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IRIDIUM CATALYST SUPPORTED ON CONDUCTIVE TITANIUM OXIDES FOR POLYMER ELECTROLYTE MEMBRANE ELECTROLYSIS

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The Ir-based Magneli phase titanium oxide supported catalyst is synthesized using the polyol approach. Its structure and activity in oxygen evolution reaction were evaluated by means of transmission electron microscopy, cyclic and linear sweep voltammetry. The catalyst structure is characterized by small Ir nanoparticles well dispersed over the support surface. The synthesized titanium suboxide supported catalyst showed very high activity in OER. Its mass activity ca. 3 times higher in comparison with the commercial IrO_x catalyst.

Keywords: *iridium, supported catalyst, Ti_4O_7, PEM, water electrolysis*

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INTRODUCTION

Hydrogen-based energy storage and supply for the modern world is currently one of the concepts under thorough evaluation and consideration. Thus the hydrogen production is a key component of hydrogen-based energy concepts. Currently, most of hydrogen is produced by steam reforming of natural gas and other hydrocarbons-based feed stock [1]. Among the various methods developed for the hydrogen production from renewable energy sources, water electrolysis is considered as one of the most practical and flexible technology. In particular, polymer electrolyte membrane (PEM) electrolysis offers a sustainable solution to produce hydrogen, which may be coupled with intermittent renewable energy sources (*e.g.* wind and solar) [2].

However, the penetration of PEM water electrolysis technology into industrial large-scale applications is slow due to the relatively high costs of its components including polymer electrolyte membrane, current collectors and noble metals-based electrocatalysts [3]. Electrochemical hydrogen evolution reaction (HER) and oxygene evolution reaction (OER) in acidic electrolyte are fast only occurring on the surface of the noble metal-based catalysts, *i.e.* Pt and Ir (IrO_2), respectively. Actually, OER takes place in harsh and severe conditions of high anodic potentials and acidic environment which determine the high corrosion rate of typical OER catalysts *i.e.* Ir oxides and Ir blacks. Thus to provide long electrolyzer service time, high Ir loadings are necessary (for instance up to 2 – 4 mg cm^{-2} of Ir loading is used currently at anode) [4]. Thus, the depositing of Iron a support material with high surface area could be an effective way to increase its utilization and to decrease its loading. However, choice of materials that can be used as Irsupports are limited [5].

Magneli phase titanium oxides own high electrical conductivity combined with excellent corrosion resistance and, thus, are promising candidates for OER catalyst support. Moreover, its hypo-d-electron character implies realization of electronic interactions with the hyper-d-electron Ir, leading to synergy and improved efficiency [6, 7]. In presented study Ir-based electrocatalysts supported on conductive titanium oxides were synthesized and evaluated. Their activities in OER were evaluated by electrochemical methods such as cyclic voltammetry and rotating disk electrode voltammetry. The data related to the structure and morphology of the catalysts were obtained using transmission electron microscopy (TEM).

EXPERIMENTAL PART

Commercial IrO_x(TKK, Japan) and $Ir_{0.7}Ru_{0.3}O_x$ synthesized by the Adams fusion method as described in [8] were taken as amorphousand a polycrystalline benchmarks respectively. The Ti_4O_7 supported catalyst with 30 wt.%Ir content was synthesized as follows. The calculated amount of the Ir nanoparticle precursor (H_2IrCl_6 $6H_2O$) was added to the three-neck flask containing the ethylene-glycol(EG), with constant stirring. A pre-homogenized solution of the Ti_4O_7support in deionized water and isopropanol was added dropwise to the reaction volume with constant stirring, after which the temperature of the mixture wasslowly increased up to 75 °C. Adsorption step was carried out with argon purging at a constant temperature of 75 °C for 2 hours. Then the temperature of the mixture was sharply increased up to 100 °C and the reduction of Ir was carried out with argon purgingas well for 4 hours. Next, the mixture was cooled down to room temperature and the resulting catalyst was washed in deionized water at least 3 times until neutral pH and dried at 70 °C for 48 hours.

Transmission electron microscopy was performed using Titan TM 80-300 S/TEM (FEI, USA). Samples were prepared by ultrasonic treatment of catalyst in EtOH for 12 min followed by pipetting the mixture onto a Lacey (thin, X-ray amorphous) carbon film supported on a copper grid.

The rotating disk electrode study methodology provided by HySA Infrastructure (South Africa) was used and validated at their facilities at North-West University. A standard ink for electrochemical measurements contained 10 mg of the catalyst powder was prepared through ultrasound treatment for 20 min in 3 ml of water and 2 ml of 2-propanol solution. Then 5 μl aliquot was pipetted onto polished polycrystalline gold electrode followed by 5 μl of 0.05% Nafion solution (10 wt%, Sigma Aldrich) capping. Electrochemical characterization of catalysts was performed in aglass three electrode cell (Pine instruments, USA) containing 0.1 M $HClO_4$ using a Pt wire as counter electrode and an Ag/AgCl/sat. KCl reference electrode equipped with MSR rotator (Pine instruments, USA). Linear polarization curves were taken in the potential range 1.2−1.6 V vs RHE at 5 mV s^{-1} sweep rate and a rotation speed of 2500 rpm. Cyclic voltammetry measurements were performed in the potential range.

Catalysts active surface area was evaluated as a voltammetric charge measured in the potential range 0.4 – 1.3 V (vs. RHE) at 100 mV s^{-1}. The average value between anodic and cathodic charge in aforementioned potential range was used [9].

RESULTS AND DISCUSSION

Fig. 1 shows the TEM images of both Ti_4O_7 support and Ti_4O_7-supported catalyst with 30 wt.% of Ir (fig. 1). The support consists of irregular-shape particles with mean particle size of 93 ± 28 nm (fig. 1 A, B). It is also seen that Ir nanoparticles of supported electrocatalyst were distributed over the support surface and mainly have spherical shape (fig. 1 C, D). The mean Ir particle size is *ca.* 2.77 nm. However, some nanoparticles form large agglomerates and is not located on the support surface.

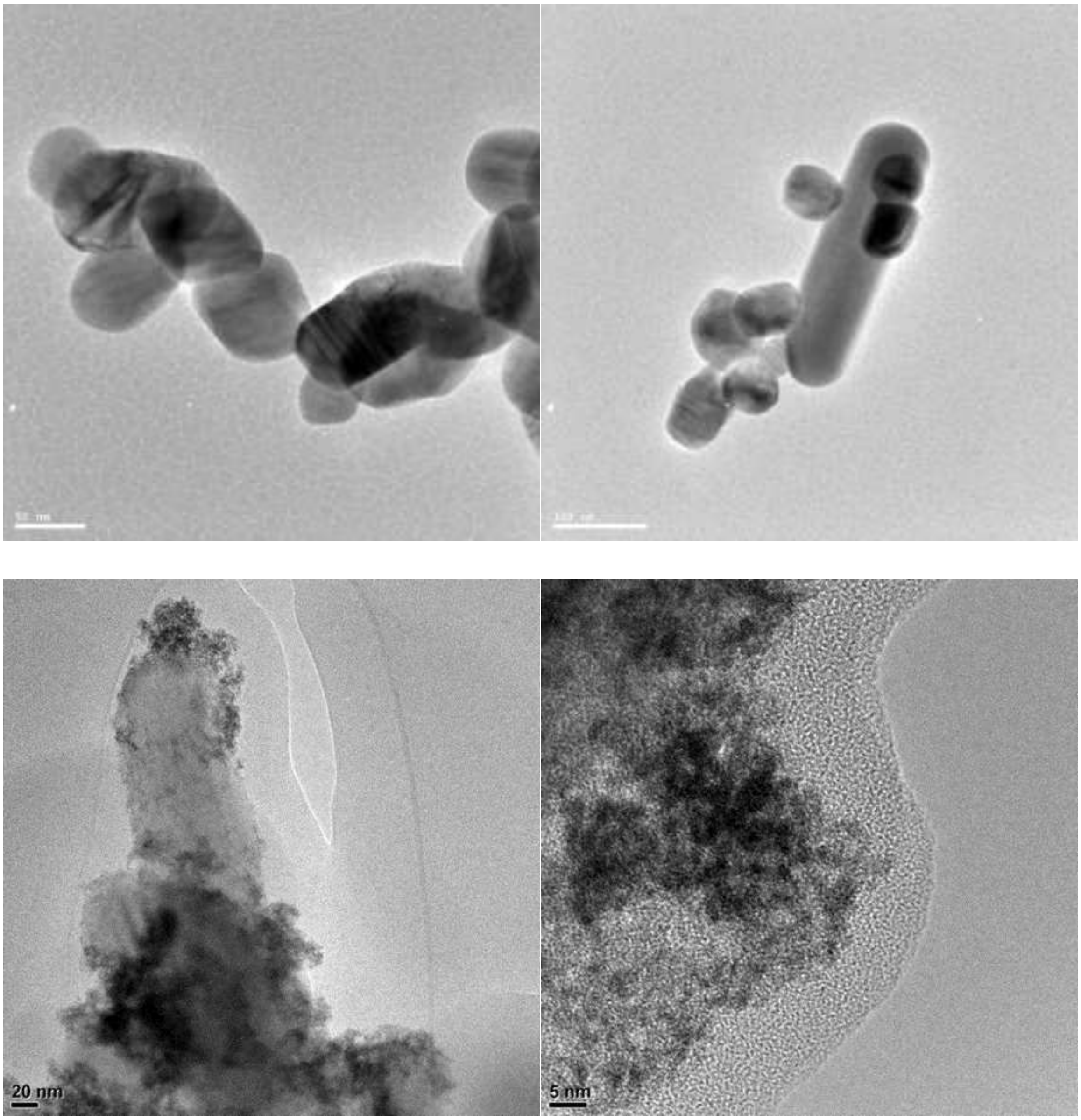

Fig. 1. TEM images of Ti_4O_7 support (A, B) and Ti_4O_7-supported catalyst (C, D).

Fig. 2 shows the cyclic voltammetry curves of studied electrocatalysts. The shape of these curves for Ir-based OER catalysts are characterized by the presence of several broad peaks at potentials > 0.4 V corresponding to the solid state redox transitions that occur due to the adsorption and oxidation of oxygenated species from the electrolyte [4]. The cyclic voltammetry curves of Ti_4O_7 are presented on the fig. 2A as well suggesting that all redox behavior is originated from the Ir nanoparticles. The IrO_x catalyst showed cyclic voltammogram (CV) specific for amorphous hydrous Ir oxides[10]. The similar CV shape of Ir^{30}/Ti_4O_7 to the IrO_x suggests that the supported electrocatalyst may have the same surface oxide structure. For the mixed oxide catalyst $Ir_{0.7}Ru_{0.3}O_x$ the CV shape is in a good agreement with literature [11] showing less defined peaks due to the overlap of both Ir and Ru redox processes.

Fig. 3 shows the polarization curves and Tafel curves of studied catalysts measured to evaluate their activity in OER and to get insight into the reaction mechanism. The current is normalized to the active surface area (measured as a charge at 0.4 – 1.3 V vs. RHE at 100 mV s^{-1}) (fig. 3A) and Ir (and Ru) mass loading (fig. 3B). Mass activity of IrO_x, $Ir_{0,7}Ru_{0,3}O_x$ and Ir^{30}/Ti_4O_7 taken at 1.48 Visca. 0.296, 0.136 and 0.752 Ag^{-1}respectively. The activity of commercial amorphous IrO_x are comparable with literature [12] taking into account the difference in experimental conditions of different authors which usually makes difficult the comparison of the results with literature.

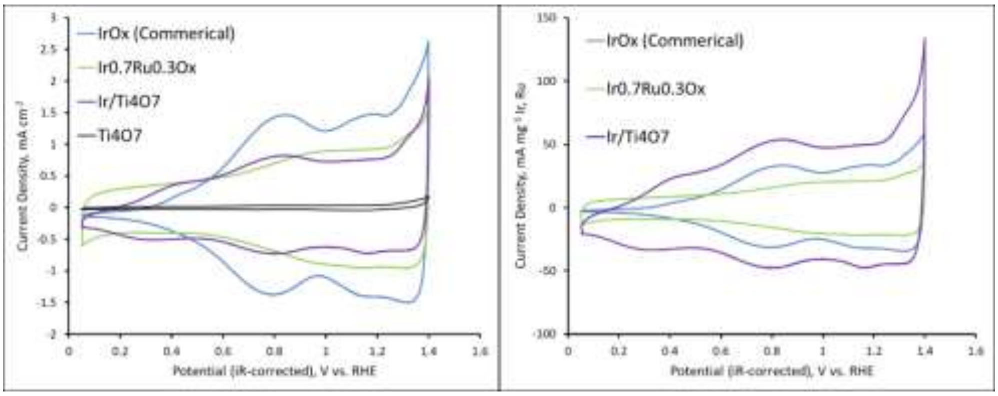

Fig. 2. Cyclic voltammetry curves of studied electrocatalysts measured in Ar-purged 0.1 M $HClO_4$ solution at 100 mV s^{-1} sweep rate and 30 °C: A – current normalized to the working electrode surface area; B - current normalized to Ir loading.

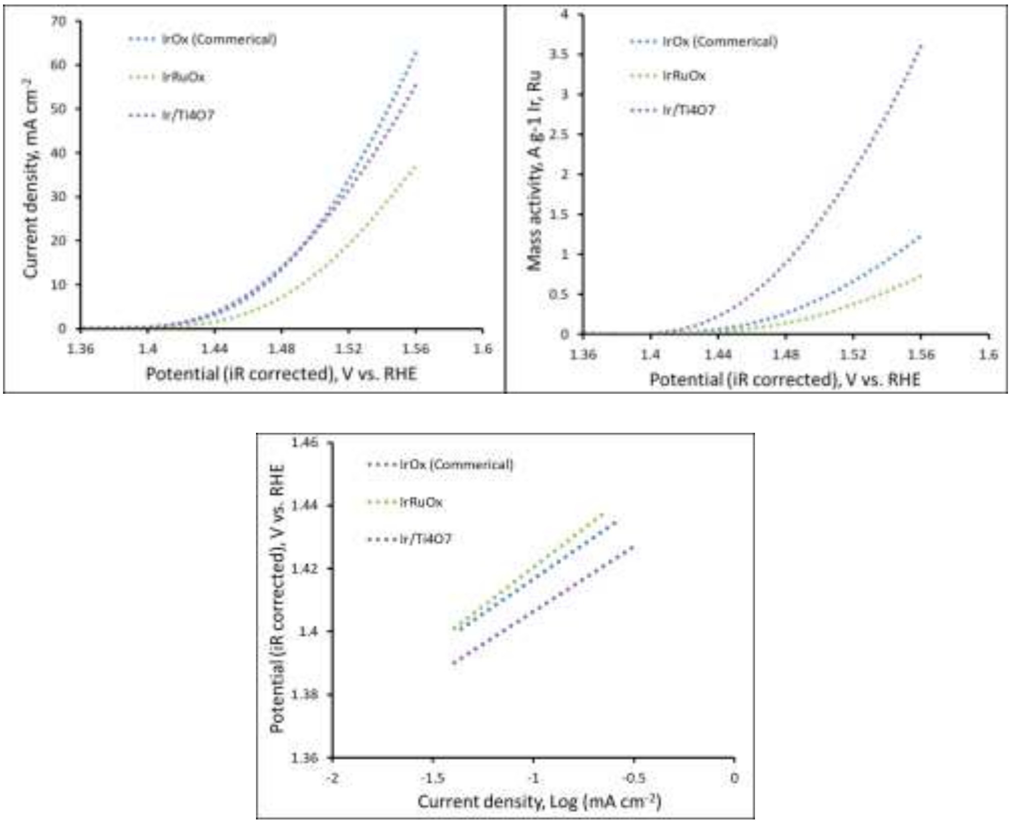

Fig. 3. Polarization curves of studied electrocatalysts measured in Ar-purged 0.1 M $HClO_4$ solution at 5 mV s^{-1} sweep rate, 30 °C and 2500 rpm (A – current normalized to the working electrode surface area; B - current normalized to Ir loading) and Tafel curves (C).

The synthesized catalyst Ir^{30}/Ti_4O_7 has significantly higher mass activity than its counter parts including the commercial one. According to the results showed in Fig.3 at he us age of supported catalysts allows to reduce the Ir loading up to 3 times maintaining the same catalyst activity. The superior activity is due to the catalyst morphology (small Ir particle size, uniform distribution over the support surface, high surface area etc.) and high conductivity of Ti_4O_7support.

Tafel slope (Fig. 3C) of IrO_x, $Ir_{0,7}Ru_{0,3}O_x$ and Ir^{30}/Ti_4O_7 is 44.1, 49.4 and40.1 mV $dec.^{-1}$. The $Ir_{0,7}Ru_{0,3}O_x$ Tafel slope value is close to the one obtained in [8]and is in good agreement with the values for mixed IrO_2 and RuO_2[13]. The values of IrO_x and Ir^{30}/Ti_4O_7Tafel slope are quite similar and close to the values typical for the hydrous Ir oxides [14]. The reaction mechanism of such an oxides are proposed in [15] and they suffer (as well as metallic Ir) from the corrosion associated with high Ir dissolution rate. So, further studies aim to improve and optimize the structure of proposed catalyst are necessary.

CONCLUSIONS

Ir-based electrocatalysts supported on conductive titanium oxides (Ti_4O_7) were synthesized, evaluated and compared with a commercial sample. The morphology and OER activity of proposed electrocatalyst were evaluated and compared to other OER catalysts including the commercial IrO_x one. Ir^{30}/Ti_4O_7 allows reducing the Ir loading up to 3 times maintaining the same OER catalyst activity. Synthesized Ti_4O_7-supported catalyst suggested to provide the OER according to the mechanism typical for the hydrous Ir oxides.

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BƏRK POLİMER ELEKTROLİTDƏ SUYUN ELEKTROLİZİ ÜÇÜN İRİDİUM VƏ TİTAN OKSİD DAŞIYICISI ƏSASINDA ELEKTROKATALİZATOR

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Ir və Maqneli fazalı titan oksidi daşıyıcısı əsasında poliol metodu ilə katalizator sintez edilib. Katalizatorun strukturu və oksigenin ayrılması reaksiyasında aktivliyi tədqiq olunub. Müəyyən edilib ki, kicik ölçülü Ir nanohissəcikləri daşıyıcı üzərində bərabər paylanıb və katalizatorun aktivliyi satış üçün mövcud elektrokatalizatordan 3 dəfə artıqdır.

Açar sözlər: *iridium, bərk polimer elektrolit, suyun elektrolizi, daşıyıcı*

ЭЛЕКТРОКАТАЛИЗАТОР НА ОСНОВЕ ИРИДИЯ И ПРОВОДЯЩИХ ОКСИДОВ ТИТАНА В КАЧЕСТВЕ НОСИТЕЛЯ ДЛЯ ЭЛЕКТРОЛИЗА ВОДЫ С ТВЕРДЫМ ПОЛИМЕРНЫМ ЭЛЕКТРОЛИТОМ

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Катализатор на основе Ir и носителя - оксида титана (фаза Магнели) был синтезирован с помощью полиольного метода. Проведены исследования его структуры и активности в реакции выделения кислорода. Структура синтезированного электрокатализатора характеризуется наночастицами Ir небольшого размера, хорошо распределенными по поверхности носителя, а его массовая активность до 3 раз выше активности коммерчески доступного электрокатализатора.

***Ключевые слова**: иридий, катализатор на носителе, Ti_4O_7, твердый полимерный электролит, электролиз воды.*