Electrocatalytic materials for solid polymer electrolyte water electrolyzers

A S Pushkarev\textsuperscript{1,2}, I V Pushkareva\textsuperscript{1,2}, S V Akelkina\textsuperscript{1}, M V Kozlova\textsuperscript{1,2}, S A Grigoriev\textsuperscript{1,2,3}, N V Kuleshov\textsuperscript{2} and D G Bessarabov\textsuperscript{3}

\textsuperscript{1} National Research Centre “Kurchatov Institute”, 1 Akademika Kurchatova Square, Moscow, 123182, Russia
\textsuperscript{2} National Research University “Moscow Power Engineering Institute”, 14 Krasnokazarmennaya Street, Moscow, 111250, Russia
\textsuperscript{3} HySA Infrastructure Center of Competence, North-West University, Private Bag X6001, Potchefstroom, 2531, South Africa

Pushkarev_as@outlook.com

Abstract. In the present work the activity and stability of the IrO$_x$/TiO$_x$ catalyst obtained by the polyol approach in the oxygen evolution reaction (OER) were studied in comparison with the commercial analogue IrO$_x$. Electrochemical studies were provided, including accelerated stress testing. The synthesized IrO$_x$/TiO$_x$ catalyst demonstrated higher OER activity and stability than the commercial IrO$_x$, and the obtained results allow to suggest and discuss possible mechanisms of the studied catalysts degradation. Tests of membrane-electrode assemblies based on synthesized IrO$_x$/TiO$_x$ catalysts in SPE water electrolyzer demonstrate the possibility to significantly reduce the noble metal content on the anode.

1. Introduction
The hydrogen energy is one of the main concepts of sustainable energy systems under development, and hydrogen production is a key component of this concept. Currently, most of the hydrogen is obtained by natural gas, hydrocarbons or alcohol steam conversion \cite{1} and, to a smaller extent, as a by-product from chlor-alkali electrolysis process. However, in recent years, water electrolysis has gained much attention since it allows the relatively quick and convenient production of pure hydrogen only from water and electricity.

Solid polymer electrolyte (SPE) water electrolysis offers a sustainable solution to produce hydrogen, which may be coupled with intermittent renewable energy sources (e.g. wind and solar) \cite{2,3}. Key advantages compared to other types of electrolyzers are a wide range of operation current densities (1-2 A cm$^{-2}$ at a thermodynamic efficiency of 60-80\%), as well as a fast response to load change. In addition, there is no need to use concentrated electrolytes, and working temperatures do not exceed 90°C \cite{2}.

The high rate of hydrogen and oxygen evolution reactions in acidic media can be achieved only using catalysts based on noble metals: Pt, Ru or Ir. Due to the high anode potential and the specific features of the oxygen evolution reaction (OER) mechanism on Ir (IrO$_x$) \cite{4}, the stability of the anode catalysts is not high enough, therefore, to ensure a sufficient SPE water electrolyzer lifespan high anode catalyst loadings on the electrode are necessary, which significantly increases the noble metals content. Furthermore, the SPE electrolysis performance significantly depends on the OER overvoltage, therefore...
the development of active and stable electrocatalysts with a substantially reduced noble metals content is necessary. The usage of supports such as different metals oxides and carbides [5,6] is a promising way to reduce noble metal loading and to increase its utilization. Titanium suboxides TiOx2-1 are promising materials as OER electrocatalyst support, which possesses high electronic conductivity [7] and high corrosion resistance in acidic media [8]. These materials have been proven as promising supports for Pt [9], Pt-Ir [10] and Ir [11] nanoparticles for hydrogen-air and reversible fuel cells as well as an anode of SPE water electrolyzer, respectively. However, the stability of OER catalysts supported on TiOx2-1 still requires clarification, since non-stoichiometric titanium oxides can be oxidized to non-conductive TiO2.

In the present work, the activity and stability of the IrOx/TiOx catalyst obtained by the polyl method in OER in comparison with the commercial analogue of IrOx were studied. An accelerated stress testing technique in a liquid electrolyte was used to evaluate the catalysts stability and to clarify possible catalysts degradation mechanisms and the role of TiOx support. Also, the synthesized IrOx/TiOx was investigated as an anode catalyst in the membrane-electrode assembly of an SPE water electrolyzer.

2. Experimental part

Commercial electrocatalyst IrOx (TKK, Japan) were used without additional treatment. The IrOx/TiOx was synthesized by the polyl method. H3IrCl6·6H2O was used as a precursor of Ir nanoparticles, and ethylene glycol was used as a reducing agent. In a typical procedure, catalyst preparation was carried out in two stages (1) adsorption of the precursor onto the support (at 75°C) and (2) reduction of the nanoparticles (at 100°C).

To deposit a catalytic layer on the working electrode surface, a catalytic “ink” was prepared and 5 μl was dropped onto a previously prepared surface of a gold disk electrode (Pine Instruments, USA) with the loading of ca. 51 μg cm-2. Finally, the catalytic layer was capped with 5 μl of a 0.05% Nafion® solution (Ion Power, USA).

Electrochemical measurements were carried out in a deaerated 0.1M HClO4 solution at 30°C in a glass three-electrode cell equipped with a Pt-wire counter electrode and an Ag/AgCl/KCl (sat.) reference electrode which was connected by Luggin capillary. A rotator (MSR, Pine Instruments) was used to rotate the working electrode, and the potentiostat (SP-150 BioLogic, USA) was used for electrochemical measurements. All potential values below are given vs. standard hydrogen electrode (SHE). Prior to experiments, the solution ohmic resistance between the working electrode and the reference electrode was measured using the built-in software procedure (EC-lab, BioLogic, USA) at a potential of 1.35 V. The activation of the working electrode was realized by potential cycling in the range of 1.2–1.6 V at a sweep rate of 100 mV s-1 for 8–10 cycles. Polarization curves were performed in the potential range 1.2–1.6 V at the sweep rate of 5 mV s-1 and a rotation speed of 2500 rpm-1. The catalyst activity was determined as the value of current density at a potential of 1.48 V obtained from polarization curves which were corrected for ohmic losses [12]. The electrochemically active surface area (EASA) of the catalysts was determined as the value of the charge obtained from the of the cyclic voltammogram (CV), measured at the sweep rate of 100 mV s-1 in the potential range 0.4–1.3 V. Accelerated stress testing (AST) [13] of catalysts was carried out by potential cycling at the rotation speed of 2500 rpm-1 in the deaerated 0.1M HClO4 solution in the potential range of 1.4–1.6 V with the potential sweep rate of 500 mV s-1.

To study the polarization curves of SPE electrolysis laboratory cell, membrane-electrode assemblies (MEAs) of a circular shape with 7 cm2 working surface area were prepared, in which Nafion® 117 membranes (Chemours Company, USA) were used as SPE. Porous titanium disks (BT-1-0 [14]) with anodic and cathodic electrocatalytic layers deposited by air-spraying of the catalyst water-alcohol suspension were used as anodic and cathodic gas diffusion electrodes (GDEs) [15]. IrOx (with the loading of 1 and 2 mg cm-2) or IrOx/TiOx (with the loading of 3 mg cm-2) were used as the anode catalyst, and Pt/Vulcan XC-72 (with the loading of 0.8 mg Pt cm-2) was used as the cathode one. MEAs were clamped in a titanium laboratory cell consisting of two thermostatically controlled half-cells [16].

3. Results and discussion
Figs. 1–2 shows the CVs of IrO₉ and IrO₉/TiOₓ catalysts, measured in deaerated 0.1M HClO₄ solution. The shape of all presented CVs are characterized by a few broad peaks mostly at potentials >0.4 V, which correspond to redox transitions, related to adsorption and oxidation of oxygenated species from the solution [17,18] according to the equation:

\[
\text{MeO}_{a} (\text{OH})_{b} + \delta \text{H}^{+} + \delta \text{e}^{-} \leftrightarrow \text{MeO}_{a-\delta} (\text{OH})_{b+\delta}
\]

where Me – Ir or Ru.

**Figure 1.** The CV of IrO₉ catalyst measured in deaerated 0.1M HClO₄ solution at 30 °C before (blue line) and after (red line) AST.

**Figure 2.** The CV of IrO₉/TiOₓ catalyst measured in deaerated 0.1M HClO₄ solution at 30 °C before (blue line) and after (red line) AST. The inset shows the initial CVs of both catalysts for comparison.

The CVs of Ir-based catalysts are characterized with two main waves (Figs. 1–2) at ca. 0.8–0.95 V and 1.0–1.2 V, related to the Ir^{III}/Ir^{IV} and Ir^{IV}/Ir^{V} transitions, respectively [19–22]. According to the results of X. Tan et al. [23], the IrO₉ (TKK) surface corresponds to the quasi-amorphous hydrated Ir^{III}/Ir^{IV} mixed oxide which confirmed by X-ray Photoelectron Spectroscopy. Also, the small wave observed at
both IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} CVs at \(-0.4\) V corresponds to the oxidation of small amount metallic Ir\textsuperscript{(0)} to Ir\textsuperscript{\textit{III}} [20]. According to the literature [24,25] the redox process observed at both IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} at 0.6–0.9 related to the Ir(OH)\textsubscript{3} transition to IrO(OH)\textsubscript{2} and suggests the same nature of IrO\textsubscript{x} particles on the titanium suboxides surface in IrO\textsubscript{x}/TiO\textsubscript{x}. The redox transition with the formation of Ir in higher oxidation states is relatively weak. It can be assumed that this process is shifted towards higher potentials and may overlap with OER, which starts at a potential value of ca. 1.4 V (Fig. 2) [20]. In fig. 1 the currents in the region of hydrogen adsorption/desorption (<0.4 V) are extremely small, which can be explained by water molecules intercalating into the oxide and preventing electron transfer in the oxide structure [26]. This effect is significantly less pronounced in the case of a catalyst on an electrically conductive support, which was also observed in [27].

The bare TiO\textsubscript{x} CV is given in fig. 2 as well, which evidenced that all charge transferring observed on the IrO\textsubscript{x}/TiO\textsubscript{x} CV relates to the IrO\textsubscript{x} nanoparticles on the support surface. The initial values of the specific active surface area and activity of both IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} catalysts are given in Table 1.

| Sample       | Specific activity at 1.48 V vs. SHE (A g\textsuperscript{-1} Ir) | Active surface area, C | Tafel slope, mV dec.\textsuperscript{-1} |
|--------------|---------------------------------------------------------------|------------------------|----------------------------------------|
| IrO\textsubscript{x} | 357±60                                                          | 1.34±0.16                | 42.4–44.7                              |
| IrO\textsubscript{x}/TiO\textsubscript{x} | 809±101                                                         | 1.94±0.30                | 39.2–40.9                              |

The mass activity of IrO\textsubscript{x} is in good agreement with the literature [28], although the comparison of the mass activity of different catalysts is very difficult due to the lack of standard methods used by all researchers and due to the difference in the experimental conditions. Significantly higher activity of IrO\textsubscript{x}/TiO\textsubscript{x} suggested being ensured by morphological factors (uniform particles distribution, their small size, high active surface area), structural factors (influence of the support on the electronic structure of IrO\textsubscript{x}) and high electrical conductivity of the support. The obtained values of the IrO\textsubscript{x}/TiO\textsubscript{x} mass activity are in good agreement with previous preliminary studies [12].

The Tafel slopes of IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} are close to each other and to the values characteristic for quasi-amorphous hydrated Ir oxides obtained by various methods [22,23,29,30], the OER on which occurs according to the mechanism associated with the participation of activated lattice oxygen atoms [31]. In figs. 1–2 the CVs of IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} catalysts measured after AST consisted of multiple triangle waves in a potential range of 1.4–1.6 V vs. SHE at 500 mV s\textsuperscript{-1} are given as well. In figs. 1–2 the CVs of IrO\textsubscript{x} and IrO\textsubscript{x}/TiO\textsubscript{x} catalysts measured after AST which consists of multiple triangle waves in the potential range of 1.4–1.6 V vs. SHE at 500 mV s\textsuperscript{-1} are given as well. It is seen that the IrO\textsubscript{x} CV profile did not undergo significant changes, although the active surface area decreased remarkably. The CV profile of IrO\textsubscript{x}/TiO\textsubscript{x} after AST has slightly changed in the region of high potential values, which may indicate an increase in the fraction of Ir atoms in higher oxidation states (IrO\textsubscript{2}(OH), IrO\textsubscript{2}), which are unstable [32]. It should be noted that in the case of catalysts based on mixed oxides of Ir and Ti [18] at Ir content of up to 20 wt.% the Ir\textsuperscript{\textit{III}}/Ir\textsuperscript{\textit{IV}} transition peak shifted to higher potential values, which is associated with a decrease in the electrical conductivity of the active layer. The absence of a noticeable shift of the Ir\textsuperscript{\textit{III}}/Ir\textsuperscript{\textit{IV}} transition peak on the IrO\textsubscript{x}/TiO\textsubscript{x} CV compared to IrO\textsubscript{x} in this work even after the AST indicates a sufficiently high conductivity of the IrO\textsubscript{x}/TiO\textsubscript{x} active layer provided during the AST process. On the other hand, a decrease in currents in the region of hydrogen adsorption/desorption after AST may indicate the slowdown of charge transfer in the surface layer of IrO\textsubscript{x}/TiO\textsubscript{x}.

The changings in the specific active surface area and the activity of studied electrocatalysts after AST are given in Figs. 3–5.
According to the data given in figs. 3–5 both catalysts showed a decrease in the active surface area, as well as in the specific activity, normalized both to the initial Ir loading and the active surface area. The mass activity of IrO$_x$ and IrO$_x$/TiO$_x$ decreased by 47 and 20% to 191.4 and 649 A g$^{-1}$ Ir, respectively, which is in good agreement with published data [30–34], according to which the quasi-amorphous Ir oxides with a highly hydrated surface and metallic Ir are characterized by low stability under OER conditions in an acidic medium. Such low stability is related to the proposed OER mechanism [4], in which the lattice oxygen atoms, which ensure the stability of the IrO$_2$ structure, are involved in the reaction and provoke the dissolution of the corresponding Ir atoms. The suggestion of the Ir dissolution due to the OER mechanism mentioned above or due to the formation of unstable high Ir oxides as the main source of IrO$_x$ degradation is supported by a significant decrease in its active surface area value.
up to 65% from the initial one. On the other hand, according to the results described in [13,35] the contribution of Ir dissolution to the catalyst degradation is not predominant when the AST conducting by the potential cycling in the range of 1.4–1.6 V vs. SHE, and the degradation process mainly occurs due to active particles morphology and structure changing (oxide film growth, nanoparticles agglomeration etc.). Taking into account a moderate decrease in the specific activity of IrOx catalysts (both per Ir loading and active surface area) followed by a slight decrease in the active surface area, a strong electronic interaction between IrOx nanoparticles and the support surface providing higher stability of the supported catalyst is suggested [6].

In fig. 6 the polarization curves of the MEA containing anodes with different catalysts and different Ir loading, measured in SPE water electrolysis cell are given. According to the obtained results, the electrolysis cell voltage at a current density of 1 A cm⁻² was 1.75 and 1.91 V for MEAs equipped with IrOx as the anode electrocatalyst (Ir loading of 2 and 1 mg Ir cm⁻², respectively), while the voltage of 1.81 V was obtained for MEA equipped with IrOx/TiOx (Ir loading of 0.9 mg Ir cm⁻²). The use of the supported catalyst allowed to reduce the voltage of the SPE water electrolyzer by ~ 100 mV when anode noble metal loading of ca. 0.9–1 mg cm⁻². However, the voltage of the MEA based on IrOx/TiOx is higher than the one of the MEA with an optimal (in terms of electrolyzer performance) Ir loading [36]. Thus, considering the design of the MEA, the use of IrOx/TiOx allows reducing the noble metal loading at the anode of the SPE water electrolyzer up to 1.5–2 times.

![Figure 6](image_url)

**Figure 6.** Polarization curves of SPE water electrolyzer MEAs with different anode catalysts and Ir loadings: (1) IrOx, 1 mg Ir cm⁻²; (2) IrOx/TiOx, 0.9 mg Ir cm⁻²; IrOx, 2 mg Ir cm⁻². Temperature - 80°C.

It should be noted that the loading of the IrOx/TiOx catalyst is quite high – 3 mg cm⁻² due to the relatively low Ir content, which leads to additional voltage losses associated with non-optimal conditions of oppositely directed water and oxygen transfer in the catalytic layer. The limitation of water access and the shielding of the OER catalyst active sites by the yielding gas bubbles can also lead to a change in the water content of the solid polymer electrolyte and induce additional polarization losses in the anode catalytic layer [37]. Therefore, further studies are needed to optimize the structure and morphology of the anode catalytic layer based on IrOx/TiOx, including the optimization of layer thickness, the noble metal content (the layer thickness decreases with its increase) and ionomer content, porosity etc.

**4. Conclusions**

In presented work, the activity and stability of the catalyst based on Ir and conductive titanium suboxides IrOx/TiOx obtained by the polyol approach were studied in the OER. The electrochemical studies and accelerated stress testing approach were used to show that the synthesized IrOx/TiOx catalyst
significantly exceeds the commercial analogue IrO$_x$ in its OER activity and stability. In addition, the degradation mechanisms of the studied catalysts were discussed and it was suggested that despite the similarity of the IrO$_x$ structure in both catalysts, the use of TiO$_x$ provides high stability of the active IrO$_x$ particles due to their strong interaction with the support. Nevertheless, further studies are needed to clarify the role of the support in the OER and IrO$_x$ degradation mechanism. The use of IrO$_x$/TiO$_x$ as the anode catalyst in the SPE water electrolyzer allows reducing the noble metal loading by 1.5–2.0 times.

**Acknowledgments**

Electrochemical measurements were financially supported by Russian Federation President Fellowship to study abroad in 2017/18 academic year (at HySA Infrastructure, North-West University, South Africa). The fabrication and testing of SPE electrolyzer MEAs were financially supported by the Russian Foundation for Basic Research (grant No 19-58-26022).

**5. References**

[1] Abdalla A M, Hossain S, Nisfindy O B, Azad A T, Dawood M and Azad A K 2018 *Energy Convers. Manag.* **165** 602–27
[2] Carmo M, Fritz D L, Mergel J and Stolten D 2013 *Int. J. Hydrogen Energy* **38** 4901–34
[3] Grigoriev S A, Fateev V N, Bessarabov D G and Millet P 2020 *Int. J. Hydrogen Energy* **45** 26036–58
[4] Kasian O, Geiger S, Li T, Grote J-P, Schweinakar K, Zhang S, Scheu C, Raabe D, Cherevko S, Gault B and Mayrhofer K J J 2019 *Energy Environ. Sci.* **12** 3548–55
[5] Karimi F and Peppley B A 2017 *Electrochim. Acta* **246** 654–70
[6] Oakton E, Lebedev D, Povia M, Abbott D F, Fabbri E, Fedorov A, Nachtegaal M, Copéret C and Schmidt T J 2017 *ACS Catal.* **7** 2346–52
[7] Arif A F, Balgis R, Ogi T, Iskandar F, Kinoshita A, Nakamura K and Okuyama K 2017 *Sci. Rep.* **7** 3646
[8] Muntean R, Pascal D T, Rost U, Holtkotte L, Nüther J, Köster F, Underberg M, Hülsler T and Brodmann M 2019 *Top. Catal.* **62** 429–38
[9] Yao C, Li F, Li X and Xia D 2012 *J. Mater. Chem.* **22** 16560
[10] Wons J-E, Kwak D-H, Han S-B, Park H-S, Park J-Y, Ma K-B, Kim D-H and Park K-W 2018 *J. Catal.* **358** 87–94
[11] Lagarteira T, Han F, Morawietz T, Hiesgen R, Garcia Sanchez D, Mendes A, Gago A and Costa R 2018 *Int. J. Hydrogen Energy* **43** 16824–33
[12] Pushkarev A S, Pushkareva I V, Du Preez S P, Ivanova N A, Grigoriev S A, Slavcheva E P, Bessarabov D G, Fateev V N and Aliyev A S 2019 *Chemical Problems* **17** 9–15
[13] Alia S M, Rasmik B, Ngo C, Neyerlin K C, Kocha S S, Pylypenko S, Xu H and Pivovar B S 2016 *J. Electrochem. Soc.* **163** F3105–12
[14] Kalinikov A A, Ostrovska S V, Porembskii V I, Pushkarev A S and Fateev V N 2018 *Russ. J. Appl. Chem.* **91** 927–9
[15] Grigoriev S, Fateev V, Pushkarev A, Pushkareva I, Ivanova N, Kalinichenko V, Yu. Presnyakov M and Wei X 2018 *Materials* **11** 1405
[16] Grigoriev S A, Pushkareva I V, Millet P, Belov A S, Novikov V V, Belaya I G and Voloshin Y Z 2017 *Int. J. Hydrogen Energy* **42** 27845–50
[17] Rozain C, Mayousses E, Guillette N and Millet P 2016 *Appl. Catal. B Environ.* **182** 153–60
[18] Bernsmeier D, Bernicke M, Schmack R, Sachse R, Paul B, Bergmann A, Strasser P, Ortel E and Kraehnert R 2018 *ChemSusChem* **11** 2367–74
[19] Minguzzi A, Locatelli C, Cappelletti G, Scavini M, Vertova A, Ghigna P and Rondinini S 2012 *J. Phys. Chem. A* **116** 6497–504
[20] Oh H S, Nong H N, Reier T, Gleich M and Strasser P 2015 *Chem. Sci.* **6** 3321–8
[21] Ouattara L, Fierro S, Frey O, Koudelka M and Comminellis C 2009 *J. Appl. Electrochem.* **39** 1361–7
[22] Yu H, Danilovic N, Wang Y, Willis W, Poozhikunnath A, Bonville L, Capuano C, Ayers K and Maric R 2018 Appl. Catal. B Environ. 239 133–46
[23] Tan X, Shen J, Semagina N and Secanell M 2019 J. Catal. 371 57–70
[24] Ooka H, Yamaguchi A, Takashima T, Hashimoto K and Nakamura R 2017 J. Phys. Chem. C 121 17873–81
[25] Steegstra P and Ahlberg E 2012 Electrochim. Acta 76 26–33
[26] Barbieri O, Hahn M, Foelske A and Kötz R 2006 J. Electrochem. Soc. 153 A2049
[27] Wang L, Lettenmeier P, Golla-Schindler U, Gazdzicki P, Cañas N A, Morawietz T, Hiesgen R, Hosseiny S S, Gago A S and Friedrich K A 2016 Phys. Chem. Chem. Phys. 18 4487–95
[28] Alia S M, Shulda S, Ngo C, Pylypenko S and Pivovar B S 2018 ACS Catal. 8 2111–20
[29] Smith R D L, Sporinova B, Fagan R D, Trudel S and Berlinguette C P 2014 Chem. Mater. 26 1654–9
[30] Abbott D F, Lebedev D, Waltar K, Povia M, Nachttegaal M, Fabbri E, Copéret C and Schmidt T J 2016 J Chem. Mater. 28 6591–604
[31] Geiger S et al 2018 Nat. Catal. 1 508–15
[32] Cherevko S, Geiger S, Kaskan O, Mingers A and Mayrhofer K J J 2016 J. Electroanal. Chem. 774 102–10
[33] Cherevko S, Geiger S, Kaskan O, Mingers A and Mayrhofer K J J 2016 J. Electroanal. Chem. 773 69–78
[34] Jovanović P et al 2017 J. Am. Chem. Soc. 139 12837–46
[35] Alia S M, Ha M-A, Anderson G C, Ngo C, Pylypenko S and Larsen R E 2019 J. Electrochem. Soc. 166 F1243–52
[36] Grigoriev S A and Kalinnikov A A 2017 Int. J. Hydrogen Energy 42 1590–7
[37] Ito H, Maeda T, Nakano A, Kato A and Yoshida T 2013 Electrochim. Acta 100 242–8