

# Effect of the composition of corrosion resistant mixed oxide-based anode and cathode electrocatalysts on the electrocatalytic performance

Laboratory Project I

**Khirdakhanim Salmanzade**

Supervisor: Dr. András Tompos

Consultants: Dr. Irina Borbáth

Renewable Energy research group

Institute of Materials and Environmental Chemistry

Research Centre for Natural Sciences



Internal consultant: Dr. Imre Miklós Szilágyi; associate professor



Budapest University of Technology and Economics

Faculty of Chemical Technology and Biotechnology

Department of Inorganic and Analytical Chemistry

## Contents

1. Introduction.....	3
2. Experimental.....	5
2.1. Electrocatalysts used.....	5
2.2. Preparation of the 20 wt.% Pt/NiWO <sub>4</sub> -rGO electrocatalysts.....	6
2.3. Electrochemical characterization.....	7
2.3.1. Electrochemical characterization by cyclic voltammetry.....	7
2.3.2. Electrochemical characterization by ORR.....	8
2.3.3. Electrochemical characterization by HOR.....	9
3. Results and discussion.....	9
3.1. Electrochemical characterization of the NiWO <sub>4</sub> -based catalysts.....	9
3.2. Electrochemical characterization of the Pd- and PdRu-based catalysts.....	13
4. Summary.....	15
5. References.....	15

## 1. Introduction

As the population grows, humankind's energy demand is increasing, making security of energy supply one of the most important tasks to be addressed today. Covering the energy demand of humanity without generating toxic or harmful substances is a particularly important challenge. Utilization of hydrogen from renewable sources is a step towards clean environmental energy production as operation of Polymer Electrolyte Membrane (PEM) fuel cells fueled with hydrogen is completely free from emission of harmful materials.

Their widespread implementation requires essentially low-cost units with high energy density and durability. Electrocatalysts, which are indispensable elements of the PEMFC electrodes have a vital influence on the performance, durability, and price of the fuel cell. Although significant efforts are spent worldwide on developing novel electrocatalysts for PEM fuel cells, state of art systems still use catalysts from the Pt/C family. The active carbon-supported Pt anode catalysts (Pt/C) used today are unfavourable in terms of CO-tolerance and stability [1, 2]. Corrosion results in either Pt dissolution or oxidation of the carbon support leading to detachment, Ostwald ripening and agglomeration of platinum nanoparticles [3, 4]. The consequence of both processes is the loss of the active surface of the catalysts. In practice this activity loss is compensated by very high Pt loadings, which in turn results in unacceptably pricey catalysts [5].

According to the literature data oxide-containing electrocatalysts are much more resistant to corrosion compared with carbon, because metals in oxides have high oxidation state and do not readily lose further electrons to become further oxidized [6]. In the last decade a range of oxide containing electrocatalyst materials were proposed for both the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR). Zhang and coworkers have listed the criteria for the selection of oxides suitable for electrocatalysts [6]: (i) high stability in acidic media for acidic fuel cells or in alkaline media for alkaline fuel cells; (ii) high resistance against electrochemical corrosion; (iii) good electronic conductivity; (iv) good proton conductivity; (v) high specific surface area (vi) appropriate porosity; (vii) compatibility with electrodes. However, even if in electrochemical experiments many of them showed excellent properties, their utilization in PEMFCs remains extremely rare.

In this respect, the choice of nickel-tungsten mixed oxides, which are stable in an acidic media and have good proton conductivity, seems to be quite promising. NiWO<sub>4</sub> nanoparticles and their composites have exhibited interesting electrochemical properties in various fields

including supercapacitors [7,8,9] and electrocatalysts for oxygen evolution reactions [10], electrocatalytic nitrogen reduction reaction [11], etc. Moreover, Pt/NiWO<sub>4</sub> system has been patented as anode electrocatalysts for alcohol oxidation in fuel cells [12].

However, NiWO<sub>4</sub> mixed oxide has relative low electrical conductivity and low specific surface area, which is disadvantageous when it is used in electrocatalysts. It is known that addition of graphene materials can increase the specific surface area and electrical conductivity of composite materials [13]. It is well known that the graphenes involve a fast electron transport and thus the electrochemical reaction is facilitated more quickly and effectively. New types of carbonaceous materials like, carbon nanotubes, reduced graphene oxides (rGOs) have also been reported to provide extreme good properties to metal oxide-carbonaceous composites due to their special electronic structure [14].

Developing Pt-free low-cost catalyst for high-performance ORR is highly desirable. Zhang et al. [15] prepared hybrid electrocatalyst based on NiCo<sub>2</sub>O<sub>4</sub>/N-doped reduced graphene oxide (NiCo<sub>2</sub>O<sub>4</sub>/N-rGO); it was found that doping of rGO with nitrogen has a beneficial effect positive on the ORR activity.

Design and preparation of novel anode materials based on Pd and Ru embedded into ordered mesoporous structures can be also a promising direction in the development of Pt-free electrocatalysts. The reasons for this choice are justified by the fact that palladium is about 50 times more abundant on Earth than platinum and consequently the price is lower than that of platinum [16]. Ruthenium possesses free states around the Pd Fermi level and it can form stable alloys with palladium or can be incorporated in the lattice with various valence states [17]. Ruthenium contains high earth abundance and it is much cheaper than other noble metals.

The aim of this work was to study the effect of composition and structure of corrosion resistant mixed oxide-based electrocatalysts on the activity in the ORR and HOR in acidic medium. The key element of the concept was to introduce oxide materials either to act as catalysts by themselves or to partly or completely replace the carbon support in the corrosion-sensitive and expensive Pt/C electrocatalysts.

In the present report catalytic systems provided to the *Renewable Energy Research Group* (RERG) by Romanian partner in the frame of cooperation with the “Ilie Murgulescu” Institute of Physical Chemistry of the Romanian Academy will be investigated.

Nickel-based nanoarchitected NiWO<sub>4</sub>, Pt/NiWO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>-SnO<sub>2</sub> materials with multiple active sites and their composites with exfoliated graphite oxides/reduced graphene oxide (rGO) was investigated in the ORR and the HOR. In additional experiment the NiWO<sub>4</sub>-rGO composite material was loaded with 20 wt.% Pt via a modified NaBH<sub>4</sub>-assisted ethylene-glycol reduction-precipitation method developed in the RERG. Moreover, Pt-free Pd and PdRu electrocatalysts supported on mesoporous SnO<sub>2</sub>-x% WO<sub>3</sub> (x= 10-30 mol%) mixed oxide prepared by different methods was investigated in the HOR.

## 2. Experimental

### 2.1. Electrocatalysts used

The catalysts for electrochemical investigation were provided by Romanian colleagues. Properties and preparation details of the NiWO<sub>4</sub>-based as well as the Pd- and PdRu-based catalysts are summarized in Table 1 and 2, respectively.

**Table 1.** Properties and preparation details of the NiWO<sub>4</sub>-based catalysts

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Sample composition & Preparation details
NiWO <sub>4</sub>	25.4	NiWO <sub>4</sub> materials with Ni/W= 1:1 ratio were synthesized by co-precipitation of Ni and W precursor compounds using ethylene glycol (EG) as template and TBAOH as pH mediator
Pt/NiWO <sub>4</sub>	22.4	8 wt.% Pt loading was done by a deposition method assisted by EG and hydrazine as reducing agents and polyvinylpyrrolidone (PVP) as dispersant/stabilizer agent
NiWO <sub>4</sub> -rGO	28.8	Composites of Ni-based materials with rGO (10 wt.%) were prepared using direct synthesis method
Pt/NiWO <sub>4</sub> -rGO	27.0	20 wt.% Pt loading was done using a modified NaBH <sub>4</sub> -assisted ethylene-glycol (EG) reduction-precipitation method
NiCoSn-rGO	8.5	Synthesis of NiCo <sub>2</sub> O <sub>4</sub> -SnO <sub>2</sub> was done by a self-assembly method using tripropylamine and diethanolamine as structural directing agents

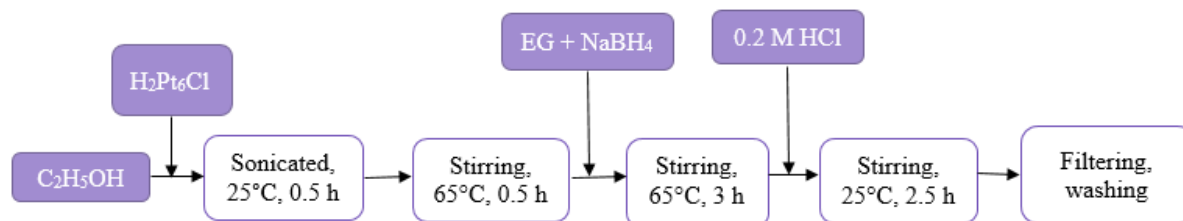
XRD analysis was performed on a Bruker D8 apparatus using the following parameters: Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 40 kV, 40 mA) at a scanning speed of 0.10 degrees/min.

**Table 2.** Properties and preparation details of the Pd- and PdRu-based catalysts

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	Sample composition & Preparation details
Sn10W-Triton	115.1	SnO <sub>2</sub> -10% WO <sub>3</sub> supports were prepared by a hydrothermal synthesis route using Triton X100 as a structural directing agent
Pd/Sn10W-Triton	102.8	the best structural organization due to the dispersion of Pd (and Ru) in the oxide matrix of Sn and W was provided by direct synthesis; Pd was reduced by hydrazine
PdRu/Sn10W-Triton	91.5	PdRu/SnO <sub>2</sub> -10%WO <sub>3</sub> (nominal composition: 10Pd30Ru50Sn10W (% mol) was prepared by hydrothermal synthesis assisted by Brij 35 and tripropylamine surfactants
RuWSn-cotton2-500	91.6	Composite was synthesized using cotton fibers as template
RuWSn-rGO-cotton2-500	49.0	Composites with rGO (10 wt.%) were prepared using direct synthesis method
Pd/RuWSn-rGO-cotton2-500	80.2	Pd (10 wt.%) was reduced by hydrazine

## 2.2. Preparation of the 20 wt.% Pt/NiWO<sub>4</sub>-rGO electrocatalysts

NiWO<sub>4</sub>-rGO composite was loaded with 20 wt.% Pt via a modified NaBH<sub>4</sub>-assisted ethylene-glycol (EG) reduction-precipitation method demonstrated schematically in Fig. 1 [18].

**Figure 1.** Flow chart for synthesis of 20 wt.% Pt/NiWO<sub>4</sub>-rGO electrocatalysts

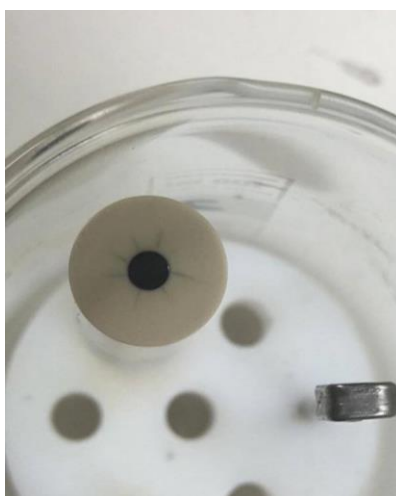
In this case 0.643 mmol H<sub>2</sub>PtCl<sub>6</sub>·x 6H<sub>2</sub>O was solved in 50 ml of ethanol and 200 mg of the samples was suspended in the solution. A solution prepared by mixing of 7.8 mmol NaBH<sub>4</sub> and 3.7 ml EG was added dropwise to the suspension at 65 °C with continuous stirring. After 3 hours of stirring at 65 °C, 15 ml 0.2 M HCl was added to the suspension and stirred for an additional 2.5 hours at room temperature in order to deposit the Pt particles onto the support material. The materials were washed three times with 50 ml water and filtered by centrifugation in order to remove the chloride ions and dried at 80 °C in an oven overnight.

## 2.3. Electrochemical characterization

### 2.3.1. Electrochemical characterization by cyclic voltammetry

All electrocatalysts were investigated by means of cyclic voltammetry (CV) in a conventional three-electrode electrochemical glass cell using a Biologic SP150 potentiostat and the EC-LAB software package. The working electrode was prepared by supporting the electrocatalysts on a glassy carbon (GC) electrode ( $d = 0.3$  cm, geometric surface area  $A = 0.0707$  cm<sup>2</sup>).

The electrode was polished by means of alumina powder (10  $\mu$ m diameter) with the addition of isopropanol in order to remove the impurities from the surface. Subsequently, the polishing alumina powder was removed from the electrode surface by rinsing with distilled water. The sample to be examined was powdered and an ink was prepared by dispersing 2 mg of the catalyst samples in 2 ml of a mixture of 1.592 ml of MilliQ water, 0.4 ml of isopropanol and 8  $\mu$ l of 5% Nafion<sup>®</sup> solution (DuPont<sup>™</sup> Nafion<sup>®</sup> PFSA Polymer Dispersions DE 520). The suspension was sonicated for 30 minutes. From this suspension a drop (3.6  $\mu$ l) was pipetted on to the dry mirror-polished GC and dried at room temperature for 20 min (see Fig. 2).



**Figure 2.** Rotating Disk Electrode with dry ink

The reference electrode was RHE. Pt was used as counter electrode. All electrochemical measurements were carried out at ambient temperature. Solutions were prepared from Millipore MilliQ water and P.A. reagents. 5.5 N Ar gas was used for deoxygenation the solutions. The electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub> (Merck).

Prior to the measurements, the electrode was activated by potential cycling for 10 times in the range 50 and 1000 mV at a scan rate of 100 mV s<sup>-1</sup>. After the activation procedure, CV measurements were done in the potential range of 50-1000 mV at a scan rate of 10 mV s<sup>-1</sup>.

### **2.3.2. Electrochemical characterization by ORR**

Catalytic activity of the catalyst samples was tested in the ORR by rotating disc electrode (RDE) technique. A RDE is a hydrodynamic working electrode used in a three-electrode system. The electrode can rotate during experiments inducing a flux of analyte to the electrode. The rotating speed of the electrode can be controlled at different levels, which yields a different flux of the analyte. It is the classical hydrodynamic electroanalytical technique used to limit the diffusion layer thickness, can be used to study the kinetics of interfacial reactions of most electrochemical processes [19].

The RDE consists of a disc (e.g. of Pt, glassy carbon and graphite) set into an insulating (PTFE) surround. The electrode is rotated about its vertical axis, typically between 225 and 10,000 rpm [20]. Although the literature suggests that the shape of the insulating mantle is critical and that exact alignment of the disk is important [21], these factors are usually not troublesome in practice, except perhaps at high rotation rates, where turbulence and vortex formation may occur. It is more important that there is no leakage of the solution between the electrode material and the insulator. The rod is attached to a motor directly by a chuck or by a flexible rotating shaft or pulley arrangement and is rotated at a certain frequency. Electrical connection is made to the electrode by means of a brush contact; the noise level observed in the current at the RDE depends on this contact [22].

The ORR measurements were done in O<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The diameter of GC electrode and Pt loading used in these experiments was the same as during CV measurements. Polarization curves were recorded by sweeping the potential between 200 and 1000 mV with 10 mVs<sup>-1</sup> sweep rate, rotating the electrode at 225, 400, 625, 900, 1225 and 1600 revolutions/min (rpm). Data were obtained from the negative scans. In order to characterize the surface state of the catalysts, before and after the RDE measurements 10 CVs between 50 and 1000 mV potential limits in Ar saturated electrolyte were also measured.



### 2.3.3. Electrochemical characterization by HOR

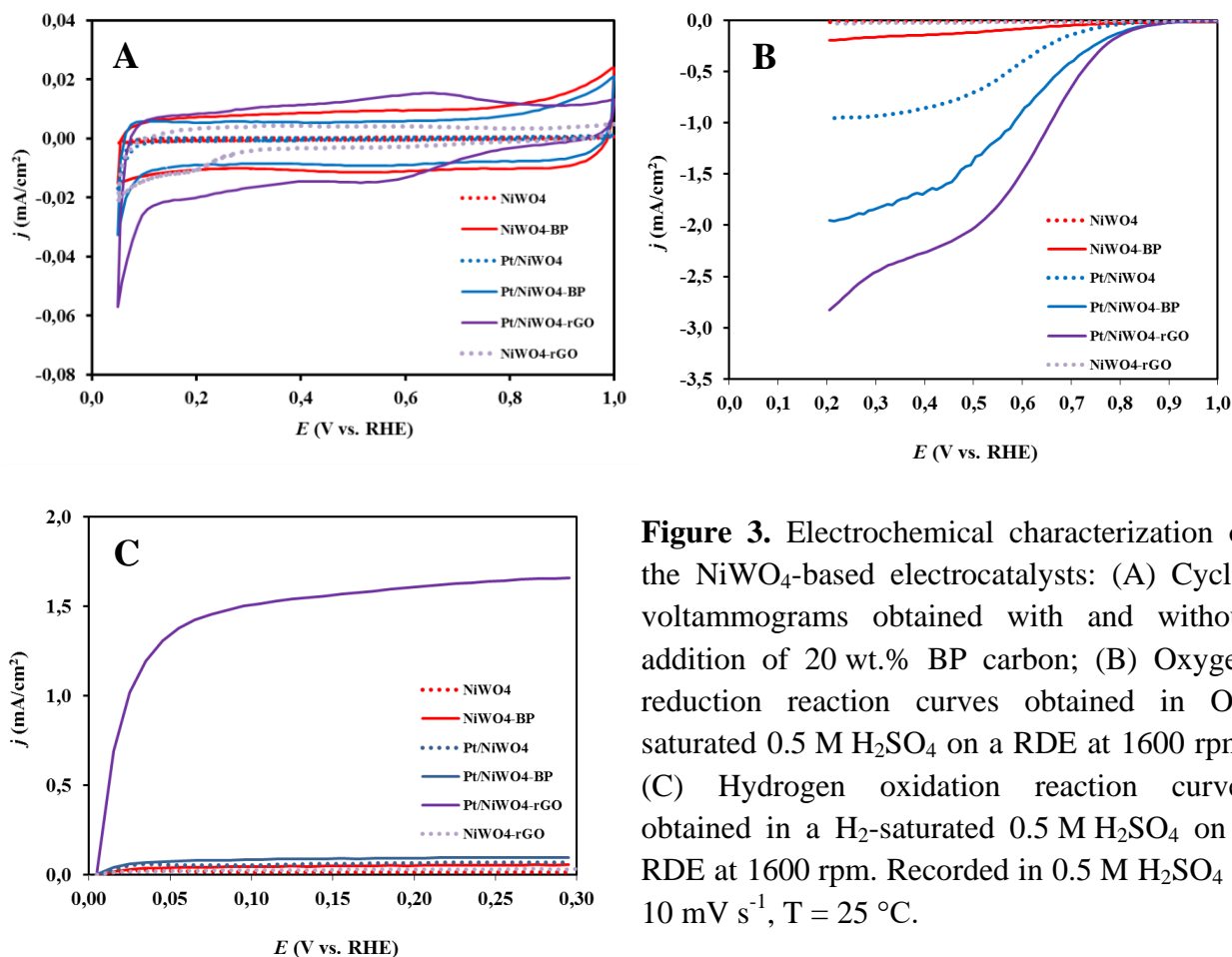
Catalytic activity in the hydrogen oxidation reaction was also investigated by RDE method in hydrogen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 400, 625, 900, 1225 and 1600 rpm. Polarization curves were recorded by sweeping the potential between 0 and 300 mV with 10 mVs<sup>-1</sup> sweep rate. The diameter of GC electrode and Pt loading used in these experiments was the same as during CV and ORR measurements.

For comparison as reference commercially available 20 wt.% Pt/C (Quintech, C-20-Pt, on Vulcan; denoted hereafter as Pt/C) was also studied by the same methods as described above.

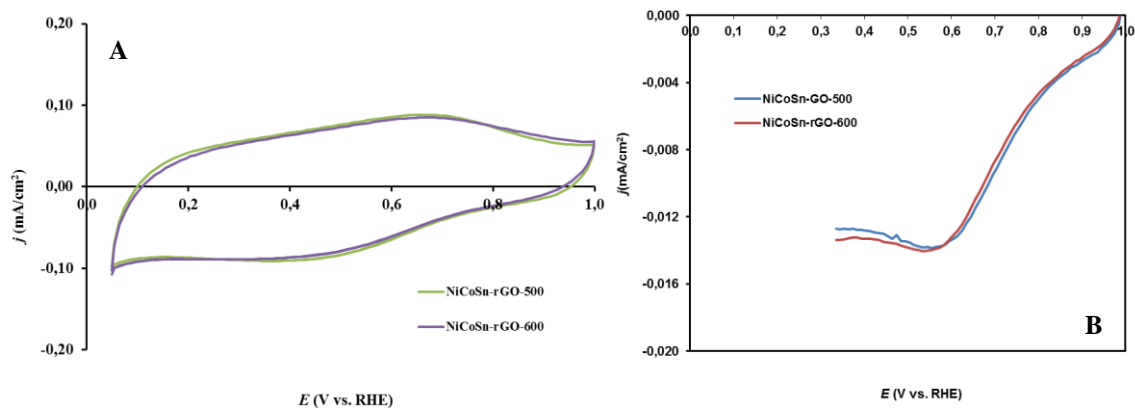
## 3. Results and discussion

### 3.1. Electrochemical characterization of the NiWO<sub>4</sub>-based catalysts

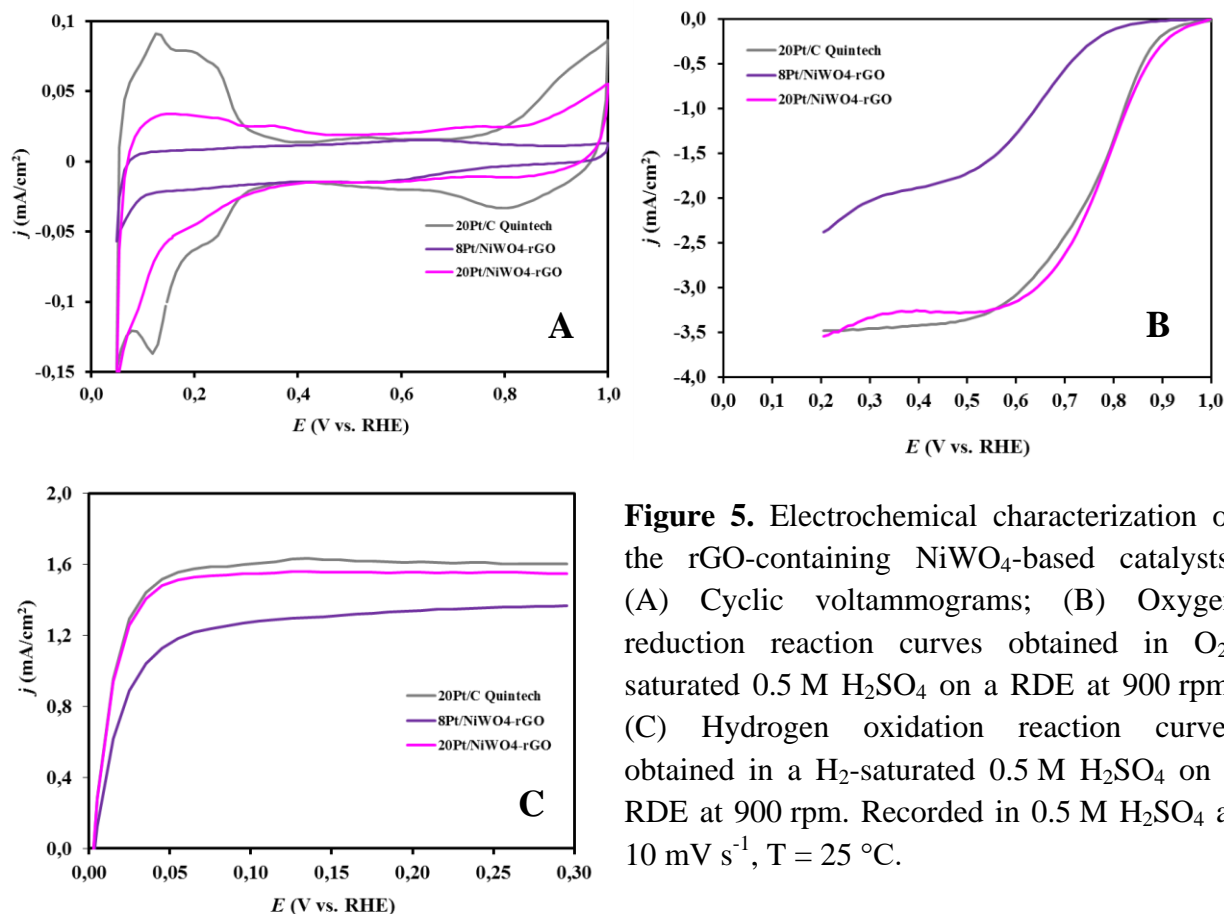
Since the NiWO<sub>x</sub> solid solution with mixed valence oxides can exhibit electrical conductivity or semiconductivity, initially the samples were tested without carbon addition. The electrocatalytic performance in the ORR and the HOR was evaluated by polarization curves measurements. Results of the electrochemical activity obtained on the NiWO<sub>4</sub>-based electrocatalysts at 1600 rpm were compared on Fig. 3. Possibly, due to the low surface area ( $S_{\text{BET}} = 22.4\text{-}28.8 \text{ m}^2/\text{g}$ ), the activity of carbon-free nickel-based NiWO<sub>4</sub> and 8 wt.% Pt/NiWO<sub>4</sub> catalysts in both reactions was very low (see Fig. 3).



Sufficient electronic conductivity can be ensured by adding during the ink preparation of 20 wt.% BP (BP: Black Pearls 2000) carbon to the catalysts. As shown in Fig. 3 after adding carbon, a significant increase in the ORR and HOR activity was observed only on the Pt/NiWO<sub>4</sub> catalyst.



**Figure 4.** (A) Cyclic voltammograms of the NiCoSn-rGO catalysts. (B) Oxygen reduction reaction curves obtained in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> on a RDE.



**Figure 5.** Electrochemical characterization of the rGO-containing NiWO<sub>4</sub>-based catalysts: (A) Cyclic voltammograms; (B) Oxygen reduction reaction curves obtained in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> on a RDE at 900 rpm; (C) Hydrogen oxidation reaction curves obtained in a H<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> on a RDE at 900 rpm. Recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 10 mV s<sup>-1</sup>, T = 25 °C.

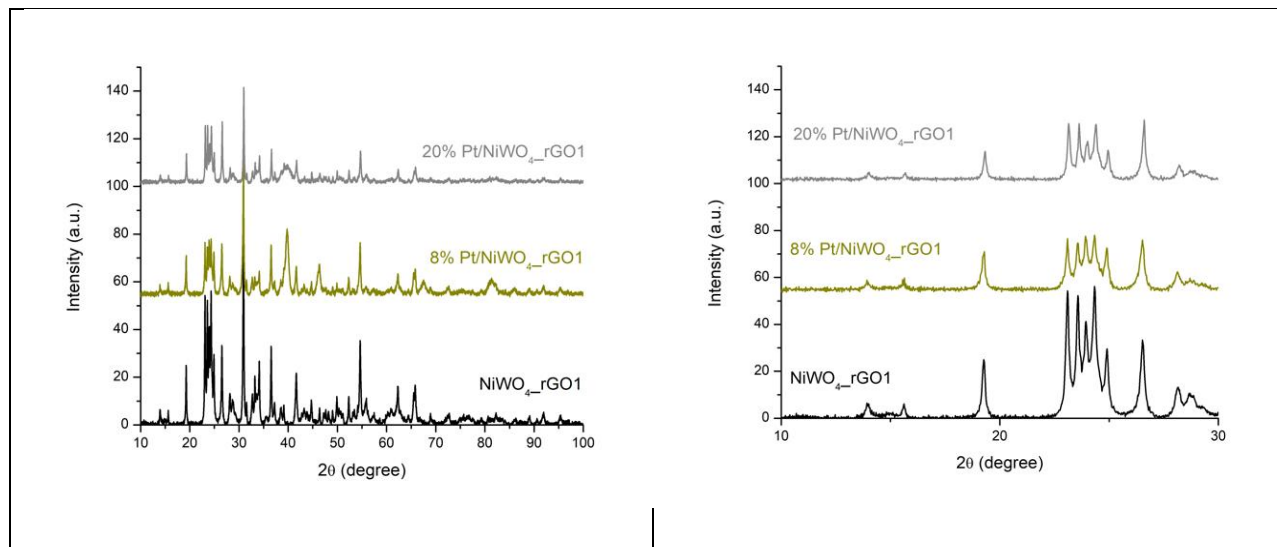
In this series of experiments, the best activity in the ORR and the HOR was obtained on the Pt catalyst supported on the composites of Ni-based materials with graphene nanoplatelets prepared using direct synthesis method (see Fig. 3), but as shown in Fig. 4 the activity of the NiCo<sub>2</sub>O<sub>4</sub>-SnO<sub>2</sub> catalyst materials remains negligible even after addition of the rGO.

In additional experiment the NiWO<sub>4</sub>-rGO composite material provided by Romanian partner was loaded with 20 wt.% Pt via a NaBH<sub>4</sub>-assisted EG reduction-precipitation method. The activity of the 20 wt.% Pt/NiWO<sub>4</sub>-rGO catalyst in the ORR and HOR was high and quite similar to the activity of the commercial reference 20 wt.% Pt/C Quintech catalyst (see Fig. 5).

A typical voltammogram of Pt electrocatalysts with the classical features of the underpotentially deposited hydrogen adsorption/desorption between 50 mV and 350 mV was observed on the 20 wt.% Pt/C catalyst (see Fig. 5.A). However, the CVs of the NiWO<sub>4</sub>-based electrocatalysts (Fig. 3.A) and even Pt/NiWO<sub>4</sub>-rGO catalyst with 20 wt.% of the Pt (Fig. 5.A) showed the rather suppressed hydrogen adsorption/desorption region.

According to the literature site-blocking effect can be caused by second metal segregated over active metal (for example, by tin segregation over Pt-Sn alloy phase in Sn-modified Pt catalysts [23]). This behavior can be a reason of the pronounced decrease of H<sub>2</sub> adsorption/desorption. It can be proposed that NiWO<sub>4</sub>-rGO composite material was not stable during Pt loading procedure; for example, some components were dissolved and re-deposited on the Pt surface during the loading procedure.

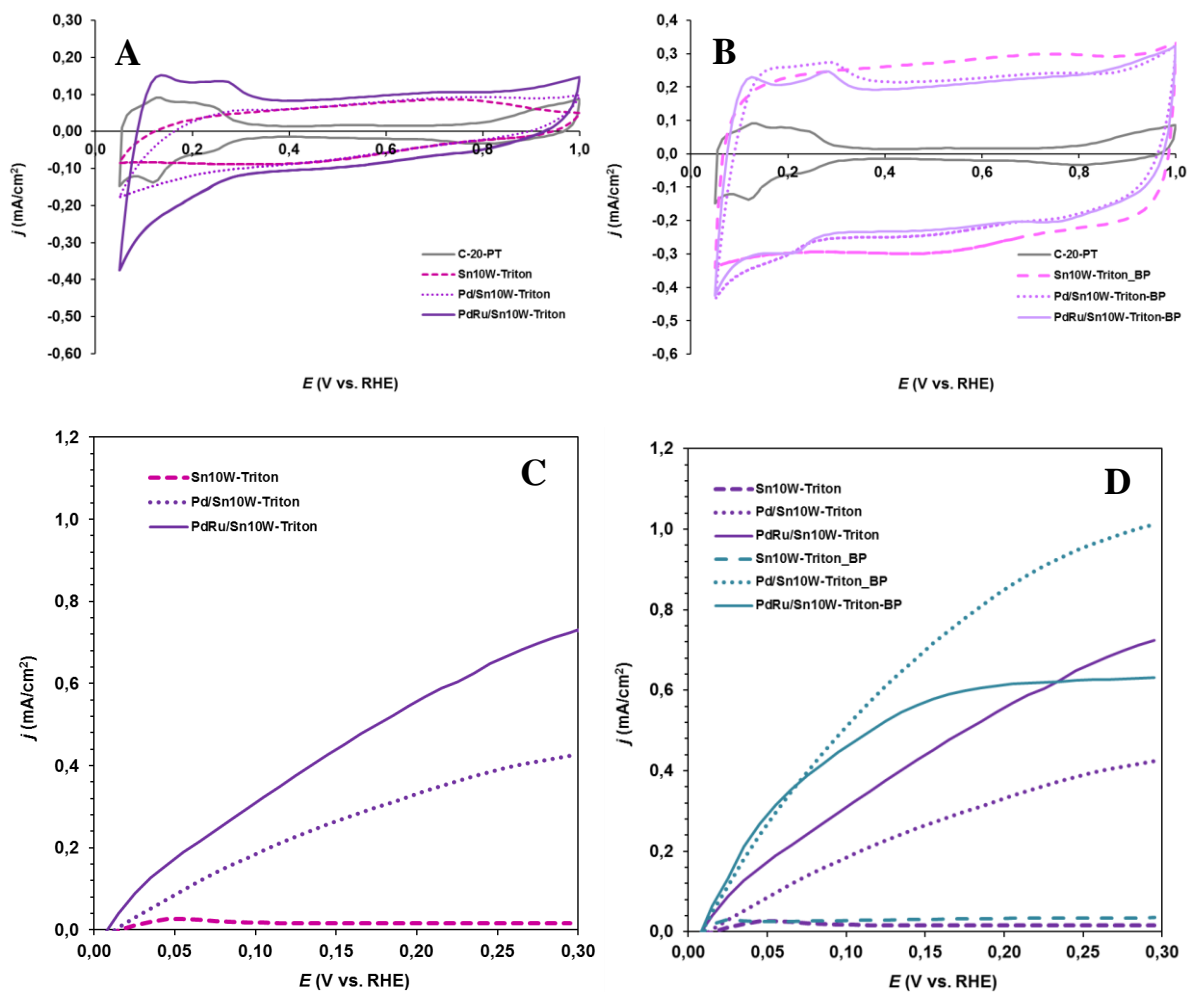
XRD patterns of nickel tungsten oxide based powders are presented in Fig. 6.



**Figure 6.** XRD patterns of the Pt/NiWO<sub>4</sub>-rGO (Pt= 0, 8 or 20 wt.%) materials

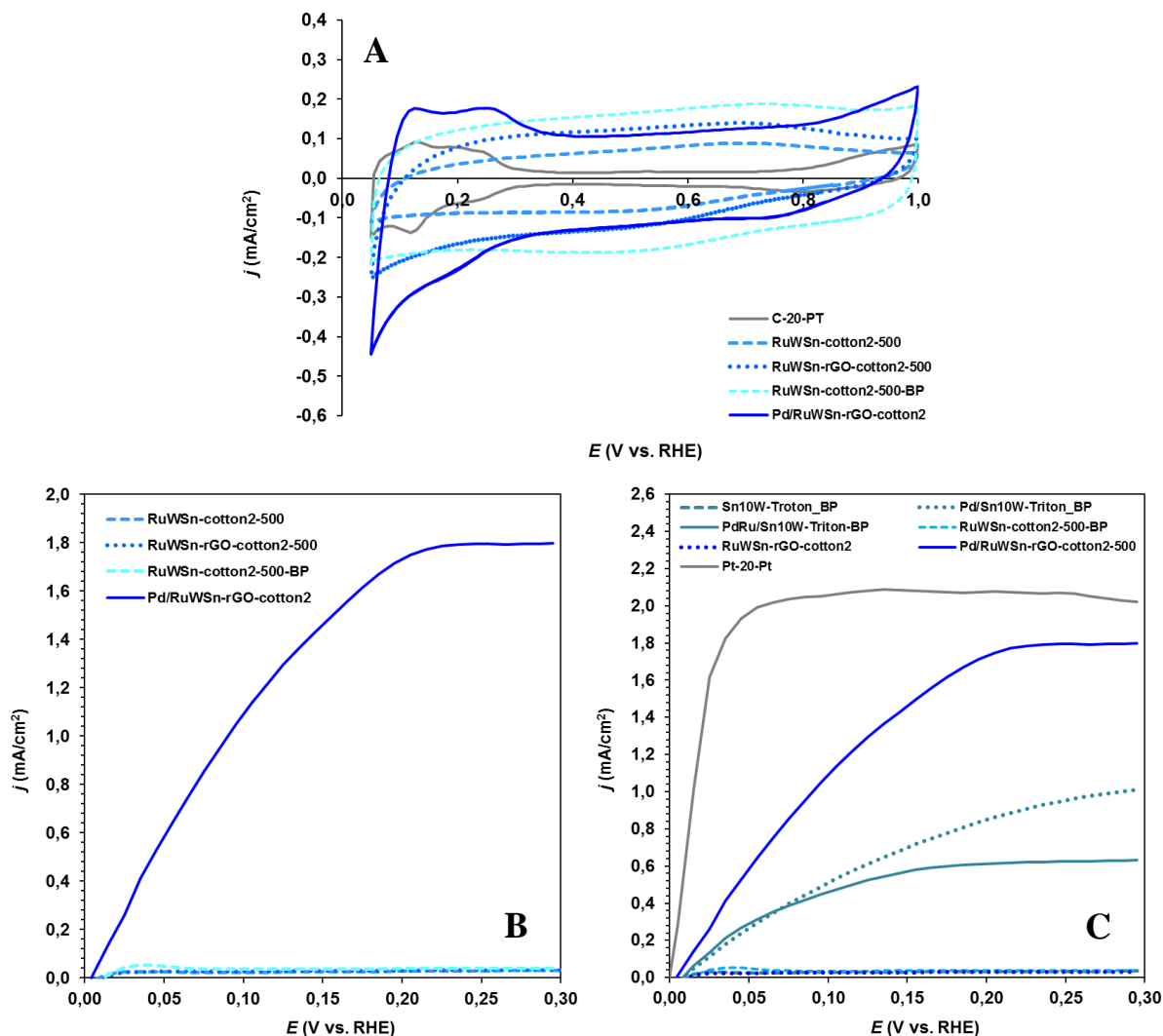
The XRD pattern of the NiWO<sub>4</sub>-rGO corresponds to a mixture of two tungsten containing phases: NiWO<sub>4</sub>, and WO<sub>3</sub>. The addition of Pt by different methods and in different amounts (8 and 20 wt.%) does not modify much the structural properties of the support, corresponding to the same phases, but with lower content of the oxide WO<sub>3</sub>, and additional peaks that are indexed to cubic Pt phase. The presence of weak cubic NiO peaks is also observed, but peak overlapping with other phases precludes a precise quantification.

### 3.2. Electrochemical characterization of the Pd- and PdRu-based catalysts



**Figure 7.** Characterization of the Sn10W-Triton-type of catalysts obtained with and without addition of 20 wt.% BP carbon. Cyclic voltammograms (A, B) recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 100 mV s<sup>-1</sup>. Results obtained on the 20 wt.% Pt/C Quintech catalyst are given for comparison. Hydrogen oxidation reaction curves (C, D) obtained in a hydrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> on a RDE at 1600 rpm. Sweep rate: 10 mV s<sup>-1</sup>.

Unfortunately, without Pd the activity in the HOR of the mesoporous SnO<sub>2</sub>-10%WO<sub>3</sub> materials prepared using Triton X100, as a structural directing agent, remains very small even after addition of the 20 wt.% BP carbon (see Fig. 7). As shown in Fig. 7.C and 7.D, after dispersion of Pd and Ru in the oxide matrix of the SnO<sub>2</sub>-10%WO<sub>3</sub> materials sizable increase of the HOR activity was observed.



**Figure 8.** Characterization of the RuWSn-type of composites and Pd catalysts synthesized using cotton fibers as template: influence of the rGO addition on the (A) cyclic voltammograms and (B) hydrogen oxidation reaction curves obtained in a hydrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> on a RDE at 1600 rpm. Sweep rate: 100 mV s<sup>-1</sup> (A) and 10 mV s<sup>-1</sup> (B). (C) Comparison of the HOR activity of RuWSn-cotton and Sn10W-Triton-type of catalysts. Results obtained on the commercial 20 wt.% Pt/C Quintech catalyst (C-20-Pt) are given for comparison (measurements were done using the same experimental condition).

In this series of experiments, the best activity was obtained on the Pd/RuWSn-rGO-cotton catalyst synthesized using cotton fibers as template (see Fig. 8.B and 8.C). Cotton fibers can be successfully applied as templates for the synthesis of mesoporous materials [24]. These electrochemical results are a good starting point for further studies.

## 4. Summary

The NiWO<sub>4</sub> materials with Ni/W= 1:1 ratio were synthesized using different methods in order to highlight the effect of preparation conditions on the electrochemical performance. After adding carbon, a significant increase in the ORR activity was observed only on the Pt/NiWO<sub>4</sub> catalyst. In this series of experiments, the best activity in the ORR was obtained on the Pt catalyst supported on the NiWO<sub>4</sub>-rGO composites prepared by direct synthesis method, but the activity of the NiCo<sub>2</sub>O<sub>4</sub>-SnO<sub>2</sub> catalyst materials remains negligible even after addition of the rGO. The activity in the ORR and HOR of the 20 wt.% Pt/NiWO<sub>4</sub>-rGO catalyst was high and quite similar to the activity of the reference 20 wt.% Pt/C Quintech catalyst.

Unfortunately, the activity of the mesoporous SnO<sub>2</sub>-10%WO<sub>3</sub> materials in the HOR remains very small even after addition of the 20 wt.% BP carbon. Sizable increase of the HOR activity was observed after dispersion of Pd and Ru in the oxide matrix of the SnO<sub>2</sub>-10%WO<sub>3</sub> materials. In this series of experiments, the best activity was obtained on the PdRu catalyst supported on SnO<sub>2</sub>-10%WO<sub>3</sub>-rGO composite synthesized using cotton fibers as template. These electrochemical results are a good starting point for further studies.

## 5. References

- 
- <sup>1</sup> J. Baschuk, X. Li, Carbon monoxide poisoning of proton exchange membrane fuel cells. *Int. J. Energy Res.* 25 (2001) 695-713.
  - <sup>2</sup> S. Shahgaldi, J. Hamelin, Improved carbon nanostructures as a novel catalyst support in the cathode side of PEMFC: a critical review. *Carbon* 94 (2015) 705-728.
  - <sup>3</sup> J.C. Meier, C. Galeano, I. Katsounaros, A.A. Topalov, A. Kostka, F. Schuüth, K.J.J. Mayrhofer, Degradation Mechanisms of Pt/C Fuel Cell Catalysts under Simulated Start-Stop Conditions. *ACS Catalysis* 2(5) (2012) 832-843.
  - <sup>4</sup> J. Zhao, X. Li, A review of polymer electrolyte membrane fuel cell durability for vehicular applications: Degradation modes and experimental techniques, *Energy Convers. Manage.* 199 (2019) 112022.
  - <sup>5</sup> B.G. Pollet, S.S. Kocha, I. Staffell, Current status of automotive fuel cells for sustainable transport, *Current Opinion in Electrochemistry* 16 (2019) 90-95.
  - <sup>6</sup> Z. Zhang, J. Liu, J. Gu, L. Su, L. Cheng, An overview of metal oxide materials as electrocatalysts and supports for polymer electrolyte fuel cells, *Energy Environ. Sci.* 7 (2014) 2535-2558.
  - <sup>7</sup> Y. Wang, C. Shen, L. Niu, Z. Sun, F. Ruan, M. Xu, S. Shan, C. Li, X. Liu, Y. Gong, High rate capability of mesoporous NiWO<sub>4</sub>-CoWO<sub>4</sub> nanocomposite as a positive material for hybrid supercapacitor, *Mater. Chem. Phys.* 182 (2016) 394-401.
  - <sup>8</sup> R.D. Kumar, Y. Andou, S. Karuppuchamy, Synthesis and characterization of nanostructured Ni-WO<sub>3</sub> and NiWO<sub>4</sub> for supercapacitor applications, *J. Alloys Compd.* 654 (2016) 349-356.
  - <sup>9</sup> J. Tian, Y. Xue, X. Yu, Y. Pei, H. Zhang, J. Wang, Solvothermal synthesis of NiWO<sub>4</sub> nanostructure and its application as a cathode material for asymmetric supercapacitors, *RSC Adv.* 8 (2018) 41740-41748.

- 
- <sup>10</sup> V.K.V.P. Srirapu, A. Kumar, P. Srivastava, R.N. Singh, A.S.K. Sinha, Nanosized CoWO<sub>4</sub> and NiWO<sub>4</sub> as efficient oxygen-evolving electrocatalysts *Electrochim. Acta* 209 (2016)75-84.
- <sup>11</sup> J. Wang, H. Jang, G. Li, M.G. Kim, Z. Wu, X. Liu, *Nanoscale* 12 (2020)1478-1483.
- <sup>12</sup> R.R. Adzic, N.S. Marinkovic, Electrocatalysts for alcohol oxidation in fuel cells, US Patent 6,183,894 B1 Feb. 6, 2001
- <sup>13</sup> F. Li, L. Long, Y. Weng, A Review on the Contemporary Development of Composite Materials Comprising Graphene/Graphene Derivatives, *Advances in Materials Science and Engineering*, Volume 2020, Article ID 7915641, 16 pages, <https://doi.org/10.1155/2020/7915641>
- <sup>14</sup> A. Halder, M. Zhang, Q. Chi, Electrocatalytic Applications of Graphene-Metal Oxide Nanohybrid Materials, In: *Advanced Catalytic Materials - Photocatalysis and Other Current Trends* (L.E. Norena, J.-A. Wang (Eds.)) 2016, Chapter 14, pp. 379-413. InTech Open Access Publishers. <http://dx.doi.org/10.5772/61808>
- <sup>15</sup> H. Zhang, H. Li, H. Wang, K. He, S. Wang, Y. Tang, J. Chen, NiCo<sub>2</sub>O<sub>4</sub>/N-doped graphene as an advanced electrocatalyst for oxygen reduction reaction. *J Power Sources* 280 (2015) 640-648.
- <sup>16</sup> E. Antolini, S.C. Zignani, S.F. Santos, E.R. Gonzalez, Palladium-based electrodes: A way to reduce platinum content in polymer electrolyte membrane fuel cells. *Electrochim. Acta* 56 (2011) 2299–2305.
- <sup>17</sup> D. Wu, K. Kusada, H. Kitagawa, Recent progress in the structure control of Pd–Ru bimetallic nanomaterials, *Science and Technology of Advanced Materials*, 17(1) (2016) 583-596. <https://doi.org/10.1080/14686996.2016.1221727>
- <sup>18</sup> Á. Vass, I. Borbáth, Z. Pászti, I. Bakos, I.E. Sajó, P. Németh, A. Tompos, Effect of Mo incorporation on electrocatalytic performance of Ti-Mo mixed oxide-carbon composite supported Pt electrocatalysts. *Reaction Kinetics Mechanisms and Catalysis* 121 (2017) 141-160.
- <sup>19</sup> S. Li, A. Thomas, In: *Advanced Nanomaterials for Electrochemical-Based Energy Conversion and Storage* (F. Ran, S. Chen (Eds.)), Chapter 12 - Emerged carbon nanomaterials from metal-organic precursors for electrochemical catalysis in energy conversion. *Micro and Nano Technologies*, 2020, pp. 393-423.
- <sup>20</sup> C.G. Zoski, *Handbook of Electrochemistry*, 2007.
- <sup>21</sup> A. C. Riddiford, *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, (P. Delahay and C. W. Tobias (Eds.)), Wiley, New York, 1966.
- <sup>22</sup> A. J. Bard and L. R. Faulkner, "Rotating Disk Electrode," in *Electrochemical Methods: Fundamentals and Applications, 2nd Edition*, New York, John Wiley & Sons, 2000, pp. 335-348.
- <sup>23</sup> I. Borbáth, D. Gubán, I. Bakos, Z. Pászti, G. Gajdos, I.E. Sajó, Á. Vass, A. Tompos, Exclusive formation of alloy phases via anchoring technique - From bimetallic catalysts to electrocatalysis, *Catal Today* 306 (2018) 58–70.
- <sup>24</sup> B. Sun, T. Fan, J. Xu, D. Zhang, Biomorphic synthesis of SnO<sub>2</sub> microtubules on cotton fibers. *Materials Letters* 59 (2005) 2325 – 2328.