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CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

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ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE*

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Rare-earth / manganese oxide-based composites for oxygen reduction reaction

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Abstract

The main objective of this research is the development of catalytic materials based on a combination of metal-oxides with extremely low-loading of Pt for oxygen reduction reactions (ORR). Materials compared were La₂O₃ with 5 mass% loading of Pt (La₂O₃-Pt) and La₂O₃/MnO₂ multioxide based material with 5 mass% loading of Pt (LMO-Pt). The electrochemical characterization of the catalytic materials has been done using cyclic voltametry (CV), linear sweep voltammetry (LSV) and galvanostatic electrochemical impedanse spectroscopy (GEIS). It was proven that both synthesized catalytic materials were ORR-active. The ORR behavior indicated that La₂O₃-Pt electrode is significantly less active than LMO-Pt. The GEIS results showed that the ORR is complex electrochemical reaction, being electrochemically and diffusion controlled. Diffusion is of mixed character due to transport of O₂ molecule and chemical reaction of oxygen reduction reaction. O₂ diffusion is the dominant process for LMO-Pt catalytic materials, while chemical reaction is dominant process for La₂O₃-Pt electrolytic material.

Keywords: hybrid materials; manganese oxide; lanthanum oxide; Pt as catalyst; fuel cell; cathode reaction

Introduction

Modern society is facing problems caused by the dominant role of fossil fuels in global energy systems. The most important ones are the exponential growth of CO₂ emission (and other greenhouse gasses) in the atmosphere and accompanying climate changes, while economical and geo-political crises occasionally appear around the globe due to the limited supplies of fossil fuels [1]. Fossil fuels must be abandoned as the main energy carriers as soon as possible and substituted by renewables. The usage of hydrogen in fuel cells is one way to replace fossil fuels. Fuel cells use noble metals like platinum, so the challenge is to find a catalyst with performance as good as noble metals.

The complicated kinetics of the electrochemical oxygen reduction reactions (ORR) is detected as the main limitation [2]. Noble metals are found to be the best catalysts, but due to their cost and limited availability, the commercialization of these catalysts is impeded [3]. In the last decades, scientists are researching ways to reduce the loading of noble metal in the electrode material while having the same activity as bulk electrode for electrochemical reactions.

Nanoparticles with a combination of the different metal compounds were found to be a good strategic materials for electrode material with wanted performances. Transition metal oxides (TMO) like MnO₂ and Co₂O₃ have been researched because of their rich oxidation states, low cost and good environmental impact [4].

Lanthanum oxide (La_2O_3) is found to have excellent electronic, photocatalytic and electrocatalytic properties [5]. Despite its exceptional electronic structure, the single oxide has low electroconductivity. Due to stated fact, the hybrid composite material is being researched to combine characteristics of metals such as perovskite oxides with ABO_3 structure. Various perovskites have been researched such as LaMnO_3 , LaCoO_3 , LaNiO_3 , LaCrO_3 and LaFeO_3 [6]. But, the systematic design and comparison of metal oxide-based electrode materials are necessary because of various synthesis procedures, structures and combinations of metals. The aim of this paper was analysis and comparison of the lanthanum and manganese-based hybrid materials for ORR of reduced Pt loading. The electrode materials based on $\text{La}_2\text{O}_3/\text{MnO}_2$ (LMO) have been synthesized with the addition of Pt low loading to enhance the activity for ORR. Transition metal oxides are used as a base due to their double-role potential, one to stabilize catalyst carrier, while the other is participating in enhancing catalytic properties of noble metals.

Materials and methods

Synthesis

All the chemicals used were commercial Sigma-Aldrich PA.

La_2O_3 -Pt was prepared by adding stoichiometric amount of H_2PtCl_4 to La_2O_3 solution with ethylene-glycol in excess to obtain La_2O_3 with 5mass% of Pt. The solution was put into the microwave reactor for 1 minute at 700W.

LMO-Pt was made by mixing starting precursor solutions to give desired stoichiometric mole ratios La:Mn = 2:5. Ethylene-glycol was used in excess as reducing agent. Commercial La_2O_3 and KMnO_4 were used in such concentrations that they give mentioned La:Mn mole ratios. The chemicals were mixed with reflux and constant mixing of the mixture at a temperature of 100 °C for 3 hours. Afterwards, stoichiometric amount of H_2PtCl_4 was added to the solution to obtain LMO with 5mass% of Pt. The solution was put into the microwave reactor for 1 minute at 700W.

Electrochemical characterization

Electrochemical behavior was analyzed by cyclic voltammetry (CV), galvanostatic electrochemical impedance spectroscopy (GEIS) and linear sweep voltammetry (LSV). Measurements were done by a three-electrode cell system in 0,1 M solution of KCl. Counter and reference electrodes were platinum wire and $\text{Hg}|\text{Hg}_2\text{Cl}_2$, respectively. The working electrode was prepared by pipetting 30 μl of the desired solution on glassy carbon. The solution was made by mixing the powder with ultrapure water in concentration of 5 mg/ml. After the 2 hours of drying in the air, the electrode was pipetted with a 20 μl solution of Nafion and water in a ratio 1:100, and dried for 2 more hours. Before the CV measurements, the cell was purged with N_2 for 30 min. Prior LSV and GEIS measurement the solution was concentrated with O_2 . For electrochemical measurements, potentiostat/galvanostat (BioLogic SAS, SP-240, Grenoble, France) was used. CV measurements were done with the scan rate of 50 mVs^{-1} between the potentials of -0,2 and 1,7 mV vs RHE at room temperature. LSV was done at the scan rate of 2 mVs^{-1} and electrode rotating rate of 1000 rpm. Measurements for GEIS were done at currents of -0,15 mA with an amplitude of 0,10mA. For all the samples the same measuring parameter was used.

Results and discussion

Figure 1. shows cyclic voltammetry (CV) measurements that were performed on La_2O_3 -Pt and LMO-Pt films dried on glassy carbon (GC). Cyclic voltammograms were recorded at a scan rate of 50 mVs^{-1} in 0,1 M KOH solution.

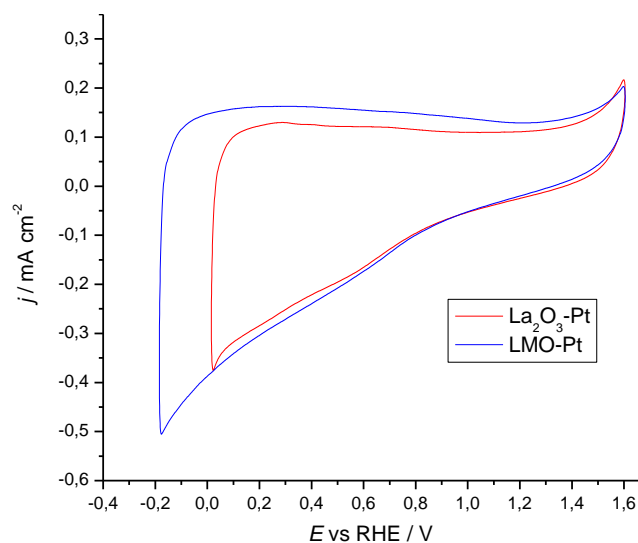


Figure 1. Stable cyclic voltammograms of $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt thin films on GC electrode at a scan rate of 50 mVs^{-1} in N_2 saturated 0.10 M KOH at room temperature.

Recorded OCP potentials vs. RHE for the prepared electrodes were 0.732 V for $\text{La}_2\text{O}_3\text{-Pt}$ and 0.883 V for LMO-Pt . It can be observed from **Figure 1** that cyclic voltammograms of these electrodes have similar look. Both voltammograms have slightly expressed peaks from hydrogen adsorption on Pt. The voltammogram currents for LMO-Pt are a little bit higher than $\text{La}_2\text{O}_3\text{-Pt}$.

The prepared electrodes were tested for ORR by using LSV method in O_2 -saturated 0.10 M KOH electrolyte. **Figure 2** presents ORR electrochemical performances of $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt thin films on glassy carbon (GC) substrate at an electrode rotating rate of 1000 rpm .

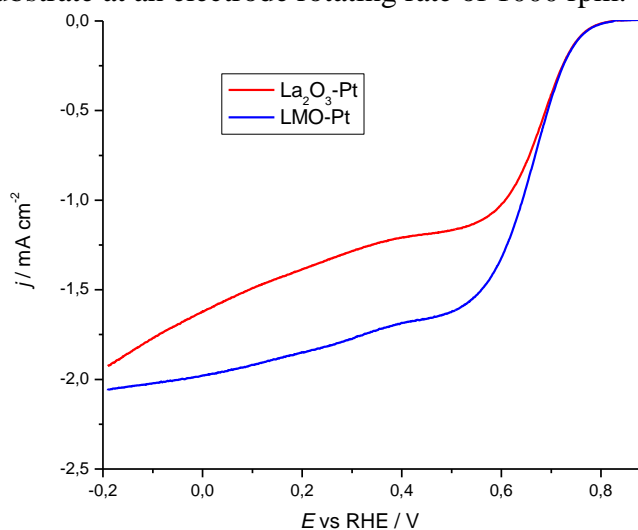


Figure 2. ORR activities of $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt electrode materials at the scan rate of 2 mV s^{-1} and electrode rotating rate of 1000 rpm .

Noticeable reduction currents can be observed when the electrolyte is saturated with O_2 , which means that the synthesized materials are ORR-active. The onset potential for $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt electrodes was approx. 0.7 V vs. RHE. The activity of these two catalysts for ORR is the same at the start of the reaction, but soon after it starts to vary significantly. The activity of LMO-Pt is quite higher and the greatest difference in currents can be seen around 0.2 V , being around 0.5 mA cm^{-2} . Galvanostatic electrochemical impedance spectroscopy (GEIS) measurements were performed at OCP and the current of -0.15 mA (with an amplitude of 0.10 mA) for both samples in O_2 -saturated

0.1 M KOH solution to evaluate the details of ORR response and electrochemical behavior of the tested electrode materials.

GEIS was recorded for $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt electrode materials in O_2 -saturated 0.10 M KOH at a current of -0.15 mA (with an amplitude of 0.10 mA). The results are shown in **Figure 3**.

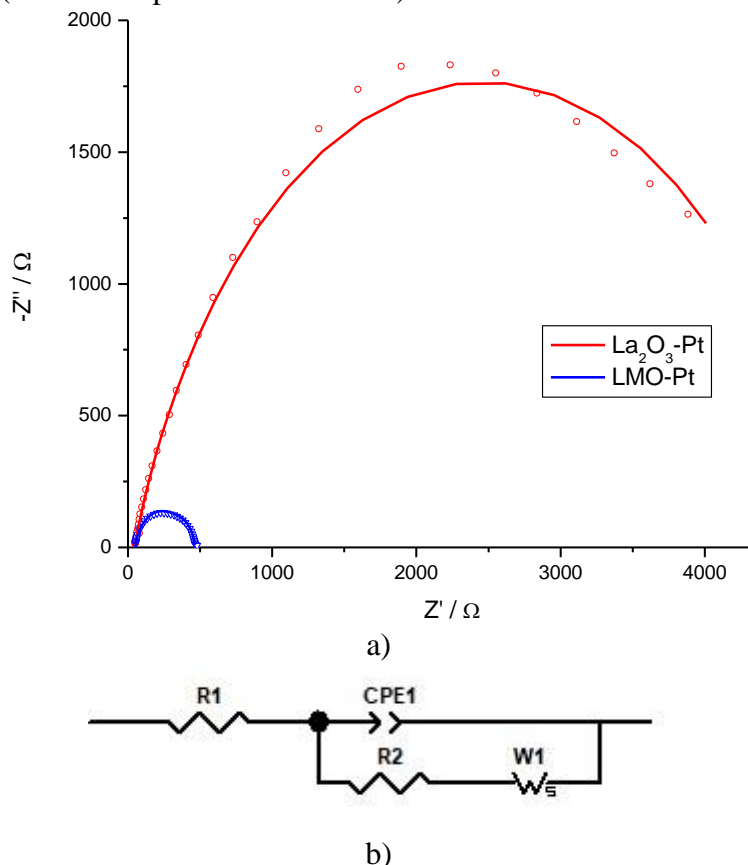


Figure 3. a) Nyquist diagrams of $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt electrolytic material in O_2 -saturated 0.10 M KOH at a current of -0.15 mA with an amplitude of 0.10 mA and b) equivalent circuits used to fit the experimental GEIS data. Equivalent electric circuit data are presented by lines in the plots.

This current range was chosen since it is in the region where the currents for the two samples vary (**Figure 2**). It can be seen from **Figure 3a**, that the semicircle of LMO-Pt is significantly lower than $\text{La}_2\text{O}_3\text{-Pt}$. This indicates that there is less resistance for charge transfer between electrode and solution in LMO-Pt sample, which indicates higher activity in that potential range. From **Figure 2** it can be seen that at a potential of -150 mV, LMO-Pt has higher currents which is in correspondence with GEIS measurements. The $\text{La}_2\text{O}_3\text{-Pt}$ radius of the first semicircle is a lot smaller than the second semicircle, while LMO-Pt has two radii of similar values. From the GEIS measurements, it can be stated that the reaction is diffusion-controlled. Hence, the one can come to a conclusion that the OR reaction is of a mixed character, being electrochemically and diffusion controlled. It can be stated that the high-frequency response corresponds to charge transfer, while the low-frequency corresponds to mass transfer. Even more, the results show that the diffusion is of mixed character due to transport of O_2 molecule and chemical reaction of oxygen reduction. O_2 diffusion is the dominant process for LMO-Pt electrolytic materials, while the chemical reaction is the dominant process for $\text{La}_2\text{O}_3\text{-Pt}$ electrode material.

The fitting results using equivalent electric circuits (EECs) for $\text{La}_2\text{O}_3\text{-Pt}$ and LMO-Pt electrolytic material of the GEIS measurements in O_2 -saturated 0.10 M KOH are given in **Table 1**.

Table 1. Galvanostatic electrochemical impedance spectroscopy data for La₂O₃-Pt and LMO-Pt electrolytic material in O₂-saturated 0.10 M KOH obtained at $i_s = -0.15$ mA with an amplitude of 0.10 mA

	CPE1-T (μ F)	CPE1-P	W1-R (Ω)	W1-T (s)	W1-P	R1 (Ω)	R2 (Ω)
La ₂ O ₃ -Pt	185.6	0.80	959.6	0.38	0.5	46.28	3853
LMO-Pt	123.5	0.84	85	0.272	0.5	47.39	332.8

Due to finite oxygen diffusion, Finite Length Warburg - Short Circuit Terminus is introduced (Ws) in EEC. This element is also known as a Generalized Finite Warburg element (GFW). For the sake of calculation, Ws-P parameter was fixed to 0.5. $W_s-T = L^2/D$, where L is the effective diffusion thickness, and D is the effective diffusion coefficient of the particle, and this parameter defines diffusion. Ws-R element of the Warburg element defines a finite resistance, and it is associated to pure chemical contribution.

Warburg element is dominant in the low-frequency region. In Warburg element, the higher Ws-T element, the bigger the real surface with the same diffusion coefficient. R1 represents the electrochemical cell resistance, while R2 shows the activity of the electrode materials towards ORR. If the resistance is a higher activity for the ORR reaction is lower. Comparing the results from Table 1 it can be seen that the presence of oxygen doubles the capacitance of the double layer. These values are even greater if the material is more active towards ORR.

Since the R2 for sample LMO-Pt is one order of magnitude smaller than of La₂O₃-Pt, it, once again, shows that LMO-Pt is a considerably more active for ORR.

Conclusion

In this research LMO and La₂O₃ with the reduced amount of noble metals supported by transition metals (LMO-Pt and La₂O₃-Pt 5 mass% Pt) were made and tested for the oxygen reduction reaction. Both catalysts were found ORR-active in alkaline solution. It was concluded from LSV curves that the activity for ORR is significantly better in the case of LMO-Pt than it is for La₂O₃-Pt.

Impedance spectroscopy measurements showed that Pt-containing material does not exhibit resistive behavior since the capacitive response is governed by Pt, which hence could appear much to populate the surface of oxide particles.

Impedance measurements indicated the ORR activity series LMO-Pt \gg La₂O₃-Pt, with oxide material showing the highest activity due to the interactive role of La oxide.

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