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Original Research Paper

# A continuous process for the ultrasonic spray pyrolysis synthesis of $RuO_2/TiO_2$ particles and their application as a coating of activated titanium anode

Milica Košević [a], Srecko Stopic [b,*], Andreas Bulan [c], Jürgen Kintrup [c], Reiner Weber [c], Jasmina Stevanović [a], Vladimir Panić [a,*], Bernd Friedrich [b]

[a] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, Belgrade, Serbia
[b] IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany
[c] Covestro Deutschland AG, Leverkusen, Germany

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ABSTRACT

Synthesis and subsequent deposition of sub-micron spherical $RuO_2/TiO_2$ particles onto titanium were performed by continuous process in two connected reactors, exclusively applied for this purpose. Synthesis of particles was achieved by ultrasonic spray pyrolysis method in the first reactor. The deposition of thus produced $RuO_2/TiO_2$ onto an expanded titanium substrate was performed at 500 °C afterwards in the second, specially constructed, reactor equipped by high-voltage electrostatic field. Basic electrochemical properties of the obtained $RuO_2/TiO_2$ particles were checked in a form of the coating on Ti deposited from the suspension of the material produced in the first reactor. Thus prepared anode was investigated by cyclic voltammetry (CV), polarization measurements in $O_2$ (OER) and $Cl_2$ (CER) evolution and the accelerated stability test in diluted chloride solution. The morphology and composition of the deposited $RuO_2/TiO_2$ were checked by scanning electron microscopy/energy dispersive X-ray spectroscopy analysis. Analysis of the results obtained for OER and CER showed that Tafel slopes for these reactions were in accordance with the values for this kind of material. The CV response was of usual characteristics too. The accelerated stability test revealed acceptable anode stability.

## 1. Introduction

$TiO_2$ is used as photocatalyst, gas sensor, inorganic membranes, pigment, for solar energy conservation [1], but also as an interlayer that improves antifungal properties of biocompatible implants [2–4] and finally stability- and surface area-enhancing component of activated titanium anodes [5]. It is found in three natural crystalline structures: tetragonal rutile and anatase and orthorhombic brookite, which show different features with respect to specific application. Hence, it is of high interest to investigate novel, simple and facile processing possibilities of nanocrystalline $TiO_2$ in order to achieve highly-ordered hierarchical structure of improved properties. Since $TiO_2$ is of semiconductive electrical features, its defined structures appear crucial for optimized conductivity of the coatings if one bears in mind the theory of formation of conductive pathways in conductive-insulating composite materials [6–8].

Ultrasonic spray pyrolysis (USP) was applied by Nedeljkovic et al. [9] for the synthesis of $TiO_2$ nanoparticles from colloidal solution of $10^{-2}$ M $TiO_2$ at 800 °C. Experimentally determined value of the mean diameter of pyrolyzed $TiO_2$ was 286 nm, what was different from the expected theoretical values ranged between 132 and 195 nm. Jokanovic et al. [10] modelled and explained the designing issues on nanostructured hollow particles by USP method. Differences in theoretically estimated and experimentally obtained wall thickness were 7–15%. The mean sub-μm particle size estimated by the theoretical model was 4.7 nm. Depending on the type of packing, the mean diameter of hollow sphere was different: for hexagonal packing, 87 nm, and for cubic packing, 95 nm, what is in accordance with theoretical model developed by Jokanovic et al. [4].

Backman et al. [11] produced nanosized $TiO_2$ particles by aerosol pyrolysis in flame reactors. The measured median size of $TiO_2$ prepared from titanium tetraisopropoxide was 13 nm at

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* Corresponding authors.
*E-mail addresses:* sstopic@metallurgie.rwth-aachen.de (S. Stopic), panic@ihtm.bg.ac.rs (V. Panić).

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600–1100 °C reactor temperature and 22 nm at 1100 °C. The disadvantage was the presence of carbon in product synthesized at 1100 °C. At higher reaction temperature (1100 °C), the coalescence, agglomeration and sintering are more dominant than at 600 °C. The desired crystalline anatase titania phase was formed at higher temperature. TEM and BET analysis of $TiO_2$ nanoparticles confirmed that the surface area and phase content can be controlled by pyrolysis temperature.

Aruna et al. [12] reported on nano-sized rutile titania particle synthesis *via* hydrothermal method without mineralizers, which contaminate the samples and induce undesirable characteristics of a product. The prepared new colloids are of the properties superior to similar materials using mineralizers. Two sets of titania colloids (with and without stirring) were prepared using a similar procedure of hydrothermal synthesis of titanium isopropoxide at pH 0.5, adjusted by nitric acid. The stirring that maintains homogeneity in the solution during the hydrothermal process was highly important when a homogeneous product was required. Rutile titania nanocrystals of about 20 nm size, prepared by hydrothermal method, have a large surface area and are of relatively stable structure at high temperatures.

$TiO_2$ powders have been synthesized *via* aerosol pyrolysis of freshly-prepared, well mixed, 0.2 M solution of titanium (IV) *n*-butoxide in *n*-butanol, in a temperature range between 200 and 580 °C in air and nitrogen atmosphere [13]. Anatase powder was formed at 500 °C in nitrogen, and in air at 580 °C. The anatase to rutile transformation took place upon subsequent annealing in air.

The preceding considerations are very important in order to better understand the aimed synthesis of $RuO_2/TiO_2$ particles for the application as a coating of activated titanium anodes. Panić et al. [14] have prepared $RuO_2/TiO_2$ particles by sol-gel method, with special attention on those of $RuO_2$ and binary oxide. The oxide materials have been prepared in the form of the coating on titanium substrate as well as in the form of composites – high surface area carbon blacks impregnated with electrochemically active Ru oxide. This study included an investigation of oxide morphology and the oxide electrochemical behavior, such as activity and stability in electrochemical reactions (chlorine evolution reaction and electro-organic synthesis) as well as pseudo-capacitive characteristics. Similarly, the aim of the study by Yao et al. [15] was to synthesize the oxide material with high activity and stability, and good capacitive properties for potential application in supercapacitators.

Pingali et al. [16] have reported that core-and-shell nanoparticles, with Ru as core and Ni as shell, were formed in the spray pyrolysis process by varying the component ratio in the precursor solution. Core-and-shell nanoparticles were formed when the ruthenium chloride–nickel chloride mole ratio in the precursor solution was 3:1 at an operating temperature of 600 °C.

Huang et al. [17] reported the formation mechanism of the core/shell $Ti_{1-x}Zr_xO_2$ solid spheres of different shapes with respect to anatase/rutile core/shell-structured titania particles. The mechanism supposed different partial phase transformation of a core and shell during anatase to rutile phase transformation and subsequent decomposition of remaining organic precursors trapped in the core. Probably the structure of the solid solutions might change as a consequence of the changes of the concentration of zirconium. Before the direct synthesis of the $TiO_2$@Ru core/shell nanoparticles by USP method, the formation mechanism of titanium oxide was analyzed by Ahonen et al. [7]. Titanium dioxide powder was formed from metal alkoxide droplet. Depending on the tubular reactor temperature, the final powder can contain either $TiO_2$ or hydrated titanium dioxide. With the increase in temperature the appearance of residual organic species was decreased.

Spherical sub-μm particles with almost perfect $TiO_2$@$RuO_2$ core/shell structure have been synthesized by Stopic et al. [18] for the very first time by employing multistep USP. The nanoparticles have been investigated by X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy techniques. The certainty and stability of the core/shell structure of the particles has been confirmed by comparison of the experimental data with those generated on the basis of a hard sphere core/shell model. It has been found that the mixing conditions of the Ru-containing aerosol with the $TiO_2$ particle stream have a significant impact on the core/shell structure formation. The method introduced in mentioned study [18] represents strong basis for preparation of mixed oxide materials within a single-step USP process that are difficult to be synthesized by other techniques.

Chlorine, produced by electrolysis of sodium chloride, is a base chemical with a variety of applications in the industry [19]. Dimensionally stable anodes (DSAs), electrodes consisted of Ti coated by a mixed $RuO_2$ and $TiO_2$ phase (or other additional noble metal oxides), are the most investigated material as electrocatalysts for chlorine evolution reaction [20] by chlor-alkali electrolysis (CAE). DSAs have been invented and patented for CAE by Beer [13]. Rutile $TiO_2$ has semiconductive properties with a band gap of 3 eV [21]. However, the doping of rutile $TiO_2$ with $RuO_2$, which is known as a good electronic conductor [22], improves electronic properties of $TiO_2$, introducing new electronic states in the region of the $TiO_2$ band gap [23,24]. Stability of DSAs in CAE, which is considerably improved by $TiO_2$, is their main advantage over previously used graphite electrodes [14].

Despite various synthesis procedures reported and analyzed in previous paragraphs, there is still continuous need to increase the activity/stability cost benefit by decreasing the amount of noble metal oxide components in carefully processed coating of DSA. In order to improve the anode performance, the suitable and facile procedures for the generation of a highly uniform coating are still to be reached. This equally concerns controllable synthesis of the mixed oxides and their appropriate deposition as coatings on Ti. The beneficial properties of the $RuO_2/TiO_2$ mixed oxide could be achieved by development of highly uniform multicomponent metal oxide structure (uniformly spherical, of bottom-stabilizing/top-active hierarchy [18]) by DSA-innovative joint USP process and consecutive coating deposition. The desired hierarchy is expected to bring benefits in noble metal savings since it is finely dispersed in a low-amount, highly reactive form over a less noble, inert, but stabilizing, $TiO_2$ component.

The aim of this work is to develop a new continuous process for the synthesis of $RuO_2/TiO_2$ particles and their electrochemical characterization, and subsequent coating deposition process onto industrial expanded titanium substrate in an electrostatic field. This approach for the preparation of DSAs within completely continuous process has not been considered so far. In order to develop this process, the two reactors were independently constructed and batched, for continuous USP [18] and coating deposition in electrostatic field at elevated temperatures, respectively. In order to characterize the USP-synthesized $RuO_2/TiO_2$ material for its basic electrochemical properties at a lab-scale level, the as-prepared material has been used for traditional preparation of a DSA. Such an anode has been subjected to the typical cyclic voltammetry measurements, polarization measurements for oxygen and chlorine evolution reaction, as well as for accelerated stability test in diluted chloride solution. The large-scale electrostatically prepared industrial anode, not suitable for relevant laboratory testing, is transferred to industrial environment and is being continuously monitored for its performance in CAE cell.

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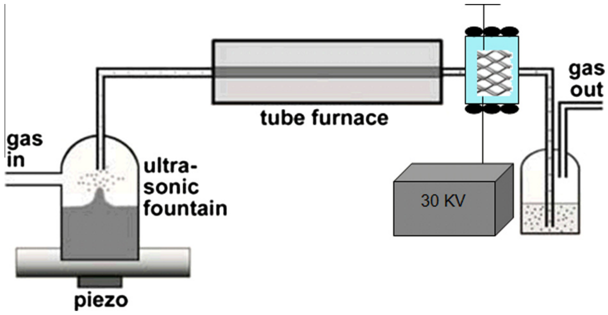

**Fig. 1.** Experimental setup for the synthesis of $RuO_2/TiO_2$ particles and their deposition on Ti by electrostatic field.

## 2. Experimental

### 2.1. Materials and procedure

Tetra-*n*-butyl orthotitanate, ruthenium(III) chloride hydrate and hydrochloric acid were used as precursors for the synthesis of $RuO_2/TiO_2$ particles USP using the equipment shown schematically in Fig. 1. All chemicals were from Merck, Germany.

The experimental setup is based on the following procedure: finely dispersed $TiO_2$ is prepared by hydrolysis of tetra-*n*-butylorthotitanate in the ultrasonic atomizer in the presence of an appropriate amount of ruthenium(III) chloride for 25:75 Ru:Ti mole ratio. Prepared $TiO_2$ suspension, along with ruthenium(III) chloride, is afterwards driven by $O_2$ as a carrier gas through tube furnace. Hence, the simultaneous conversion of Ru chloride to oxide and the transformation to crystalline structure of both $TiO_2$ and $RuO_2$ are expected at elevated temperature in tube furnace. These are known usual transformations in calcinations of corresponding precursors into binary Ru and Ti oxide [25,26].

The most important parts of the equipment for synthesis are within the first reactor, consisted of the ultrasonic atomizer and the tube furnace with three separated heating zones. The temperature and pressure control was adjusted using three independent thermostats/vacuum pumps assemblies. Fountainization of the obtained solution mixture of precursors took place at room temperature in an ultrasonic atomizer (Gapusol 9001, RBI/France) with one transducer to create the aerosol. With regards to our previous results, the resonant frequency was selected to be 2.5 MHz. Under spray pyrolysis conditions, the oxygen carrying the fine droplets of precursors is passing continuously through the tube furnace (Thermostar, Aachen) at a flow rate of the 3 L/min in order to transfer the precursors to mixed oxide at 800 °C. After formation of $RuO_2/TiO_2$, the produced particles were transferred to second reactor in order to coat an expanded titanium anode in an electrostatic field with high voltage of 30 kV at 500 °C, as shown at Fig. 2. Owing to surface charge of the particles, they are electrostatically collected at the expanded titanium by application of high intensity electrostatic field and simultaneously thermally treated in order to insure the particles adhesion and structure stability. The electrostatic field was generated by a high voltage device (30 kV, 0.08 mA) from Eltex, Elektrostatik-GmbH, Weil am Rhein, Germany.

$RuO_2/TiO_2$ particles, which are not deposited on a titanium anode, were collected in a bottle filled by water (Fig. 1).

Expanded titanium is inserted (Fig. 2a) in a specially constructed furnace (second reactor) made of quartz (Fig. 2b). Electric field is generated at the temperature of 500 °C by titanium and an auxiliary plate as the poles of the field. Sand-blasted expanded titanium (mechanically cleaned) was treated with oxalic acid prior to mounting into the second reactor, in order to remove passive film and to degrease the surface, which enables a better adhesion of formed particles to the anode surface.

### 2.2. Microscopic and spectroscopic characterization

A scanning electron microscope (MIRA VP) from Large Chamber Scanning Electron Microscopy (SEM), Central Facility for Electron Microscopy GFE, Aachen, Germany, was used for the characterization of oxide particles incorporation into a titanium anode. SEM/energy dispersive spectroscopy (EDS) method was used to check the composition of the particles, surface appearance and cross-section of lab-scale DSA. Si(Bi) X-ray detector connected to the SEM and a multi-channel analyzer have been employed.

### 2.3. Anode preparation for electrochemical testing of $RuO_2/TiO_2$ material

A 17.5 mg cm$^{-3}$ suspension of obtained $RuO_2/TiO_2$ particles in 2-propanol was ultrasonically prepared (40 kHz, 70 W). The suspension was pasted onto the Ti rod (3 mm in diameter) up to the height 1 cm.

Before $RuO_2/TiO_2$ layer deposition, the sand-blasted titanium surface was cleaned in hot HCl for *ca.* 15 min. Coating was depos-

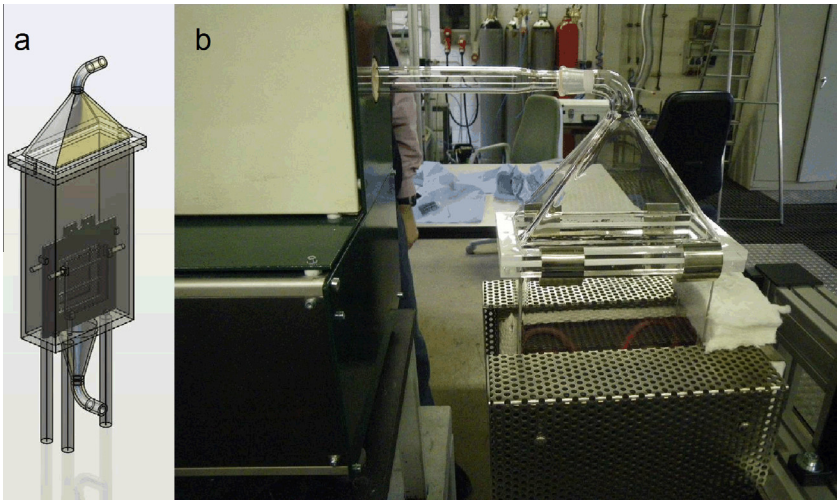

**Fig. 2.** Scheme (a) and a photograph (b) of specially constructed reactor for coating deposition from USP generated aerosol of $RuO_2/TiO_2$.

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ited from obtained suspension onto prepared Ti substrate in 6 pasting steps. After each step, the layer was dried at 120 °C and annealed at 450 °C, for 5 min. When 1 mg cm$^{-2}$ of the coating was reached, the anode was finally annealed at 450 °C for 20 min.

### 2.4. Electrochemical measurements

The $RuO_2/TiO_2$ activated titanium anode was electrochemically examined by cyclic voltammetry (CV), polarization measurements in oxygen (OER) and chlorine evolution reaction (CER) and by the accelerated stability test (AST). CV measurements were performed in 1 M $H_2SO_4$ aqueous solution (prepared with the distilled water) at a sweep rate of 50 mV s$^{-1}$ before and after the AST. The polarization measurements were performed quasi-stationary with an anodic sweep rate of 1 mV s$^{-1}$, in 1 M $H_2SO_4$ (OER) and 5 M NaCl (CER). The anode was pre-conditioned potentiostatically at 0.90 V *vs.* Ag/AgCl for 15 min.

The electrochemical measurements were recorded at room temperature, using SAS Bio-Logic potentiostat/galvanostat, model SP-200 (Bio-Logic SAS, Grenoble, France). Three-electrode cell consisted of Ag/AgCl reference electrode (all potentials are given in Ag/AgCl scale), platinum plate as a counter electrode and prepared $RuO_2/TiO_2/Ti$ anode as a working electrode.

AST of the prepared anode was conducted galvanostatically in 0.5 M NaCl, pH 2, 21 °C, at constant current density of 2.0 A cm$^{-2}$. Pt plate was used as a cathode. The pH was held constant by the addition of an HCl solution. The cell voltage is recorded continuously and the loss of the anode activity is indicated by time required for the cell voltage to start to increase continuously.

## 3. Results and discussion

### 3.1. SEM/EDS characterization of the coated titanium

The $RuO_2/TiO_2$ material electrostatically deposited onto expanded titanium, as well as the lab-scale $RuO_2/TiO_2$ coating, was analyzed by SEM/EDS.

The important aim was to check the morphology of obtained $RuO_2/TiO_2$ particles and their incorporation onto Ti substrate surface by electrostatic field. Fig. 3 shows the photograph of an anode, the SEM surface appearance of the Ti substrate at the beginning of the electrostatic coating deposition process and EDS spectrum of the coating. The sub-μm-sized spherical particles of $RuO_2/TiO_2$ obtained by USP method were identified at both expanded titanium coated in electrostatic field and Ti substrate for electrochemical investigations. The initialy-generated spherical particles [18] seem not suffering from morphological transformations upon subsequent depositions either by electrostatic field at elevated temperature (Fig. 3) or from a suspension by thermal treatment (Fig. 4). The particles appear adherent to the surface in clusters at the initial stage of deposition, whereas uniform coating clearly made of spheres is seen in pasting deposition procedure. Owing to the thermal treatment, the *ca.* 0.5–2 μm-wide cracks between large particle gatherings are formed (Fig. 4a). This kind of a coating morphology is different from usually registered for traditional thermally-prepared coating, having the “mud-crack” structure of the rather compact islands separated by the cracks [27,28]. The SEM image of cross-section of an activated Ti rod (Fig. 4b) shows that the coating of an average thickness of *ca.* 20 μm is formed. This thickness is considerably larger than the value expected according to applied coating amount (for 1 mg cm$^{-2}$ and projected coating composition, the approximate calculation according to the densities of oxides and system geometry gives the value of *ca.* 2 μm for ideally compact coating) and the literature data reporting the thickness of 2–3 μm [29]. This appears to be the consequence of uniform spherical structure generated by USP, which produces highly porous coating by ordered packing of the sub-micron-sized spheres. It could be beneficial for the efficient coating electrochemical performance, since the coating material is more easily accessed by the electrolyte. On the other hand, the electrolyte penetration path toward Ti substrate is considerably longer with respect to thinner, more compact, coating, which could improve the anode service life in CAE [30,31].

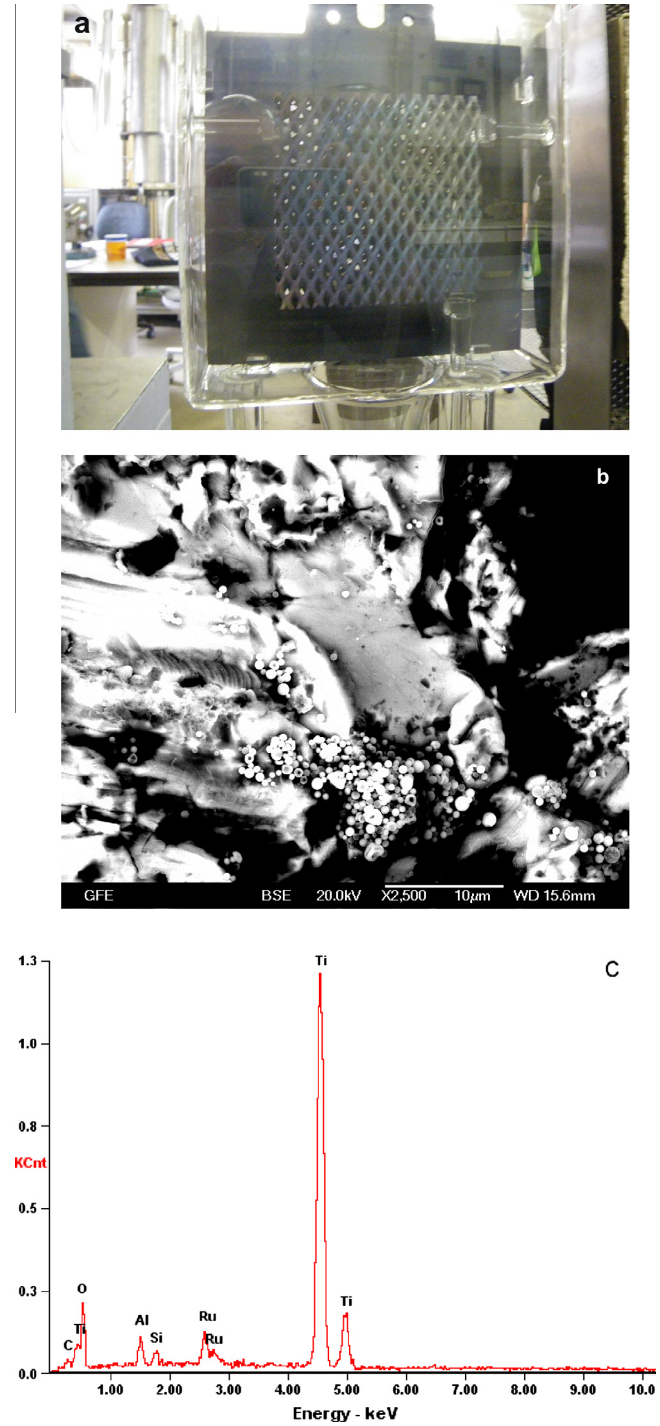

**Fig. 3.** (a) Activated titanium anode just after electrostatic deposition of the coating, (b) SEM surface appearance of the coated anode and (c) EDS analysis of the coating.

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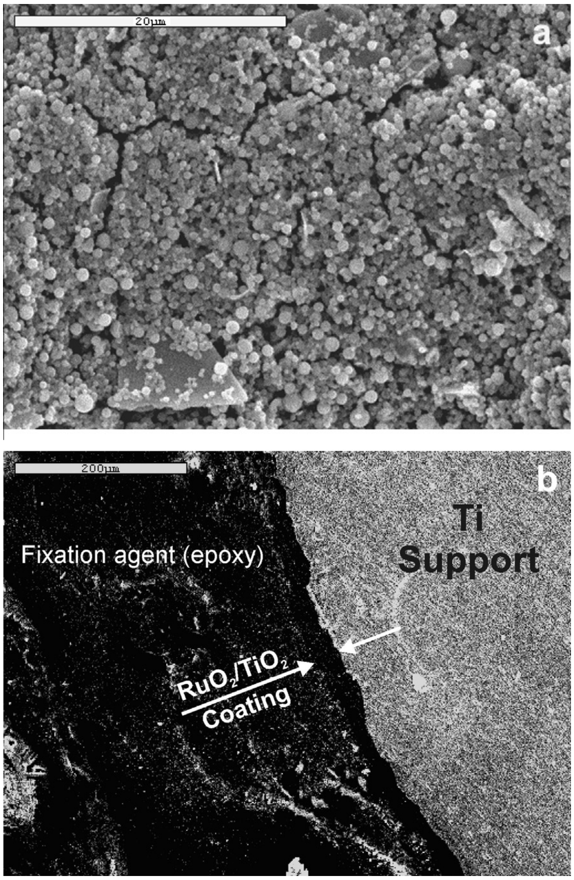

**Fig. 4.** (a) Top view and (b) cross-sectional SEM images of Ti rod with $RuO_2/TiO_2$ coating.

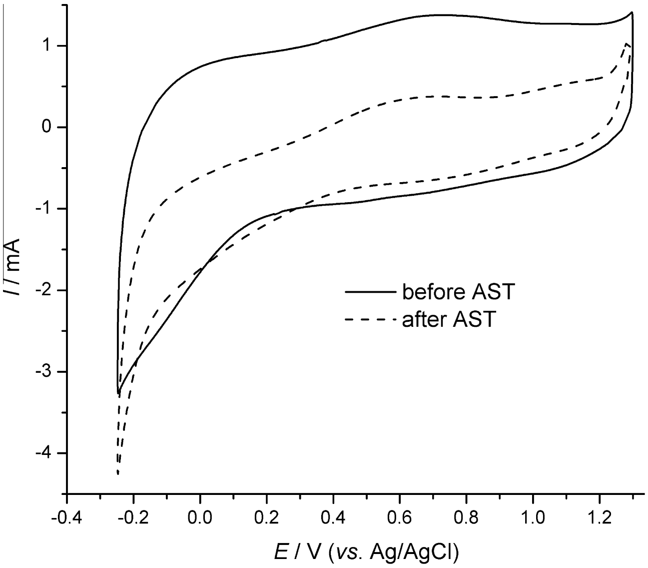

**Fig. 5.** Cyclic voltammetry curves for the $RuO_2/TiO_2/Ti$ anode, registered before and after the accelerated stability test; electrolyte: 1 M $H_2SO_4$, room temperature, sweep rate: 50 mV $s^{-1}$.

### 3.2. Electrochemical characterization

The CV curves for $RuO_2/TiO_2/Ti$ anode recorded in 1 M $H_2SO_4$ at a sweep rate of 50 mV $s^{-1}$ before and after the AST are shown in Fig. 5.

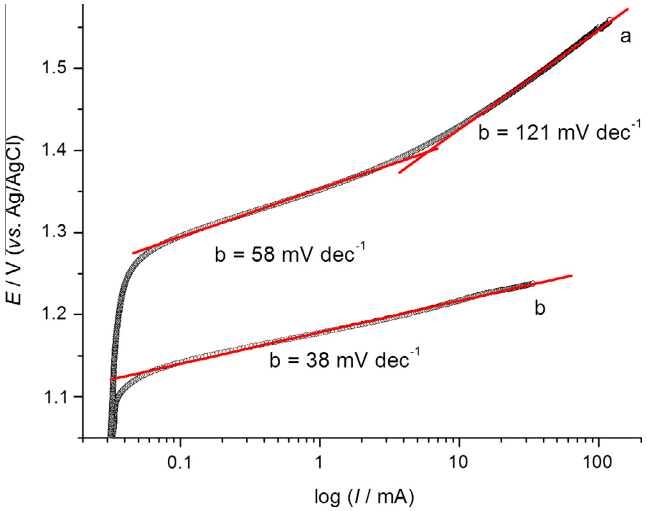

**Fig. 6.** Quasi-steady-state polarization curves for the $RuO_2/TiO_2/Ti$ anode in 1 M $H_2SO_4$ (a) and 5 M NaCl (b) solutions; room temperature, sweep rate: 1 mV $s^{-1}$.

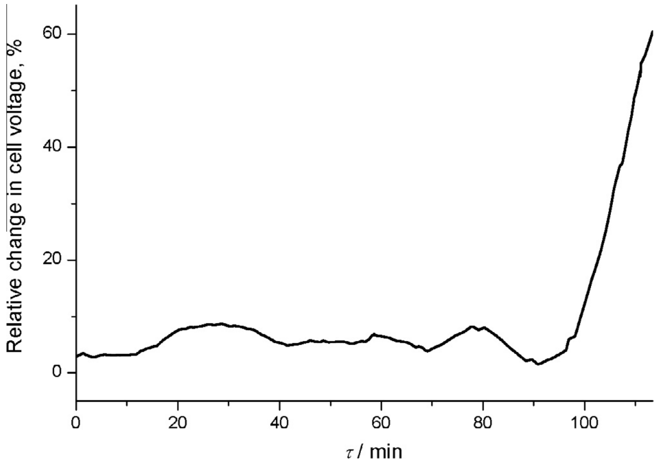

**Fig. 7.** Results of the accelerated stability test for the $RuO_2/TiO_2/Ti$ anode. Electrolyte, 0.5 M NaCl; pH 2; temperature 21 °C; $j$: 2.0 A $cm^{-2}$. Coating amount: 1 mg $cm^{-2}$.

The anode got stable response upon few CV cycles. The shape of CV curves before AST is usual for DSA-type electrodes [5,25]. There is appearance of broad redox peaks around 0.6 V, typical for well-known pseudocapacitive response of well-developed rutile structure of $RuO_2$ [32]. They are recognized as a consequence of proton-assisted solid state surface redox transition, generally presented as:

$$RuO_x(H_2O) \rightleftarrows RuO_{(x+\delta)}H_2O_{(y-\delta)} + 2\delta H^+ + 2\delta e^-, \quad 0 \leqslant \delta \leqslant x \tag{1}$$

The proton insertion into the hydrated structure of the oxide takes part during the cathodic sweep at the potentials negative to 0.2 V (Fig. 5). The corresponding ejection according to Eq. (1) is extended to rather wide potential range in subsequent anodic sweep. These CV features are quite comfortable electrochemical confirmation of typical rutile structure of investigated type of mixed oxides [33].

CV response registered after AST shows significant reduction of CV currents in comparison to those registered before AST. AST causes the changes in the coating structure: electrochemical dissolution of the $RuO_2$ as an active coating component and mechanical coating depletion, both changes leading to the decrease in $RuO_2$ amount and consequently the decrease in CV currents [30,31].

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There is also pronounced tilt of a CV after AST, suggesting high internal resistance of the sample. This is due to enrichment of the coating by insulating $TiO_2$ layer caused by $RuO_2$ dissolution and partially due to oxidation of a Ti substrate during the AST.

Quasi-steady-state polarization curves, corrected for the ohmic drop, for $O_2$ (curve a) and $Cl_2$ (curve b) evolution reactions are shown in Fig. 6.

For the oxygen reaction, the Tafel slopes for both low (<1.4 V) and high overpotential (>1.4 V) regions were observed. The Tafel slope of 60 mV $dec^{-1}$, registered below 1.4 V, shifts to 121 mV $dec^{-1}$ with increasing potential. These are usual values registered for this type of the material and confirmed by the theoretical considerations [33,34].

On the other hand, a single Tafel slope below 40 mV $dec^{-1}$ was obtained for CER. This value is in accordance with the literature data for the $RuO_2$-coated anode [13,27,35] and shows excellent electrocatalytic activity of the synthesized anode for CER. A value of 40 mV $dec^{-1}$ shows that the investigated material reflects much behavior of pure $RuO_2$ as the consequence of the characteristic $RuO_2/TiO_2$ structure.

The results of the AST are shown in Fig. 7.

As seen in Fig. 7, the cell voltage during the AST gives stable reading not exceeding the 10% of the initial value. The values increase sharply after *ca.* 100 min of the electrolysis (approx. 1 h 45 min). This time is known as estimated lifetime of anode and is comparable to lifetimes of DSA-type of anodes [27,30,31].

## 4. Conclusion

Spherical $RuO_2/TiO_2$ particles have been synthesized by single-step ultrasonic spray pyrolysis (USP) and subsequently applied within a continuous process as a coating onto expanded titanium substrate in order to prepare an industrial type of activated titanium anode. SEM/EDS analysis showed that the particles appear adherent to the surface, arranged in clusters without substantial changes of the initial particle texture. This texture is preserved also when the suspension of the particles is applied to coat Ti for the investigation of $RuO_2/TiO_2$ electrochemical properties. Owing to defined spherical structure, the coating appears much thicker for a given coating mass.

The investigation of basic electrochemical properties of the synthesized $RuO_2/TiO_2$ coating showed that the USP coating is of typical electrochemical properties for activated titanium anodes. It shows good electrocatalytic activity for oxygen and chlorine evolution reactions and acceptable stability in electrolysis of diluted chloride solutions.

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