

MAGNETRON SPUTTERED IRIIDIUM OXIDE AS ANODE CATALYST FOR PEM HYDROGEN GENERATION*¹

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Thin films of iridium oxide are deposited by reactive magnetron sputtering. The influence of oxygen partial pressure in the sputtering plasma on the composition, surface structure and morphology of the films has been studied by XRD, SEM, AFM and XPS analysis. An optimal combination of sputtering parameters yields stable microporous amorphous films with highly extended fractal surface. The electrochemical properties of these films are investigated in view of their application as catalysts for PEM water splitting, using the electrochemical techniques of cyclovoltammetry and steady state polarization. A morphology factor assessing the catalyst active surface for a series of sputtered samples with varying thickness/loading is determined and correlated to the catalytic efficiency. It has been proven that iridium oxide is a very efficient catalyst for oxygen evolution reaction (OER). The best performance with anodic current density of 0.3 A cm^{-2} at potential of 1.55 V (*vs.* RHE) shows the 500 nm thick film containing 0.2 mg cm^{-2} catalyst. These results combined with the established long-term mechanical stability of the sputtered iridium oxide films (SIROFs) prove the advantages of the reactive magnetron sputtering as simple and reliable method for preparation of catalysts with precisely controlled composition, loading, and surface characteristics.

Keywords: iridium oxide catalysts; reactive magnetron sputtering; thin films; composition, surface structure and morphology; anodic process; PEM hydrogen generation

ИРИДИУМ–ОКСИД НАНЕСЕН СО МАГНЕТРОНСКО РАСПРСКУВАЊЕ КАКО АНОДЕН КАТАЛИЗАТОР ЗА ДОБИВАЊЕ ВОДОРОД ВО ЌЕЛИИ СО ПЕМ

Нанесувани се тенки филмови од иридиум–оксид со помош на реактивен магнетронски распрснувач. Следено е влијанието на парцијалниот притисок на кислородот во распрснувачката плазма врз составот, површинската структура и морфологијата на филмовите со помош на анализите XRD, SEM, AFM и XPS анализа. При оптимална комбинација на параметрите на распрскувањето се постига формирање на стабилни микропорозни аморфни филмови, со високо развиена фрактална површина. Електрохемиското однесување на овие филмови е проучувано од аспект на нивна примена како катализатори за електролиза на вода во ќелии со протоноизменувачки мембрани (ПЕМ), користејќи циклична волтаметрија и стационарен галваностатски метод. За проценка на вредноста на активната површина на катализаторот е определен морфолошки фактор за серија примероци формирани со магнетронско распрскување, со варирање на дебелината/количеството катализатор, а потоа е воспоставена корелација меѓу овој фактор и каталитичката активност. Беше покажано дека иридиум–оксидот е многу ефикасен катализатор за реакцијата на развивање на кислород (OER).

* Dedicated to Professor Svetomir Hadži Jordanov on the occasion of his 70th birthday.

Најдобри резултати со анодна густина на струјата од $0.3 \text{ A} \cdot \text{cm}^{-2}$ при потенцијал од 1.55 V (во однос на RHE–референтна водородна електрода) покажа филмот со дебелина од 500 nm кој содржи $0.2 \text{ mg} \cdot \text{cm}^{-2}$ катализатор. Овие резултати комбинирани со утврдената механичка стабилност на филмовите од иридиум–оксид формирани со распрскување (SIROFs) ги докажуваат предностите на реактивното магнетронско распрскување како едноставен и сигурен метод за подготовка на катализатори со прецизно контролиран состав, количество катализатор и површински карактеристики.

Клучни зборови: иридиум–оксидни катализатори; реактивно распрскување со магнетрон; тенки филмови; состав, површинска структура и морфологија; аноден процес; генерирање водород во ќелии со протоноизменувачки мембрани (PEM).

1. INTRODUCTION

Hydrogen generation via polymer electrolyte membrane electrolysis is a comparatively new technology inspired and imposed by the intensive development of polymer electrolyte fuel cells (PEMFCs). The main advantages of PEM electrolysis over the conventional alkaline one are the lack of circulating liquid electrolyte, the substantially higher current densities ($1\text{--}3 \text{ A cm}^{-2}$ compared to 0.2 A cm^{-2}), the wide range of power loads, the lower parasitic energy losses, the very rapid power-up/power-down rates and the substantially higher purity of the produced hydrogen [1–3]. In addition, the PEM water electrolyzers (PEMWEs) can work at higher pressures thus, avoiding the compression of the hydrogen required for its transport. They allow variation of the input energy and are compatible with the renewable energy sources, which are variable by nature. The PEMWEs are ideal decision for small and remote plants and households with low and erratic energy consumption. Nevertheless the achieved essential progress in the field the PEMWEs are still not broadly used since the efficiency, service life, and especially the cost are still unsatisfactory. The main drawback of proton conducting PEM electrolysis is the relatively high anodic overpotential during the oxygen evolution reaction (OER) with respect to alkaline process. This partial electrode reaction is the major source of energy consumption during the electrolytic generation of hydrogen. Beside the required high catalytic activity, the anodic catalysts should possess excellent mechanical and chemical stability including

resistance toward oxidation at the high anodic potentials where the oxygen evolution takes place. During the last years, high performance has been reported for catalysts such as Ir, Pt–Ir, Ir–Ru and Ir–Ta oxides, while Ir–Ru has been proven to be the most active OER composition [3–6]. However, issues such as the reduction of catalyst loading and lifetime are still of continuous research interest. Essential cost reduction can be achieved by development of cheaper catalysts with enhanced activity, as well as by improvement of the utilization and decreasing of the catalyst loadings.

The method of magnetron sputtering is a well known and broadly used technique for preparation of variety of thin films with specific applications, mainly in the field of silicon microtechnology. In the last decade it has been introduced as an alternative to the classical methods for PEM catalysts preparation [7–9] offering several advantages. Contrary to the conventional methods such as thermal decomposition of metal precursors, the sol gel method, the wet chemical reduction, etc. [10–13] which produce catalytic powders, the catalysts prepared by magnetron sputtering are deposited as thin compact mono, bi- or poly-metallic and/or oxide films upon a selected substrate material or even directly onto the polymer proton conductive membrane. Thus, the numerous processes necessary to assemble the major component of the electrochemical processor, such as the preparation of catalyst ink, the following spreading of the ink on the substrate at several consecutive steps, etc. can be essentially reduced and simplified.

The parameters of the sputtering process (temperature, partial pressure of the inert and reactive gases, dc power, distance target – substrate) have a decisive effect on the properties of the deposited films such as density, surface morphology, porosity, mechanical stability. Other important characteristics of the catalysts prepared by this technique are the excellent homogeneous distribution of the metal particles on the support and the extremely low metal loadings (down to $10 \mu\text{g}\cdot\text{cm}^{-2}$) which can be achieved [8].

Iridium oxide is a material of increased interest in the modern material science due to its interesting properties and variety of technical applications. It has enhanced electrochemical activity, excellent electrical conductivity, electrochromatic properties, and biocompatibility [14–16]. The method of reactive magnetron sputtering allows preparation of homogeneous thin iridium oxide films with precisely controlled surface structure, morphology and thickness on various substrates [17–19]. These films known as sputtered iridium oxide films (SIROF) are well known for their improved chemical and mechanical stability in comparison to IrO_2 obtained by other methods. This paper summarises our work on development of optimised process for SIROF deposition, demonstrates the decisive role of the sputter regime on the film properties, and presents the application of SIROFs as anode catalysts for hydrogen generation via PEM water electrolysis.

2. EXPERIMENTAL

The iridium oxide films are fabricated by reactive dc magnetron sputtering from an Ir target in Ar/O_2 plasma using commercial equipment Nordiko 2550. The sputtering chamber is connected to gas lines delivering Ar and O_2 to the reactor. The inlet gas flow rates (F_{Ar} and F_{O_2}) are measured in standard cubic centimetres per minute [sccm]. The outlet gas flow rate depends on the effective pumping power of the cryogenic pump which determines the partial pressure of both gases and the

total pressure in the chamber. The effective pumping power is regulated by the opening of a throttle valve, S , measured in percents. The sputtering process is performed in a dc mode applying a power of 100 W without heating. SIROFs are deposited on hydrophobic carbon paper substrates upon 50 nm thick adhesive Ti sublayer. The thickness of the films is used to calculate the deposition rate R_d . It is measured with a surface profiler Tencorr P-10 using a control sample deposited on glass substrate via a lift off process. The structure of the films is analyzed by X-ray diffraction technique with a Philips X-ray diffractometer PW 3010. The surface morphology is examined by scanning electron microscopy using a Zeiss Gemini 982 microscope and the surface roughness is studied by atomic force microscopy with Quesant Instrument Q Scope 250. The electrochemical properties of the SIROF samples are tested in acid aqueous solution ($0.5 \text{ M H}_2\text{SO}_4$) and in a polymer proton conductive electrolyte. In the latter case they are integrated in membrane electrode assemblies consisting of SIROF anode and a Pt cathode (both having loading of $0.2 \text{ mg}_{\text{cat}}\cdot\text{cm}^{-2}$) attached on both sides of a polymer membrane Nafion 117 via hot pressing following a procedure described in details elsewhere [20]. The investigation is carried out using the electrochemical methods of the cyclic voltammetry (CV) and steady state polarisation measurements. The details about the specific polarization measurements are given in the captions under the figures. All electrochemical tests are performed using an EG&G PAR 283 potentiostat controlled by a commercial software.

3. RESULTS AND DISCUSSION

3.1. Optimisation of the sputtering process

The optimisation procedure includes varying of several parameters of the sputter process which influence essentially the chemical composition, structure, morphology, and electrochemical characteristics of SIROFs. The

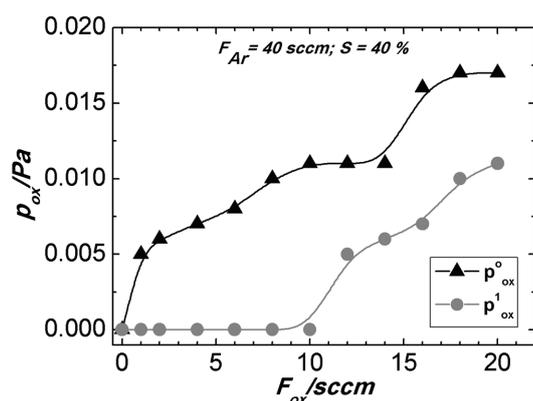


Fig. 1. Generic curves of dc reactive magnetron sputtering of iridium oxide films ($S = 40\%$; $L = 78$ mm; $P = 100$ W)

power of the applied electric field, P , is fixed to 100 W, while the flow rate of the argon gas, F_{Ar} , feeding the reactor is varied in the range 0–80 sccm; the valve opening of the pump, S , evacuating the gases from the chamber is changed in the range 15–80% and the substrates are positioned at two different distances, L , from Ir target (78 mm and 85 mm). For each combination $F_{Ar} - S - L$ the flow of the reactive oxygen gas, F_{ox} , is increased from 0 to 40 sccm in order to obtain the so called generic curves of the process, representing the influence of F_{ox} on the reactive gas partial pressure, p_{ox} , and the deposition rate, R_d . Among all 16 combinations of sputtering parameters tested, the characteristic point of the process, indicating an abrupt change in the trend of p_{ox} was unambiguously seen only on the generic curves recorded at the parameter set $F_{Ar} = 40$ sccm – $S = 40\%$ (Figure 1). For this sputter regime the initial increase of F_{ox} up to 10 sccm does not influence the partial pressure in the chamber, while at $F_{ox} = 10$ sccm the p_{ox} value increases abruptly indicating deviation of the system from steady state. This characteristic point of the curve is known as “transition point” of the sputtering process. The further increase in F_{ox} affects only slightly p_{ox} . Accordingly, after the initial rapid increase in the vicinity of the transition point R_d reaches a maximal value of 9.5 nm min^{-1} and further on does not change essentially. This set of process parameters ($F_{Ar} = 40$ sccm;

$S = 40\%$; $L = 78$ mm; $P = 100$ W; $F_{ox} = 8$ – 12 sccm) is considered as an optimal sputter regime. It is used to deposit a series of test samples varying the oxygen flow in the range 0–40 sccm and to investigate the influence of F_{ox} on the SIROF composition, surface structure and morphology.

3.2. Physical characterisation of SIROF

The X-ray diffraction spectra of all SIROFs showed iridium reflections with very low intensity, indicating an amorphous state of the deposited oxide layers. The SEM images presented in Figure 2 demonstrate that the film morphology and surface structure depend essentially on the oxygen flow. The pure iridium is composed of uniform, densely packed granular particles with a feature size of about 70 nm, the SIROFs obtained near the transition point have microporous structure, while at much higher F_{ox} the films become dendrite. The average roughness factor, R_a , calculated from the AFM data show that surface roughness increases rapidly with the increase of F_{ox} up to 12 sccm, does not change much in the range 12–20

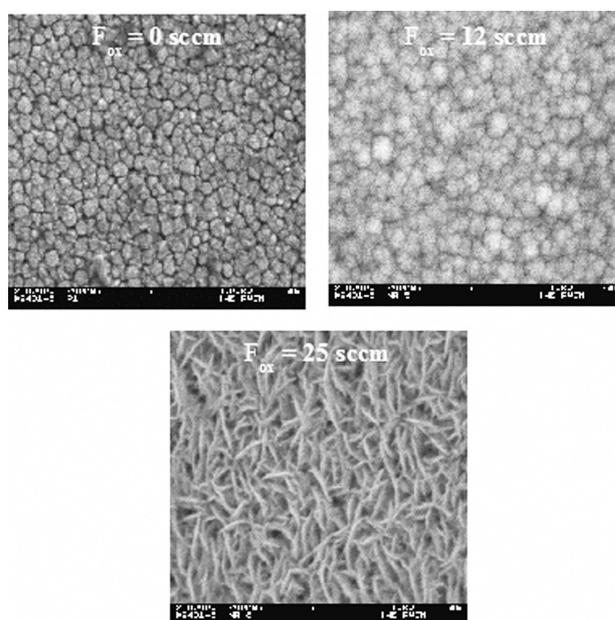


Fig. 2. SEM images of selected SIROFs obtained at optimized sputtering parameters ($F_{Ar} = 40$ sccm; $S = 40\%$; $L = 78$ mm; $P = 100$ W) and different oxygen flow

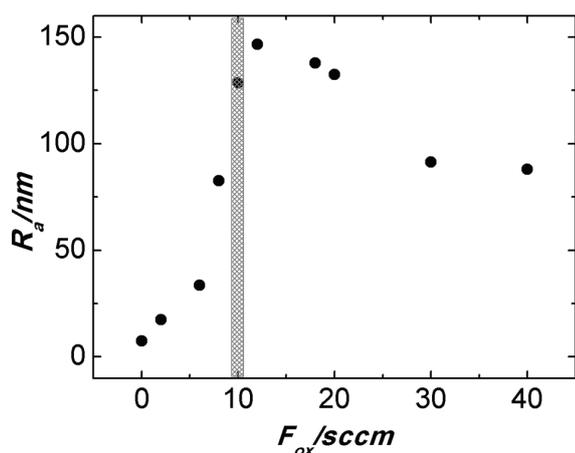


Fig. 3. Influence of oxygen flow on the roughness of SIROFs determined by AFM analysis.

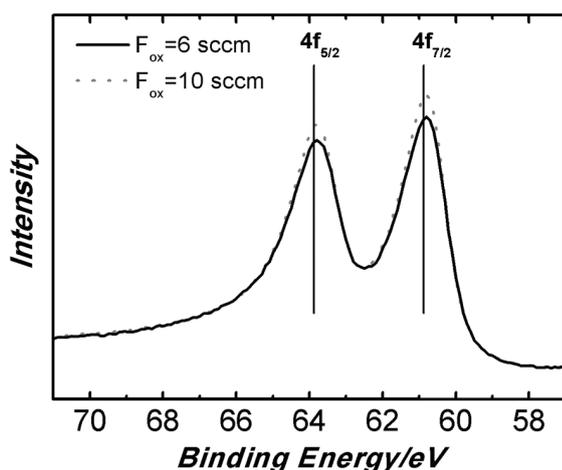


Fig. 4. XPS spectra of Ir 4f level of selected SIROFs deposited at optimized sputtering parameters and different F_{ox} values

sccm, while at higher oxygen flows the trend is back to smoother surfaces (Figure 3). To follow the effect of F_{ox} on the surface composition of the sputtered films they are studied by XPS (Figure 4). The position of the Ir 4f band is independent of the oxygen flow rate at which the films are sputtered. The binding energy of the 4f_{7/2} peak corresponds to the standard value for the pure iridium metal (60.9 eV) and the 4f_{5/2} peak is shifted in the positive direction, indicating a surface layer with Ir in higher

oxidation state [21]. The calculated data of the surface composition showed that the ratio between the pure iridium atoms and the iridium oxide molecules in the sputtered films gradually decreases with the increase in F_{ox} . At the same time, the ratio between the bound iridium and the oxygen atoms is nearly constant and very close to 1:2 suggesting that the deposited SIROFs consist predominantly of IrO₂. However, a definite correlation of the experimental binding energy with the oxidation state of Ir cannot be made from the available data. The sputtered films, even at $F_{ox} = 40$ sccm, still contain an essential amount of pure unbound iridium metal. The performed analysis showed that the oxygen flow has a decisive influence on the film morphology, respectively on the available active surface per unity geometric area which is an important factor affecting the optimal loading and its utilisation in case of electrocatalytic applications. The samples deposited at: $F_{Ar} = 40$ sccm; $S = 40\%$; $L = 78$ mm; $P = 100$ W; $F_{ox} = 8-12$ sccm possess homogeneous microporous structure combined with a highly developed surface and are expected to show superior performance characteristics. Their electrochemical performance as OER catalysts is investigated both in aqueous acidic and in polymer proton conductive membrane electrolytes.

3.3. Electrochemical tests in 0.5M H₂SO₄

It is well known that the continuous potential cycling of iridium in aqueous electrolytes results in formation of hydrated iridium oxide films [22–24]. The procedure is appropriately called “activation” because during this process the amount of charge transferred through the electrode/electrolyte interface gradually increases to reach a maximal value for the system under study [23, 25]. Therefore, all electrochemical data reported in this work are obtained after preliminary activation of the samples to a constant integral charge according the procedure described in details elsewhere [26]. Repetitive potential cycling at scan rate of 100 mVs⁻¹ is applied in the “water window” of the system (e.g. between the potentials of hydro-

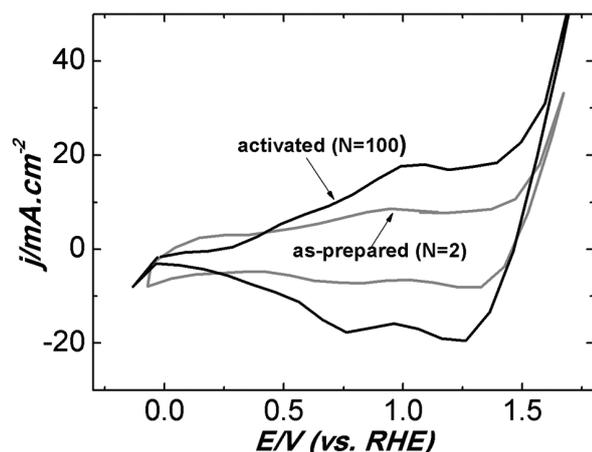


Fig. 5. Cyclic voltammograms of SIROF recorded after different number of activation cycles N in 0.5 M H_2SO_4 at 20 °C; scan rate $100 \text{ mV}\cdot\text{s}^{-1}$.

gen and oxygen evolution) until a stable shape of the CV is reached. The characteristic expansion of the voltammogram with the cycling is illustrated in Figure 5. The main feature of the CV curves is the symmetry along the potential axis and the equality of the integral anodic and cathodic charges passing through the phase boundary electrode/electrolyte. The observed increase in the total integral charge during the activation is attributed to hydration of the film and spreading of the electrolyte to more surface regions of difficult accessibility [27–29]. The consequence is a high ratio active to geometric electrode surface, allowing reduction of the catalyst loading without a sacrifice of efficiency and thus, resulting in lower cost of catalysis. The CV curve of the activated sample is dominated by current peaks located in the potential range above 0.7 V corresponding to hydration and oxidation/reduction reactions in the film. The peaks are broad and not very well depicted, suggesting an existence of variety of active surface sites with different formal potentials which is consistent with the amorphous state of the iridium oxide.

3.4. SIROFs as catalyst for PEM electrochemical water splitting

The selection of highly efficient electrode materials for production of clean hydrogen fuel requires detail knowledge on the electrochemical

behaviour of the catalysts in the specific electrolyte and working conditions, as well as optimisation of the catalytic loading and electrode structure in order to achieve maximal efficiency at minimal costs. The catalytic properties of the SIROFs sputtered at the established optimal regime are investigated in electrolytic cell with proton conductive membrane *Nafion* 117, which is the most broadly used polymer electrolyte. The membrane electrode assemblies with SIROF anode and sputtered Pt cathode catalysts are investigated after initial activation similar to that carried out in aqueous acidic solution. As it is shown in Figure 6, the increase in the applied potential cycles leads to the characteristic symmetrical broadening of the area under the CVs, related to gradual hydration of SIROF and penetration of the reactant in the pores of the catalytic film. CVs are dominated by current peaks in the potential range above 0.7 V, due to reversible redox processes and changes in the iridium oxidation state $\text{Ir}^{3+}/\text{Ir}^{4+}$. The SIROF catalysts before and after activation are examined by XPS analysis. The results in Figure 7 show presence of Ir in several oxidation states. The peaks at 60.7 and 62 eV are due to Ir^0 и Ir^{4+} , respectively [30, 31]. In accordance with the suggested activation hypothesis in the Ir 4f spectrum of the activated film, there are no peaks due to pure metallic iridium. It consists mainly of Ir^{3+} and Ir^{4+} (the peaks at 61.9 and 63.7 eV, respectively) [30].

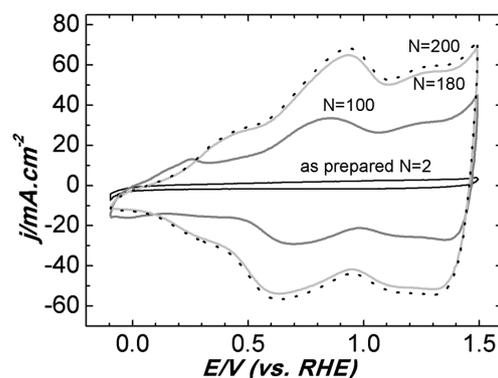


Fig. 6. Cyclic voltammograms of SIROFs integrated in MEA with *Nafion* 117 polymer electrolyte after different number of activation cycles N ; scan rate $100 \text{ mV}\cdot\text{S}^{-1}$; 20 °C.

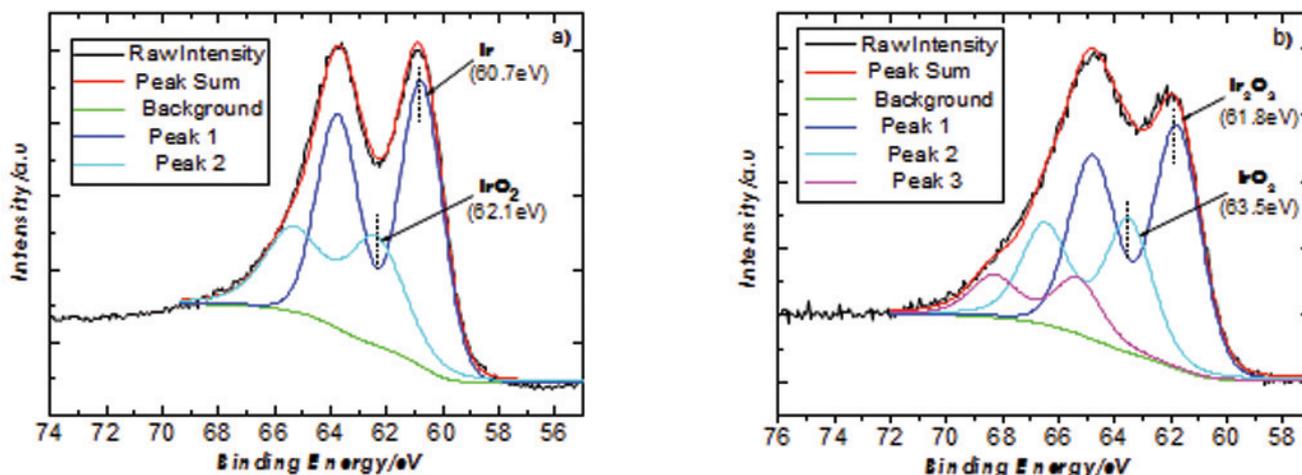


Fig. 7. XPS spectra of SIROFs before (a) and after (b) activation in Nafion 117 polymer electrolyte

One of the approaches to reduce the cost of the hydrogen produced by PEM water electrolysis is the reduction of the catalyst loading at preserved efficiency. For this purpose a series of SIROFs with different thickness/catalytic loading in the range 100–1000 nm/0.04–0.4 mg·cm⁻² were deposited. In order to optimise the catalysts loading it is necessary to access the real surface available for the reaction and to see how it is influenced by the film thickness. Following the method developed by Da Silva et al. [28], repetitive potential cycling in the water window potential range (–0.1 to 1.5 V) at varying scan rates (5–300 mVs⁻¹) are applied and the anodic current density, j_a , at potential just before the commence of intensive oxygen evolution reaction (1.31 V) is determined. Figure 8 presents the dependence of j_a on the scan rate. The slope of the liner section of the curves at low scan rates is a measure for the capacity of the total electrode surface C_t , while the slope at high cycling rates represents the “external”, e.g. the easily accessible electrode surface, C_{ext} . The difference between both values gives the “internal”, e.g. difficult to access part of the catalytic film. The morphology factor, f , determined by the ratio $f = C_{int}/C_t$ is a measure for the unusable part of the catalyst. The higher the value of f is, the lower is the catalyst utilization. It is seen that for the thin-

ner films (300 и 500 nm or 0.12 и 0.2 mg·cm⁻², respectively) j_a increases linearly with v in the whole interval of scan rates tested, suggesting that for these films nearly the whole catalyst takes part in the electrochemical charge transfer reaction. On the other hand, the j_a/v curves of the thicker samples (750 and 1000 nm or 0.3 и 0.4 mg·cm⁻², respectively) have two different linear sections, implying that at high scan rates part of the catalytic film is not accessible, e.g. it is inactive and does not contribute to the efficiency. According to the obtained values of the morphology factor (Table 1) the optimal SIROF thickness is 500 nm, which corresponds to a load 0.2 mg·cm⁻².

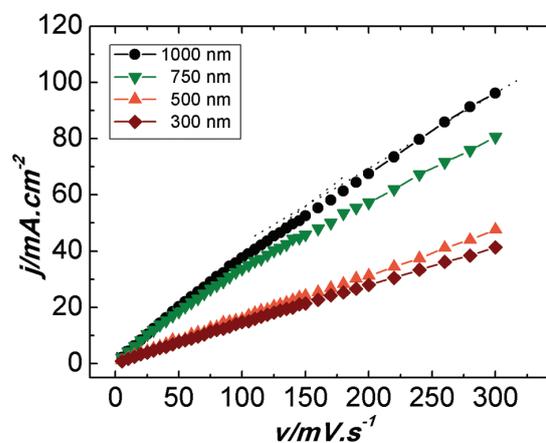


Fig. 8. Dependence of current density j_a at 1.31 V on the scan rate for catalytic films with different SIROF thickness/loading at test temperature of 20 °C

Table 1

Catalytic loading, charge capacity, morphology factor, and Tafel constants of SIROFs during PEM water electrolysis

$\delta, \mu\text{'nm}$	$l, \text{mg}\cdot\text{cm}^{-2}$	$Q_{\text{CDC}}, \text{mC}\cdot\text{cm}^{-2}$	morphology factor, f	$b_1, \text{mV}\cdot\text{dec}^{-1}$	$b_2, \text{mV}\cdot\text{dec}^{-1}$
1000	0.4	768	0.43	55	222
750	0.3	694	0.37	49	167
500	0.2	377	0.08	39	116
300	0.12	304	0.1	44	110

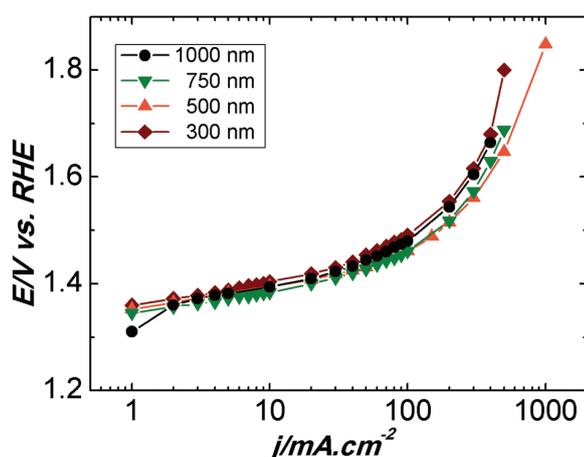


Fig. 9. Anodic steady state polarisation curves of SIROFs at temperature of 80 °C

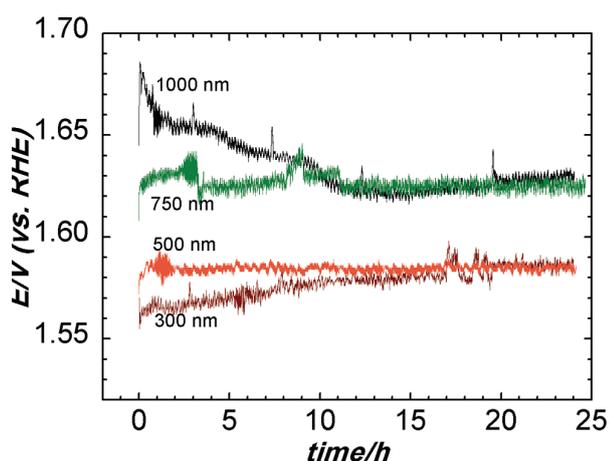


Fig. 10. Long term performance of the SIROFs recorded in a galvanostatic mode at current density of $0.3 \text{ A}\cdot\text{cm}^{-2}$ and temperature of 80 °C

The steady state anodic polarisation curves of the samples under study are presented in Figure 9. The oxygen evolution initiates at about 1.31 V and intensifies essentially with the increase of the potential. Two linear segments can be seen, corresponding to two Tafel slopes (b_1 , b_2) for the low and the high current density domains, respectively. These results are in good agreement with other literature data for pure and mixed IrO_2 prepared by thermal decomposition [3, 32, 33]. The results from the polarisation tests are summarised in Table 1. The process is most efficient and proceeds with lowest overpotential (current density of $0.5 \text{ A}\cdot\text{cm}^{-2}$ at 1.7 V) on the electrode with SIROF loading $0.2 \text{ mg}\cdot\text{cm}^{-2}$ which has also the lowest morphological factor and therefore, the most optimized structure. The usage of higher catalyst loadings would result only in increased cost of the electrolysis without improving its efficiency.

To check the stability of the sputtered iridium oxide films, the development of the electrode potential with time is followed for a period of 24 h under galvanostatic conditions at current density of $0.3 \text{ A}\cdot\text{cm}^{-2}$. A stable potential value is established in the beginning of the test (1.55 to 1.70 V depending on the thickness of the catalytic film). This value does not change essentially during the test duration (Figure 10), indicating a stable behaviour. In accordance with the steady state curves the electrode containing 500 nm SIROF shows a superior behaviour. This electrode is tested for a longer period of 168 h. On completion of the polarisation experiment the CVs were re-measured. They were identical to

those obtained before the long-term experiment suggesting a constancy of the catalytic properties combined with corrosion and mechanical stability of the iridium oxide film. The stability in the electrochemical performance (despite the usage of carbon paper substrate) is due to the deposited thin Ti sublayer which excludes the substrate from the aggressive oxygen radicals formed during the oxygen evolution. The measured current densities are comparable with those reported in the literature for IrO₂ obtained by other methods at much higher catalysts loadings [5, 33]. The excellent catalytic activity of our SIROFs is better demonstrated when presented as catalytic mass activity, j_m , and compared with the available literature data. The best mass activity of 0.5 A·g⁻¹_{cat} at cell voltage of 1.56 V has been reported by Marshall et al. [5] for IrO₂ obtained by thermal decomposition of iridium salts. In comparison, the developed SIROF has achieved 1.5 A·g⁻¹_{cat} at the same voltage [34].

4. CONCLUSIONS

The results presented in this work demonstrate the possibilities offered by the method of dc magnetron sputtering for deposition of thin iridium oxide films with strictly controlled properties, including composition, morphology, surface structure, density, electrochemical activity, etc. The advantages of the developed SIROFs as anodic catalysts for oxygen evolution in PEM water electrolysis are unambiguously demonstrated. The reaction starts at 1.31 V (about 0.2 V earlier than on Pt) and proceeds with low overpotential. Although iridium is a noble and expensive metal, the determined optimal catalyst loading of only 0.2 mg·cm⁻² is very low and guarantees high efficiency, mass activity and catalyst utilisation, thus giving serious promises for cost reduction of the PEM water electrolysis.

REFERENCES

- [1] P. Millet, M. Pineri, R. Durand, New Solid Polymer Electrolyte composites for water electrolysis, *J. Appl. Electrochem.*, **19** (1989), 162.
- [2] Y. Nishimura, K. Yashuda, Z. Siroma, K. Asaka, High current density solid polymer electrolyte water electrolysis, *Denki Kagaku oyobi kogyo butsuri Kagaku*, **65** (1997), 1122.
- [3] E. Rasten, G. Hagen, R. Tunold, Electrocatalysis in water electrolysis with solid polymer electrolyte, *Electrochim. Acta*, **48** (2003), 3945.
- [4] S. A. Grigoriev, V. I. Porembsky, V. N. Fateev, Pure hydrogen production by PEM electrolysis for hydrogen energy, *Int. J. Hydrogen Energy*, **31** (2006), 171.
- [5] A. Marshall, B. Børresen, G. Hagen, M. Tsyppkin, R. Tunold, Electrochemical characterisation of Ir_xSn_{1-x}O₂ powders as oxygen evolution electrocatalysts, *Electrochim. Acta*, **51** (2006), 3161.
- [6] F. Andolfatto, R. Durand, A. Michas, P. Millet, P. Stevens, F. Andolfatto, R. Durand, A. Michas, P. Millet, P. Stevens, *Int. J. Hydrogen Energy* **19** (1994) 421.
- [7] R. O'Hayre, S.-J. Lee, S.-W. Cha, F.B. Prinz, A Sharp Peak in the Performance of Sputtered Platinum Fuel Cells at Ultra-Low Platinum Loading, *J. Power Sources*, **109** (2002), 483.
- [8] D. Gruber, N. Ponath, J. Müller, F. Lindstaedt, Sputter-deposited ultra-low catalyst loadings for PEM fuel cells, *J. Power Sources*, **150** (2005), 67.
- [9] D. R. McIntyre, A. Vossen, J. R. Wilde, G. T. Burstein, Electrocatalytic properties of a nickel-tantalum-carbon alloy in an acidic electrolyte, *J. Power Sources*, **108** (2002), 1.
- [10] T. Teda, H. Igarashi, H. Uccida, M. Watanabe, Enhancement of the Electroreduction of Oxygen on Pt Alloys with Fe, Ni, and Co, *J. Electrochem. Soc.*, **146** (1999), 3750.
- [11] M. M. Jaksic, Hypo-hyper-d-electronic interactive nature of interionic synergism in catalysis and electrocatalysis for hydrogen reactions, *Int. J. Hydrogen Energy*, **26** (2001), 559.
- [12] E. Antolini, Formation of carbon-supported PtM alloys for low temperature fuel cells: a review, *Mat. Chem. Phys.*, **78** (2003), 563.
- [13] H. Boenemann, R. Richards, Nanoscopic metal par-

- tics—synthetic methods and potential applications, *Eur. J. Inorg. Chem.*, (2001), 2455.
- [14] H. J. Cho, H. Horii, C. S. Hwang, J. W. Kim, C. S. Kang, B. T. Lee, S. I. Lee, Y. B. Koh, and M. Y. Lee, Preparation and Characterization of Iridium Oxide Thin Films Grown by DC Reactive Sputtering, *Jap. J. Appl. Phys. Part 1*, **36** (1997), 1722.
- [15] C. U. Pinnow, I. Kasko, N. Nagel, S. Poppa, T. Mikolajick, C. Dehm, W. Hosler, F. Bleyl, F. Jahnel, M. Seibt, U. Geyer, and K. Samwer, Influence of deposition conditions on Ir/IrO₂ oxygen barrier effectiveness, *J. Appl. Phys.*, **91** (2002), 9591.
- [16] 16. H. S. Lee, W. S. Um, K. T. Hwang, H. G. Shin, Y. B. Kim, and K. H. Auh, Ferroelectric properties of Pb(Zr,Ti)O₃ thin films deposited on annealed IrO₂ and Ir bottom electrodes, *J. Vac. Sci. Techn. A* **17** (1999) 2939
- [17] 17. T. Pauporte, D. Aberdam, J. L. Hazemann, R. Faure, and R. Durand, X-ray absorption in relation to valency of iridium in sputtered iridium oxide films, *J. Electroanal. Chem.* **465** (1999) 88
- [18] N. Bestaoui, E. Prouzet, P. Deniard, and R. Brec, Structural and analytical characterization of an iridium oxide thin layer, *Thin Solid Films*, **235** (1993), 35.
- [19] R. H. Horng, D. S. Wu, L. H. Wu, M. K. Lee, Formation process and material properties of reactive sputtered IrO₂ thin films, *Thin Solid Films*, **373** (2000), 231.
- [20] E. Slavcheva, I. Radev, S. Bliznakov, G. Topalov, P. Andreev, E. Budevski, Sputtered iridium oxide films for water splitting via PEM electrolysis, *Electrochim. Acta*, **52** (2007), 3889.
- [21] S. Thanawala, D. G. Georgiev, R. J. Baird, G. Auner, Characterization of Iridium Oxide Films Deposited by Pulsed-Direct-Current Reactive Sputtering, *Thin Solid Films*, **515** (2007), 7059.
- [22] S. Gottesfeld, S. Srinivasan, Electrochemical and optical studies of thick oxide layers on iridium and their electrocatalytic activities for the oxygen evolution reaction, *J. Electroanal. Chem.*, **86** (1978), 89.
- [23] J. O. Zerbino, N. R. de Tacconi, A. J. Arvia, The Activation and Deactivation of Iridium Electrodes in Acid Electrolytes, *J. Electrochem. Soc.*, **125** (1978), 1266.
- [24] S. Hackwood, L. M. Schiavone, W. C. Dautremont-Smith, G. Beni, "Anodic Evolution of Oxygen on Sputtered Iridium Oxide Films, *J. Electrochem. Soc.*, **128** (1981), 2569.
- [25] C. Bock, V. I. Birss, Anion and water involvement in hydrous Ir oxide redox reactions in acidic solutions, *J. Electroanal. Chem.*, **475** (1999), 20.
- [26] E. Slavcheva, R. Vitushinsky, W. Mokwa, U. Schnackenberg, Sputtered Iridium Oxide Films as Charge Injection Material for Functional Electrostimulation, *J. Electrochem. Soc.*, **151** (2004), E226.
- [27] I. S. Lee, C. N. Whang, K. Choi, M. S. Choo, Y. H. Lee, **Characterization of iridium film as a stimulating neural electrode**, *Biomaterials*, **23** (2002), 2375.
- [28] L. A. Da Silva, V. A. Alves, M. A. P. Da Silva, S. Trasatti, J. F. C. Boodts, Oxygen evolution in acid solution on IrO₂ + TiO₂ ceramic films. A study by impedance, voltammetry and SEM *Electrochim. Acta*, **42** (1997), 271.
- [29] T. M. Silva, A. M. P. Simoes, M. G. S. Ferreira, M. Walls, M. Da Cunha Belo, Electronic structure of iridium oxide films formed in neutral phosphate buffer solution, *J. Electroanal. Chem.*, **44** (1998), 5.
- [30] S. B. Brummer, L. S. Robblee, F. T. Hambrecher, Criteria for selecting electrodes for electrical stimulation: theoretical and practical considerations, *Ann. N.Y. Acad. Sci.*, **405** (1983), 159.
- [31] S. B. Brummer and M. T. Turner, Electrochemical considerations for safe electrical stimulation of the nervous system with platinum electrodes, *IEEE Trans. Biomed. Eng.*, **BME-24** (1977), 59.
- [32] S. Trasatti, Electrocatalysis: understanding the success of DSA®, *Electrochim. Acta*, **45** (2000), 2377.
- [33] L. A. Da Silva, V. A. Alves, S. C. de Castro, J. F. C. Boodts, XPS study of the state of iridium, platinum, titanium and oxygen in thermally formed IrO₂+TiO₂+PtO_x films, *Colloid Surf. A: Physicochem. Eng. Aspects*, **170** (2000), 119.
- [34] D. Labou, E. Slavcheva, U. Shnakenberg, S. Neophytides, Performance of laboratory polymer electrolyte membrane hydrogen generator with sputtered iridium oxide anode, *J. Power Sources*, **185** (2008), 1073.