Plasma Deposited Thin Iron Oxide Films as Electrocatalyst for Oxygen Reduction Reaction in Proton Exchange Membrane Fuel Cells

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The possibility of using plasma deposited thin films of iron oxides as electrocatalyst for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFC) was examined. Results of energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) analysis indicated that the plasma deposit consisted mainly of FeO_X structures with the X parameter close to 1.5. For as deposited material iron atoms are almost exclusively in the Fe^{3+} oxidation state without annealing in oxygen containing atmosphere. However, the annealing procedure can be used to remove the remains of carbon deposit from surface. The single cell test (SCT) was performed to determine the suitability of the produced material for ORR. Preliminary results showed that power density of 0.23 mW/cm^2 could be reached in the tested cell.

Keywords: plasma deposition, iron oxide electrocatalyst, oxygen reduction reaction, fuel cell.

1. INTRODUCTION

The fuel cells belong to the modern class of current generation devices. Like all electrochemical cells, the fuel cell has a pair of half-electrodes immersed in a basic electrolyte or mounted on both sides of the solid state proton-conductive membrane (PEM). To date, there is no better catalyst than platinum black, which is used at concentration of 10 % to 60 % [1]. Despite the fact that platinum is the most effective, it is also expensive rare element, which is easy to contaminate by gas impurities usually leading to dramatic power losses. Several ways have been proposed to lower prices and improve accessibility of proton exchange membrane fuel cells (PEMFC). The main approach is based on the reduction of platinum content while maintaining catalyst effectiveness, for example, by the catalyst surface area modification [2]. There have been some attempts to prepare a new electrocatalysts as platinum composites with other noble metals [3 – 5] and the nano-composites of platinum group metals with non-noble metals compounds [3, 6]. The other approach is to use electrocatalyst made of non-noble metals and their derivatives [7 – 11].

Electrocatalysts can be prepared by means of various methods like solvothermal methods, sol-gel reduction or coprecipitation, thermal synthesis and electrodeposition. The most used techniques are based on sol-gel or hydrothermal methods that give small, well defined crystals of active species. However, there are also a lot of disadvantages of these methods such as generation of wastes and large energy consumption. Furthermore, the materials produced this way are composed of small sized particles but not as small as they can be using plasma methods. By means of plasma enhanced chemical vapor deposition (PECVD), nanostructured thin films of

electroactive materials can be deposited with strong adhesion directly on an electron-conductive substrate (e.g. carbon paper). By selecting the deposition parameters, it is possible to obtain different structures characterized by the same chemical composition but various physicochemical properties. In this paper, the effectiveness of the plasma-deposited iron oxides was investigated as an electrocatalyst for PEMFC.

2. EXPERIMENTAL

Thin films containing FeO_X were deposited in a parallel-plate RF (13.56 MHz) plasma reactor presented in [12], using iron pentacarbonyl (Sigma Aldrich, 99 %) as the precursor and mixture of oxygen (99.999 %) and nitrogen (99.999 %), in a ratio of 1:4, as a carrier gas. Both the precursor container and the entire gas feed line were heated up to 329 K. The total pressure in the reactor chamber was 5.2 Pa, the glow discharge power density was 355 W/dm^3, and the flow rates of precursor vapor and carrier gas were 0.035 sccm and 0.90 sccm, respectively.

Chemical composition of the investigated materials was determined by a scanning electron microscope (SEM FEI Quanta 200 FEG) equipped with an energy-dispersive X-ray spectrometer (EDX Oxford INCA 250). EDX measurements were taken at ten different spots for a given sample, and then the average atom concentration and its standard deviation were calculated for each of identified elements. Electron energy of 3.5 keV was used in all tests. Quantitative and structural surface analysis were performed by an ESCA-XPS (Kratos AXIS Ultra) spectrometer using monochromatic Al K$_\alpha$ X-Rays source of excitation energy equal to 1486.6 eV. For both EDX and XPS tests, thin films of investigated material were plasma-deposited onto silicon wafers.

For the single cell test (SCT), the investigated material was plasma-deposited directly on a disk shape carbon paper (SpectraCarb) with diameter of 15 mm, which was

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then used as a cathode. The same disk of carbon paper covered by 0.4 mg/cm² of Pt was used as the anode. The membrane was made of Nafion® (N-215 from FuelCell-Store). The cell was fed with pure hydrogen and oxygen (both AirLiquide, 99.999 %).

Some of plasma-deposited samples were used directly for structural tests while others before the investigations were subjected to an annealing procedure during 45 min in electric oven at 723 K under air atmosphere.

3. RESULTS

Atomic composition of the plasma-deposited films containing FeO_X was studied by means of EDX spectrometry. Results obtained for both "as deposited" and annealed materials (Table 1) revealed that no significant change occurred after the thermal treatment. The material consists mainly of iron and oxygen atoms (together 87 at.%).

Table 1. Atomic composition of investigated materials (EDX)

| Element	As deposited, at.%	After annealing, at.%
Fe	32.3 ± 0.1	32.4 ± 0.1
O	54.8 ± 0.1	54.8 ± 0.1
N	6.1 ± 0.1	5.86 ± 0.08
C	6.90 ± 0.05	6.85 ± 0.05

The ratio of oxygen to iron is equal to X = 1.7, which, assuming that not all oxygen atoms are chemically bonded with iron atoms, could suggest that the film dominant structure is represented by the stoichiometric Fe_2O_3. The mass deposition rate (2.2 μg/cm²min) in the plasma deposition process was estimated from the EDX results obtained for series of films deposited at the same process parameters but at different deposition times. The calculation algorithm based on Kanaya-Okayama electron depth penetration formula [13] is described elsewhere in detail [14]. Due to the fact that electron penetration depth is in the range of the deposited film thickness, the data presented in Table 1 can be regarded as volume-average values.

On the other hand, XPS is a well-known spectroscopy technique to probe the thin surface of the material, which usually means a few atomic layers. The atomic compositions measured by this technique for "as deposited" and annealed samples are not the same (Table 2). In general, the results are similar to these obtained by means of EDX but some differences are clearly seen. Before annealing, the surface of plasma deposit is richer with carbon structures (approx. 17 at.%). During the annealing process the carbon deposit was removed revealing FeO_X structures, which amount increases from 78.5 at.% to 93 at.%. The ratio of oxygen to iron, measured by XPS, was equal to X = 1.53 – very close to the stoichiometric Fe_2O_3. Furthermore, it should be noted that during the annealing process all nitrogen atoms are removed from the material surface (Table 2).

Table 2. Atomic composition of investigated materials (XPS)

Element	As deposited, at.%	After annealing, at.%
Fe	30.4 ± 0.5	36.9 ± 0.9
O	48.1 ± 0.5	56.4 ± 0.7
N	4.2 ± 0.2	0.00
C	17.4 ± 0.2	6.8 ± 1.5

The XPS Fe 3p and O 1s peaks for both "as deposited" and annealed samples are presented in Fig. 1, Fig. 2 and Fig. 3, Fig. 4, respectively. The Fe 3p peak was selected for analysis because the Fe 2p peak is much more complex in shape, having multiple secondary or satellite peaks [15].
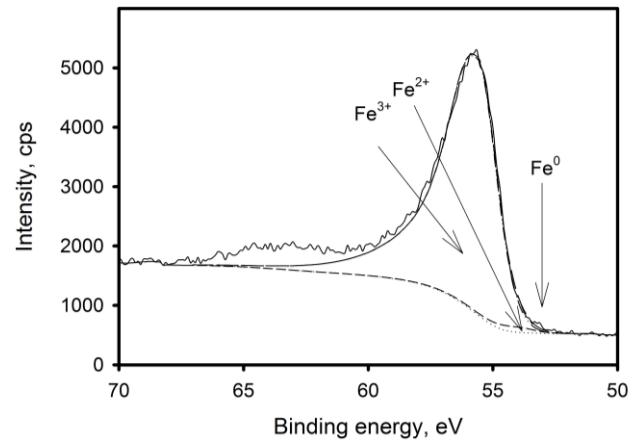
Fig. 1. XPS Fe 3p spectra of the FeO_X film plasma deposited for 60 min (as deposited sample)
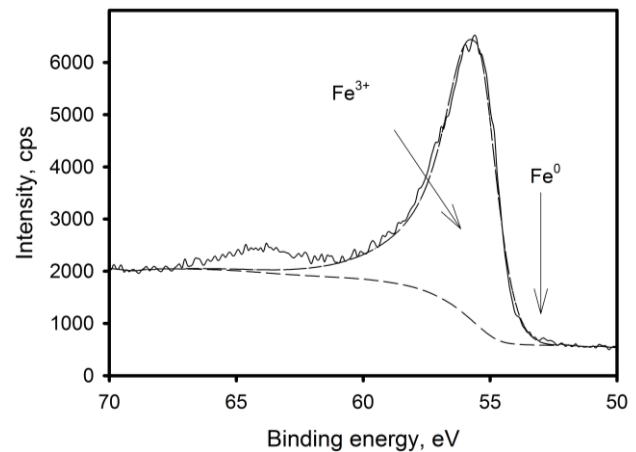
Fig. 2. XPS Fe 3p spectra of the FeO_X film plasma deposited for 60 min (annealed sample)

The deconvolution procedure of Fe 3p region was based on background and peaks parameters described previously by Yamashita and Hayes [16, 17]. As a result, relative shares of Fe^{2+} and Fe^{3+} compounds were estimated and placed in Table 3 including peaks positions and corresponding FWHMs. It is clearly seen that iron atoms are almost exclusively in the Fe^{3+} oxidation state. Only in "as deposited" material the Fe^{2+} component was observed but its estimated percentage was less than 2 at.%. Both "as deposited" and annealed samples showed no signal of metallic Fe. The expected position of the Fe^0 peak [18] is indicated in Fig. 1 and Fig. 2.

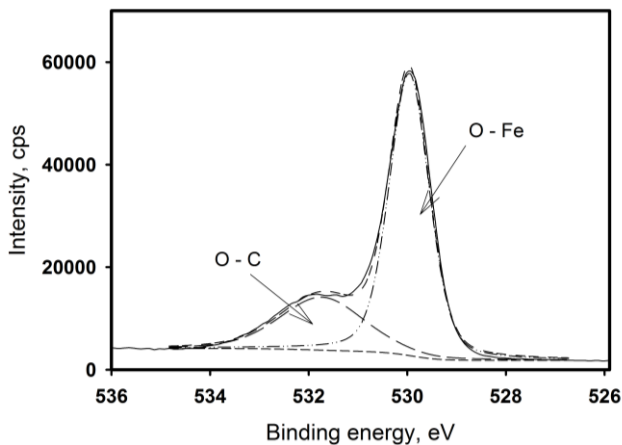**Table 3.** Parameters of the XPS Fe 3p peak fits

Sample	Peak.	Position,eV	FWHM,eV	Relative area at., %
As deposited	Fe^{2+}	54.0	2.08	1.7
	Fe^{3+}	55.6	2.45	98.3
Annealed	Fe^{3+}	55.5	2.45	100

The differences in XPS spectra before and after annealing are well seen in O 1s region (Fig. 3 and Fig. 4,

and Table 4), which confirms above conclusion on removing carbon component (high-energy part of the band) from the film surface and uncovering underlying FeO_X structures (low-energy part of the band) [19].
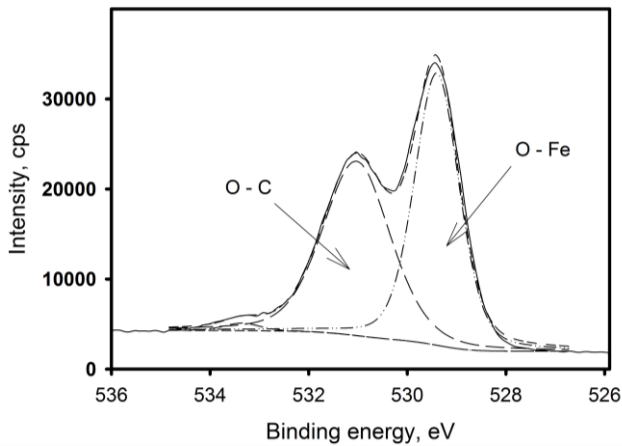
Fig. 3. XPS O 1s spectra of the FeO_X film plasma deposited for 60 min (as deposited sample)

**Fig. 4.** XPS O 1s spectra of the FeO_X film plasma deposited for 60 min (annealed sample)

Table 4. Parameters of the XPS O 1s peak fits

| Sample	Bonds	Position, eV	FWHM, eV	Area, %
As deposited	O – Fe	529.4	1.07	50.9
	O – C	531.0	1.61	49.1
Annealed	O – Fe	530.0	0.96	71.3
	O – C	531.7	2.04	28.7

In the case of the investigated FeO_X films, the annealing procedure is not crucial for desired material composition (Fe_2O_3) that, as a result of oxygen rich plasma, is formed already during plasma deposition. However, annealing process cleans the material surface from nitrogen and carbon deposit increasing the contact surface of Fe_2O_3. Hence, all further electrochemical analyses were carried out only on annealed samples.

Single cell characteristics measured for the PEMFC with the plasma-deposited FeO_X catalyst (60 min deposition) are shown in Fig. 5 and Fig. 6. The FeO_X load in this cell was equal to 130 µg/cm². For such a cell, typical values of open circuit voltage (OCV) and Tafel slope were 0.4 V and 120 mV/dec, respectively. Maximum of power density 0.23 mW/cm² was measured at cell current density 1.6 mA/cm² and potential value of 140 mV. Although the produced FeO_X electrocatalyst is far less effective than platinum [14], the presented results should be considered preliminary, which encourage for further research.
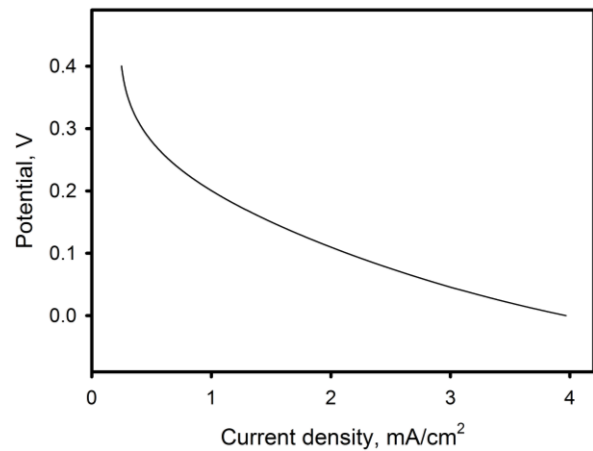
Fig. 5. Cell potential vs. current density measured for fuel cell with FeO_X film (60 min plasma deposited) as ORR catalyst
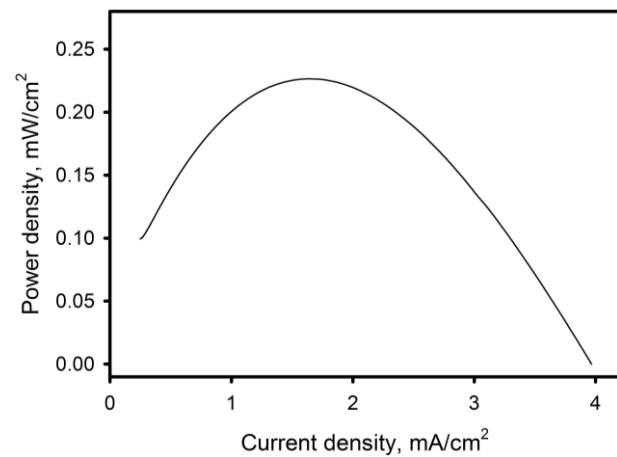
Fig. 6. Power density vs. current density measured for fuel cell with FeO_X film (60 min plasma deposited) as ORR catalyst

4. CONCLUSIONS

Thin films consisted mainly of FeO_X were produced in low temperature plasma with mass deposition rate of 2.2 µg/cm²min. The residual carbon deposit can be easily removed during 45 min annealing in electric oven at 723 K under air atmosphere increasing amount of FeO_X on the surface up to 93 %. Analysis of the XPS Fe 3p indicates that all iron atoms are chemically bonded with oxygen. The estimated percentage of Fe^{2+} and Fe^{3+} oxidation states was found to be about 1.7 at.% and 98.3 at.%, respectively, for "as deposited" material, while after annealing only Fe^{3+} states remained. The ratio of oxygen to iron, measured by XPS, was close to 1.5. The obtained material showed catalytic activity for the oxygen reduction reaction. It was found that the fuel cell with platinum as the anode and FeO_X deposit (130 µg/cm²) as the cathode was characterized by OCV of 0.4 V and maximum power density of 0.23 mW/cm². This catalyst is far less effective than pla-

tinum, however, is much cheaper than any noble element. Investigations will be continued to improve its efficiency.

REFERENCES

1. **Liu, C.C., Sung, C.C.** A Review of the Performance and Analysis of Proton Exchange Membrane Fuel Cell Membrane Electrode Assemblies *Journal of Power Sources* 220 2012: pp. 348 – 353.
http://dx.doi.org/10.1016/j.jpowsour.2012.07.090

2. **Guo, S., Dong, S., Wang, E.** Gold/platinum Hybrid Nanoparticles Supported on Multiwalled Carbon Nanotube/Silica Coaxial Nanocables: Preparation and Application as Electrocatalysts for Oxygen Reaction *International Journal of Hydrogen Energy* 39 2014: pp. 6462 – 6469.
http://dx.doi.org/10.1021/jp0772629

3. **Sanchez-Padilla, N.M., Morales-Acosta, D., Morales-Acosta, M.D., Montemayor, S.M., Rodriguez-Varela, F.J.,** Catalytic Activity and Selectivity for the ORR of Rapidly Synthesized M@Pt (M=Pd, Fe_3O_4, Ru) Core-Shell Nanostructures *International Journal of Hydrogen Energy* 39 2014: pp. 16706 – 16714.
http://dx.doi.org/10.1016/j.ijhydene.2014.03.223

4. **Antolini, E., Zignani, S.C., Santos, S.F., Gonzalez, E.R.** Palladium-based Electrodes: A Way to Reduce Platinum Content in Polymer Electrolyte Membrane Fuel Cells *Electrochimica Acta* 56 2011: pp. 2299 – 2305.
http://dx.doi.org/10.1016/j.electacta.2010.11.101

5. **Uribe-Godinez, J., Garcia-Montalvo, V., Jimenez-Sandoval, O.** Development of Ir based and Rh Based Catalyst Electrodes for PEM Fuel Cell Applications *International Journal of Hydrogen Energy* 38 2013: pp. 7680 – 7683.
http://dx.doi.org/10.1016/j.ijhydene.2012.10.060

6. **Neergat, M., Gunasekar, V., Rahul, R.** Carbon-supported Pd-Fe Electrocatalysts for Oxygen Reduction Reaction (ORR) and Their Methanol Tolerance *Journal of Electroanalytical Chemistry* 658 2011: pp. 25 – 32.
http://dx.doi.org/10.1016/j.ijhydene.2012.10.060

7. **Zhang, J., Wang, X., Qin, D., Xue, Z., Lu, X.** Fabrication of Iron-Doped Cobalt Oxide Nanocomposite Films by Electrodeposition and Application as Electrocatalyst for Oxygen Reduction Reaction *Applied Surface Science* 320 2014: pp. 73 – 82.
http://dx.doi.org/10.1016/j.apsusc.2014.09.056

8. **Zhang, L., Zhang, J., Wilkinson, D.P., Wang, H.** Progress in Preparation of Non-Noble Electrocatalysts for PEM Fuel Cell Reactions *Journal of Power Sources* 156 2006: pp. 171 – 182.
http://dx.doi.org/10.1016/j.jpowsour.2005.05.069

9. **Song, C., Zhang, J.** Electrocatalytic Oxygen Reduction Reaction, In: Zhang, J. (Ed.), PEM Fuel Cell Electrocatalysts and Catalyst Layers – Fundamentals and Applications, Springer-Verlag, London, 2008: pp. 89 – 134.
https://doi.org/10.1007/978-1-84800-936-3_2

10. **Wang, M., Zhang, H., Zhong, H., Ma, Y.** Cobalt Oxyphosphide as Oxygen Reduction Electrocatalyst in Proton Exchange Membrane Fuel Cell *International Journal of Hydrogen Energy* 36 2011: pp. 720 – 724.
http://dx.doi.org/10.1016/j.ijhydene.2010.09.065

11. **Ahmed, J., Yuan, Y., Zhou, L., Kim, S.** Carbon Supported Cobalt Oxide Nanoparticle-Iron Phthalocyanine as Alternative Cathode Catalyst for Oxygen Reduction in Microbial Fuel Cells *Journal of Power Sources* 208 2012: pp. 170 – 175.
http://dx.doi.org/10.1016/j.jpowsour.2012.02.005

12. **Kapica, R., Redzynia, W., Tyczkowski, J.** Characterization of Palladium-Based Thin Films Prepared by Plasma-Enhanced Metalorganic Chemical Vapor Deposition *Materials Science (Medžiagotyra)* 18 2012: pp. 128 – 131.
http://dx.doi.org/10.5755/j01.ms.18.2.1913

13. **Kanaya, K., Okayama, S.** Penetration and Energy-Loss Theory of Electrons in Solid Targets *Journal of Physics D: Applied Physics* 5 1972: pp. 43 – 58.
http://dx.doi.org/10.1088/0022-3727/5/1/308

14. **Kazimierski, P., Jozwiak, L., Sielski, J., Tyczkowski, J.** Cobalt Oxide-Based Catalysts Deposited by Cold Plasma for Proton Exchange Membrane Fuel Cells *Thin Solid Films* 594 2015: pp. 5 – 11.
http://dx.doi.org/10.1016/j.tsf.2015.10.006

15. **Biesinger, M.C., Payne, B.P., Grosvenor, A.P., Lau, L.W.M., Gerson, A.R., Smart, R.St.C.** Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Cr, Mn, Fe, Co and Ni *Applied Surface Science* 252 2011: pp. 2717 – 2730.
http://dx.doi.org/10.1016/j.apsusc.2010.10.051

16. **Yamashita, T., Hayes, P.** Effect of Curve Fitting Parameters on Quantitative Analysis of $Fe_{0,94}O$ and Fe_2O_3 using XPS *Journal of Electron Spectroscopy and Related Phenomena* 152 2006: pp. 6 – 11.
http://dx.doi.org/10.1016/j.elspec.2006.02.002

17. **Yamashita, T., Hayes, P.** Analysis of XPS Spectra of Fe^{2+} and Fe^{3+} Ions in Oxide Materials *Applied Surface Science* 254 2008: pp. 2441 – 2449.
http://dx.doi.org/10.1016/j.apsusc.2007.09.063

18. **McIntyre, N.S., Zetaruk, D.G.** X-ray Photoelectron Spectroscopic Studies of Iron Oxides *Analytical Chemistry* 49 (11) 1977: pp. 1521 – 1529.
http://dx.doi.org/10.1021/ac50019a016

19. **Grosvenor, A.P., Kobe, B.A., McIntyre, N.S.** Studies of the Oxidation of Iron by Water Vapour Using X-Ray Photoelectron Spectroscopy and QUASES *Surface Science* 572 2004: pp. 217 – 227.
http://dx.doi.org/10.1016/j.susc.2004.08.035