Exploring $BaTiO_3$-Derived Materials for Advancing SOFC Electrode Performance

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Significance and Relevance

The present work has significance in addressing one of the key challenges in new air-electrode materials for solid oxide fuel cells (SOFCs), the reduction of critical raw materials (CRMs) such as cobalt (Co) and lanthanum (La). By focusing on $BaTiO_3$-derived perovskites, this study contributes to the development of alternative materials with both environmental and economic advantages, focusing on a more sustainable approach to energy conversion technologies. Additionally, this research establishes a methodology of characterization for future novel materials.

Preferred and 2nd choice for the topic: Sustainable and clean energy production and transport. *Second choice:* green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

One of the current challenges in solid oxide fuel cell (SOFC) development is the removal or reduction of critical raw materials (CRMs), like Co, La and Sr[1], in electrode materials while maintaining adequate electrochemical activity and ionic conduction. On the other hand, non-critical alternatives such as barium titanate $BaTiO_3$ (BTO) show significantly lower activity. The objective of the present work is to take advantage of the capability of ABO_3 perovskite oxides to accommodate various cation substitutions at A- and/or B-site to embed the needed functions. In practice, we target the design of BTO-derived perovskites with increased redox activity and improved ionic conductivity, which is a promising starting point for low-CRM materials.

For example, substituting Ti^{4+} by Fe^{3+} at B-site of $BaTiO_3$ is expected to bring additional redox functions, while modifying the total cationic charge leads to structural rearrangements to maintain neutrality. In general, varying the ionic radii, the formal charge of the cations or the A/B ratio is expected to cause structural disorders which can sustain ionic conductivity or favor the ex-solvation of an additional crystal phase.[2] Moreover, A-site deficient perovskite materials have demonstrated improved redox activity over the stoichiometric counterparts.[3]

In this work, we target the selection of BTO-based oxides modified by the substitution of A-site cations (Ba^{2+}) and/or B-site cations (Ti^{4+}). To this end, the following dopants were chosen to substitute the A- and B-sites of BTO, to form a series of BTO-derived samples: Ca^{2+} and La^{3+} ions for the A-site, and Pr^{3+}, Ni^{2+}, Fe^{3+} and Cu^{2+} ions for the B-site.

Our research focuses on a comprehensive investigation of BTO-derived perovskites, examining their structure, including minority phases, redox properties, surface composition and ionic conductivity.

Materials and Methods

The BaTiO3-derived samples were prepared using the citrate complexation method, accompanied by some samples synthesized with the conventional ceramic (solid-state) method and samples made with an autocombustion synthesis.

Several characterization techniques (SSA, TGA-DSC, TPR-TPO, XRD, and XPS) were used. Moreover, operando Raman spectroscopy was run by means of a dedicated environmental cell (Harrick Scientific) and a HR800 Horiba spectrometer equipped with several lasers allowing excitation wavelengths of 633, 532 or 457nm. XPS has been performed by means of a Kratos Analytical Axis UltraDLD spectrometer. Quasi in-situ measurements were made using the catalytic cell, where the samples were thermally pretreated under gaseous reactant flow at atmospheric pressure and transferred to the analysis chamber under UHV.

Results and Discussion

XRD, Raman, and XPS analyses revealed ex-solved crystalline phases in some of the samples. Preliminary results of a $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ sample show some reducibility by TPR, making it suitable for H2 reduction. Fig. 1 shows in-situ Raman spectra collected during H_2/O_2 cycling. H_2-TPR induced clear spectral modifications beyond thermal effects, notably a shift to lower frequencies, decreased intensity at 505 cm^{-1}, and increased intensity at 730 cm^{-1}. O_2-TPO restored the initial Raman spectrum, indicating sample regeneration upon redox cycling.

The sample's reducibility correlates with its iron content, as evidenced by the quasi in-situ XPS spectra in Fig. 1. Metallic iron is formed after reduction at 800°C and disappears upon reoxidation, suggesting that the observed reduction is linked to Fe cations. Further analysis using complementary techniques will provide a detailed discussion of this phenomenon

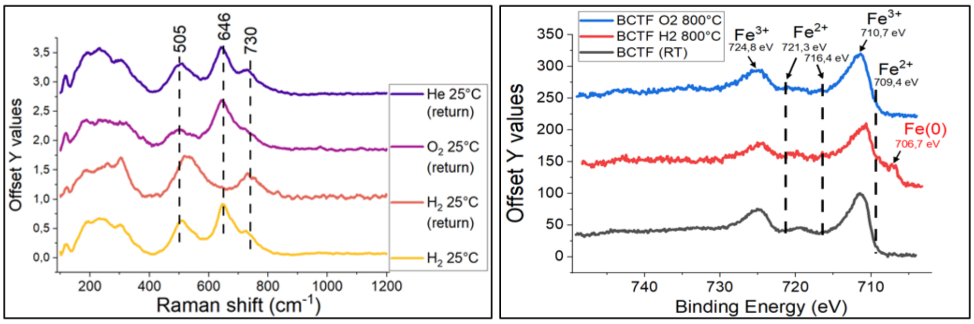

Figure 1. *Left: evolution of the Raman spectra at λ = 633 nm of $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ during in-situ measurements. Right: quasi in-situ XPS spectra of $Ba_{0.85}Ca_{0.15}Ti_{0.80}Fe_{0.20}O_3$ showing the Fe 2p orbitals after H_2 reduction at 800°C and O_2 oxidation at 800°C.*

In conclusion, combining in-situ Raman experiments, XPS measurements, and the other characterization techniques, it becomes possible to estimate the performance of a possible SOFC electrode material. Additionally, the activity of the perovskite materials is influenced by their synthesis method.

References

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