

# A new method of one-pot synthesis of efficient Au/SnO<sub>2</sub> electrocatalysts for fuel cells

AGNIESZKA MARTYLA<sup>1\*</sup>, MONIKA OSINSKA-BRONIARZ<sup>1</sup>,  
MACIEJ KOPCZYK<sup>1</sup>, BOGNA SZTORCH<sup>2</sup>, MARTA DOBROSIELSKA<sup>2</sup>,  
ROBERT E. PRZEKOP<sup>2</sup>

1. Institute of Non Ferrous Metal, Division in Poznan, Central Laboratory of Batteries and Cells  
Forteczna Street 12, 61-362 Poznan  
Poland
2. Centre of Advanced Technologies, Adam Mickiewicz University in Poznan,  
Umultowska 89c, 61-614 Poznan  
Poland

\*agnieszka.martyla@claiopoznan.pl <http://www.claiopoznan.pl>

*Abstract:* Electro-oxidation of methanol in acidic solution was investigated on Au/SnO<sub>2</sub> based electrocatalyst obtained by the sol-gel method. Au/SnO<sub>2</sub> systems were prepared by one-pot synthesis using a sol-gel method and tin (IV) acetate as a precursor of SnO<sub>2</sub> and water solution of HAuCl<sub>4</sub> acid as a source of metallic phase. The described method, thanks to its simplicity and mild processing temperature, offers uniform dispersion of metal phase in the bulk of the gel forming as a result of hydrolysis and condensation of tin precursor. It has been found that the obtained system exhibits high electrocatalytic activity.

*Key-Words:* Sol-gel, One-pot method, Electrocatalyst, Fuel Cells

## 1 Introduction

Fuel cells are one of alternative electric energy sources whose rapid development has been observed in recent years. They are characterized by one of the highest output power factor from a unit volume of fuel, no toxic fumes emission at very high energy conversion efficiency. Fuel cells can work with many types of fuel and the cells are classified according to the type of fuel used. One of the fuel cell types are Direct Methanol Fuel Cells (DMFC) with methanol as fuel. Thanks to the platinum catalyst, hydrogen is liberated at the anode to which methane is supplied and then it undergoes decomposition into electrons and protons. The protons migrate through the electrolytic membrane towards the cathode. Also electrons move towards the cathode through the external electric circuit. At the anode the carbon atoms coming from methanol react with the oxygen atoms from water to form carbon dioxide (CO<sub>2</sub>). At the cathode the protons and electrons react with oxygen atoms supplied from outside to form water [1]. DMFCs have

relatively simple structure, simple operation, are safe, can be exploited at low temperatures and can be easily and fast set to work, however, the ways to improve its performance are continuously searched for. One of the elements that should be worked upon is the catalyst. The commonly used platinum [2] is expensive and relatively fast undergoes poisoning with the intermediate products of methanol oxidation so it is fast deactivated. Often platinum is combined with other metals or it is dispersed on carbon [3] or oxide [4] supports. The Pt/SnO<sub>2</sub> systems show high activity in the oxidation [5] reactions. Tin(IV) oxide (SnO<sub>2</sub>) is one of the most promising catalyst supports, in view of its chemical stability and catalytic effects. The structure of this oxide permits e.g. the control of pore size in this support, which is important when metallic phase [6] is deposited on it. The search for new materials to be used in DMFCs and ways of their syntheses is still a challenge. In this report we propose a new catalyst for this type of cells in which the metallic phase is gold which is deposited on SnO<sub>2</sub> obtained by sol-gel synthesis. The systems Au/SnO<sub>2</sub> are

known to be active in the sensors of CO [7,8] and other gases [9,10]. When dispersed on solid supports gold is a very attractive catalyst because of its high activity, high stability and ease of regeneration [11,12]. The Au-Pt alloy catalyst supported on carbon has been applied in methanol oxidation in which its activity was higher than that of Pt/C catalyst [13,14]. In this paper we want to present the results of studies on the application of Au/SnO<sub>2</sub> as the catalyst of methanol oxidation. The catalysts proposed differed in the content of gold, varied from 4.1%, 8.2% to 16.4%, and were obtained in one-pot synthesis. This method permits obtaining complex materials in a single reaction with no need to remove intermediate products. The Au/SnO<sub>2</sub> systems were characterized by XRD, TEM, and finally by cyclic voltamperometry which permits checking the possibility of using the catalyst proposed in a fuel cell.

The systems Au/SnO<sub>2</sub> were obtained following the procedure described in [4], using water solution of HAuCl<sub>4</sub> as the precursor of metallic phase Au (1.39, 2.78, 5.57 cm<sup>3</sup>, respectively). The final samples contained 4.1, 8.2 and 16.4 wt. % of the metallic phase.

## 2 Experimental

### 2.1. Preparation

The preparation of Au/SnO<sub>2</sub> systems was carried out according to the procedure described in the [4] work, using an aqueous solution of HAuCl<sub>4</sub>, as the precursor of the metallic Au phase. Finally, the samples contained 4.1 wt%, 8.2 wt% and 16.4 wt% metallic phase. After precursor solution dosing, the systems were dispersed in an ultrasonic bath at 323 K for 12 hours. The encapsulated solvents were removed from the gel by evaporative drying. The samples were heated in the oxygen atmosphere. The composition and the names of the obtained materials are presented in Table 1.

**Table 1.** The composition and the names of the obtained materials

| Sample              | A     | B     | C      |
|---------------------|-------|-------|--------|
| Au/SnO <sub>2</sub> | 4.1 % | 8.2 % | 16.4 % |

### 2.2. Physicochemical characteristics

The phase identification and the influence of the thermal treatment on Au/SnO<sub>2</sub> systems was performed using an X-ray diffraction (XRD) powder diffractometer (X'Pert<sup>3</sup> Powder, Panalytical) using CuK $\alpha$  lamp radiation and Ni filter. X-ray spectra were recorded in the angular range of 5–80 [2theta].

Imaging the surface was performed with TEM electron microscopy (JOEL JEM 1200 EX).

The cyclic voltammetry (CV) experiment was performed in a two-electrode cell of Swagelok type with the application of ECLAB V10.12 VMP model 0.3 potentiostat/galvanostat by Bio-Logic, in the range of potential from – 0.5 to 1.0 V. The scan rate of 0.05 mVs<sup>-1</sup> was applied. The catalyst powders were suspended in solution of PVdF-HFP in acetone with graphite and applied onto a stainless steel electrode. The cell's configuration was: steel-Pt/SnO<sub>2</sub>| separator | steel. The electrolyte contained 1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.5 mol/dm<sup>3</sup> CH<sub>3</sub>OH.

The catalyst powders were suspended in solution of PVdF-HFP in acetone with graphite and applied onto a stainless steel electrode. PVdF-HFP was used as a binder [15], in lithium-ion cells, it is also used as an electrolyte [16]. The cell's configuration was: steel-Pt/SnO<sub>2</sub>| separator | steel. The electrolyte contained 1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> and 0.5 mol/dm<sup>3</sup> CH<sub>3</sub>OH.

## 3 Results and discussion

XRD studies were carried out in order to check the effect of temperature and content of metallic phase on the catalytic activity of Au/SnO<sub>2</sub> systems. The materials studied directly after synthesis are characterized by high amorphousness, (Fig. 1, 2, 3, 293 K), which is attributed to the gel structures dried at room temperature. Annealing of the samples leads to increased intensity of the reflections, both those assigned to SnO<sub>2</sub> (cassiterite) and those assigned to metallic gold. The reflections at the following 2 theta angles ~ 26, ~ 33, ~ 51 and ~ 66 correspond to the tetragons rutile structure of SnO<sub>2</sub> (PDF 4+ Card File No 04-003-5853), while those at 2 theta angles of ~ 38, ~ 44, ~ 65 and ~ 78 should be assigned to Au (PDF 4+ Card File No 04-007- 8790).

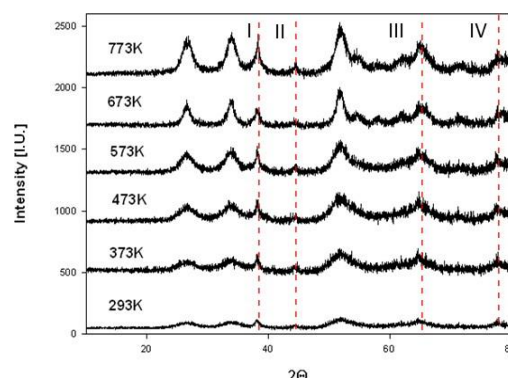
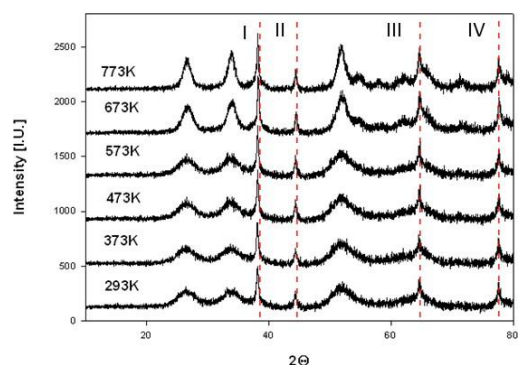
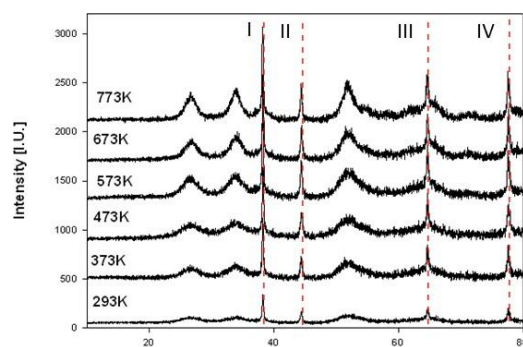


Fig. 1. XRD patterns of 4.1% Au/SnO<sub>2</sub> systemsFig. 2. XRD patterns of 8.2% Au/SnO<sub>2</sub> systemsFig. 3. XRD patterns of 16.4% Au/SnO<sub>2</sub> systems

For all samples the thermal treatment leads to increase in the intensity of reflections, assigned to both SnO<sub>2</sub> and to gold. The reflections of the highest intensity were recorded for the sample with the highest content of metallic phase.

Transmission electron microscope images of the samples studied are presented in Fig. 4. They show well-defined mesoporous structure of SnO<sub>2</sub> and Au clusters. For the samples with the lowest loading with metallic phase (4.1% Au), annealed at 373 K, (Fig. 4A, 4C, 4E) the images show the structure of uncalcined (amorphous, acetic) SnO<sub>2</sub> gel [4] and gold crystallites of the size from 12 to 30 nm, so rather large. As proved in earlier studies [4] the limiting temperature of thermal treatment of SnO<sub>2</sub> obtained from tin acetate is 673 K.

As a result of thermal treatment, the amorphous acetic gel is transformed into nanocrystalline tin oxide (Fig. 4D). Interestingly, for the systems treated at temperatures from the range 573-773 K, no sintering was observed and thus no growth of gold crystallites related to this phenomenon, both for the sample loaded with 4.1% Au and that with 8.2% Au. The thermal treatment of samples loaded with 16.4% Au leads to formation of systems characterized by high dispersion and the presence of

spherical nanoparticles of gold of the sizes from the range 10 - 100 nm (Fig. 4E).

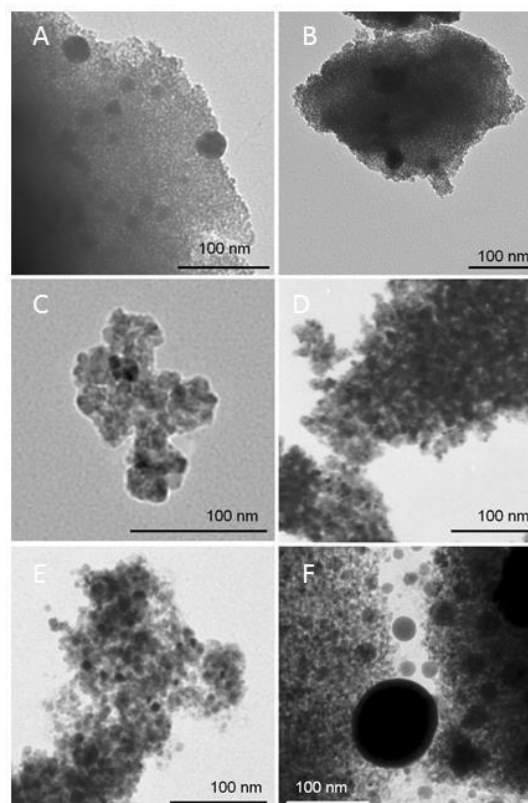


Fig. 4. HR-TEM images of: A) 4.1% Au 373 K, B) 4.1% Au 673 K, C) 4.1% Au 373 K, D) 8.2% Au 673 K, E) 16.4% Au 373 K, F) 16.4% Au 673 K

The performance of Au/SnO<sub>2</sub> systems as catalysts of methanol oxidation was checked by cyclic voltamperometry. The studies were carried out for each system, observing the effect of metallic phase content and heating temperature on the electrocatalytic activity. Fig. 5 presents the cyclic voltamperometry curves recorded for particular Au/SnO<sub>2</sub> catalysts in the medium of 1.0 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> with addition of 0.5 mol/dm<sup>3</sup> CH<sub>3</sub>OH. All curves show a peak in the range 0.5-0.8V, which can be assigned to methanol oxidation. The peak can change its position depending on the content of gold and temperature of thermal treatment.

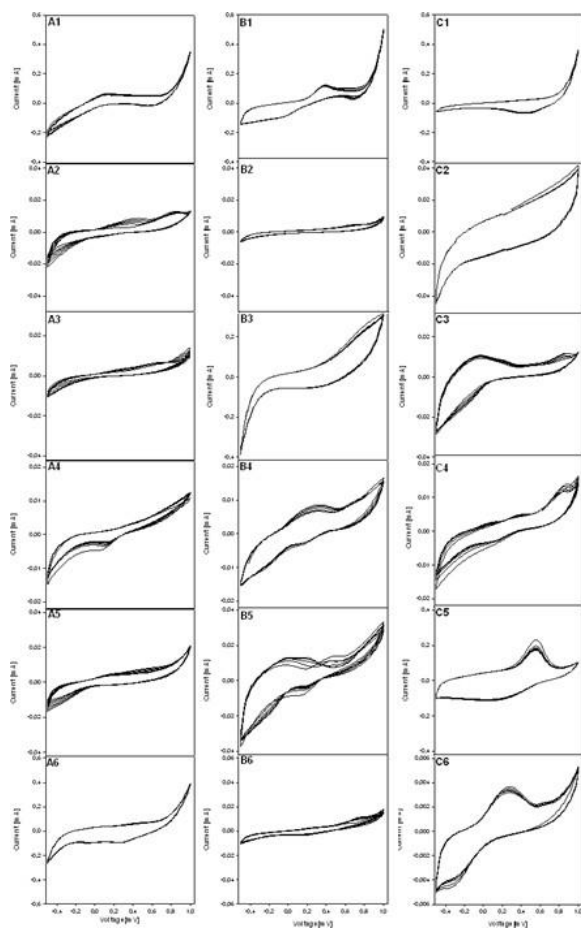


Fig. 5. Cyclic voltammetry of the Au/SnO<sub>2</sub> systems: A) 4.1% Au, B) 8.2% Au, C) 16.4% Au, after thermal treatment. Temperatures of thermal treatment: 1-293 K, 2-373 K, 3-473 K, 4-573 K, 5-673 K, 6-773 K.

The hydrated acid H<sub>2</sub>AuCl<sub>4</sub> (gold precursor) is inactive in the electrochemical process. Removal of water results in an increase in catalytic activity. For the system with the lowest gold loading the current decreases with increasing temperature of the catalyst annealing. For the system with the lowest gold loading, the current generated decreased with increasing temperature of catalyst heating. The most pronounced influence of temperature on methanol oxidation was noted for the systems with high gold loading. The sample containing 8.4% of metallic phase was active in methanol oxidation already at room temperature, but with increasing temperature the current intensity decreased. A similar effect was observed for the sample with 16.8% Au, but annealing of this catalyst at 673 K resulted in increased current intensity and had significant effect on the methanol oxidation reaction. On the basis of the above arguments, the sample with 16.8%

content of metallic phase was the best from the series studied. The results obtained confirmed that for the systems with gold no sintering takes place that would block the metallic phase activity and proved that individual clusters of gold catalyze methanol oxidation.

The process of methanol oxidation depends on the structure of the catalyst used. The reflections assigned to gold in the diffractograms of the catalysts indicate that in this reaction the following hkl planes are active: {110}, {200}, {220}, {311}. The analogous results obtained for platinum as the metallic phase also indicated the same planes as active in methanol oxidation [4]. In particular, the Au plane {110} seems the most active in this process. Similarly as for the systems with platinum [4], the catalysts activity depends on temperature. The Au/SnO<sub>2</sub> sample containing 16.8% of the metallic phase, after heating/ annealing at 673K generates the highest current intensity from among the other systems studied in the same conditions.

The curves presented in Fig. 5 illustrate considerable differences in activity between the catalysts samples studied. The differences are attributed to the thermal treatment which determines the final form of the metallic phase. The process of H<sub>2</sub>AuCl<sub>4</sub> decomposition can proceed according to the two following mechanisms [17].

Different character of the redox processes, evidenced by differences in the voltamperometric curves makes it difficult to draw any comparisons. The activities of all systems quickly increase after the removal of coordination water, which is the most pronounced for the samples with high gold loading. On the basis of results of our studies it can be concluded that the oxidation state of gold determines its activity.

## 4 Conclusion

Au/SnO<sub>2</sub> nanoparticles were synthesized by one-pot sol-gel technique. The proposed method of synthesis and thermal treatment allow for good control of the size of metal and stabilization of nanoparticles within the pores of the support. It was possible to obtain uniform and well dispersed gold nanoparticles, which was confirmed by XRD and TEM. After thermal treatment, Au particle did not migration and coalescence on the surface wasn't observed. However, this process required higher temperatures in comparison to multi-stage synthesis methods thanks to stabilization of small Au clusters in the gel structure. Au/SnO<sub>2</sub> - based electrocatalyst showed electrochemical activity during methanol oxidation reaction in acid solution. The CV results

demonstrated that the oxidation state of Au is a determining factor of its activity. One-pot reaction allow to obtain materials with high dispersion of metal particles which are active in oxidation process and they have possibilities to application in fuel cells.

#### Competing interests

The authors declare that they have no competing interests.

#### Acknowledgments

The study was financially supported by statutory activity within the Institute of Non-Ferrous Metals Division in Poznan, Central Laboratory of Batteries and Cells and Centre of Advanced Technologies, Adam Mickiewicz University in Poznan

#### References:

- [1] F. Samimi, M. R. Rahimpour, Chapter 20 – Methanol Production in Thermally Coupled, Fluidized-Bed, Bubble-Column and Membrane Reactors, Methanol, Science and Engineering, 2018, pp. 381–397.
- [2] R. N. Singh, A. Singh and Anindita, Electrocatalytic activity of binary and ternary composite films of Pd, MWCNT, and Ni for ethanol electro-oxidation in alkaline solutions, *Carbon*, vol. no 34, 2009, pp. 271-278.
- [3] C. A. Bessel, K. Laubernds, N. M. Rodriguez and R. T. K. Baker, Characteristics of Copper Particles Supported on Various Types of Graphite Nanofibers, *J. Phys. Chem. B*, vol no 105, 2001, pp. 1115–1118.
- [4] A. Martyla, M. Kopczyk, P. Marciniak, R. Przekop, One-pot method of synthesis of Pt/SnO<sub>2</sub> system and its electrocatalytic activity, *Chemistry Central Journal*, 8:49, 2014, 11 pages.
- [5] F. Takasaki, S. Matsuie, Y. Takabatake, X. Noda, A. Hayashi, Y. Shiratori, K. Ito, K. Sasaki, Carbon free Pt electrocatalysts supported SnO<sub>2</sub> for polymer electrolyte fuel cells: electrocatalytic activity and durability, *J Electrochem Soc*, vol. 158, 2011, pp: 1270–1275
- [6] P. Zhang, S. Y. Huang, B. N. Popov, Mesoporous tin oxide as an oxidation-resistant catalyst support for proton exchange membrane fuel cells, *J Electrochem Soc*, vol no 157, 2010, pp: 1163–1172.
- [7] V. Zielasek, B. Jurgens, C. Schulz, J. Biener M. M. Biener, A. V. Hamza, M. Baumer, Gold catalysts: nanoporous gold foams, *Angew Chem Int Ed*, vol. no 45, 2006, pp: 8241-8244.
- [8] M. Ojeda, B. Z. Yhan, E. Iglesia, Mechanistic interpretation of CO oxidation turnover rates on supported Au clusters, *J. Catal*, vol. no 285, pp: 92-102.
- [9] S. E. Davis, B. N. Zope, R. J. Davis, On the mechanism of selective oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over supported Pt and Au catalysts, *Green Chem*, vol no 14, 2012, pp: 143-147.
- [10] T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, K. Kaneda, Supported gold nanoparticles as a reusable catalyst for synthesis of lactones from diols using molecular oxygen as an oxidant under mild conditions, *Green Chem.*, vol. no 11, 2009, pp: 793-797.
- [11] Z. Zhang, X. J. Cui, F. Shi, Z. Q. Deng, Nano-Gold Catalysis in Fine Chemical Synthesis, *Chem Rev*, vol. no 112, 2011, pp: 2467- 2505.
- [12] A. Leyva-Perez, A. Corma, Similarities and differences between the “relativistic” triad gold, platinum, and mercury in catalysis, *Angew Chem, Int Ed*, vol. no 51, 2012, pp: 614- 635.
- [13] G. Selvarani, S. V. Selvaganesh, S. Krishnamurthy, G. V. M. Kiruthika, P. Sridhar, S. Pitchumani, A. K. Shukla, A Methanol-Tolerant Carbon-Supported Pt–Au Alloy Cathode Catalyst for Direct Methanol Fuel Cells and Its Evaluation by DFT, *J. Phys. Chem. C*, vol. no 113, 2009, pp: 7461- 7468.
- [14] C. Jeyabharathi, P. Venkateshkumar, J. Mathiyarasu, K. L. N. Phani, Platinum - tin bimetallic nanoparticles for methanol tolerant oxygen-reduction activity, *Electrochim. Acta*, vol. no 54, 2008, pp: 448-454.
- [15] V. Barsykov, V. Khomenko, The influence of polymer binders on the performance of cathodes for lithium-ion batteries, *Sci J Riga Tech Univ Mat Sci Appl Chem*, vol no 1, 2010, pp: 67-71.
- [16] S. Sharma, N. Dhiman, D. Pathak, R. Kumar Effect of nano-size fumed silica on ionic conductivity of PVdF-HFP-based plasticized nano-composite polymer electrolytes, *Ionics*, vol no 22, 2016, pp: 1865-1872.
- [17] K. Otto, I. Oja Acik, M. Krunks, K. Tõnsuaadu, Mere, Thermal decomposition study of HAuCl<sub>4</sub>·3H<sub>2</sub>O and AgNO<sub>3</sub> as precursors for plasmonic metal nanoparticles, *J Therm Anal Calorim*, vol no 118, 2014, pp: 1065-1072.