Palladium-based electrocatalysts for PEM applications

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ABSTRACT:
The goal of present study is development and investigation of nano-structured Pd-based electrocatalysts for hydrogen oxidation and proton reduction in proton exchange membrane (PEM) fuel cells and electrolyzers. Electro-active metallic structures were obtained by chemical reduction of precursor salts (including on Vulcan XC-72 carbon carrier) using ethylene glycol with addition of formaldehyde or using borohydride. Alternatively, Pd nano-clusters have been obtained from chemical reduction of precursor salts in perfluorinated polymer Nafion® membrane. Using the synthesized Pd-based catalyst membrane-electrode assemblies (MEAs) have been prepared and successfully tested in single fuel and electrolysis cells. Comparison of MEAs performances based on Pt, PtPd- and Pd-based electrocatalysts were provided. The present study demonstrates the principal possibility of partial or total replacement of the Pt by the Pd on the hydrogen electrode of PEM systems.

KEYWORDS: Palladium/carbon; Electrocatalyst; Fuel cell; Electrolyser; Proton exchange membrane (PEM).

1. Introduction

Fuel cells and electrolyzers based on PEM technology are being developed worldwide as high effective and environmentally-friendly energy conversion devices both for mobile and stationary application. One of the main components of these systems responsible for theirs efficiency and cost is the electrocatalytic layer. Pt is widely used as electrocatalyst in R&D programs on PEM fuel cells and water electrolyzers. But because of elevated price and limited resources, Pt cannot be used for large-scale applications and alternative materials are needed.

One of the ways for cutting down the Pt consumption in PEM-systems is to reduce metal loadings [1, 2]. Other ways deals with development of biological catalysts [3, 4], non-platinum metal catalysts, for example, based on porphyrins of metals [5-7] or mixed catalysts with reduced Pt content, mainly PtRu [8-10] and PtSn [11] (for fuel cells) and Ru, Ir and theirs oxides and alloys [12-15] (for electrolyser). Pd, which is more abundant than Pt, has been less extensively studied for such applications despite interesting electrocatalytical properties. For example, preliminary tests have shown that Pd deposited onto carbon nanotubes exhibits a high catalytic activity for the oxidation of hydrazine [16, 17]. In paper [18] Pd-based structures on activated carbon and Vulcan XC-72 (2 and 4 wt%) were synthesized, electrochemically characterized and tested on the cathode of PEM fuel cell. In Ref. [19] PtPd/C-based anode catalysts for direct ethanol fuel cells were fabricated and characterized. In Ref. [20] electrocatalysts based on Pt and Pd on charcoal have been prepared and tested on the anodic side of PEM fuel cells. Evaluation of electrochemical activity of Pd catalysts on carbon in alkaline solutions for the oxidation of hydrogen, methanol, formaldehyde and ethylene glycol and reduction of oxygen was done in [21]. In Ref. [22] Pd was tested in anodic and cathodic conditions of PEM electrolyser.

In the present study, nano-structured Pd-based catalysts have been developed and tested, both for hydrogen electro-oxidation and electro-evolution in PEM-systems.
2. Experimental

2.1. Catalyst synthesis

Pt and/or Pd catalysts were synthesized in the form of metal nano-particles on Vulcan XC-72 carbon carrier (SBET=250 m²/g) using chemical reduction of Pt or Pd complexes by means of ethylene glycol with addition of formaldehyde. The simultaneous sorption/reduction technique briefly explained below was used. The required amount of precursor (0.1 M H₂PtCl₆ or PdCl₂) and suspension of bi-distilled water, 2-propanol and Vulcan were mixed, the pH of the mixture was conditioned up to 8 using Na₂CO₃ solution. Suspension was added to ethylene glycol, after that formaldehyde was added dropwise. The temperature of the obtained mixture was kept constant at 95°C during 2 hours and after the heating was switched off. After 12 hours, the excess of the solution was poured out and the deposit (Pt or Pd on Vulcan) was washed off (8-10 times) by decantation method in bi-distilled water. Finally, the synthesized catalyst was dried up and activated in Ar-H₂ atmosphere.

Pt, Pd and Ir metal black were synthesized using sodium borohydride as reducing agent. For example, for Ir-black synthesis pH of H₂IrCl₆ water solution was conditioned up to 13-13.5 by addition of KOH. Then to this mixture NaBH₄ solution in 1 M NaOH was added at room temperature and continuous agitating. Agitating of a reactionary mixture proceeds before the termination of gas evolution. Then a deposit is washed by a decantation method up to achievement of pH of drain solution 6-6.5. The washed metal catalyst is dried up at temperature 60-70°C.

A number of electrocatalysts were synthesized using the above described techniques. In particular, using simultaneous sorption/reduction techniques, Pt₄₀/Vulcan-XC72, Pt₃/Pd₄₀/Vulcan-XC72 and Pd₄₀/Vulcan-XC72 catalytic structures have been prepared (where 40 is amount of the metal in wt %).

Alternatively, in situ Pd nano-clusters have been obtained from chemical reduction of precursor salts in perfluorinated polymer materials such as Nafion® membrane (SEM picture is shown on Fig. 1). This technique is used for the preparation of sup-nanometer range Pd particles. Preliminary tests have been made concerning hydrogen evolution on these particles and full results will be presented elsewhere.

Fig. 1. SEM picture of Nafion-embedded nano-Pd particles (INPG, Grenoble).
2.2. Characterization of electrocatalysts

The electrochemical characterization of catalysts was made using cyclic voltammetry. The working electrode was a porous titanium disk of 0.4 cm² area with an electrocatalytic layer (catalyst with 5% wt of ion-exchange polymer) sprayed onto it. Working electrode with electrocatalytic layer was installed into a three-electrode cell. The reference electrode was saturated silver-silver chloride electrode (SSCE), platinum wire was used as the counter electrode. Experiments were made in 1M H₂SO₄ solution in bi-distilled water. Argon was bubbled through the cell in order to eliminate the influence of oxygen dissolved in electrolyte and to mix the solution. Potentiodynamic measurements were programmed and conducted by the potentiostat (Solartron 1285). Preliminary cleaning (ca. 10 minutes) of the electrode surface using anode-cathode activation process from $E = -0.2$ to $+1.1$ V vs. SSCE was applied before each experiment in order to obtain stable area and shape of hydrogen part of the potentiodynamic curve. The curves were recorded at 25°C with cycling of the potential from -0.17 up to +1.20 V (vs. SSCE) with a scan rate of 20 mV s⁻¹ (this rate allows to obtain clear peaks of hydrogen adsorption and desorption).

2.3. Preparation of the MEAs

Prepared electrocatalysts were tested as components of electrocatalytic layer for a hydrogen electrode of PEM fuel cell and electrolyser. Nafion®-1135 membrane preliminary washed within 10% HCl, 1 M KOH and deionised water (in order to remove various impurities) was used as membrane material to prepare the MEAs for fuel cell. MEAs with 25 cm² operating area have been prepared using the synthesized Pt40/Vulcan-XC72, Pt1Pd140/Vulcan-XC72 and Pd40/Vulcan-XC72 catalysts for anode. Pt40/Vulcan-XC72 with 10% wt of PTFE was used on a cathode in all cases. The catalytic composition for anode and cathode contained 15% wt of the ion-exchange polymer (with respect to the weight of catalyst) and was applied onto Nafion membrane by spray technique. Metal loading for anode and cathode was 0.35 mg cm⁻². Standard carbon paper Sigracet 10bb with micro-porous sub-layer has been used as gas diffusion electrodes. Formation of MEAs was finalized by a method of a hot pressing at t=120°C, p=50 kg cm⁻² and 5 min of pressing time. The MEAs evaluation was carried out using Fuel Cell Test Station (Fuel Cell Technologies, Inc.).

For electrolyser Nafion 115 membrane was used. Pt or Pd loading for the cathode was 0.7 mg/cm². As an anode catalyst Ir-black (2.0 mg/cm²) was applied. As current collectors, preliminary washed porous titanium sheets with thickness 850 microns and porosity ca. 30% have been applied. Anode water supply was organized.

3. Results and discussion

3.1. Parameters of the synthesized electrocatalysts

Cyclic voltamperograms of 0.4 cm² electrodes based on Pt40/Vulcan XC-72, Pt1Pd140/Vulcan XC-72 and Pd40/Vulcan XC-72 catalysts prepared using simultaneous sorption/reduction technique are shown on Fig. 2. The curves for platinum- and palladium-based electrodes have the forms typical for these metals. The difference of the potentiodynamic curve for Pt1Pd1 catalyst specifies on the formation of an alloy of these metals. This fact has been proved by the x-ray analysis as well.
Fig. 2. Cyclic voltammograms (20 mV s$^{-1}$) of electrodes based on synthesized catalyst. 1 – Pt40/Vulcan-XC72, 2 – Pt$_{0.1}$Pd$_{0.1}$/Vulcan-XC72 and 3 – Pd40/Vulcan-XC72.

Cyclic voltammograms were employed to obtain the electrochemical active surface area (EAS) of synthesized catalysts (see the Table 1). The EAS of the platinum catalyst was determined using the coulombic charge for hydrogen desorption ($Q_H$). Calculation of the charge $Q_H$ was carried out using the method described in [23-25] by integration of hydrogen part of potentiodynamic curve and adjusting this value to charging of carbon substrate $Q_C$ (capacitance component): $Q_H = Q_S - Q_C$. Determination of EAS for palladium-based catalyst was done using the peak of chemisorbed oxygen reduction, the adjusting to a charge of a carbon substrate was employed as well. For platinum-palladium catalyst the EAS was obtained as the mean value between the amounts of charge corresponding to hydrogen and oxygen peaks. The average size of metal particle in electrocatalysts was estimated using electronic microscopy (see Table 1).

Table 1. Characteristics of synthesized catalysts.

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>EAS, m$^2$ g$^{-1}$</th>
<th>Particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt40/Vulcan-XC72</td>
<td>44 ± 4</td>
<td>6.4 ± 0.9</td>
</tr>
<tr>
<td>Pt$<em>{0.1}$Pd$</em>{0.1}$/Vulcan-XC72</td>
<td>39 ± 4</td>
<td>9.2 ± 1.3</td>
</tr>
<tr>
<td>Pd40/Vulcan-XC72</td>
<td>33 ± 3</td>
<td>14.9 ± 2.1</td>
</tr>
<tr>
<td>Pt-black</td>
<td>30 ± 3</td>
<td>19.0 ± 2.7</td>
</tr>
<tr>
<td>Pd-black</td>
<td>26 ± 2</td>
<td>12.5 ± 1.8</td>
</tr>
</tbody>
</table>

The same methods were used to study parameters of catalysts synthesized with preliminary sorption of the precursor(s). These catalysts, contrary to the catalysts prepared using simultaneous sorption/reduction technique, have rather low specific surfaces (for example, 14 m$^2$ g$^{-1}$ for Pd40/Vulcan-XC72). One can suppose that preliminary sorption results to autocatalytic growth of particles with formation of theirs agglomerates during synthesis.
It is remarkable that using simultaneous sorption/reduction technique, the EAS of obtained catalysts increase significantly. For example, Pd40/Vulcan-XC72 catalysts synthesized using this technique have specific surfaces of 33 m$^2$ g$^{-1}$ (see Table 1). In our opinion the exclusion of preliminary precursor(s) adsorption on the carrier avoid the aggregating of the synthesized particles during precursor reduction and results in increasing of catalyst active surface.

In general, the obtained results show that reduction of Pd and/or Pt precursor salts using ethylene glycol with addition of formaldehyde and polyvinylpyrrolidone is a promising method for the preparation of electrocatalysts.

Potentiodynamic curves obtained for Pt- and Pd-black synthesized using boron hydride are shown on a Fig. 3.

![Cyclic voltammograms (20 mV s$^{-1}$) of electrodes based on synthesized catalyst. 1 – Pt-black; 2 – Pd-black.](image)

**Fig. 3.** Cyclic voltammograms (20 mV s$^{-1}$) of electrodes based on synthesized catalyst. 1 – Pt-black; 2 – Pd-black.

### 3.2. Results of MEA tests

The synthesized catalysts were used for fabrication of anodes for MEAs. Using these MEAs single fuel cells were assembled and tested, the results for catalysts fabricated using simultaneous sorption/reduction technique are presented on Fig. 4. Fuel cell performance obtained with MEA using mixed Pt$_x$Pd$_{1-x}$ catalyst is very similar to one on the basis of pure Pt on carbon catalyst. In particular, at the operating voltage of ca. 0.7 V the performances of both MEAs are the same. Thus, we have shown an opportunity of partial replacement (at least 50% in tested conditions) of the Pt by the Pd on the hydrogen electrode of PEM fuel cell without loss of performances.
Fig. 4. Current-voltage performances of single fuel cells with MEAs fabricated using Pt, Pt-Pd, and Pd-based anode catalysts prepared by simultaneous sorption/reduction technique.

Anode catalyst: 1 – Pt40/Vulcan-XC72; 2 – Pt-Pd40/Vulcan-XC72 and 3 – Pd40/Vulcan-XC72.
Cathode catalyst: Pt40/Vulcan-XC72 + 10% wt of PTFE. Nafion®-1135 membrane.
Metal loading on cathode and anode 0.35 mg/cm².

Operating conditions: Hydrogen and oxygen flow rates of 600 ml min⁻¹. Air flow rate 3000 ml min⁻¹.

Fuel cell fabricated with MEA on the basis of pure Pd on carbon catalyst demonstrates performance, which is slightly lower in comparison with pure Pt on carbon catalyst. For example, at operating voltage of 0.7 V the current density of MEA with Pd catalyst is about 250-300 mA cm⁻² less in comparison to fuel cell with pure Pt on carbon catalyst. It is additional confirmation of the possibility to replace the Pt by the Pd on the anode electrode of PEM fuel cells.

The difference between performances of tested MEAs is roughly proportional to the difference in EAS of prepared electrocatalysts, which is caused by the sizes of metal particles, see Table 1. The catalysts...
fabricated using preliminary sorption technique have significantly small values of EAS. As the consequence, fuel cells using these catalysts demonstrate performances which are significantly low to ones presented on Fig. 4. Thus, we have confirmed the essential influence of a technique of synthesis on metal particle size and EAS of catalysts and, thus, on the performance of fuel cells.

Characteristics of MEAs with catalysts prepared by simultaneous sorption/reduction technique were compared with MEAs on the basis of Pt$_x$Pd$_{1-x}$ (40% wt of metal on the carrier) prepared by the microemulsion method [20]. It can be noted, that MEAs prepared in this work have lower (about twice) total metal loading in comparison to ones studied in paper [20] and demonstrate higher performances. Underline also the difference in the thickness of membranes, which were used in [20] and in the present work for fabrication of MEAs. This comparison confirms the importance of the technique of catalyst synthesis and MEA fabrication on fuel cell performances.

The obtained with Pd catalysts performances of PEM fuel cells are comparable with the results obtained with conventional E-Tek MEA with platinum catalyst (for the same metal loading).

Volt-amperic curves of PEM electrolysers using Pt and Pd as cathode catalysts in a range of operating current densities (0.5-1 A/cm$^2$) practically coincide (see Fig. 5). The typical voltage of PEM electrolysis cell with Pd-based catalyst on the cathode is 1.65 V at a current density of 1 A/cm$^2$.

![Fig. 5. Comparison of the current-voltage performances of single electrolysis cell with MEAs using Pt and Pd-based cathode catalysts at 90°C and atmospheric pressure of gases. Solid polymer electrolyte is Nafion®-115 membrane. Cathode catalyst: Pt, Pt40/V, Pd, Pd40/V – 0.7 mg/cm$^2$; anode catalyst: Ir – 2.0 mg/cm$^2$.](image)

Tests of PEM cells on the basis of Pd catalysts during 80 hours have shown the acceptable stability of the performance.

4. Conclusions

Thus, as a result of the present work, Pd-based nano-structured electrocatalysts have been synthesized and characterized. It was shown that performance of PEM-systems containing the Pd electrocatalysts on hydrogen electrode is comparable to that on the basis of the Pt electrocatalysts.

The methods used in the present work for the synthesis of catalyst powder and for the preparation of MEAs allow us to obtain, with Pd as catalyst, the best fuel cell performances (even for lower metal loading) in comparison with previously published data. Thus, the present study demonstrates the principal possibility of partial or total replacement of the Pt by the Pd on the hydrogen electrode of PEM systems.

Acknowledgements

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References