

SYNTHESIS OF PEROVSKITES $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ SUPPORTED ON CARBON MATERIALS AND THEIR APPLICATION IN THE OXYGEN REDUCTION REACTION

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Introduction

Fuel cells and metal-air batteries are promising devices that can substitute the actual energy providers, fossil fuels, promoting the use of renewable energies. However, the oxygen reduction reaction (ORR) that takes place in the cathode presents sluggish kinetics; therefore, catalysts with great performance are needed. Perovskite-based materials are promising materials because, due to their tuneable physicochemical properties, they can result into different catalytic properties¹. As perovskite materials present low conductivity, they need to be supported on a conductive material. Carbon materials, apart from providing properties such as high electrical conductivity and high surface area, improve significantly the activity of the electrocatalysts due to synergetic effects²⁻³. In this investigation, we propose the development of perovskite nanoparticles with the formula $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ supported on Vulcan as a promising alternative to the commercial catalysts in alkaline conditions.

Materials and Methods

The synthesis of $\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskites ($x = 0, 0.3, 0.5, 0.7,$ and 1) was performed by a sol-gel method similar to that described in the literature¹ but modified by the addition of cobalt. The perovskite materials were characterized by physicochemical and electrochemical techniques. To prepare Vulcan/perovskite materials, a ratio 1:1 of both materials were mixed physically in order to obtain a homogenous catalytic material.

Results and Discussion

$\text{LaMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite materials exhibit two different crystal structure that is affected by the amount of cobalt introduced into the LaMnO_3 perovskite. The perovskite material with $x \leq 0.5$ has a cubic structure, whereas with $0.7 \leq x \leq 1$ has a rhombohedral hexagonal structure. To get a better performance, it is preferable to have a more symmetric structure in order not disturb the BO_6 octahedra that seem to play the catalytic role in ORR⁵. Moreover, the manganese substitution by cobalt in the perovskites increases the crystal size and, thus, less active sites are available for the

ORR. However, the addition of cobalt generates a new redox couple that is beneficial for ORR.

Table 1 shows the electrocatalytic parameters of the ORR results from the supported and the unsupported perovskite materials compared to Vulcan support. The perovskite materials exhibit a better activity when a low concentration of cobalt is introduced into LaMnO₃ perovskite, with the lowest activity for LaCoO₃ perovskite. Interestingly, the supported perovskite materials show an enhancement in the activity due to the synergistic effect of both materials. The perovskite that contains less amount of cobalt presents again the best performance towards ORR

Table 1: Parameters of the catalytic activity towards ORR.

Sample	Onset potential (at -0.25 mA/cm ²) / V	N° electron (at -1 mA/cm ²)	Limiting current (at 0.4 V vs RHE)/- mA/cm ²	Vulcan/Perovskite sample		
				Onset potential (at -0.25 mA/cm ²) / V	N° electron (at -1 mA/cm ²)	Limiting current (at 0.4 V vs RHE) / - mA/cm ²
Vulcan	0.74	2.29	-3.17	-	-	-
LaMnO ₃	0.71	2.88	-2.20	0.82	3.84	-3.8
LaMn _{0.7} Co _{0.3} O ₃	0.70	3.10	-2.51	0.81	3.85	-4.77
LaMn _{0.5} Co _{0.5} O ₃	0.66	2.94	-2.06	0.81	3.85	-4.70
LaMn _{0.3} Co _{0.7} O ₃	0.67	2.93	-2.30	0.78	3.83	-4.43
LaCoO ₃	0.66	2.57	-1.85	0.77	3.20	-3.73

Conclusions

The supported perovskite LaMn_{0.7}Co_{0.3}O/Vulcan₃ shows the best activity towards ORR. This perovskite has a cubic crystal structure and it has the smallest crystallite size; therefore, more active sites are available for ORR. Moreover, the introduction of a redox couple from cobalt generates more active sites for a better performance towards ORR.

Therefore, this perovskite can be a promising catalyst to substitute the current commercial electrocatalysts based on platinum.

Acknowledgment

The authors thank MINECO and FEDER (MAT2016-76595-R and ENE2017-90932-REDT) for the financial support. J.X.F.-L. gratefully acknowledges MINECO for the financial support through FPI contract (BES-2017-081598).

References

1. Y. Zhu, W. Zhou, Z. Shao, Perovskite/Carbon Composites: Applications in Oxygen Electrocatalysis, *Small*, 13 (2017) 1–25.
2. G. Kéranguéven, S. Royer, E. Savinova, Synthesis of efficient Vulcan-LaMnO₃ perovskite nanocomposite for the oxygen reduction reaction, *Electrochem. Commun.* 50 (2015) 28–31.
3. K. Liu, J. Li, Q. Wang, X. Wang, D. Qian, J. Jiang, J. Li, Z. Chen, Designed synthesis of LaCoO₃/N-doped reduced graphene oxide nanohybrid as an efficient bifunctional electrocatalyst for ORR and OER in alkaline medium, *J. Alloys Compd.* 725 (2017) 260–269.
4. C. Li, Z. Yu, H. Liu, K. Chen, High surface area LaMnO₃ nanoparticles enhancing electrochemical catalytic activity for rechargeable lithium-air batteries, *J. Phys. Chem. Solids*, 113 (2018) 151–156.
5. J. Suntivich, H.A. Gasteiger, N. Yabuuchi, H. Nakanishi, J.B. Goodenough, Y. Shao-Horn, Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries, *Nat. Chem.* 3 (2011) 546–550.