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Investigations of mixed oxides Mg/Ni/Al(O) from layered double hydroxides as catalyst support for proton exchange membrane water electrolysis

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Various alternatives of electrocatalyst supports are being searched. The conformation of the multi-cationic Layered Double Hydroxides (LDHs) Mg/Ni/Al after calcination - mixed oxide Mg/Ni/Al(O) are proposed as advanced support for electrocatalysis. LDHs, a new class of basic mixed hydroxides exhibiting layered structure, proved to be good substrates to be loaded with noble metals and non noble metals, also having properties of electron donor promoters. The aim of this work is a characterization of the structure of Pt-catalysts appropriate for electrochemical water splitting. These catalysts are prepared by deposition of Pt on supports mixed oxides Mg/Ni/Al(O), obtained by calcination of multicationic LDH. These materials are characterized by means of structural (XRD, TEM) and electrochemical methods: cyclic voltammetry (CV) and steady-state polarization techniques, in view of their possible application as electrocatalytic support for oxygen evolution reaction in proton exchange membrane water electrolysis.

Keywords: catalyst support material, Pt_Mg/Ni/Al(O)**,** PEMWEs, oxygen evolution reaction, Pt

1. INTRODUCTION

The proton exchange membrane water electrolysis (PEMWEs) is efficient method to produce hydrogen with higher purity and it offers several advantages over the traditional technologies [1]. Even if the electrolyte and the membrane electrode assembly have been widely studied, degradation of the materials, especially the carbon supports of the electrode, and the high cost of the Pt loaded electrodes are now the new issues to overcome. Few researches have been carried out, aiming to replace the carbon support and decrease the Pt loading. It came out that using divers metal oxide powder as a support would significantly decrease the cost of the PEMWEs but also would increase its stability and thus the life time of the cell. Pt nanoparticles and their alloys are usually dispersed on porous carbon black (e.g., Vulcan XC–72) to function as PEMWEs anode and cathode catalysts, which are one of the most important and most expensive components in PEM water electrolysis. Suitable support materials must be electrically conductive and corrosion inert [2]. The big disadvantage of carbon is its lack of stability at high anodic potentials, where oxygen evolution takes place [3]. The stability of carbon support affects the loss of platinum surface area following both, the platinum particle sintering and the platinum release from the carbon support [4]. Therefore, various alternatives of electrocatalyst supports are being searched. A good candidate as a catalyst support could be a material which manifests the stability and the specific property - strong metal-support interaction (SMSI) effect [5–7], which presumed the lower Pt loadings and the greater efficiency. This fort interaction between support and particles is due to intensive electronic transfer. Surprisingly, interaction and cooperation between nanosized metal particles and basic supports have been scarcely investigated. A recent review considering the metal-support interaction ("electron transfer") and the metal-support cooperation ("metal-base bifunctional catalysis") has shown the great potential of the layered double hydroxides (LDH) as precursors of the metal particles on basic supports with very unique properties [8, 9]. LDHs of the general formula of $[M^{2+}_{1-x} M^{3+}_{x}(OH)_2][A^{n-}]_{x/n}.mH_2O$ can contain different M^{2+} and M^{3+} metal cations in their brucite-like sheets, and various A^{n-} charge-compensating anions in their interlayer space. LDH compounds easily decompose into mixed oxides of the $M^{2+}M^{3+}(O)$ type after calcination [10–12], these materials having both basic and redox functions as catalysts. Three general routes are available for synthesis of the LDHs precursors: first, the synthesis of the LDHs, containing M^{2+} and/or M^{3+}elements with redox behavior within the sheets;

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second, the exchange with anionic metal precursors of the desired metal in the interlayer space of the LDHs; and third, the deposition or grafting of inorganic or organometallic precursors onto the calcined precursor LDH. The choice of this material is based on its properties of an electron donor promoter. [13]. It is known also that LDHs are good precursors for loading noble metals and non noble metals [14]. The aim of this research is to investigate the possible apply of the LDHs materials as a support material of metal catalysts, used in PEMWEs. In this work we use the conformation of multi-cationic Layered Double Hydroxides LDHs NO_3 – Mg/Ni/Al after calcination – mixed oxide Mg/Ni/Al(O) which are proposed as advanced Pt catalyst support for electrocatalysis.

2. EXPERIMENTAL

2.1. Catalyst synthesis

The initial multi-cationic structure NO_3 – Mg/Ni/Al was synthesized by coprecipitation at constant pH (~11) of suitable amounts of $Mg(NO_3)_2.6H_2O$ (0.2 M), $Al(NO_3)_3.6H_2O$ (0.1 M) and $Ni(NO)_2.6H_2O$ (0.05 M) with a solution of NaOH (2.0 M). The addition of the alkaline solution was controlled by using a pH-STAT Titrino (Metrohm) apparatus to keep the pH constant. The suspension was stirred overnight at 80ºC for 17 h, and then the solid was separated by centrifugation, washed thoroughly with distilled water, and dried overnight at 80ºC. The support of mixed oxide Mg/Ni/Al(O) was obtained by calcination of multi-cationic LDH NO_3 – Mg/Ni/Al, at 450ºC for 5 hours under air. One part of the sample was impregnated by platinum (II) acetylacetonate using the sol-gel method to prepare supported Pt catalysts. These samples were gradually heated in hydrogen atmosphere until the the temperature of 240ºC was reached, than they were held for 2 h under these conditions, and gradually cooled. This first part of samples were hereafter labeled as Mg/Ni/Al(O) –Pt. Another part was kept without platinum impregnation, these samples were labeled as Mg/Ni/Al(O).

2.2. Electrode preparation

The electrodes have a complex multilayered structure, consisting of gas diffusion layer, catalytic nanoparticle mixture layer, and a support of mixed oxide Mg/Ni/Al(O). The last layer is made of a catalyst and support mixture, deposited on a thin carbon cloth, serving as a gas diffusion layer. The catalytic layer is spread upon the carbon cloth at several steps. After each step the electrode was dried for 30 min at ambient temperature and weighted using an analytical microbalance. The procedure has been repeated until a metal loading of 0.5 mg. cm^{-2} was reached. Then the electrode was hot pressed onto the PEM. The hot pressing is performed stepwise in the regime of gradual temperature and pressure increase, starting at 50°C and 6 kg. cm^{-2}, and ending at 120ºC and 12 kg. cm^{-2}, respectively.

2.3. Physical characterization

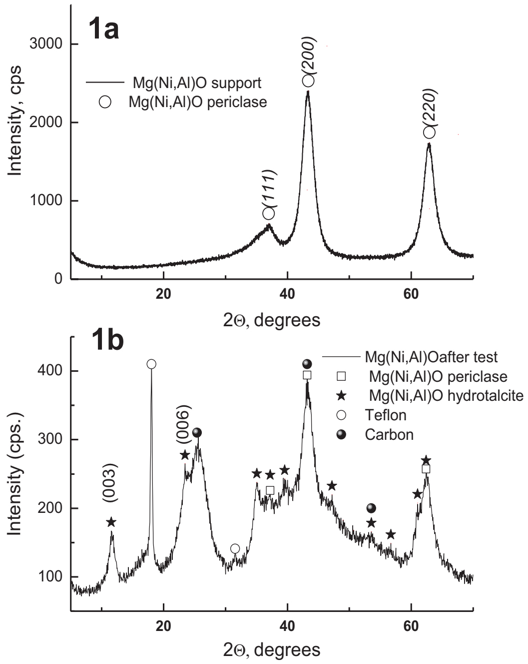
XRD patterns were recorded on a Bruker D8 Advance instrument using the Cu $K\alpha_1$ radiation (λ= 1.542 Å, 40 kV, and 50 mA). TEM analysis of samples was performed using a JEOL 1200 EXII microscope, operated at 80 kV on samples, previously calcined at 450ºC. Measurements of the reduced platinum particle sizes on several micrographs led to the determination of the mean particle sizes.

2.4. Electrochemical characterization

The catalysts under study are investigated as electrodes for the oxygen evolution reaction. The electrochemical tests were performed on membrane electrode assemblies (MEAs), using a Nafion 117 membrane as an electrolyte. The performance characteristics of thus prepared MEA were investigated in a self made laboratory PEM electrolytic cell. The electrochemical behavior of the prepared Pt_Mg/Ni/Al(O) –composites as catalysts for oxygen evolution reaction (OER) were studied and compared to that of the support Mg/Ni/Al(O) using the techniques of cyclic voltammetry and steady state polarisation. All electrochemical measurements were carried out with a commercial Galvanostat/ Potentiostat POS 2 Bank Electronik, Germany.

3. RESULTS AND DISCUSSION

The XRD analyst show that the support corresponds to Mg(Ni,Al)O periclase, (Figure 1a). The crystallite size is around 4.5 nm (Table 1). After the electrochemical test, the support partially reconstructed in layered structure of multicationic LDH (type hydrotalcite, Mg(Ni)–Al). Figure 2 presents the XRD spectra of the samples with different Pt-content (10% and 20%), deposited on Mg(Ni,Al)O periclase support. The average Pt-crystalline size on catalyst with 20% Pt is 14-17 nm, and the size does not change after electrochemical tests. For the sample with 10% Pt, the crystalline sizes are of 10-11 nm (Table 1). After the electrochemical tests (Fig. 2b), the diffraction peak disappears at around 63 degree.



Fig, 1. XRD spectra of catalyst support: a) before electrochemical and b) after electrochemical test.

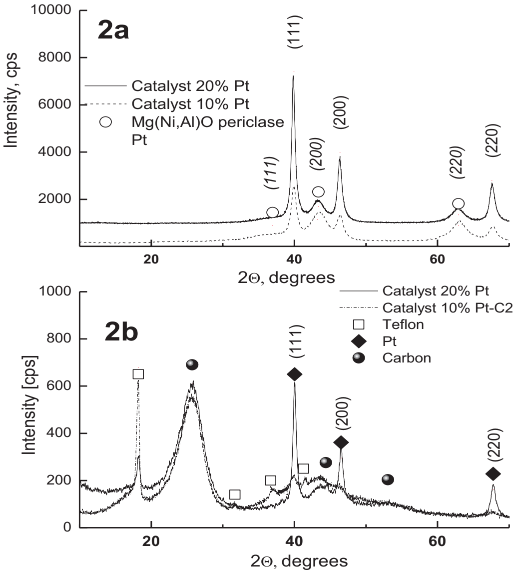


Fig. 2. XRD spectra of Pt catalyst a/ before and b/ after electrochemical test.

No intensive diffraction peaks were observed in the *x*-ray spectra of hydrotalcite. All this subjects the complementary analysis of the support structure after the electrochemical test. Our previous results showed that the CV-curves of Mg/Ni/Al(O) – substrate (without Pt) was active up to the 30th cycle, and then its activity dropped down sharply.

Table 1. Crystallite size of the Mg(Ni,Al)O-support, and Pt/Mg(Ni,Al)O catalysts

Sample	Crystallite size, nm	
Support	$D_{(200)}$	4.00
	$D_{(220)}$	5.00
Pt (20%)	$D_{(111)}$ $D_{(200)}$	17.00
		14.00
Pt (10%)	$D_{(111)}$	11.00
	$D_{(200)}$	10.00

This result is explained with the degradation of Mg/Ni/Al(O) or in other words, the reconstruction which was confirmed by the XRD patterns [15]. Similar effect was observed in the catalyst with 10% Pt. The anodic curves, corresponding to the oxygen evolution (Fig. 4), show that the catalytic activity of tested catalyst is lower. The best activity exhibits the electrode with a higher platinum content. This result may be associated with the XRD- results. The higher Pt-content prevents to a greater degree the reconstruction of the support. This may be due to the strong interaction between small Pt-particles and mixed oxide. The same results are observed for the Ni-catalyst based on LDH [16].

TEM

The materials were characterized by TEM in order to compare the size distribution of the metal particles before and after the electrocatalytic test (Figure 3).

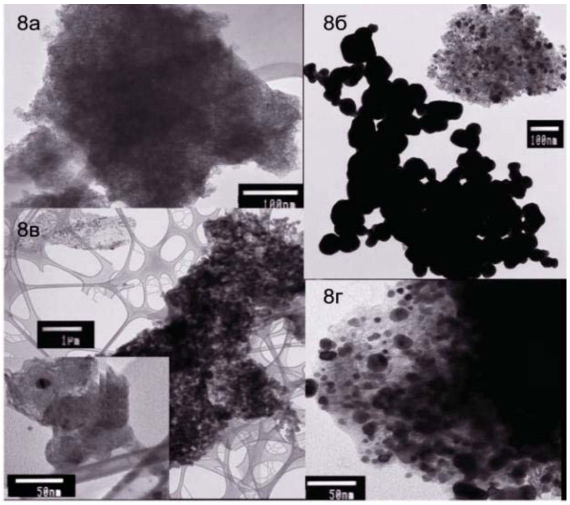


Fig. 3. TEM images:1a – support of Mg(Ni,Al)O periclase;1b – impregnated sample with Pt;1c - the sample after electrode preparation before electro-chemical test;1d – the electrode after electrochemical test.

These observations on the catalyst Pt-loading sample (0.5 mg.cm^{-2}) showed the formation of different-sized Pt- particles on the mixed oxide support (3–15 nm), while the massive clusters of Pt (23–115 nm) were formed outside of the support.

These results suppose the excess of platinum. They also allow us to compare the TEM images of the samples of Pt-catalyst before and after work of the electrode. The results show that Pt particles remain of the same size. Again, the control of the metal dispersion state may be due to the fort interaction between the support and the small particles.

3.3. Electrochemical characterization

The cyclovoltammetric experiments have been performed in the whole potential range between the hydrogen and the oxygen evolution. Our previous results showed that the CV curve of the Pt_Mg/Ni/Al(O) sample has the typical behavior of the monometallic platinum in regards to the hydrogen and the oxygen regions, and its character does not change with the cycling – it has clearly delineated the oxidation and the reduction peaks, and the double layer region. The CV-curves of Mg/Ni/Al(O) (without Pt) electrode have rather different profile, their peaks are not clearly defined. The electrode was active up to the 30th cycle, and then its activity dropped down sharply. This result can be explained with the degradation of Mg/Ni/Al(O) or in other words, with the reconstruction which was confirmed by the XRD patterns. In the presence of platinum, this effect is not observed and the electrode is stable [17].

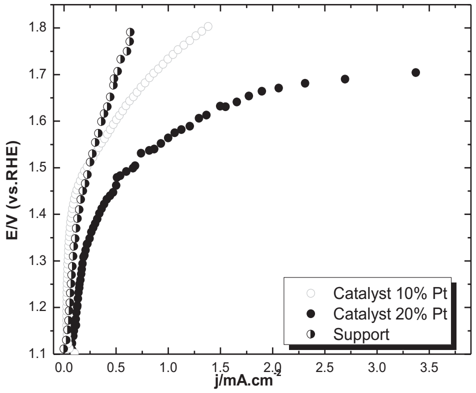


Fig. 4. Steady state polarisation curves at 80ºC.

Figure 4 shows the polarization curves. The polarization test showed the OER proceeds with a higher rate on the Pt_Mg/Ni/Al(O), compared to the none-containing platinum electrode. The curve demonstrates a stable behavior of the catalyst, due to the endurance of the substrate by these anodic potentials.

4. CONCLUSIONS AND PERSPECTIVES

It was shown that the preparation of catalyst leads to small Pt particles, supported on a Ni/Mg/Al/O mixed oxide matrix. The Pt particles have the same mean size of 3–15 nm before and after operation of the electrode. The massive clusters of Pt (23–115 nm), which were observed outside the support, suppose the excess of platinum which can be reduced for further work, and thus decrease the quantity of the noble metal (Pt) in the catalyst. The use of oxide mixed in LDHs leads to solids, exhibiting higher metal dispersion, and to stability of the particle size distribution under the electrocatalytic test. The solid, obtained from co-precipitated Ni/Mg/Al LDH calcinated, and the non impregnated reveals the interesting result of 170 cycles before the reconstruction of its structure. These Ni-containing materials offer interesting outlooks for electrocatalytic applications due to their better stability and higher conductivity. The main hindrances for the application of the mixed oxide Mg/Ni/Al(O) are in the first place the low electronic conductivity and secondly the memory effect which lead to reconstruction in the HDL layered structure. There is also a possibility of reducing the quantity of noble metals used (Pt-catalyst) or replaced by a none-noble metal. Further modifications in the support composition reveal an opportunity to increase its conductivity and its stability. The investigations showed that the conformation oxide of LDHs Ni/Mg/Al, can be successfully applied as an electrocatalyst supporting material in PEM water electrolysis. It was observed that strong connections between the metal particles and the support are established. The support has a beneficial influence on the particle-size.

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Изследване на смесени оксиди Mg/Ni/Al(O) получени от двуслойни хидроксиди като каталитичен носител за ПЕМ водна електролиза

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(Резюме)

Търсени са различни алтернативи за електрокаталитични носители. Кристалната конформация смесен оксид Mg/Ni/Al(O), получен чрез калциниране на нитратна форма на мултикатионен двуслоен хидрооксид (ДСХ) Mg/Ni/Al-NO3 - е разглеждан като перспективен носител за електрокатализа. ДСХ са клас от основни смесени хидрооксиди със слоестта структура, които се проявяват като добри носители за натоварване с благородни и неблагородни метали и притежават свойства на електронни донори. Целта на настоящата работа е охарактеризиране на структурата на Pt-катализатори, подходящи за електрохимично разлагане на вода. Тези катализатори са синтезирани чрез отлагане върху носители от смесени оксиди Mg/Ni/Al(O), получени при калциниране на мултикатионен ДСХ. Материалите са изследвани със структурни (XRD, TEM) и електрохимични методи: циклична волтаметрия (CV) и стационарна поляризационна техника, с оглед евентуалното им приложение като електрокаталитични носители по отношение на реакцията на отделяне на кислород при ПЕМ водна електролиза.

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