New trends in application of photo and electro catalysis

Proceedings of the 7th Czech-Austrian workshop

Josef Krýsa
EDITOR


Hnanice, Czech Republic
PREFACE

Czech - Austrian workshops „New trends in application of photo and electro catalysis“ represent a successful series of the conferences organized jointly by the University of Chemistry and Technology, Prague and Vienna University of Technology. The first Czech – Austrian workshop was held in November 2006 in Hnanice, Czech Republic. The 2nd workshop was held in December 2008 in Telč, the 3rd, 4th, 5th and 6th workshops were held in in Hnanice in 2009, 2011, 2012 and 2013, respectively.

The 7th Czech - Austrian workshop „New trends in application of photo and electro catalysis“ was held in Hnanice, Czech Republic from 25th to 27th May 2015. Participants were from six Czech institutions: University of Chemistry and Technology, Prague; Jaroslav Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic; Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic; Faculty of Chemical Technology, Technical University Brno, Institute of Physics, Academy of Sciences of the Czech Republic and University of South Bohemia in České Budějovice, two Austrian institutions: Vienna University of Technology and University of Salzburg and one French institution: CNRS/Université de Versailles.

The objective of the workshop was to further intensify the exchange of experience and new ideas in the field of semiconductor photocatalysis and photoelectrochemistry, dye sensitised solar cells, electrochemically prepared self organised structures, fuel cells, electrochemical engineering and modelling of electrochemical processes. Workshop was especially useful for PhD students who could present their results at the international forum.

The positive aspect of the workshop was the participation of colleagues from University of Salzburg. This time there were no participants from other European countries (Slovakia, Germany and Slovenia) as was the case of previous workshops. But it is believed that this situation will change and the next bilateral Czech – Austrian workshop will have more attendees from other European countries. Especially due to the fact that next (8th) workshop is planned to be organised in autumn 2016 where we will celebrate the 10 years anniversary in the history of Czech – Austrian workshops „New trends in application of photo and electro catalysis“.

Josef Krýsa and Guenter Fafilek

Acknowledgement

The workshop and proceedings were financially supported by the Ministry of Education, Youth and Sports of the Czech Republic and OEAD Austria (project number Aktion 72p6).

Financováno z prostředků programu AKTION Česká republika - Rakousko, spolupráce ve vědě a vzdělávání.

The event is co-funded by AKTION CR – Austria programme.
Content

List of authors ........................................................................................................................................... 6
List of participants ........................................................................................................................................ 7
Programme of the Workshop .................................................................................................................... 8
Diamond Electrode for Dye-Sensitized Solar Cell ....................................................................................... 11
Porphyrin Adsorption Studies on MgO Nanocubes ................................................................................... 13
Experimental Results of La0.8Sr0.2CrO3 / SrTiO3(100) Heterostructure Used for a High Temperature Photovoltaic Cell .................................................................................................................. 14
Photocathodes for Dye-Sensitized Solar Cells ........................................................................................... 17
Electrocoagulation: Electrochemistry in Wastewater Treatment ............................................................... 19
Removal of Toxic Metals by Electrocoagulation Using Mild Steel and Aluminum Electrodes .................. 20
Titanium Dioxide Photocatalyst Prepared by Lyophilization From Titanyl Sulphate: Activity in UV and Visible Light ........................................................................................................................................ 22
Inks Containing Resazurin and Acid Violet 7 as a Testing Method for Self-Cleaning Paints. 24
Photoelectrochemical Hydrogen Production on TiO2 And Fe2O3 Thin Films ........................................... 26
1-D Nanostructures of TiO2 and Fe2O3 for Electrochemical Water Splitting – Review ................. 28
Hydrogen Permeability of Selected Proton Exchange Membranes in Water Electrolysis Process .......... 30
Effect of Operating Conditions and Anode Composition on Kinetic Parameters of Oxygen Evolution Reaction in SOEC .................................................................................................................................. 32
Enhanced PEC Water Splitting Efficiency of Hematite Thin Photoanodes – the Role of Texture ............ 34
WO3 Films for Photo-Electrochemical Water Splitting ............................................................................ 36
Defects in Wet-Chemically Synthesized WO3 Nanostructures: Impact on Photoelectrocatalytic Properties ........................................................................................................................................ 38
Origin of Electrocatalytic Activity of the RGO Towards Hydrogen Evolution Reaction in an Alkaline Water Electrolysis ...................................................................................................................................... 39
Sol-Gel TiO2 Blocking Layers: Electrochemical Properties and Electrochemical Doping .......... 41
Printed Titania Photoanodes with Organosilica Binder ............................................................................. 43
Inkjet Printed Interdigitated Conductivity Sensors ..................................................................................... 45
Influence of pH on the Photocatalytic Treatment of Cyanide ................................................................. 48
Mechanism of H3PO3 Electrochemical Oxidation on Platinum in Context of High Temperature PEM Fuel Cell Operation ........................................................................................................ 50
Analysis of Mass and Charge Distribution in HT PEM Fuel Cell Stack by 3D Mathematical Model ...... 52
Electrochemical Preparation of Nanostructured Photocatalytic TiO2 Layers ................................................... 54
The Synthesis of One-Dimensional TiO2 Nanostructures and Study on their Electrochemical Behaviors ........................................... 56
List of authors

Anta J. A. ........................................38
Bastl Z. ........................................41
Baudys M. ......................................24
Berger T. ........................................13, 38
Boubínová R. ....................................20
Bousa M. ........................................41
Bouzek K. .......................................30, 32, 39, 50, 52
Brüger A. .......................................48
Brunauer G. .....................................14
Bystroň T. .......................................50
Chanda D. .......................................39
Čada M. ..........................................34
Diwald O. .......................................13
Dobrota A. ......................................39
Drakselová M. ..................................52
Drbohlavová J. ..................................54
Dzik P. ............................................43, 45
Fafilek G. .......................................14, 48
Gao F. .............................................17
Haenen K. .......................................17
Han H. ............................................56
Havlíček D. ......................................41
Hnát J. ............................................39
Hubička Z. .......................................26, 34
Karas F. ..........................................32
Kavan L. .........................................11, 17, 41
Klusáčková M. ..................................46
Klusoň P. .........................................19, 20
Kment Š. .........................................26, 28, 34
Kodým R. .........................................32, 52
Krýsa J. ..........................................22, 24, 26, 28, 34, 36
Krýsová H. ......................................17
Krystynik P. .....................................19, 20
Maes W. .........................................17
Mališ J. ..........................................30
Márquez A. ......................................38
Morozová M. ...................................26
Nebel C. E. ......................................17
Neumann-Spallart M. .........................43, 45, 48
Olejníček J. .....................................34
Oskam G. .........................................38
Ponweiser K. ....................................14
Paidar M. .......................................30, 32, 39
Pasti I. ............................................39
Paušová Š. .......................................28
Petrák V. .........................................17
Pližingrová E. ...................................22
Prokop M. ........................................50
Přikrylová K. ....................................54
Rodríguez M. ...................................38
Rotter B. .........................................14
Schneider J. .....................................13
Šnita D. ..........................................52
Šubrt J. ...........................................22
Tarábková H. ...................................46
Tito D. ............................................19, 20
Verstappen P. ...................................17
Veselý M. ........................................43, 45
Walch G. ..........................................14
Yeap W. S. .......................................17
Zbořil R. .........................................34
Zlámal M. .......................................26, 36
Zukalová M. ....................................41
List of participants

Austria
Vienna University of Technology, Institute of Chemical Technologies and Analytics
Assoc. Prof. Dr. Guenter Fafilek
Dr. Andreas Brueger
Georg Brunauer, M.Sc

University of Salzburg, Dept. of Materials Science and Physics
Prof. Oliver Diwald
Dr. Thomas Berger
Augusto Márquez, M.Sc.
Johannes Schneider, M.Sc.

Czech Republic
University of Chemistry and Technology, Prague, Dept. of Inorganic Technology
Prof. Dr. Ing. Karel Bouzek
Prof. Dr. Ing. Josef Krýsa
Doc. Ing. Martin Paidar
Ing. Hana Bartková, Ph.D.
Ing. Šárka Paušová, Ph.D.
Ing. Martin Zlámal, Ph.D.
Ing. Michal Baudys
Ing. Michaela Brunclíková
Ing. Monika Drakselová
Ing. Debabrata Chanda
Ing. Filip Karas
Ing. Jakub Mališ
Ing. Eva Plížingrová
Ing. Martin Prokop

J. Heyrovský Institute of Physical Chemistry AS CR
Prof. Ladislav Kavan, DSc.
Ing. Hana Krýsová, Ph.D.
RNDr. Markéta Zukalová, PhD.

Institute of Chemical Process Fundamentals AS CR
Ing. Pavel Krystyník, Ph.D.
Duarte N. Tito, M.Sc., Ph.D.

Institute of Physics AS CR
RNDr. Zdeněk Hubička, PhD.
Ing. Štěpán Kment, PhD.
Hyungkyu Han, M.Sc.

Brno University of Technology
Faculty of Chemistry
Doc. Ing. Michal Veselý, Ph.D.
Ing. Petr Dzik, Ph.D.

Faculty of Electrical Engineering and Communication
Ing. Jana Drbohlavová, Ph.D.
Ing. Kateřina Příkrylová

University of South Bohemia in České Budějovice
Mgr. Pavel Černý

Other countries
CNRS/Université de Versailles, France
Dr. Michael Neumann-Spallart
Programme of the Workshop

Monday, 25th May

12.30-13.00 – arrival
13.00-13.30 – registration of participants
13.30 – welcome talk

Chair: Josef Krýsa

13.40 Ladislav Kavan
Diamond Electrode for Dye-Sensitized Solar Cell

14.10 Johannes Schneider, Thomas Berger, Oliver Diwald
Porphyrin Adsorption Studies on MgO Nanocubes

14.30 Zdeněk Hubička, Štepán Kment, Martin Čada
Effect of the Substrate Ion Bombardment During Reactive Pulsed Sputtering Deposition of Thin Films

Experimental Investigation of La$_{1-x}$Sr$_x$CrO$_3$/SrTiO$_3$(100) Heterostructure Used for a High-Temperature Photovoltaic Cell

15.10-15.40 – coffee break

Chair: Michael Neumann-Spallart

15.40 Hana Krýsová, V. Petrák, W.S.Yeap, Ch.E. Nebel, K. Haenen, L. Kavan
Photocathodes for Dye-Sensitized Solar Cells

16.00 Duarte N. Tito
Electrocoagulation – Electrochemistry in Wastewater Treatment

16.20 Pavol Krystyník, Petr Klusoň, Duarte N. Tito, R. Boubínová
Removal of Toxic Metals by Electrocoagulation Using Stainless Steel and Aluminum Electrodes

16.40 Eva Plížingrová, Jan Šubrt, Josef Krýsa
Titanium Dioxide Photocatalyst Prepared by Lyophilization from Titanyl Sulphate: Activity in UV and Visible Light

17.00 Michal Baudys, Josef Krýsa
Inks Containing Resazurin and Acid Violet 7 as a Testing Method for Self-Cleaning Paints

19.30 – common dinner
Tuesday, 26th May

Chair: Oliver Diwald

9.00 Josef Krýsa, Magda Morozová, Martin Zlámal, Štěpán Kment, Zdeněk Hubička
Photoelectrochemical Hydrogen Evolution with n-Type Semiconductor Photoanode

9.20 Šárka Paušová, Štěpán Kment, Josef Krýsa
1-D Nanostructures of TiO$_2$ and Fe$_2$O$_3$ for Photoelectrochemical Water Splitting – Review

9.40 Jakub Mališ, Martin Paidar, Karel Bouzek
Hydrogen Permeability of Selected Proton Exchange Membranes in Water Electrolysis Process

10.00 Filip Karas, Roman Kodým, Martin Paidar, Karel Bouzek
Effect of Operating Conditions on Kinetic Parameters of Oxygen Evolution Reaction in SOEC

10.20-10.50 – coffee break

Chair: Ladislav Kavan

10.50 Štěpán Kment, Zdeněk Hubička, Josef Krýsa, Z. Remeš, J. Tuček, J. Olejníček, Radek Zbořil
Enhanced PEC Water Splitting Efficiency of Hematite Thin Photoanodes – the Role of Substrate Type

11.10 Martin Zlámal, Josef Krýsa
Tungsten Oxide Layers for Photoelectrochemical Water Splitting

11.30 Augusto Márquez, Manuel Rodríguez, Juan A. Anta, Gerko Oskam, Thomas Berger
Defects in Wet-Chemically Synthesized WO$_3$ Nanostructures: Impact on Photoelectrocatalytic Properties

11.50 Debabrata Chanda, A. Dobrota, Jaromír Hnát, Martin Paidar, Igor Pasti, Karel Bouzek
Origin of Electrocatalytic Activity of the RGO towards Hydrogen Evolution Reaction in an Alkaline Water Electrolysis

12.10 – lunch
14.00-18.00 – individual discussions
19.30 – common dinner

21.00 – Informal discussions of teachers, young researchers and PhD students about the aspects and experiences from Czech-Austrian exchange programme
**Wednesday, 27th May**

*Chair: Karel Bouzek*

**9.00** Markéta Zukalová
Sol-Gel TiO₂ Blocking Layers: Electrochemical Properties and Electrochemical Doping

**9.20** Petr Dzik, Michael Neumann Spallart, Michal Veselý, Mária Veselá
Ink Jet Printing of Nanoparticulate Titania Consolidated by Organosilica Binder and Application Examples - Part I

**9.40** Petr Dzik, Michael Neumann Spallart, Michal Veselý, Mária Veselá
Ink Jet Printing of Nanoparticulate Titania Consolidated by Organosilica Binder and Application Examples – Part II

**10.00** Andreas Brüger, Guenter Fafilek, Michael Neumann-Spallart
Influence of pH on the Photocatalytic Treatment of Cyanide

**10.20-11.00** – coffee break, check out from the hotel

*Chair: Guenter Fafilek*

**11.00** Martin Prokop, Tomáš Bystroň, Karel Bouzek

**11.20** Monika Drakselová, Roman Kodým, Dalimil Šnita, Karel Bouzek
Analysis of Mass and Charge Distribution in HT PEM Fuel Cell Stack by 3D Mathematical Model

**11.40** Kateřina Přikrylová, Jana Drbohlavová
Electrochemical Preparation of Nanostructured Photocatalytic TiO₂ Layers

**12.00** Hyungkyu Han
The Synthesis of One-Dimensional TiO₂ Nanostructures and Study on Their Electrochemical Behaviors

**12.30** – final remarks

**13.00** – lunch

**14.00** – departures
DIAMOND ELECTRODE FOR DYE-SENSITIZED SOLAR CELL

L. Kavan

J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic (kavan@jh-inst.cas.cz)

Dye-sensitized solar cell (DSC) is based on spectral sensitization of wide-band gap semiconductor electrodes to visible light. The most successful device employing n-TiO₂ photoanode achieved 13% solar conversion efficiency [1]. A mirror alternative of this solar cell uses dye-sensitized photocathode, such as p-NiO. However, the efficiency of p-DSC is still by a factor of 10 smaller [2,3].

B-doped nanocrystalline diamond (BDD) is outperforming p-NiO in chemical and electrochemically stability [4], optical transparency [5,6] and high hole diffusion coefficient (2-30 cm²/s) [7] (cf. the value for p-NiO, 4·10⁻⁸ cm²/s). [8] Under 1 sun illumination (AM1.5G: 100 mW/cm²) the sensitized p-NiO can deliver short-circuit photocurrents of ca. 5 mA/cm², but the BDD electrode provided photocurrents by 3 orders of magnitude smaller. [6] Hence, the improvement of p-DSC with diamond photocathode is currently attracting dynamic research activities. [6,9-14]

Nanocrystalline boron doped diamond films are grown by a microwave plasma enhanced chemical vapor deposition. [15,16] Electrochemical impedance spectroscopy can provide the flatband potentials and concentrations of acceptors, which relate to the B-concentrations from the neutron depth profiling. Electrochemical cleaning of the surface from sp² carbon impurities was demonstrated by Raman spectroscopy. [15]

Spectral sensitization of diamond surface by organic dyes has been pioneered in 2008 by Zhong et al. [10] who anchored covalently dicyanovinyl-bithiophene and C₆₀-bithiophene through Suzuki coupling to H-terminated BDD. They observed photocurrents of ca. 120 nA/cm² under white light illumination (150 W halogen lamp) in aqueous electrolyte solution with dimethylviologen acting as the electron carrier. Later on, photocurrents of ca. 4-6 µA/cm² were observed in similar systems under 1 sun illumination. [6]

Sensitization of BDD by manganese phtalocyanine [11,12] and Ru(SCN)₂(pbca)₂ (pbca = 2,2’-bipyridine, 4,4’-dicarboxylate) (commonly coded N₃ dye) [13] provided rather low photocurrents, typically of the order of 1-10 nA/cm² under ca. 1 sun illumination. Yeap et al. [9] modified the diamond surface with thiophene derivatives through a combination of diazonium electrografting and Suzuki cross-coupling and observed photocurrents of ca. 150 nA/cm² under white light illumination (15 mW/cm² intensity).

Krysova et al. [14] reported on non-covalent anchoring of 4-(bis-{4-[5-(2,2-dicyano vinyl)-thiophene-2-yl]-phenyl}-amino)-benzoic acid (coded P₁) dye. In a two-step procedure, polyethyleneimine (PEI) was adsorbed on H-terminated BDD, and subsequently modified with P₁. This dye is known to be successful for the sensitization of p-NiO [17,18]. Interestingly, the same P₁ dye is applicable also for the sensitization of n-TiO₂ [18] which is reminiscent of the activity of N₃ dye in both systems. [13]

The P₁-sensitized diamond electrode exhibited stable cathodic photocurrents under visible light illumination in aqueous electrolyte solution with dimethylviologen electron mediator. [14] The found photocurrents were about 100-150 nA/cm² at the white light intensity of 18 mW/cm². In spite of the simplicity of the surface sensitization protocol, the photoelectrochemical performance is similar or better compared to that of other sensitized diamond electrodes which were reported in previous studies. [6,9-14]

Acknowledgment

This work was supported by the Grant Agency of the Czech Republic (contract No. 13-31783S).
References


Porphyridin molecules play an important role both in nature and technology. Their tunable and versatile functional properties result from the manifold possibilities to functionalize the tetrapyrole unit and to introduce different metal ions at the porphyrin core thereby forming stable organometallic complexes. A technological exploitation of related phenomena as well as the successful implementation of functionalized particles in macroscopic, functional devices still requires a better understanding of the microscopic interaction between porphyrins and inorganic components in optical [1], optoelectronic [2] or photochemical applications [3].

We have studied on particle powders of morphologically well-defined MgO cubes the adsorption of 2H-Tetraphenylporphyrin (2H-TPP) both from toluene solution and via the gasphase. Using DR-UV/Vis and photoluminescence spectroscopy we observed on MgO nanocubes porphyrin metalation and the persistent adsorption of Mg-TPP at the oxide surface. Interestingly, no significant surface metalation was observed on the larger MgO cubes. As evidenced by detailed transmission electron microscopy and X-ray diffraction studies the morphology and crystal structure of the particle powders does not change significantly upon porphyrin adsorption. Whereas porphyrin metalation at metal surfaces [4] and at metal clusters pre-deposited on oxide surfaces [5] have previously been reported, here first evidence for porphyrin metalation on a pure metal oxide surface is presented.

References
EXPERIMENTAL RESULTS OF La_{0.8}Sr_{0.2}CrO_3 / SrTiO_3(100) HETEROSTRUCTURE USED FOR A HIGHTEMPERATURE PHOTOVOLTAIC CELL

G.C. Brunauer^1,3, G. Walch^2, B. Rotter^1, E. Esmaeili^1, A. K. Opitz^2, G. Fafilek^2, K. Ponweiser^1, J. Fleig^2

^1TU Wien, Institute for Energy Systems und Thermodynamics, ^2TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9, 1060 Vienna, Austria ^3NOVAPECC GmbH, Hildebrandgasse 28, 1180 Vienna, Austria

Abstract
The absorption of light by semiconducting materials results in a partial conversion of the radiative energy into electrical energy, a process of great importance and interest in energy technology. The solar spectrum can be classified into a high energetic part (short wave length) and a lower energetic part (long wave length). Both can be used by the special type of high temperature photovoltaic cell (HT-PV) under consideration, which consists of solid oxide materials, especially perovskite oxides with the general formula ABO_3. In fact, strontium doped lanthanum chromium oxide (La_{1-x}Sr_xCrO_3) and strontium titanate (SrTiO_3) are not only attractive candidates as semiconducting oxide materials for a HT-PV cell, but also for driving an electrochemical reaction used in a Solid Oxide Photo-Electrochemical Cell (SOPEC).

Material Characterisation
This paper shows the results of investigating the heterostructure La_{0.8}Sr_{0.2}CrO_3/SrTiO_3(100) under ultra-violet (UV) radiation at temperatures from 400°C up to 500°C. The HT-PV cell consists of a SrTiO_3 (STO) single crystal in the orientation 100 with a La_{0.8}Sr_{0.2}CrO_3 thin-film deposited by pulsed laser deposition (PLD). Both perovskites are large band gap (E_g) semiconducting metal oxides. It is well known that the E_g of STO is about 3.2 eV. Furthermore, optical measurements of 20% doped strontium LaCrO_3 (La_{0.8}Sr_{0.2}CrO_3) have shown that its E_g should be around 2.8 – 3.1 eV. For the excitation of electron-hole charge carriers (e^−, h^+) photons in wave-length \nu equal to or larger than around 385 nm are necessary. Any photon’s energy that is higher or lower than E_g is converted into heat. Given the high E_g of the La_{0.8}Sr_{0.2}CrO_3/ SrTiO_3(100)-system, electrons (e^-) can be excited from the valence band (VB) to the conduction band (CB) at temperatures up to 600°C. In contrast, e become thermally excited at relatively low temperatures when using low-band gap materials such as Si-based semiconductors (~1.1eV).

Research Process and Results
In a first step, the HT-PV cells were characterized by measuring current-voltage (I-V) curves. The I-V measurement was performed depending on a) temperature, b) light intensity and c) wave-length. For this test series, HT-PV cells with the dimension of 10x10x0.5 mm
were used. The results of open-circuit voltage and ($U_{oc}$) short-circuit ($I_{sc}$) current are shown in Fig. 2a and 2b.

![Graphs](image1)

The measurements have shown that $U_{PV,oc}$ is decreasing with rising temperature, whereas $I_{PV,sc}$ is increasing. In that context, it is interesting that the voltage at the HT-PV cell $\eta_{PV}$ remains more or less stable over temperature. In the next step, the HT-PV cell was packed on top of an electrolyte supported cell (ESC) consisting of a polycrystalline 3 mol% yttria-stabilised zirconia (YSZ) substrate ($\Omega20x0.3$ mm) coated on both sides with porous strontium doped lanthanum cobaltite (LSC) as electrode material for oxygen reaction. Voltage and current in the operation point ($U_{PEC}$, $I_{PEC}$) of the cell shown in Fig. 3 were measured at different temperatures. The measurements have shown that $U_{PEC}$ decreases dramatically with rising temperature (Fig. 2a), whereas $I_{PEC}$ increases (Fig. 2b).

Further on, the cell in Fig. 3 has been implemented in an experimental setup with gas-tight chambers and light-coupling by a quartz bar. When the light (LED 10W/365 nm) is switched on, oxygen is incorporated (Eq.1) at the cathode (1) due to the applied current and voltage from the HT-PV cell. Oxygen ions going through the YSZ following Kröger–Vink nomenclature (Eq. 2) and leaves the cell at the anode (2), Eq. 3.

\[
\frac{1}{2}O_2 + 2e^\prime \rightleftharpoons O^{2-} \quad \text{Eq. 1}
\]

\[
\frac{1}{2}O_2 + 2V_{O^\prime\prime} \rightleftharpoons 2O^\delta + 2h^\star \quad \text{Eq. 2}
\]

\[
O^{2-} \rightleftharpoons \frac{1}{2}O_2 + 2e^\prime \quad \text{Eq. 3}
\]

In a sequence of light off-and-on, voltage, current, and oxygen concentration have been measured at a temperature of 450°C, as shown in Fig. 4.
The voltage in the operation point under illumination has reached its maximum at nearly 0.5 V (Fig. 4.a). That has led to an electrical current of more than 0.8 mA (Fig. 4.b). Finally, the oxygen concentration has been shifted from 640 to 400 ppm O$_2$ (Fig. 4.c). Overall, it could be shown that the La$_{0.8}$Sr$_{0.2}$CrO$_3$/SrTiO$_3$(100) heterostructure is a promising material system for photo-electrochemical energy conversion.

**Acknowledgement**

This work was financed by the Austrian Research Promotion Agency (FFG) under the project no. 838562.
PHOTOCATHODES FOR DYE-SENSITIZED SOLAR CELLS

Hana Krýsová¹, Václav Petrák², Weng Siang Yeap³, Pieter Verstappen³, Wouter Maes³, Ken Haenen³, Fang Gao⁴, Christoph E. Nebel⁴, Ladislav Kavan¹

¹ J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague 8, Czech Republic (hana.krysova@jh-inst.cas.cz)
² Institute of Physics, v.v.i., ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic
³ Hasselt University, Institute for Materials Research, B-3590 Diepenbeek, Belgium
⁴ Department of Micro and Nano Sensors, Fraunhofer IAF, Freiburg 79108, Germany

The sensitization of wide band-gap semiconductors to visible light is intensively studied in the area of n-doped electrode materials, such as TiO₂, which forms a basis for the dye-sensitized solar cell (DSC). The most successful material for an active photocathode is p-doped NiO, but the highest efficiency obtained so far for the p-DSC is only 1.3%.[1,2] The final goal of these efforts is obviously a tandem device (p,n-DSC) in which both electrodes are the photoactive semiconductors. The tandem cells are attractive due to their enhanced voltage, which is not controlled by the redox potential of the mediator anymore,[3] but these cells cannot rival the efficiencies of the optimized n-DSCs at the moment.

Among the alternative photocathode materials, the B-doped nanocrystalline diamond (BDD) can be considered a promising replacement of p-NiO. Diamond films made by CVD are attractive due to their excellent chemical and electrochemical stability, optical transparency and favorable electrical properties. BDD is better optically transparent than p-NiO, approaching the optical quality of indium-tin oxide (ITO) at certain levels of doping.[4,5]

A light-harvesting efficiency of a monolayer of dye molecules on a flat surface of B-doped nanocrystalline diamond is inherently small. The growth of nano-textured mesoporous diamond films was attempted by templating with SiO₂ fibers and SiO₂ spheres. So called nanodiamond foam was grown by using SiO₂ spheres (500 nm in diameter) as templates, on which a thin BDD layer was deposited by standard chemical vapour deposition growth. The template was subsequently etched away by HF solution, leaving hollow spheres of diamond which replicated the SiO₂ template.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig.1A,B: SEM images of B-doped diamond foam sensitized with BT-Rho.</td>
<td></td>
</tr>
</tbody>
</table>

To directly compare flat diamond films and diamond foams, we have functionalized the diamond foams with the same dyes ((E)-2-(4-[2-(6-bromo-4,4-diethyl-4Hcyclopenta[1,2-b:5,4-b']dithiophen-2-yl)vinyl]-3-cyano-5,5-dimethylfuran-2(5H)-ylidene)malononitrile (coded CPDT-Fur) and (Z)-2-[(5’-bromo-[2,2’-bithiophen]-5-yl)methylene]-4-oxo-2-
thioxothiazolidin-3-yl) acetic acid (coded BT-Rho)) as applied in our previous work on flat BDD films.[6] These molecules were anchored by the Suzuki coupling protocol through a phenyl linker, which was attached to the originally H-terminated diamond surface by diazonium electrografting.

The prepared materials were tested as electrodes in the dark and upon illumination in an aqueous electrolyte solution with methyl viologen acting as a reversible electron acceptor. Reference experiments were carried out with standard flat BDD films, too.

Cathodic photocurrent densities for a fresh foam electrode sensitized with both CPDT-Fur and BT-Rho illuminated by white light (20 mW/cm²; simulated AM 1.5G solar spectrum) are approximately 3-times larger than those on flat diamond, which is attributed to the enhanced surface area of the foam electrodes.

**Acknowledgment**
This work was supported by the Grant Agency of the Czech Republic (contract No. 13-31783S).

**References**
Today's world faces a strategic and global challenge that extends beyond political borders, beliefs or origins - the sustainable management of Water Resources. In a reality where population growth is expected to reach (at least) 9 billion by 2050, how to manage this finite and fundamental resource whilst meeting the needs of Industry, Agriculture and individuals across the globe?

The solution lies in improving public attitude towards water consumption through education and raised awareness. Coupled with that, improved technology is needed to make more efficient use of the existing resources. Undoubtedly, no particular technology will solve all issues but rather a multitude a solutions will be required to meet a broad range of specific scenarios.

Wastewater treatment is one area where great potential for water reuse exists but where improved public perception and technology are needed. Crisis such as the ongoing California drought (2015) have helped change public perception and highlighted the value of wastewater as a reusable resource.

The fundamental objectives of the water treatment process are: the provision of safe drinking water, protection of human health and protection of the environment. Although the process details can change significantly from site to site, the process is broadly divided in three stages: Primary (removal of large objects and heavy solids), Secondary (removal of dissolved and suspended contaminants) and Tertiary (removal of trace contaminants and disinfection).

A wide range of contaminants (e.g. nutrients, suspended solids, heavy metals) is removed during Secondary stage in a process called Coagulation. Chemically this involves the addition of a precipitation agent (typically Fe or Al) that promotes particle aggregation and precipitation, leading to accumulation of the contaminants into a sludge that can be separated from the aqueous phase by physical techniques (e.g. sedimentation, flotation). Typically, coagulation is done by chemical addition of Fe or Al salts (e.g. FeCl₃ or Al₂(SO₄)₃) that (at the appropriate pH) readily form insoluble hydroxides which ad(ab)sorb contaminants in solution thus inducing their removal.

Although a well-established process, Chemical Coagulation requires the transport, handling and storage of large volumes of aqueous solutions which are corrosive and pose an environment risk if accidentally spilled. Electro-coagulation is the electrochemical alternative where the use of salt solutions is replaced by metallic electrodes (Fe or Al). The electrochemical process employs controlled anodic corrosion to produce the relevant metal hydroxides (Fe(OH)₃ or Al(OH)₃) at a rate determined by current intensity. From Faraday's law, metal concentration can be estimated which correlates well with experimental values.

The implementation of electrochemistry not only avoids the issues listed above but also significantly reduces the volume required to store the precipitating agent as aqueous solutions are replaced by metallic plate (reduction of 40x by volume). This enables the development of compact systems that can be employed in a wide range of scenarios from portable handheld systems, large-scale moveable plants to full industrial scale systems.
Given its fundamental role in supporting life and ecosystems, water should be regarded as the major and most valuable resource that can be found on Earth. However, despite its importance, there are several threats causing water pollution that compromise its fundamental role. One of major threats results from poorly managed industry directly disposing various wastes into environment and consequently endangering sources of water. Presented contribution is focused on testing of innovative method for toxic metals removal from contaminated water by method of electrochemical coagulation.

Electrocoagulation (EC) is a method of coagulation that does not require the use of other chemicals. It is a technique that utilizes electrochemical dissolution of electrode and formation of small hydroxide particles (coagulants) in solutions. These small particles aggregate to larger particles (floc) that tend to create ferric ions with iron dissolved from electrode as well as with the iron dissolved as pollutant. It is a phenomenon during which charged particles in colloidal suspension are neutralized by mutual collision with counter ions and they are agglomerated, followed by sedimentation. Electrodes are usually made of Al or various types of steel. The rate of sacrificial electrode is driven by current input.

To determine the current input efficiency, the amount of iron generated was calculated by using Faraday’s Law:

$$w = \frac{I \cdot t \cdot M}{z \cdot F}$$

where $w$ is the amount of dosed iron at specific current density with relevant current input (A), $t$ is a residence time in the EC cell (s), $M$ is molecular weight of Fe (55,485 g/mol), $z$ is number of electrons transferred per Fe atom and $F$ is Faraday’s constant. When operated the EC at steady state, the Fe (dosed) concentration was a function of the current input and contact time of treated water with anodic surface. By adjusting the operating current input and flow rate of treated water, a desired Fe (dosed) concentration was obtained. The results have that calculated data correspond with theoretical assumptions well.

First of all, various operational parameters of electro-coagulation (EC) were optimized, namely inputting concentration of toxic metal, the amount of in-situ electrochemically dosed coagulant by electrochemical dissolution of anode, pH of treated effluent, current density. Optimization experiments were performed with model effluents contaminated by lead and cadmium. All the experiments were performed with two types of electrodes – iron and aluminum. Comparison of both electrode performances has shown that aluminum electrode revealed higher efficiencies in toxic metals removal.
Fig. 1: Removal efficiency of lead and cadmium as a function of inputting concentration and contamination concentration/dosed coagulant ratio

Optimal experimental conditions, based on results obtained with model effluents, were applied on industrially polluted effluents (RW1 to RW3). Those effluents originally came from various industrial sites. It is evident that most of the contaminating ions revealed high removal efficiency up to 99.9% depending on the type of contaminant. It has been shown that electrocoagulation is very promising technology in removal of toxic metals from model and industrial effluents.

Tab. 1: Removal efficiency of industrial pollutants in real effluents

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RW1</th>
<th>RW2</th>
<th>RW3</th>
<th>Removal efficiency [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.29</td>
<td>-</td>
<td>-</td>
<td>97.7</td>
</tr>
<tr>
<td>Sb</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>59.1</td>
</tr>
<tr>
<td>Pb</td>
<td>6.04</td>
<td>-</td>
<td>-</td>
<td>99.9</td>
</tr>
<tr>
<td>Ni</td>
<td>34.6</td>
<td>1.67</td>
<td>-</td>
<td>97.8</td>
</tr>
<tr>
<td>Zn</td>
<td>47.8</td>
<td>-</td>
<td>1.4</td>
<td>99.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.64</td>
<td>1.8</td>
<td>1.4</td>
<td>89.2</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>0.86</td>
<td>-</td>
<td>74.4</td>
</tr>
</tbody>
</table>

Acknowledgement

This work was supported by the Technology Agency of the Czech Republic (TA04020130).
TITANIUM DIOXIDE PHOTOCATALYST PREPARED BY LYOPHILIZATION FROM TITANYL SULPHATE: ACTIVITY IN UV AND VISIBLE LIGHT

Eva Plížingrová1, Šubrt2, Josef Krýša1

1 University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic (eva.plizingrova@vscht.cz)

Nanoparticles of titanium dioxide (TiO2) are considered as the most effective material with respect to its nontoxicity, high photoactivity and low price. Titania-based photocatalysts are still the most widely used material for photocatalytic water cleaning, air purification, and the photocatalytic production of hydrogen from water.

There are several different methods for the preparation of TiO2 photocatalyst. Our group deals with the preparation of TiO2 foam from an aqueous solution of titanyl sulphate [1,2,3]. The advantage of the preparation of TiO2 foam in comparison with the sol-gel method is that it does not require organic compounds for the synthesis of TiO2. In addition, the preparation is simple and uses cheap raw materials.

In the first step of the preparation of non-doped material, titanyl sulphate (TiOSO4·xH2O) was dissolved in distilled water at 35 °C. The colourless solution was precipitated by ammonia solution until it reaches pH 8. The white precipitate was filtered and washed to remove sulphate anions formed in the reaction. Then the pH value was reduced by H2O2. The resulting yellow transparent colloidal solution of peroxo-polytitanic acid was lyophilized, and subsequently annealed at 500, 650, 800 and 950 °C [2,3].

In the case of doped samples, dopant was added in the first step of synthesis, rest of the preparation was the same as described above. The samples were doped with Ag, Au and Nd. Amount of dopant was 1 at. % towards Ti.

The synthesized samples were studied by X-ray diffraction, electron microscopy, and the specific surface area was determined by the B.E.T. method. The photocatalytic activity was characterized using 4-chlorophenol (4-CP) in an aqueous solution as a model compound.

The lyophilized samples are amorphous. Annealing at 500 °C results in the formation of anatase crystalline structure. In non-doped samples, further increase in annealing temperature to 950 °C means an increase of size of anatase crystallites from 35 to 140 nm and decrease in the value of specific surface area from 35 to 11 m²·g⁻¹. In comparison with non-doped samples, doping with Nd causes a decrease of the size of anatase crystallites for all temperatures of annealing. Doping with Ag, Au does not influence growing anatase crystallites except temperature 950 °C where the size of anatase crystallite was almost twofold. The presence of dopant was confirmed from EDS. Fig. 1 shows HRTEM micrographs of doped samples annealed at 650 °C.

For temperatures 500, 650 and 800 °C neodymium was not observed as a separated phase in HRTEM. The diffraction pattern of sample annealed at 950 °C showed three different phases - anatase, rutile and neodymium titanium oxide. At lower temperatures only anatase phase was observed. Nd seems to be predominantly built in the structure of TiO2.

In HRTEM, silver and gold nanoparticles were observed already in lyophilized sample as a visibly separated phase. Ag and Au seems to be both, built in the structure as well as separated nanoparticles. Silver and gold nanoparticles had around 20 nm.

None of the doped samples resulted in an increase of the photocatalytic activity in UV region in comparison with non-doped sample and P25 (Evonik-Degussa) often considered as so far the most active commercial photocatalyst (Fig. 2). The photocatalytic activity in visible region was almost negligible, about 2 orders lower than in UV. The rate constants for all samples are summarized in the Tab. I.
Fig. 1. HRTEM study: (a) sample doped with Nd (b) sample doped with Ag (c) sample doped with Au

Fig. 2. Results of photodegradation of 4-CP in UV light for the samples annealed at 800 °C, initial 4-CP concentration = 5\times10^{-5} \text{ mol} \cdot \text{l}^{-1}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rate constant (min^{-1})</th>
<th>UV light</th>
<th>Visible light</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIG-Au-800</td>
<td>0.014</td>
<td>0.00013</td>
<td></td>
</tr>
<tr>
<td>TIG-Ag-800</td>
<td>0.025</td>
<td>0.00006</td>
<td></td>
</tr>
<tr>
<td>TIG-Nd-800</td>
<td>0.024</td>
<td>0.00019</td>
<td></td>
</tr>
<tr>
<td>TIG-800</td>
<td>0.051</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>P25</td>
<td>0.030</td>
<td>0.00009</td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgement

This work was partly supported from specific university research (MSMT No 20/2015), partly from project ENVIMOD (CZ.1.07/2.2.00/28.0205) and partly from the Grant Agency of the Czech Republic (project number P108/12/2104).

References

This paper deals with application of new rapid method of photocatalytic activity assessment which can be used on various photocatalytic paints. The method is based on irreversible reductive color change of Resazurin (Rz) or Acid Violet 7 (AV7) dyes (Fig. 1a and Fig. 1b) in ink containing glycerol as a sacrificial electron donor. The principle of the method is schematically shown in Fig. 2. Water based acrylic paint with TiO$_2$ photocatalyst (8% TiO$_2$ P25, Evonik) and two commercial paint, namely exterior (CP1) and interior (CP2), were applied as an example of self-cleaning paints.

The aim of this work was to investigate influence of weathering test in QUV on photocatalytic activity.

Using a recently published procedure [1], photocatalytic activity of these paints was determined as a time in which 90% of overall color change of Resazurin or Acid Violet 7 ink occurs.

Ttb90 values are summarized in Table 1. Commercial paints CP1 and CP2 exhibit different photocatalytic activities. Whereas CP2 shows very low photocatalytic activity with Ttb90 of Rz ink about 4000 s, CP1 shows very high photocatalytic activity so the reduction of Rz ink is...
very quick. Thus to determine photocatalytic activity we have to use Acid Violet 7 ink, which has Ttb\textsubscript{90} about 340 s.

<table>
<thead>
<tr>
<th>paint</th>
<th>Resazurin ink(Rz)</th>
<th>Acid Violet 7 (AV7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO\textsubscript{2} paint</td>
<td>90±15</td>
<td>3000±75</td>
</tr>
<tr>
<td>Interior paint (CP2)</td>
<td>Too fast</td>
<td>340±25</td>
</tr>
<tr>
<td>Exterior paint (CP1)</td>
<td>4000±60</td>
<td>Too slow</td>
</tr>
</tbody>
</table>

Table 1: Results of photocatalytic activity expressed as Ttb\textsubscript{90}

In case of TiO\textsubscript{2} paint two different Ttb\textsubscript{90} values for each paint were calculated. In the case of Resazurin Ttb\textsubscript{90} was calculated as 90 s. Using Acid Violet 7 the Ttb\textsubscript{90} was(33x times higher) about 3000 s.

It can be assumed that to develope full photo catalytic activity a certain time of weathering is needed [2,3]. From this reason samples were exposed to accelerated weathering test in QUV panel using the following cycle: i) UV irradiation (maximum 340 nm), intensity 1 W/m\textsuperscript{2}/nm, 8 h, (ii) spraying with water, 7 dm\textsuperscript{3}/min, 4 min, (iii) condensation of steam, temperature 70 °C, 4 h and (iv) spraying with water, 7 dm\textsuperscript{3}/min, 4 min. Exposition in QUV panel simulates accelerated weathering effects such as rain dew and UV light The scheme of QUV is illustrated on Fig. 3

During weathering polymer binder partially degrades resulting in an increase of surface exposed concentration of TiO\textsubscript{2} particles [4]. The photocatalytic activity was expressed as a time of exposition in QUV. TiO\textsubscript{2} paint seems to be stable and no significant destruction of binder was observed. Paradoxically the CP2 paint in which no significant resistance against weather conditions can be assumed seems to be stable and only small chalking was observed. On the contrary CP1 paint shows very low stability against weathering. Already after 350 hours of exposition the whole paint almost disappeared.

In the case of TiO\textsubscript{2} paint, during exposition in QUV photocatalytic activity gradually increases and after 600 hours of weathering the reciprocal Ttb\textsubscript{90} was 3,5 higher compared to unexposed paint. In the case of CP2 paint a dramatic increase of photocatalytic activity was observed after 500 hours of exposition and reciprocal value of Ttb 90 was 12x higher compared to unexposed paint. The reason for high activity of CP2 (which is one order of magnitude higher compared to TiO\textsubscript{2} paint) is probably in higher amount of the photocatalyst (higher than 8% as in the case of TiO\textsubscript{2} paint).

Acknowledgement

Financial support of INTEC project (FP7-NMP-2012-CSA-6, GA No. 319210 and specific university research (MSMT No 20/2015) is acknowledged.

References

Photoelectrochemical hydrogen production on TiO$_2$ and Fe$_2$O$_3$ thin films

Josef Krýsa$^1$, Martin Zlátal$^1$, Magda Morozova$^1$, Stepan Kment$^2$, Zdenek Hubicka$^2$

$^1$ University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic (josef.krysa@vscht.cz)
$^2$ Institute of Physics AS CR, v.v.i., Na Slovance 1999/2, 182 21 Prague 8, Czech Republic

Titania (TiO$_2$) and iron oxide (α-Fe$_2$O$_3$) hematite thin films have the potential applications as photoanodes for hydrogen production via photoelectrochemical water splitting. Great advantages of TiO$_2$ are its low price, high stability and nontoxicity. However, for practical applications, there is a huge disadvantage consisting in utilization of very small part of sunlight (4%). Iron oxide (α-Fe$_2$O$_3$) has favourable band gap (2.0–2.2 eV), which allows absorbing a substantial fraction of solar spectrum, resulting in the theoretical maximal solar-to-hydrogen (STH) conversion efficiency 15% [1]. But there are also limitations, e. g. the nonideal position of hematite’s conduction band, which is too low for spontaneous water reduction. Therefore the aim of the present work was the comparison of TiO$_2$ and Fe$_2$O$_3$ photoanodes and the efficiency evaluation for hydrogen evolution via water splitting.

TiO$_2$ and Fe$_2$O$_3$ films were prepared on FTO glass by sol–gel [2] and advanced pulsed plasma deposition method of High Power Impulse Magnetron Sputtering (HiPIMS) [3]. For both techniques, subsequent calcination was found necessary. The films were judged on the basis of physical properties such as crystalline structure, optical absorption and surface topography. The functional properties (photocurrent, open circuit potential) were investigated under simulated photoelectrochemical (PEC) water splitting conditions in a three electrode arrangement. Standard solar illumination conditions (AM 1.5 G) was used as excitation light, solution of Na$_2$SO$_4$ for TiO$_2$ and NaOH for Fe$_2$O$_3$ thin films were used as the electrolytic media. For the straightforward comparison of the films the measured potentials vs Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale. Optimised semiconductor films were applied as photoanodes in a two compartment single band gap PEC cell and hydrogen evolution rate evaluated.

Polarization curves for thin films of TiO$_2$ and Fe$_2$O$_3$ are compared in Fig. 1. TiO$_2$ films exhibit an photocurrent onset at 0.2 V (RHE) and then plateau from about 0.8 V to 2.0 V (RHE). Fe$_2$O$_3$ films exhibits an photocurrent onset at more positive potential (1.1 V (RHE) then there is almost linear increase of photocurrent with applied potential.

Regarding the PEC activity of the TiO$_2$ films, a higher photoresponse (about 20%) was evident for sol-gel films in comparison to HIPIMS films. A different situation was observed for the hematite films. In this case the plasmatic films showed a tenfold enhancement of the stable photocurrent density over the sol-gel hematite films. A very high concentration of the surface states acting as the recombination centres might be the reason for the poor activity of the hematite sol-gel films. As far as the plasmatic hematite films are concerned, some of the abovementioned drawbacks for its application for the PEC water splitting were addressed in
this study by deposition of very thin films of hematite (25 nm) and by doping the hematite with Sn.

Fig. 2 shows the time dependence of photocurrent and evolved hydrogen for applied potential 1 V (vs. Ag/AgCl). Both anodic and cathodic compartments were bubbled with argon and the outlet gas from cathodic compartment was injected to gas chromatograph with TCD detector. In agreement with polarization curve photocurrents for applied potential 1 and 0.5 V are very similar (60-50 µA). The concentration of evolved hydrogen in outlet gas from cathodic compartment increases with irradiation time and after about 2-3 hours reaches the fairly constant value. The fact that the concentration of hydrogen increases with time can be explained by the fact that even the solution was bubbled by Ar before and during water splitting experiments there was significant amount of dissolved oxygen which could be reduced instead of water. Furthermore produced hydrogen is at first dissolved in electrolyte and then enter the gas phase which is analysed. Similarly as photocurrents for both applied potentials steady state concentrations of evolved hydrogen in outlet gas are almost the same (about 350 ppm). This suggests that the current efficiency of produced hydrogen is for both applied potentials almost the same.

It can be concluded that photocurrent and corresponding hydrogen evolution rate is significantly higher for hematite films than for the other two materials. For hematite photoanode in 1 M NaOH, and applied potential 0.55 V (Ag/AgCl) the observed photocurrent density was 0.9 mW/cm², hydrogen production rate was 125 µmol/h/cm² and faradaic efficiency for hydrogen production was around 95 %. For TiO₂ photoanode the hydrogen production rate was only 25 mmol/h/cm² but the applied bias was significantly lower (0.5 V).

Acknowledgement
This work was supported by the Grant Agency of the Czech Republic (project number P108/12/2104).

References
1-D NANOSTRUCTURES OF TiO₂ AND Fe₂O₃ FOR ELECTROCHEMICAL WATER SPLITTING – REVIEW

Šárka Paušová¹, Štěpán Kmen², Josef Krýsa³

¹ University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic (sarka.pausova@vscht.cz)
² Institute of Physics AS CR, v.v.i, Na Slovance 1999/2, 182 21 Prague 8, Czech Republic

With increasing demands on energy supply, necessity of usage of an efficient renewable source of energy is growing. One of the possibilities is conversion of solar light to electricity or fuel. Since the photocatalytic water splitting on titanium dioxide was discovered by Fujishima and Honda [1], the great effort has been devoted to application of TiO₂ in energy conversion. Although TiO₂ is a suitable candidate for water splitting some main drawbacks have to be overcome, such as high electron-hole recombination or short excited state life time. Using 1-D nanostructures (nanotubes, nanorods, nanowires or nanofibers) seems to be one of the possible ways how to increase the TiO₂ effectivity. However, even usage of TiO₂ nanostructures is limited by usage of UV light irradiation (TiO₂ band gap energy is 3.2 eV), so the modification of the TiO₂ with metal and/or non-metal ion doping to narrow the bandgap or sensitization by quantum dots or plasmon enhancement is necessary or application of another semiconducting material active under visible light irradiation. Hematite and its pure or modified nanostructures show even better characteristics (band gap energy 2.0 eV, very good stability and abundance) which make Fe₂O₃ one of the best choices for solar water splitting.

1-D nanostructures of TiO₂ and Fe₂O₃ can be prepared by many different methods. Nanotubes are commonly prepared by anodization of Ti or Fe substrates or Ti or Fe thin layers [2, 3], by template synthesis [4, 5] or hydrothermal synthesis (in the case of TiO₂) [6]; nanorods can be prepared by oblique-angle deposition [7] or metal-organic chemical vapour deposition [8] for TiO₂, hydrothermal synthesis used for both TiO₂ and Fe₂O₃ [9], template synthesis [10, 11] or anodization of Fe substrates or Fe thin layers [12]; nanowires or nanofibers of TiO₂ can be prepared by template synthesis [13], electrospinning synthesis [14], hydrothermal synthesis [15] or hydrothermal corrosion of Ti metal substrate [16], and nanowires or nanofibers of Fe₂O₃ by plasma oxidation of Fe sheets [17], thermal oxidation of Fe sheets [18], hydrothermal synthesis [19] or thermal decomposition of Fe compounds [20].

To compare the results of prepared nanostructures is not a simple thing. A lot of authors have used different conditions for the measurement of photoelectrochemical properties, such as different light intensity or wavelengths, different electrolyte or different applied potential and referent electrode. Differences in referent electrodes and electrolyte pH can be overcome by recalculation of applied potential to RHE. However, due to differences in light intensity, light wavelengths and electrolytes are the results incomparable.

So far for pristine TiO₂, nanorods seems to be the nanostructure exhibiting the highest usability for water splitting showing photocurrent density of 1.0 ma/cm² at 0.62 V vs RHE [11]. Among the modified structures, CdTe quantum dots modified TiO₂ nanotubes exhibit photocurrent density six times higher than pristine TiO₂ ~ 6 ma/cm² at 0.6 V vs RHE [3]. In the case of Fe₂O₃, pristine nanostructures exhibiting the best results are nanotubes with photocurrent density 2.2 ma/cm² at 1.43 V vs RHE [5] and for modified structures nanorods doped by Pt showed photocurrent density 10 ma/cm² at 1.5 V vs RHE [10].

Acknowledgements

Authors acknowledge the financial support from Grant Agency of the Czech Republic (project number 15-19705S).
References
Increasing installed capacity of renewable electric energy sources make new demands on electric grid. Main problem of renewable sources is unpredictable production of energy, which is difficult to store. One possibilities is using pump hydro-plants for energy storage, but this solution is limited by geographical conditions. On the other hand hydrogen economy represents viable solution of energy storage, because capacity of such system is limited only by storage capacity of hydrogen. Overproduction of electric energy is converted to chemical energy of hydrogen, which can be stored and can be converted back to electric energy in time of elevated consumption of electric energy. Hydrogen can be produced by water electrolysis process, which can be realized by three ways [1,2]. One way is alkaline process, which represents mature technology, typical of large scale installations. Second way is PEM water electrolysis which is more effective and more flexible than alkaline process. Third way is high temperature electrolysis, which is still available only in laboratory scale. PEM electrolyzer consists of three main parts, like any electrochemical reactors: cathode, anode and electrolyte. Electrolyte is here represented by proton exchange membrane (PEM), which also separates both electrodes chambers of electrolyzer. While hydrogen is produced on the cathode, oxygen is evolved on the anode. Water is decomposed on catalyst particles fixed in the gas diffusion electrodes. Membrane have to be ionic conductive to ensure contact between anode and cathode.

Main disadvantage of PEM electrolysis is high investment costs, which is given by necessity of using catalysts based on platinum metals and expensive membrane. Most promising method for catalysts loading reduction is to operate at elevated temperature above 100°C [2]. The electrode kinetics will be enhanced and therefore the overpotential at both electrodes is reduced. It also enables decrease of catalysts loading.

Elevated operation temperature requires thermaly stable materials. Membrane, which is typically based on perfluorinated sulfonated polymer [1,2], have to be hydrated for ensure ionic conductivity. Water is necessary in liquid form for hydration of membrane and preservation high intensity of process. Presence of the swelling water in the bulk of the membrane forms pathways in the membrane allowing the transport of the gas molecules. Operation at elevated pressure is favourable, because generated hydrogen is already compressed. By this way it is possible to save some energy necessary for compression of gases for gasholders store.

The aim of this work was to determine permeation of the produced gases through the separator represented by the polymer electrolyte membrane under PEM water electrolysis conditions. It is because permeation of oxygen and hydrogen in this cell represents significant problem from two points of view. At first, mixture containing 4,0 vol.% of hydrogen in oxygen is explosive. At the same time, permeation of gasses across the membrane represents loss of the process faradaic efficiency. As separator it was used membrane made from perfluorinated sulphonated polymer. Those types of membranes were originally developed for chlor-alkali electrolysis [2], where permeation of generated gases is not a main problem. Also operation temperature of chlor-alkali electrolysis is typically under 90°C. Application of perfluorinated sulfonated membranes in process with operation temperature over 100°C is not well described. Even the membrane material is formally considered as dense and more or less impermeable, its swelling (induced by the presence of the functional groups in the polymer
molecule structure) has to be considered. It thus means that beside thickness also the chemical composition and structure of the polymer has an impact on its permeability.

In the present study it was tested most used type of perfluorinated sulphonated membrane Nafion® 117. Cathode was presented by commercial electrodes E-TEK with catalyst loading 0.5 mg of Pt per cm². Anode was presented by homemade electrode, which consists from IrO₂ catalyst deposited on titanium felt. The catalyst loading was 1 mg of IrO₂ per cm². Active area of electrolyser was 4 cm². Asymmetric pressure operation mode was used in this work. Oxygen was generated at atmospheric pressure while hydrogen pressure was set to overpressure 200 kPa. Generated oxygen was analysed by gas chromatography.

Diffusion of hydrogen through membrane was studied in temperature range 40-120°C. Data from these measurements are presented on the figure 1. According to the expectations, permeability increases with increasing temperature. It is connected to increased expansion of the membrane and decreasing viscosity of the pore fluid. Data measured for other pressure differences were qualitative same. Concentration of hydrogen in oxygen decreases with increasing current densities. Explanation this effect is, that with increasing current densities increase volume of generated gases faster than volume of hydrogen, which penetrated through membrane into anode chamber.

![Figure 1: Volume concentration of hydrogen in generated oxygen at pressure difference 200 kPa](image)

Measured data presents safety area of operation parameters of PEM water electrolyzer, because all concentrations are under critical concentration 4.0 vol.%. Elevated permeation of hydrogen can form explosive mixture at higher pressure differences.

**Acknowledgement**
This work was supported by the specific university research (MSMT No 20/2015).

**References**

Hydrogen production by steam electrolysis in the solid oxide electrolysis cell (SOEC) attracted a great interest of researchers especially within last decade. This is due to the promising properties of hydrogen with respect to its potential utilization in the field of energy storage. In this concept, the SOEC system can be connected either with solar concentrators, where it could serve as a technology for the efficient large scale hydrogen production, or with nuclear reactors of fourth generation for effective leveling of the electric power generation. Such hydrogen can be subsequently used either in various processes as a valuable raw material or it can serve for other purposes such as fuel for hydrogen powered vehicles, or for electricity generation.

Through the fact, that SOEC has many advantages in comparison with the low temperature water electrolysis processes, such as high process efficiency, no need of platinum metals based catalysts or possibility of reversible operation, i.e. in electrolysis (SOEC) or fuel cell (SOFC) regime, there are still some issues to be overcome. One of the significant problems represents anode (oxygen electrode) performance and stability. Therefore, it was a subject of this work to optimize composition of the oxygen electrode and to determine kinetic parameters of oxygen evolution reaction in dependence of operating conditions.

So far, the most frequently used SOEC anodes material is strontium doped lanthanum manganate (LSM). LSM is characterized by its perovskite structure and mixed ionic and electronic conductivity. However, its ionic conductivity is rather poor when compared to the electronic one. Anodes prepared from pure LSM also suffer from delamination from the electrolyte during operation in water electrolysis regime. Therefore, the yttria stabilized zirconia (YSZ), i.e. the electrolyte phase, is usually added to the anode structure to form the composite electrode. Resulting microstructure of anode and the ratio between LSM and YSZ is crucial to obtain good anode performance.

Within the framework of this work, the oxygen evolution reaction was studied on five composites with different LSM/YSZ ratio. These anode composites were prepared using commercial powder precursors and deposited on the YSZ electrolyte pellet by screen printing method. They were subsequently tested in a form of symmetrical cells (i.e. electrochemical cell with both electrodes of same composition) in the three electrode set-up. The pseudostationary voltammetric curves were recorded upon working electrode polarization within the electrode potential range of ±1 V vs. electrode reversible potential. Since the reference electrode has the same composition as the working electrode and it was subjected to the same environment (gas composition), the reversible cell voltage has a value of 0 V. Thus, study of oxygen electrode was accomplished both in electrolysis and fuel cell regime, i.e. anodic and cathodic polarization of the working electrode.

Besides the electrode composition (YSZ/LSM ratio), the effect of operating temperature and oxygen concentration on the oxygen electrode performance was studied. Finally, the kinetic parameters $j_0$ $V$ [A m$^{-3}$] (exchange volumetric current) and $\alpha$ (charge transfer coefficient) of oxygen evolution reaction were evaluated from the global polarisation data by means of 2-dimensional mathematical model of porous electrode. The model was solved by the finite element method implemented in COMSOL Multiphysics$^\text{TM}$. A two-parameters ($j_0 V$, $\alpha$) optimization routine fminsearch incorporated in MATLAB code was employed to search
for the minimum of the sum of the squares of the errors between the modeled and experimentally determined voltammetric curves.

Experimentally measured voltammetric curves for all electrode compositions and two operational temperatures (600 °C and 800 °C) are shown in Fig. 1. Measured data show the optimal composition of oxygen electrode to change with increasing operational temperature from 60 wt. % LSM at 600 °C to 50 wt. % LSM at 800 °C. This is caused by increase in ionic conductivity of YSZ and electronic conductivity of LSM with increasing temperature. Thus, the composition of anode mixture was successfully optimized and well performing stable anode was prepared.

![Voltammetric curves recorded at 600 °C and 800 °C; working and reference electrode gas – 20 vol. % O₂ in N₂, counter electrode gas – pure O₂](image)

Fig. 1: Voltammetric curves recorded at 600 °C and 800 °C; working and reference electrode gas – 20 vol. % O₂ in N₂, counter electrode gas – pure O₂

Fig. 2 shows example of kinetic parameters evaluated as a function of oxygen concentration at 800 °C. These results confirm that even small addition of YSZ phase to the oxygen electrode significantly improve its performance, presumably predominantly by extension of electrochemically active surface area of the electrode. Moreover, as the parameter α decreases with increasing amount of YSZ present in the electrode, it might be assumed that either rate determining step of the process or even whole reaction mechanism is changing upon YSZ addition. Fig. 2 also shows that oxygen concentration has almost no effect on the electrode performance i.e. only minor changes of \( j_0^V \) parameter were identified for increasing concentration of O₂.

![Kinetic parameters \( (j_0^V, \alpha) \) evaluated for operational temperature of 800 °C as a function of oxygen concentration](image)

Fig. 2: Kinetic parameters \( (j_0^V, \alpha) \) evaluated for operational temperature of 800 °C as a function of oxygen concentration

**Acknowledgement**

This work was supported by the Technology Agency of the CR under project no: TA01020930 and from specific university research (MSMT No 20/2015).
ENHANCED PEC WATER SPLITTING EFFICIENCY OF HEMATITE THIN PHOTOANODES – THE ROLE OF TEXTURE

S. Kment*, Z. Hubiška*, M. Čada†, J. Olejniček†, R. Zbořil‡, J. Krýsa§

1 Institute of Physics AS CR, v.v.i., Na Slovance 2, Prague, Czech Republic (kment@fzu.cz)
2 Palacky University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic
3 University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic

Hydrogen production from photoelectrochemical (PEC) water splitting driven by solar power is one of the clean technologies that can be used for environmentally friendly fuel production that is hydrogen. Iron oxide (α-Fe₂O₃) with hematite crystalline structure possesses many advantageous properties. The material’s substantial light absorption, offering potential conversion of up to 17% of the sun’s energy into hydrogen (band gap energy between 2.0–2.2 eV),1 nontoxicity, high stability in aqueous environments, ample abundance and low cost are generally superior compared to other photoanodes. [1]

In the present work, we attempted to tune the crystal orientation and texture of hematite photoanodes by carefully controlling the energy of particles bombarding the substrate during a plasma assisted deposition procedure, i.e., a magnetron sputtering process.

The highly oriented hematite films examined in this study were fabricated by DC pulse reactive magnetron sputtering of a pure iron target working as a cathode in an Ar/O₂ gas mixture. Three different pulsing regimes of deposition magnetron discharge were used: (i) high impulse power magnetron sputtering mode (HiPIMS, 0.1 kHz), (ii) pulsing sputtering mode (PS, 1 kHz), and (iii) medium frequency sputtering mode (MFS, 50 kHz). As a result of different pulsing frequencies, f_P, and duty factors of a pulsing cycle, d_u, used, various cathode pulse current densities were reached.

![X-ray diffraction patterns](image)

Fig. 1: (a) X-ray diffraction patterns of hematite films deposited on the amorphous fused silica substrates; (b) models of the hematite crystal lattice with (104) and (110) preferentially oriented planes displayed; (c) simulated PEC water splitting activity of hematite photoanodes deposited under different energy of substrate ion bombardment. The PEC characteristics were recorded under solar light AM 1.5 simulated conditions with an intensity of 100 mW cm⁻², using 1 M KOH solution as the electrolyte, and with a scan rate of 1 mV s⁻¹.

XRD patterns of films are presented in Figure 1a. It can be seen that the main variation was in the two most intense diffraction peaks corresponding to (110) and (104) reflections (in hexagonal coordinates) due to hematite, α-Fe₂O₃. Only in the case of the MFS films, both these diffraction peaks occurred, suggesting the common polycrystalline hematite form. The main reflection observed in the spectrum for the PS film was from the (104) plane, whereas the desired preferential phase orientation along the (110) plane was unambiguously identified in the XRD pattern of the HiPIMS film. The (110) reflection peak broadening suggested that
the HiPIMS films were composed of nanocrystalline grains when compared to the remaining types of tested photoanodes (MFS, PS). Generally, the short duty cycles and low repetition frequency of the HiPIMS discharge resulted in a high power density (4 kW/cm²) and high plasma density (∼10¹⁸–10¹⁹ m⁻³) in the pulse, however, the values averaged over the whole period were much smaller (comparable or even lower than in the DC mode). Owing to the high power of the HiPIMS pulse, a large fraction of the sputtered metal (here Fe) particles were ionized in the target region. Thus, the high energy ion flux, bombarding the substrate, was considerably enhanced, potentially hugely affecting the film crystallinity, texture, grain size, microstructure, density, adhesion, etc., by influencing surface diffusion. Energetic bombardment in the HiPIMS mode removes adsorbed impurities and facilitates surface diffusion and migration, allowing adatoms to be accommodated in certain preferential plane orientation, in this study, orientation along the (110) plane. In comparison with the HiPIMS approach, the energy of particles impinging the substrate is negligible in the case of the MFS mode. Thus, this mode resulted in formation of polycrystalline grains without any preferential plane orientations, which was consistent with XRD data of natural isotropic hematite powder (JCPDS 33-0664). On the other hand, the reflection peak at 2θ = 33.3°, presented in the PS photoanode XRD spectrum, was attributed to (104) reflection. The pulse discharge current during the PS deposition was tenfold smaller than that for the HiPIMS mode. Thus, the energy of particles bombarding the substrate surface was lower in the former case but still much higher than expected in the MFS method. As a result, hematite adatoms tended to assemble in a different way, ultimately leading to the (104) texture.

Large differences in the PEC simulated water splitting performance were observed between the tested films (Figure 1c). In these experiments, J-V polarization curves were measured under standard AM 1.5 G (intensity 100 mW cm⁻²) chopped light illumination. The highest photocurrent values (0.28 mA cm⁻² at 1.23 V and 0.65 mA cm⁻² at 1.55 V vs. RHE) were obtained with the HiPIMS fabricated hematite photoanodes. Since all experimental conditions were kept identical and the examined photoanodes differed principally in the preferential alignment of the crystallites, the excellent photoactivity of the HiPIMS photoanode was most likely due to the favorable conductivity of the majority carriers (electrons) along the [110] axis (c-axis) perpendicularly connected to the FTO substrate. The second highly textured hematite photoanode deposited using the PS mode exhibited an almost negligible plateau photocurrent of 0.02 mA cm⁻² at 1.23 V vs. RHE, which remained almost constant until the water oxidation dark current onset. This drastic decrease can be explained by the synergistic effect of low electron and hole mobilities within the (104) plane oriented parallel to the c-axis and its non-ideal oxygen dominated surface termination, which is believed to cause much higher surface recombination due to the high density of surface states acting as traps. The most cathodically shifted dark current onset corresponding to the PS photoanode can also be attributed to the surface or defect states. In between the two extremes (HiPIMS and PS films), the photoactivity of the untextured MFS films showed a photocurrent maxima of 0.14 mA cm⁻² at 1.23 V and 0.38 mA cm⁻² at 1.55 V vs. RHE. This result is consistent with the XRD patterns, which showed that both discussed planes were present almost equally.

Acknowledgement
This work was supported by the Grant Agency of the Czech Republic – projects P108/12/2104 and 15-00863S; and by the Academy of Sciences of the Czech Republic – project M100101215.

References
**WO\textsubscript{3} FILMS FOR PHOTO-ELECTROCHEMICAL WATER SPLITTING**

*Martin Zlámal, Josef Krýsa*

University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic (zlamalm@vscht.cz)

Tungsten trioxide together with other metal oxides such as titanium oxide and zinc oxide is widely used for photocatalytic experiments. It is indirect band gap semiconductor ($E_g \approx 2.5–2.8$ eV) that can capture approximately 12\% of the solar spectrum and can absorb light in the visible spectrum up to 500 nm [1]. It is also convenient material to be used for hydrogen production via photoelectrochemical water splitting [2].

Layers formed by particles of material have advance in relatively high specific surface area usable for the reactions. But the mechanical stability and conductivity of these layers are very low due to weak adhesion of the particles. Both can be improved by layer calcination. The aim of the present work was therefore the comparison of photoelectrochemical and mechanical properties of particulate WO\textsubscript{3} layers and layers prepared by spray-pyrolysis of several precursors.

Tungsten trioxide particle layers were prepared on fluorine doped tin oxide layered glass (FTO) substrates by sedimentation of commercial WO\textsubscript{3} (99\%, Fluka) from its water suspension. Different amounts of WO\textsubscript{3} at the layer can be achieved by changing the concentration of the suspension. Further annealing at different temperatures improves adhesion of WO\textsubscript{3} particles in the layer.

Spray pyrolysis was done by semi-automatic spray device consisting of nozzle (EST 616, Czech Republic) fed with air (5 bar) and solution of precursor (2.7 cm\textsuperscript{3}/min). Nozzle is mounted on linear motion (20 cm/s) and atomized precursor solution is delivered downwards to the heated support FTO glass. Spraying was repeated up to several hundred times to obtain sufficient amount of WO\textsubscript{3} in the layer. Two different precursors were used for spray-pyrolysis deposition of the WO\textsubscript{3} on FTO substrates.

i) Acetylated peroxotungstic acid (AcPTA) precursor was prepared by several consequent steps [1] including reaction of metal tungsten with hydrogen peroxide, reaction of produced peroxotungstic acid with glacial acetic acid under reflux for 24 hours at 55 °C, evaporation and drying followed by dissolution of formed AcPTA in ethanol. Solution was sprayed to the FTO substrates heated to 150° C to form gray-black layers of partly degraded AcPTA. Wide variety of spray counts was used. Samples were annealed at 500 °C after spray deposition.

![Fig. 1: SEM image of the WO\textsubscript{3} layers produced by the spray-pyrolysis of AcPTA (A) and APT (B); topview (left) and cross section (right).](image)

ii) Ammonium paratungstate (APT) was prepared by reaction of tungsten oxide in ammonium solution at 80 °C with further recrystallization. Water solution of APT was used for spray-pyrolysis at 450 °C [3].

Both precursors produce monoclinic WO\textsubscript{3} (reference code 01-083-0950) according to XRD analysis with similar peak height proportions. Linear voltammetry of prepared WO\textsubscript{3} layers was measured within periodically chopped light illumination. Different excitation lights were used: three with very narrow single peak at light spectra (315, 365 and 404 nm) and fourth at
the standard solar illumination conditions (AM 1.5 G). Better adhesion at higher annealing temperatures results in more stable layers with higher photocurrent. Increasing of the annealing temperature to 600 °C caused the formation of undesirable crystal phases (produced by the reaction of WO₃ and FTO layer) and significant decrease in photocurrent/IPCE (incident photon to current efficiency).

Key parameters of semiconductor layers for photoelectrochemical water splitting application are maximum photocurrent and the layer stability. It was experimentally proved that both parameters can be significantly improved by thermal annealing at 450-500 °C for particulate layers of WO₃ [4].

![Fig. 2: Photocurrents of prepared WO₃ layers under AM1.5G light.](image)

Spray-pyrolysis of AcPTA produces homogeneous WO₃ layers with photocurrents comparable to the particular layers. However with increasing amount of formed WO₃ adhesion is decreasing resulting to the pealing of the thick layers as can be seen at Fig. 1A. Deposition of APT by spray pyrolysis (Fig. 1B) produce layers with lower photocurrents, but with very good mechanical properties (Fig. 2). Subsequent temperature annealing at 500 °C of the layers formed by APT spray-pyrolysis has no positive effect to their photocurrents.

**Acknowledgement**
Authors acknowledge Grant Agency of the Czech Republic (P108/12/2104) for the financial support.

**References**
DEFECTS IN WET-CHEMICALLY SYNTHESIZED WO₃ NANOSTRUCTURES: IMPACT ON PHOTOELECTROCATALYTIC PROPERTIES

Augusto Márquez¹, Manuel Rodríguez², Juan A. Anta³, Gerko Oskam⁴, Thomas Berger³

¹ Universidad Pablo de Olavide, Dept. of Physical, Chemical and Natural Systems, Spain
² CINVESTAV-IPN, Dept. of Applied Physics, México
³ University of Salzburg, Dept. of Material Science & Physics, Austria

Mesoporous WO₃ films have gained considerable interest in the past due to their use in electrochromic devices [1]. In addition, WO₃ is a promising candidate for photoelectrochemical water oxidation due to its high photocorrosion resistance in acidic media [2].

Monoclinic WO₃ was synthesized by alcoholysis and partial hydrolysis of WCl₆ in ethanol assisted by solvothermal conditions.[3] Mesoporous electrodes were then prepared by casting the particle suspension on a conductive substrate (fluorine-doped tin oxide, tungsten or titanium foil) followed by a sintering step at 450 °C or 550 °C, respectively. Whereas WO₃ shows a high stability in acidic media it is well known that electrochemical proton insertion leads to the formation of colored tungsten bronze. This process, which is exploited in electrochromic applications, is related to significant structural changes in the oxide.[4] On the other hand it is know from TiO₂ that a charge transfer reductive doping procedure, which consists of the concerted electron and proton accumulation in the oxide, may significantly improve the photocatalytic properties of the semiconductor.[5]

In this presentation we will discuss the influence of a concerted electron and proton uptake on the photoelectrocatalytic properties of WO₃ electrodes in water photooxidation. The electrochemical study will be complemented by UV-Vis and IR spectroelectrochemical measurements. Our results show that an electrochemical doping can enhance the photoelectrocatalytic activity only in the case of thin films sintered at low temperatures (450 °C). For these electrodes high defect concentrations at the nanocrystal surface are expected. These defects possibly result from the wet-chemical origin of the oxide and cannot be healed at the low sintering temperature. Excessive doping leads to an activity loss on all the studied electrodes (sinter temperatures: 450 °C and 550 °C) due to the irreversible electrochemical introduction of recombination sites.

References
The growing energy demands of developed societies occurring in parallel with increasing pressure on environmental protection and reduction of pollutions has inspired active research in the field of environmentally friendly energy production and storage methods. In this domain hydrogen represents one of the most promising energy carriers of the future. Water electrolysis as an inseparable part of the hydrogen cycle represents a technology capable of efficiently converting electrical energy from renewable power sources, such as solar or wind, into the chemical energy of hydrogen. The latest trend in electrochemical water splitting research represents anion selective membrane water electrolysis (ASMWE) attracting currently a lot of interest. Main advantages of this process consist in the higher system compactness, low rate of hydrogen cross-over and higher flexibility.

However, many ASMWE devices rely on use of noble metals like Pt for hydrogen evolution reaction (HER), although their low abundancy and high cost. To develop a highly efficient ASMWE system for practical application, finding a stable, low cost catalyst for HER represents one of the key points. Mostly, transition metal based electrodes serve as a HER catalyst in alkaline medium, but, their activity is far lower when comparing to Pt. Carbon-containing compounds, like graphene, graphene oxide (GO), i.e. graphene containing a significant amount of oxygen atoms in different functional groups, and reduced graphene oxide (RGO) are also of interest showing promising properties in this direction. Following examples may be mentioned at this place. MoS₂ nanoparticles grown on RGO have shown good photocatalytic activity towards the HER in photo-electrochemical water splitting process. Yang et al. reported WS₂ deposited on RGO as an efficient HER catalyst for acidic water electrolysis. Porous NiO/RGO hybrid can extensively catalyse the OER in alkaline medium. However, to the best of our knowledge, no information has been published to date on the RGO comparable regarding its electrocatalytic activity towards HER in alkaline water electrolysis to Pt.

Graphene (Geim and Novoselov 2010 Nobel Prize) has attracted a lot of attention in recent years due to its potential application in many energy-related technological fields. Graphene is defined as a planar hexagonal ring containing sp² hybridized carbon atom with a two-dimensional (2D) honeycomb lattice. Over the years, graphene-supported metal nanoparticles attracted a lot of attention and it was found that in these systems graphene acts as an active support. For example, when it comes to hydrogen storage graphene enhances the performance of the composite material through H spillover, with a possibility to further tune its properties by introduction defects and/or dopants to its structure. In HER catalysis, the same process is of immense importance, as it enables cleaning of the catalyst surface due to the transfer of discharged H to the active support where it recombines to H₂, allowing on this way the electrode reaction to proceed. In this work, a RGO/Ni foam catalyst is described that, even when compared with a commercial Pt catalyst, exhibits high HER activity in alkaline solution.

The objective of the present study is to verify suitability of RGO for application as a catalyst for the HER in ASMWE. In order to prepare desired RGO, an improved and mild method was proposed for preparation of graphite oxide. Resulting graphite oxide was exfoliated to GO by ultrasonication. Subsequently, GO was reduced to RGO electrochemically on nickel foam electrode. Produced RGO was characterized by a broad
range of spectroscopic techniques. In the next step its stability and activity towards HER in alkaline water electrolysis was investigated by means of linear sweep voltammetry and in single alkaline water electrolysis cell. As shown in Figure 1, current density obtained using bare Ni foam cathode during the water electrolysis test was 54 mA cm$^{-2}$ at a cell voltage of 1.85 V. In the case of the cathode modified with RGO current density under identical conditions attained 223 mA cm$^{-2}$.

Based on the thermodynamic considerations which relied on theDensity Functional Theory (DFT) calculations, an atomic-level justification is put forward for the superb catalytic activity of a RGO/Ni foam electrode. It led to a conclusion that H atoms, formed upon H$_2$O discharge on Ni, spill onto RGO serving as an H ad-atom acceptor (Figure 2). It continuously clears active Ni sites. This mode of action is rendered by unique reactivity of RGO, which arises due to the presence of O surface groups within the graphene structure and which is not expected for pristine graphene.

![Figure 1](image1.png)

**Figure 1.** V–i characteristics of a single-cell electrolyzer. Experimental conditions: 50 °C; 10 wt % KOH solution; anode: bare Ni foam; cathode: bare Ni foam, 0.15 mg cm$^{-2}$ RGO coated Ni foam & 0.15 mg cm$^{-2}$ Pt + qPPO binder (85:15); electrode area 3.8 cm$^2$; electrolyte flow rate 350 ml min$^{-1}$. Assignment of electrodes is indicated for all experiments in the figure.

![Figure 2](image2.png)

**Figure 2.** Comparison of hydrogen binding energies on the considered RGO model surfaces with hydrogen adsorption/absorption energetics on the Ni(001) surface. Shaded areas represent the range of hydrogen binding energies on a particular surface. Hydrogen binding energy on pristine graphene is indicated by a thick horizontal line. Even at very low H coverage, H binding presents an energetically favourable alternative to the formation of subsurface H atoms in the Ni phase.

**Acknowledgement**

The financial support from Technology Agency of the Czech Republic under project No. TA03010594 is gratefully acknowledged.
Compact TiO\textsubscript{2} thin films are used as blocking layers in solid state dye sensitized solar cells (DSCs), and in the perovskite solar cells. Here, the TiO\textsubscript{2} film serves as an electron collector and simultaneously as a buffer layer, preventing recombination of photoexcited electrons from the substrate, typically F-doped SnO\textsubscript{2} conducting glass (FTO) with the hole conductor\cite{1, 2}. The compact TiO\textsubscript{2} film is grown on top of FTO, usually by spray pyrolysis, DC-magnetron sputtering, electrochemical deposition, atomic layer deposition and spin coating. Recently, we developed a facile sol-gel dip coating technique producing dense and extremely mechanically stable TiO\textsubscript{2} thin films on various substrates from precursor solutions containing poly(hexafluorobutylmethacrylate), PHFM or hexafluorobutyl methacrylate, HFM as the structure-directing agents\cite{3}. Compact TiO\textsubscript{2} films were characterized by scanning electron microscopy, X-ray diffraction, adsorption measurements, UV-vis spectroscopy, Raman spectroscopy, atomic force microscopy and cyclic voltammetry of Li insertion\cite{3}. The films are quasi-amorphous, but crystallize to TiO\textsubscript{2} (anatase) upon heat treatment at 500\textdegree{}C.

An electrochemical study shows that the films grown with the aid of PHFM or HFM provide excellent rectifying interface for charge-transfer reactions of model redox probes. Blocking properties of the films were tested by cyclic voltammetry using [Fe(CN)\textsubscript{6}]\textsuperscript{3/4-} in aqueous electrolyte solution\cite{4}. The redox potential of [Fe(CN)\textsubscript{6}]\textsuperscript{3/4-} (0.24 V vs. Ag/AgCl) is sufficiently positive to the flat-band potential of TiO\textsubscript{2} (anatase) at all pH values in aqueous electrolyte solutions. The flat-FB of anatase single-crystal electrode shows the Nernstian pH-dependence:

$$\varphi_{FB} = -0.36 - 0.059 \cdot \text{pH} \text{ (in V vs. Ag/AgCl)} \quad (1)$$

Good-quality anatase blocking layers make a rectifying interface, at which no anodic currents of ferrocyanide oxidation flows, because titania is in the depletion regime at these potentials. The onset of cathodic current (ferricyanide reduction) appears at the potentials negative to the $\varphi_{FB}$, when the titania electrode is in the accumulation regime. The defects in the blocking layer are thus sensitively monitored by the occurrence of anodic current, which is assigned to the ferrocyanide oxidation at the naked FTO areas in pinholes. The as-grown films was found to produce an excellent rectifying interface with almost no pinholes\cite{4}. However, anatase crystallization induced by heat treatment at 500\textdegree{}C in air partially decreases blocking quality of dense sol-gel TiO\textsubscript{2} layers. The overall area of thermally induced pinholes is comparable to that in spray-pyrolyzed titania films. The flat-band potentials, $\varphi_{FB}$ of the as-grown films are upshifted by about 0.2–0.4 V against the values predicted for a perfect anatase single-crystal surface (eq. 1), but they still follow the Nernstian pH dependence\cite{4}. The same test was repeated by spiro-OMeTAD in dichloromethane electrolyte solution\cite{4}. In this case blocking is excellent, obviously due to the fact that large spiro-OMeTAD molecule cannot penetrate the very narrow pores in the blocking layer, which are still accessible for [Fe(CN)\textsubscript{6}]\textsuperscript{3/4-}.

Proton insertion into titania takes place during electrochemical n-doping in aqueous acidic electrolyte solution at sufficiently negative potential\cite{5}. The n-doping of TiO\textsubscript{2} can be
conveniently carried out by electrochemical reduction. In the absence of any other redox couple in an aqueous electrolyte solution, the proton insertion, described by equation 2, is the only faradaic process occurring on the titania electrode at sufficiently negative potentials in acidic electrolyte solutions:

\[
\text{TiO}_2 + e^- + H^+ \rightarrow \text{TiOOH}
\]  

(2)

Electrochemical doping was carried out simply by keeping the potential for a selected time at \(-1\) V vs Ag/AgCl, which is well below the \(\Delta_{\text{FB}}\) (eq 1). The proton insertion occurs with the accumulation of electrons (eq 2). Doping manifests itself by permanent color changes and by characteristic morphological differences on the surface[5]. The good-quality films are ideally compact, mimicking the properties of a macroscopic single crystal electrode. In contrast to porous polycrystalline electrodes, the doping of our dense films persists for at least weeks, if the electrode is stored in air at room temperature. Stirring at 250 rpm causes stronger electrochemical doping, as compared to doping in unstirred solution: the currents are expectedly larger, and we observe massive hydrogen evolution with the concomitant H$_2$ oxidation as on pure FTO[5]. Similarly to the previous case, the doping persists upon storage in air. The doped films still accommodate Li$^+$ by electrochemical insertion, but competition between Li$^+$ and H$^+$ ions in the lattice is detected by cyclic voltammograms.

Acknowledgement
This research was supported by the Grant Agency of the Czech Republic (contracts No. 13-07724S and 15-06511S) and COST Action CM1104.

References
PRINTED TITANIA PHOTOANODES WITH ORGANOSILICA BINDER

P. Dzik¹, M. Veselý¹, M. Neumann - Spallart²

¹ Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic (dzik@fch.vutbr.cz)
² Groupe d'Étude de la Matière Condensée (GEMaC), CNRS/Université de Versailles, 45, avenue des États-Unis, 78035 Versailles CEDEX, France

The mixture of titania-silica represents a perspective group of materials that have recently been used as catalysts and supporting materials¹². Titania-silica mixtures were found that improve the photocatalytic properties of pure titanium dioxide³, increase the specific surface area⁴ and improve the adsorption properties⁵. In this paper, we report on the fabrication of titanium dioxide layers by direct inkjet patterning of nanocrystalline suspensions. A recently reported organo-silica binder⁶ was mixed with commercial titania nanoparticles in order to improve printed layer mechanical properties. Inkjet printable formulations with various ratios of titania to binder were formulated and patterns of different thickness were printed onto soda-lime, Pyrex and FTO glass substrates. Printed green body patterns were further processed by thermal treatment or UV curing. The physical, chemical, electrical and photocatalytic properties of printed, sintered and UV-cured patterns were investigated in detail and the influence of post-deposition processing on printed layer properties was elucidated.

For the sake of convenient testing of various silica-titania ratios, stock dispersions of titanium dioxide in anhydrous ethanol were mixed first, having the same dry mass content as the silica binder solution. The printing formulation was then prepared by mixing varying volumes of silica binder solution, titania dispersion and viscosity-controlling solvent (butanol) in 20 mL glass vials. Approximately 3 g of 1 mm diameter glass balls were added to each vial and they were kept shaking for minimum 2 days on an oscillating plate shaker set to 900 rpm. Printing of prepared inks was performed with an experimental inkjet printer Fujifilm Dimatix 2831 following a standard procedure described previously⁷. The deposition process was finalized by curing. One copy of each sample set let to dry at ambient temperature and is further referred to as “printed” (P) sample set. The second one was calcined at 450 °C in air and is further referred to as “sintered” (S) sample set. The third one was immersed into demineralized water and placed 30 cm under an industrial processing UV lamp (model 80 BQL7, 248 W, Ultralight AG, Liechtenstein) for 10 hours and was called “UV cured” sample set (UV).

Photoelectrochemical characterization was performed by linear sweep voltammetry at room temperature using a two-electrode setup with the 1 cm² titania patches. The printed FTO slide was scratched with a diamond knife and thus two isolated FTO strips were created. One strip with the printed titania patch served as the working electrode and the opposite naked FTO strip as the counter electrode. This setup was fitted into a custom build quartz cuvette. The cuvette was filled with 0.1 M phosphate buffer (pH = 7) and fitted onto an optical bench equipped with a fluorescent UV-A lamp emitting a broad peak centered at 365 (Sylvania Lynx-L 11 W). A magnetic stirrer was placed beneath the cuvette and a magnetic flea inside the cuvette provided efficient electrolyte mixing. The lamp emission was monitored by Gigahertz Optic X97 Irradiance Meter with a UV-3701 probe and the irradiance was set to 3 mW/cm² by adjusting the lamp-to-cuvette distance. Measurements of generated photocurrents were performed with an electrometer build on the basis of National Instruments Labview platform and supplying a linear voltage gradient of 10 mV/s from -0.5 to 2 V.
Fig. 1: Photocurrents delivered by electrodes treated by various processes (print formulation containing 63 wt.% titania and 35 wt.% of binder) and a summary for all samples.

As depicted in the figures above, photocurrent density is increasing with titania content in all three studied processing options since the fraction of photosensitive component is increasing. For all tested formulations, sintering resulted into appr. 2.5 times greater photocurrent values than in the case of UV-cured electrodes. So while sintering remains the superior processing method for inorganic substrates, UV-curing provides a sound option for heat sensitive substrates.

Acknowledgement

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic for support through project LD14131.

References

INKJET PRINTED INTERDIGITATED CONDUCTIVITY SENSORS

M. Neumann-Spallart\textsuperscript{1}, P. Dzik\textsuperscript{2}, M. Veselý\textsuperscript{2}

\textsuperscript{1} Groupe d'Étude de la Matière Condensée (GEMaC), CNRS/Université de Versailles, 45, avenue des États-Unis, 78035 Versailles CEDEX, France,
\textsuperscript{2} Brno University of Technology, Faculty of Chemistry, Purkyňova 118, 612 00 Brno, Czech Republic

In this paper we report on the fabrication process and physical properties of cells for measuring electrolyte conductance. We utilized the benefits of inkjet printing and prepared gold conductive tracks on alumina with interdigitated design and variable finger density. Such cells are of use in measuring the conductance of electrolytes of low ionic strength\textsuperscript{1}. Further applications may involve various capacitive sensors\textsuperscript{2-3} and photoelectrochemical cells\textsuperscript{4}. Due to the materials used in this study, the printed electrodes are curable at high temperature if contaminating deposits are to be removed, e.g. when biological samples had been measured\textsuperscript{5}.

Pattern printing was performed with an experimental inkjet printer Fujifilm Dimatix 2831 whose features and benefits have been described previously\textsuperscript{6}. Gold resinate solution RL Au 01913 (art. no. 89960429, a product under development in 2014) was purchased from Heraeus. Alumina sheets 26 x 76 mm, 0.635 mm thickness (Elceram Inc., Czech Republic) were used as substrates. The interdigitated electrode patterns with finger widths between 200 and 2000 µm were drawn as vector graphics using Corel Draw. Three layers were overprinted in a wet-to-wet manner using optimized printing settings and substrate treatment. The layers were dried on a hot-plate at 120 °C and then fired at 800 °C for 30 min.

The studied sample series yielded a sheet resistance down to 0.27 Ω, corresponding to a specific resistivity of only three times higher than bulk Au. The design of the devices, which is based on an interdigitated photoelectrochemical cell fabricated by conventional lithography\textsuperscript{4} is outlined in Fig. 1, with \( w \), the finger width and \( s \), the distance between fingers.

![Fig. 1: Interdigitated finger device cross section](image)

The conductivity cell constant, \( \kappa \), of a sensor is defined by:

\[
R = \rho \cdot \kappa
\]

(1)

where \( R \) is the measured resistance and \( \rho \) is the specific resistivity of the electrolyte, with \( \sigma \), the specific conductivity equaling \( 1/\rho \).

Using the measured values of \( s \), \( w \), and \( L \) (the finger length), and the resulting number of fingers, \( N \), in the mask-delimited zone, the conductivity cell constants were calculated using an analytical solution derived by Olthuis\textsuperscript{7}:

\[
\kappa = \frac{1}{(N-1)L} \frac{2K(k)}{K[(1-k^2)^{1/2}]}
\]

(2)

where

\[
k = \cos \left( \frac{\pi w}{2s+w} \right)
\]

(3)
The incomplete elliptic integrals of the first kind (eq. 4) were evaluated numerically. In Fig. 2, theoretical values of $\kappa$ as a function of the number of fingers are plotted together with experimentally determined values in aqueous electrolytes of different specific conductivity, using a commercial, calibrated conductivity cell with $\kappa = 0.125$ cm$^{-1}$ as standard.

Cell constants between 0.008 and 0.09 cm$^{-1}$ were obtained. It can be seen that measured and theoretically predicted values are very close for all electrolytes. The cell with the lowest cell constant found in this series (0.008 cm$^{-1}$) is the most appropriate for measuring the specific conductivity, $\sigma$, of very dilute electrolytes. For cells with an overall active area of the size used in this work (16 mm $\times$ 52 mm), increasing the number of finger pairs further would not lead to a significant decrease of $\kappa$ as the curve $\kappa$ vs. $N$ flattens at high number of finger pairs, $N$. As $\sigma = R/\kappa$, the measured resistance, $R$, is low for cells with low $\kappa$ and can therefore be obtained conveniently with instruments of limited high resistance input range. In this way, the specific conductivity of distilled, ion-exchange and reverse osmosis purified water samples was measured successfully.

**Fig. 2:** Cell constants of interdigitated devices. The labels refer to the finger widths. Open spheres indicate theoretical values according to eq. 2.
Fig. 3. Impedance spectroscopy of interdigitated devices in 0.1 mM KNO₃. IDE 250, IDE 500, IDE 750 and IDE 1000 stand for devices with the corresponding finger with and gap (in µm) which are compared to a conventional parallel plate cell with $\kappa = 0.125$ cm⁻¹. The amplitude of the perturbing signal was 0.01 V rms.

Cells with $w = s =$ 1000, 750, 500, and 250 µm in contact with 0.1 mM aqueous KNO₃ solution were subjected to impedance spectroscopy. Fig. 2 shows that the amplitude, $r (|=|Z|)$, of the impedance of the solution, can be conveniently obtained down to low frequencies of 200 Hz (above which frequency the influence of diffusion layer capacitance ceases to influence the response) up to and above 2 kHz.

References
The toxicity of cyanide in water, air and soil is an excepted fact. However to find serious exposure limits is a difficult task. Data for the evaluation is often old and difficult to use in contemporary requirements, on the other hand, studies about the toxicity of cyanide are getting more complicated due to the growing knowledge of its hazardousness.

One of the basic arguments for the definition of exposure limits in air is the detoxification rate of cyanide in the human body. Two values are still in discussion in recent literature. The rate of 17 µg/kg body weight/min is based on studies from Loevenhart (1918) [1], who tested the impact of NaCN seriously ill patients, ignoring the fact that free cyanide is not stable in solutions at high pH. The rate of 1 mg/kg body weight/min is found in a more recent publication from Schulz (1982) [2], although no explanation was found for citations of fatalities after consumption of similar cyanide concentrations in the same paper. Hence, an amount of cyanide being metabolised in the body must be below this value.

The volatilisation rate of HCN in different pH values is a crucial point in the estimation of the hazardousness of cyanide in the environment and further treatment opportunities. The photoelectrocatalytic treatment, using TiO$_2$ on conducting glass (FTO) was investigated by the authors in previous studies. Treatment of solutions with a pH value of 10.5 resulted in a low degradation rate, compared to experiments with other substances [3]. In plotting the degradation rate against the distance of the redox potential to the energy of the valence band, a correlation is found (Fig. 1)

\[
p = \frac{k V F}{i_{\text{photo}}}
\]

\(p\): ratio between the rate constant of the oxidation of the oxidisable additive \((k)\) and the rate of water oxidation in a batch reactor with the total volume \(V\) of the solution.

\(F\): Faradaic constant.

\(i_{\text{photo}}\): photocurrent produced with irradiation of UV-light.

Fig. 1: Linear free energy relationship - constant \(p\) against the difference of the energy of the valence band to the redox potential of different species
The assumption of a relationship between the reaction rate and the difference of the energy of the valence band to the redox potential can be confirmed if the reaction rate changes with \((E_{VB} - E_{\text{redox}})\). If the oxidation of cyanide proceeds via the direct route

\[
\text{CN}^- + \text{h}^+ \rightleftharpoons \text{CN}^*
\]

it should be pH independent and the difference to the pH dependent valence band level increases. Experiments for the investigation of this relationship were done with TiO\(_2\) layers on FTO glass and a steel counter electrode in a photoelectrocatalytic setup, using UVA light (Fig. 2).

Fig. 2: Total and detailed Cyanide loss in a degradation experiment, using 400 mg/l Cyanide solutions in buffered solutions of different pH values.

Besides the strong increase of volatilisation, the increase of cyanide oxidation with decreasing pH is confirmed. Experiments were done in a closed setup with cyanide-contaminated air suction through an absorption flask (1M NaOH). Experiments with other materials will follow to investigate the acidic region and to prove the relationship on other species.

Additional investigations of the processes in photoelectrocatalysis at different pH will help to improve the detoxification capability of TiO\(_2\) in gold mining. Furthermore, the cyanide management in gold processing has to be improved to minimise the intake of NaCN. With a new discussion of cyanide-limits in gold mining based on recent investigations of the toxicity, the further reduction of cyanide contaminations will require advanced technologies for the degradation and the analysis as well.

References
MECHANISM OF H₃PO₃ ELECTROCHEMICAL OXIDATION ON PLATINUM IN CONTEXT OF HIGH TEMPERATURE PEM FUEL CELL OPERATION

M. Prokop, T. Bystroň, K. Bouzek

University of Chemistry and Technology, Prague, Dept. of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic (prokopm@vscht.cz)

High temperature fuel cells with proton exchange membrane (HT PEM FC) represent a compromise between low temperature PEM FCs and high temperature systems in context of catalyst poisoning resistance and construction material demands. Due to the operating temperature above 130 °C HT PEM FCs utilize membrane based on polybenzimidazole doped with H₃PO₄.

Phosphoric acid could be reduced both electrochemically at potentials of H⁻-adsorption and chemically by H₂ at temperatures over 70 °C to phosphorus compounds with lower oxidation state than P(V). These impurities that are specifically adsorbed on Pt significantly decrease electrochemically active surface area of the electrode. Lately H₃PO₃ was identified as one of the main products of H₃PO₄ reduction [1]. During HT PEM FC operation H₃PO₃ is produced in the anode compartment and could be possibly transported to cathode where undergoes anodic oxidation.

Basic information about H₃PO₃ electrochemical behaviour on Pt was included in our previously published work [2]. Goal of the present work is to determine mechanism and kinetics of electrochemical oxidation of H₃PO₃ on Pt electrode. With complex information on H₃PO₃ oxidation it could be potentially possible to modify HT PEM FC operation regime to partly avoid production of H₃PO₃ or remove it from the electrolyte.

All measurements were performed in three-electrode arrangement on a working bulk Pt electrode (1.11 cm²), Pt foil counter electrode and using Hg|HgSO₄|K₂SO₄ (saturated) reference electrode (MSE) separated from electrolyte by double liquid junction (1st stage filled with corresponding electrolyte and 2nd with saturated K₂SO₄ solution). All potential values in this paper are related to this electrode. Tempering was realized in glass jacketed cell, temperature was controlled by cryostat Julabo B12. In case of measurements performed at 160 °C a PTFE cell was placed in aluminium block heated to required temperature. HEKA PG310 potentiostat was used for cyclic voltammetry measurements and potentiostatic sampling voltammetry measurements inside faraday cage were performed on AUTOLAB PGSTAT302N potentiostat. Electrolytes were prepared using demineralized water and extra pure chemicals; 98% H₂SO₄ (Sigma), 98% H₃PO₃ and 85% H₃PO₄ (both from Acros Organics). Before use H₃PO₄ was treated with 30% H₂O₂ (Penta) at 160 °C for 24 h, volume ratio H₃PO₄:H₂O₂ 1:1. Na₂H₂P₂O₇·6H₂O was prepared according to procedure described by Remy and Falius [3]. Its purity was 99 % as determined by TGA and XRD analysis.

Main oxidation peak maximum of H₃PO₃ on a bulk Pt electrode was located around 0.15 V. At concentrations of H₃PO₃ below 10⁻⁴ mol dm⁻³ its oxidation proceeded mainly on bare Pt surface while at higher concentrations peak maximum was located well in potential area of Pt surface oxide formation. On the reverse scan the second H₃PO₃ oxidation peak was observed around 0 V especially at high H₃PO₃ concentrations and elevated temperatures. This peak probably corresponds to H₃PO₃ oxidation on renewed Pt surface. Examined H₃PO₃ electrochemical behaviour was similar in 0.5 mol dm⁻³ H₂SO₄ and H₃PO₄. Main difference is that oxidation peaks in H₂SO₄ are more pronounced. This is caused by stronger supporting electrolyte anion adsorption on Pt surface in H₃PO₄ in comparison to H₂SO₄ solution.

Determined adsorption isotherms show interesting property of H₃PO₃; while surface coverage of Pt by H₃PO₄ increases exponentially with concentration and decreases with temperature, in case of H₃PO₃ adsorption isotherm follows S-shape and surface coverage
increases with raising temperature. Reason consists in presence of tautomeric equilibria between thermodynamically stable passive form and more adsorbing active form of H$_3$PO$_3$.

Electrochemical kinetics of H$_3$PO$_3$ oxidation was examined by Tafel analysis. Tafel slope was surprisingly concentration-dependent varying from 300 to 100 mV dec$^{-1}$. Charge transfer coefficient varied with surface coverage from 0.2 to 0.5. For H$_3$PO$_3$ concentrations over 4·10$^{-4}$ mol dm$^{-3}$ Tafel slope was 100 mV dec$^{-1}$ and charge transfer coefficient raised to value 0.5. According to experimental kinetic data two mechanisms of H$_3$PO$_3$ oxidation were proposed, both including multiple electrochemical and chemical steps with P(IV) compound as possible intermediate. Following measurements of Na$_2$H$_2$P$_2$O$_7$.6H$_2$O electrochemical behaviour showed that its oxidation proceeds in the area of PtO$_x$ formation, thus supporting P(IV) compound status as possible intermediate during H$_3$PO$_3$ oxidation. However intensity of Na$_2$H$_2$P$_2$O$_7$.6H$_2$O oxidation peaks was not proportional with intermediate peaks on H$_3$PO$_3$ voltammograms.

Electrochemical behaviour of 95% H$_3$PO$_3$ at 160 °C is comparable to its behaviour in diluted H$_3$PO$_4$ at 25 °C. Because of high temperature H$_3$PO$_3$ oxidation peaks are shifted to more negative potential values with maximum around 0.05 V. Maximum of the peak in this case lies in double-layer area of Pt voltammogram so H$_3$PO$_3$ oxidation proceeds only on bare Pt surface. Preliminary results didn’t show any significant dependence of Tafel slope (85 mV dec$^{-1}$) and charge transfer coefficient (1) on concentration of H$_3$PO$_3$. In comparison with H$_3$PO$_3$ oxidation at 25 and 70 °C change in reaction mechanism is expected according to values of charge transfer coefficients.

H$_3$PO$_3$ is specifically adsorbed on Pt surface blocking significant part of active surface. From adsorption isotherms of H$_3$PO$_3$ was confirmed that surface coverage by H$_3$PO$_3$ increases with raising temperature due to the tautomeric equilibria. Tafel kinetics of H$_3$PO$_3$ electrochemical oxidation on a bulk Pt was determined and consequently two mechanism of H$_3$PO$_3$ oxidation were proposed. Both mechanisms include multiple steps including both the electrochemical and the chemical ones. P(IV) compound is probably one of the intermediates. Oxidation of H$_3$PO$_3$ in H$_3$PO$_4$ at temperature 160 °C probably undergoes different mechanism than at 25 and 70 °C.

Acknowledgement

Financial support of this project by FCH JU within the framework of project No: 325368 and by MSMT CR within the framework of project No: 7HX13002 is gratefully acknowledged.

References
The fuel cells (FCs) with polymer electrolyte membrane (PEM) are promising candidates for transportation, stationary and portable electric power generations due to their simplicity, high energy density and zero emission of pollutants. Nowadays, research is focused on high temperature (HT) PEM FCs operating at temperatures above 120 °C. Increasing of the temperature enhances electrochemical reactions kinetics, facilitates water management, enables more effective utilization of a waste heat and also improves the tolerance of Pt-C based catalyst to CO contained in the hydrogen originating from hydrocarbons reforming. In this kind of FC a polybenzimidazole (PBI) membrane doped by phosphoric acid is used as a solid polymer electrolyte. A certain number of single cells has to be used in a form of a stack to reach sufficient unit performance. The stacks represents typical device with plate-and-frame setup. This configuration brings advantages such as a simple assembly geometry and scale-up ability. Generally, the scale-up can lead to local inhomogeneity in flow of mass, heat or charge which might cause the loss of performance and/or reduction of lifetime. Experimental study and development of such large devices is very time demanding and costly. The mathematical modelling offers an option to visualise local distributions of various physical quantities, which significantly helps to study and optimize the system.

Description of a whole stack by means of detailed mathematical model is very computational demanding. Industrial scale unit consists of high number of layers and phase interphases. It makes the system to be “stiff” and extremely difficult to numerical discretization. Therefore, a sufficiently effective mathematical modelling approach has to be developed to describe such a system. Within this work, a novel modelling concept based on macrohomogeneous approach is presented. This approach assumes that system appears continuous (macrohomogeneous) in the through-plane direction. The individual continuous phases are characterized by effective transport parameters and volumetric fractions, and they are interconnected via source/sink terms in corresponding balance equations. The anisotropic structure of the real system is expressed by means of anisotropic transport parameters, i.e. the parameters are dependent on the position in space.

Fig. 1: (left) Model system geometry, (right) cross-section through the stack in x-y plane, light and dark arrows indicate main flow direction in anode and cathode gas stream respectively.
Aim of this work was to apply this modelling approach to describe behaviour of the FC stack consisting of 100 cells. The three dimensional (3D) stationary model was proposed. The operating temperature was 160 °C. Flow field with parallel channels was considered. The system geometry and x-y cross-section through the stack is shown in Figure 1.

Oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR) were considered in the system. The kinetics of HOR was assumed to be significantly faster in contrast with ORR. Due to this fact, the contribution of HOR to total overvoltage was neglected at this stage. The kinetics of ORR was described by Butler-Volmer type equation. The reactants crossover was not considered. The anode gas stream contained pure hydrogen in stoichiometric excess of $\lambda_{H2} = 1.2$. The cathode gas stream contained mixture of oxygen, nitrogen, and water vapour. Stoichiometric excess of $\lambda_{O2} = 2$ was considered. The model consisted of 7 dependent variables and included mass balance of both gas streams, material balances of individual gaseous components and charge balance.

The proposed model enabled visualisation of local distribution of various physical variables. For instance, Figure 2 shows local distribution of current density for current 0.4 A cm$^{-2}$. The local current density decreases from inlet to outlet (in x-coordinate) with decreasing concentration of oxygen. We can also see that the value of local current density notably varies in y-coordinate due to nonuniform flow of gas in the flow field channels. This non-uniformity can lead to the locally different behaviour. The conditions favourable for degradation can occur in some places.

The macrohomogeneous model of the HT PEM FC was successfully realized in 3D representation. For the proposed geometry the model calculations revealed a uniform behaviour of the individual stack cells, but non-uniform distribution of properties in the in-plane direction (x-y plane). This is caused by high gas flow resistance of the flow field horizontal channels. It is evident that the presented stack configuration is far from optimal.

Acknowledgement

Financial support of this research by FCH JU within the framework of Grant Agreement No. 325262 and by the MSMT CR within the project No. 7HX13001 is gratefully acknowledged.

References

ELECTROCHEMICAL PREPARATION OF NANOSTRUCTURED PHOTOCATALYTIC TiO₂ LAYERS

K. Přikrylová, J. Drbohlavová

Department of Microelectronics, Faculty of Electrical Engineering and Communication, Brno University of Technology Technická 3058/10, 616 00 Brno, (xprik26@stud.feec.vutbr.cz) Central European Institute of Technology, Brno University of Technology, Technická 3058/10, 616 00 Brno, Czech Republic

The titanium dioxide is an important wide bandgap semiconductor in the field of photocatalysis due to its strong oxidizing ability [1], superhydrophilicity, chemical stability, long durability, nontoxicity, low cost and transparency in visible light. Self-ordered TiO₂ nanostructured and nanoporous surfaces have great potential as a superior photocatalyst due to their valuable high surface area. Also it is not necessary to remove photocatalyst nanoparticles as in the case of TiO₂ suspensions. [2]

The TiO₂ nanostructured and nanoporous surfaces can be fabricated by many different approaches, for example using template [3], sol-gel [4], hydrothermal [5] or anodic oxidation (AO) methods [6]. AO has become one of the most popular method because it is relatively fast, low cost, highly tunable, and reproducible. Morphological structure of anodized TiO₂ can be modified by changing the preparation conditions such as AO time, applied voltage, temperature, Ti layer thickness and electrolyte composition (e.g. content of fluoride, water or organic additives) viscosity, conductivity, and pH. [5,7]

The present research demonstrates a method for the fabrication of TiO₂ surfaces via either one-step or two-step AO of thin Ti layer in organic electrolyte containing ethylene glycol, ammonium fluoride and water. [8] One-step anodization was performed at 60 V and room temperature. In the case of two-step AO, we applied an ultrasonic treatment between the steps and the potential was kept at 60 V in the first step, while it varied from 40 V to 100 V in the second step. [9]

![Fig. 1: SEM images of anodic TiO₂ nanoporous/nanotubular structure prepared via two-step AO.](image)

The prepared TiO₂ surfaces were characterized by scanning electron microscopy (SEM). SEM images revealed the one-step anodized titania surfaces have nanoporous character while two-step ones have unique nanotubular character with upper nanoporous layer (Fig. 1). This
upper layer is formed by dissolution of upper Al oxide layer caused by aggression of fluoride ions. Such a nanoporous layer can serve as a protective layer for nanotubes below or as a stable matrix for supporting various nanoparticles. This TiO$_2$ nanoporous layer can be further doped with noble metals (e. g. silver or gold) in order to improve the photocatalytical efficiency in VIS region. To conclude, these TiO$_2$ nanostructured surfaces have higher uniform configuration and higher surface area. Thus they have better potential for future photocatalytic application in comparison to nanoporous structures prepared by one step AO.

Acknowledgement
The research was supported by project no. FEKT-S-14-2300 A new types of electronic circuits and sensors for specific applications.

References
THE SYNTHESIS OF ONE-DIMENSIONAL TiO$_2$ NANOSTRUCTURES AND STUDY ON THEIR ELECTROCHEMICAL BEHAVIORS

H. Han$^{1,2}$

$^1$Institute of Physics AS CR, v.v.i., Na Slovance 2, Prague, Czech Republic
(hyungkyu.han@upol.cz)

$^2$Palacky University, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic

TiO$_2$ has received attention as an alternative anode for high power lithium rechargeable batteries due to abundance, low cost, structural stability during lithium insertion/extraction, and high working voltage enables high rate operation. However, the poor rate capability of TiO$_2$ electrodes, which results from their intrinsic physicochemical properties, limits their practical use. Considerable efforts have been made to investigate a variety of titanium dioxide based nanostructures and composites to solve the problem of poor rate capability. In this thesis, we synthesized nitridated TiO$_2$ hollow nanofibers, directly grown TiO$_2$ nanotubes array on current collector, and TiO$_2$ nanotubes branched tree on carbon nanofiber to consider the improvement of electrochemical characteristic by the experimental results and theoretical analysis. Nitridated TiO$_2$ hollow nanofibers showed more improved cyclability and rate capability due to hollow morphology and highly conducting TiN layers compared to TiO$_2$ nanofibers.$^1$ However there is still problem of the high resistance between active material and current collector. To improve this problem, directly grown TiO$_2$ unsealed nanotubes on current collector without insulating binder were proposed. The structure shows 6.2 times higher rate capability at 10C compared to typical composite film of TiO$_2$ hollow nanofibers active material/conducting agent/binder (80:10:10, weight ratio) result from high electronic resistance at the interface acting as a huge barrier for electron injection from the current collector to the electrode. Especially, the use of electrically insulating binder and the physical contact between active material and current collector leads to significant degradation of the electronic conductivity of the overall electrode system by theoretical analysis.$^2$ But low areal capacity of the anode still prohibits its practical use. The energy density per unit area (areal capacity ; mAhcm$^{-2}$) is a critical for practical application. The increase in the areal capacity can be achieved by increasing the TiO$_2$ thickness. However, there exists a trade-off between the electrode thickness and the electronic resistivity, which leads to significant degradation of the rate capability.

Fig. 1: Cross section SEM images of the TiO$_2$ NTs arrays with a length of 0.5 µm (a), 4 µm (b), 8 µm (c) and the TiO$_2$ NT – CNF nanostructure (d) on the metal current collector. Top-view SEM images of the TiO$_2$ NT – CNF nanostructure ((e)-(f)).$^3$
Fig. 2: TEM images of the TiO$_2$ NTs array with a length of µm and the TiO$_2$ NT – CNF nanostructure. Low magnification ((a) and (d)), high magnification ((b) and (e)) and high resolution TEM images ((c) and (f)) for the TiO$_2$ NTs array with a length of 4 µm and the TiO$_2$ NT – CNF nanostructure, respectively.$^3$

Fig. 3: Electrochemical characteristics of the TiO$_2$ NTs arrays with a different length and the TiO$_2$ NT – CNF nanostructure electrodes. (a) Voltage profiles for the first cycle (b) cyclic performance at a current density (40 mA g$^{-1}$). (Closed circle – capacity retention; Open circle – coulombic efficiency)(c) Rate capability at different current densities.$^3$

Finally, we suggest an architecture based on TiO$_2$ nanotubes branched on carbon nanofibers (CNF). The CNF backbone, with direct electric contact of the TiO$_2$ nanotube branched on carbon nanofibers nanostructure electrode to the current collector, provides both an efficient electron transport pathway and a large space for dense TiO$_2$ active material loading, which enable significant improvement in rate capability as well as the achievement of high area energy density. The strategy presented here offers a design guideline to prepare TiO$_2$ based anode materials for next generation LIBs.

Acknowledgement
Author wish to thank to the Grant Agency of the Czech Republic – project 13-29241P and to the Academy of Sciences of the Czech Republic – project M100101215.

References
1 Han, H. et al. Nitridated TiO2 hollow nanofibers as an anode material for high power lithium ion batteries. Energ Environ Sci 4, 4532-4536, (2011).