Arabian Journal of Chemistry (2021) **14**, 103101

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Novel multifunctional two layer catalytic activated titanium electrodes for various technological and environmental processes

Vesna Krstić [a,b,*], **Branka Pešovski** [b,*]

[a] *Mining and Metallurgy Institute Bor, Zeleni Bulevar 35, 19210 Bor, Serbia*
[b] *University of Belgrade, Technical Faculty Bor, VJ 12, 19210 Bor, Serbia*

KEYWORDS

Surface modified anode;
Mixed metal oxide layers;
Electrocatalysis;
Crotonaldehyde hydrogenation;
Heterogeneous catalysis;
Wastewater treatment

Abstract In this review article different systems of dimensionally stable electrodes (DSEs) are presented with an emphasis on the application of catalytic activated titanium electrodes with a double layer platinum-group of metals (PGMs). The role of platinum metals mixed oxides (RuO_2, IrO_2, TiO_2) as excellent catalysts on the surface of dimensionally stable anodes (DSAs) and a wide area of their application in various technological processes such as electrochemical engineering, wastewater treatment, degradation of pollutants, crotonaldehyde hydrogenation and fuel cells development has also been discussed. A method of forming new electrodes by using aqueous solutions of PGM chlorides which are placed on the surface of titanium substrate is also shown in this work. Very good bonding properties between the layers and the substrate contribute to the long working period of the above mentioned electrodes. One of the possible processes of surface modification of the new titanium DSAs could be the alloying of the above mentioned platinum metals on specific catalyst supports at low temperatures for the reaction of hydrogenation of crotonaldehyde. The application of DSAs could enable lower power consumption for obtaining copper and other heavy metals using electrolysis and could give cleaner deposits. On the other hand, to remove copper and other heavy metals from mining wastewater using electrolysis results in less environmental pollution.

1. Introduction

Research in the field of the electrochemical and electrocatalytic behavior of different electrode materials, primarily insoluble anodes, opens up new possibilities for the application of platinum metals in their production. Bearing in mind the current knowledge in this area, it should be noted that the variety of appropriate materials for the production of insoluble anodes in earlier periods of research related to the use of graphite anodes (Janssen, 1974), various ferrous alloys, non-ferrous

---

[*] Corresponding authors.
E-mail addresses: vesna.krstic@irmbor.co.rs (V. Krstić), branka.pesovski@irmbor.co.rs (B. Pešovski).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.arabjc.2021.103101

alloys (Spasojević et al., 2013), the platinum-group of metal alloys, lead anodes (McBurney and Gabe, 1979; Bagshaw and Wright, 1992), and platinum and titanium anodes (Gabe, 1981). Many electro-catalytic processes, especially those that take place in extremely unfavorable conditions, such as wastewater treatment (Krstić et al., 2018; Krstić, 2021), chlor-alkali electrolysis, electrochemical deposition of non ferrous and precious metals, require the development and application of a new insoluble and electro-catalytic activated anode, and this is therefore a new area for the development of modern electrochemistry. It was found in an earlier period of research that as platinum, because of its nobility and catalytic ability can withstand working in extremely adverse corrosion conditions, its use as an anode material was in the form of electrochemically platinised titanium electrodes (Vijh, 1981; Brauer and Grube, 1981; Brauer and Grube, 1981). Recent progress in electrocatalysis has attracted extensive attention for its opportunities in converting chemical energy of fuel cells into electrical energy (Elezovic et al., 2015; Gojković et al., 2010). This new knowledge indicates a better way to rationally design and produce noble metal-based nanostructures and to optimize nanocatalysts from the viewpoint of surface and interface engineering, in terms of both cost and performance (Wang et al., 2015). It is known that the market price of platinum is very high. Therefore the development of new manufacturing techniques using a nano catalyst with a reduced Pt content and good catalytic properties of its surface is the priority in this area of science (White et al., 2009; Jung et al., 2010). Today industrial electrochemical processes are increasingly using a corrosion resistant dimensionally stable electrode (DSE). Titanium electrode surfaces activated with a layer of mixed platinum metals oxides are among the DSEs. These electrodes have excellent electrocatalytic, electro-mechanical and corrosion properties (Zhang et al., 2017; Balko, 1991), and by working with DSEs high efficiency could be achieved and could yield an excellent quality metal deposit. Modern research into mixed metal oxides (MMO) anodes for electrochemical oxidation of organic pollutants in water include the use of different types of MMO anodes, different types of support, and the combination of mixed oxides (Wu et al., 2014; Krstić, 2021). DSAs based on mixed oxides of the platinum metals group on the titanium substrate have found wide application in wastewater treatment, in organic chemical and pharmaceutical industries. Various types of recalcitrant organic pollutants which can be degraded by MMO anodes are pesticides and herbicides (Malpass et al., 2006, Pesovski et al., 2007), phenolic compounds (Wang and Wang, 2008), plasticizers (Wang et al., 2010), chelating agents (Pinhedo et al., 2005; Li et al., 2013a,b,c; Shao et al., 2006) and microcystin toxins (Shi et al., 2005).

The obtaining of unsaturated alcohols by selective hydrogenation of α,β-unsaturated aldehyde, such as crotonaldehyde ($CH_3{-}CH{=}CH{-}CHO$ or but-2-enal), is a very important reaction in industry and attracts much interest for fundamental research in catalysis (Ponec, 1997; Delbecq et al., 2016; Marinelli and Ponec, 1995; Claus and Hofmeister 1999; Mohr et al., 2003; Krstić, 2021). One important step is the selective hydrogenation of the carbonyl bond ($C{=}O$) to obtain crotyl alcohol, when the olefin ($C{=}C$) bond remains unaffected. This reaction is good for investigation and controls the intermolecular ability of catalytic activity and the selectivity of monometallic catalysts (Bachiller-Baeza et al., 2001; Bailie et al., 2001; Gutierrez et al., 2012; Ramos-Fernández et al., 2010; Reyes et al., 2000; Ruiz-Martínez et al., 2008), as well as influencing by the addition of a second metal (bimetallic or promoter) (Blanco et al., 2008; Delbecq and Sautet, 2003; Margitfalvi et al., 1998; Merlo et al., 2006; Silvestre-Albero et al., 2006) in order to improve the catalysts' selectivity to crotyl alcohol (Claus, 1998; Gallezot and Richard, 1998). The influence of the support on which the active catalytic phase is incorporated (Vannice, 1975, 1990; Tauster et al., 1978; Ruppert and Paryjczak, 2007; Dandekar and Vannice, 1999; Abid et al., 2006; Serrano-Ruiz et al., 2006; Vannice and Sen, 1989), also plays an important role in understanding the catalysts' function mechanism. Their synthesis and characterization contribute to the function and stability (Ammari et al., 2004; Blanco-Delgado et al., 2011; Liberkova et al., 2002; Lin et al., 2015; Ramos-Fernández et al., 2008a,b; Sen and Vannice, 1988; Sepulveda-Escribano et al., 1998) as well as a better understanding of the working mechanisms of the catalytic processes.

Titanium as a support of catalysts and a material with excellent physical and chemical characteristics and oxide layers to improve its performance, found an important place in the study of materials suitable for work in a variety of adverse conditions. Diebold (2003) has made a significant contribution to research, working on a comprehensive study that deals with the TiO_2 surface. A review of bioanalysis with mesoporous TiO_2 materials was made by Dai and Ju (2012). They concluded that TiO_2 has enormous significance in the field of technological development in electronic devices because of its electrical and semiconductor properties. As a semiconductor material TiO_2 offers a wide range of applications, including biosensors and catalysis (Astuti et al., 2009; Bao et al., 2008; Fattakhova-Rohlfing et al., 2007; Lu et al., 2006; Jia et al., 2008; Roddick-Lanzilotta and McQuillan, 2000; Liu and Chen, 2005). A hybrid supporting material for Pt-based catalysts consisting of TiO_2 and nanostructured carbon was developed to improve the electronic conductivity of Pt catalysts (Huang et al., 2014). Jiang et al. (2012) has reported that combined TiO_2 substrates with carbon materials improved the electrical conductivity of Pt-based catalysts and Pt/TiO_2-C catalysts and showed excellent electrochemical properties when tested under direct methanol fuel cells (DMFCs) conditions.

In recent years, to improve the characteristics of lead anodes as electrolytic materials, a significant number of researchers have been working (Hrussanova et al., 2001; Huang et al., 2010; Ma et al., 2016; Nidola, 1989; Zhang and Houlachi, 2010; Zhou et al., 2017; Ivanov et al., 2000a; Ivanov et al., 2000b). Clancy et al. (2013) gave an overview of the possibilities for alloying Pb and their electrochemical influence in electrowinning. The biggest costs in copper production are costs of electrolysis. Therefore great efforts are continuously being made in research to obtain the copper at a lower price (Haghighi et al., 2013; Nikoloski and Barmi, 2013; Najminoori et al., 2015; Ehsani et al., 2016; Ciumag et al., 2016).

The aim of this review paper is to propose possibilities to improve the working parameters in copper electrolysis, as well as to remove the copper from mining wastewater. For this reason, the results of surface modification, which are the active form of electro-catalytic anode surface of new DSE, will be considered. It is shown that surface alloying of platinum metals on specific catalysts at low temperatures, is one of the possible surface catalytic DSE modifications. Different ways of titanium surface modification, as the material with excellent characteristics for use in the copper electrolysis process, would contribute to obtaining the lower price of copper and its better quality. In this way, the impact on the environment contamination would be significantly reduced.

2. General characteristics and application of titanium dimensionally stable anode

Due to its physical and chemical characteristics, titanium is suitable anode material used as a substrate on thin coatings and activated titanium anodes. On this point, it is interesting to note the electrochemistry of titanium, on which a lot of research was done in the seventies (Vijh, 1981). Titanium is considered a base metal (Ti^{2+}/Ti, $E^0 = -1{,}63$ V) in normal use, but when it is used in the chemical and electrochemical conditions allowing the formation of a single oxide TiO_2, it may have a noble character, since it is sensitive to modifications, and therefore is an interesting anode material (Wu et al., 2014; Diebold, 2003). Potential–pH diagram in Fig. 1 shows that the TiO_2 is stable in the full range of pH in the anodic conditions, except for the HF with the catalytic participation of a minimum amount of platinum in the solution (Gabe, 1981).

When used in electrochemistry, the downside of titanium electrodes is the high electrode potential of oxygen and hydrogen separation (Vijh, 1981). However, the galvanic applying of a thin layer of anodic platinum protects titanium from corrosion in the solutions and provides greater electrical conductivity of the TiO_2 film formed on the surface of the titanium electrodes. These titanium properties can also be achieved by adding platinum metals cations in electrolyte and/or alloying of titanium with platinum metals.

It is known that the platinum ions in the solution may act as titanium corrosion inhibitors. Studies have shown that traces of platinum (10^{-6} g ions L^{-1}) are sufficient to reduce the corrosion of titanium to a negligible degree. For this purpose, initially Pt, Pd and Au were used. In a further phase of the study it was considered that the alloying of titanium with platinum and precious metals is the preferred application method of these metals for titanium processing. The required amount of alloying metals was 0.1–0.5 wt% depending on the selected metals (Vijh, 1981; Diebold, 2003; Krstić 2021). However, as only the surface properties of titanium electrodes are required, rather than their total mass, the alloying of mass is proved to be an uneconomical method for protecting titanium anodes.

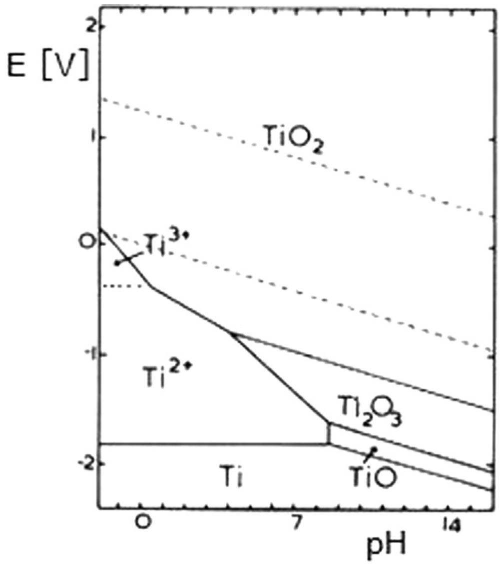


Fig. 1 Potential–pH diagram for the Ti-H_2O system at 25 °C (Gabe, 1981).

3. Titanium anodes with mixed metal oxide layers

Modern electrochemical studies in recent decades have opened the possibility for the development of a special direction for the study of the mixed metal oxide coatings. This group of electrode materials, known as MMO coatings, was primarily studied in the processes of chlorine and chlorate electro-synthesis (Eberil et al., 2000; Hansen et al., 2010; Lassali et al., 1994; Yi et al., 2007), where high density and current efficiency are required. Because of their good properties, such as corrosion and general chemical stability, catalytic power, mechanical strength and relatively easy fabrication, they are now used in various electrochemical processes such as wastewater treatment, which also speeds up their further development (Evdokimov, 2001; Spasojević et al., 2006, 2012, 1987; Krstajić et al., 1984, 1986; Pavlović et al., 1988).

Beer and Magnetochemie (1970), as explained in his patent, referred to the composition of the mixed metal oxide coatings. The essence is in the electrode of conductive metal such as Ti, Ta, Zr, Bi, Nb, W or their alloys, with oxide film formed on its surface. The surface of these metals is coated with a crystalline metal oxide mixture, containing about 50 mol.% of thin film layer, together with the platinum metals such as Ru, Rh and Pt, and Cu, Ni and Pb are also possible. In the early period of their study, a typical method of production involves the use of titanium chloride ($TiCl_3$) and ruthenium chloride ($RuCl_3$), which are coated on previously prepared titanium electrodes by sand blasting, degreasing and etching. This is followed by solvent evaporation and by heat treatment for 15 min to 2 h under different temperature modes from 300 to 800 °C. Factors that affect the service life of these electrodes are: the composition of mixture oxide, the size of their particles, the total thickness of the oxide layer, and calcinations conditions. The presence of $TiCl_3$ in the mixture is necessary, because TiO_2 on the surface increases the adhesion of RuO_2 (Vijh, 1981; Gabe, 1981). In addition to applications in the chlor-alkali electrolysis (Eberil et al., 2000), today these electrodes are increasingly used in various galvanic processes, where pure electrolytes and cleaner cathode metal deposits are needed. Over-voltage of oxygen separation on these anodes is much lower, which affects the greater energy savings (Kiros et al., 2006).

Surface activated titanium anodes are now increasingly used as a substitute for all other types of dimensionally stable electrodes, primarily expensive anodes with a coating of platinum, and Ru, Ir, Ti oxide (Barison et al., 2000, 2004). Modern electrochemistry is still focused on their research using different methods and combinations of platinum metals, usually on a titanium substrate. Bearing in mind the limited resources of raw materials, as well as the high price of platinum, aspirations in further research are focused on a more economical consumption of platinum metals, to achieve the best possible results for their application. High cost and a limited supply of Pt, and the reducing of the Pt loadings are a fundamental requirement for hydrogen and fuel cells production (Fontelles-Carceller et al., 2017), reduction of nitrate in water (Soares et al., 2012) etc. Different synthesis methods to reduce the Pt content have been reported (Vignarooban et al., 2015; Mukerjee and Srinivasan, 1993).

Electrolysis is an important final reducing phase of electrochemical copper production. The basis for this kind of assertion is in enhancing treatment of low copper ores percentage by leaching on the crowd, followed by solvent extraction and electrolysis. There is continuing research into bio-hydrometallurgical processes for the treatment of copper sulphide concentrates. These processes will have great advantages in terms of energy savings and the protection of the environment. In all these processes electrolysis is an inevitable procedure (Nikoloski and Barmi, 2013; Najminoori et al., 2015; Ehsani et al., 2016). Numerous improvements to increase copper production ensure the future application of the electrolytic processes (Haghighi et al., 2013; Nikoloski and Barmi, 2013; Najminoori et al., 2015; Ehsani et al., 2016; Ciumag et al., 2016), and therefore the application of new DSAs.

The production of the copper cathode by leaching on the crowd (mostly oxide ores), using techniques of solvent extraction and electrolysis with insoluble anodes, has significantly increased in recent years. By using these methods, about 20% of the total world production of copper is obtained, and it is estimated that until 2020 this percentage will increase to 40% (Cooper, 1985; Gilbertson, 2000).

Leaching of large quantities of poor sulphide and oxide ore on piles, aided by rapid development of bio-leaching processes of sulphide concentrates by solvent extraction and electrolysis, contributes to an increase in copper production with certain advantages, when compared to pyrometallurgical production, in terms of investment and production costs as well as environmental benefits.

The main and the greatest costs in hydrometallurgical copper production are the electrolysis costs which are 8 to 10 times higher than with electrolytic refining of copper anodes (2 kWh kg^{-1} compared to 0.25 kWh kg^{-1}) (Gilbertson, 2000). High consumption of electric energy in the electrolysis process is a problem for many researchers who have worked and strive to optimize the process. The consumption of electricity in electrolysis can be reduced by the reduction of the voltage on the cell, by reducing the oxygen over-voltage and/or by changing the anode reaction.

3.1. Dimensionally stable titanium anodes

The industrial success of and the successive rapid development in the field of fundamental research into the new DSA® materials is one of the greatest technological inventions of the last 50 years in electrochemistry. Many scientists have contributed towards the development of these new materials and among them a significant place belongs to Trasatti (2000). His work in the field of electrocatalysis, using PGMs for obtaining dimensionally stable electrode materials, contributes to a better understanding of the properties that make these materials so interesting.

Cornell et al. (2003) has investigated ruthenium based DSA® in chlorate electrolyte using rotating discs made from commercial electrodes. The obtained potential and current density of bending curves has been defined as the critical potential, E_{cr}, and the critical current density, i_{cr}. New anodes operate at a relatively high potential, $> E_{cr}$. An increase in real surface area and thereby a decrease in anode potential, has an effect on the selectivity for oxygen formation at the beginning of the working process.

Stainless steel is also used as a material for DSAs. For this reason Olsson and Landolt (2003) have studied the chemistry of passive films on stainless steels, perfecting in situ methods for the study of passive films with atomic resolution, obtaining real time information on film chemistry and their growth. *In situ* investigations indicate that charge transfer at the metal/film or the film/solution interface limits the rate of film growth on stainless steels at short times. The passive film growth occurs in seconds or minutes, but long range film forming is a slower process which takes several hours. Oxide film composition confirms the similar rating of in situ techniques with previous data obtained with *ex situ* techniques.

Graphite electrode materials also have found their use as DSAs. Pace and Stauter (1974) examined the electrolysis of copper from the synthetic electrolyte with a high content of copper and at the same time they introduced SO_2 into the electrolyte in the presence of the graphite electrode. They showed that the copper cathodes can be manufactured with a higher current efficiency than a current in a conventional electrolytic practice from the electrolyte with the copper content ranges from 1 to 2 mol L^{-3} in the presence of iron at 10 g L^{-3}. A significant reduction in the cell voltage in the electrolysis of copper may occur if the conventional anodic reaction is replaced with reactions (1) and (2), with the standard reduction potentials in aqueous solution at 25 ℃:

$$2H_2O + SO_2 = SO_4^{2-} + 4H^+ + 2e^- \quad (\mathrm{E}^0 = +0.2\ \mathrm{V}) \tag{1}$$

$$Fe^{2+} = Fe^{3+} + e^- \quad (\mathrm{E}^0 = +0.771\ \mathrm{V}) \tag{2}$$

Oxidation reactions using SO_2 and reactions of conventional oxygen separation based on the thermodynamic values related with (3) and (4) reactions:

cell reaction to - SO_2 process:

$$CuSO_4 + H_2SO_3 + H_2O = Cu + 2H_2SO_4 \tag{3}$$

$\Delta H^0 = -77.28$ kJ mol^{-1} Cu
$\Delta G^0 = -31.76$ kJ mol^{-1} Cu

cell reaction to - conventional process:

$$CuSO_4 + H_2O = Cu + 1/2\,O_2 + H_2SO_4 \tag{4}$$

$\Delta H^0 = +221.46$ kJ mol^{-1} Cu
$\Delta G^0 = -172.21$ kJ mol^{-1} Cu

The enthalpy difference between the two reactions in the copper amount of 298.74 kJ mol^{-1} is in favor of the SO_2 reaction. In this case, the power consumption is less than 1.3 kWh t^{-1} of copper for the SO_2 process. Based on the free energy reaction, it can be shown that the SO_2 process takes place at the theoretical potential that is lower for 1.05 V than the conventional electrolysis process. Quite slow oxidation kinetics using sulfur dioxide, particularly at higher current densities, do not significantly reduce the anode voltage and do not show the advantages indicated by thermodynamic analysis. Dependencies of the anodic polarization from agitation electrolyte by aeration on the anode surface, and mechanical oscillations of the anode, have made it possible to examine and improve the transfer of fero ions (Pace and Stauter, 1974).

Devilliers and Mahe (2010) have investigated the selective electrodeposition of lead dioxide on Ti/TiO_2 substrates. They concluded that there is a drastic decrease of the resistance of the electrode when a PbO_2 layer is electrodeposited onto a Ti/TiO_2 structure of such electrodes. This would enable the preparation and the application of these electrodes as a cheaper variant of DSAs. It is known that the presence of the passive layer of titanium oxide on the DSA surface may cause the corrosion resistance and surface passivation. Precisely because of this passive layer, titanium cannot be used directly as the anode material. Modification of the surface of a Ti/TiO_2 substrate may lead to the formation of new electrode materials such as Ti/TiO_2/M or Ti/TiO_2/OX, in which M is a metal such as platinum and the platinum group of metals and OX a conducting oxide with electrocatalytic properties (Devilliers and Mahe, 2010).

Forty et al. (2001) prepared a new ternary coating of DSA®-type coatings with nominal composition $Ti/Ru_{0.3}$-$Ti_{(0.7-x)}Sn_xO_2$ deposited on a Ti substrate by thermal decomposition of $RuCl_3$ and polymeric precursors of Sn and Ti at 400 °C. Compared with a traditional method of thermal decomposition of the chloride salts, they found that the polymeric precursor maintains a good yield between the nominal and experimental composition and a higher coating stability, which has been confirmed by accelerated life tests in 1.0 mol L^{-3} of aqueous $HClO_4$ and an anodic current of 400 mA cm^{-2}. Such DSAs, based on ternary oxides show high stability during the oxygen evolution reaction (OER).

Cestarolli and De Andrade (2003) examined a similar ternary coating electrode system with the nominal composition of $Ti/Ru_{0.3}Pb_{(0.7-x)}Ti_xO_2$ ($0 \leq x \leq 0.7$), deposited on Ti. They found that the replacing of Ti with Pb extends the service life and gives better catalytic activity for OER, and the heat treatment at 550 °C gives a higher coating stability. The new electrode was prepared by the thermal decomposition of Ru, Ti and Pb inorganic salts dissolved in isopropanol. Electrochemical analyses were conducted in an acid medium containing $HClO_4$ and H_2SO_4. They investigated changes in the temperature of heat treatment, heating time and the supporting electrolyte in order to obtain optimal parameters for application in electrolysis processes.

Gueneau et al. (2003) investigated the morphology, composition and the electrical and electrochemical behavior of the anodic microporous layer which is prepared by the galvanostatic anodisation of Ti, followed by galvanostatic deposition of Pt or Ir. It was found that Pt is deposited within some of the micropores of the oxide film, whereas Ir is deposited preferentially on the top surface by forming Ti/TiO_2/Ir new electrode. It was also found that the electrochemically formed hydrated Ir oxide is catalytically less stable, than the iridium oxide film which is subjected to a heat treatment, and also used in Cu electrowinning. It has been observed that these electrodes function as DSAs.

3.2. *The surface modified DSA based on the mixed metal oxides layers RuO_2-TiO_2/Pt-IrO_2*

Due to the catalytic processes of nucleation and the formation of oxygen bubbles, the polarization of the anode and oxygen overvoltage are reduced. Thereby the applying of new DSAs, based on platinum metals oxides, reduces the charge of the cell about 0.35 V in comparison with lead anodes (Spasojević et al., 2012). The analysis of results by Spasojevic et al. (2006, 2012, 2013) and Pesovski et al. (2007), shows that the new anode with a double layer catalyst of RuO_2-TiO_2/Pt-IrO_2, in addition to the particular application for chloride ions anodic oxidation from the concentrated and diluted sodium chloride solution, could be used in electrowinning of Cu from acid sulphate solution.

A 10 g m^{-2} of active film on the first layer consists of a 40 mol.% RuO_2 and 60 mol.% TiO_2 and was prepared from the chloride solution of $RuCl_3 \cdot H_2O$ and $TiCl_3$ dissolved in 20% HCl (Spasojevic et al., 2012). The new, two layer electrode, was prepared from the 2% solution of H_2PtCl_6 and $IrCl_3$ (referring to pure metals) in 2-propanol, by Spasojevic et al. (2012), and was deposited onto the second layer. After deposition of the solution, the electrode was dried at 50 °C until complete evaporation of the solvent and then was heated for 10 min at 450 °C. The Pt/Ir ratio was 60/40. Anodes of RuO_2/TiO_2 degrade relatively rapidly during anodic oxygen separation from acid sulphate solution, which prevents their use in industrial plants. The resulting diffraction patterns, presented by Spasojevic et al. (2006), showed that the first layer of the optimal composition active coating consists of a RuO_2 and titanium rutile structure phase of solid solution, as illustrated in Fig. 2. XRD. Patterns recorded after thermal treatment forming a second layer, showed that the double layer film consists of RuO_2 and TiO_2 rutile structure phase of solid solution (the first layer), and of the Pt and Ir metals solid solution phase, with Ir content less than 1% in the form of rutile structure IrO_2 (second layer).

From an analysis of their results, Spasojevic et al. (2006, 2012, 2013) suggest that a new anode with a double layer RuO_2-TiO_2/Pt-IrO_2 catalysts could be used successfully, for example in the electrolytic process of copper from acid sulphate baths, as shown in Scheme 1 Pesovski et al. (2007). Applying the above mentioned anodes for copper production, a lower energy consumption per kilogram of obtained metal could be provided, resulting in cleaner copper and less environmental pollution.

Classical lead-antimony alloyed electrodes have about 350–400 mV higher oxygen separation overvoltage than new electrodes, which makes them less economical. The use of titanium anodes with an active RuO_2-TiO_2/Pt-IrO_2 film in the plating process of precious metals would result in very pure deposits, Scheme 1.

Use of electrocatalysis with MMO anodes in the electrochemical degradation of organic pollutants is one method for wastewater treatment. Table 1 shows various types for organic pollutants in wastewater treatment, which have been studied for oxidation and degradation with different MMO anodes, based on the combination of Ti-substrate and Ru, Ir or Pt metal oxides layers. With suitable MMO anodes used in the appropriate operating conditions for electrochemical oxidation, most organics can be completely removed or be in acceptable concentration levels for further treatment (Wu et al., 2014; Anjum et al., 2019).

The catalytic activity of the new double-layer electrode with RuO_2-TiO_2/IrO_2-Pt catalyst was tested for chlorine evolution reaction from acid concentrated solutions of alkali chloride. In the rapid corrosion test it was found that new anodes have about twelve times greater stability than the anode with RuO_2/

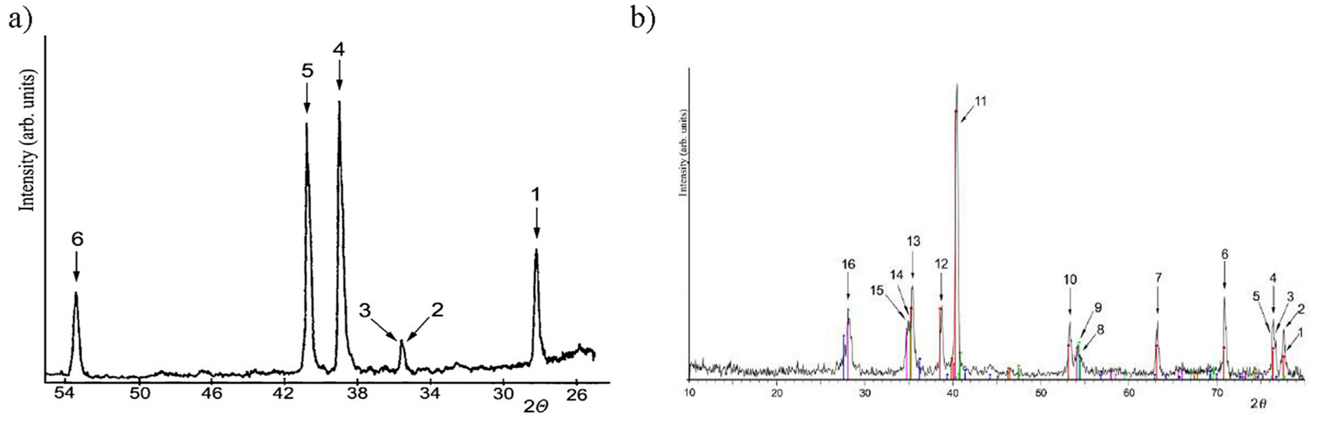
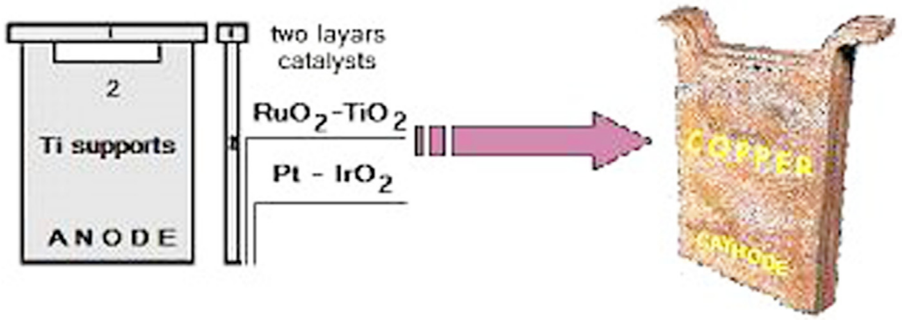


Fig. 2 XRD pattern of a: a) first coating layer of the composite electrocatalyst containing 40 mol.% RuO_2 and 60 mol.% TiO_2, and b) second coating layer of RuO_2-TiO_2/Pt-IrO_2 (Spasojevic et al., 2012).



Scheme 1 Scheme of two layer catalytic activated titanium electrode for copper obtaining and for Cu contaminated wastewater treatment.

TiO_2 film (Barison et al., 2000; Devilliers and Mahe, 2010; Evdokimov, 2001; Spasojeviæ et al., 2013; Spasojević et al., 1983, 1984). Cost effective application of these electrodes in industrial cells for chlorine production depends on the ratio of the price of platinum metal salts on the world market.

4. Surface alloying of platinum metals on specific catalysts at low temperatures

The effect of temperature reduction on the Ru-Ir/ZnO catalysts for selective hydrogenation of crotonaldehyde was examined by Yu et al. (2014). Li et al. (2013a,b,c) also examined the activity and selectivity of the catalyst for this reaction but using a Ru/ZnO catalyst with a different content of Ru and bimetallic Ru-Ir/ZnO catalyst. In comparison to the monometallic Ru/ZnO catalyst, the bimetallic Ru-Ir/ZnO catalyst showed a better performance. They concluded that the addition of Ir can effectively improve the catalytic properties, particularly the stability of the catalyst. The improved stability may be attributed to the changed electronic properties of Ru and Ir metals, forming RuIr alloy on the surface, as well as the reduction of surface acidity as compared to the Ru/ZnO catalyst. The effect of temperature reduction on the catalytic properties of Ir/TiO_2 catalyst for hydrogenation of crotonaldehyde was also examined by Chen et al. (2012). It was found that a lower temperature (300 °C) can cause a significant effect on the resulting catalytic properties, because the chemical-physical nature of the catalyst can be modified after thermal treatment.

Yu et al. (2014) studied the Ru-Ir/ZnO catalyst with the participation of 3 wt% Ru and Ir, too, at different temperatures in the range of 150 to 400 °C. The catalytic activity and selectivity were tested for the reaction of crotonaldehyde hydrogenation in gas phase at 80 °C. Characterization of surface properties was carried out by the different techniques such as XRD, XPS, NH_3–TPD and RS. Li et al. (2013a,b,c) prepared the Ru-xIr/ZnO catalysts by impregnating the support with aqueous solution of $RuCl_3$ and H_2IrCl_6. The samples were dried at 60 °C for 12 h and then calcined at 400 °C for 2 h in air.

Yu et al. (2014) presented XRD diffraction patterns of catalysts at different temperatures, as shown in Fig. 3. The diffraction peaks of ZnO support for RuIr metal phase are dominant in all the catalysts. With increasing reduction temperature, the diffraction peak ($2\theta = 44.0°$) weakens, because of the metal Ru^0, and peak at about 43.7° for RuIr alloy [JCPS 65–5982, RuIr (1 1 0) to 43.7°]. At a higher reduction temperature, intensities of two peaks become stronger. It can be concluded that an increase in reduction temperature leads to the aggregation of Ru particles and the possible formation of an RuIr alloy. Possible forming of this RuIr alloy was verified

Table 1 Some organic pollutants which can be degraded by different catalytic activated titanium MMO anodes.

	Compound	MMO anode type	Curent density(mA cm^{-2})[a]	Removal efficiency[b]	Current efficiency	Service life (h)	Reference
Phenolic compounds	Phenol	Ti/SnO2-Sb-Ru		0.82 [COD]	0.386	34	Xu et al. (2012)
		Ti/TaOx-IrOx/BiOx-TiO2/BiOx-TiO2	P	–	0.6	–	Park et al. (2012)
		Ti/TiO2-BiOx	14.7	0.60 [Phenol]	0.67	–	Park et al. (2009)
	Chlorophenol	Ti/IrO2/RuO2	39	0.9 [COD]	–	–	Wang and Wang (2008)
Nitrophenol	4-Nitrophenol	Ti/CeO2-RuO2-SnO2	20	0.86 [COD]	0.336	340	Liu et al. (2012)
	4-Nitrophenol	Ti/SnO2-Sb2O5-IrO2	P	0.75 [TOC]	0.468		Chu et al. (2012)
Pharmaceuticals, antibiotics, hormones	Acetaminophen	Ti/TiO2/RuO2 Ti/Ta$_2$O5/IrO$_2$	24–180	0.90 [COD] 0.40 [COD]			de Oliveira et al. (2011)
	Pharmaceuticals	Ti/Pt/SnO2-Sb2O4	10–30	0.17–0.82[COD]	0.45–0.88	–	Santos et al. (2013)
	Ofloxacin	Ti/IrO2/Ta2O5	20	0.30 [COD]	–	–	Carlesi Jara et al. (2007)
Pesticides andherbicides	Atrazine	Ti/Rux Sn1 − xO2	10	0.21 [COD]			Malpass et al. (2010)
		Ti/Ru0.3Ti0.7O2	10–120	0.04–0.46 [TOC]	–	–	Malpass et al. (2006, 2007)
	Carbaryl	Ti/Ru0.3Ti0.7O2	40	0.58 [COD]	–	–	Malpass et al. (2013)
	Cyanuric acid	Ti/Ru0.3Ti0.7O2	5–50	0.13–0.56[TOC]	–	–	Malpass et al. (2009)
	Glyphosate	Ti/(RuO2)0.7 (Ta2O5)0.3 Ti/Ru0.3X0.7O2 (X = Ti, Sn or Pb) Ti/Ir0.3Sn0.7O2		0.81–0.91[COD]	0.20–0.40	–	Neto and De Andrade (2009)
Chelating agents	Humic acid	Ti/TiO2-RuO2	20	0.25–0.65 [TOC]	–	–	Pinhedo et al. (2005)
	Humic acid	Ti/RuO2-IrO2	13.1–56.3	0.88 [COD]	0.30		Li et al. (2013a, b,c)
	Humic substances	Ti/TiO2-lrO2-RuO2	100	0.56 [COD]	0.15–0.65		Shao et al. (2006)
Dyes and dyeeffluent	Indigo carmine	Ti/IrO2-SnO2-Sb2 O5	5–20	0.99 [COD]	–	–	Rodríguez et al. (2013)
	Industrial dye effluent	Ti/RuO2/IrO2	10–25	0.56–1 [COD]	–	–	Raghu et al. (2009)
	Industrial dye	Ti/Ru-Ti-O	10–50	0.53–0.83	0.47–0.89	–	Basha et al. (2012)
	Methyl orange	Ti/IrO2 -SnO2 - Sb2 O5	P	0.98 [Color]	–	–	Chaiyont et al. (2013)
	Reactive Black	Ti/RuO2-IrO2	31.7	0.32 [COD]	–	–	Wu et al. (2012)
	Reactive Blue	Ti/TiO2-RuO2-IrO2	21.66	0.56 [COD]	–	–	Rajkumar et al. (2007)
	Reactive Blue	Ti/IrO2/TaO2/RuO2	16.2	0.44 [COD]	0.04–0.065	–	Karuppiah and Raju (2009)
	Reactive	Ti/SnO2-Sb-Pt	125	0.9–0.95 [COD]	–	990	del Río et al. (2010)
	Reactive Red	Ti/IrO2-RuO2	15–50	0.32–0.43[COD]	0.13	–	Panakoulias et al. (2010)
	Reactive Red	Ti/Ru0.3Ti0.7 O2	5–89	0.40–0.80[TOC]	–	–	Catanho et al. (2006)
	Selected disperse dyes	Ti/RhOx-TiO2	30	0.40 [Color]	0.1–0.2	–	Szpyrkowicz et al. (2005)
	Selected reactive dyes	Ti/SnO2-Sb-Pt	125	0.99 [Color]			Sala et al., 2012
	Selected reactive	Ti/TiO2-RuO2-IrO$_2$	72.2	0.735 [COD]	–	–	Rajkumar and

(*continued on next page*)

Table 1 (*continued*)

	Compound	MMO anode type	Curent density(mA cm^{-2})[a]	Removal efficiency[b]	Current efficiency	Service life (h)	Reference
	dyes						Kim (2006)
	Synthetic dye effluent	Ti/Ti-Pt-Ir-O	5–14	0.55–0.86	0.045–0.314	–	Chatzisymeon et al. (2006)
Plasticizers	Bisphenol-A	Ti/TiO2 -RuO2	6.5–30	0.09 [COD]	–	–	Pereira et al. (2012)
	Dietyl phthalate	Ti/IrO2/RuO2	39	0.40 [COD]	–	–	Wang et al. (2010)
Microcystin toxins	Microcystin RRMicrocystin LR	Ti/RuO2-IrO2	4.44–8.89	0.43–1 [MCRR] 0.43–1 [MLRR]	–	–	Shi et al. (2005)

[a] P - Operated at potentiostatic mode.

[b] Removal efficiency: determined by COD, TOC, Color and pollutant concentration.

by comparing the diffractograms of Ru-Ir/ZnO-400 with the Ru/ZnO-400 catalyst. The Ru-Ir/ZnO-400 catalyst shows overlapping of peaks at 43.7° and 44.0°, respectively. This confirms the possibility of alloying, while Ru/ZnO-400 only shows a weak peak at 44.0°

In a study by Li et al. 2013a TEM images were given of the reduced catalyst (see Fig. 4). Aggregations of metal particles are indicated by circles. Size distributions are also listed and help to understand more fully the possible mechanism of alloy formations.

Chen et al. (2012), showed XRD patterns of reduced Ru-xIr/ZnO catalysts at Fig. 5. They concluded that very strong diffraction peaks corresponding to ZnO catalyst support can be observed. Weak diffraction peak ($2\theta = 44.0°$) to Ru/ZnO catalyst was observed, because of the metal Ru^0. Ru-Ir/ZnO catalysts were observed as expressed lines at 43.7° and their intensity becomes stronger with increasing Ir content in the catalyst. This diffraction peak could mark the formation of the RuIr alloy [JCPS 65–5982, RuIr (1 0 1) to 43.7°]. The content of RuIr alloys increases with the addition of Ir in the catalyst, as shown in Fig. 5.

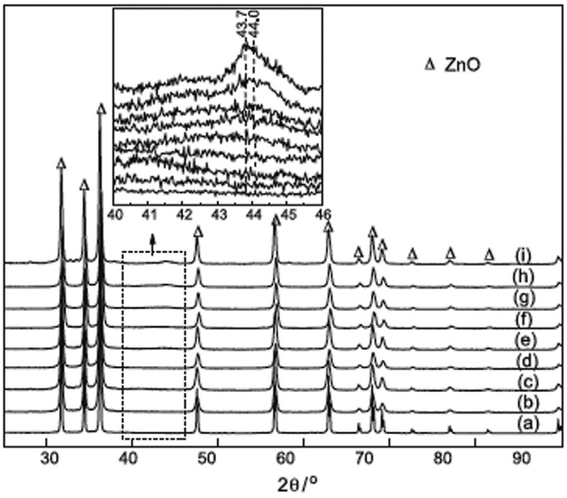


Fig. 3 XRD patterns of reduced catalyst: (a) ZnO, (b) Ir/ZnO-200, (c) Ir/ZnO-400, (d) Ru/ZnO-200, (e) Ru/ZnO-400, (f) Ru-Ir/ZnO-150, (g) Ru-Ir/ZnO-200, (h) Ru-Ir/ZnO-300 and (i) Ru-Ir/ZnO-400 (Yu et al., 2014).

Catalysts based on Ru-Ir have shown a very good catalytic ability for the reaction of hydrogenation of crotonaldehyde. For example, the Ru-Ir/ZnO-400 catalyst showed 94.6% of the selectivity to crotyl alcohol for the activity of 43%. The hydrogenation reaction of crotonaldehyde on ZnO support was explained by Yu et al. (2014) and Li et al. (2013a,b) in their work on these catalysts. Their conclusions and methods of preparation of ZnO-supported catalysts could help obtain a better understanding of the physical and chemical mechanisms on the surface of activated titanium DSAs, and could enhance the electrocatalytic properties of the anodes themselves. Such or similar methods of producing the surface modified DSAs affords the possibility of their application in different technical purposes, such as an application for wastewater treatment and/or obtaining cheaper and pure copper cathode (Elezović et al., 2010; Gojković et al., 2010). The links between the surface structure of MMOs and their electrocatalytic performances are still not clearly established in literature, and because of this, more such information is required by careful characterization with different analysis techniques (Krstajic et al., 2004).

5. Some important applications of platinum electrocatalysts and discussion

The catalytic electrode system presented, with double-layer platinum catalysts RuO_2-TiO_2/Pt-IrO_2 could be used for a variety of industrial electrochemical processes such as direct ethanol fuel cells (DEFCs) and degradation of phenols. Its application, with a further adjustment of operating parameters in a given electrochemical process, could significantly contribute to environmental protection. For example, DEFCs are very important as a power source in numerous applications due to ethanol non-toxicity and high density energy carrier, and wide availability from various kinds of biomass (Song and Tsiakaras, 2006; Antolini, 2007). In research by Camara and Iwasita (2005) it was shown that the complete electrooxidation of ethanol is a very complicated reaction because of relatively slow reaction rate on Pt, and the production of partially and incompletely oxidized acetaldehyde and acetic acid as the main products in acidic media, instead of com-

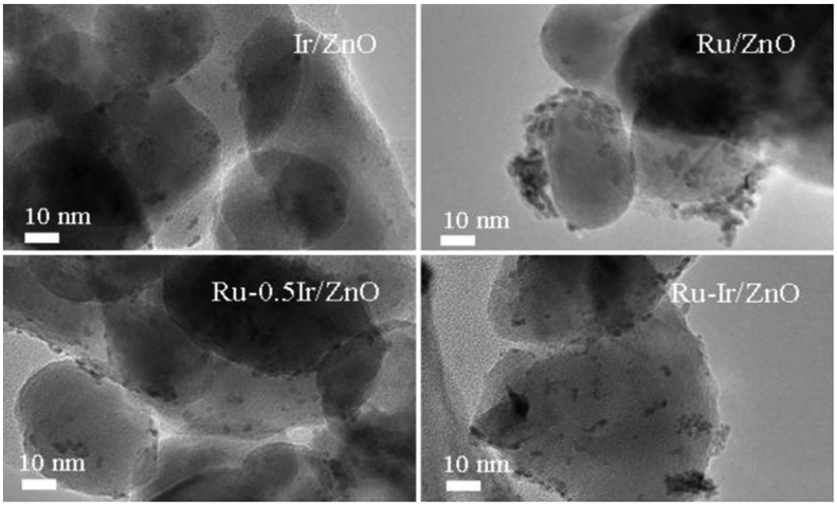


Fig. 4 TEM images of reduced catalysts: (a) Ir/ZnO-200, (b) Ru/ZnO-200, (c) Ru-Ir/ZnO-150, (d) Ru-Ir/ZnO-200, (e) Ru-Ir/ZnO-300 and (f) Ru-Ir/ZnO-400 (Yu et al., 2014).

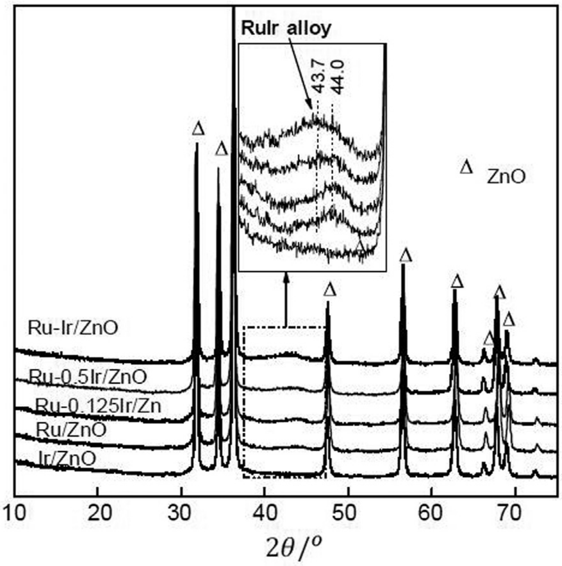


Fig. 5 XRD patterns of Ru–xIr/ZnO catalysts (Chen et al., 2012).

pletely oxidized CO_2. Therefore the development of novel catalysts with high catalytic activity for the complete oxidation of ethanol, especially anode electrocatalysts, is an important research topic for the use of ethanol as a fuel for DEFCs.

The addition of a secondary element such as Ru, Sn or Rh to Pt can enhance the ethanol oxidation reaction (Rousseau et al., 2006; Wang et al., 2007; Jiang et al., 2005; de Souza et al., 2002; Li et al., 2010), but these kinds of alloys usually show relatively low selectivity for CO_2 formation compared with Pt alone (Rousseau et al., 2006; Wang et al., 2007). de Souza et al. (2002) studied the electrochemical behavior of the ethanol on Pt, Rh, and Pt-Rh electrodes. They found that Rh has a relatively low electrocatalytic activity to ethanol oxidation. Compared with $Pt_{73}Rh_{10}$, pure Pt electrodes show similar electric current density, but this alloy has high CO_2 production activity. Li et al. (2010) found that the addition of Rh in Pt-SnO_2/C enhances the catalyst capacity to break C—C bonds, and in the same time enhances the electric current for ethanol oxidation.

Many researchers describe the use of Ir in catalysts for ethanol electro-oxidation. Cao et al. (2007) found that Ir based catalysts such as Ir_3Sn/C gave improved catalytic performances for the ethanol oxidation reaction (EOR) compared with Pt_3-Sn/C. This might be due to the formation of IrO_2 on Pt, bearing in mind that Pt-IrO_2 has been reported to be a good catalyst for the EOR (Calegaro et al., 2006). Ribeiro et al. (2007) informed that Ir and Sn co-doped catalyst $Pt_{68}Sn_9Ir_{23}$/C has also been an excellent EOR promoter. Fatih et al. (2010) synthesized a series of quaternary PtRuIrSn/C catalysts and found that $Pt_{30}Ru_{30}Ir_{10}Sn_{30}$/C catalyst gave the best performance for the complete oxidation of ethanol and excellent long-term stability. Zhao et al. (2011) prepared a series of Pt-Ir-SnO_2/C electrocatalysts by the modified Bönnemann method (Bönnemann et al., 1991; Higuchi et al., 2011). The role of each element in these catalytic activities has not been well investigated because of the complexity of the catalytic system. However, it was found that the Pt-$Ir_{0.07}$-SnO_2/C electrocatalyst showed both higher EOR current density and selectivity for CO_2 formation at 0.5 V compared with those of Pt/C and Pt-SnO_2/C at 25 °C. Adding a suitable amount of Ir to the binary Pt-SnO_2/C catalyst enhances catalytic activity during ethanol oxidation, contributing to Pt-Ir-SnO_2/C becoming an efficient catalyst for the cleavage of C–C bond of ethanol in a relatively low potential region, therefore the Pt-Ir-SnO_2/C catalyst may be an ideal catalyst for the direct ethanol fuel cells (Zhao et al., 2011; Fontelles-Carceller et al., 2017).

Examining the electrochemical degradation of 2-chlorophenol using Ti/β-PbO_2 and Ti/α-PbO_2/β-PbO_2 electrodes, Zhang et al. (2015) found that the removal rate was 100% after 180 min of electrolysis under optimal conditions. As noted, the oxygen evolution potential of a cauliflower-structured Ti/α-PbO_2/β-PbO_2 electrode is 3.1 V, which is much higher than that of Ti/β-PbO_2 (1.6 V), or 1.8 V on Ti/PbO_2 electrode that some researchers also considered (Li et al., 2011). Anodic oxygen evolution leads to losses of electrical energy in organic wastewater treatment, because the oxygen evolution is supporting a reaction that reduces the current efficiency of the organic oxidation, and oxygen evolution is an undesirable concurrent reaction (Calegaro et al., 2006). Thus, the use of an anode with high oxygen evolution overpotential favors the electrochemical oxidation of organic components. Ti/α-PbO_2/β-PbO_2 electrodes are an example of new non-platinum electrode materials that can be successfully used in wastewater treatment and environmental protection.

Conventional DSAs with a thin active layer of rutile-structured 40 mol.% RuO_2 and 60 mol.% TiO_2 nanocrystalline solid solution, coated on a titanium metal substrate by thermal deposition, have a wide use in cells for active chlorine production and in chlor-alkaline and chlorate elestrolysis (Cornell et al., 2003; Kiros et al., 2006; Yi et al., 2007; Khelifa et al., 2009; Hansen et al., 2010). These electrodes also have a high catalytic activity for oxygen evolution from acid sulphate solutions, but they are corrosion unstable and dissolve in these solutions. A titanium oxide layer, simultaneously formed on the titanium metal–coating interphase has a poor conductivity and cannot be used in metal electrowinning and in proton exchange membrane water electrolysis (Chen et al., 2011).

Modern research into DSAs is focused on coatings containing nanocrystals of metallic platinum, iridium and ruthenium dioxides, and oxides of some non-precious metals such as SnO_2, Sb_2O_5, and Ta_2O_5. The new DSAs were showing a high corrosion stability and high catalytic activity for oxygen evolution from acid sulphate solutions and therefore they have been suitable for electroplating and metal electrowinning of various non-ferrous metals, and in proton exchange membrane water electrolysis (Chen et al., 2002; Yao et al., 2007; Ye et al., 2010).

Modern research in the field of elecrolysis with insoluble anodes has achieved significant progress. Overall, the results are related to the increase of current density and reducing voltage on the cell, by using alternative types of anodes. Thus, the problem of high power consumption can be reduced by using new DSAs in electrocatalytic reactions on the surface which cause changes in anodical reactions.

Only a few examples of the use of new very significant catalytic systems have been presented, however the scope of their potential applications is very wide, indicating the need for further research on their development and for their implementation (Jović et al., 2016; Lačnjevać et al., 2015; Krstić and Pešovski, 2019) as an important link in environmental and social responsibility (Lončar et al., 2019).

6. Conclusions and future perspectives

The production of new electrodes presented in this review is based on the use of aqueous solutions of platinum metals chloride salts. The work of developing new DSA production methods will allow the use of more contemporary materials with a direct application in industrial processes, with a decrease in cost operations, an increase in product quality and affording better environmental protection. The above mentioned features of the new electrocatalytic activated anodes provide their direct application in electro-metallurgical processes, where corrosion resistant DSAs and clean electrolytes are required. These anodes could be used for the purposes of wastewater treatment, electro-plating of rhodium, chromium and heavy metals, copper, gold, in the industry of chlorine, iodine, bromine, mercury, and for membrane and hydrogen cells. Their excellent electrocatalytic properties could allow the selective cathode deposition of metals from complex electrolytes. Generally, the role of the expensive platinum and platinum group of metals in the preparation of these electrodes is of particular importance, and therefore future investigations should be directed towards their rational use.

For all these reasons, further research should be directed towards the study of the surface modification of titanium, with a special emphasis on the study of the electrocatalytic mechanisms on the surface, to discover the best solution for their application in different technologies. Contribution to this area of research will also involve studying the possibility of surface alloying of platinum metals such as Ru and Ir, on specific catalysts at low temperatures, which would further clarify the mechanisms of surface reactions of new catalytic systems.

Acknowledgements

This review was financially supported by the Ministry of Education and Science of the Republic of Serbia. The authors are grateful for Registration No. 451-03-9/2021-14/200052 . The authors also are grateful to Prof. Nicola Bolton for its overall support and the selfless assistance in the preparation of this article.

References

Abid, M., Paul-Boncour, V., Touroude, R., 2006. Pt/CeO2 catalysts in crotonaldehyde hydrogenation: Selectivity, metal particle size and SMSI states. Appl. Catal. A Gen. 297, 48–59. https://doi.org/10.1016/j.apcata.2005.08.048.

Ammari, F., Lamotte, J., Touroude, R., 2004. An emergent catalytic material: Pt/ZnO catalyst for selective hydrogenation of crotonaldehyde. J. Catal. 221, 32–42. https://doi.org/10.1016/S0021-9517(03)00290-2.

Anjum, MMiandad, R., Waqas, M., Gehany, F., Barakat, M.A.,, 2019. Remediation of wastewater using various nanomaterials. Arabian J. Chem. 12 (8), 4897–4919. https://doi.org/10.1016/j.arabjc.2016.10.004.

Antolini, E., 2007. Catalysts for direct ethanol fuel cells. J. Power Sources 170, 1–12. https://doi.org/10.1016/j.jpowsour.2007.04.009.

Astuti, Y., Topoglidis, E., Cass, A.G., Durrant, J.R., 2009. Direct spectroelectrochemistry of peroxidases immobilised on mesoporous metal oxide electrodes: Towards reagentless hydrogen peroxide sensing. Anal. Chim. Acta 648, 2–6. https://doi.org/10.1016/j.aca.2009.06.031.

Bailie, J.E., Abdullah, H.A., Anderson, J.A., Rochester, C.H., Richardson, N.V., Hodge, N., Zhang, J.G., Burrows, A., Kiely, C.J., Hutchings, G.J., 2001. Hydrogenation of but-2-enal over supported Au/ZnO catalysts. Phys. Chem. Chem. Phys. 3, 4113–4121. https://doi.org/10.1039/B103880J.

Balko, E.N.,1991. Chapter 10 - Electrochemical Applications of the Platinum Group Metals: Platinum Group Metal Coated Anodes, Stud. Inorg. Chem. 11, 267-301. https://doi.org/10.1016/B978-0-444-88189-2.50015-8.

Bao, S.J., Li, C.M., Zang, J.F., Cui, X.Q., Qiao, Y., Guo, J., 2008. New Nanostructured TiO_2 for Direct Electrochemistry and Glucose Sensor Applications. Adv. Funct. Mater. 18, 591–599. https://doi.org/10.1002/adfm.200700728.

Barison, S., Battisti, A.D., Fabrizio, M., Daollo, S., Piccirillo, C., 2000. Surface chemistry of RuO2/IrO2/TiO2 mixed-oxide electrodes: secondary ion mass spectrometric study of the changes induced by electrochemical treatment. Rapid Commun. Mass Spectrom. 14, 2165–2169. https://doi.org/10.1002/1097-0231(20001215)14:23 < 2165::AID-RCM148 > 3.0.CO;2-H.

Barison, S., Daolio, S., Fabrizio, M., Battisti, A.D., 2004. Surface chemistry study of $RuO_2/IrO_2/TiO_2$ mixed-oxide electrodes. Rapid Commun. Mass Spectrom. 18, 278–284. https://doi.org/10.1002/rcm.1326.

Beer, H.B.(Magnetochemie N.V.), British Patent 1, 195, 871, 1970.

Blanco-Delgado, C., Krstić, V.R., Pesquera-Gonzalez, C., González-Martinez, F., 2011. Modified clays, PILC'S, applied in catalysis. Chem. Ind. 65, 37–42. https://doi.org/10.2298/HEMIND100906066D.

Blanco, C., Krstic, V., Pesquera, C., Perdigon, A., González, F., 2008. Mesoporous materials as supports of Rh catalysts. Synthesis, characterization and catalytic application. Studies Surf. Sci. Catal. 174B, 1343–1346. https://doi.org/10.1016/S0167-2991(08)80138-3.

Bönnemann, H., Brijoux, W., Brinkmann, R., Dinjus, E., Joussen, T., Korall, B., 1991. Formation of Colloidal Transition Metals in Organic Phases and Their Application in Catalysis. Angew. Chem. Int. Ed. Engl. 30, 1312–1314. https://doi.org/10.1002/anie.199113121.

Brauer, G., Grube, H. J., Handbuch der Preparativen Anorganischen Chemie, Stuttgart, 1981, pp. 1704-1751

Bachiller-Baeza, B., Rodríguez-Ramos, I., Guerrero-Ruiz, A., 2001. Influence of Mg and Ce addition to ruthenium based catalysts used in the selective hydrogenation of α,β-unsaturated aldehydes. Appl. Catal. A: Gen. 205, 227–237. https://doi.org/10.1016/S0926-860X(00)00562-7.

Calegaro, M.L., Suffredini, H.B., Machado, S.A.S., Avaca, L.A., 2006. Preparation, characterization and utilization of a new electrocatalyst for ethanol oxidation obtained by the sol–gel method. J. Power. Sources 156, 300–305. https://doi.org/10.1016/j.jpowsour.2005.06.015.

Carlesi Jara, C., Fino, D., Specchia, V., Saracco, G., Spinelli, P., 2007. Electrochemical removal of antibiotics from wastewaters. Appl. Catal. B Environ. 70, 479–487. https://doi.org/10.1016/j.apcatb.2005.11.035.

Camara, G.A., Iwasita, T., 2005. Parallel pathways of ethanol oxidation: The effect of ethanol concentration. J. Electroanal. Chem. 578, 315–321. https://doi.org/10.1016/j.jelechem.2005.01.013.

Cao, L., Sun, G., Li, H., Xin, Q., 2007. Carbon-supported IrSn catalysts for direct ethanol fuel cell. Fuel Cells Bulletin 11, 12–16. https://doi.org/10.1016/S1464-2859(08)70142-1.

Catanho, M., Malpass, G.R.P., Motheo, A.J., 2006. Photoelectrochemical treatment of the dye reactive red 198 using DSA® electrodes. Appl. Catal. B: Environ. 62, 193–200. https://doi.org/10.1016/j.apcatb.2005.07.011.

Cestarolli, D.T., De Andrade, A.R., 2003. Electrochemical and morphological properties of $Ti/Ru_{0.3}Pb_{(0.7-x)}TixO_2$-coated electrodes. Electrochim. Acta 48, 4137–4142. https://doi.org/10.1016/S0013-4686(03)00581-4.

Chaiyont, R., Badoe, C., de León, C.P., Nava, J.L., Recio, F.J., Sirés, I., Herrasti, P., Walsh, F.C., 2013. Decolorization of Methyl Orange Dye at IrO2-SnO2-Sb2O5 Coated Titanium Anodes. Chem. Eng. Technol. 36, 123–129. https://doi.org/10.1002/ceat.201200231.

Chatzisymeon, E., Xekoukoulotakis, N.P., Coz, A., Kalogerakis, N., Mantzavi-nos, D., 2006. Electrochemical treatment of textile dyes and dyehouse effluents. J. Hazard. Mater. 137, 998–1007. https://doi.org/10.1016/j.jhazmat.2006.03.032.

Chen, G., Chen, X., Yue, P.L., 2002. Electrochemical Behavior of Novel $Ti/IrO_x-Sb_2O_5-SnO_2$ Anodes. J. Phys. Chem. B 106, 4364–4369. https://doi.org/10.1021/jp013547o.

Chen, S., Zheng, Y., Wang, S., Chen, X., 2011. Ti/RuO2–Sb2O5–SnO2 electrodes for chlorine evolution from seawater. Chem. Eng. J. 172, 47–51. https://doi.org/10.1016/j.cej.2011.05.059.

Chen, P., Lu, J.-Q., Xie, G.-Q., Hu, G.-S., Zhu, L., Luo, L.-F., Huang, W.-X., Luo, M.-F., 2012. Effect of reduction temperature on selective hydrogenation of crotonaldehyde over Ir/TiO2 catalysts. Appl. Catal. A: Gen. 433–434, 236–242. https://doi.org/10.1016/j.apcata.2012.05.024.

Chu, Y.Y., Qian, Y., Wang, W.J., Deng, X.L., 2012. A dual-cathode electro-Fenton oxidation coupled with anodic oxidation system used for 4-nitrophenol degradation. J. Hazard. Mater. 199, 179–185. https://doi.org/10.1016/j.jhazmat.2011.10.079.

Ciumag, M., Gibilaro, M., Massot, L., Laucournet, R., Chamelot, P., 2016. Neodymium electrowinning into copper-neodymium alloys by mixed oxide reduction in molten fluoride media. J. Fluorine Chem. 184, 1–7. https://doi.org/10.1016/j.jfluchem.2016.02.001.

Clancy, M., Bettles, C.J., Stuart, A., Birbilis, N., 2013. The influence of alloying elements on the electrochemistry of lead anodes for electrowinning of metals: A review. Hydrometallurgy 131–132, 144–157. https://doi.org/10.1016/j.hydromet.2012.11.001.

Claus, P., 1998. Selective hydrogenation of ά,β-unsaturated aldehydes and other C = O and C = C bonds containing compounds. Top. Catal. 5, 51–62. https://doi.org/10.1023/A:1019177330810.

Claus, P., Hofmeister, H., 1999. Electron Microscopy and Catalytic Study of Silver Catalysts: Structure Sensitivity of the Hydrogenation of Crotonaldehyde. J. Phys. Chem. B 103, 2766–2775. https://doi.org/10.1021/jp983857f.

Cornell, A., Hakansson, B., Lindbergh, G., 2003. Ruthenium based DSA® in chlorate electrolysis—critical anode potential and reaction kinetics. Electrochim. Acta 48, 473–481. https://doi.org/10.1016/S0013-4686(02)00679-5.

Cooper, W.C., 1985. Advances and future prospects in copper electrowinning. J. Appl. Electrochem. 15, 789–805. https://doi.org/10.1007/BF00614357.

Dai, Z., Ju, H., 2012. Bioanalysis based on nanoporous materials. Trends Anal. Chem. 39, 149–162. https://doi.org/10.1016/j.trac.2012.05.008.

Dandekar, A., Vannice, M.A., 1999. Crotonaldehyde Hydrogenation on Pt/TiO2and Ni/TiO2SMSI Catalysts. J. Catal. 183, 344–354. https://doi.org/10.1006/jcat.1999.2419.

Delbecq, F., Sautet, P., 2003. Influence of Sn additives on the selectivity of hydrogenation of α-β-unsaturated aldehydes with Pt catalysts: a density functional study of molecular adsorption. J. Catal. 220, 115–126. https://doi.org/10.1016/S0021-9517(03)00249-5.

Delbecq, F., Li, Y., Loffreda, D., 2016. Metal–support interaction effects on chemo–regioselectivity: Hydrogenation of crotonaldehyde on $Pt_{13}/CeO_2(1\ 1\ 1)$. J. Catal. 334, 68–78. https://doi.org/10.1016/j.jcat.2015.10.028.

Devilliers, D., Mahe, E., 2010. Modified titanium electrodes: Application to Ti/TiO2/PbO2 dimensionally stable anodes. Electrochim. Acta 55, 8207–8214. https://doi.org/10.1016/j.electacta.2010.01.098.

Diebold, U., 2003. The surface science of titanium dioxide. Surf. Sci. Rep. 48, 53–229. https://doi.org/10.1016/S0167-5729(02)00100-0.

Eberil, V.I., Fedotova, N.S., Novikov, E.A., Mazanko, A.F., 2000. Studying the Link between the Potential of a Metal-Oxide Anode, the Current Efficiency for Chlorate, and the Current Losses for the Oxygen and Chlorine Evolution in a Wide Range of the Chlorate Electrolysis Conditions. Russ. J. Electrochem. 36, 1296–1302. https://doi.org/10.1023/A:1026603714489.

Ehsani, A., Yazici, E.Y., Deveci, H., 2016. Influence of polyoxometallates as additive on electro-winning of copper. Hydrometallurgy 162, 79–85. https://doi.org/10.1023/A:1026603714489.

Elezović, N.R., Babić, B.M., Gajić-Krstajić, Lj, Radmilović, V., Krstajić, N.V., Vračare, L.J., 2010. Synthesis, characterization and electrocatalytical behavior of Nb–TiO2/Pt nanocatalyst for oxygen reduction reaction. J. Power Sources 195, 3961–3968. https://doi.org/10.1016/j.jpowsour.2010.01.035.

Elezovic, N.R., Ercius, P., Kovać, J., Radmilović, V.R., Babić, B.M., Krstajić, N.V., 2015. Synthesis and characterization of Pt nanocatalyst on Ru0.7Ti0.3O2 support as a cathode for fuel cells application. J. Electroanalyt. Chem. 739, 164–171. https://doi.org/10.1016/j.jelechem.2014.12.033.

Evdokimov, S.W., 2001. Electrochemical and Corrosion Behavior of Dimensionally Stable Anodes in Chlorate Electrolysis: Efficiency of the Sodium Chlorate Production at Elevated Temperatures. Russ. J. Electrochem. 37, 363–371. https://doi.org/10.1023/A:1016669821615.

Fattakhova-Rohlfing, D., Wark, M., Brezesinski, T., Smarsly, B.M., Rathousky, J., 2007. Highly Organized Mesoporous TiO$_2$ Films with Controlled Crystallinity: A Li-Insertion Study. Adv. Funct. Mater. 17, 123–132. https://doi.org/10.1002/adfm.200600425.

Fatih, K., Neburchilov, V., Alzate, V., Neagu, R., Wang, H., 2010. Synthesis and characterization of quaternary PtRuIrSn/C electrocatalysts for direct ethanol fuel cells. J. Power Sources 195, 7168–7175. https://doi.org/10.1016/j.jpowsour.2010.05.038.

Fontelles-Carceller, O., Muñoz-Batista, M.J., Rodríguez-Castellón, E., Conesa, J.C., Fernández-García, M., Kubacka, A., 2017. Measuring and interpreting quantum efficiency for hydrogen photo-production using Pt-titania catalysts. J. Catal. 347, 157–169. https://doi.org/10.1016/j.jcat.2017.01.012.

Forty, J.C., Olivi, P., De Andrade, A.R., 2001. Characterisation of DSA®-type coatings with nominal composition Ti/Ru$_{0.3}$Ti$_{(0.7-x)}$-Sn$_x$O$_2$ prepared via a polymeric precursor. Electrochim. Acta 47, 913–920. https://doi.org/10.1016/S0013-4686(01)00791-5.

Gabe, D.R., 1981. Oxide films on anodes during electrodeposition. In: Vijh, A.K. (Ed.), Oxide and Oxide Films. Marcel Dekker Inc, New York, pp. 210–238.

Krstajic, G., Lj, M., Trisovic, T. Lj., Krstajić, N.V., 2004. Spectrophotometric study of the anodic corrosion of Ti/RuO2 electrode in acid sulfate solution. Corrosion Sci. 46, 65–74. https://doi.org/10.1016/S0010-938X(03)00111-2.

Gallezot, P., Richard, D., 1998. Selective Hydrogenation of α,β-Unsaturated Aldehydes. Catal. Rev. Sci. Eng. 40, 81–126. https://doi.org/10.1080/01614949808007106.

Gilbertson, B.P., 2000. Creating value through innovation: biotechnology in mining. Mineral Processing and Extractive Metallurgy IMM Transactions: Section C 109, 61-67. https://doi.org/10.1179/mpm.2000.109.2.61.

Gojković, S. Lj., Babić, B.M., Radmilović, V.R., Krstajić, N.V., 2010. Nb-doped TiO$_2$ as a support of Pt and Pt–Ru anode catalyst for PEMFCs. J. Electroanalyt. Chem. 639, 161–166. https://doi.org/10.1016/j.jelechem.2009.12.004.

Gueneau, J.P., Macpherson, J.V., Delplancke, J.L., 2003. Characterisation and behaviour of Ti/TiO2/noble metal anodes. Electrochim. Acta 48, 1131–1141. https://doi.org/10.1016/S0013-4686(02)00824-1.

Gutierrez, V., Dennehy, M., Diez, A., Volpe, M.A., 2012. Liquid phase hydrogenation of crotonaldehyde over copper incorporated in MCM-48. Appl. Catal. A: Gen. 437–438, 72–78. https://doi.org/10.1016/j.apcata.2012.06.011.

Haghighi, H.K., Moradkhani, D., Sedaghat, B., Najafabadi, M.R., Behnamfard, A., 2013. Production of copper cathode from oxidized copper ores by acidic leaching and two-step precipitation followed by electrowinning. Hydrometallurgy 133, 111–117. https://doi.org/10.1016/j.hydromet.2012.12.004.

Hansen, H.A., Man, I.C., Studt, F., Abild-Pedersen, F., Bligaard, T., Rossmeisl, J., 2010. Electrochemical chlorine evolution at rutile oxide (110) surfaces. Phys. Chem. Chem. Phys. 12, 283–290. https://doi.org/10.1039/B917459A.

Higuchi, E., Miyata, K., Takase, T., Inoue, H., 2011. Ethanol oxidation reaction activity of highly dispersed Pt/SnO2 double nanoparticles on carbon black. J. Power Sources 196, 1730–1737. https://doi.org/10.1016/j.jpowsour.2010.10.008.

Hrussanova, A., Mirkova, L., Dobrev, Ts, 2001. Anodic behaviour of the Pb–Co3O4 composite coating in copper electrowinning. Hydrometallurgy 60, 199–213. https://doi.org/10.1016/S0304-386X(00)00190-0.

Huang, H., Guo, Z.-C., Li, J.-K., Chen, B.-M., 2010. Effect of added cobalt ion on copper electrowinning from sulfate bath using doped polyaniline and Pb-Ag anodes. Trans. Nonferrous Met. Soc. China 20, s55–s59. https://doi.org/10.1016/S1003-6326(10)60012-X.

Huang, Y.Q., Huang, H.L., Gao, Q.Z., Gan, C.F., Liu, Y.J., Fang, Y.P., 2014. Electroless synthesis of two-dimensional sandwich-like Pt/Mn3O4/reduced-graphene-oxide nanocomposites with enhanced electrochemical performance for methanol oxidation. Electrochim. Acta 149, 34–41. https://doi.org/10.1016/j.electacta.2014.10.102.

Ivanov, I., Stefanov, Y., Noncheva, Z., Petrova, M., Dobrev, Ts., Mirkova, L., Vermeersch, R., Demaerel, J.-P., 2000. Hydrometallurgy 57, 109-124.

Ivanov, I., Stefanov, Y., Noncheva, Z., Petrova, M., Dobrev, Ts., Mirkova, L., Vermeersch, R., Demaerel, J.-P., 2000. Hydrometallurgy 57, 125-139.

Janssen, L.J.J., 1974. The mechanism of the chlorine evolution on different types of graphite anodes during the electrolysis of an acidic NaCl solution. Electrochim. Acta 19, 257–265. https://doi.org/10.1016/0013-4686(74)85076-0.

Jia, N.Q., Wen, Y.L., Yang, G.F., Lian, Q., Xu, C.J., Shen, H.B., 2008. Direct electrochemistry and enzymatic activity of hemoglobin immobilized in ordered mesoporous titanium oxide matrix. Electrochem. Commun. 10, 774–777. https://doi.org/10.1016/j.elecom.2008.01.044.

Jiang, L.H., Sun, G.Q., Sun, S.G., Liu, J.G., Tang, Sh.H., Li, H.Q., Zhou, B., Xin, Q., 2005. Structure and chemical composition of supported Pt–Sn electrocatalysts for ethanol oxidation. Acta 50, 5384–5389. https://doi.org/10.1016/j.electacta.2005.03.018.

Jiang, Z.Z., Wang, Z.B., Qu, W.L., Gu, D.M., Yin, G.P., 2012. Synthesis and characterization of carbon riveted Pt/MWCNTs@TiO2–TiC catalyst with high durability for PEMFCs application. Appl. Catal. B: Environ. 123–124, 214–220. https://doi.org/10.1016/j.apcatb.2012.04.040.

Jović, B.M., Jović, V.D., Lačnjevać, U.Č., Stevanović, S.I., Kovač, J., Radović, M., Krstajić, N.V., 2016. Ru layers electrodeposited onto highly stable Ti2AlC substrates as cathodes for hydrogen evolution in sulfuric acid solutions. J. Electroanalytical Chem. 766, 78–86. https://doi.org/10.1016/j.jelechem.2016.01.038.

Jung, D.S., Park, S.B., Kang, Y.C., 2010. Design of particles by spray pyrolysis and recent progress in its application. Korean J. Chem. Eng. 27, 1621–1645. https://doi.org/10.1007/s11814-010-0402-5.

Karuppiah, M.T., Raju, G.B., 2009. Anodic Degradation of CI Reactive Blue 221 Using Graphite and IrO$_2$/TaO$_2$/RuO$_2$ Coated Titanium Electrodes. Ind. Eng. Chem. Res. 48, 2149–2156. https://doi.org/10.1021/ie801291h.

Khelifa, A., Aoudj, S., Moulay, S., Hecini, M., De Petris-Werr, M., 2009. Degradation of EDTA by in-situ electrogenerated active chlorine in an electroflotation cell. Desalin. Water Treat. 7, 119–123. https://doi.org/10.5004/dwt.2009.706.

Kiros, Y., Pirjamali, M., Bursell, M., 2006. Oxygen reduction electrodes for electrolysis in chlor-alkali cells. Electrochim. Acta 51, 3346–3350. https://doi.org/10.1016/j.electacta.2005.10.024.

Krstajić, N., Spasojević, M., Jakšić, M., 1984. A selective catalyst for titanium anodes: development and Optimization: I. Catalyst Structure, Activity and Durability. J. Res Inst. Catalysis, Hokkaido Univ. 32, 19–28. https://doi.org/10.1016/2115/25149.

Krstajić, N.V., Spasojević, M.D., Jakšić, M.M., 1986. A selective catalyst for titanium anodes. J. Mol. Catal. 38, 81–88. https://doi.org/10.1016/0304-5102(86)87051-1.

Krstić, VUrošević, T., Pešovski, B.,, 2018. A review on adsorbents for treatment of water and wastewaters containing copper ions. Chemical Engineering Science 192, 273–287. https://doi.org/10.1016/j.ces.2018.07.022.

Krstić, VPešovski, B.,, 2019. Reviews the research on some dimensionally stable anodes (DSA) based on titanium. Hydrometallurgy 185, 71–75. https://doi.org/10.1016/j.hydromet.2019.01.018.

Krstić, V, 2021. Some Effective Methods for Treatment of Wastewater from Cu Production. Water Pollution and Remediation: Heavy Metals. Environmental Chemistry for a Sustainable World, 53. Inamuddin, Ahamed M.I., Lichtfouse E., Springer Nature, pp. 313–440.

Lačnjevać, U.C., Radmilović, V.V., Radmilović, V.R., Krstajić, N. V., 2015. RuOx nanoparticles deposited on TiO$_2$ nanotube arrays by ion-exchange method as electrocatalysts for the hydrogen evolution reaction in acid solution. Electrochimica Acta 168, 178–190. https://doi.org/10.1016/j.electacta.2015.04.012.

Lassali, T., Boodts, J., Trassati, S., 1994. Electrocatalytic activity of the ternary oxide Ru0.3PtxTi(0.7-x)O2 for chlorine evolution. Electrochim. Acta 39, 1545–1549. https://doi.org/10.1016/0013-4686(94)85133-6.

Li, B., Hong, X., Lin, J.-J., Hu, G.-S., Yu, Q., Wang, Y.-J., Luo, M.-F., Lu, J.-Q., 2013a. Promoting effect of Ir on the catalytic property of Ru/ZnO catalysts for selective hydrogenation of crotonaldehyde. Appl. Sur. Sci. 280, 179-185. https://doi.org/10.1016/j.apsusc.2013.04.122..

Li, B., Hu, G.-S., Jin, L.-Y., Hong, X., Lu, J-Q., Luo, M.-F., 2013b. Characterizations of Ru/ZnO catalysts with different Ru contents for selective hydrogenation of crotonaldehyde. J. Ind. Eng. Chem. 19 (1), 250-255. https://doi.org/10.1016/j.jiec.2012.08.008..

Li, G. T., Yip , H. Y., Wong , K. H., Hu, C., Qu, J. H., Wong, P. K., 2011. Photoelectrochemical degradation of Methylene Blue with β-PbO2 electrodes driven by visible light irradiation. J. Environ. Sci. 23 (6), 998-1003. https://doi.org/10.1016/S1001-0742(10)60489-5.

Li, M., Kowal, A., Sasaki, K., Marinkovic, N., Su, D., Korach, E., Liu, P., Adzic, R.R., 2010. Ethanol oxidation on the ternary Pt–Rh–SnO2/C electrocatalysts with varied Pt:Rh:Sn ratios. Electrochim. Acta 55, 4331–4338. https://doi.org/10.1016/j.electacta.2009.12.071.

Li, X.Y., Wang, C.W., Qian, Y., Wang, Y.J., Zhang, L.W., 2013c. Simultaneous removal of chemical oxygen demand, turbidity and hardness from biologically treated citric acid wastewater by electrochemical oxidation for reuse. Sep. Purif. Technol. 107, 281-288. https://doi.org/10.1016/j.seppur.2013.01.008..

Liberkova, K., Touroude, R., Murzin, D.Y., 2002. Analysis of deactivation and selectivity pattern in catalytic hydrogenation of a molecule with different functional groups: crotonaldehyde hydrogenation on Pt/SnO$_2$. Chem. Eng. Sci. 57, 2519–2529. https://doi.org/10.1016/S0009-2509(02)00134-3.

Lin, H., Zheng, J., Zheng, X., Gu, Z., Yuan, Y., Yang, Y., 2015. Improved chemoselective hydrogenation of crotonaldehyde over bimetallic AuAg/SBA-15 catalyst. J. Catal. 330, 135–144. https://doi.org/10.1016/j.jcat.2015.07.022.

Liu, S., Chen, A., 2005. Coadsorption of Horseradish Peroxidase with Thionine on TiO2 Nanotubes for Biosensing. Langmuir 21, 8409–8413. https://doi.org/10.1021/la050875x.

Lončar, DPaunković, J., Jovanović, V., Krstić, V.,, 2019. Environmental and social responsibility of companies across European Union countries - panel data analysis. Science of the Total Environment 657, 287–296. https://doi.org/10.1016/j.scitotenv.2018.11.482.

Lu, H.Y., Yang, J., Rusling, J.F., Hu, N.F., 2006. Vapor-Surface Sol-Gel Deposition of Titania Alternated with Protein Adsorption for Assembly of Electroactive, Enzyme-Active Films. Electroanalysis 18, 379–390. https://doi.org/10.1002/elan.200503420.

Liu, Y., Liu, H.L., Ma, J., Li, J.J., 2012. Preparation and electrochemical properties of Ce–Ru–SnO2 ternary oxide anode and electrochemical oxidation of nitrophenols. J. Hazard. Mater. 213-214, 222–229. https://doi.org/10.1016/j.jhazmat.2012.01.090.

Ma, R., Cheng, S., Zhang, X., Li, S., Liu, Z., Li, X., 2016. Oxygen evolution and corrosion behavior of low-MnO2-content Pb-MnO2 composite anodes for metal electrowinning. Hydrometallurgy 159, 6–11. https://doi.org/10.1016/j.hydromet.2015.10.031.

Malpass, G.R., Miwa, D.W., Machado, S.A., Olivi, P., Motheo, A.J., 2006. Oxidation of the pesticide atrazine at DSA® electrodes. J. Hazard. Mater. 137, 565–572. https://doi.org/10.1016/j.jhazmat.2006.02.045.

Malpass, G.R.P., Miwa, D.W., Miwa, A.C.P., Machado, S.A.S., Motheo, A.J., 2007. Photo-Assisted Electrochemical Oxidation of Atrazine on a Commercial Ti/Ru0.3Ti0.7O2 DSA Electrode. Environ. Sci. Technol. 41, 7120–7125. https://doi.org/10.1021/es070798n.

Malpass, G.R.P., Miwa, D.W., Miwa, A.C.P., Machado, S.A.S., Motheo, A.J., 2009. Study of photo-assisted electrochemical degradation of carbaryl at dimensionally stable anodes (DSA®). J. Hazard. Mater. 167, 224–229. https://doi.org/10.1016/j.jhazmat.2008.12.109.

Malpass, G.R., Miwa, D.W., Machado, S.A., Motheo, A.J., 2010. SnO2-based materials for pesticide degradation. J. Hazard. Mater. 180, 145–151. https://doi.org/10.1016/j.jhazmat.2010.04.006.

Malpass, G.R.P., Salazar-Banda, G.R., Miwa, D.W., Machado, S.A. S., Motheo, A.J., 2013. Comparing atrazine and cyanuric acid electro-oxidation on mixed oxide and boron-doped diamond electrodes. Environ. Technol. 34, 1043–1051. https://doi.org/10.1080/09593330.2012.733420.

Marinelli, T.B.L.W., Ponec, V., 1995. A Study on the Selectivity in Acrolein Hydrogenation on Platinum Catalysts: A Model for Hydrogenation of α,β-Unsaturated Aldehydes. J. Catal. 156, 51–59. https://doi.org/10.1006/jcat.1995.1230.

Margitfalvi, J.L., Tompos, A., Kolosova, I., Valyon, J., 1998. Reaction Induced Selectivity Improvement in the Hydrogenation of Crotonaldehyde over Sn–Pt/SiO2Catalysts. J. Catal. 174, 246–249. https://doi.org/10.1006/jcat.1998.1966.

Merlo, A.B., Santori, G.F., Sambeth, J., Siria, G.J., Casella, M.L., Ferretti, O.A., 2006. Hydrogenation of crotonaldehyde and butyraldehyde on silica supported Pt and PtSn catalysts: A drifts study. Catal. Commun. 7, 204–208. https://doi.org/10.1016/j.catcom.2005.11.002.

McBurney, M.J.P., Gabe, D.R., 1979. Filming behaviour of lead anodes for chromium electroplating. Surfc. Technol. 9 (4), 253–266. https://doi.org/10.1016/0376-4583(79)90100-6.

Mohr, C., Hofmeister, H., Radnik, J., Claus, P., 2003. Identification of Active Sites in Gold-Catalyzed Hydrogenation of Acrolein. J. Am. Chem. Soc. 125, 1905–1911. https://doi.org/10.1021/ja027321q.

Mukerjee, S., Srinivasan, S., 1993. . Enhanced electrocatalysis of oxygen reduction on platinum alloys in proton exchange membrane fuel cells. J. Electroanal. Chem. 357, 201–224. https://doi.org/10.1016/0022-0728(93)80380-Z.

Najminoori, M., Mohebbi, A., Arabi, B.G., Daneshpajouh, S., 2015. CFD simulation of an industrial copper electrowinning cell. Hydrometallurgy 153, 88–97. https://doi.org/10.1016/j.hydromet.2015.02.005.

Neto, S.A., De Andrade, A.R., 2009. Electrochemical degradation of glyphosate formulations at DSA® anodes in chloride medium: an AOX formation study. J. Appl. Electrochem. 39, 1863–1870. https://doi.org/10.1007/s10800-009-9890-6.

Nidola, A., 1989. Electrode materials for oxygen evolution cobalt treated lead vs. commercial lead and lead alloys. Mater. Chem. Phys. 22, 183–201. https://doi.org/10.1016/0254-0584(89)90037-0.

Nikoloski, A.N., Barmi, M.J., 2013. Novel lead–cobalt composite anodes for copper electrowinning. Hydrometallurgy 137, 45–52. https://doi.org/10.1016/j.hydromet.2013.05.004.

de Oliveira, M.C.Q., Tanaka, A.A., los Lanza, M.R.D., Sotomayor, M.D.T., 2011. Electro-analysis 23, 2616-2621.

Olsson, C.O.A., Landolt, D., 2003. Passive films on stainless steels-chemistry, structure and growth. Electrochim. Acta 48, 1093–1104. https://doi.org/10.1016/S0013-4686(02)00841-1.

Pace, G.F., Stauter, J.C., 1974. Direct electrowinning of copper from synthetic pregnant leach soulutions utiliying SO2 and graphite anodes, pilot plant results. CIM Bulletin 67, 85–90.

Panakoulias, T., Kalatzis, P., Kalderis, D., Katsaounis, A., 2010. Electrochemical degradation of Reactive Red 120 using DSA and

BDD anodes. J. Appl. Electrochem. 40, 1759–1765. https://doi.org/10.1007/s10800-010-0138-2.

Park, H., Vecitis, C.D., Hoffmann, M.R., 2009. Electrochemical Water Splitting Coupled with Organic Compound Oxidation: The Role of Active Chlorine Species. J. Phys. Chem. C 113, 7935–7945. https://doi.org/10.1021/jp810331w.

Park, H., Bak, A., Ahn, Y.Y., Choi, J., Hoffmannn, M.R., 2012. Photoelectrochemical performance of multi-layered BiOx–TiO2/Ti electrodes for degradation of phenol and production of molecular hydrogen in water. J. Hazard. Mater. 211-212, 47–54. https://doi.org/10.1016/j.jhazmat.2011.05.009.

Pavlović, O.Ž., Krstajić, N.V., Spasojević, M.D., 1988. Formation of bromates at a RuO_2TiO_2 titanium anode. Surf. Coatings Technology 34, 177–183. https://doi.org/10.1016/0257-8972(88)90079-5.

Pereira, G.F., Rocha-Filho, R.C., Bocchi, N., Biaggio, S.R., 2012. Electrochemical degradation of bisphenol A using a flow reactor with a boron-doped diamond anode. Chem. Eng. J. 198–199, 282–288. https://doi.org/10.1016/j.cej.2012.05.057.

Pesovski, B., Cvetkovski, V., Spasojeviæ, M., 2007. The new titanium electrode surfaces activated by oxide metal layer. Copper 32, 49–56. UDC: 669.295:669.056(045) = 861.

Pinhedo, L., Pelegrini, R., Bertazzoli, R., Motheo, A.J., 2005. Photoelectrochemical degradation of humic acid on a (TiO2)0.7 (RuO2)0.3 dimensionally stable anode. Appl. Catal. B: Environ. 57, 75–81. https://doi.org/10.1016/j.apcatb.2004.10.006.

Ponec, V., 1997. On the role of promoters in hydrogenations on metals; α,β-unsaturated aldehydes and ketones. Appl. Catal. A: Gen. 149, 27–48. https://doi.org/10.1016/S0926-860X(96)00250-5.

Raghu, S., Lee, C.W., Chellammal, S., Palanichamy, S., Basha, C.A., 2009. Evaluation of electrochemical oxidation techniques for degradation of dye effluents—A comparative approach. J. Hazard. Mater. 171, 748–754. https://doi.org/10.1016/j.jhazmat.2009.06.063.

Rajkumar, D., Kim, J.G., 2006. Oxidation of various reactive dyes with in situ electro-generated active chlorine for textile dyeing industry wastewater treatment. J. Hazard. Mater. 136, 203–212. https://doi.org/10.1016/j.jhazmat.2005.11.096.

Rajkumar, D., Song, B.J., Kim, J.G., 2007. Electrochemical degradation of Reactive Blue 19 in chloride medium for the treatment of textile dyeing wastewater with identification of intermediate compounds. Dyes Pigments 72, 1–7. https://doi.org/10.1016/j.dyepig.2005.07.015.

Ramos-Fernández, E.V., Silvestre-Albero, J., Sepúlveda-Escribano, A., Rodríguez-Reinoso, F., 2010. Effect of the metal precursor on the properties of Ru/ZnO catalysts. Appl. Catal. A: Gen. 374, 221–227. https://doi.org/10.1016/j.apcata.2009.12.014.

Reyes, P., Aguirre, M.C., Pecchia, G., Fierro, J.L.G., 2000. Crotonaldehyde hydrogenation on Ir supported catalysts. J. Mol. Catal. A 164, 245–251. https://doi.org/10.1016/S1381-1169(00)00329-0.

Ribeiro, J., dos Anjos, D.M., Kokoh, K.B., Coutanceau, C., Léger, J.-M., Olivi, P., de Andrade, A.R., 2007. Carbon-supported ternary PtSnIr catalysts for direct ethanol fuel cell. Electrochim. Acta 52, 6997–7006. https://doi.org/10.1016/j.electacta.2007.05.017.

del Río, A.I., Fernández, J., Molina, J., Bonastre, J., Cases, F., 2010. On the behaviour of doped SnO2 anodes stabilized with platinum in the electrochemical degradation of reactive dyes. Electrochim. Acta 55, 7282–7289. https://doi.org/10.1016/j.electacta.2010.07.008.

Rodríguez, F.A., Mateo, M.N., Aceves, J.M., Rivero, E.P., González, I., 2013. Electrochemical oxidation of bio-refractory dye in a simulated textile industry effluent using DSA electrodes in a filter-press type FM01-LC reactor. Environ. Technol. 34, 573–583. https://doi.org/10.1080/09593330.2012.706645.

Roddick-Lanzilotta, A.D., McQuillan, A.J., 2000. An in situ Infrared Spectroscopic Study of Glutamic Acid and of Aspartic Acid Adsorbed on TiO2: Implications for the Biocompatibility of Titanium. J. Colloid Interface Sci. 227, 48–54. https://doi.org/10.1006/jcis.2000.6864.

Rousseau, S., Coutanceau, C., Lamy, C., Léger, J.M., 2006. Direct ethanol fuel cell (DEFC): Electrical performances and reaction products distribution under operating conditions with different platinum-based anodes. J. Power Sources 158, 18–24. https://doi.org/10.1016/j.jpowsour.2005.08.027.

Ruiz-Martínez, J., Fukui, Y., Komatsu, T., Sepuúlveda-Escribano, A., 2008. Ru–Ti intermetallic catalysts for the selective hydrogenation of crotonaldehyde. J. Catal. 260, 150–156. https://doi.org/10.1016/j.jcat.2008.09.024.

Ruppert, A.M., Paryjczak, T., 2007. Pt/ZrO2/TiO2 catalysts for selective hydrogenation of crotonaldehyde: Tuning the SMSI effect for optimum performance. Appl. Catal. A: Gen. 320, 80–90. https://doi.org/10.1016/j.apcata.2006.12.019.

Sala, M., Del Río, A.I., Molina, J., Cases, F., Gutiérrez-Bouzán, M. C., 2012. Influence of cell design and electrode materials on the decolouration of dyeing effluents. Int. J. Electrochem. Sci. 7, 12470–12488.

Santos, D., Pacheco, M.J., Gomes, A., Lopes, A., Ciriaco, L., 2013. Preparation of Ti/Pt/SnO2–Sb2O4 electrodes for anodic oxidation of pharmaceutical drugs. J. Appl. Electrochem. 43, 407–416. https://doi.org/10.1007/s10800-013-0527-4.

Sen, B., Vannice, M.A., 1988. Metal-support effects on acetone hydrogenation over platinum catalysts. J. Catal. 113, 52–71. https://doi.org/10.1016/0021-9517(88)90237-0.

Sepulveda-Escribano, A., Coloma, E., Rodriguez-Reinoso, F., 1998. Promoting Effect of Ceria on the Gas Phase Hydrogenation of Crotonaldehyde over Platinum Catalysts. J. Catal. 178, 649–657. https://doi.org/10.1006/jcat.1998.2199.

Serrano-Ruiz, J.C., Luettich, J., Sepulveda-Escribano, A., Rodriguez-Reinoso, F., 2006. Effect of the support composition on the vapor-phase hydrogenation of crotonaldehyde over $Pt/Ce_xZr_{1-x}O_2$ catalysts. J. Catal. 241, 45–55. https://doi.org/10.1016/j.jcat.2006.04.006.

Shao, L., He, P., Xue, J., Li, G., 2006. Electrolytic degradation of biorefractory organics and ammonia in leachate from bioreactor landfill. Water Sci. Technol. 53, 143–150. https://doi.org/10.2166/wst.2006.347.

Shi, H.X., Qu, J.H., Wang, A.M., Ge, J.T., 2005. Degradation of microcystins in aqueous solution with in situ electrogenerated active chlorine. Chemosphere 60, 326–333. https://doi.org/10.1016/j.chemosphere.2004.11.070.

Silvestre-Albero, J., Coloma, F., Sepúlveda-Escribano, A., Rodríguez-Reinoso, F., 2006. Effect of the presence of chlorine in bimetallic PtZn/CeO2 catalysts for the vapor-phase hydrogenation of crotonaldehyde. Appl. Catal. A: Gen. 304, 159–167. https://doi.org/10.1016/j.apcata.2006.02.039.

Soares, O.S.G.P., Jardim, E.O., Reyes-Carmona, A., Ruiz-Martínez, J., Silvestre-Albero, J., Rodríguez-Castellón, E., Orfao, J.J.M., Sepúlveda-Escribano, A., Pereira, M.F.R., 2012. Effect of support and pre-treatment conditions on Pt–Sn catalysts: Application to nitrate reduction in water. J. Colloid Interface Sci. 369, 294–301. https://doi.org/10.1016/j.jcis.2011.11.059.

Song, S., Tsiakaras, P., 2006. Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs). Appl. Catal. B: Environ. 63, 187–193. https://doi.org/10.1016/j.apcatb.2005.09.018.

de Souza, J.P.I., Queiroz, S.L., Bergamaske, K., Gonzalez, E.R., Nart, F.C., 2002. Electro-Oxidation of Ethanol on Pt, Rh, and PtRh Electrodes. A Study Using DEMS and in-Situ FTIR Techniques. J. Phys. Chem. B 106, 9825–9830. https://doi.org/10.1021/jp014645c.

Spasojević, M., Krstajić, N., Jakšić, M., 1983. Optimization of an anodic electrocatalyst: Ru02/TiO2 on titanium. J. Res Inst. Catal. Hokkaido Univ. 31, 77–94. https://doi.org/10.1016/2115/28061.

Spasojević, M., Krstajić, N., Jakšić, M., 1984. A selective catalyst for titanium anodes: development and optimization II. Selectivity Features. J. Res Inst. Catal. Hokkaido Univ. 32, 29–36. https://doi.org/10.1016/2115/25150.

Spasojević, M.D., Krstajić, N.V., Jakšić, M.M., 1987. A selective catalyst for titanium anodes: development and optimization II. Selectivity Features. J. Mol. Catal. 40, 311–326. https://doi.org/10.1016/2115/25150.

Spasojević, M., Cvetkovski, V., Stevanović, R., Ribić, L., Pešovski, B., Rafailović, L., 2006. Serbian Patent P-2006/0678.

Spasojević, M., Maričić, A., Ribić Zelenović, L., Krstajić, N., Spasojević, P., 2013. The kinetics of hydrogen absorption/desorption within nanostructured composite Ni79.1Co18.6Cu2.3 alloy using resistometry. J. Alloys Compd. 551, 660–666. https://doi.org/10.1016/j.jallcom.2012.10.187.

Spasojeviæ, M., Trišoviæ, T., Ribiæ-Zelenoviæ, L., Spasojeviæ, P., 2013. Development of RuO2/TiO2 titanium anodes and a device for in situ active chlorine generation. Hem. Ind. 67, 313–321.

Spasojević, M., Ribic-Zelenović, L., Spasojević, P., 2012. Microstructure of new composite electrocatalyst and its anodic behavior for chlorine and oxygen evolution. Ceram. Int. 38, 5827–5833. https://doi.org/10.1016/j.ceramint.2012.04.032.

Szpyrkowicz, L., Cherbanski, R., Kelsall, G.H., 2005. Hydrodynamic Effects on the Performance of an Electrochemical Reactor for Destruction of Disperse Dyes. Ind. Eng. Chem. Res. 44, 2058–2068. https://doi.org/10.1021/ie049444k.

Spasojević, M., Ribic-Zelenović, L., Spasojević, P., 2012. Microstructure of new composite electrocatalyst and its anodic behavior for chlorine and oxygen evolution. Ceram. Int. 38 (7), 5827-5833. https://doi.org/10.1016/j.ceramint.2012.04.032.

Tauster, S.J., Fung, S.C., Garten, R.L., 1978. Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide. J. Am. Chem. Soc. 100, 170–175. https://doi.org/10.1021/ja00469a029.

Trasatti, S., 2000. Electrocatalysis: understanding the success of DSA®. Electrochim. Acta 45, 2377–2385. https://doi.org/10.1016/S0013-4686(00)00338-8.

Vannice, M.A., Sen, B., 1989. Metal-support effects on the intramolecular selectivity of crotonaldehyde hydrogenation over platinum. J. Catal. 115, 65–78. https://doi.org/10.1016/0021-9517(89)90007-9.

Vignarooban, K., Lin, J., Arvay, A., Kolli, S., Kruusenberg, I., Tammeveski, K., Munukutla, L., Kannan, A.M., 2015. Nanoelectrocatalyst materials for low temperature fuel cells: A review. Chin. J. Catal. 36, 458–472. https://doi.org/10.1016/S1872-2067(14)60175-3.

Vijh, A.K., Oxide and Oxide Films - Volume 6, ed., Marcel Dekker, Inc., New York, 1981.

Wang, Q., Sun, G.Q., Jiang, L.H., Xin, Q., Sun, S.G., Jiang, Y.X., Chen, S.P., Jusys, Z., Behm, R.J., 2007. Adsorption and oxidation of ethanol on colloid-based Pt/C, PtRu/C and Pt3Sn/C catalysts: In situFTIR spectroscopy and on-line DEMS studies. Phys. Chem. Chem. Phys. 9, 2686–2696. https://doi.org/10.1039/b700676b.

Wang, H., Wang, J.L., 2008. The cooperative electrochemical oxidation of chlorophenols in anode–cathode compartments. J. Hazard. Mater. 154, 44–50. https://doi.org/10.1016/j.jhazmat.2007.09.102.

Wang, H., Sun, D.Z., Bian, Z.Y., 2010. Degradation mechanism of diethyl phthalate with electrogenerated hydroxyl radical on a Pd/C gas-diffusion electrode. J. Hazard. Mater. 180, 710–715. https://doi.org/10.1016/j.jhazmat.2010.04.095.

Wang, C., Bai, S., Xiong, Y., 2015. Recent advances in surface and interface engineering for electrocatalysis. Chin. J. Catal. 36, 1476–1493. https://doi.org/10.1016/S1872-2067(15)60911-1.

White, R.J., Luque, R., Budarin, V.L., Clark, J.H., Macquarrie, D., 2009. Supported metal nanoparticles on porous materials. Methods and applications. J. Chem. Soc. Rev. 38, 481–494. https://doi.org/10.1039/B802654H.

Wu, W., Huang, Z.-H., Lim, T.-T., 2014. Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. Appl. Catal. A: Gen. 480, 58–78. https://doi.org/10.1016/j.apcata.2014.04.035.

Wu, J., Liu, F., Zhang, H., Zhang, J.H., Li, L., 2012. Decolorization of CI Reactive Black 8 by electrochemical process with/without ultrasonic irradiation. Desalination Water Treat. 44, 36–43. https://doi.org/10.1080/19443994.2012.691739.

Xu, H., Li, A.-P., Qi, Q., Jiang, W., Sun, Y.-M., 2012. Electrochemical degradation of phenol on the La and Ru doped Ti/SnO2-Sb electrodes. Korean J. Chem. Eng. 29, 1178–1186. https://doi.org/10.1007/s11814-012-0014-3.

Yao, W., Yang, J., Wang, J., Nuli, Y., 2007. Chemical deposition of platinum nanoparticles on iridium oxide for oxygen electrode of unitized regenerative fuel cell. Electrochem. Commun. 9, 1029–1034. https://doi.org/10.1016/j.elecom.2006.12.017.

Ye, F., Li, J., Wang, X., Wang, T., Li, S., Christensen, E., 2010. Electrocatalytic properties of Ti/Pt–IrO2 anode for oxygen evolution in PEM water electrolysis. Int. J. Hydrogen Energy 35, 8049–8055. https://doi.org/10.1016/j.ijhydene.2010.01.094.

Yi, Z., Kangning, C., Wei, W., Wang, J., Lee, S., 2007. Effect of IrO_2 loading on RuO_2–IrO_2–TiO_2 anodes: A study of microstructure and working life for the chlorine evolution reaction. Ceram. Int. 33, 1087–1091. https://doi.org/10.1016/j.ceramint.2006.03.025.

Yu, Q., Zhang, X., Li, B., Lu, J., Hu, G., Jia, A., Luo, C., Hong, Q., Song, Y., Luo, M., 2014. Effect of reduction temperature on Ru–Ir/ZnO catalyst for selective hydrogenation of crotonaldehyde. J. Molec. Catal. A: Chem. 392, 89–96. https://doi.org/10.1016/j.molcata.2014.04.022.

Zhang, W., Houlachi, G., 2010. Electrochemical studies of the performance of different Pb–Ag anodes during and after zinc electrowinning. Hydrometallurgy 104, 129–135. https://doi.org/10.1016/j.hydromet.2010.05.007.

Zhang, W., Ghali, E., Houlachi, G., 2017. Review of oxide coated catalytic titanium anodes performance for metal electrowinning. Hydrometallurgy 169, 456–467. https://doi.org/10.1016/j.hydromet.2017.02.014.

Zhang, Q., Guo, X., Cao, X., Wang, D., Wei, J., 2015. Facile preparation of a Ti/α-PbO2/β-PbO2 electrode for the electrochemical degradation of 2-chlorophenol. Chin. J. Catal. 36, 975–981. https://doi.org/10.1016/S1872-2067(15)60851-8.

Zhao, L., Mitsushima, S., Ishihara, A., Matsuzawa, K., Ota, K., 2011. Electrocatalysts for Ethanol Oxidation in Acidic Media. Chin. J. Catal. 32, 1856–1863. https://doi.org/10.1016/S1872-2067(10)60297-5.

Zhou, H., Su, M., Lee, P.-H., Shih, K., 2017. Synthesis of submicron lead oxide particles from the simulated spent lead paste for battery anodes. J. Alloys Compounds 609, 101–107. https://doi.org/10.1016/j.jallcom.2016.08.094.