OPTIMIZATION THE SYNTHESIS CONDITIONS USING SOL-GEL METHOD OF CATALYSTS MATERIALS FOR PEM WATER SPLITTING

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ABSTRACT

The Pt-nanomaterials on different supports (Vulcan+TiO\textsubscript{2}, and Ebonex) are synthesized at different conditions by sol-gel method. The influence of temperature and reduction atmosphere on structural and electrocatalytic properties toward oxygen evolution reactions (OER) in PEM electrolyzer is investigated. The best results are obtained for the catalyst prepared at 200\degree C and mixed reducing atmosphere (95 \% Ar + 5 \% H\textsubscript{2}). The enhanced catalytic activity is explained with the observed smaller Pt-crystallite size and respectively high active surface, participating in the reaction.

Keywords: Pt-nanomaterials, TiO\textsubscript{2} Ebonex, catalytic efficiency, PEM water electrolysis, oxygen evolution reactions.

INTRODUCTION

The proton exchange membrane water electrolysis (PEMWEs) is an efficient method to produce hydrogen with higher purity which offers several advantages over the traditional technologies like higher current density and compatibility with the renewable energy sources. The anodic reaction of oxygen evolution (OER) is of particular research interest since it is the main source of energy losses and electrode degradation problems [1, 2].

One way to enhance the catalytic activity is to increase the real surface area of the catalysts by lowering the particles size applying an appropriate method for their synthesis. Among the existing different preparation methods [3-11] the wet sol-gel method is one of the most effective [3, 4]. However, even for this technique the formation of large particles during some preparation steps, such as heat treatment and reduction conditions, is still a problem.

On the other hand, the dispersion of Pt on a suitable substrate has a significant impact on the catalytic efficiency. A promising alternative of the commonly used carbon substrates are some ceramics materials such as TiO\textsubscript{2} and non-stoichiometric Magneli phase titanium oxide (Ti\textsubscript{n}O\textsubscript{2n-1}) known under the registered trade name Ebonex (Ataverda Inc, UK). These materials when used as supports for Pt-catalysts provide a strong hypo-hyper-d-electron interaction, resulting in considerable increase of the catalytic activity [3, 12-14].

The conditions of the synthesis also play an important role over the formation and growth of the catalytic crystallites.

These considerations determined the aim of the recent work, namely - preparation of Pt nanosized electrocatalysts for PEM water electrolysis by sol-gel method using different catalysts supports (carbon black containing 20 wt. \% TiO\textsubscript{2} and non-stoichiometric titanium oxide Ti\textsubscript{n}O\textsubscript{2n-1} (Ebonex), mechanically activated) and optimisation the heat treatment and reducing conditions of the synthesis.

EXPERIMENTAL

Catalyst synthesis

The synthesis of the chosen composite materials consisted in direct selective grafting of platinum from acetylacetonate precursor (Pt[\(\text{C}_5\text{H}_7\text{O}_2\text{]_m}\) or Pt-
acac). The supports used were titanium dioxide and a commercial Ebonex powder. The titanium dioxide was preliminary impregnated upon a carbon black (Vulcan XC-72) powder using Ti-isopropoxide (Ti[OCH(CH₃)₂]₄) as a precursor. The Ebonex powder was subjected to mechanical treatment in a planetary ball mill for 40h. The content of TiO₂ in the first composite as well as the metallic part in each of the catalysts was 20 wt. %. The synthesis was carried out at 200 and 250°C. The reduction atmosphere was pure H₂ and a mixture of 95 % Ar + 5 % H₂. The preparation procedure was described in details elsewhere [4].

Physical Characterization

The phase composition, morphology and surface structure of the prepared materials were studied by XRD, TEM and XPS.

The X-Ray diffraction spectra were recorded by X-ray diffractometer Philips APD15 with Cu Ka radiation. The diffraction data were collected at a constant rate of 0.02 °s⁻¹ over an angle range of 2θ = 10 – 90 degrees. TEM investigations are carried on JEOL-200 CX transmission electron microscope.

The XPS of the samples were recorded with an ESCALAB MK II (VG Scientific, England) electron spectrometer. The photoelectrons were excited with a twin anode X-ray source using Al Kα (hν = 1486.6 eV) radiation. C 1s photoelectron line at 284.8 eV was used as a reference for calibration.

Laboratory PEM cell and test procedure

The electrochemical tests were performed on membrane electrode assemblies (MEAs), using a Nafion 117 membrane as an electrolyte. The catalysts under study were investigated as electrodes for the oxygen evolution reaction (OER), while a commercial E-TEK catalyst containing 20 wt. % Pt on carbon support was used to prepare both the hydrogen (HE) and the reference (RE) electrodes. The electrodes have a complex multilayered structure, consisting of gas diffusion, backing, and catalytic layers.

The performance characteristics of thus prepared MEA were investigated in a self made laboratory PEM electrolytic cell. It consists of two gas compartments where hydrogen and oxygen evolution take place, separated by the membrane electrode assembly under study. A reference electrode is situated in the hydrogen evolution compartment. The electrochemical behavior of the prepared Pt-composites on Pt/TiO₂+Vulcan and Pt/Ebonex supports was studied using the common electrochemical techniques of cyclic voltammetry and steady state polarisation at operating temperature of 20 and 80°C. All electrochemical measurements were carried out with a commercial Galvanostat/ Potentiostat POS 2 Bank Electronik, Germany.

RESULTS AND DISCUSSION

Structural analyses

Generally, the rate of a chemical reaction depends on the concentration of reactants or/and products as well on the process parameters such as temperature T, pressure P etc.

In our case, the heat treatment of the prepared Pt-catalysts in a reducing atmosphere is a solid state–gas reaction. Therefore, the rate of Pt crystal growth depends first of all, on the concentration of the reducing gas. Secondly, according the formal kinetics the rate of the Pt crystal growth can be described with the equation:

\[ \frac{da}{dt} = k(T) f(\alpha) = A \exp(-E/RT) f(\alpha) \]  

where a is the degree of conversion, f(α) is a function, describing the reaction mechanism; T is the temperature; k(T)=Aexp(-E/RT) is the rate constant with Arrhenius
Taking into account the above, we carried out the study in two stages. First, we investigated the influence of the reduction atmosphere at constant temperature (250°C). The reduction procedure was performed in pure hydrogen and in a gas mixture 95% Ar + 5% H₂. Fig. 1 presents the normalized XRD spectra of the composite catalysts synthesized at different reduction gas flow.

The mixture of the hydrogen with argon leads to widening of the diffraction peaks (inset in Fig. 1), indicating a formation of smaller particles. This was confirmed by the values of Pt crystallites size determined by Scherrer equation [17].

\[
D = \frac{k \lambda}{\beta \cos \theta}
\]

(2)

where D is the average dimension of crystallites; k is the Scherrer constant in the range 0.85–1.0 in dependence on the crystal type (is usually assumed to be k≈0.9); \( \lambda \) is the X-ray wavelength; \( \theta \) is the Bragg angle and \( \beta \) is the peak broadening in radians.

The results obtained showed that in pure hydrogen the size of the Pt/EBONEX crystallites is around 20 nm, while in the mixed gas flow (95% Ar + 5% H₂) it falls down to 11-13 nm (Table 1).

As already mentioned another way to reduce the Pt particle size is to decrease the temperature of the heat treatment which in turn, should affect the value of the rate constant. To verify this, the tests in the reduction atmosphere producing smaller crystallites (95 % Ar + 5 % H₂) were carried out also at lower temperatures. The XRD spectra presented in Fig.2 show that the smallest crystals size was obtained for Pt/TiO₂+Vulcan (2-3 nm) followed by Pt/EBONEX (5-6 nm) catalysts, prepared at temperature of 200°C.

In Fig. 3 are presented TEM images of the composite catalyst Pt/TiO₂+Vulcan at different temperatures. A good correlation with the XRD results is observed. The titanium oxide deposited on carbon black is in amorphous state. The large specific surface area characteristic for carbon black is preserved.

The Pt-surface area is connected with the particle size by equation:

\[ S_p = \frac{6}{\pi D} \]

(3)

Table 1. Calculated Pt crystallites size and specific surface.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>synthesis conditions</th>
<th>D, nm</th>
<th>S, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/EBONEX</td>
<td>250°C, H₂</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>Pt/EBONEX</td>
<td>250°C, Ar+H₂</td>
<td>14</td>
<td>20</td>
</tr>
<tr>
<td>Pt/EBONEX</td>
<td>200°C, Ar+H₂</td>
<td>6</td>
<td>47</td>
</tr>
<tr>
<td>Pt/TiO₂+Vulcan</td>
<td>250°C, H₂</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td>Pt/TiO₂+Vulcan</td>
<td>250°C, Ar+H₂</td>
<td>13</td>
<td>22</td>
</tr>
<tr>
<td>Pt/TiO₂+Vulcan</td>
<td>200°C, Ar+H₂</td>
<td>3</td>
<td>109</td>
</tr>
</tbody>
</table>
where $S_{pt}$, $\rho$, $D$ are the surface area, the relative density, and the size of Pt particles estimated from full width of half maximum (FWHM), respectively. The higher surface area is obtained for the catalysts synthesized at lower temperature.

The XPS investigations confirmed the results published in our previous work [18] - the Pt is in metallic state with small amount of Pt$^{2+}$ and Pt$^{4+}$, while titanium is present only in one valence state (Ti$^{4+}$) for the catalyst Pt/TiO$_2$+Vulcan and in two valence states (Ti$^{3+}$ and Ti$^{4+}$) for Pt/Ebonex.

**Electrochemical investigations**

As an illustration of the influence of preparation conditions on the electrochemical behavior of the catalysts, in Fig. 4 are presented the cyclic voltammetry curves for the catalyst Pt/Ebonex at operating temperature $80^\circ$C typical for PEMWE.

The results suggest that Pt/Ebonex ($200^\circ$C, Ar + $H_2$) facilitates stronger the oxygen evolution reaction which starts at lower overpotentials and proceeds with higher rate compared to Pt/Ebonex ($250^\circ$C, $H_2$) catalysts with the same loading. There is a small difference in the character of both curves.

The quasi steady state polarization tests of the anodic partial electrode reaction involved in the electrolytic water splitting were performed for Pt/Ebonex catalysts synthesized under different conditions (Fig. 5).

The results show that the difference in the activity of both catalysts is essential as Pt/Ebonex ($200^\circ$C) (Ar+$H_2$)
is much more efficient. The demonstrated enhanced catalytic activity is entirely logical, having in mind the results from the physical analysis of the synthesized materials and can be explained with the smaller particle crystal size respectively, with the higher specific surface area of this catalyst.

CONCLUSIONS

The composition, morphology and surface structure of Pt-nanomaterials dispersed on different supports (Vulcan+TiO₂ and Ebonex) by sol gel synthesis performed at different conditions were studied by bulk and surface analysis. It was found that Pt is predominantly in metallic state. Smaller Pt-crystallite size and respectively, higher active surface were observed for samples prepared at 200°C under mixed (Ar + H₂) reducing atmosphere. The electrochemical tests proved that Pt/Ebonex (200°C) (Ar + H₂) facilitates stronger the oxygen evolution reaction which starts at lower overpotential and proceeds with higher rate compared to Pt/Ebonex (250°C, H₂) catalysts with the same loading. The improved catalytic activity was explained with the established higher specific surface area of this catalyst.

Acknowledgements

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REFERENCES


