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Preparation of CO-tolerant anode electrocatalysts for polymer electrolyte membrane fuel-cells

PhD Thesis

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1. Introduction

Hydrogen has a key role in resolving one of the most important issues of our time: to meet the ever increasing energy demand of the world from clean and renewable sources. Fuel cells can convert chemical energy stored in hydrogen or in other compounds with hydrogen content to electricity without any emission of pollutants. Currently catalysts with high loading of Pt are required for the oxidation and reduction on the anode and cathode side of the cell, respectively. These catalysts are expensive and not effective enough. The hydrogen fuel is usually produced by reforming so that it contains a few ppm of CO, which irreversibly binds to the active Pt sites. This CO poisoning hinders the operation of the cell by preventing the access of the hydrogen fuel to the active sites of the catalyst, resulting in the prohibition of the hydrogen oxidation reaction. Furthermore by dipole interaction strongly bound CO reduces the activity of the remaining free sites. If alcohols are directly used as fuels, CO is always present as an intermediate product in the electrooxidation reaction. So it is necessary to develop CO-tolerant electrocatalysts. A promising method is to design Pt-based catalysts that are CO-tolerant due to their structure, which means the ability to oxidize the blocking CO species on lower potentials, ensuring the accessibility of the active catalytic sites for the electrooxidation of the fuel.

Another issue with the commonly used carbon-supported Pt catalysts is that the support tends to corrode under the fast load change conditions encountered frequently in fuel cells used in transportation applications. Corrosion of the support rapidly deteriorates the electrocatalyst, which results in declining performance of the fuel cell.

In this thesis work Pt-based CO-tolerant electrocatalysts for polymer electrolyte membrane (PEM) fuel cell applications were developed by modifying the Pt/C system by oxophilic metals (W, Sn). The goal was to develop stable catalysts, which are not only active in the CO-oxidation reaction, but also in the electrooxidation of the fuel itself, providing the possibility for the reduction of the Pt content and as a consequence the price of the catalysts.

2. State of art

Fuel cells are electrochemical devices that convert the chemical energy of the fuel directly to electricity by chemical reaction, so they have excellent efficiency. The principle of their operation is that the oxidation of the chemical energy carrier (fuel) and the reduction of the oxidant (oxygen) are carried out separately, the material flow is ensured by an ionic conductor, which connects the anode and cathode side, while the electrons released during the oxidation are led through electrical loads to the cathode side. Their electrochemical efficiency can reach 80 %. Generally, every compound that can be oxidized could be used as a fuel, and every oxidant can be introduced to the cathode site which has the ability to reduce. Hydrogen gas can be directly fed onto the anode; the hydrogen content of methanol could be released either before feeding it into the fuel cell, or directly in the cell. The latter method is sufficient primarily for small, portable applications.¹

Since the anode reaction is 5-7 times faster than the reduction on the cathode, the catalytic issues on the anode are not due the slow kinetics, but rather caused by the pollutants (CO) or reaction intermediates which poison the catalytic sites.² Further disadvantages of pure carbon supported Pt catalysts are their high price, the limited availability of Pt, and the electrocorrosion-sensitivity of the carbon support.³ These problems give a firm ground for research to realize CO-tolerant fuel cells.

One of the most promising solutions is to apply CO-tolerant electrocatalysts, since they can provide high efficiency without technical issues (such as complex devices). Most often a second oxophilic metal is used as a modifier, which upon water activation can provide the

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² J. Zhang, *PEM Fuel Cell Electrocatalysts and Catalyst Layers*, 2008, Spinger

³ Y.-C. Park, K. Kakinuma, M. Uchida, D. A. Tryk, T. Kamino, H. Uchida, M. Watanabe, *Electrochim. Acta* 91 (2013) 195-207.

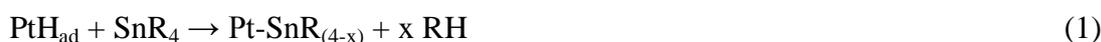
necessary OH_{ad} species for the oxidation of CO at less positive potentials than Pt, or it could enhance CO-tolerance by the electronic effect. The most popular modifiers are Ru, Sn, Co, Cr, W, Fe, Ni, Pd, Os, Mo and Mn. The co-catalytic effect of the modifier can be attributed to the following effects:

- 1. Bifunctional effect:** the modifier metal with stronger affinity for oxygen than platinum sites provides the necessary oxygen containing OH_{ad} species at less positive potentials than Pt.⁴
- 2. Ligand (or electronic) effect:** the electronic structure of the catalytic active site is modified by the second component, the promoter, so that the adsorption/desorption behaviour of the reagents/reaction intermediates are modified. As an example Fe-Pt or Ru-Pt systems could be mentioned,⁵ which can decrease the adsorption of CO.
- 3. Morphologic effect:** the dilution of the active component with a catalytically inactive modifier changes the distribution of the metal, creating new possible reaction paths.⁶

The catalysts can be modified by alloying the active Pt with an oxophilic modifier, or the second metal can be immobilized in the structure of the support.

According to the literature of the electrooxidation of alcohols, tin-modified Pt/C is a very promising electrocatalyst.^{7,8} Many methods exist in the literature for the synthesis of Sn-Pt/C catalysts. However, most of them lead to products with a wide range of phases, such as metallic Pt, Pt-oxide, various tin-oxides, Sn-Pt alloys or Pt_(1-x)Sn_x solid solutions with diverse stoichiometry.^{9,10} It has been demonstrated⁷ that Pt₃Sn phase is the most stable and active catalysts among Sn-Pt alloys for the CO oxidation reaction.^{7,11} Although, by analyzing the reports it emerges that the exclusive production of Pt₃Sn alloy phase rarely occurs, and its presence strongly depends on the synthetic procedure.¹²

During decades of research activity our research group has accumulated a detailed knowledge on the preparation of different types of supported E_x-M_y (E= Sn, Ge; M= Pt, Pd, Rh, Ru) catalysts with exclusive formation of metal-metal interaction and high E/M ratios. It has been demonstrated^{13,14,15} that exclusive formation of Sn-Pt alloys with different Pt/Sn ratios can be achieved by Controlled Surface Reaction (CSR). Our research group is one of the pioneers of the CSR method.¹⁶ During CSR hydrogen adsorbed on Pt reacts with tetraalkyl-tin compounds (SnR₄). The basic surface chemistry can be written as follows:^{13,16}



The use of the above two-step CSR method guarantees the exclusive introduction of tin onto platinum, i.e. the suppression of Sn-support interaction. In case of the Pt-Sn system the

⁴ M. Watanabe, S. Motoo, *Electroanal. Chem. Interfacial Electrochem.* 60 (1975) 275-283.

⁵ L. G. S. Pereira, V. A. Paganin, E. A. Ticianelli, *Electrochim. Acta* 54 (2009) 1992-1998.

⁶ W. Vielstich, A. Lamm, H. A. Gasteige, *Handbook of Fuel Cells*, Wiley, 2003

⁷ S. García-Rodríguez, F. Somodi, I. Borbáth, J.L. Margitfalvi, M.A. Peña, J.L.G. Fierro, S. Rojas, *Appl. Catal. B: Env.* 91 (2009) 83-91.

⁸ S. Garcia-Rodríguez, M.A. Peña, J.L.G. Fierro, S. Rojas, *J. Power Sources* 195 (2010) 5564-5572.

⁹ E. Antolini, E. R. Gonzalez, *Electrochim. Acta* 55 (2010) 6485-6490.

¹⁰ M. Arenz, V. Stamenkovic, B.B. Blizanac, K.J. Mayrhofer, N.M. Markovic, P.N. Ross, *J. Catal.* 232 (2005) 402-410

¹¹ V.R. Stamenkovic, M. Arenz, C.A. Lucas, M.E. Gallagher, P.N. Ross, N.M. Markovic, *J. Am. Chem. Soc.* 125 (2003) 2736-2745.

¹² E. Antolini, E. R. Gonzales, *Catal. Today* 160 (2010) 28-38.

¹³ J.L. Margitfalvi, I. Borbáth, E. Tfirst, A. Tompos, *Catal.Today* 43 (1998) 29-49.

¹⁴ J.L. Margitfalvi, I. Borbáth, M. Hegedűs, A. Tompos, *Appl. Catal. A: General* 229 (2002) 35-49.

¹⁵ J.L. Margitfalvi, I. Borbáth, K. Lázár, E. Tfirst, Á. Szegedi, M. Hegedűs, S. Gőbölös, *J. Catal.* 203 (2001) 94-103.

¹⁶ J. Margitfalvi, M. Hegedűs, S. Gőbölös, E. Kern-Tálas, P. Szedlacek, S. Szabó, F. Nagy, in: *Proc. 8th Int. Congress on Catalysis*, Vol. 4, Berlin (West), 2-6 July 1984, pp. 903-912.

net result is the exclusive formation of Sn-Pt alloy phases.¹⁷ In the previous studies of our research group the modes and ways to increase the amount of tin introduced directly onto the parent metal has also been established.^{13,18} It has been demonstrated^{7,19} that the use of extremely high SnR₄ concentration should be avoided, since it can lead to the concentration gradient of the anchored modifier. In those studies it has already proved that long reaction time, high reaction temperature and high [SnEt₄] concentration leads to the non-desired reaction between the surface groups of the support and the tin precursor. The use of consecutive reaction steps avoids any inhomogeneity of the modifier over the metallic particles.

As aforementioned stable and CO-tolerant catalysts can be formed not only by the formation of platinum alloys, but also by the modification of the support with oxophilic metals. Numerous studies can be found in the literature about W-based CO-tolerant electrocatalyst, which was realized either by the modification of Pt with tungsten or by the deposition of Pt onto the surface of WO₃.^{20,21} The co-catalytic effect of the tungsten was assigned to the quick and easy oxidation-state changes. Based on the literature results enhanced CO-tolerance of the W-modified anode electrocatalysts was explained not only in the frame of bifunctional mechanism and/or by the influence of W on the interaction between Pt and adsorbed CO (electronic effect). Comparing to other popular modifiers the promotional effect of tungsten was also to increase catalytic activity through „hydrogen spill-over” effect.^{22,23} It has been demonstrated²² that the proton conducting tungsten bronze (H_xWO₃ (0.3<x<0.5)) provides rapid hydrogen oxidation leading to the improvement of the overall catalytic activity.

It is known that W can be easily oxidized to WO₃ even at lower potentials, so it cannot be applied in fuel cells in metallic form, furthermore WO₃ is an n-type semiconductor with a band gap of 2,6-2,7 eV, so it cannot be used as a support for electrocatalysts. Recent literature suggests,²⁰ however, that the beneficial properties of the tungsten co-catalyst can be preserved if it is incorporated into TiO₂. TiO₂ is an n-type semiconductor, but it has excellent mechanical, chemical and redox stability, low cost, non-toxicity and corrosion resistance in acidic environment, furthermore its conductivity can be substantially improved by cation substitution. Since the ionic radius of W is similar to that of Ti²⁴, it is a promising substituent to modify TiO₂ and form a conductive Ti_(1-x)W_xO₂ mixed oxide.

Electroconductive Ti_{0,7}W_{0,3}O₂ mixed oxide has been applied as a support for Pt in anode electrocatalysts.²⁵ These materials showed unique CO-tolerance compared to commercial catalysts,²⁵ although in order to ensure sufficient conductivity 20 wt% activated carbon was added to the catalyst ink before the measurements.

Upon the development of novel electrocatalysts in this thesis two pathways were followed: (i) alloying the active noble metal (Pt) with another oxophilic metal (Sn) and (ii) modification of the active carbon support by more corrosion resistant, electrical conductive W-containing Ti_(1-x)W_xO₂ mixed oxide.

In the development of the Pt-Sn/C catalysts the goal was to determine the optimal synthesis parameters of the CSR method for the exclusive formation of the Pt₃Sn phase, which shows enhanced catalytic behaviour in both CO and methanol oxidation reactions.

¹⁷ Cs. Vèrtes, E. Tálás, I. Czako-Nagy, J. Ryzckovski, S. Góbbölös, A. Vèrtes, J. Margitfalvi, *Appl. Catal.* 68 (1991) 149-159.

¹⁸ J.L. Margitfalvi, I. Borbáth, M. Hegedús, E. Tfirst, S. Góbbölös, K. Lázár, *J. Catal.* 196. (2000) 200-204.

¹⁹ J.L. Margitfalvi, I. Borbáth, M. Hegedús, S. Góbbölös, *Appl. Catal. A: General* 219 (2001) 171-182.

²⁰ D. Wang, C.V. Subban, H. Wang, E. Rus, F.J. DiSalvo, H.D. Abruña, *J. Am. Chem. Soc.* 132 (2010) 10218-10220.

²¹ L.G.S. Pereira, F.R. dos Santos, M.E. Pereira, V.A. Paganin, E.A. Ticianelli, *Electrochim. Acta* 51 (2006) 4061-4066.

²² J. Zeng, J.Y. Lee. *Int. J. Hydrogen Energy* 32 (2007) 4389-4396

²³ E. Maillard, Y. Peyrelade, Y. Soldo-Olivier, M. Chatenet, E. Chaînet, R. Faure. *Electrochim. Acta* 52 (2007) 1958-1967.

²⁴ R.D. Shannon, *Acta Crystallogr.* A32 (1976) 751-767.

²⁵ C.V. Subban, Q. Zhou, A. Hu, T.E. Moylan, F.T. Wagner, F.J. DiSalvo, *J. Am. Chem. Soc.* 132 (2010) 17531-17536.

Following the second pathway the goal was to prepare a W-modified CO-tolerant and stable catalyst support with sufficient electroconductivity. The stabilization of the modifier from leaching in acidic electrolyte was attempted by isovalent substitution of tungsten into the rutile-TiO₂ lattice, while the conductivity and corrosion resistance across the anticipated potential/pH window was ensured by a Ti-W mixed oxide – activated carbon composite type structure. The main goal was to study the influence of the experimental conditions, mainly the preparation method used and the multistep heat treatment applied on (i) the rutile/anatase phase ratio, (ii) oxidation state of W, and (iii) presence or absence of free WO₃ and/or WO₂ phases, not incorporated into the rutile crystal-lattice. My efforts were concentrated on finding the optimum experimental conditions for synthesizing Pt/Ti_{0.7}W_{0.3}O₂-C catalysts with good electrochemical stability and enhanced CO tolerance, and understanding the relationships between the synthesis parameters, structure development and electrocatalytic properties.

3. Experimental part

40 wt% commercial Pt/C catalyst (Quintech) was modified with tetraethyltin (SnEt₄) by CSR in order to obtain Sn-Pt/C electrocatalysts with Pt/Sn=1.8-3.0 ratios. The Pt/C catalyst was suspended in *n*-decane in a stainless steel autoclave, then after adjusting the H₂ pressure to 5 bar, the reactor was heated to 170 °C. After reaching the desired temperature the first amount of SnEt₄ solved in *n*-decane was added under vigorous stirring. The requested amount of SnEt₄ was divided into 3, 4 or 5 uniform portions and was introduced to the reactor after equal periods of time, each anchoring period was 1 hour. After the modification procedure, the catalyst was separated by centrifugation and carefully washed. Then, the powder was dried at 60 °C for 1 hour, and was treated in hydrogen atmosphere by Temperature Programmed Reduction (TPR) at 250, 350 or 400 °C.

The conductive Ti-W mixed-oxide – carbon composites were prepared by three different synthesis methods: (i) microwave-assisted solvothermal synthesis route I, (ii) sol-gel synthesis route II, and (iii) a low temperature sol-gel-based multistep synthesis route III. The scheme of the synthesis routes is shown on Fig. 1. The supports were loaded with 40 wt% of Pt by NaBH₄-assisted ethylene-glycol reduction method.

The crystalline structure of the samples was examined by XRD, and the particle size distribution was determined by TEM. The chemical composition of the samples was determined by several methods (SEM, EDS, XRF, XPS), and the chemical states were identified by XPS. The electrocatalytic activity was measured by cyclic voltammetry.

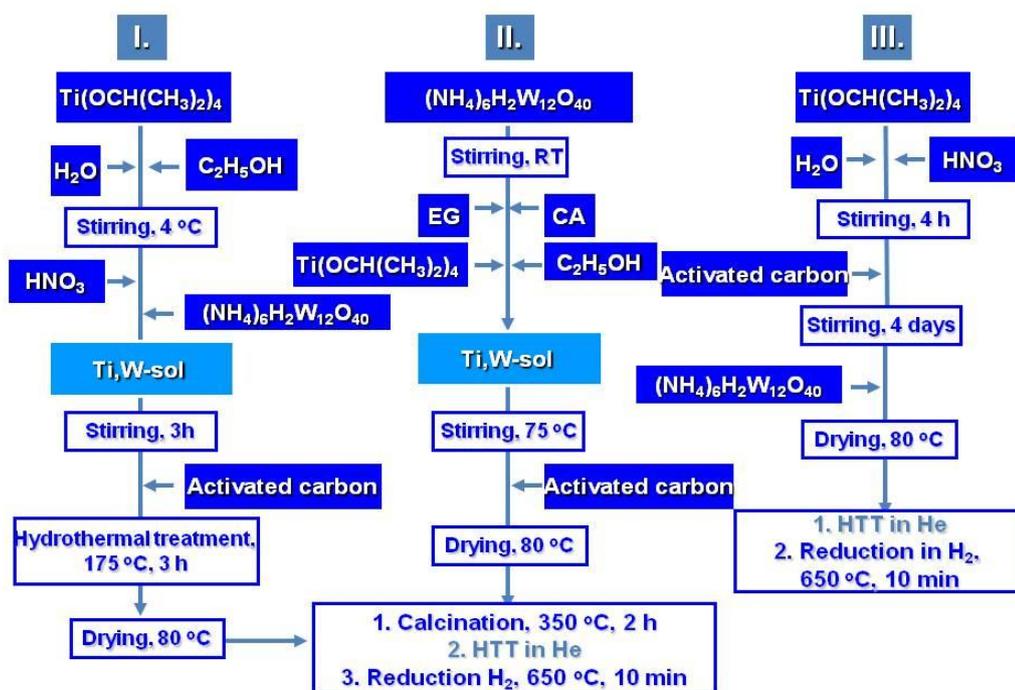


Fig. 1. Flow chart for preparing $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite materials.

4. Results

4.1. Synthesis and characterization of Pt electrocatalysts supported on $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite materials

A new synthesis route was designed to prepare Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ type catalysts. The synthesis parameters, the structure and chemical properties of the novel $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite materials were determined by various methods. Three synthesis methods were compared and the parameters of the synthesis (time of room temperature aging, conditions of high temperature treatment (HTT) and reduction) were optimized. The most important results are the followings:

- Results of powder X-ray diffraction indicated that upon using the synthesis route III high reproducibility in the formation of rutile phase with high crystallinity (98-100 %) and almost exclusive tungsten incorporation can be achieved [1].
- The samples prepared by three different routes were characterized by XRD before and after the heat treatment steps. Prior to any heat treatments, a mixture of anatase and WO_2 phases were achieved by synthesis route I, the second method resulted in amorphous precipitates, while pure rutile phase was achieved by route III. A two-step heat treatment (annealing for 8 h at 750°C in He, followed by reduction for 10 min at 650°C in H_2) produced a mixture of rutile TiO_2 with some tungsten incorporation and anatase for synthesis route I, anatase and non-incorporated WO_2 for synthesis route II and a high level of tungsten incorporation into rutile for synthesis route III [1]. According to these results, in case of the sample prepared by synthesis route II the lack of crystalline rutile phase hindered the incorporation of W, and as a consequence free WO_2 phase not incorporated into the titania was observed.
- The comparison of the three methods supports the idea that anatase or amorphous-type TiO_2 starting structure hinders the formation of mixed oxide with rutile lattice and high level of W incorporation in the presence of activated carbon. This confirms that synthesis

route III is the most sufficient method to prepare $\text{Ti}_{(1-x)}\text{W}_x\text{O}_2$ in the presence of carbon with high reproducibility, since upon using of this method the necessary rutile crystallites are formed at room temperature [1,2].

- Since one of the most critical parameters of the synthesis route III is the duration of the aging at room temperature, its effect on the structure of the materials was revealed by XRD measurements [1,2,4]. The results showed that at least 2 days of aging is necessary to obtain pure rutile phase. After the heat treatment high level of crystallinity and high degree of W incorporation ($W_{\text{subst}} = 30\%$) was achieved in case of the sample aged for 4 days. It is important to note that the longer aging time did not increase the crystallite size of the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite materials [1].
- Decomposition of the W precursor compound and its subsequent reduction was studied by TPR [1]. According to TPR results the hydrogen consumed in the range $\sim 220\text{ }^\circ\text{C} \leq T \leq 650\text{ }^\circ\text{C}$ was only slightly higher than the amount of H_2 calculated for the reduction of $\text{W}^{6+} \rightarrow \text{W}^{4+}$. In accordance with the above findings, the temperature of the reductive treatment was set to $650\text{ }^\circ\text{C}$.
- Upon using the composite materials prepared by synthesis route I the influence of the final temperature and duration of the HTT in He on the rutile/anatase phase ratio and oxidation state of W was investigated [1]. It was demonstrated by XRD that HTT at $750\text{ }^\circ\text{C}$ for 8 h followed with reduction at $650\text{ }^\circ\text{C}$ resulted in the disappearance of free, non-incorporated tungsten-oxide phases and almost total incorporation of W.
- XPS measurements were carried out to determine the chemical state of tungsten before and after reduction in samples prepared by synthesis routes II and III (see Fig. 2.A). In line with the TPR findings the results of XPS measurements confirmed that in spite of the air exposure, incorporated tungsten predominantly was in the +4 oxidation state [1].
- The valence band XPS spectra of the non-reduced and reduced carbon-free $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ samples were compared with the spectra of TiO_2 , WO_3 and WO_2 (see Fig. 2.B) [1]. The appearance of the emission at the Fermi energy in the reduced $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ sample (similar to WO_2) confirmed the presence of W^{4+} species with a metallic-like electronic structure in the mixed oxide. The data, along with those obtained during the *in situ* XPS study of the two-step annealing process [2] confirm that enhanced tungsten incorporation and activation was achieved by the short reduction, which transforms the material into a metallic state.

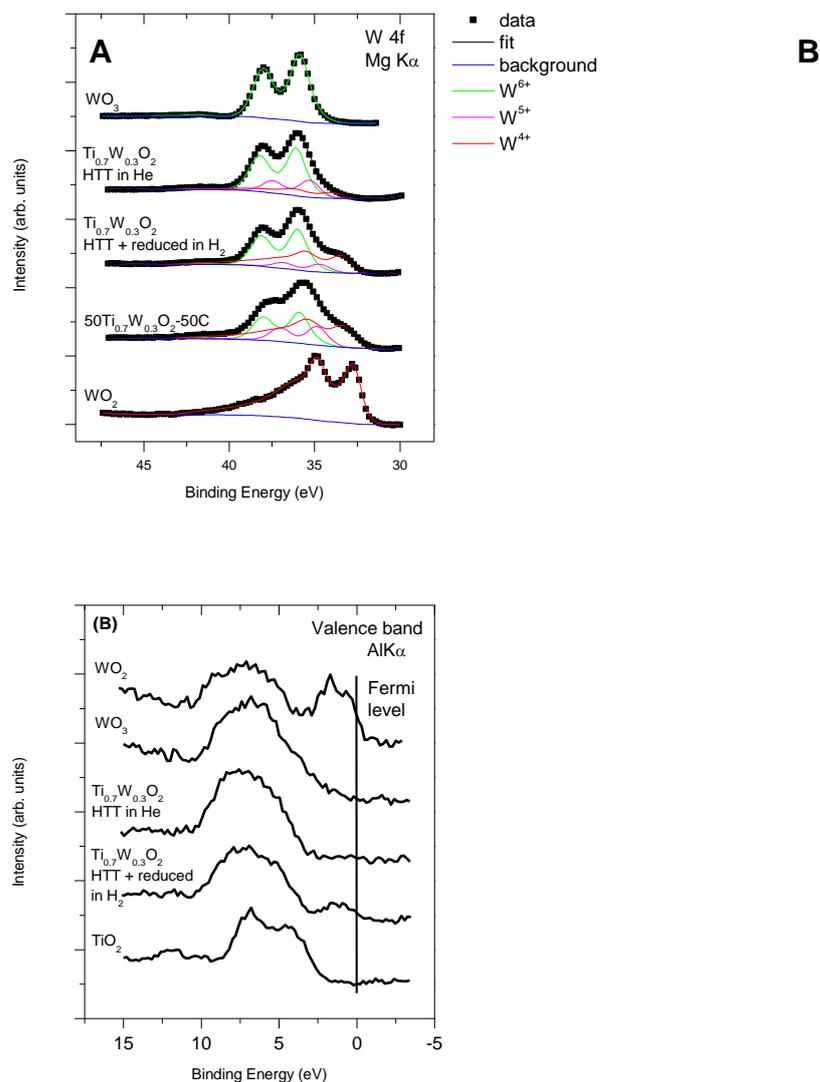
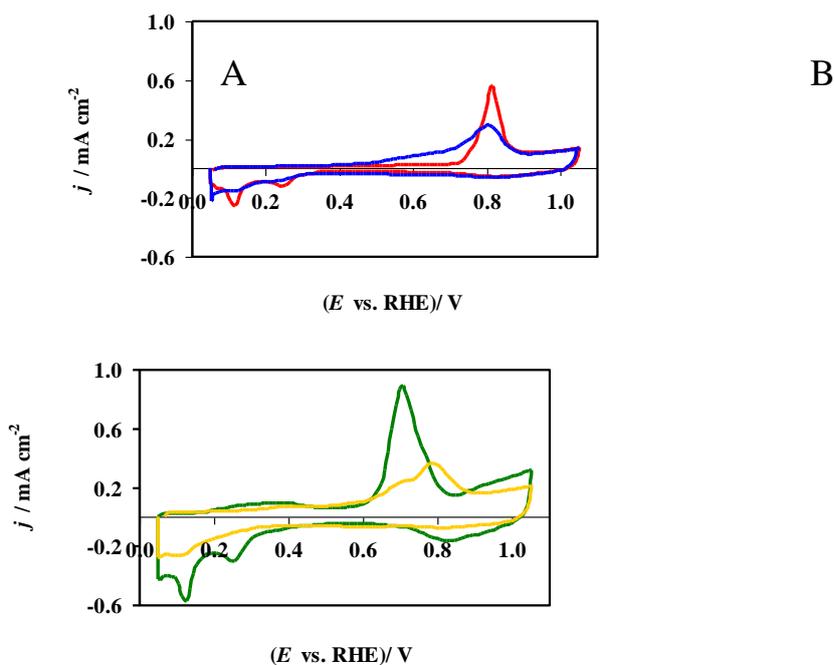


Fig. 2. (A): W 4f core level spectra of the non-reduced and the reduced carbon-free $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ samples (route II), and the reduced $50\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-50C}$ composite (route III) along with the WO_3 and WO_2 references. (B): valence band spectra of the non-reduced and reduced carbon-free $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ samples (route II) compared with the spectra of WO_3 , WO_2 and TiO_2 .

- According to results of the EDS, XRF and XPS measurements the Ti/W and $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2/\text{C}$ ratios are in a good agreement with the expected ones, so the composition of the samples can be successfully controlled by varying the amount of the activated carbon and Ti and W precursors [1,2,4].
- The uniform distribution of highly dispersed Pt particles (2.3 ± 0.8 nm) in 40 wt% Pt/ $50\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-50C}$ anode electrocatalysts was verified via TEM technique. In case of the composite support materials the main Pt particle size was significantly smaller than that of 40 wt% Pt/C catalyst (4.5 ± 1.8 nm) [1-3]. Our results confirm that the presence of TiO_2 prevents the Pt particles from agglomeration and helps to control the nanostructure of the catalyst.

The electrocatalytic behaviour and CO-tolerance of the catalysts were examined by cyclic voltammetry.

- Enhanced CO tolerance of the electrocatalyst prepared using the composite material synthesized in route III was evidenced by the appearance of a CO-oxidation related “pre-peak” between 150 and 540 mV and by a shift of the maximum of the main CO oxidation peak by ca. 110 mV towards less positive potential compared to Pt/C in the CO_{ads} stripping voltammogram (see Fig. 3.A-B) [1-3].
- Upon using the H₂-purged CO_{ads} stripping (see Fig. 3.C) an immediate and pronounced increase of the current in the “pre-peak” potential range between 0.05 and 0.60 mV was demonstrated for the Pt/Ti_{0.7}W_{0.3}O₂-C electrocatalyst (route III) compared to the PtRu/C benchmark (Quintech C-20-/10-Pt/Ru, Pt= 20 wt%, Ru= 10 wt% on Vulcan). On the contrary, on the parent Pt/C catalyst the adsorbed CO blocks the Pt catalytic sites in the potential region studied, independently of the atmosphere used upon purging [1,3].
- The electrochemically active surface area (ECSA) value of the composite supported Pt catalyst (33.4 m²/g_{Pt}), which was calculated from the charge associated with a CO monolayer adsorbed onto the Pt nanoparticles (ECSA_{CO}), is significantly higher than that of the unmodified home made Pt/C (12.6 m²/g_{Pt}) or the carbon-free Pt/Ti_{0.7}W_{0.3}O₂ sample (13.8 m²/g_{Pt}) [2]. This observation is in agreement with TEM results, which showed that the Pt nanoparticles are highly dispersed on the Ti_{0.7}W_{0.3}O₂-C composite support.
- It was demonstrated that H insertion/deinsertion into the WO_x support influenced the Coulombic charge of the hydrogen region by the so called hydrogen “spill-over” effect. The difference observed between the ECSA_{CO} and the charge calculated from hydrogen adsorption/desorption region (ECSA_{H-UPD}) values for the Pt/Ti_{0.7}W_{0.3}O₂-C catalyst was related to the formation of tungsten bronzes H_xWO₃ [2]. In accordance with the literature²³ H⁺ insertion at low electrode potentials were claimed to be responsible for the high tolerance to CO of the composite supported electrocatalyst.



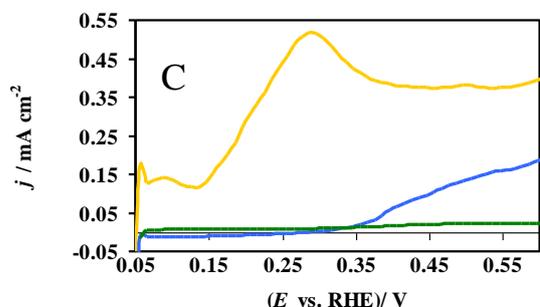


Fig. 3. Ar purged CO_{ad} stripping voltammograms recorded on (A) Pt/C, (red) and PtRu/C (blue) catalysts, and on (B) Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ (yellow, after mixing 20% of activated carbon prior to the measurements) and Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ (green, synthesis route III) catalysts. (C) CO_{ad} stripping voltammogram after H_2 purging in the “pre-peak” potential range between 0,05 and 0,6 V on Pt/C (green), PtRu/C (blue) and Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ (yellow, synthesis route III) catalysts. Recorded in 0.5 M H_2SO_4 , at 10 mV/s, $T = 25^\circ\text{C}$. The current density j was normalized to the geometrical surface area.

- A major issue concerning the catalyst support durability is carbon corrosion, which occurs at potentials above 0.9 V (vs. RHE). Electrochemical corrosion of the carbon supports causes the agglomeration and sintering of the Pt particles, which result in decrease of the ECSA values. After 5000 cycles (see Fig. 4) the loss in the integrated Coulombic charge associated with hydrogen adsorption/desorption ($Q_{\text{H-UPD}}$) for Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ was ca. 30 %, while on Pt/C this value was more than 70 % [1].
- After the electrochemical stability test experiments the Pt particle size distribution was verified via TEM technique [1,2]. After 5000 cycles, some extent of sintering and agglomeration of the Pt nanoparticles was observed for both catalysts. On the Pt/C catalyst the Pt particle size grew from 4.5 ± 1.8 nm to 10.0 ± 5.7 nm, while on the composite-supported catalyst after 5000 cycles the particle size was 6.5 ± 2.3 nm. These results confirm that upon using of the composite support, more effective protection of the Pt particles from agglomeration can be reached.

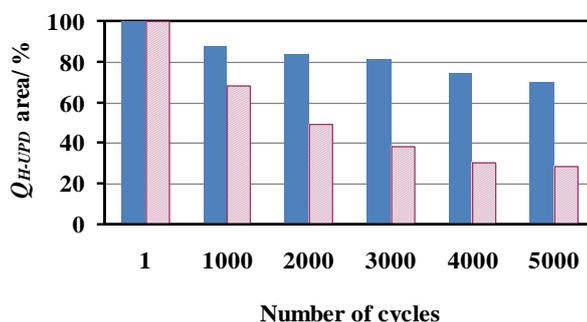


Fig. 4. Electrochemical stability study by cyclic polarization: the loss of $Q_{\text{H-UPD}}$ charges associated with hydrogen adsorption/desorption as a function of the number of cycles on the Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ catalyst prepared by route III (blue) and the home made Pt/C (red). Recorded at $v=50$ mV/s scan rate between 0.05 and 1.25 V in 0.5 M H_2SO_4 , at 25°C for 66.7 h.

- The measurements in the fuel cell test device showed that the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite-supported catalyst prepared by route III has similar activity than Pt/C in the hydrogen oxidation reaction. However, upon using the Pt/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ catalyst 100 ppm CO concentration in the H_2 fuel caused 140 mV voltage loss at 1 A/cm^2 current density, while in

the case of Pt/C catalyst the loss was 360 mV, confirming its CO tolerance even under true reaction conditions.

4.2. Synthesis and characterization of Sn-Pt/C electrocatalysts

The formation of carbon supported Sn-Pt alloys with different Pt/Sn ratios (Pt/Sn= 1.8-3.0) have been achieved by CSR. Optimum experimental conditions were found for the controlled synthesis of Sn-Pt/C electrocatalysts containing Pt₃Sn alloy phase almost exclusively. During the preparation of the Sn-Pt/C catalysts the effect of the number of consecutive tin anchoring periods, the amount of added tin in each period and the influence of the final temperature (T_{red}) of the reduction in the second step of the CSR on (i) the actual composition of formed bimetallic phases, (ii) chemical state of Sn and Pt, and (iii) presence or absence of both unmodified Pt and SnO_x phases was studied extensively. It was demonstrated that the method of CSR is a powerful tool to create Pt-Sn bimetallic nanoparticles, without tin deposition onto the carbon support.

- XRD demonstrated that the electrocatalysts with the desired Pt/Sn= 3 ratio contain a near-stoichiometric fcc Pt₃Sn alloy phase (75-85 %) along with a certain amount of the Pt-rich Pt_(1-x)Sn_x solid solution. The presence of a solid solution phase was evidenced by the broadening of the diffraction peaks at their higher diffraction angle side. Superlattice reflections ascribed to the fcc Pt₃Sn alloy phase were also observed (see Fig. 5). In the catalysts with higher tin content (Pt/Sn ≤ 2.2) the formation of hcp PtSn phase (Pt:Sn= 1:1) was also demonstrated. No evidence of the presence of SnO₂ phase was found by means of the XRD analysis [5].
- The content and dispersion of the fcc Pt₃Sn phase within the electrocatalysts depends on (i) the amount and concentration of *n*-decane solution of SnEt₄, (ii) the number of consecutive tin anchoring periods, and (iii) final temperature of H₂ pre-treatment (T_{red}) applied during TPR (the second step of the CSR) [3,5].

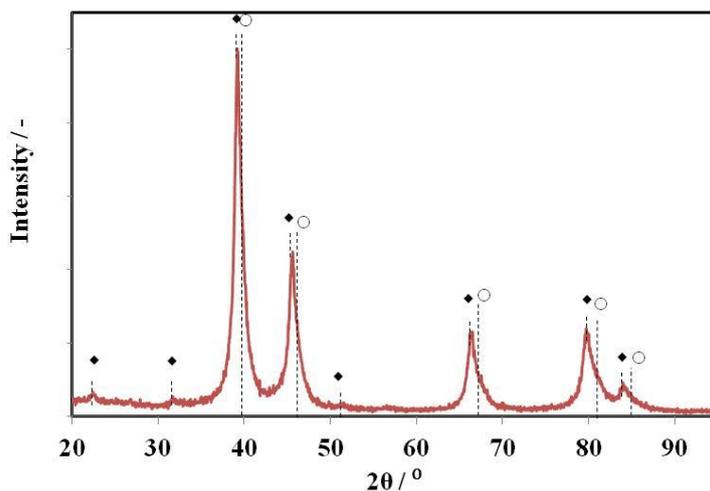


Fig. 5. X-ray diffraction pattern of the tin modified Pt/C sample. ◆: Pt₃Sn, ○: Pt_(1-x)Sn_x

- According to XRD and TEM results upon reduction at T_{red} = 250°C the size of bimetallic particles in the Sn-Pt/C catalysts was rather smaller than after treatment in H₂ at 350°C. Taking into account the fact that relative abundance of Pt₃Sn phase in samples treated at 350°C and 250°C was quite similar (ca. 80 %), the use of the 250°C as a final temperature in step II was recommended [5].
- The mean particle size of the best Sn-Pt/C catalyst with the desired Pt/Sn= 2.9 atomic ratio prepared using the lowest concentration of SnEt₄ in *n*-decane and four consecutive tin anchoring periods was 5.0 ± 1.9 nm. According to TEM images the incorporation of tin

resulted only in a small increase of the mean size comparing to that observed on the parent Pt/C catalyst (4.1 ± 1.6 nm) [5].

- Homogeneous distribution of tin in the Pt matrix was evidenced by EDS analysis. Mean atomic Pt/Sn ratio (Pt/Sn= 2.86) was in a good agreement with the nominal values calculated from the amount of tin introduced during CSR (Pt/Sn= 2.90). In line with XRD results, no evidence of tin segregation or presence of SnO₂ phases in the Sn-modified Pt/C samples were found by means of the EDS analysis [3,5].
- According to XPS studies (see Fig. 6.), the air-exposed Sn-Pt/C catalyst contained both SnO₂ and metallic Sn. An *in situ* treatment in hydrogen at 350°C resulted in complete reduction of the ionic tin to Sn⁰ [3,5]. A one day air exposure of the H₂-treated sample partially restored the SnO₂ content. This behaviour confirms the presence of exclusive Sn-Pt interactions as it is in good agreement with the previous results of our research group,^{15,26} evidencing the enrichment of tin in the surface layers of the alloy-type SnPt catalysts. In those studies it was established that in the presence of O₂ and H₂ the reversible interconversion of PtSn ↔ Sn⁴⁺ + Pt can easily proceed even at room temperature [5].

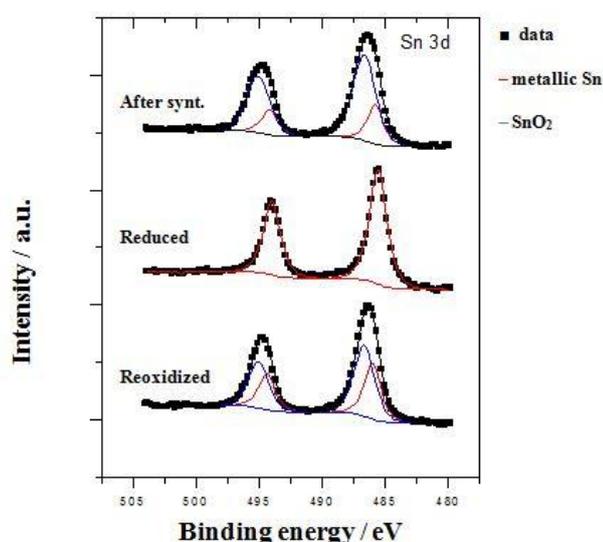


Fig. 6. Sn 3d core level spectra of the Sn-Pt/C sample with Pt/Sn = 3.0 ratio after storage of the synthesis product in air, after reduction at 350 °C in H₂ and after re-oxidation. Fitting components due to metallic Sn and SnO₂ are presented by means of red and blue lines, respectively.

The electrocatalytic activity of the catalysts in the oxidation of CO (see Fig. 7.A) and methanol (see Fig. 7.B) was evaluated by means of cyclic voltammetry.

- Upon addition of tin the onset potential of CO oxidation has been shifted by 500 mV to less positive potentials, which indicates a significant improvement in the CO oxidation ability of the Sn-modified samples in comparison to the Pt/C catalysts (see Fig. 7.A) [3,5]. Also, the shape of the peaks is rather different; CO_{ad} oxidation on Sn-modified Pt/C is a broad peak from ca. 200 to 800 mV, whereas a rather well-defined peak is recorded for the CO_{ad} electrooxidation on Pt/C. The difference of the shapes of the CO oxidation

²⁶ J.L. Margitfalvi, I. Borbáth, M. Hegedűs, Á. Szegedi, K. Lázár, S. Gőbölös, S. Kristyán, Catal. Today 73 (2002) 343-353.

peak indicates that Sn sites nucleate OH_{ad} species necessary for the CO_{ad} oxidation at less positive potentials than Pt.

- CO and methanol electrooxidation activity was the highest over the catalyst prepared using the lowest concentration of SnEt_4 in *n*-decane ($[\text{SnEt}_4] = 0.023 \text{ M}$) and four consecutive tin anchoring periods. It was demonstrated that the increasing tin content above a certain (optimal Pt/Sn= 3) amount gives rise to a negative effect on the catalyst performance in the CO and methanol electrooxidation. The high activity is mainly attributed to the (i) small particle size, (ii) the presence of fcc Pt_3Sn phase and (iii) the absence of hcp Sn-Pt phase [3,5].
- The performance of the Pt/C and the most active Sn-Pt/C catalyst for the electrooxidation of CO_{ad} and methanol has been also evaluated by *in-situ* EC-IRAS technique. The obtained results confirmed that Sn is a good promoter for both oxidation reactions on Pt-based catalysts.

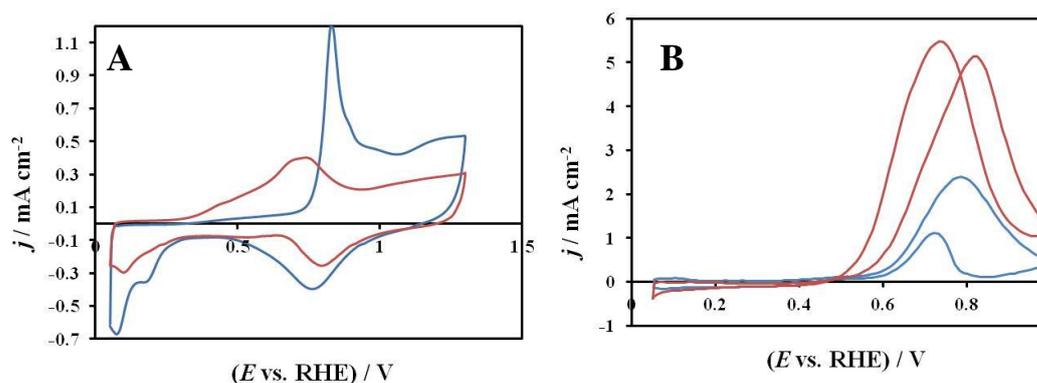


Fig. 7. (A) CO and (B) methanol oxidation on Pt/C (*blue*) and Sn-Pt/C catalyst with Pt/Sn = 3.0 ratio (*red*). Recorded in 0.5 M H_2SO_4 , at 10 mV/s, $T = 25 \text{ }^\circ\text{C}$. The current density j was normalized to the geometrical surface area.

- It was demonstrated that tin had a strong dilution effect of the platinum sites decreasing the number of Pt ensembles necessary for the methanol dehydrogenation to CO. As deduced from the results of the *in situ* EC-IRAS the actual reaction pathway on Pt/C and Sn-Pt/C catalysts is different, the direct oxidation of methanol to CO_2 is promoted in the Sn-modified electrodes [5].

5. Theses

1. Optimum experimental conditions were found to synthesize rutile phase, isovalent tungsten-doped $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ mixed oxide – activated carbon composites.
 - 1.1. It was shown that the presence of rutile phase before the high temperature treatment is prerequisite for complete W incorporation. A sol-gel preparation method was developed to achieve rutile crystallites on the activated carbon at room temperature [1-4].
 - 1.2. It was shown by means of the combination of several analytical methods that the desired $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ mixed oxide – activated carbon composite structure is formed by the high temperature treatment in inert atmosphere followed by reduction in hydrogen of the products of the sol-gel synthesis. The parameters of the high temperature treatment were optimized in order to minimize the presence of metallic W and non-incorporated WO_2/WO_3 phases [1].

2. Enhanced CO tolerance of the electrocatalyst prepared using the composite material synthesized in route III was evidenced by the appearance of a CO-oxidation related “pre-peak” and by pronounced shift of the maximum of the main CO oxidation peak towards less positive potential compared to Pt/C [1-3]. The electrochemical stability tests revealed that the degradation rate of the Pt/Ti_{0.7}W_{0.3}O₂-C catalyst is much smaller than that of the Pt/C catalyst [1-3]. The electrochemical activity and CO-tolerance was confirmed by measurements in a fuel-cell test device as well.
3. It was shown that the structure of the Sn-Pt/C-type catalysts can be tuned by the parameters of the Controlled Surface Reaction. The synthesis led to the exclusive formation of Sn-Pt alloy phases with high content of fcc Pt₃Sn phase. No evidence of the presence of SnO₂ phases were found, therefore the interaction between Sn and the carbon support was avoided, Sn interacts solely with Pt [3,5].
4. Direct correlation was observed between the Pt₃Sn content of the catalysts and the electrocatalytic activity. The onset potential of the CO_{ad} oxidation reaction shifted by 500 mV to less positive potentials compared to Pt/C, together with an increased activity in the methanol electrooxidation reaction. The reasons of the enhanced activity are (i) the small particle size, (ii) the presence of fcc Pt₃Sn phase and (iii) the absence of hcp Sn-Pt phase [5].

6. Application possibilities

The novel 40 wt% Pt/Ti_{0.7}W_{0.3}O₂-C electrocatalysts are suitable candidates for the application in PEM fuel cells. Successful investigations in a fuel cell test device demonstrate the suitability of the material for real life applications. Since the catalysts increased CO-tolerance, even hydrogen produced by reforming can be introduced to the anode of the system. Stability tests showed that the support is resistant towards electrocorrosion, the assembled PEM fuel cells can be used in vehicles as well, where the high potential during start/stop switches would otherwise lead to severe carbon corrosion in case of conventional Pt/C catalysts.

The Sn-Pt/C type catalysts prepared by Controlled Surface Reaction could be applied in direct methanol fuel cells (DMFC) as anode electrocatalysts. DMFCs are promising energy sources for smaller mobile applications or vehicles, due to the easy handling and transportation of the liquid-phase fuel.

In general, for the widespread application of fuel cells it is necessary to reduce the price of the systems. A major part of the price is contributed to the noble metal content of the catalysts, therefore more in-depth research is needed to improve the performance and decrease the Pt-content of the catalysts.

7. Articles and presentations

Publications in the subject of the dissertation

1. **Dorottya Gubán**, Irina Borbáth, Zoltán Pászti, István E. Sajó, Eszter Drotár, Mihály Hegedűs, András Tompos:
Preparation and characterization of novel $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2\text{-C}$ composite materials for Pt-based anode electrocatalysts with enhanced CO tolerance
Applied Catalysis B: Environmental 174: (2015) 455-470. **IF(2014): 6.007**
2. **Dorottya Gubán**, Zoltán Pászti, Irina Borbáth, István Bakos, Eszter Drotár, István E. Sajó, András Tompos:
Design and preparation of CO tolerant anode electrocatalysts for PEM fuel cells
Periodica Polytechnica- Chemical Engineering (2015), DOI: 10.3311/PPCh.8227, accepted for publication. **IF(2014): 0.296**
3. Borbáth Irina, Pászti Zoltán, **Gubán Dorottya**, Vass Ádám, Tompos András:
CO toleráns anódoldali elektrokatalizátorok fejlesztése PEM tüzelőanyag-cellákhoz
Magyar Kémiai Folyóirat (2015), közlésre elfogadva. **ISSN: 1418-9933**
4. **Gubán Dorottya**, Borbáth Irina, Pászti Zoltán, Sajó István, Drotár Eszter, Tompos András:
Anódoldali elektrokatalizátor fejlesztése hidrogén-üzemű PEM tüzelőanyag-cellákhoz
In: Bohner Báborka, Endrődi Balázs (Szerk.) *XXXVII. Kémiai Előadói Napok*. Szeged, Magyarország, 2014.11.03-2014.11.05. Magyar Kémikusok Egyesülete, Budapest; Szeged, 2014, pp. 80-84. ISBN 978-963-9970-53-3
5. Irina Borbáth, **Dorottya Gubán**, Zoltán Pászti, István E. Sajó, Eszter Drotár, Jose Luis de la Fuente, Tirma Herranz, Sergio Rojas, András Tompos:
Controlled synthesis of $\text{Pt}_3\text{Sn/C}$ electrocatalysts with exclusive Sn-Pt interaction designed for use in direct methanol fuel cells
Topics in Catalysis 56: (2013) 1033-1046. **IF: 2.22**

Other publications

6. L. Grand, A. Pongrácz, E. Vázsonyi, G. Márton, **D. Gubán**, R. Fiáth, B.P. Kerekes, G. Karmos, I. Ulbert, G. Battistig:
A novel multisite silicon probe for high quality laminar neural recordings
Sensors and Actuators A- Physical 166: (2011) 14-21. **IF: 1,802**

Oral and poster presentations

1. **D. Gubán**, I. Borbáth, F. Hirth, A. Tompos, Z. Pászti, I. Sajó, J.L. Margitfalvi:
Design of CO tolerant anode electrocatalysts for hydrogen fueled PEM fuel cells
15th International Congress on Catalysis, Munich, Germany, July 1 - 6, 2012.
2. **D. Gubán**, A. Beck, I. Borbáth, L. Gucci, A. Tompos, Z. Pászti, I. Sajó:
Tin modified Pt electrocatalysts for methanol electrooxidation designed for use in direct methanol fuel cells
15th International Congress on Catalysis, Munich, Germany, July 1 - 6, 2012.
3. I. Borbáth, **D. Gubán**, Z. Pászti, I. Sajó, A. Tompos:
Controlled synthesis of $\text{Pt}_3\text{Sn/C}$ electrocatalysts with exclusive Sn-Pt interaction designed for use in direct methanol fuel cells

IX International Conference „Mechanism of Catalytic Reactions” St. Petersburg, October 22-25, 2012.

4. **D. Gubán**, I. Borbáth, A. Tompos, Z. Pászti, I. Sajó:
CO-toleráns anód elektrokatalizátor fejlesztése polimer elektrolit membrán (PEM) tüzelőanyag-cellához
Kálmán Erika Doktori Konferencia, MTA Természettudományi Kutatóközpont, Mátraháza, Magyarország, 2012. szeptember 18-20.
5. I. Borbáth, **D. Gubán**, Z. Pászti, I.E. Sajó, E. Drotár, J.L.G. de la Fuente, T. Herranz, S. Rojas, A. Tompos:
Application of Controlled Surface Reactions for the preparation of highly active Pt₃Sn/C catalysts for electrooxidation of CO and methanol
International Symposium of the Romanian Catalysis Societ (RomCat 2013), Cluj-Napoca, Romania, May 29-31, 2013.
6. **D. Gubán**, I. Borbáth, A. Tompos, Z. Pászti, I. Sajó, E. Drotár:
Preparation of Pt catalysts supported on composite of titania-tungsten mixed oxide and activated carbon. Novel CO-tolerant anod electrocatalysts
11th European Congress on Catalysis (EuropaCat-XI), Lyon, France, September 1-6, 2013, paper reference: S8-T1-DS4-06, abstract_0518.
7. **D. Gubán**, I. Borbáth, Z. Pászti, I. Sajó, E. Drotár, A. Tompos:
A new way to obtain CO-tolerant Pt/Ti_xW_(1-x)O₂-C anode electrocatalysts. Application for hydrogen fueled PEM fuel cells.
12th Pannonian Symposium on Catalysis, Castle Trest, 2014, September 16 - 20.
8. **D. Gubán**, I. Borbáth, Z. Pászti, I. Sajó, E. Drotár, A. Tompos:
Anódoldali elektrokatalizátor fejlesztése hidrogén-üzemű PEM tüzelőanyag-cellákhoz.
XXXVII. Kémiai Előadói Napok, Szeged, 2014. November 3-5.

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Number of presentations in the subject of the dissertation:	8
Number of articles:	6
Total impact factor:	10.325
Total number of independent citations:	4