Highly active bifunctional $LaMO_3$ (M=Cr, Mn, Fe, Co, Ni) perovskites for oxygen reduction and oxygen evolution reaction in alkaline media

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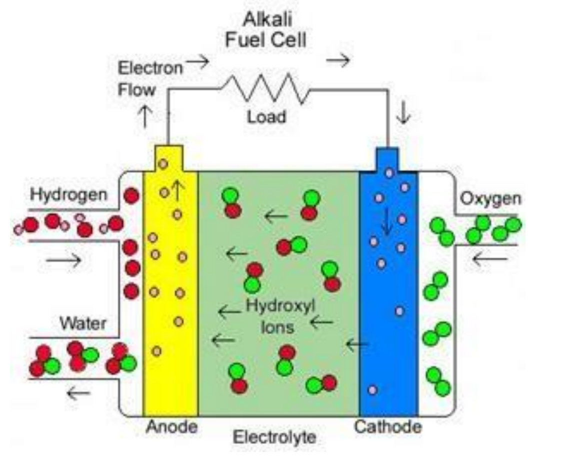
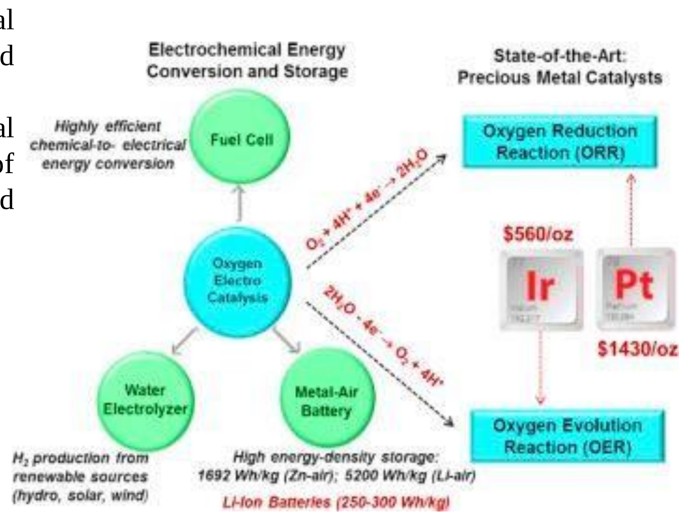
Abstract: Lanthanum based electrocatalytically active perovskites, $LaMO_3$ (M=Cr, Mn, Fe, Co, Ni), were synthesized using a single step solution combustion synthesis technique. The perovskites showed exceptional performance for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline medium. Based on the experimental results and literature survey, it is suggested that the exceptional activity of Mn and Co based lanthanum perovskite catalyst could be due to the optimum stabilization of reaction intermediates involved in the rate-determining step (RDS) of ORR/OER.

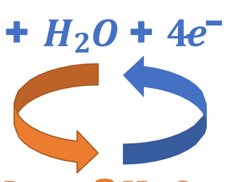
Introduction

- A fuel cell is a device that generates electricity by a chemical reaction.
- Every fuel cell has two electrodes called, respectively, the anode and cathode.
- Alkali fuel cells operate on compressed hydrogen and oxygen.
- They generally use a solution of potassium hydroxide in water as their electrolyte.
- Efficiency is about 70 percent
- Alkali cells were used in Apollo spacecraft to provide both electricity and drinking water.
- However, their platinum electrode catalysts are expensive.
- Develop a non-precious and readily available bifunctional catalyst suitable of simultaneously activating the ORR and OER.
- Combining the two functionalities in one single bifunctional oxygen redox electrode would greatly simplify the design of energy conversion devices or enhance the mobility and power-to-weight ratio



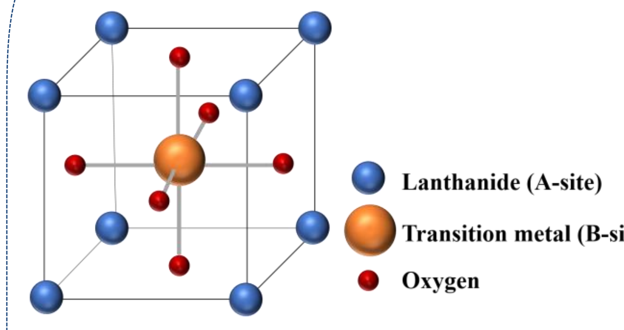


ORR − $O_2 + H_2O + 4e^- \rightarrow 4OH^-$

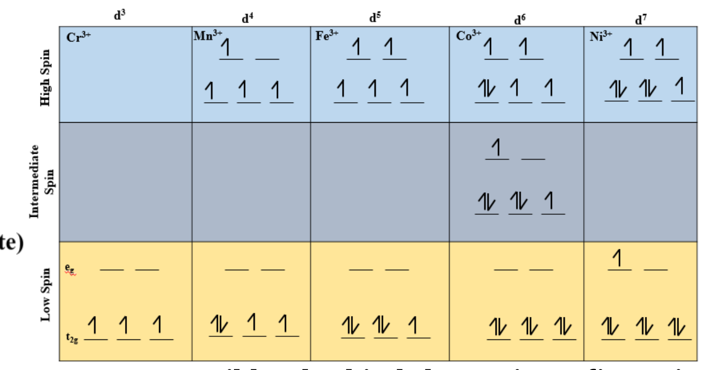


OER − $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

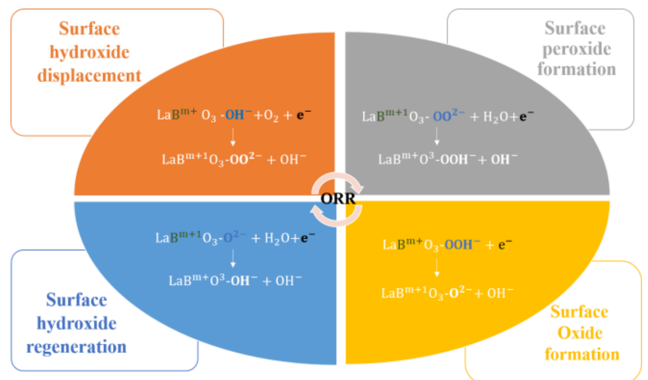
Mechanism of ORR /OER in Pervoskites

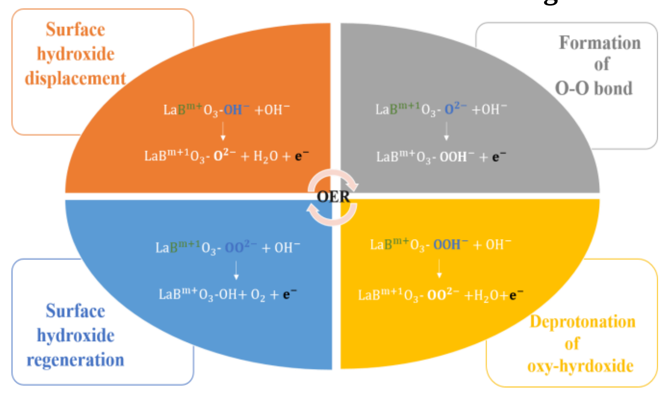


Unit cell ABO_3 perovskite structure



Possible 3d orbital electronic configuration





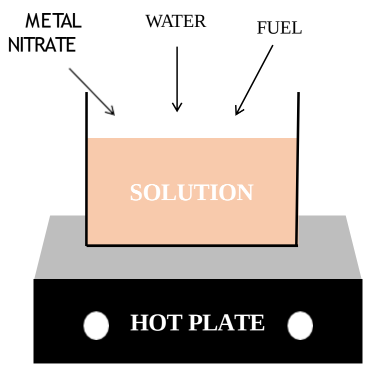
Proposed four electron ORR and OER mechanism on perovskite surface

Low e_g orbital filling ⟶ strong adsorption of oxygenated species on the B site (strong B-OH bond)

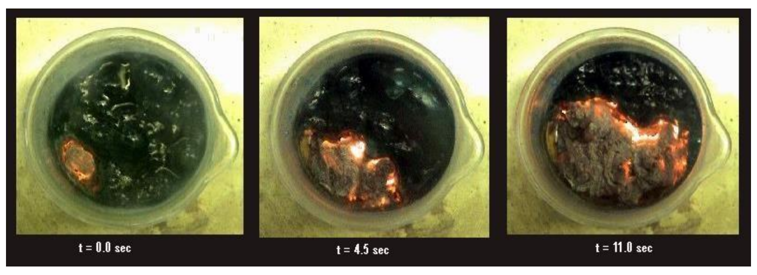
High e_g orbital filling ⟶ weak adsorption of oxygenated species that limits the reaction through the slow adsorption of reactants

Optimize the e_g=1 ⟶ Balance the adsorption and desorption of reactants and the intermediate

Catalyst Preparation



Volume combustion synthesis



Combustion front movement

Key features: Molecular level homogenization ,high temperature (~1000 ˚C), short process time, evolution of gases, porous and high surface area

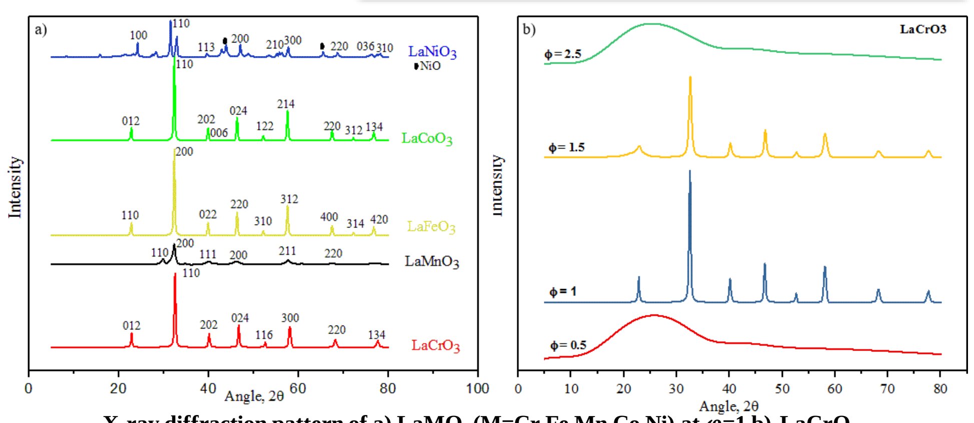
Fuel: e.g. glycine, urea, hydrazine etc.

$$Me^{v}(NO_3)_v + \frac{5}{9}v\varphi NH_2CH_2COOH + \frac{5}{4}v(\varphi-1)O_2 \rightarrow MeO_{\frac{v}{2}} + \frac{10}{9}v\varphi CO_2 + \frac{25}{18}v\varphi H_2O + \left(\frac{5\varphi+9}{18}\right)vN_2$$

Metal Oxide — Gas Phase Products

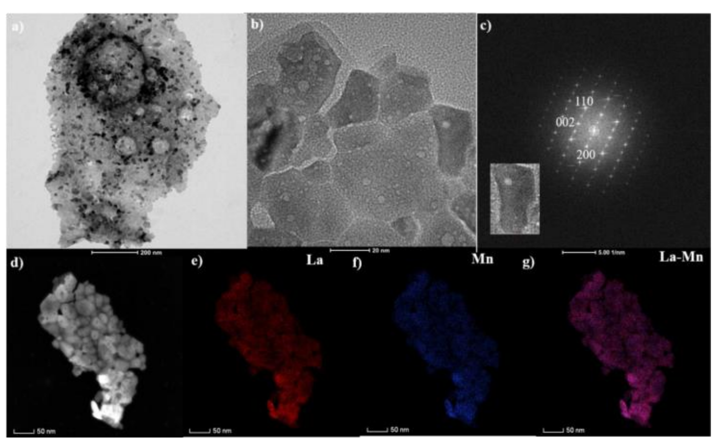
Where φ is fuel to oxidizer ratio
φ = 1, Stoichiometric mixture
φ > 1, Fuel rich
φ < 1, Fuel lean

Catalyst Characterization

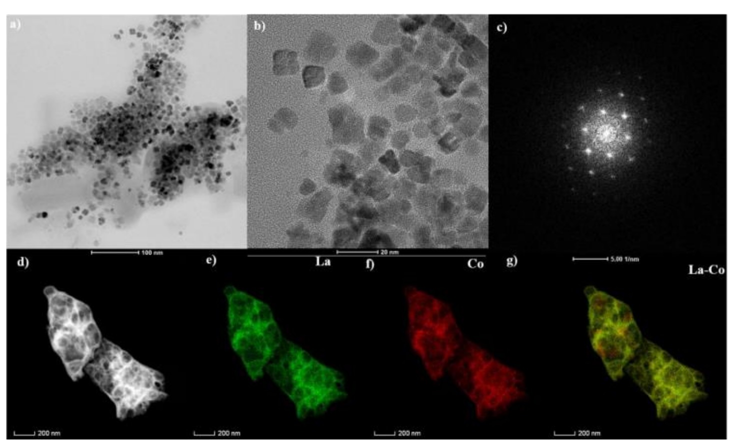


X-ray diffraction pattern of a) $LaMO_3$ (M=Cr,Fe,Mn,Co,Ni) at φ=1 b) $LaCrO_3$

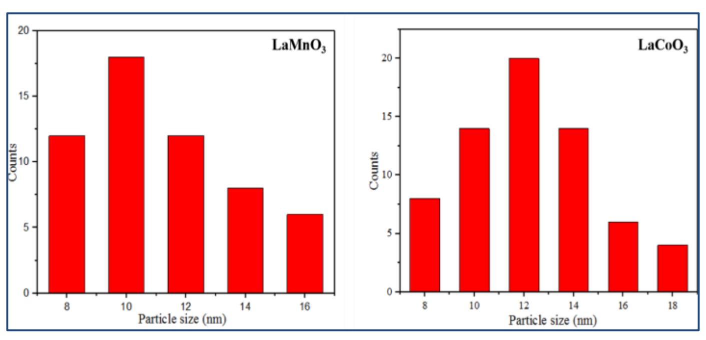
- $LaNiO_3$ particularly contain two different phases, $LaNiO_3$ and NiO,
- All other compounds are completely in the perovskite form.
- Combustion temperature obtained at φ =0.5 and φ = 2.5 does not provide enough energy for the crystallite structure formation.



HRTEM image and c) SAED pattern of LaMnO3 (d-g) EDX elemental mapping of La, Mn and overlapped La-Mn.



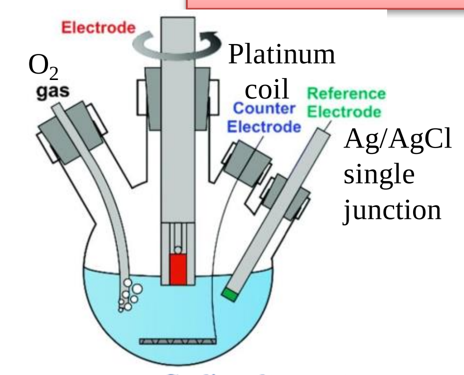
HRTEM image and c) SAED pattern of LaCoO3 (d-g) EDX elemental mapping of La, Co and overlapped La-Co.

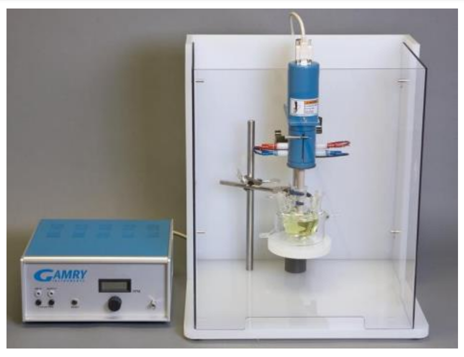


Particle size distribution histogram of a) $LaMnO_3$ b) $LaCoO_3$

- The particle distribution over selected region on $LaMnO_3$ and $LaCoO_3$ suggests the presence of particles in the range between 8 -20 nm along with some level of agglomeration.
- . EDX elemental mapping indicates the presence of La and Mn in equal ratio everywhere on the catalyst

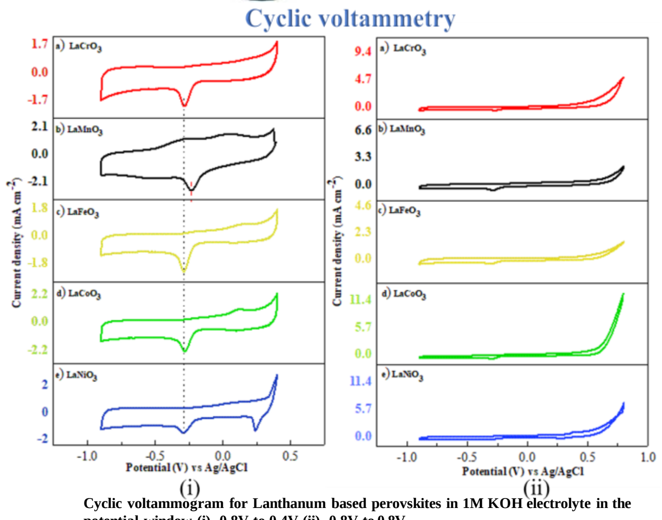
Electrocatalytic ORR/OER Reaction





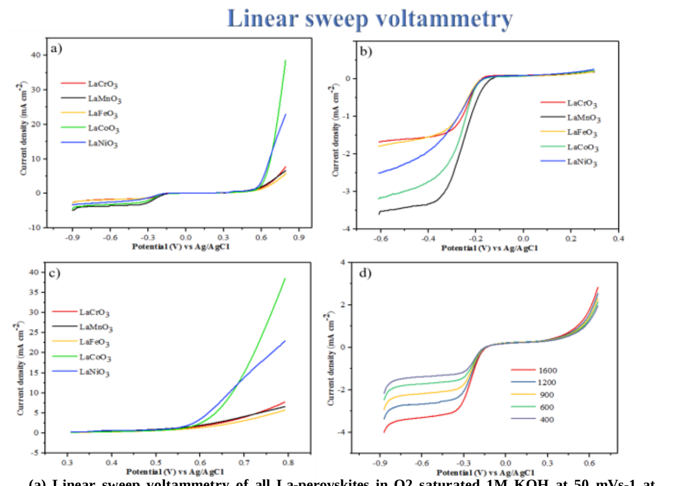
PINE instruments bipotentiostat (WaveDriver 20) connected with rotating disc electrode (RDE) Speed – 400 to 1600 rpm

Cyclic voltammetry



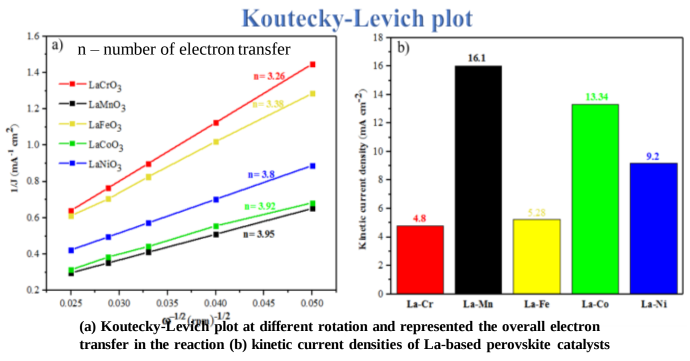
Cyclic voltammogram for Lanthanum based perovskites in 1M KOH electrolyte in the potential window (i) -0.8V to 0.4V (ii) -0.8V to 0.8V.

Linear sweep voltammetry



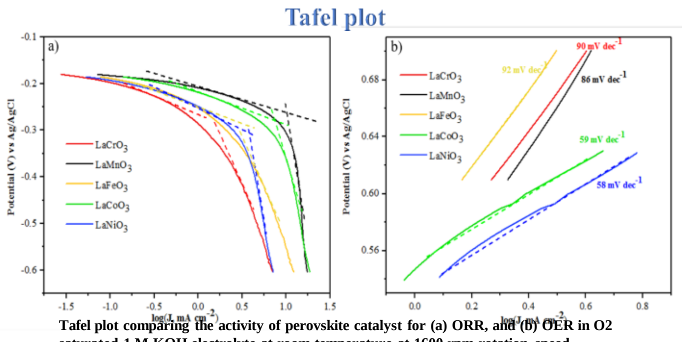
(a) Linear sweep voltammetry of all La-perovskites in O2 saturated 1M KOH at 50 mVs-1 at 1600 rpm in the potential range of -0.9V to 0.8V, (b) oxygen reduction reaction (ORR) current densities at 1600 rpm (c) OER current densities in the potential between 0.3V to 0.8V, d) ORR current density of $LaMnO_3$ at different rotation speed (400 to 1600rpm)

Koutecky-Levich plot



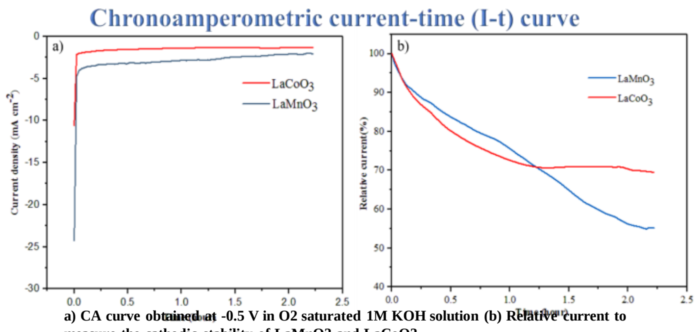
(a) Koutecky-Levich plot at different rotation and represented the overall electron transfer in the reaction (b) kinetic current densities of La-based perovskite catalysts

Tafel plot



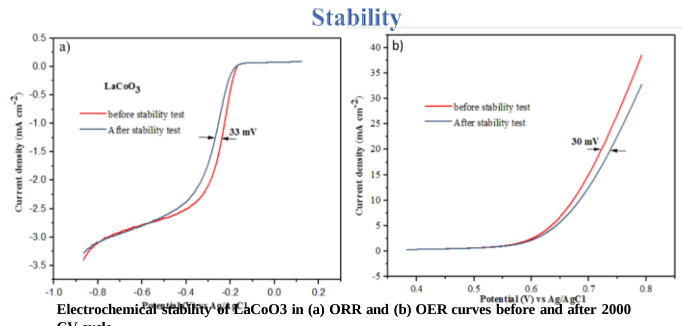
Tafel plot comparing the activity of perovskite catalyst for (a) ORR, and (b) OER in O2 saturated 1 M KOH electrolyte at room temperature at 1600 rpm rotation speed.

Chronoamperometric current-time (I-t) curve



a) CA curve obtained at -0.5 V in O2 saturated 1M KOH solution (b) Relative current to measure the cathodic stability of LaMnO3 and LaCoO3

Stability



Electrochemical stability of LaCoO3 in (a) ORR and (b) OER curves before and after 2000 CV cycle

Conclusion

- $LaMnO_3$ shows the maximum current density for oxygen reduction reaction, whereas $LaCoO_3$ shows better performance for oxygen evolution reaction.
- The ORR kinetics was improved in the order of **$LaCrO_3 < LaFeO_3 < LaNiO_3 < LaCoO_3 < LaMnO_3$.**
- Chronoamperometric results show that at -0.5V $LaMnO_3$ holds the maximum current density with poor stability.
- The $LaCoO_3$ catalyst showed better stability for oxygen reduction and oxygen evolution reactions with continuous cycling for 2000 cycles between -0.3V to 0.6V

Reference

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Acknowledgement

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