



FUNDAMENTAL STUDIES OF THE ELECTROOXIDATION OF METHANOL ON PEROVSKITES OXIDES

KEY WORDS: electrocatalysis, perovskite oxides, methanol, bio-based energy, hydrogen

Mariana Amaral Dotta (IQ-Unicamp), Swathi Raju (IQ-Unicamp), Rafael Vicente (IQ-Unicamp), Daniela Zanchet (IQ-Unicamp) and Pablo Fernández (IQ-Unicamp).

INTRODUCTION:

Pollution, climate change, global warming, and their consequences call for an urgent change in the way society perceives the usage and production of energy¹. In this scenario, the opportunities for greener sources of energy create a fertile ambient for bio-based economies.

There is a large variety of abundant and cost-effective biomass-derived resources, such as ethanol², glycerol³, and glucose⁴, that can be used to produce a wide range of fine chemicals for different industries and applications. Besides, if the electrooxidation of these substances is performed at the anode of an electrolyzer, while water is reduced at the cathode, these fine chemicals can be produced concomitantly along with high-purity hydrogen⁵, which will be likely the most important energy carrier of this century.

Methanol is the simplest organic alcohol, making it a potential probe molecule to understand the electrooxidation of more complex alcohols or polyols, for instance, glycerol, that can form in its direct oxidation value-added chemicals such as glyceric acid, dihydroxyacetone, and much more⁶. In addition, it makes fundamental studies easier, for example, by decreasing the computational cost to perform computational experiments. Besides, methanol (or biomass-derived compounds) can be used in an electrolyzer, as shown in Figure 1. The organic molecule is inserted at the anode compartment, where it is oxidized. At the cathode, water reduction reaction takes place, producing high-purity hydrogen. The standard potentials for the oxidation of H₂O to O₂ and methanol to CO₂ are 1.23 and 0.03V, respectively⁷. Thus, electrolysis in the presence of methanol (and several other small organic molecules) proceeds at a much lower voltage than conventional water electrolysis⁸, making this approach more energy efficient for hydrogen production.

Apart from these thermodynamic considerations, better catalysts for anodes of electrolyzers are being intensely researched. By tuning the properties of the catalysts by changing the composition, shape, and size, etc., it is possible to reduce the energy input to run the electrolyzer at a desired current density. Besides, these changes will also impact the reaction selectivity, which also depends on the applied potential, temperature, pH, among many other factors.

Most of the studies in the field of oxidation of alcohols/polyols have been performed with noble metal-based electrocatalysts, which are expensive and scarce. In this context, perovskite oxides (PO) emerge as versatile materials to be used for the electrooxidation of alcohols. PO are a general name for oxides with the structural formula ABO₃ or A₂BO₄. In the oxides with the formula ABO₃, which are the object of study of this work, the A site

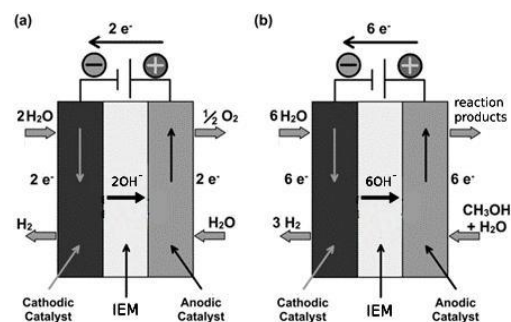


Figure 1: comparative representation of a) water electrolysis and b) aqueous methanol electrolysis with an Ion Exchange Membrane (IEM). Figure adapted from literature⁸.

is a 12-fold coordinated cation, whereas the B site is a 6-fold cation coordinated with 6 oxygen atoms⁹ (Figure 2). They can be synthesized by a variety of routes, being obtained in the form of films, powders, and nanoparticles, among other possibilities¹⁰. The properties of these materials can be tuned by varying the A and B site elements of the PO. By controlling the structure, it has been shown that we can obtain materials with different properties, such as high structural stability, different oxidation states of A and B sites, and distinct content of oxygen vacancy, among others^{9,10}.

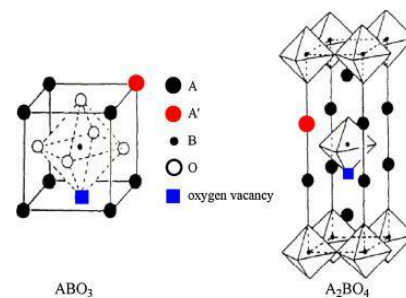


Figure 2: structure of ABO_3 and A_2BO_4 perovskite oxides. Figure extracted from literature¹⁰.

In this work, we will use a set of $LaBO_3$ perovskite oxides, in which the B site is substituted by different metals, to study their activity for the electrooxidation of methanol (EOM) and the selectivity of the reaction by using *in-situ* FTIR. Besides, we discuss the effect of the electrolyte composition and of methanol concentration on the rate of electrooxidation and the reaction selectivity.

MATERIALS AND METHODS:

Perovskite oxides:

The PO were synthesized by using a combination of the citrate¹¹ and the microwave-assisted methods^{12,13}. The compositions of PO are $LaBO_3$ with $B = Fe, Mn, Ni, Co$.

Electrochemical measurements:

The measurements were performed in a conventional three-electrode electrochemical cell connected to a potentiostat/galvanostat (Autolab, Methrom). A 5 mm diameter glassy carbon electrode was used as PO support. For the working electrode (WE) preparation, the PO powders were sonicated in water, with a ratio of 5 mg of oxides to 0.5 mL of ultrapure (Milli-Q) water for 9 hours to acquire homogeneous dispersion of PO for deposition. After that, POs were deposited by drop casting on the glassy carbon surface with a material loading of 10 μL . The electrode was dried in an oven for 15 minutes.

The counter electrode (CE) was a Platinum (Pt) foil, and the reference electrode (RE) was a reversible hydrogen electrode (RHE). Cyclic voltammetry linear scans (CV) were performed, with a potential window of 0,05 to 1,6V. All the potential mentioned here are referenced with respect to RHE. CV measurements were performed in alkaline media (0.1 mol/L and 0.5 mol/L NaOH) with 0.3 mol/L and 1.0 mol/L methanol. The scan rate was 20mV/s.

Electrocatalyst characterization:

PO were characterized by X-ray diffraction (XRD) using a STOE STADI P with a molybdenum source and a germanium (111) monochromator in transmission mode. The samples were binned into a quartz tube, in powder form, and scanned from 2° to 60° in a step-scan mode with a step size of 0.015°.

FTIR measurements:

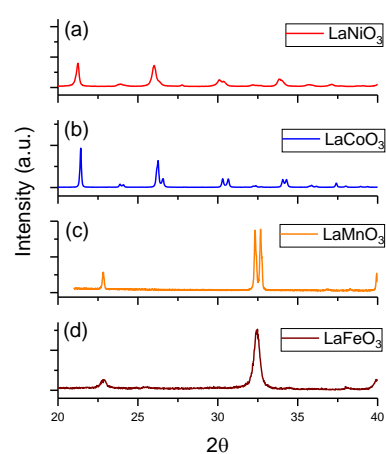
In-situ infrared experiments were carried out with a Shimadzu IR Prestige-21 spectrometer with a mercury cadmium telluride (MCT) detector. Details about the *in-situ* FTIR technique can be found elsewhere¹⁴. To perform the *in-situ* FTIR measurements, a three-electrode spectroelectrochemical cell (SEC) equipped with a CaF_2 prism placed on top of a specular reflection accessory (VeeMax II, Pike Technologies) was used. The SEC was composed

of the CE, which was a Pt foil, and the RHE. First, the WE was polarized at 0.05V, and then inserted in the SEC, put in contact with the electrolyte, and gently pressed against the prism to form the thin layer with a thickness of about 50 μm . This thin layer configuration is important to decrease the radiation loss due to the absorption of IR radiation by water. In this experiment, the spectra were obtained during stepped chronoamperometry in a range of 0.05 V – 1.7V. At each potential, 256 interferograms with a resolution of 4 cm^{-1} were acquired. The spectra were plotted as the ratio of R/R_0 , where R_0 is the reference spectrum that will be 0.05V and R is the sample spectra as a function of the potential. All measurements were performed using H_2O . All the data were represented in Transmittance (%). The bands pointing upwards are related to the consumption of the species, while the bands going downwards are related to the formation of products during the reaction.

RESULTS AND DISCUSSION:

Electrocatalyst characterization

In order to characterize the bulk crystallographic structure of perovskite oxides, XRD measurements were



performed. The samples were characterized based on the Crystallography Open Database (COD) and Inorganic Crystal Structure Database (ICSD). Results can be seen in Figure 3. For all the materials, a predominance of the perovskite phase was observed.

For LaNiO_3 , besides the peaks associated with the pure PO material, an additional peak corresponding to nickel oxide (NiO) can also be seen. The presence of this peak indicates that not all the nickel precursor was converted into the perovskite structure.

Figure 3: XRD measurements for the synthesized materials of a) LaNiO_3 ; b) LaCoO_3 ; c) LaMnO_3 ; and d) LaFeO_3 . Figure extracted from literature¹⁵.

Electrochemical measurements

Figure 4 shows the CV results obtained in 0.1 mol/L NaOH with and without the presence of 0.3 mol/L methanol. It shows that LaNiO_3 and LaCoO_3 are active for EOM, while LaFeO_3 and LaMnO_3 are rather inactive. It is worth noting that this result is similar to those reported by Santiago et al. for the electrooxidation of glycerol¹⁶.

To study the effects of methanol concentration, we performed experiments in 0.1 mol/L NaOH and 1 mol/L methanol. Figure 5 shows the comparison between measurements with 0.3M and 1M methanol. Results show that increasing methanol concentration does not increase the oxidation current. This result indicates that, in this concentration range, the EOG is not limited by the availability of organic molecules.

To study the effects of pH, we performed experiments in 0.5 mol/L NaOH and 0.3 mol/L methanol. Figure 6 compares the results with 0.1 mol/L and 0.5 mol/L NaOH. While the oxidation currents do not change for LaCoO_3 , they clearly decrease for LaNiO_3 . A closer look at the blank voltammogram shows that while the response is independent of the pH for Co's catalysts, the material containing Ni changes its profile, suggesting a modification on its surface.

Santiago et al.¹⁶, based on the ideas of Chen et al.¹⁷, proposed that the electro-oxidation of glycerol occurs through a "chemical" process, i.e., the PO in alkaline media form M(OH)O (metal oxyhydroxide species) after applying a positively enough electrochemical potential. For instance, this is indicated by the peak around 1.4V (Figures 4d, 5b and 6b) in the blank CV for LaNiO_3 . Thus, these reactive species then chemically react with the

organic molecule to form oxidized products. The fact that the rate of oxidation seems to be rather insensitive to the concentration of the alcohol, suggests that in these conditions, the reaction is limited by the availability of $M(OH)O$ species on both catalysts.

On the other hand, for $LaNiO_3$, we observed a dependence of the activity with the pH. The blank CVs at different concentrations of NaOH show that the surface of the catalysts is affected by the pH, altering the redox properties of the material and, consequently, changing its activity. More experiments need to be performed to understand how the pH affects the formation of more $M(OH)O$ reactive species.

In addition, Santiago. et. al. showed that, for glycerol, the activity trends for the same materials was $LaMnO_3 < LaFeO_3 < LaCoO_3 < LaNiO_3$. They suggested that the chemical reactivity of $M(OH)O$ species increases with the increasing atomic number of M elements at the B site. In addition, they claimed that these species are highly active for Co and Ni, and inactive for Fe and Mn. The same trends were observed with methanol in this work, suggesting that the catalytic behavior of PO might be analogous for both methanol and glycerol oxidation.

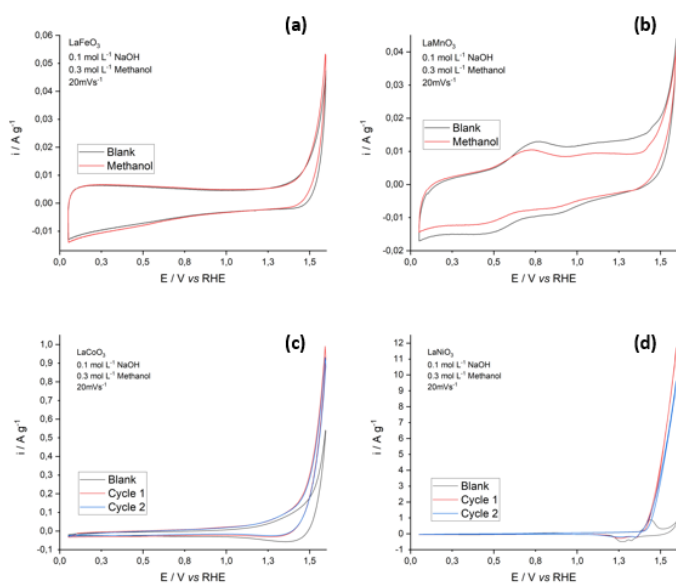


Figure 4: Cyclic voltammograms linear scans of EOM performed with: a) $LaFeO_3$; b) $LaMnO_3$; c) $LaCoO_3$; and d) $LaNiO_3$. All results are standardized by PO mass and were performed in 0.1 mol/L NaOH and 0.3 mol/L methanol.

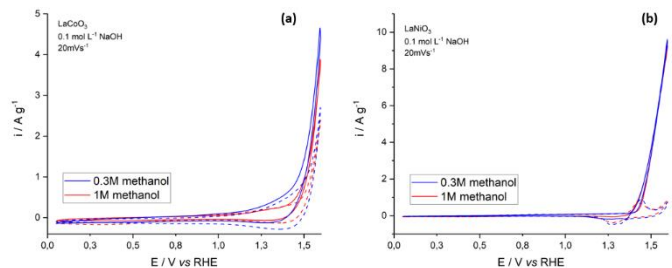


Figure 5: Cyclic voltammograms linear scans of EOM performed with: a) $LaCoO_3$; and b) $LaNiO_3$. All results are standardized by PO mass. Figure shows the comparison between measurements with 0.3M and 1M methanol (0.1M NaOH).

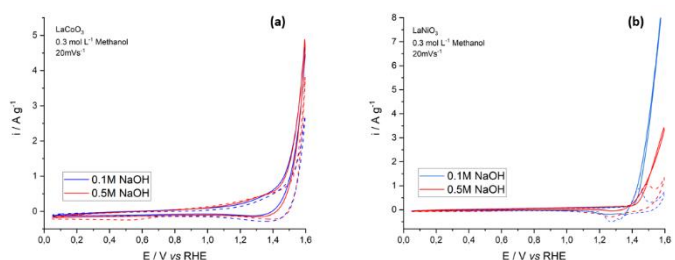


Figure 6: Cyclic voltammograms linear scans of EOM performed with: a) $LaCoO_3$; and b) $LaNiO_3$. All results are standardized by PO mass. Figure shows the comparison between measurements in 0.1M and 0.5M NaOH (0.3M methanol).

FTIR measurements

The EOM on both $LaNiO_3$ and $LaCoO_3$ was investigated by FTIR to determine the reaction selectivity and formed products. The spectra obtained at different potentials are presented in Figure 7. The experiments were performed with 0.1 mol/L NaOH and 0.3 mol/L methanol, with an applied voltage of 1.0 to 1.7V.

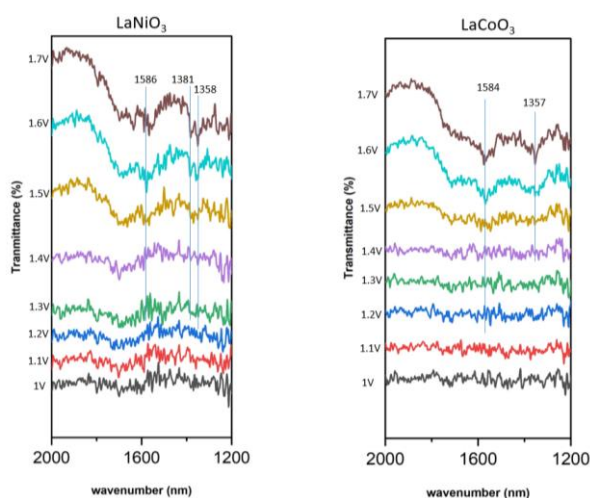


Figure 7: FTIR spectra for $LaNiO_3$ and $LaCoO_3$ obtained by *in-situ* FTIR in 0.1 mol/L NaOH and 0.3 mol/L methanol. Spectra are composed by 256 interferograms with 4 cm^{-1} of resolution. Reference spectra acquired at 0.8V.

The spectra obtained at different potentials are presented in Figure 7. The experiments were performed with 0.1 mol/L NaOH and 0.3 mol/L methanol, with an applied voltage of 1.0 to 1.7V.

The results for $LaNiO_3$ show the appearance of three bands (1585 cm^{-1} , 1380 cm^{-1} and 1360 cm^{-1}) at potentials higher than 1.4V. Formate presents defined bands at 1580 cm^{-1} , 1380 cm^{-1} and 1350 cm^{-1} , which are related to C-O asymmetric stretching, COO rocking and C-O symmetric stretching, respectively^{18,19}. $LaCoO_3$ results show the appearance of two bands (1584 cm^{-1} and 1357 cm^{-1}), which are also related to the formation of formate. Thus, we can see

that LaNiO₃ and LaCoO₃ PO are selective to the EOM pathway that leads to formate generation as product.

CONCLUSIONS AND PERSPECTIVES:

The modification of the PO composition, with the substitution of the B site by different transition metals, severely affects the electrocatalytic activity. While LaNiO₃ and LaCoO₃ are active for the EOM, LaMnO₃ and LaFeO₃ do not oxidize the alcohol.

Modifications in the electrolyte composition can also affect the reaction of methanol electrooxidation when using the LaNiO₃, which is related to the formation of more reactive species, namely M(OH)O metal oxyhydroxide species. The methanol concentration in solution, however, does not have an effect in the obtained current from the reaction, which, indicates that, in this concentration range, the EOG is not limited by the availability of organic molecules, leading to the evidence of existence of a saturation point of methanol concentration in the PO surface.

In-situ FTIR experiments show the formation of formate when the electrooxidation reaction is performed with LaNiO₃ and LaCoO₃ perovskites. The formation of this product may be of great interest, since it is a chemical with greater market value than methanol. Thus, the coupling of methanol electrooxidation with the reduction of water, besides being a way to produce green hydrogen, can also be a way to produce fine chemicals.

It is worth noting that the presented results in this work are similar to those reported by Santiago et al.¹⁶ and Chen et. al.¹⁷ for the electrooxidation of other alcohols and polyols, for instance, glycerol. In this way, we can see that methanol takes the role of an important model molecule for fundamental studies in the field of electrooxidation of alcohols and polyols. Being the simplest organic alcohol, the study of this molecule allows researchers to understand mechanisms and the reaction selectivity for the aforementioned PO electrocatalysts, turning studies in the area simpler and, for example, decreasing the computational cost to perform computational and theoretical experiments.

The research group still has several experiments ongoing to identify the selectivity of the use of Ni and Co perovskites, mapping the generated products of the reaction, alongside with understanding of the reaction mechanisms. Electrolysis and HPLC measurements should be performed to understand the reaction selectivity and quantify the formed products.

REFERENCES:

- [1] Shell Global. Sky scenario | Shell Global.
- [2] Sun, J.; Wang, Y. Recent Advances in Catalytic Conversion of Ethanol to Chemicals. *ACS Catalysis*. 2014. <https://doi.org/10.1021/cs4011343>.
- [3] Bagheri, S.; Julkapli, N. M.; Yehye, W. A. Catalytic Conversion of Biodiesel Derived Raw Glycerol to Value Added Products. *Renewable and Sustainable Energy Reviews*. 2015. <https://doi.org/10.1016/j.rser.2014.08.031>.
- [4] Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass. *U.S. Dep. Energy*. 2004. <https://doi.org/10.2172/926125>.
- [5] Coutanceau, C.; Baranton, S.; Kouamé, R. S. B. Selective Electrooxidation of Glycerol into Value-Added Chemicals: A Short Overview. *Frontiers in Chemistry*. 2019. <https://doi.org/10.3389/fchem.2019.00100>
- [6] Kaur, J.; Sarma, A.; Jha, M.; Gera, P. Valorisation of crude glycerol to value-added products: perspectives of technology, economics and environmental issues. *Biotechnology Reports*, 2020. <https://doi.org/10.1016/j.btre.2020.e00487>
- [7] Take, T.; Tsurutani, K.; Umeda, M. Hydrogen production by methanol-water solution electrolysis. *Journal of Power Sources*. 2007. <https://doi.org/10.1016/j.jpowsour.2006.10.011>
- [8] Menia, S.; Tebibel, H.; Lassouane, F.; Khellaf, A.; Nouicer, I. Hydrogen production by methanol aqueous electrolysis using photovoltaic energy: Algerian potential. *Elsevier*. 2016. <https://doi.org/10.1016/j.ijhydene.2016.11.178>
- [9] Hwang, J. et al. Perovskites in catalysis and electrocatalysis. *Science* 358, 751–756 (2017).
- [10] Zhu, J. et al. Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis. *ACS Catal.* 4, 2917–2940 (2014).
- [11] Garcia, J. Perovskitas Preparadas Pelo Método Do Citrato Como Catalisadores Para a Reação de Redução de NO Com CO. 2011.
- [12] Galal, A.; Atta, N. F.; Ali, S. M. Optimization of the Synthesis Conditions for LaNiO₃ Catalyst by Microwave Assisted Citrate Method for Hydrogen Production. *Appl. Catal. A Gen.* 2011, 409–410, 202–208. <https://doi.org/10.1016/j.apcata.2011.10.005>.
- [13] Rao, K. J.; Vaidhyanathan, B.; Ganguli, M.; Ramakrishnan, P. A. Synthesis of Inorganic Solids Using Microwaves. *Chem. Mater.* 1999, 11 (4), 882–895. <https://doi.org/10.1021/cm9803859>.
- [14] Ye, J.; Jiang, Y.; Sheng, T.; Sun, S. In-situ FTIR spectroscopy studies of electrocatalytic reactions and processes. *Nano Energy*. 2016. <https://doi.org/10.1016/j.nanoen.2016.06.023>
- [15] Santiago, P. V. B.; Lima, C. C.; Bott-Neto, J. L.; Fernández, P. S.; Angelucci, C. A.; Souza-Garcia, J. Perovskite oxides as electrocatalyst for glycerol oxidation. *Journal of Electroanalytical Chemistry*. 2021. <https://doi.org/10.1016/j.jelechem.2021.115198>
- [16] Santiago, P. V. B.; Raju, S. P.; Akkiraju, K.; Vicente, R. A.; Silva, M. A.; Yuan, S.; Zanchet, D.; Shao-Horn, Y.; Fernández, P. S. Perovskite Oxides as an opportunity to systematically study the electrooxidation of alcohols and polyols on materials based on abundant elements: learning from the experience using pure metals and metallic oxides in electrocatalysis. *Energy Materials*, 2023. <https://doi.org/10.1021/acsaem.3c00492>
- [17] He, Z.; Hwang, J.; Gong, Z.; Zhou, M.; Zhang, N.; Kang, X.; Han, J. W.; Chen, Y. Promoting biomass electrooxidation via modulating proton and oxygen anion deintercalation in hydroxide. *Nature Communications*, 2022. <https://doi.org/10.1038/s41467-022-31484-0>
- [18] P. Gopal. Evidence for production of surface formate upon direct reaction of CO with alumina and magnesia. *J. Catal.*, 105 (1987), pp. 366-372.
- [19] K. Ito, H.J. Bernstein. The vibrational spectra of the formate, acetate, and oxalate ions. *Can. J. Chem.*, 34 (1956), pp. 170-178.