Pt/Ebonex® electrodes. The data recorded at a frequency of 5 Hz obey Mott-Schottky relationship in wide range of potentials.

Anodic polarization of Pt /Ebonex® above flatband potential leads to carrier depletion, decrease in electrode capacitance and increase in slope of polarization curve represented in semilogarithmic scale. We observed an increase of the flatband potential (Table 2) with thermal treatment temperature, and the donor concentration decreases induced both oxidation of Pt with phase oxides formation and TiO_2 formation that leads, as a result, to reduction of free electrons number.

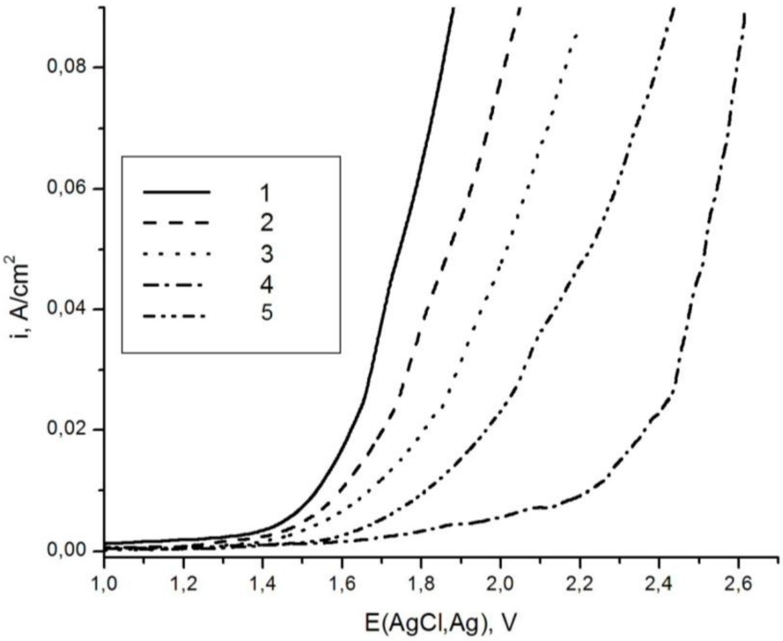


Figure 5. Polarization curves in 1 M $HClO_4$ for Ebonex®/Pt-electrodes, obtained without thermal treatment (1) and thermally treated at 230 (2), 310 (3) and 410^{0}C (4,5). Duration of thermal treatment 1 h (2,3,5) or 2 h (4). Potential scan rate – 5 mV/s.

Table 2. Electrochemical and semiconductor properties of Ebonex®/Pt-electrodes

Treatment temperature of Ebonex®/Pt-electrodes, ^{0}C	Intercept and slope of polarization curves in semilogarithmic scale		Flatband potentials and donor concentrations calculated from Mott-Schottky plot	
	a, V	b, V	E_{FB}, V	$N \times 10^{-23}$, cm^{-3}
25	2.12	0.294	0.465	100
230	2.21	0.307	0.570	28
410	3.07	0.425	0.666	0.027

In accordance with the data of Table 2, an anodic photocurrent is recorded upon irradiation of unmodified Ebonex® with UV light (Fig. 6A). The photocurrent increases when the material is heated at T > 400°C in keeping the the discussed increase of the mean O/Ti stoichiometric ratio, as also generally observed for TiO_{2-x} partially reduced electrodes [32].

It is interesting to note that the thermal treatment of unmodified Ebonex® at 410^{0}C results in a higher electrocatalytic activity compared with pristine material (Fig. 7), which seems to be in contrast with the abov discussed results. Apparently, the oxidation of low Magneli phases [8] accompaniying bonding energy changes are correlated with electrocatalytic properties of oxide materials [33]. In general case the electrocatalytic activity of an electrode toward any kind of oxygen-transfer reactions strongly depends on bond strength of chemisorbed oxygen-containing particles with the electrode surface. Since no *in situ* electrochemical data are available for oxides, the evolution of the prediction possibility of electrocatalytic activity could be based on the experimental data taken from neighboring fields.

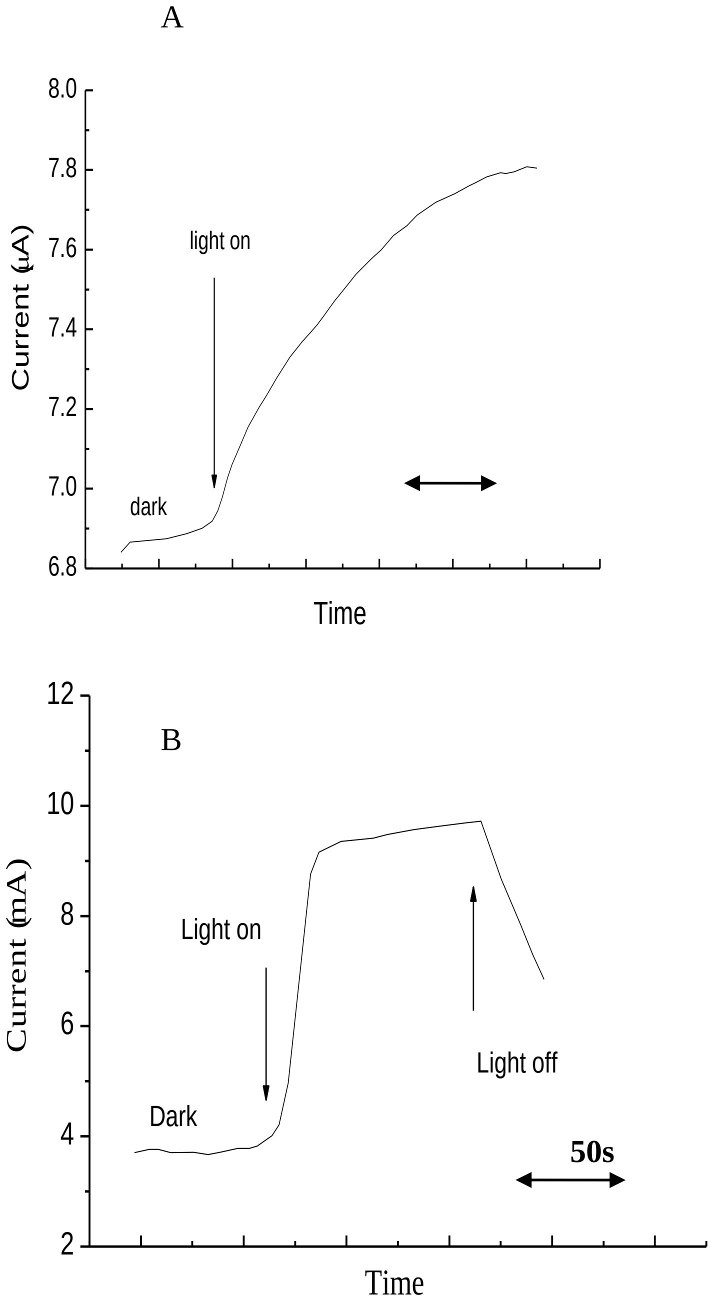


Figure 6. Photoelectrochemical Current-Time Transients for Ebonex in 1M HClO4 with no thermal treatment and after 2h at 410°C. Electrode area: 1.3 cm^2. Irradiarion at $\lambda > 300$ nm.

The parameter which is expected to parallel the energy change occurring during the electrochemical reaction is the enthalpy of transition of the oxide from a lower to a higher oxidation state [32]. Standard enthalpy for lower to higher oxide transition for TiO_2 ($Ti_2O_3 \rightarrow TiO_2$) is 574.47 kJ mol^{-1} that higher than for other titanium oxides. Increase of the enthalpy indicates a growth of bond strength of chemisorbed oxygen -containing particles on the electrode surface. When oxygen evolution reaction at Ebonex® electrode in acidic solution is limited by a first electron transfer [33], so called “electrochemical adsorption” stage, the increase of bond strength leads to acceleration of OER (Fig. 7).

The same effect we observed for Ebonex®/Pt-electrode , thermally treated at 410^{0}C for 4 hours (Fig. 8). No anodic current plateau due to platinum phase oxides formation is noted on cyclic voltammogram what indicates oxidation of Pt by atmospheric oxygen during thermal treatment with formation of stable phase oxides. Hysteresis observed at oxygen evolution potentials clearly indicates changes in the state of the surface).

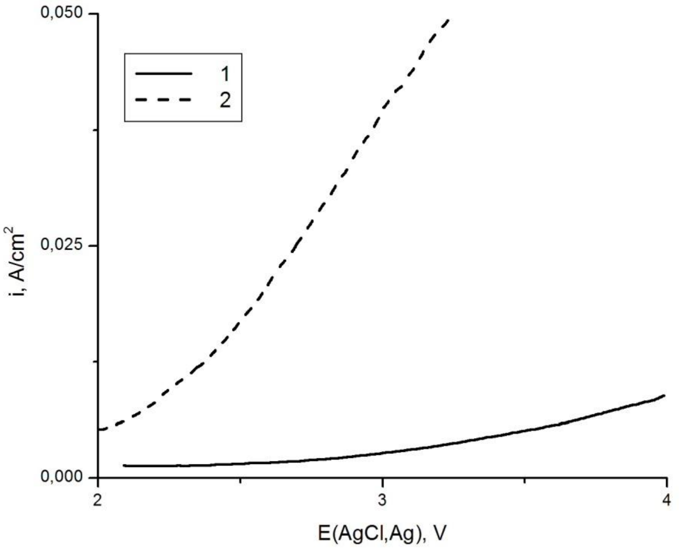


Figure 7. Polarization curves in 1 M $HClO_4$ for Ebonex® (1) and Ebonex® thermally treated at 410^{0}C (2) . Potential scan rate – 5 mV/s.

4. CONCLUSIONS

In this work we have examined the effects of thermal treatment of Ebonex® and Pt/Ebonex® electrodes on their physicochemical and electrocatalytic activity.

The temperature of treatment significantly affects the catalytic activity of both Ebonex® and Pt /Ebonex® electrodes through surface area, chemical composition and semiconductor properties, i.e., shift of flatband potential to positive values and decrease in donor concentration .

An increase in treatment temperature leads to rearrangement of the Pt overlayer by thermal surface diffusion (230 to 310°C) and deeper into pores of the substrate at still higher temperature (410°C). The voltammetry reduction peak of Pt phase oxides formed at high anodic potentials characterizes quantity of electrochemically active platinum on Ebonex®-surface and can be correlated with electrocatalytic activity of thermally treated Ebonex®/Pt-electrodes.

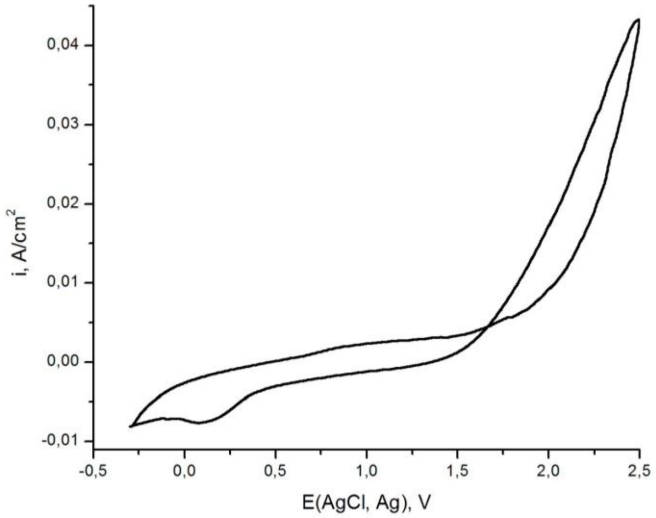


Figure 8. Cyclic voltammograms in 1 M $HClO_4$ for the Ebonex®/Pt-electrodes, thermally treated at 410^0C for 4 h. Potential scan rate – 100 mV/s.

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