

MEA with carbon free Pt-Fe catalysts and gas diffusion layers for application in PEM water electrolysis

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Received September 10, 2012; revised November 15, 2012

Mono and bimetallic compositions containing Pt and Pt-Fe supported on Magneli phase titania (Ebonex®) are integrated in membrane electrode assemblies with novel carbon-free gas diffusion layers and investigated in relation to their electrocatalytic activity and stability toward the oxygen evolution reaction in PEM water electrolysis. The investigated Pt-Fe/Ebonex exhibits enhanced efficiency compared to pure Pt with the same catalytic loading due to formation of surface oxides and electronic hypo hyper-d-electron interactions between the hypo-d metallic components (Fe and Ti), on one hand and the hyper-d Pt, on the other hand. The utilization of the catalysts is assessed applying a repetitive potential cycling at varying scan rate to determine the morphology factor f , serving as a measure for the unusable part of the catalyst. The results obtained show that the part of the Pt-Fe/Ebonex not accessible for the electrochemical reaction, is less than that for the pure platinum catalyst. The Ebonex-based GDL has a good electrical conductivity and is more resistant to oxidation than a commercial carbon black GDL which has a positive impact on the stability of the catalyst, the oxygen electrode, and the MEA.

Keywords: PEM water electrolysis, oxygen evolution reaction, Pt, Fe, Ebonex, GDL

INTRODUCTION

The electrocatalysts play an important role in the electrochemical energy systems such as hydrogen generators based on electrolysis of water in polymer electrolyte membrane (PEM) cells. In this regard, the development of highly active and durable catalysts, particularly for the oxygen evolution reaction (OER) is one of the most important issues with great impact both on the efficiency and the cost of PEM water electrolysis (PEMWE). To date, Pt-based materials are the most successful PEMWE catalysts employed in the practice. However, even these expensive and highly active materials are not capable to accelerate significantly the naturally sluggish OER kinetics. There are intensive research efforts to reduce or replace Pt with less expensive metal alloys in form of nanoparticles [1-5]. One of the main approaches is the development of composite catalysts with increased activity through realization of synergetic effects between the metallic components of the catalyst and the catalytic substrate. In this way, partial or total replacement of Pt with cheaper metals can be achieved without sacrifice of OER efficiency.

Another successful approach to reduce the cost of catalysis is the dispersion of the catalytic nanoparticles on proper supports, ensuring highly developed active surface and thus, better utilization of Pt. It is commonly recognized that the supporting material plays a critical role in both the activity and durability of the catalyst. Carbon and graphite are the most widely used catalyst supports, offering excellent electrical conductivity and large active surface (up to 200-300 m².g⁻¹). However, the majority of the C-based supporting materials are not stable at the aggressive operating conditions of PEMWE anode (high anodic potentials, moisture, oxygen, enhanced temperature) which in turn often leads to gradual degradation of the anode and severe performance losses [6]. Therefore, in order to improve durability of PEM water electrolysis cells, it is necessary to explore novel more stable alternatives.

The gas diffusion layer (GDL) is another essential component of the polymer electrolyte membrane assembly. It distributes the reactant over the catalyst layer and conducts the electrons from the reaction sites to the outer electric circuit. Therefore, the structure of GDL is also essential for MEA performance.

It has been shown recently that nonstoichiometry Magneli phase titania is a good candidate as catalyst support. Our previous results

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have demonstrated that the partial substitution of Ebonex-supported Pt catalyst with Fe increases the mass activity toward oxygen evolution reaction (OER) in PEM water electrolysis. The supporting material of choice is known for its stable behaviour and good corrosion resistance at the high anodic potentials of intensive oxygen evolution and its ability to contribute to the catalytic efficiency via electronic interactions with the metallic components (the so called strong metal support interaction, SMSI) [7]. However, since these composite Ebonex-supported catalysts were spread onto carbon GDL, gradual degradation of the anode in the course of electrolysis was observed [8]. The objective of this work is to investigate the efficiency and reliability of Pt-Fe/Ebonex as anode catalyst integrated in MEA with a novel carbon-free GDL, prepared by mixing Ebonex powder with a hydrophobic agent polytetrafluoroethylene (PTFE, Teflon®).

EXPERIMENTAL

The synthesis of the chosen composite catalysts consisted in direct selective grafting of the metals from acetylacetonate precursors ($M((C_5H_7O_2)_n)_m$ or M-acac (M = Pt, Fe). The substrate used was a commercial Ebonex powder (non-stoichiometric titanium oxide with common formula Ti_nO_{2n-1}) with average particle size 5 μm . Before synthesis it was subjected to mechanical treatment in a planetary ball mill for 40h, resulting in reduced particle size and increased surface. The metallic part in each of the catalysts was 20 wt. % while the Pt:Fe weight ratio in the precursors was 1:1. The preparation procedure included two steps. The first one was the pretreatment of the support and the precursors using magnetic stirrer and ultrasonic bath, their mixing and heating at temperature 60°C until a fine gel was obtained. In the second step of the synthesis, the mixture was heated in inert atmosphere at temperature at 200 °C (for Pt/Ebonex) and 250°C (for Pt-Fe/Ebonex. The reduction atmosphere was 100% H₂ and 95% Ar + 5% H₂, respectively.

The composition, morphology and surface structure of the prepared materials were studied by bulk and surface analysis, such as EDX, XRD, and SEM. The catalysts composition was examined by energy-dispersive X-ray spectroscopy (EDX) as a part of scanning electron microscope appliance. XRD spectra were recorded by X-ray diffractometer Philips APD15. The diffraction data were collected at a constant rate of 0.02 °.s⁻¹ over an angle range of $2\theta = 10 - 90$ degrees. The size of Pt

crystallites was determined by Scherrer equation [9]. The morphology and surface structure were studied by scanning electron microscopy (SEM) using a ZEISS GEMINI 982 microscope with an acceleration voltage 10 kV.

The electrochemical tests were performed on membrane electrode assemblies (MEAs) with a commercial polymer membrane Nafion 117 (Alfa Aesar), as an electrolyte. MEA was prepared by hot pressing of the electrodes for hydrogen and oxygen evolution on both sides of the membrane using a 5% Nafion solution as a binder. The electrodes with geometric area of 0.5 cm² had a double layered structure, consisting of a hydrophobic backing layer (GDL) and an active catalytic one. The synthesized Ebonex-supported catalysts were used to prepare the electrode for the oxygen evolution reaction (OER). A commercial E-TEK catalyst containing 20% Pt on carbon support was used for the reference (RE) and the hydrogen (HE) electrodes.

The catalytic layers were spread upon the backing one as an ink (catalyst particles mixed with diluted Nafion ionomer) at several steps as after each one the electrode was dried for 30 min at 80°C. The procedure was repeated until a metal loading of 0.5 mg.cm⁻¹ was reached. The gas diffusion layer for the anode was prepared mixing Ebonex with 30 wt.% Teflon emulsion as described elsewhere [10].

The performance characteristics of the prepared MEA were investigated in a self made laboratory PEM electrolytic cell, consisting of two gas compartments where hydrogen and oxygen evolution take place, separated by the membrane electrode assembly under study. A reference electrode was situated in the hydrogen evolution compartment. The catalytic activity of the prepared catalysts was studied using the techniques of cyclic voltammetry and steady state polarization at temperatures of 20°C and 80°C. All electrochemical measurements were carried out with a commercial Galvanostat/Potentiostat POS 2 Bank Elektronik, Germany.

RESULTS AND DISCUSSION

The XRD spectra of the synthesized Pt/Ebonex and Pt-Fe/Ebonex catalysts are presented in Figure 1. For easier phase identification the spectrum of the Ebonex support is also included. In all spectra the characteristic peaks of the Magneli phase titanium oxide are registered. The typical fcc Pt peaks that appear on the spectrum of the pure Pt/Ebonex shift significantly to higher diffraction angles with Fe addition. The new positions are closer to the PtM₃

crystal phases than to PtM (M=Fe) [11]. The cell parameter decreases from 3.916 Å for Pt/Ebonex to 3.769 Å for Pt-Fe/Ebonex (Table 1).

Table 1. Calculated Pt crystallite size and cell parameters

Sample	Pt/Ebonex	Pt-Fe/Ebonex
Crystallite size D_{111} , nm	14	6
Pt cell parameter, Å	3.916	3.769

The results indicate that most of Fe atoms are incorporated in the Pt crystal cell. Additionally, Fe_3O_4 phase is also identified.

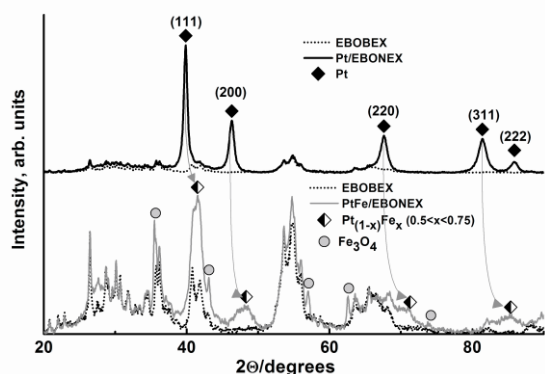


Fig.1. XPD spectra of the composite catalysts

SEM images of the investigated catalysts are presented in Figure 2. It can be seen that the catalytic particles are uniformly distributed on the Ebonex- surface. There is a correlation between the results of the XRD spectra and SEM images. For Pt/Ebonex (Fig. 2a) the size of Pt- particles is larger than this of Pt-Fe (Fig. 2b). Moreover Pt-Fe particles are less contrast due to the presence of Fe_3O_4 phase of the surface.

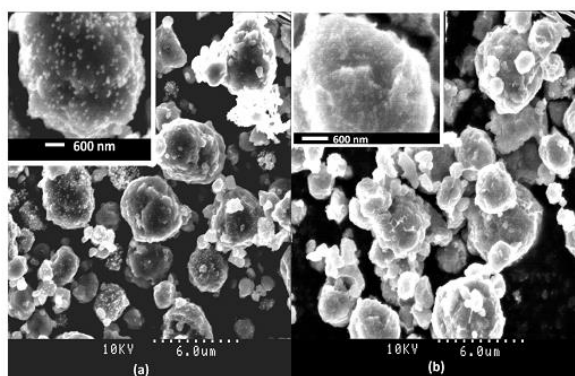


Fig. 2. SEM images of the composite catalysts: (a) Pt/Ebonex; (b) Pt-Fe/Ebonex

The composition of the synthesized materials was determined by EDX analysis and is presented in Table 2.

Table 2. EDX data for Pt/Ebonex and Pt-Fe/Ebonex

Catalyst	Pt/Ebonex		Pt-Fe/Ebonex	
	Weight %	Atomic %	Weight %	Atomic %
Ti	76.8	94.6	81.7	88.3
Pt	23.2	5.3	8.0	2.2
Fe	-	-	10.3	9.5

The determined Pt:Ti ratio in Pt/Ebonex is 0.23:0.77. The metallic part in Pt-Fe/Ebonex (Pt and Fe) is around 18 wt. % and the ratio between both metals is Pt:Fe \approx 0.8:1, i.e. almost identical to the ratio of both metals in the precursors. The cyclovoltammetry tests at temperature of 20°C were performed to obtain a qualitative information about the nature of the processes occurring on the catalyst surface (Fig.3).

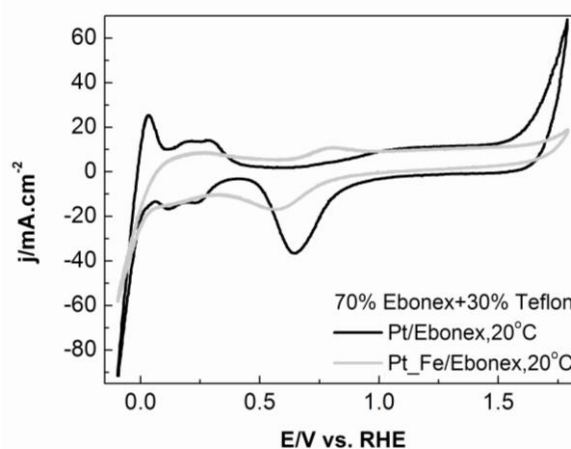


Fig.3. CV curves of Pt/Ebonex and Pt-Fe/Ebonex at 20°C and 100 mV.s⁻¹

On the CV curve of Pt/Ebonex all current peaks typical for Pt are well represented at the corresponding potentials in the hydrogen and oxygen regions. The shape of the curve is characteristic for an electrode with comparatively low porosity and a crystalline Pt catalyst with a prevailing (111) orientation [10]. At the same time, the characteristic anodic current peak at about 0.7-0.8V which almost always presents on CVs of electrodes with carbon-based GDLs does not appear in this case. The CV of the Pt-Fe/Ebonex shows two nearly reversible anodic and cathodic peaks situated in the potential range 0.75 – 0.80 V. These peaks are prescribed to the redox Fe^{3+}/Fe^{2+} transition. Their existence corresponds well with the results from XRD and the previously published XPS analysis [8], indicating an existence of Fe_3O_4 phase.

One of the goals in this study was to estimate the real active surface area of the anode when the conventional carbon based GDL in the MEA is replaced by GDL consisting of Magnelli phase

titanium. This was done determining the value of morphological factor (f) which is a measure for the unusable part of the catalyst. The approach, firstly suggested by de Silva is based on a repetitive potential cycling in the water window potential range (0 - 1.8 V) at varying scanning rate (5 – 300 $\text{mV}\cdot\text{s}^{-1}$), followed by determination of the anodic current density (j_a) at fixed potential, just before the beginning of intensive oxygen evolution [12]. Fig 4 presents the j_a/v plot of both catalysts. As seen, there are two linear sections with different slopes at low and high potential scan rates. This is an indication that at high rates, respectively at the high operative overvoltages, part of the catalytic loading is not used for the electrochemical reaction of interest. The determined morphological factors are 0.725 for Pt/Ebonex and 0.570 for Pt-Fe/Ebonex. These values are significantly higher than those for Pt/Ebonex catalyst integrated in MEA with GDL containing carbon black Vulcan XC72 [13]. The corresponding utilization of platinum in Pt/Ebonex is only about 30%, while the morphological factor for the bi-metallic catalyst indicates a slightly better utilization. The results can be explained with the low surface area of the catalysts, spread on GDL with insufficient porosity.

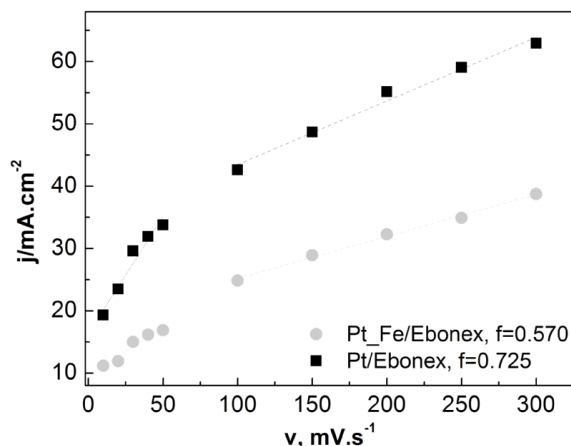


Fig. 4. Dependence of current density j_a at 1.6 V on the potential scan rate v

Figure 5 shows the results obtained from polarization experiments carried out at the typical PEMWE working temperature of 80°C. It should be noted that the content of Pt in the bimetallic Pt-Fe/Ebonex is essentially reduced compared to pure Pt/Ebonex, leading to much lower noble metal loading. That is way, for better comparison the anodic current of the oxygen evolution reaction was normalised relative to the Pt content and presented as mass activity, $j_m / \text{mA}\cdot\text{mgPt}^{-1}$.

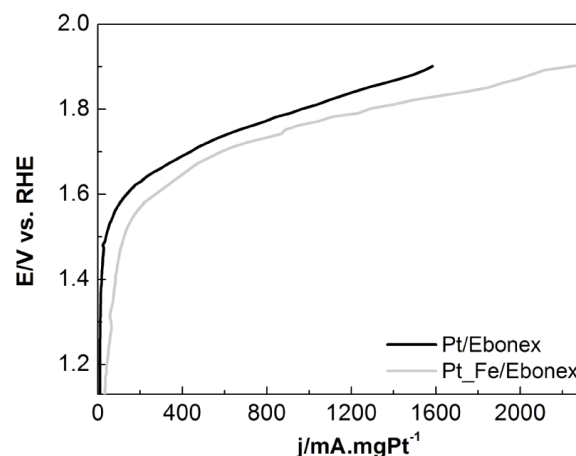


Fig. 5. Polarization curves of Pt/Ebonex and Pt-Fe/Ebonex at 80°C and scan rate $1 \text{ mV}\cdot\text{s}^{-1}$

The polarization curves demonstrate an enhanced efficiency of the binary Pt-Fe/Ebonex. It can be seen that the OER on the bimetallic Ebonex-supported catalyst starts at lower potentials compared to pure Pt. Similarly, an improved efficiency of OER in presence of Pt-Fe/Ebonex was found previously when these catalysts were integrated in MEA with carbon-based GDL. The effect was prescribed to occurrence of hypo-hyperd-electron interaction between Pt and Fe, leading to changes in the electron density of Pt d-orbital [8]. The data in Table 1 show that in the recent case, structural effects and geometry factors (smaller particle size, respectively the higher active surface area available for the electrochemical reaction) also contribute to the increased efficiency of Pt-Fe/Ebonex. An additional positive effect of the second metallic component, related to the cost of catalysis, is the nearly double reduction of Pt-loading.

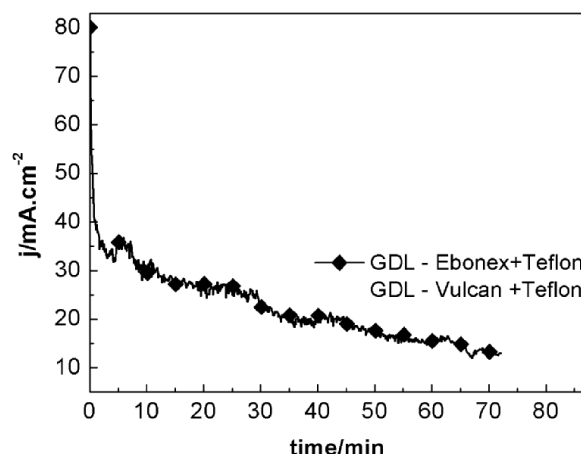


Fig. 6. Potentiostatic polarization curves obtained at 1.8V and 80°C

Having in mind the stable behaviour and good corrosion resistance of Ebonex at the high anodic

potentials of intensive oxygen evolution it was to be expected that the replacement of carbon in the GDL with Ebonex should increase additionally the anode stability and thus, the MEA durability. In the research presented herein, this effect was verified. It is illustrated in Fig. 6, presenting durability tests of anodes with identical catalytic layers spread on different (carbon- and Ebonex-based) GDLs.

The results confirm the suitability of Ebonex as a reliable electrode material at aggressive operative conditions of intensive oxygen evolution, moisture, and high temperature. This conductive oxide is not only an attractive alternative of carbon as catalytic support but can be also considered as a promising material for fabrication of gas diffusion layers with specific application in PEMWE.

CONCLUSIONS

The bimetallic Pt-Fe catalyst dispersed on mechanically treated Ebonex support and integrated in anode with a carbon-free GDL possess higher mass activity toward oxygen evolution in PEM water electrolysis than pure Pt, resulting from realization of electronic interactions between the components of the catalyst and geometry factors related to the size of the catalyst crystallites, the increased active surface, and the improved catalyst utilization. A realization of synergetic effect as a result of hypo-hyper-d-electronic interactions between the catalyst and the support, which further increases the OER efficiency, is also assumed. The used newly developed Ebonex-based GDL is resistant to oxidation and degradation phenomena which has an additional positive impact on the stability of the anode and durability of the MEA

Acknowledgment: The authors would like to acknowledge the financial support of Bulgarian Ministry of Youth, Education and Science, project BG 051PO001-3.3.05/0001, contract № DO2 –552 for dissemination of the research results.

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МЕП С НЕСЪДЪРЖАЩИ ВЪГЛЕРОД Pt-Fe КАТАЛИЗАТОР И ГАЗОДИФУЗИОНЕН СЛОЙ ЗА ПЕМ ВОДНА ЕЛЕКТРОЛИЗА

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Постъпила на 10 септември 2012 г.; Коригирана на 15 ноември, 2012 г.

(Резюме)

Моно- и биметални композиции, съдържащи Pt и Pt-Fe върху носител Ебонекс са интегрирани в мембранни електродни пакети (МЕП) с нов, несъдържащ въглерод газодифузионен слой. Изследвани са тяхната електрокаталитична активност и стабилност по отношение на реакцията на отделяне на кислород в ПЕМ водна електролиза. Синтезираните Pt-Fe/Ebonex катализатори показват увеличена ефективност в сравнение с чистата Pt при едно и също каталитично натоварване, дължащи се на формиране на повърхностни оксиди и hypo hyper-d-електронни взаимодействия между hypo-d металните компоненти (Fe и Ti) от една страна и hyper-d Pt от друга. За оценка на използваемостта на катализатора е изчислен морфологичния му фактор (f) чрез снемане на циклични криви в една и съща потенциална област при различни скорости на сканиране на потенциала. Резултатите показват, че недостъпната за електродната реакция повърхност за Pt-Fe/Ebonex е по-малка от тази за катализатора, съдържащ чиста платина. Газодифузионният слой, базиран на Ебонекс, има добра електропроводимост и е по-устойчив към окисление спрямо комерсиалния, съдържащ въглен, което влияе положително върху стабилността на катализатора, кислородния електрод и МЕП.