

Effects of divalent B-site cations upon the structural and catalytic properties on Fe-based mixed conductors

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Introduction

Solid oxide fuel cells (SOFCs) show great promise for generating clean power from a variety of fuels. The major roadblock against their implementation is a large cathodic resistance, which causes insufficient power densities and high fabrication costs. The large cathodic resistance is caused by slow oxygen activation kinetics and oxide ion transport of the current Mn-based cathode [1]. Mixed (electronic and ionic) conductors have been demonstrated to increase performance through the expansion of the electrochemically active area. The oxygen reduction behavior of mixed conductors is co-limited by the oxygen surface exchange and bulk ionic transport [2]. Despite the improved performance compared to Mn-based materials, no mixed conductor exhibits the optimal balance of oxygen reduction kinetics and system compatibility. The present work examines the effects of divalent doping upon the structural and catalytic properties of Fe-based mixed conductors.

Materials and Methods

Fe-based mixed conductors are based on the perovskite (ABO_3) unit cell. The perovskite-type materials are prepared by solid-state techniques with the formula $(La_{0.60}Sr_{0.40})(Co_{0.18}Fe_{0.72}X_{0.1})O_{3-\delta}$ where X is Zn, Cu, or Ni. Data for $(La_{0.60}Sr_{0.40})(Co_{0.20}Fe_{0.80})O_{3-\delta}$ is provided for comparison. Unit cell parameters are determined by X-ray diffraction (XRD). High-temperature structural properties, such as unit cell parameters and oxygen vacancy formation, are examined using *in-situ* XRD and temperature-programmed techniques. Oxygen-surface interactions are characterized using temperature-programmed techniques, oxygen equilibration experiments, and differential scanning calorimetry. Voltammetry and impedance experiments are performed to examine the electrochemical performance of the materials. Complementary data are provided by techniques such as BET surface area measurements, X-ray photoelectron spectroscopy (XPS), and vibrational spectroscopy.

Results and Discussion

The addition of divalent cations on the B-site causes variations in the structural and catalytic properties of the mixed conductors. Changes in the unit cell parameters are explained through changes in cationic valence and size effects. Moreover as shown in Figure 1, the addition of the divalent cations leads to an increase in oxygen vacancy formation at elevated temperatures in air. Since oxygen vacancies are necessary for the oxygen surface exchange reaction and ionic mobility, these materials are expected to demonstrate improved performance compared to the formulation free of divalent species on the B-site. In particular, the addition of Zn, the cation with the largest ionic radii, leads to the creation of oxygen vacancies with greatest ease. An optimization of the Zn and Co levels will result in even improved oxygen vacancy formation.

In agreement with the larger unit cell, calorimetric and spectroscopic results reveal that oxygen is more weakly bound (and thus more mobile) in the perovskite lattice for the mixed conductors doped with the divalent cations.

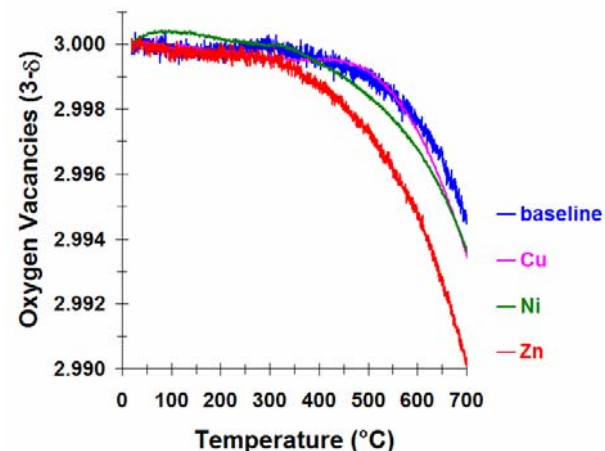


Figure 1. Oxygen content (δ in $ABO_{3-\delta}$) in air as a function of temperature for perovskite – type materials of the formula $(La_{0.60}Sr_{0.40})(Co_{0.18}Fe_{0.72}X_{0.1})O_{3-\delta}$. Data for $(La_{0.60}Sr_{0.40})(Co_{0.20}Fe_{0.80})O_{3-\delta}$ is provided for comparison as a baseline material.

Tests are performed to examine the compatibility of the new materials with potential electrolytes such as yttria-stabilized zirconia. Compatibility properties examined include chemical and thermal expansion and chemical reactivity.

A novel series of potential SOFC cathode materials has been synthesized by the incorporation of divalent cations into perovskite-type mixed conductors. The formulations demonstrate increased oxygen vacancy formations compared to similar materials without the divalent doping.

Significance

The development of novel cathode formulations with improved catalytic properties and electrolyte compatibility is necessary for the commercialization of SOFCs.

References

1. Ormerod, R.M., *Solid oxide fuel cells*. Chem. Soc. Rev., 2003. 32: p. 17.
2. Adler, S.B., *Factors Governing Oxygen Reduction in Solid Oxide Fuel Cell Cathodes*. Chemical Reviews, 2004. 104: p. 4791.