



Low-critical elements perovskite oxides for clean energy production and CO₂ conversion

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Significance and Relevance

To make Solid Oxide Cells (SOCs) competitive for a sustainable future, satisfactory electrocatalysts for oxygen reduction reaction, ORR, and/or for CO₂ reduction reaction CO₂RR, and sustainable materials and processes, are required at the same time. This work concerns the optimization, through doping and synthesis strategies, of the properties of ABO₃ perovskite oxides, the most promising class of SOCs electrocatalysts for clean energy production and CO₂ conversion. The aim is to decrease the critical elements content and to increase the materials performance, by exploiting the knowledge on synthesis-structure-properties relationships.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport and CO₂ utilization and recycling

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Clean energy transition entails CO₂ utilization and recycling as energy vectors and/or chemicals. Solid oxide cells (SOCs) offer the possibility of producing green energy, working as solid oxide fuel cell (SOFC), and/or to convert CO₂ into valuable fuels, operating as solid oxide electrolysis cell (SOEC). For SOCs, a key technological issue is the development of performing electrocatalysts with structural chemical/thermal stability, peculiar surface and redox properties, good ionic-electronic conductivity and electrocatalytic features towards ORR and/or CO₂RR¹. Furthermore, a sustainable technology moves together with sustainable materials first in terms of critical element content². Perovskite oxides seem to meet all these requirements, if appropriately doped in A-, B-, or O- sites and tailored by synthesis procedures³. Doped-La(Sr)FeO₃ represent a versatile class of perovskites with a good balance between stability/activity/conductivity. It is expected that the replacement of critical Sr with not critical² La, Sm or Ce mainly affects mixed ionic-electronic conductivity, whereas electrocatalytic performance is primarily determined by B-site elements as Fe and Al, for ORR, and Fe, Co, Ni and Cu, for CO₂RR. In this work, A- and B-sites co-doping and the less known O-site doping were explored, by selecting compositions with low-content of critical elements. In details, Ce/Sm/Y/Al-doped SrFeO₃ were explored for ORR, whereas Cu/Ni/F-doped La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ were studied for CO₂RR. The fine-tuning of their chemical-physical properties was also attained through the synthesis procedures, using solution combustion synthesis or citrate assisted method⁴.

Materials and Methods

Herein two class of perovskite oxides are presented for ORR and CO₂RR, respectively. As electrocatalysts for ORR SrFeO₃ doped in A-site with Sm, Ce or Y and in B-site with Al were studied. For CO₂RR three different doping strategies were explored for La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃: i) doping the B-site with Cu or Ni ii) fluorine-doping in O-site and iii) co-doping B- and O-sites with Cu/Ni and F. Solution combustion synthesis (SCS) and citrate-assisted method were employed as effective synthesis methodologies in producing perovskite oxides. Structural, surface, textural and redox properties were investigated by X-ray diffraction (XRD) with Rietveld analysis, X-Ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and temperature programmed reduction (TPR) in controlled

atmospheres. Electrochemical tests were performed on symmetrical cells by electrochemical impedance spectroscopy (EIS).

Results and Discussion

Figure 1A displays an example of graphical Rietveld fitting of XRD data. X-ray diffraction associated with Rietveld analysis evidenced the incorporation of dopants in the rhombohedral perovskite crystal structures for all studied compositions. H_2 -temperature programmed reduction profiles showed that this class of materials exhibits reduction properties and oxygen mobility in the SOCs working temperature range. A satisfactory oxygen vacancies distribution is crucial for oxygen adsorption and oxygen ion drift along the electrocatalyst. Therefore, XPS and TGA experiments were carried out for the evaluation of the suprafacial oxygen vacancies and as well of the bulk oxygen mobility at high temperature (above 400 °C). Figure 1B depicts, for differently doped-SrFeO₃, the results relative to TPD step under N₂ flow, carried out during TGA after air treatment. The Sm-doped sample seems to release the highest amount of gaseous O₂, corresponding to the highest weight loss, suggesting that this sample may have the highest amount of oxygen vacancies and bulk oxygen mobility. CO₂-chemisorption properties of doped-La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ evaluated by CO₂-thermogravimetric analysis evidenced a positive effect of copper and fluorine doping (Figure 1C). Structural, redox and surface results were correlated with those obtained by electrochemical impedance spectroscopy in air for doped SrFeO₃ and in CO₂ for doped- La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ on symmetrical cells configuration with Ce_{0.8}Sm_{0.2}O₂ as electrolyte.

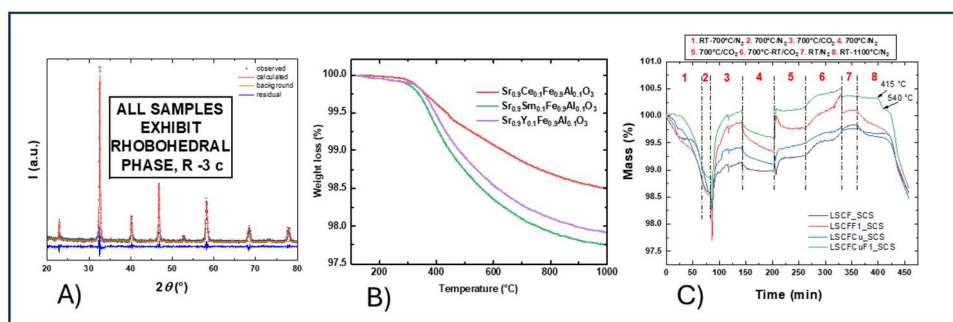


Figure 1. A) Rietveld analysis of XRD data; B) TPD-step of a TGA experiment in air; C) CO₂-TGA experiment consisting of CO₂ chemisorption at 700 °C (2 cycles) and subsequent TPD step.

References

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