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Electrochemical characterization of metal oxides as catalysts for oxygen evolution in alkaline media

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An investigation of $LaCoO_3$ catalysts for Oxygen Evolution Reaction (OER) in alkaline media is presented. The material has been obtained by an original one step method. The effect of various parameters such as the catalyst and PTFE loading, catalyst layer thickness and fabrication technique on the electrode performance are described. The catalytic activity of the OER in 0.1 M KOH was determined from Tafel plots, obtained from galvanostatic current-voltage measurements as well as by the Rotating Disk Electrode (RDE) method. Long term tests have been conducted showing a good stability of the catalysts for the OER in 0.1 M KOH

Keywords: Alkaline, Electrolysis, Oxide

INTRODUCTION

In Polymer Electrolyte Conduction ($PEM.OH^-$) OH^- Cation electrolysis significant overpotential is found to occur at the anode where the oxygen evolution reaction (OER) takes place. For this reason, the oxygen evolution reaction (OER) has been intensively studied for many decades in order to elucidate the reaction mechanism and minimize the energy loss during water electrolysis. Improving the OER kinetics would indeed favor a widespread market penetration of ($PEM.OH^-$) electrolysers. There are several chemical aspects of the steps of the reaction mechanisms that have been used to rationalize and explain the trends in catalytic activity of OER catalysts in an alkaline electrolyte (alkaline and PEM), such as acid–base properties [1], redox potentials of the catalyst [2], binding energies of the metal component to hydroxyl ions [3], binding energies of the metal component of the catalyst to oxygen [4], to the number of d-electrons [5] and the geometrical factors [6]. The catalyst that generally shows the best trade-off between catalytic activity and stability, both in acidic and alkaline media, is IrO_2. However, since iridium is quite expensive and limited as a typical secondary metal resource, research efforts have been directed towards the development of OER catalysts with a reduced amount of Ir or based on other transition metal oxides. This is particularly the case for ($PEM.OH^-$) electrolysers since base metals such as cobalt, nickel and perovskite oxides were proven to be quite stable and active in alkaline media.

Perovskite oxides (ABO_3) with alkaline or rare-earth cations in the A-site and first-row transition-metal cations in the B-site have shown the potential of being efficient oxygen electrodes in alkaline solutions[7-9]. Bockris and coworkers [5, 10, 11] correlated the activity of perovskite oxygen-evolving electrodes in alkaline solutions with the enthalpy of formation for the corresponding metal hydroxides and the bond strength of M–OH estimated by a modified version of one of the Ruetschi and Delahay’s methods [3]. Note that the type of A-ion in the perovskite ABO3 compounds had little effect on the oxygen evolution activity of their catalysts, the correlation was based on the B-ion of the catalyst [10]. However, lanthanum-based perovskites containing different transition metal active sites ($LaBO_3$, B = Ni, Ni, Fe, Co, Mn) are synthesized by a general colloidal method, yielding phase pure catalysts of homogeneous morphology and surface area (8−14 m^2/g)[12-14].

The present study represents a continuing effort in the search for more active OER in alkaline media electrode materials. We report herein a study on the electrochemical properties of $LaCoO_3$ as a catalyst synthesized using the solid state reaction route and used as an electrode in the form of a coating on a nickel foam support. The effect of various parameters such as the catalyst and PTFE loading, catalyst layer thickness and fabrication technique on the electrode performance are studied, in comparison with a commercial IrO_2 catalyst. The catalytic activity towards the OER of catalysts was

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determined from Tafel plots obtained from galvanostatic current-voltage measurements. The electrocatalytic activity toward the ORR in 0.1 M KOH was studied by the Rotating Disk Electrode (RDE) method at room temperature.

EXPERIMENTAL

Material synthesis

The $LaCoO_3$ (LCO) perovskite powder was synthesized using the solid state reaction route from stoichiometric amounts of La_2O_3 and Co_3O_4 powder as precursors. Following dry mixing of the precursors, thermal treatment in air was applied in order to obtain the targeted single phase material. This synthesis method is presented in detail in the work of S. Enache, M. Dragan, A. Soare, D. Ion-Ebrasu, A. Zaulet, M. Varlam, K. Petrov, "One step solid-state synthesis of lanthanum cobalt oxide perovskites as catalysts for oxygen evolution in alkaline media".

The electrodes were prepared on rounded shapes of Ni foam with 93% porosity acquired from Goodfellow, having different catalyst and PTFE loading (Table 1). Moreover, in order to improve the electrode conductivity, silver was added in different ratios. The electrodes were prepared by an in house method: the catalyst was mixed with PTFE and silver and added on to the Ni foam support that was then placed in a matrix. The electrode surface is 1 cm^2. The catalyst/Ni foam was pressed at 300 kgf, for 1 minute at 300° C.

Table 1. LCO catalyst, PTFE and silver loading

Catalyst (mg)	Silver (mg)	PTFE (mg)	Support	Sample name
150mg IrO_2	-	20	Ni foam	150IrO_2/20PTFE/Nifoam
150 $LaCoO_3$	-	20	Ni foam	150LCO/20PTFE/Nifoam
100 $LaCoO_3$	-	16,6	Ni foam	100LCO/16.6PTFE/Nifoam
75 $LaCoO_3$	-	10	Ni foam	75LCO/10PTFE/Nifoam
65 $LaCoO_3$	10	10	Ni foam	65LCO/10Ag/10PTFE/Nifoam
60 $LaCoO_3$	15	10	Ni foam	60LCO/15Ag/10PTFE/Nifoam
50 $LaCoO_3$	25	15	Ni foam	50LCO/25Ag/10PTFE/Nifoam

Electrochemical measurements

Electrochemical tests include both stationary and non-stationary methods.The galvanostatic experiments were conducted using a three conventional three-kept for electrode Pyrex glass cell using a programable power source HMP4040 with four channels. The measurements were carried out at room temperature, using Hydrofelx Hydrogen Reference Electrode (RHE) as reference electrode, 1 M KOH and a Pt plate as the counter electrode. A potassium hydroxide 1M solution was prepared using Milli-Q ultrapure water. The samples were then mounted in a glass tube sealed with an encapsulant paste from Dupont.

In order to measure catalyst stability, the 150LCO/20PTFE/Nifoam sample was kept at 5 mA for 888 hours and at 50 mA for 720 hours respectively. After each long term measurement, the current-voltage curves were recorded.

Electrocatalytic activities with respect to the ORR were studied by the Rotating Disk Electrode (RDE) method. An OrigaFlex 5 A potentiostat/ galvanostat controlled by commercial software was used in the experiments. Electrochemical measurements were carried out in a conventional three-electrode Pyrex glass cell. The working electrode was an OrigaTrod glassy carbon rotating disk electrode (RDE) with a geometric area of 0.196 cm^2 embedded in polytetrafluoroethylene (PTFE). A catalyst ink including 5 mg of catalyst, 20 µl of a Fumion® FAA-3-Solut-10 solution and 240 µl of isopropanol was sonicated and mixed overnight. An aliquot of 10 µl was deposited on the glassy-carbon disk. Prior to deposition, the RDE was polished to a mirror finish with 1.0 μm alumina and 0.05 μm diamond paste (PK-3 Electrode Polishing Kit) in sequence. After each polishing step, the RDE electrodes were ultrasonically cleaned in Milli-Q water. Finally, the glassy carbon (GC) electrode was ultrasonically cleaned in Milli-Q water in sequence and dried under argon flow. A Hydrofelx Hydrogen Reference Electrode (RHE) was used as a reference and a platinum plate as the counter-electrode. The experiments are carried out at room temperature in a 0.1 M KOH electrolyte which was purged with high purity O_2 for 30 minutes. All potentials in this paper are reported vs. a RHE reference electrode

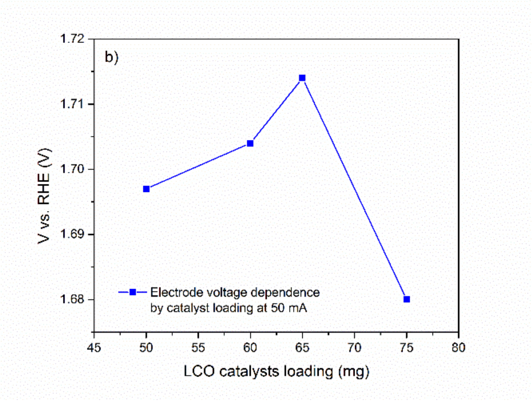
RESULTS AND DISCUSSIONS

Galvanostatic measurements

To determine the effect of catalyst loading and the impact of silver inclusion, the electrode voltage dependence was plotted at 50 mA. Figure 1 (a) shows the increase in the electrode voltage as a function of the decrease in catalyst load. From Figure 1 (b) we can deduce a different trend of the electrode voltage when silver is added to the LCO powder. The voltage decreases with the increase in silver quantity, but this value (1.70 V) is higher than the one corresponding to the sample containing 75 mg of LCO (1.68 V), without a precious metal. This behavior can be explained by the incomplete coverage of the electrode when the catalysts loading is lower than 75 mg, followed by the enhanced contribution of the Ni foam to the overall performance of the electrode.

Presented in Figure 2 are the galvanostatic current-voltage curves recorded for different LCO/PTFE loading in comparison with the IrO_2 commercial catalyst, in the range 0÷100 mA.

Figure 3 shows the Tafel plots (log j) versus V and the slopes calculated from the curves presented in Figure 2. The slopes for the LCO samples are in the domain of 93 mV/decade (75 mg LCO) to 133 mV/decade (150 mg LCO). This is because the overpotential will rise slower if the current density is increasing when using this material as a catalyst in the OER. Since the overpotential is the energy loss during the OER, the smaller slope indicates a better catalysis performance. The value of the slope for a *75LCO/10PTFE/Ni foam* sample is close to the one corresponding to the commercial IrO_2 catalyst (87 mV/decade), which indicates that this probe can be considered to have the best electrode structure and composition for a OER in alkaline media related to the perovskite catalyst presented in this work. These considerations confirm that the OER proceeds along four paths since this reaction involves four electrons and is in accordance with the results presented in the next paragraph [15-18].



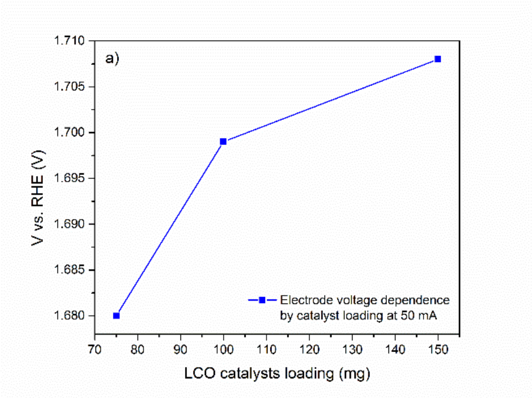


Fig. 1 Electrode voltage dependence versus LCO catalysts loading calculated at 50 mA (without silver); (b) with silver mixed with LCO powder.

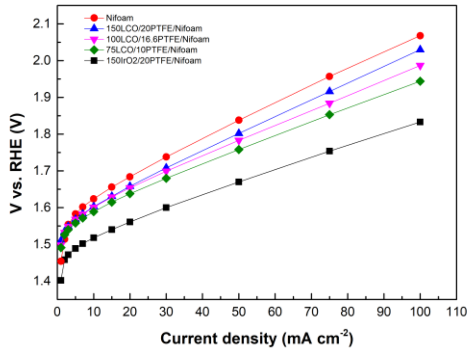


Fig. 2. Galvanostatic current-voltage curves recorded for different LCO/PTFE loading in comparison with an IrO_2 commercial catalyst, in the range 0÷100 mA.

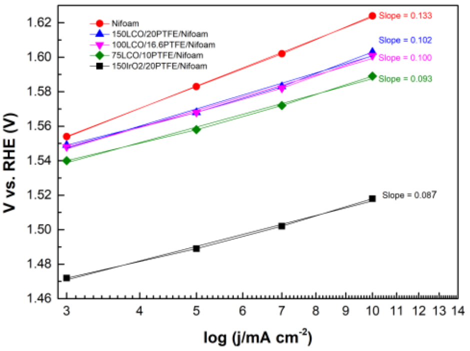


Fig. 3. Tafel plots recorded for different LCO/PTFE loading in comparison with an IrO_2 commercial catalyst, in the range 3÷10 mA.

In order to increase the $LaCoO_3$ oxide based electrode, different quantities of silver were added by substituting part of the LCO catalyst. Figure 4 (galvanostatic current-voltage curves recorded for different LCO/PTFE/Ag loadings on Ni foam) and Figure 5 (Tafel plots) respectively, indicate that there is no noticeable improvement in electrode conduction after silver introduction. Therefore, we conclude that doing this does not make sense, since it will increase the cost of electrode production.

However, further experiments may be carried out by keeping constant the 75 mg of LCO and adding controlled quantities of silver.

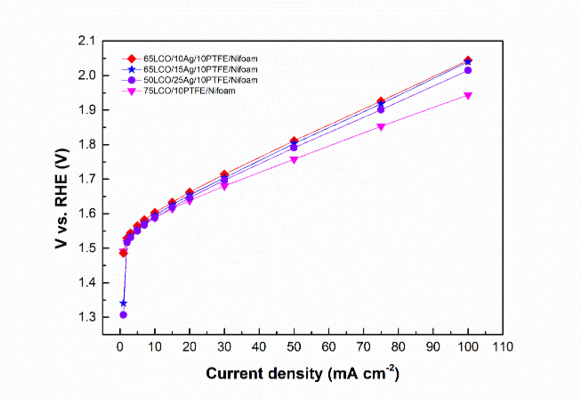


Fig. 4. Galvanostatic current-voltage curves recorded for different LCO/PTFE/Ag loadings on Ni foam

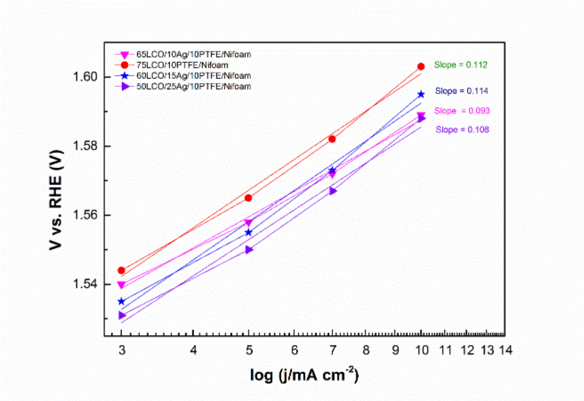


Fig. 5. Tafel plots recorded for different LCO/PTFE/Ag loadings on Ni foam

RDE Measurements

The catalytic performance of LCO with respect to the oxygen reduction reaction(ORR) was evaluated in a 0.1 M KOH solution using the RDE cycling voltammetry method. All the RDE voltammetric experiments were carried out under bench top conditions at an ambient temperature (24 ± 1 °C) in an oxygen saturated atmosphere.

The effect of sweep rate variation from 5 to 500 mV/s is shown in Figure 6. Voltammograms were plotted from 0.5V to -0.55 V, 0.5 to -0.5 V *vs.* RHE and the solution was purged with oxygen for 15 minutes after each voltammogram. The results show that the anodic and cathodic peaks increase with the increasing sweep rate and the ORR peak becomes sharper. This behavior proves that the LCO catalyst has a good stability with respect to the ORR.

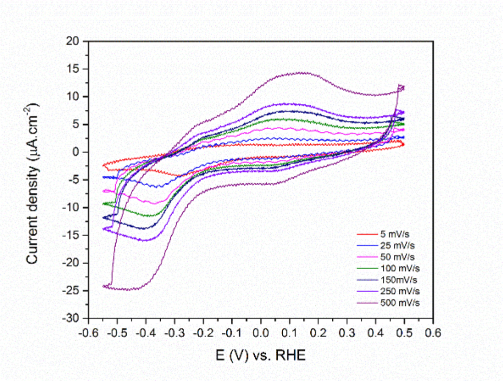


Fig. 6. Cycling voltammograms showing the effect of sweep rate for the LCO catalyst.

Stability measurements of the samples were carried out using one step pulse chronoamperometry in 0.1 M KOH exposed to atmospheric oxygen at -0.15 V over a test period of two hours and a 200 rpm rotation speed. In Figure 7 we observe a relatively stable performance of the catalysts with respect to the oxygen reduction reaction (ORR)/

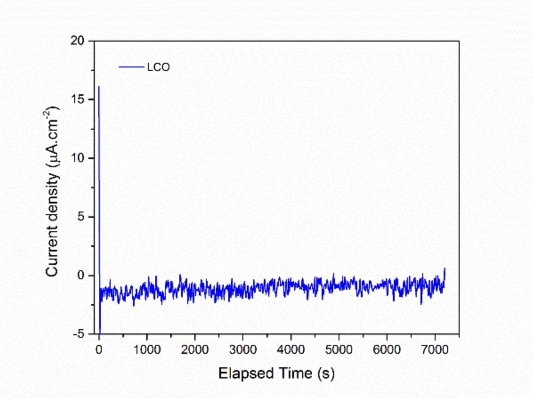


Fig. 7. Chronoamperometric stability measurements for the ORR recorded at-0.15V vs. RHE and rotation at 500 rpm in 0.1 M KOH saturated with oxygen

The kinetics of the catalytic oxygen-reduction reaction of LCO was studied by linear sweep voltammetry (LSV) measurements using the RDE electrode. We carried out LSV measurements at different rotation speeds from 400 to 1400 rpm on RDE in 0.1 M KOH saturated with O_2. As shown in Figure 8, it can be seen that the onset potential moves to more negative values, the current is increasing and all the current-potential curves are smooth with the increase in rotation rate.

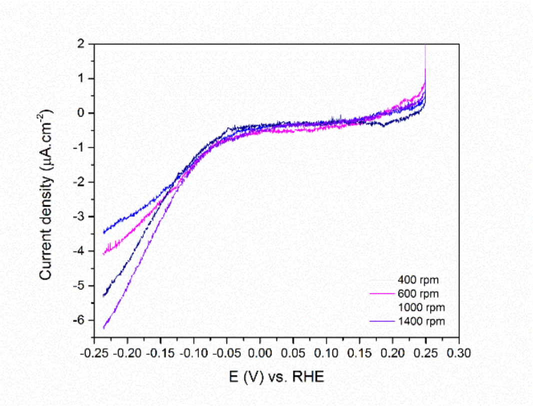


Fig. 8. LSV curves for LCO at different rotation speeds between 400 to 1400 rpm on RDE in 0.1 M KOH saturated with O_2.

Figure 9 shows the fitted Koutecky–Levich plots (Current density^{-1} (mA^{-1}/cm$^{2}_{geo}$) vs. $w^{-1/2}$)(rad/s$^{-1/2}$)) of the LCO catalyst calculated from LSV currents under variable rotation rates in the potential range -0.15 to -0.24 V. The plots show a good linearity for all potentials and a slope of between 1.4 and 1.8. Moreover, the calculated *n* number of moles of electrons transferred in the half reaction is close to 4 corresponding to a ORR in alkaline media proceeding by direct four-electron reduction (ec. 1) [14]:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \qquad (1)$$

The stability of the LCO catalyst was measured for the 150LCO/20PTFE/Ni foam sample. From Figures 10 and 11 it can be seen that the electrode is stable over more than 700 hours, both at a low current (5 mA) as well as at a higher current (50 mA).

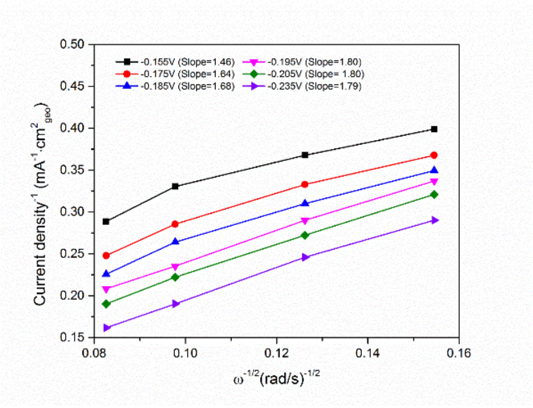


Fig. 9. Fitted Koutecky–Levich plots of the LCO catalyst calculated from LSV currents under different rates of rotation in the potential range -0.15 to -0.24 V.

The results presented above confirm the catalytic activity and stability of LCO for the OER and the fact that the best sample is the one with 75 mg of LCO and 10 mg of PTFE.

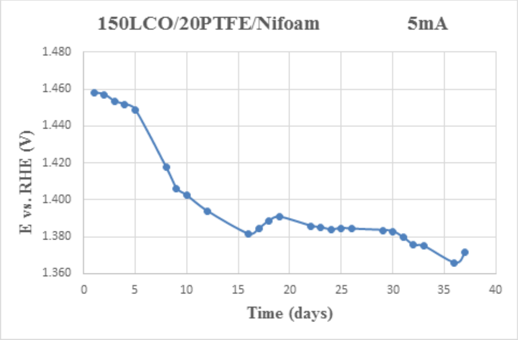


Fig. 10. Long term measurements of 150LCO/20PTFE/Nifoam at 5 mA for 888 hours.

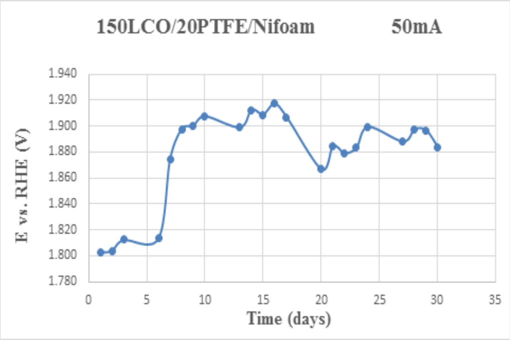


Fig. 11. Long term measurements of 150LCO/20PTFE/Nifoam at 50 mA for 720 hours.

CONCLUSIONS

We have shown in this paper that the catalyst $LaCoO_3$ perovskite synthesized using the solid state reaction route manifests good catalytic activity and stability for the OER. Silver added to the LCO powder together with PTFE doesn't noticeably improve the electrode conductivity therefore we can conclude that the addition of silver does not make sense, since this will increase the cost of electrode production. However, further experiments may be carried out by keeping constant the 75 mg of LCO and adding controlled quantities of silver.

The RDE cycling voltammetry measurements prove that the LCO catalyst has a good stability with respect to the ORR. Chronoamperometry shows the performance of the LCO perovskite catalyst to be relatively stable with respect to the oxygen reduction reaction (ORR).

However, the number of electrons transferred in the half reaction is close to 4 corresponding to the ORR in alkaline media that proceeds by direct four-electron reduction and hence the mechanism of the ORR is complementary to the $LaCoO_3$ catalysts presented in this paper and corresponds to a direct reduction of O_2 to OH^-.

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ЕЛЕКТРОХИМИЧНО ОХАРАКТЕРИЗИРАНЕ НА МЕТАЛНИ ОКСИДИ КАТО КАТАЛИЗАТОРИ ЗА ОТДЕЛЯНЕ НА КИСЛОРОД В АЛКАЛНИ СРЕДИ

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(Резюме)

Изследвани са катализатори на база $LaCoO_3$ за реакции на отделяне на кислород в алкална среда. Материалът е получен по оригинален метод (едностъпков). Изследвано е въздействието на различни параметри като тефлонизиране на катализатора, дебелината на каталитичния слой и техниката на изработка на електрода. Каталитичната активност при реакцията на отделяне на кислород в 0.1 M KOH се определя от Тафеловите наклони, получени от поляризационнните криви на галваностатичните измервания, както и от измерванията с ротиращ дисков електрод. Проведени са дългосрочни тестове за дълготрайна стабилност на катализаторите за отделяне на кислород в 0.1 M KOH.

Ключови думи: перовскит- $LaCoO_3$, метални оксиди, отделяне на кислород