Montmorillonite as a catalytic support in water electrolysis

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The paper presents a research on the phyllosilicate mineral Montmorillonite (MMT) in regard to its properties as catalytic support for hydrogen generation via electrochemical water splitting. MMT is loaded with noble metal nanoparticles (Ir) having well proven high catalytic activity toward the oxygen evolution reaction (OER). The metal is deposited by the well-established sol gel technique. The catalytic loading is varied in the range 10-30 wt. %. The obtained montmorillonite-supported catalysts (Ir/MMT) are studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersion X-ray (EDX) analysis. Their electrochemical performance and OER catalytic efficiency are investigated by cyclic voltammetry and quasi steady state polarization curves in aqueous acid solution. The performed morphological and electrochemical investigations showed that the Ir/MMT catalysts under study possess superior performance in regard to both activity and durability compared to the previously studied iridium catalysts supported on commercial electrically conductive ceramic support Magnelli phase titania.

Key words: hydrogen technologies, water electrolysis, oxygen evolution reaction, electrocatalysts, non-carbon catalytic supports.

INTRODUCTION

The electrochemical water splitting is a viable method for production of clean hydrogen. The classical alkaline water electrolysis is still the most commonly used production technology for this purpose. In the last decades an intensive research has been carried out on development of acidic polymer electrolyte membrane water electrolysis cells (PEMEC). This new and environmentally friendly method has some advantages over the classical alkaline electrolysis, primarily in regard to the process intensity, efficiency, purity of the generated gases, and compatibility with the renewable energy sources [1-3]. PEMEC is considered as one of the key technologies that can be powered by renewable energy sources and used for the large scale production of clean hydrogen [4]. The partial hydrogen (HER) and oxygen (OER) evolution reactions are of special importance in both fundamental and applied electrochemistry. The OER is fundamentally less studied, as it is much more complex. The efficient oxidation of water is greatly hindered by the OER, which proceeds as a multistep proton-coupled electron transfer process [5]. It is the most critical step severely limiting the overall efficiency of the water splitting due to the intrinsically slow kinetics requiring considerable overpotential to achieve rational process rate [3, 4]. The rate and mechanism of OER depend strongly on the chemical nature, surface structure, and morphology of the used electrocatalysts, as well as on the process operative conditions (type of the electrolyte, temperature, etc.). The proper combination of these factors is essential to lower the energy barrier and enhance the energy conversion rate.

The major drawback of the PEMEC is the fact that the required electrocatalysts are predominately based on the platinum group metals, their alloys and/or oxides. In 1966 Damjanov et al. studied the kinetics of the OER on Rh, Ir, and Pt-Rh alloys using a liquid electrolyte, showing the increase of activities in the following order: Pt < Pt-Rh < Rh < Ir [6, 7]. Later on, it was proven that iridium (IrO_2) and ruthenium (RuO_2) oxides are the most representative and effective OER electrocatalysts [8-10]. However, the large-scale application of these catalysts is strongly hindered by their low abundance and the associated high cost.

The usual approach to decrease the cost of the catalysis and thus, the capital expense of PEMEC, is to deposit the noble metal particles on catalytic support with highly developed surface. The most broadly used catalytic supports are various carbon materials (carbon blacks, nanotubes, nanorods, etc.). OER at the anode takes place at relatively high potentials (1.5–1.8V vs. RHE) which in combination with the intensive gassing, high humidity and elevated temperatures creates critical operative conditions, prohibiting the use of carbon-

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based materials as catalyst support, since the carbon is oxidized at potential of +0.206 V vs. RHE [11, 12] according the reaction: $C + 2H_2O \quad CO_2 + 4H^+ + 4e-$

For this reason, to achieve not only high OER activity but also cost efficiency and durability the IrO_2 particles should be supported on electro-conductive material with much higher corrosion stability (titanium nitride, tantalum carbide, doped or reduced forms of titanium, tin oxide etc.). Another approach is to synthesize complex catalytic compositions mixing IrO_2 with inexpensive and electrochemically inert materials such as TiO_2, SnO_2, Ta_2O etc. catalyst layer in order to form Ir-based mixed oxides. In the last decade, a great number of papers using the former approach have been published [13-20]. However, along with the nonsufficient stability of most of those new supports at long term service in oxidizing environment [21], the reported noble metal loadings remained quite high, most often in the range 1.5-5.0 mg cm^{-2} [4, 22].

The aim of this work is to explore one natural mineral (Montmorillonite, MMT) as catalytic support and to assess the efficiency of the composite MMT-supported IrO_2 toward OER in acidic electrochemical water splitting. MMT is a phyllosilicate layered clay with 2:1 type sheet structure, high cation exchange capacity, high surface area and low cost [23]. Chemically, it is a complex mixture of hydrated phyllosilicates, having rather complex general chemical formula: $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$.

Clay minerals in general, are layered porous materials which can "trap" significant amount of different fluids (air, water, saline water, etc.) in the pores or/and in the interlayer space. The electrical conductivity of the clay depends on both the type of the fluid and the chemical nature of the matrix. It is attributed to exchange of cations or proton transfer between the dissociated interlayer water and the matrix. The small particle size of the clay minerals (1-2 µm in diameter) results in significantly high surface area per unit volume, where a large number of cations can be adsorbed, thus leading to significant level of electrical conductivity [24].

According to our knowledge, up to now Montmorillonite has not been investigated as catalytic support in water electrolysis.

EXPERIMENTAL

The catalysts under study are synthesized by sol-gel method from Ir-acetilacetonate $(Ir((C_5H_7O_2)_n)_m$ precursor, Ir-acac, following the next procedure: (i) pretreatment of the support and the precursor in iso-propanol using magnetic stirrer and ultrasonic bath, their mixing and heating at temperature 60 °C until a fine gel is obtained; (ii) thermal treatment at temperature 240 °C for 4 h in H_2 gaseous atmosphere.

Five different test samples with iridium loadings of 10, 15, 20, 25, and 30 wt.% Ir supported on MMT are prepared and investigated.

Their structural and phase composition are examined by X-ray diffraction (XRD). The diffraction data are collected using X-ray diffractometer Philips ADP15 with Cu-K radiation (λ = 1.54178 Å) at a constant rate of 0.02° s^{-1} over an angle range 2 = 4° ÷ 80°.

SEM and EDX analysis are obtained using JEOL JSM 6390 electron microscope (images in secondary and back-scattered electrons), equipped with INCA Oxford elemental detector.

The electrochemical performance and catalytic efficiency are studied by cyclovoltammetry and chronoamperometry (potentiodynamic and potentiostatic polarization) methods using a commercial Galvanostat/ Potentiosat POS 2 (Bank Electronik, Germany). The cyclic voltammograms (CV) are recorded in the "water window" potential range (between the hydrogen and oxygen evolution potentials) at scan rate of 100 mV s^{-1}. The quasi steady state polarization tests are carried out in potentiodynamic mode with scan rate of 1 mV s^{-1}. To investigate the stability of the catalysts performance with time, chronoamperometric tests at constant potential of 1.8 V are performed.

All electrochemical tests are performed in 0.5 M H_2SO_4 at room temperature in a conventional 3-electrode electrochemical cell. Pt wire is used as counter electrode and Ag/AgCl as reference electrode. The working area of the test electrode is 0.5 cm^{-2} and all test samples contain 0.5 mg$_{Ir}$cm^{-2}.

RESULTS AND DISCUSSION

The XRD patterns of the synthesized Montmorillonite supported catalysts are presented in Fig. 1 together with those of the pure support (MMT clay) and the Ir-acac precursor according Inorganic Crystal Structure Database, ICSD (PDF#23-1711). The phase identification shows presence of MMT and non-destructed Ir-acac in all test samples. Ir or IrO_2 are not registered which does not exclude their presence in amorphous state.

The inset in the Fig. 1 is a zoomed image of XRD patterns in the 5-10° 2θ range. It shows a shift of the (001) diffraction peak corresponding to basal $d_{(001)}$ spacing of the catalyzed MMT samples. The shift to lower 2 angles after deposition of iridium indicates an increase in the interlayer distance

compared to that in the unloaded MMT. In the literature such an increase has been prescribed to intercalation of metal cations (in our case Ir^+ and/or Ir-organometallic cations) into the clay structure [25, 26].
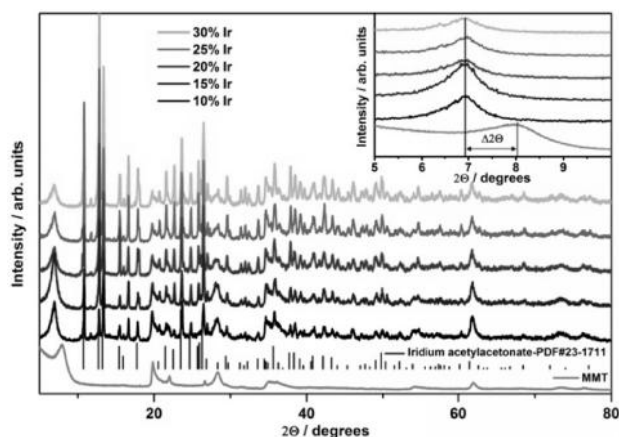

Fig. 1. XRD patterns of the synthesized catalysts, pure MMT and Ir-acac.

The synthesized Ir/MMT catalysts with target content of Ir in the range 5 to 30 wt.% are studied by EDX analysis to determine their exact noble metal content. The results obtained (Table 1) demonstrate high efficiency of the applied method of synthesis which ensures close to 100% utilization of the metal precursor. In the same table are shown experimental data from the performed electrochemical tests.

Table 1. Iridium content in the test samples determined by EDX analysis and kinetic data assessing their catalytic activity.

| Sample	Ir wt. %		OER	
			E=1.7V	*Tafel Slopes mV.dec^{-1}*
	target	obtained	*j/mA.cm^{-2}*	*b*
Ir 10	10	9.85	10.32	180
Ir 15	15	15.03	15.02	200
Ir 20	20	18.84	26.27	160
Ir 25	25	24.96	20.07	170
Ir 30	30	28.73	23.10	170

The morphology of the synthesized catalysts was studied by scanning electron microscopy (SEM). The microscopic images (Figure 2) show highly developed surface and porous structure of the individual clusters (agglomerates), which is an important prerequisite for achieving high utilization of the catalyst.
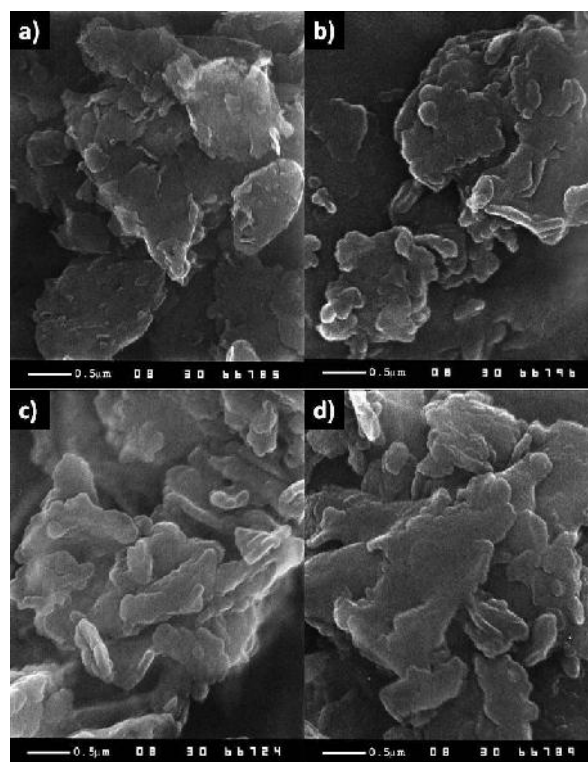
Fig. 2. SEM image of a) pure MMT, b) Ir10/MMT, c) Ir25/MMT and d) Ir30/MMT.

Electrochemical measurements

In Fig. 3 are shown the obtained cyclic voltammograms of five test electrodes with equal iridium loading (0.5mg.cm^{-2}) and different Ir/MM ratio. The CV curves are recorded in the potential range between -0.45 and 1.45 V vs. Ag/AgCl reference electrode at scan rate of 100 mV s^{-1}.
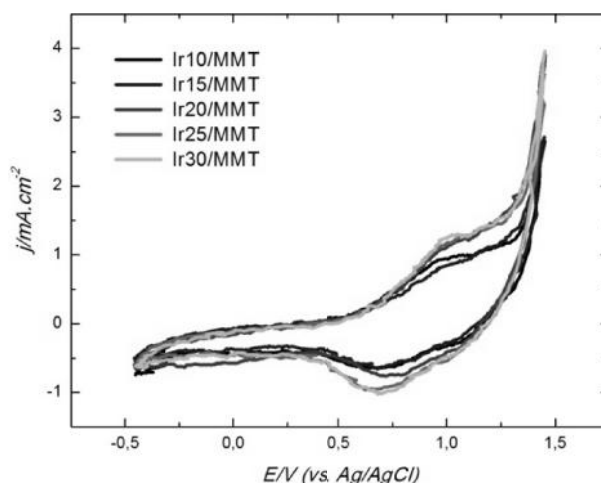

Fig. 3. Cyclic voltammograms of Ir/MMT catalysts in 0.5M H_2SO_4 at room temperature; potential scan rate 100 mV s^{-1}.

The reversible current peaks typical for transformation of iridium oxidation state in acid media (Ir/Ir^{2+}, Ir^{2+}/Ir^{3+} and Ir^{3+}/Ir^{4+}) are well depicted. The peaks on the voltammograms of the

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samples Ir20/MMT, Ir25/MMT and Ir30/MMT are visibly broader than those of the electrodes prepared from samples with lower Ir/MMT ratio, indicating higher active surface of these electrodes.

Fig. 4 presents the partial electrode reaction of oxygen evolution for the same electrodes. All polarization curves demonstrate intensive oxygen evolution at potentials above 1.5 V. The reaction proceeds with highest rate on the electrode with Ir20/MMT. The obtained current densities on Ir30/MMT and Ir25/MMT slightly lower, while on Ir10/MMT and Ir15/MMT the oxygen evolution proceeds much slower.
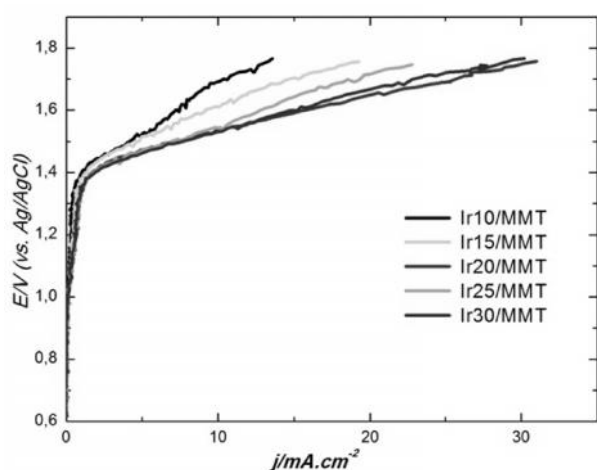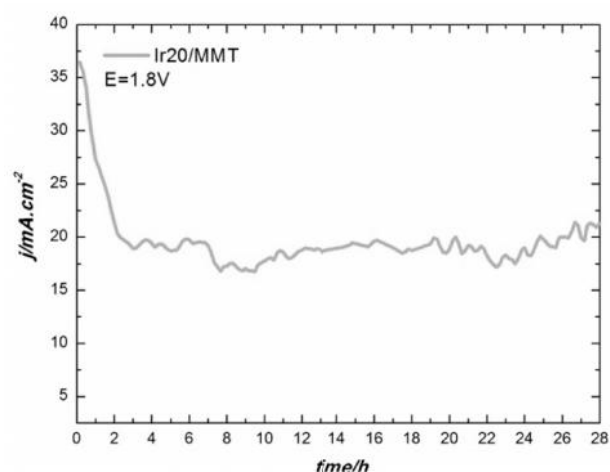

Fig. 4. Anodic polarization curves of the Ir/MMT in 0.5M H_2SO_4 at room temperature; potential scan rate 1 mV s^{-1}.

In order to obtain some data on the electrochemical kinetics and the mechanism of OER in Fig. 5 are presented the semi-logarithmically plotted current–potential curves (Tafel plots). The calculated values of the Tafel plots and the achieved current densities at 1.7 V are summarized in Table 1. They confirm the best efficiency (highest current density) combined with lower Tafel constant b of the catalyst Ir20/MMT.
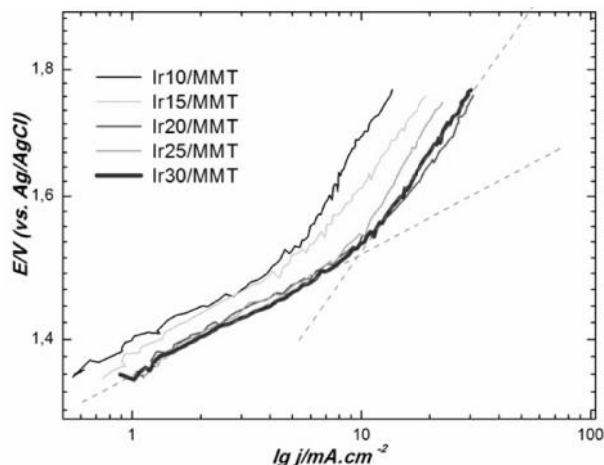
Fig. 5. ORR Tafel plots of the Ir/MMT in 0.5M H_2SO_4 at room temperature; scan rate 1 mV.s^{-1}.

Finally, to evaluate the stability of the Ir20/MMT catalytic performance at long service, potentiostatic polarisation tests (chrono-amperometry) are carried out at constant potential of 1.8 V where an intensive oxygen evolution takes place. Fig. 6 presents the results obtained in 30-hour experiment. It is seen that after initial slight decrease of the measured current density, the reaction rate stabilizes around 20 mA cm^{-2} and does not change for the whole duration of the experiment, indicating both efficiency and durability of the catalyst performance.
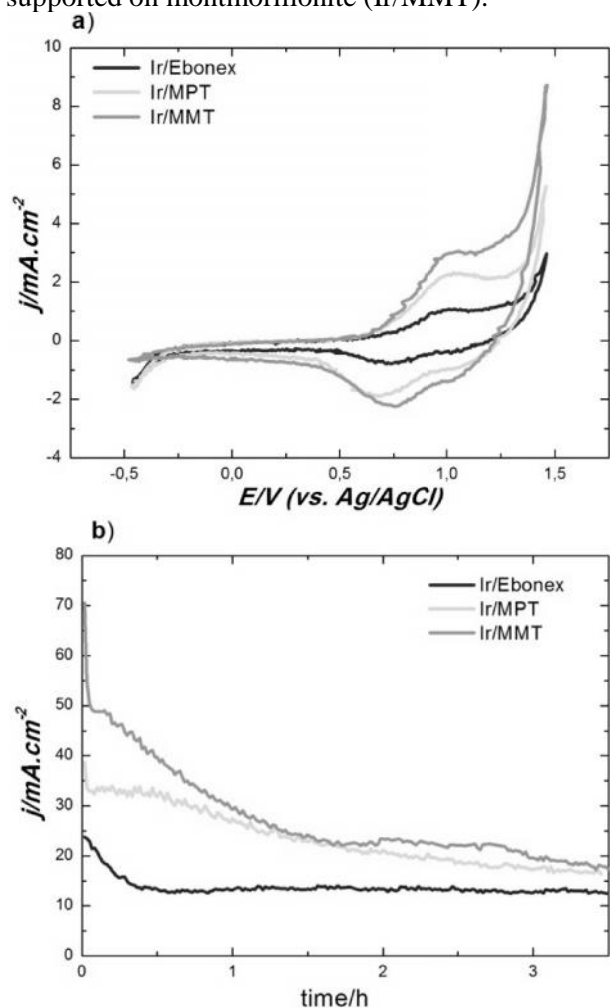

Fig. 6. Potentiostaic polarization curves of Ir/MMT in 0.5 M H_2SO_4, at room temperature; E=1.8 V.

In our previous study it was shown that Ir deposited on different commercial ceramic supports also increase essentially the OER. The best efficiency was obtained for Ir supported on Magnelli phase titania (MPT) - a nonstoichiometric mixture of titanium oxides with common formula Ti_nO_{2n-1} that possesses excellent electrical conductivity combined with high corrosion resistance both in acidic and in alkaline media. The research performed with two different commercial products of Magnelli phase titania (Ebonex, Atraverda, UK and MPT, Ti-dynamics, China) proved that the Ebonex-supported iridium has better catalytic efficiency toward oxygen evolution reaction, comparable to the best data published in the literature [27]. It demonstrated enhanced stability during accelerated tests however, the utilization was not satisfactory due to the low surface area of the substrate. The MPT-supported iridium showed even higher efficiency but lower stability at long tests.

In order to evaluate the properties of the herein studied novel catalytic support MMT, in Fig.7 are compared cyclic voltammograms and polarization curves of identical electrodes containing equal loadings of iridium deposited on Ebonex, MPT and MMT, respectively. The results indicate highest

active surface (broadest CV) combined with superior efficiency and stability of the catalyst supported on montmorillonite (Ir/MMT).

Fig. 7. Cyclic voltammograms, scan rate 100 mV.s^{-1} (a) and potentiostatic polarization curves, E=1.8 V (b) of Ir/Ebonex, Ir/MPT, and Ir/MMT in 0.5M H$_2$SO$_4$ at room temperature.

Fig. 8 presents the SEM images of the studied supports. The Ebonex has the largest particles size with smooth surface. The small MPT particles size (100-200 nm) and the rough surface of the MMT particles ensure a higher specific surface area compared to Ebonex and it is a precondition for higher electrochemical activity of the catalysts on MMT and MPT supports.
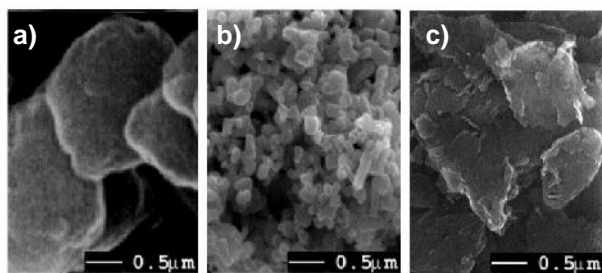
Fig. 8. SEM image of a) Ebonex, b) MPT and c) MMT.

In addition, the XRD analysis showed chemical interaction between iridium and the MMT substrate, resulting in structural changes of the clay, namely an increase in the basal spacing between parallel layers. These two effects (the cation intercalation and the increase of surface area) explain the superior catalytic efficiency of the Ir/MMT catalyst.

CONCLUSIONS

The work demonstrates that the investigated phyllosilicate mineral montmorillonite (MMT) is a promising alternative of the conventional carbon materials for application as anode catalyst support for hydrogen generation via electrochemical water splitting. Ir/MMT showed superior performance in regard to both activity and stability compared to Magnelli phase titania supports (Ebonex, Atraverda and MPT, Ti-Dynamics). The specific morphology and layered structure of the MMT influence the efficiency of the electrode reaction ensuring much higher current densities at equal catalytic loading. The registered Ir intercalation into MMT crystal structure contributes significantly to the catalytic efficiency.

Further research focused on the catalyst-support electronic and/or interionic interactions and their effect on activity is in progress.

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Mg)$_2$(Si$_4$O$_{10}$)(OH)$_2$.nH$_2$O   .

                                                          .   /   Ir   Ir-

                        -              .   ,

Ir/

                        (SEM),   (XRD)   (EDX).

                                                                                  (OER)   0.5   .

H$_2$SO$_4$.

                        Ir   Ir   Ir//MMT   -

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