

## Morphology and phase composition of platinized Ebonex<sup>®</sup> materials

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The influence of the synthesis conditions on the morphology of an Ebonex<sup>®</sup>/Pt surface and the phase composition has been established. It is shown that during electrochemical deposition of platinum onto an Ebonex<sup>®</sup> surface, the coating is not continuous, but is represented by individual islands of metal with weak crystallinity deposited on the substrate. After the heat treatment, the surface morphology becomes similar to that of pure Ebonex<sup>®</sup>, and the only difference resides in a small amount of tiny platinum crystals fused into the substrate. Chemical interactions of metallic platinum with the titanium oxides, accompanied by encapsulation of the metal by oxides at high temperatures, are likely. It was found that, without thermal treatment, the platinum coating is largely X-ray amorphous, and its crystallinity increases with increasing annealing temperature and time. In parallel, the internal stress of the coating is reduced by a factor 4.

Platinized Ebonex<sup>®</sup> / Thermal treatment / Morphology / Phase composition

### 1. Introduction

Ebonex<sup>®</sup> ceramic is a metallic-type conductor with potential applications as a commercial electrode to rank alongside existing materials such as graphite, magnetite, silicon iron, and the family of noble metal oxide-coated titanium anodes [1]. Its conductivity is similar to that of carbon, but the resistance to corrosion and oxidation is much higher. The empirical formula of this substance is Ti<sub>4</sub>O<sub>7</sub> [2]. The structure is rutile titanium dioxide, which can be described as a network of TiO<sub>6</sub> octahedra, sharing vertices in the plane *ab* and edges along the 4-fold axes perpendicular to this plane. Ti<sub>4</sub>O<sub>7</sub> contains for every three layers TiO<sub>2</sub> a single layer TiO. The TiO layer is connected to adjacent TiO<sub>2</sub> layers via common faces instead of shared atoms, as in the case of rutile titania. The result is a conductive strip closely surrounded by TiO<sub>2</sub>. The TiO layer provides conductivity, and chemical resistance is provided by the TiO<sub>2</sub> part [3,4]. However, Ebonex<sup>®</sup> alone has a number of disadvantages due to its propensity for passivation by anodic polarization because of the increasing amount of oxygen, which results in the formation of titanium(IV) oxide over time. The latter is an n-type semiconductor with low carrier content. A thin layer of platinum group metals that will be used as donor

carriers in the semiconductor is applied to the Ebonex<sup>®</sup> in order to overcome these shortcomings [5,6]. In this regard, establishment of the effect of synthesis conditions of Ebonex<sup>®</sup>/Pt materials on their physicochemical properties is of considerable interest for both theory and applications. Since the electrocatalytic activity of anode materials in oxygen transfer reactions is determined by chemical and structural factors, in this paper we consider the effect of the synthesis conditions on the morphology of the Ebonex<sup>®</sup>/Pt surface and the phase composition.

### 2. Experimental

All the chemicals used in this work were reagent grade. A monolithic block of Ebonex<sup>®</sup> (density 8.5 g·cm<sup>-3</sup>, porosity 12-18 vol.%), supplied by Atraverda Ltd, was cut with a diamond-cutter into 10 mm×10 mm square samples, which were used as substrates. The Ebonex<sup>®</sup> was treated by the following procedure before platinum electrodeposition: i) polishing by moist abrasive paper and rinsing; ii) chemical etching in a 0.5 M HCl + 0.1 M CH<sub>3</sub>COOH + 0.02 M NaF solution at 50 °C for 60 min; iii) rinsing and ultrasonic treatment in water to remove remains of etchant from the Ebonex<sup>®</sup> pores.

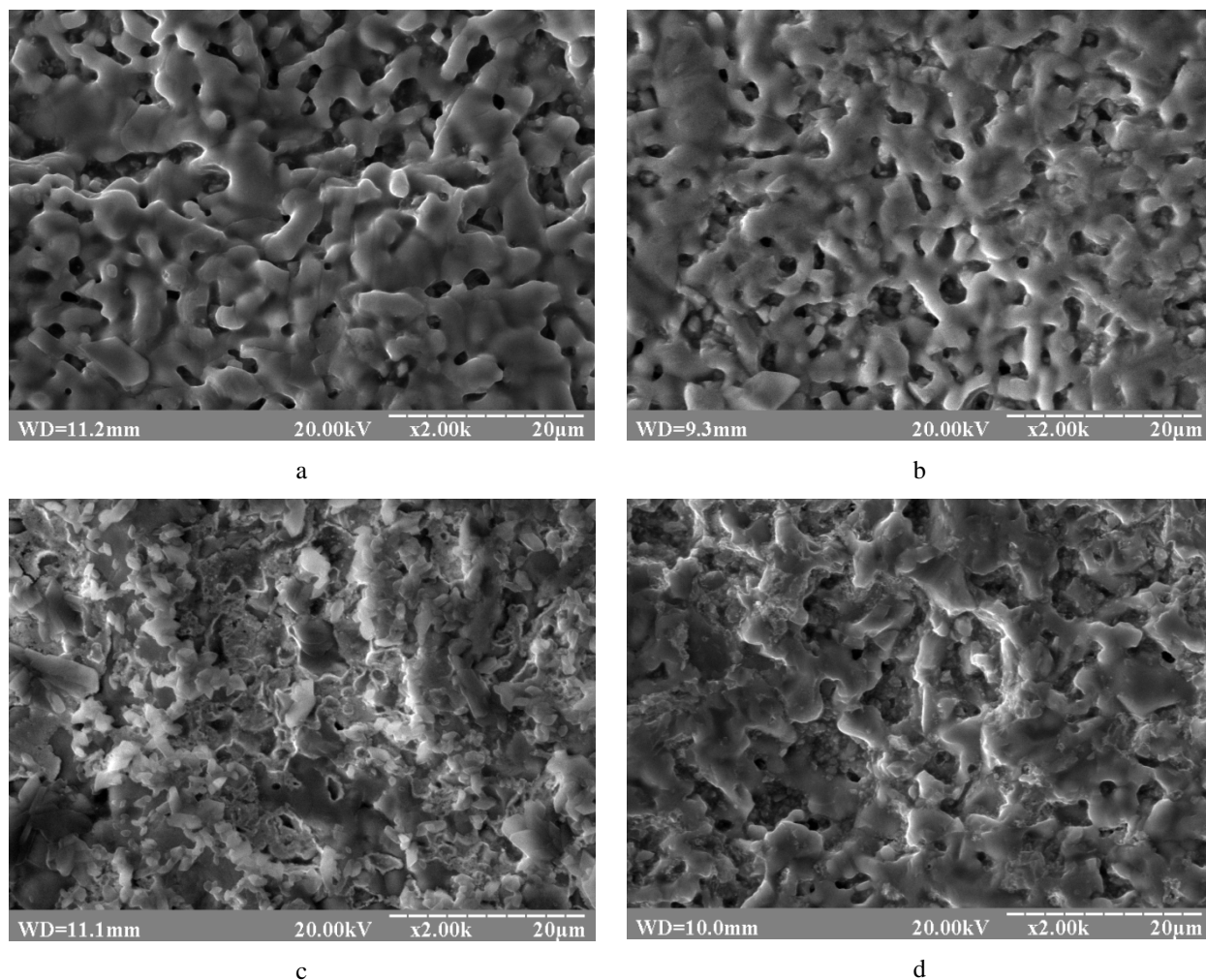
Then platinum was electrodeposited at 80 °C at a cathodic current density of 20 mA·cm<sup>-2</sup> from 0.05 M K<sub>2</sub>PtCl<sub>6</sub> + 1.5 M NaNO<sub>2</sub> + 10 M NH<sub>3</sub> [7]. The coating thickness was about 1 or 4 μm (~2 or 8 mg Pt per cm<sup>2</sup>). Some initial and platinized samples were thermally treated in air using a tube furnace at 230, 310 or 410 °C for 1 h.

The surface morphology was studied by the scanning electron microscopy (SEM) technique using a REM-106I microscope. Phase analysis was performed using X-ray powder diffraction (DRON-2.0 M diffractometer with Fe K $\alpha$ -radiation, Bragg-Brentano geometry,  $\theta/2\theta$ -scanning,  $10.00 \leq 2\theta \leq 125.00$  range with a scanning step of  $0.050^\circ 2\theta$  and 3 s exposure time). The observed diffraction intensities were compared with reference powder patterns of known binary and ternary phases using PowderCell and STOE WinXPOW program packages. Crystal structure refinements were performed using the Rietveld method. Calculations of

the unit cell parameters and theoretical patterns were performed using WinPLOTR program packages.

### 3. Results and discussion

The original Ebonex<sup>®</sup> has a morphology typical for materials obtained by sintering powders in an inert or reducing atmosphere and is characterized by a fairly developed porous surface (Fig. 1a). There is gradual destruction of fused amorphous zones with the appearance of chaotically oriented small crystals as the temperature rises, which can be seen from Fig. 1b. Most likely, the changes observed in the morphology are caused by the rearrangement of titanium oxides due to the absorption of oxygen from the air and its diffusion deep into the solid phase. The changes are rather slow, due to the relatively low oxygen partial pressure and low solid phase diffusion rates.



**Fig. 1** SEM-images of an Ebonex<sup>®</sup> surface (a) heat-treated at 410 °C (b) and an Ebonex<sup>®</sup>/Pt surface (c) heat-treated at 410 °C (d).

During the electrochemical deposition of platinum onto the Ebonex<sup>®</sup> surface, the coating is not continuous but consists of individual islands of metal with weak crystallinity deposited on the substrate (Fig. 1c). After the heat treatment, the surface morphology becomes similar to that of pure Ebonex<sup>®</sup>, and the only difference is a small amount of tiny platinum crystals fused into the substrate (Fig. 1d). This allows us to assume there is chemical interaction of metallic platinum with titanium oxides, accompanied by encapsulation of the metal by oxides at high temperatures.

An increase of the temperature also promotes diffusion of platinum into the substrate bulk, which leads to visual similarity of the morphologies of heat-treated Ebonex<sup>®</sup> and Ebonex<sup>®</sup>/Pt.

An increase of the amount of electrodeposited platinum leads to a significant increase of the coverage of the coating (not shown), although even in this case the metal layer is not defect-free and continuous. Islands of non-covering are observed both in pores and on the substrate surface. An increase of the annealing temperature leads to disintegration of the coating and a decrease of the size of the polycrystalline blocks, as well as a visual decrease of the amount of platinum on the substrate surface. These changes are clearly visible when the temperature is increased up to 410 °C, where areas of substrate that are not covered by platinum begin to appear more and more. The reasons for the observed phenomenon are the same as those described above. The only difference is that, with large amounts of platinum, the changes are less significant because of the low rates of diffusion of the metal into the substrate bulk.

X-ray diffraction was used to assess the changes in the phase composition of the electrodes, for different conditions of preparation. As follows from the titanium-oxygen phase diagram described by Hayfield [1], changes in temperature and composition lead to significant changes in the phase composition and formation of different titanium oxides, which in turn affects other physicochemical properties of the electrodes, including a number of semiconductor and electrochemical properties.

It was found [8,9] that titanium oxides of the general formula  $Ti_nO_{2n-1}$  ( $n = 4-10$  among which  $Ti_4O_7$ ,  $Ti_5O_9$ ,  $Ti_6O_{11}$ ,  $Ti_7O_{13}$ ,  $Ti_8O_{15}$ ,  $Ti_9O_{17}$ ,  $Ti_{10}O_{19}$ , obtained by various methods) form the basis of the Ebonex<sup>®</sup> ceramic material.  $Ti_4O_7$ ,  $Ti_5O_9$ , and  $Ti_6O_{11}$  prevail by mass ratio.

The results of the X-ray diffraction analysis of the samples are presented in Table 1. As one can see from the data obtained, the main phase of commercial Ebonex<sup>®</sup> is  $Ti_6O_{11}$ . During the thermal treatment, the system begins to take up oxygen and, already at 230 °C, titanium dioxide appears as one of the phases in the form of hollandite,  $TiO_2(H)$ , which is a hygroscopic form of the oxide. This polymorphic form contains double chains of  $TiO_6$  octahedra forming tunnels, which facilitate the diffusion of cations

through the structure [10,11]. The  $Ti_6O_{11}$  phase seems to split into two,  $Ti_5O_9$  and  $TiO_2$ , at this temperature, which is most likely due to the insufficient rate of oxygen diffusion from the gas phase into the solid. In this regard, the thermodynamically more stable titanium dioxide takes oxygen from the  $Ti_6O_{11}$  phase.

A new titanium oxide phase, identified in [12], appears at 310 °C instead of  $Ti_5O_9$  for a fixed annealing time. The amount of oxygen in the system increases at 410 °C and leads to the appearance of additional  $TiO_2$  in the form of rutile. In this case, an increase of the annealing time leads to complete disappearance of the  $Ti_5O_9$  phase. Thus, the annealing temperature and time of Ebonex<sup>®</sup> has a significant impact on the phase composition of the system.

Fig. 2 shows that reflections of platinum have appeared on the Ebonex<sup>®</sup>/Pt samples with a low content of platinum in the active layer. With an increase of the processing temperature (or time for heat treatment at 410 °C), the degree of crystallinity of the grains of the platinum phase increases – a transition is observed from semi-amorphous halos for samples without heat treatment to satisfactorily formed reflections for materials obtained at 410 °C. The unit-cell parameter of the face-centered cubic lattice of platinum in the coating (face-centered cubic (fcc), structural type copper) is equal to  $\sim 3.90$  Å, which is slightly less than for pure platinum ( $a = 3.9236$  Å). Due to the fact that the reflections from platinum in the coating intersect with groups of reflections from the substrate of the Ebonex<sup>®</sup> phases, it is not possible to accurately determine the unit-cell parameter or determine the grain size of the platinum phase.

Reflections of platinum forming the main phase in the coating are clearly determined for the Ebonex<sup>®</sup>/Pt samples with higher platinum contents (Fig. 3). It can be seen that the degree of crystallinity of the grains of the platinum phase increases with increasing annealing temperature. Since the reflections of the platinum phase grains from the coating suppress the groups of reflections of the Ebonex<sup>®</sup> phase substrate, in this case it becomes possible to satisfactorily determine the unit-cell parameters, as well as the microstructure, especially for samples treated at 410 °C (Table 2).

As one can see from Table 2, heat treatment of coatings at higher temperatures and/or an increase of the time of the heat treatment significantly increase the grain size and also the unit-cell parameter of the platinum phase, the latter approaching that of pure platinum. It should be noted that, along with this, the internal stress of the metal coating is significantly reduced (by almost a factor 4), which improves the mechanical stability of the electrodes during their operation. This is very important, since one of the problems of oxide-metal systems is internal stress, which leads to rapid mechanical destruction of the DSA<sup>®</sup> active layer and, as a result, low service life of such electrodes.

The intensity of the semi-amorphous peaks-halo of the platinum grains increases and the phase composition of the Ebonex<sup>®</sup> ceramic is preserved when the thickness of the coating is increased in samples submitted to no thermal treatment. However, reflections of the Ti<sub>5</sub>O<sub>9</sub> phase appear in addition

to those of the Ti<sub>6</sub>O<sub>11</sub> phase at higher platinum contents.

The intensity of the reflections from the platinum grains and the degree of crystallinity of the grains increase for an increase of the annealing time up to 4 h (Fig. 3).

**Table 1** X-ray diffraction phase analysis of Ebonex<sup>®</sup>.

Sample and heat treatment conditions	Phase composition, space group / Pearson symbol*	Unit-cell parameters (Å, °)**			Ref.
		<i>a</i> / $\alpha$	<i>b</i> / $\beta$	<i>c</i> / $\gamma$	
Ebonex <sup>®</sup>	Ti <sub>6</sub> O <sub>11</sub> <i>P</i> -1 / <i>aP</i> 34	5.554 / 89.81	7.128 / 79.78	9.715 / 71.51	13
Ebonex <sup>®</sup> 230 °C, 1 h	Ti <sub>5</sub> O <sub>9</sub> <i>P</i> -1 / <i>aP</i> 28	5.567 / 69.80	7.114 / 74.97	8.485 / 71.52	14
	Ti <sub>6</sub> O <sub>11</sub> <i>P</i> -1 / <i>aP</i> 34	5.553 / 89.78	7.127 / 79.76	9.716 / 71.48	13
	TiO <sub>2</sub> hollandite <i>I</i> 4/ <i>m</i> / <i>tI</i> 24	10.061		2.944	15
Ebonex <sup>®</sup> 310 °C, 1 h	Ti <sub>6</sub> O <sub>11</sub> <i>P</i> -1 / <i>aP</i> 34	5.553 / 89.77	7.126 / 79.77	9.716 / 71.51	13
	TiO <sub>2</sub> hollandite <i>I</i> 4/ <i>m</i> / <i>tI</i> 24 unidentified***	10.240		2.870	15
Ebonex <sup>®</sup> 410 °C, 1 h	Ti <sub>5</sub> O <sub>9</sub> <i>P</i> -1 / <i>aP</i> 28	5.565 / 69.81	7.112 / 75.01	8.483 / 71.55	14
	Ti <sub>6</sub> O <sub>11</sub> <i>P</i> -1 / <i>aP</i> 34	5.548 / 89.77	7.122 / 79.76	9.712 / 71.51	13
	TiO <sub>2</sub> hollandite <i>I</i> 4/ <i>m</i> / <i>tI</i> 24	10.178		2.981	15
	TiO <sub>2</sub> rutile <i>P</i> 4 <sub>2</sub> / <i>mnm</i> / <i>tP</i> 6	4.595		2.950	
Ebonex <sup>®</sup> 410 °C, 4 h	Ti <sub>6</sub> O <sub>11</sub> <i>P</i> -1 / <i>aP</i> 34	5.540 / 89.85	7.141 / 79.87	9.731 / 71.70	13
	TiO <sub>2</sub> hollandite <i>I</i> 4/ <i>m</i> / <i>tI</i> 24	10.261		2.870	15
	TiO <sub>2</sub> rutile <i>P</i> 4 <sub>2</sub> / <i>mnm</i> / <i>tP</i> 6	4.603		2.966	

\* Standardized unit cells.

\*\* Refined parameters are given with average standard deviations of 0.005 for unit-cell lengths and 0.01 for angles.

\*\*\* Unidentified phase. A strong peak appears at  $\sim 14.80^\circ 2\theta$ .

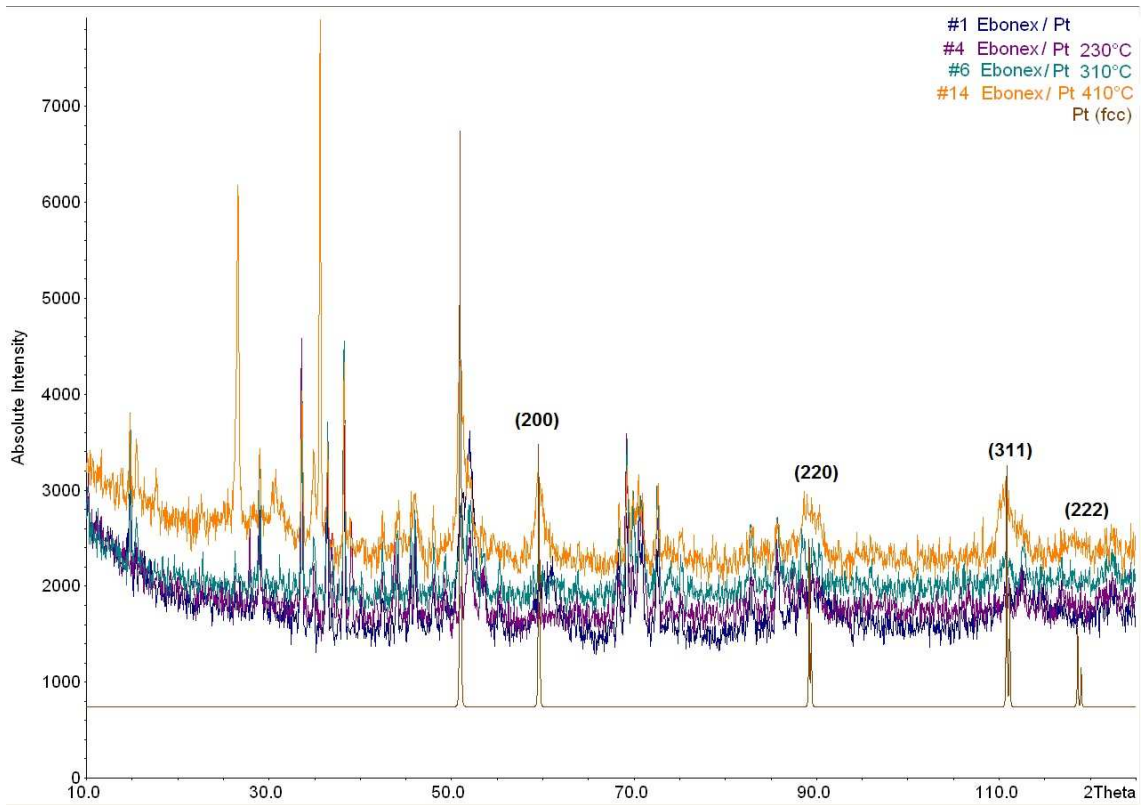
**Table 2** Unit-cell parameter of the platinum phase (space group *Fm-3m*, Pearson symbol *cF*4, structural type Cu) as a component of the coating on Ebonex<sup>®</sup>/Pt (4 μm thickness) and characteristics of the microstructure.

Sample and treatment conditions	Unit-cell parameter <i>a</i> (Å)	Average size of domains of coherent scattering (Å)*	Average maximum internal stress (%)**
Ebonex <sup>®</sup> /Pt	3.840(3)	47±23	198(70)
Ebonex <sup>®</sup> /Pt 230 °C, 1 h	3.842(4)	46±24	207(77)
Ebonex <sup>®</sup> /Pt 310 °C, 1 h	3.854(8)	53±19	161(49)
Ebonex <sup>®</sup> /Pt 410 °C, 1 h	3.898(3)	67±16	116(5)
Ebonex <sup>®</sup> /Pt 410 °C, 4 h	3.9111(17)	154±26	51(8)

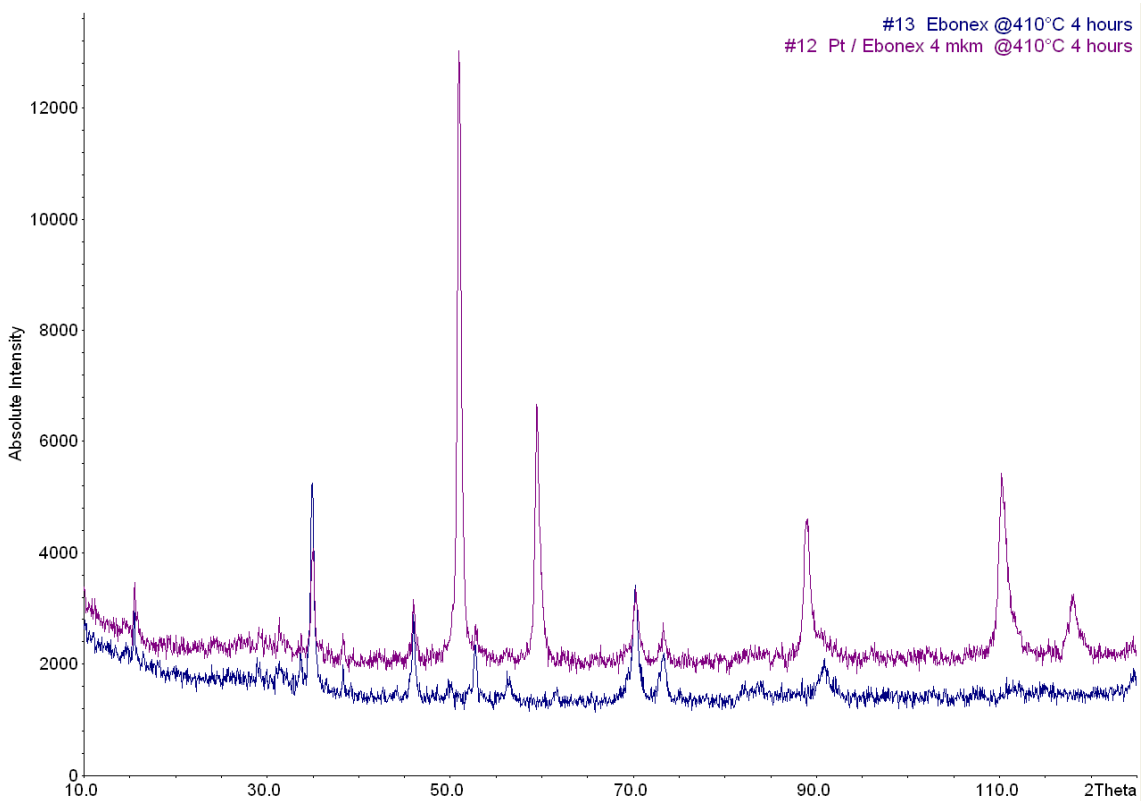
\* As a first approximation the average grain size of the phase.

\*\* Deformation is microstress in the crystal lattice.





**Fig. 2** X-ray diffractograms of Ebonex<sup>®</sup>/Pt coatings compared to metallic Pt. Digits indicate the Miller indices  $hkl$  of the reflections of platinum.



**Fig. 3** X-ray diffractograms of Ebonex<sup>®</sup> and Ebonex<sup>®</sup>/Pt coatings after 4 h treatment at 410 °C.

## Conclusions

The morphology of the surface of the electrodes, as well as their phase composition, depends on the platinum content, annealing temperature and time. The titanium dioxide phase hollandite is formed during the thermal treatment; this phase facilitates the diffusion of platinum into the substrate bulk and can lead to a significant change in the physicochemical properties of materials. It was found that, without thermal treatment, the platinum coating is largely X-ray amorphous, and its crystallinity increases with increasing annealing temperature and time. At the same time, the internal stress of the coating is reduced by a factor 4.

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