Catalytic activity of co-sputtered PtIr thin films toward oxygen reduction

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The work presents a research on the preparation, physical characterisation, and electrochemical activity of bimetallic platinum-iridium (Pt-Ir) thin films with varying metal ratio as oxygen reduction reaction (ORR) catalysts. The films are deposited upon gas permeable hydrophobic carbon paper substrates by co-sputtering from Pt and Ir pure metal targets. To achieve different metal ratios, the sputtering power applied on the iridium target is varied in the range 0 - 100 W at constant power of the Pt target. The ORR catalytic activity is investigated in 0.5M H₂SO₄ and proton conductive polymer electrolyte Naftion. The study reveals that the efficiency of the co-sputtered Pt-Ir catalysts is superior compared to pure Pt and depends on the sputter regime and alloy composition.

Keywords: oxygen reduction, magnetron sputtering, platinum iridium electrocatalysts, PEM fuel cell

INTRODUCTION

The oxygen reduction reaction (ORR) is the main source of energy dissipation in the polymer electrolyte membrane fuel cells (PEFC) [1]. The best ORR catalyst among the pure metals is Pt but its performance even at comparatively high loadings (0.4 mg.cm⁻²) is not fully satisfactory for PEFC mass production. To improve the ORR efficiency, catalysts with enhanced activity and better utilisation at decreased catalytic loadings are required [2,3]. The stability and durability are also a serious challenge for the successful PEMFC commercialisation. Various Pt alloys have shown improved catalytic activity compared to pure Pt. Typical examples are the alloys of Pt with transition metals (Cr, Fe, Co, Ni, Cu, etc.) which have been studied intensively over the last decades [4-6]. However, these metals are not stable in acidic media and can be easily leached out from the alloy, causing degradation of the catalyst, poisoning of the polymer electrolyte, and gradual decay in the fuel cell performance.

The platinum group metals (Au, Pd, Ir, Os, Ru, Rh) on the other hand, have excellent chemical stability and are attractive alloying elements capable to enhance the activity of Pt, at the same time improving the catalyst durability [7-9]. Among these metals, iridium is of particular interest since it shows extremely high stability. The existing literature data on the catalytic performance of Pt-Ir alloys are still scarce and refer mainly to Pt-Ir nanoparticles prepared by wet chemical reduction or thermal decomposition of metal salts. Ioroi and Yasuda investigated unsupported Pt-Ir alloys with varying Ir-content as oxygen reduction catalysts [8]. In acidic solutions they observed increase in the kinetic current density by a factor of about 1.5 for Pt-Ir samples containing 5-20 wt. % Ir. Similarly, under PEMFC working conditions, the dependence between Ir content and the specific current density showed an enhanced ORR activity at Ir concentration in the range 5-20 wt.%. Popov et al. studied mixtures of unsupported Pt- and Ir-black as catalysts for unitized regenerative fuel cells [9]. They reported that the Pt-Ir mixed catalyst with 15 wt. % Ir and electrochemical active surface area comparable to that of Pt-black, showed the highest round-trip efficiency at various current densities. At the same time, the fuel cell performance of this catalytic mixture was very similar to the efficiency of the Pt-black, despite the fact that Ir is known to possess lower ORR activity than Pt. In the last decade there is an increased interest to the method of magnetron sputtering as an alternative catalysts preparation technique [10-15]. It can be easily

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adopted for direct incorporation of variety of catalytic materials into the active PEMFC element – the membrane electrode assembly (MEA) [12,13]. The method offers advantages related both to the optimisation of the catalytic properties and the assembling of the MEA [14,16]. The surface structure and morphology of the catalytic film can be strictly controlled by simple variation of the process parameters [10,17,18]. Other advantageous feature of the method is its excellent reproducibility as well as the possibility to deposit not only pure metals but also alloys (co-sputtering) and compounds (reactive sputtering). In a more recent work an optimal regime for sputtering of low Pt loaded catalytic films directly on gas diffusion substrates was found [14]. This paper is focused on the fabrication of thin bimetallic Pt-Ir films by co-sputtering from Pt and Ir pure metal targets. The aim is by varying the power of the applied electrical field to optimise the composition and morphology in order to obtain catalysts with high ORR efficiency at low overall metal loading. Intra-atomic electronic interactions between both metals, resulting in increased ORR efficiency are also expected.

EXPERIMENTAL

The co-sputtered Pt-Ir films were deposited on commercial gas diffusion electrodes (hydrophobic carbon paper E-TEK 120/30 WP) over a thin Ti-adhesion layer [18]. The pressure of the argon plasma (p_Ar), the working distance between the metal target and the substrate (WD), and the dc power applied to the Pt target (P_Pt) were held constant for each sample (9 Pa, 78 mm, and 100 W, respectfully). To provide thin Pt-Ir films with various metal ratio the power of the Ir target (P_Ir) was varied in the range between 20 and 100 W. Further in the text the samples are referred in accordance to the power of the Ir target (Pt-Ir20 stays for the sample sputtered at P_Pt = 100 W and P_Ir = 20 W).

The films were characterised by energy dispersive X-ray spectroscopy (EDX), X-Ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) [19]. The influence of the Pt-Ir ratio on the catalytic activity toward oxygen reduction in 0.5 M H_2SO_4 electrolyte was studied at room temperature by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) on rotating disc electrode (EG&G PARC, Model 616). The experiments were performed in a three electrode electrochemical cell with Pt wire counter electrode and saturated Ag/AgCl reference electrode. In the text all potentials are referred to reference hydrogen electrode (RHE). The Pt and Pt-Ir catalytic films deposited on commercial gas diffusion layers (carbon Toray paper, 30% water proofed, 300 µm thick) were attached mechanically to a glassy carbon disk electrode, leaving working area of 0.5 cm² exposed to the electrolyte. The CV measurements were carried out in Ar-saturated electrolyte. The electrochemical active surface area (S_A) was calculated via integration of the area under the hydrogen adsorption/desorption peaks according a common electrochemical procedure [2]. The polarisation curves were obtained in oxygen saturated electrolyte. The activity of the catalysts was assessed comparing the current density in the kinetic range of the curves (j at 0.9 V vs. RHE). Selected samples were integrated in membrane electrode assemblies using a commercial Nafion 117 membrane (Alfa Aesar) and tested as cathodes in a single cell hardware supplied with Pt hydrogen reference electrode (Fuel Cell Technologies Inc.). The testing conditions were: 80 °C, total pressure of 2.5 atm abs., fully humidified hydrogen and air. The electrochemical experiments were performed using Solartron Analytical 1287 Electrochemical Interface potentiostat and CorrWare™ software.

RESULTS AND DISCUSSION

Structural and morphological characterisation

![Fig. 1. Influence of sputtering power on the content of Ir in the co-sputtered Pt-Ir films; Cell parameter of Pt-Ir films as function of Ir content (inset figure).](image)

The iridium content (m_Ir, at.%) determined via EDX is given in Table 1. In the same table are included the measured catalytic loadings and some
structural data extracted by the XRD analysis. The established linear dependence between \( m_{Ir} \) and \( P_{Ir} \) (Fig. 1) allows an easy control of the catalyst composition and loading by simple variation of the sputtering power and duration of the process. The results show that although the sputtering time was kept constant for all samples, their catalytic loadings \( (I_{cat}) \) are not identical. A general trend of decrease in \( I_{cat} \) with the increasing \( P_{Ir} \) is observed. This is related to the lower deposition rate of Ir which grows in a more disordered columnar structure with smaller crystallites compared to Pt [20]. For this reason the increase in \( m_{Ir} \) leads to formation of layers with higher porosity, more open structure and lower density.

The effect of \( P_{Ir} \) on the surface morphology and film structure the Pt-Ir samples was investigated using SEM and XRD analysis and these results have been presented in details elsewhere [17,19]. Briefly, the size of the particles decreases with the increasing \( P_{Ir} \), varying in the range 20-10 nm, while the increase in Ir content leads to changes in the crystallites shape and formation of elongated structures, more clearly seen on the samples obtained at \( P_{Ir} \geq 30 \text{ W} \). The observed changes in the morphology are related to the increasing amount of Ir atoms taking part in the film growth that compete with the sputtered Pt for the most favourable surface sites, leading to change in the preferential plains of the crystal growth and formation of smaller crystallites with different crystal habitus. The XRD analysis revealed displacement of the diffraction peaks with the increasing \( m_{Ir} \) to higher angles in respect to pure Pt, indicating a lattice contraction due to the inclusion of Ir atoms. The increase in \( m_{Ir} \) leads also to decrease in the cell parameter following a linear trend (the inset in fig. 1) and in accordance with the empirical Vegard’s law proves a substitution of a solid solution type [21]. The estimated structural characteristics of the catalysts are summarized in Table 1.

### Table 1. Structural characteristics of Pt-Ir films co-sputtered at various power of Ir target \((P_{Ir})\) on carbon paper; \( WD = 78 \text{ mm} ; P_{Ar} = 9 \text{ Pa} ; P_{Pt} = 100 \text{ W} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( P_{Ir} ) [W]</th>
<th>( I_{cat} ) [mg.cm(^{-2})]</th>
<th>( m_{Ir} ) [at.%]</th>
<th>( D_{111} ) [nm]</th>
<th>( D_{200} ) [nm]</th>
<th>( a ) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0</td>
<td>0.143</td>
<td>0</td>
<td>11.8</td>
<td>7.7</td>
<td>3.9244</td>
</tr>
<tr>
<td>PtIr20</td>
<td>20</td>
<td>0.108</td>
<td>6.8</td>
<td>11.7</td>
<td>8.7</td>
<td>3.9202</td>
</tr>
<tr>
<td>PtIr30</td>
<td>30</td>
<td>0.107</td>
<td>10.7</td>
<td>11.0</td>
<td>8.2</td>
<td>3.9167</td>
</tr>
<tr>
<td>PtIr40</td>
<td>40</td>
<td>0.118</td>
<td>15.3</td>
<td>10.4</td>
<td>11.5</td>
<td>3.9100</td>
</tr>
<tr>
<td>PtIr50</td>
<td>50</td>
<td>0.110</td>
<td>20.5</td>
<td>9.7</td>
<td>10.7</td>
<td>3.9065</td>
</tr>
<tr>
<td>PtIr100</td>
<td>100</td>
<td>0.078</td>
<td>42.5</td>
<td>7.6</td>
<td>7.9</td>
<td>3.8846</td>
</tr>
<tr>
<td>Pure Ir</td>
<td>100</td>
<td>0.067</td>
<td>100</td>
<td>6.0</td>
<td>5.0</td>
<td>3.8403</td>
</tr>
</tbody>
</table>

The positions of Pt 4f\(_{3/2}\) and Ir 4f\(_{3/2}\) peaks (at bonding energies of 71.2–71.6 eV and 60.6–61 eV, respectively) derived from XPS spectra [19] indicated that both components are in metallic form. With the increase of Ir content a shift of about 0.3 – 0.4 eV to higher binding energies was registered for the Pt4f\(_{3/2}\) line. At the same time the Ir 4f\(_{3/2}\) peak was equally shifted to lower binding. The observed displacements in the binding energy of the core-level orbital are related to changes in the electron density, indicating an intra-atomic charge transfer [8].

**Electrochemical tests**

The electrochemical activity of the co-sputtered Pt-Ir films was investigated using linear sweep voltammetry (LSV) on rotating disk electrode (RDE). Figure 2 shows the polarisation curves of the Pt-Ir30 sample obtained at varying rotation rate \((\omega)\). The typical regions of kinetic, mixed and diffusion control of the reaction are well distinguished. The inset in fig. 2 presents the current-potential curves of the Pt-Ir films having an enhanced ORR efficiency compared to the pure Pt at rotation rate of 1200 rpm. The the oxygen reduction is most intensive on the Pt-Ir30 catalyst. In order to
evaluate the catalytic efficiency of each sample, it is necessary to determine the kinetic current density \((j_k)\), to construct the Tafel plots, and using the equation \(\eta = a + b \log j_k\), to calculate the exchange current density \((j_0)\), which is a measure for the intrinsic catalytic activity.

According to the Levich RDE theory, the overall disk current \((j)\) is related to the diffusion limited current \((j_{lim})\), the kinetic current \((j_k)\), and the reaction order \((m)\) according to eq. (1):

\[
\log j = m \log(1 - jj_{lim}) + \log j_k
\]

while, the limiting current density is represented by eq. (2):

\[
j_{lim} = 0.62nFCD_o^{2/3}v^{1/6}\omega^{1/2}
\]

where \(n\) is the number of electrons transferred per molecule of O\(_2\), \(F\) - the Faraday constant, \(C_o\) - the bulk concentration of oxygen, \(D\) - its diffusion coefficient, \(v\) - the kinematic viscosity, and \(\omega\) - the electrode rotation rate.

The equation (2) is an ideal response of a fast electron transfer processes. For reactions proceeding under mixed transport-kinetic control, the electrode current is described by the modified Koutecky-Levich equation (3):

\[
1/j = 1/j_{lim} + 1/j_k
\]

According the RDE theory, for fixed overpotentials the plots \(1/j\) vs. \(1/\omega^{1/2}\) should generate straight lines with intercepts proportional to \(j_k\) and slopes independent on the potential and proportional to \(n\). The Koutecky-Levich analysis is broadly used to estimate the kinetic current density.

However, it should be noted that Eq. (3) is valid only for first order reactions [6,22-24]. In order to verify its validity for the catalysts under study the plots of \(\log j\) vs. \(\log (1-j/j_{lim})\) for the sputtered Pt (Fig. 3 a) and Pt-Ir30 (Fig. 3 b) catalytic films were built at different rotation rates and electrode potentials. The obtained slopes of the straight lines were higher than 1 (in the range 1.32-1.45), showing a deviation of the ORR from the first order kinetics.

The observed deviations in the hydrodynamics of the studied systems most probably are related to the highly porous structure of the electrodes. In this case the Koutecky-Levich analysis is not valid and the catalytic activity can be compared using the current density at low overvoltages normalized by the real surface area of the electrode, \(S_A\) [14, 23]. The values of \(S_A\) for the Pt-Ir samples (Table 2) were determined by cyclic voltammetry (Fig. 4) following the well established experimental procedure [2]. The \(S_A\) of the Pt-Ir sample under study does not differ significantly as Pt-Ir20 and Pt-Ir30 have slightly higher active surfaces than pure Pt.

### Table 2. Electrochemical data obtained from the cyclic voltammetry curves and the Tafel plots.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(j_{ave})</th>
<th>(S_A)</th>
<th>Tafel slope (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mA cm(^{-2})</td>
<td>cm(^2) real cm(^{-2})</td>
<td>mV dec(^{-1})</td>
</tr>
<tr>
<td>Pt</td>
<td>4.7 x 10(^{-5})</td>
<td>22.5</td>
<td>110</td>
</tr>
<tr>
<td>Pt-Ir20</td>
<td>7.22 x 10(^{-5})</td>
<td>23.9</td>
<td>102</td>
</tr>
<tr>
<td>Pt-Ir30</td>
<td>10.2 x 10(^{-5})</td>
<td>25.5</td>
<td>98</td>
</tr>
<tr>
<td>Pt-Ir40</td>
<td>5.4 x 10(^{-5})</td>
<td>25.4</td>
<td>108</td>
</tr>
</tbody>
</table>

The data in Table 2 show that the oxygen reduction is most intensive on the Pt-Ir30 catalyst. Fig. 5 presents the current density \(j\) normalised to the \(S_A\) vs. potential in the kinetic range where the mass transport effects are negligible (0.9V vs. RHE). The values of the Tafel slope \(b\) determined from these plots are included in Table 2. The lowest is the slope for the Pt-Ir30 sample but in general, the values for all samples are very close (101-111).

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**Fig. 3.** Reaction order plots for Pt (a) and Pt-Ir30 (b) catalytic films in 0.5M H\(_2\)SO\(_4\) at various electrode potentials
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Fig. 4. Cyclic voltammetry curves of selected sputtered Pt-Ir films recorded at 100 mV.s\(^{-1}\) scan rate in 0.5M H\(_2\)SO\(_4\).

Fig. 5. Tafel kinetic plots for selected sputtered Pt-Ir films in 0.5M H\(_2\)SO\(_4\) mV.dec\(^{-1}\), suggesting that the rate determining step is the transfer of the first electron to the oxygen molecule (\(b = 120\) mV.dec\(^{-1}\)). The comparison of all the results obtained indicates that the bimetallic Pt-Ir films are more efficient ORR catalysts than the pure Pt film. With the increase of \(m_{Ir}\), the rate of the reaction increases, goes through maximum at concentrations around 11 at.% Ir (for Pt-Ir30 the increase is by factor of 2.2 compared to Pt), and at higher \(m_{Ir}\) decreases again.

While Pt is known to possess the highest ORR activity among the pure metals, including those from the Pt group (Pt > Pd > Ir > Rh), numerous theoretical calculations and experimental data have shown that various Pt alloys (if properly designed) demonstrate an improved catalytic behavior compared to pure Pt [24-26]. The enhanced ORR activity is related to geometry factors such as particle size effect and the Pt-Pt nearest neighbour bond distance and/or electronic factors such as intra atomic interactions resulting in modification of Pt electronic structure [27]. The results obtained in this study show that the concentration of Ir influences strongly the catalytic efficiency of the sputtered Pt-Ir alloy as both groups of the aforementioned factors are involved. The performed XRD and SEM analysis registered systematic change in the morphology, particle size, and lattice parameter with the change of the sputtering power, respectively with the content of Ir in the sputtered film. The alloying leads to shrinkage of the metal lattice and decrease of the Pt-Pt nearest neighbour distance thus, inducing low energy Pt surface sites for enhanced oxygen adsorption. At the same time due to the stronger affinity of Ir to OH adsorption, the formation of Ir-OH\(_{ads}\) starts at less positive potentials than the Pt-OH\(_{ads}\) surface coverage (Fig. 4). The earlier formation of Ir-OH coverage and the steric hindrance between the already adsorbed OH-groups leave more free active Pt sites for the adsorption of oxygen. It should be noticed that both the decrease in the lattice parameter and the increase of Ir concentration follow a linear trend with the increasing sputtering power \(P_{Ir}\), while the electrochemical measurements proved a superior catalytic activity for the Pt-Ir30. This most active catalyst has moderate lattice parameter and Ir content of ~11 at.%. Obviously, at higher Ir concentration (\(m_{Ir} > 15\) at.%), the discussed positive effects induced by Ir diminish due to the accompanying decrease of the Pt active surface sites which in turn, hinders the adsorption of oxygen and results in lower ORR intensity. The observed enhanced activity of the Pt-Ir films can be related also to the electronic interactions between both metals registered by the XPS analysis [19]. The displacement in the binding energies of Pt 4F\(_{7/2}\) and Ir 4F\(_{7/2}\) is a result of changes in the electron density, indicating an intra-atomic charge transfer between both metals. In general, the partial electron transfer in an alloy occurs from the less

Fig. 6. ORR polarisation curves in PEMFC presented as mass activity.
electronegative to the more electronegative component. The electronegativity values of Pt and Ir are 2.18 and 2.22 respectively. Therefore, in Pt-Ir alloy the partial electron transfer should be from Pt to Ir. This assumption is in agreement with the XPS analysis where a positive shift in the binding energy of the core level electrons of Pt atom is observed.

Since the sputtered PtIr films are envisaged for fuel cell applications PtIr30, PtIr50 and the pure Pt were integrated in membrane electrode assemblies and investigated in laboratory PEMFC. The obtained polarisation curves are shown in fig. 6 where the current density is normalized to the catalytic loading and presented as mass activity, \( j_m \). In accordance with the results obtained in sulfuric acid solution, the performance of MEA with PtIr30 cathode (mass activity per overpotential) in the potentials range 0.75 – 0.5 V vs. RHE exceeds by a factor of 2 that of MEA with a pure Pt cathode.

CONCLUSIONS

The influence of Ir sputtering power on the film composition, structure and morphology, and the ORR electrocatalytic activity were studied in details. It was found that the increasing power results in gradual Ir enrichment of the film, leading to formation of catalysts with higher porosity, decrease in the particles size, and shrinkage of the metal lattice. Electronic interactions and intra-atom charge transfer between both metals were also registered. It was shown that these effects reflect on the catalytic activity of the co-sputtered films that goes through maximum at Ir concentrations in the range 10-15 at.% The results obtained give credence to consider the co-sputtered PtIr films as promising durable cathodes for PEFC applications capable to offer enhanced ORR efficiency at relatively low metal loading.

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КАТАЛИТИЧНА АКТИВНОСТ НА СЪ-РАЗПРАШЕНИ ФИЛМИ ОТ Pt-Ir СПРЯМО РЕДУКЦИЯ НА КИСЛОРОД

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(Резюме)

Настоящата статия е посветена на приготвяне, физико-химично характеризиране и оценка на електрохимичната активност на биметални платина-иридий (Pt-Ir) тънки филми с различно съотношение между двата метала като катализатори спрямо редукция на кислород. Филмите са отложени върху газо-пропусклива хидрофобизирана въглеродна хартия посредством съ-разпрашване на Pt и Ir метали мишени. За да се постигнат различни Pt-Ir съотношения, мощността на разпрашване, приложена върху иридиевата мишена е променяна в диапазона 0 - 100 W при постоянна мощност на платиновата мишена. Електро-каталитичната активност спрямо редукция на кислород е изследвана в 0,5 M H2SO4 и протон проводящ полимерен електролит Nafion. Резултатите показват, че електро-каталитичната активност на съ-разпрашените Pt-Ir катализатори е по-висока в сравнение с тази на Pt и силно се повлиява от режима на разпрашване и състава на сплавта.