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Thermodynamic data of $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ SOFC cathode material

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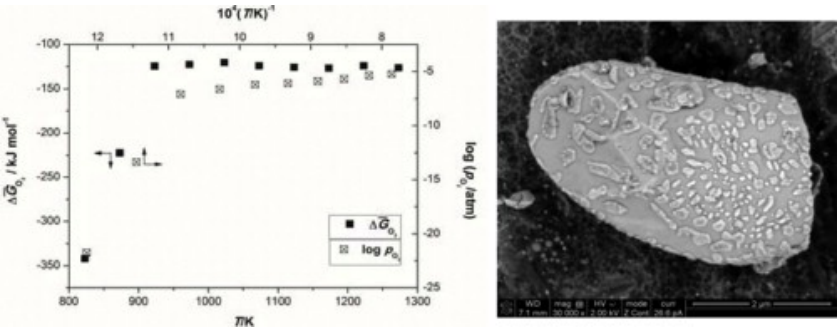
Abstract

The compound $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ with perovskite structure has been studied focusing mainly on the thermodynamic stability in correlation to the change in the oxygen stoichiometry. The thermochemical behavior has been investigated from room temperature to 1300K by thermal gravimetry and differential thermal analysis in air and by calorimetry in scanning mode in Argon. The temperature dependence of enthalpy (ΔH^T_{298}) in the temperature range of 300–900K was measured by drop calorimetry. Thermodynamic properties represented by the relative partial molar free energies, enthalpies and entropies of oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been obtained in the temperature range of 823–1273K using solid electrolyte electrochemical cells (EMF). The influence of the oxygen stoichiometry on the thermodynamic properties was examined using a coulometric titration technique coupled with EMF measurements. The results are discussed based on the strong correlation between the energetic parameters and the charge compensation of the material system.

Graphical abstract

Partial molar energy of oxygen dissolution ($\Delta\bar{G}_{O_2}$) and equilibrium partial pressure of oxygen ($\log p_{O_2}$) of perovskite material with the composition $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as a function of temperature.



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Introduction

Searching for new materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs), the mixed ionic-electronic conducting (MIEC) perovskite oxides (Ba,Sr)(Co,Fe)$O_{3-\delta}$ (BSCF) have received great attention [1], [2], [3], [4], [5], [6], [7], [8]. These oxides may show a high electronic conductivity due to the mixed valence states of the transitional metals and high oxide ion conductivity related to the high oxygen vacancy concentration. The properties of the BSCF compounds can be tailored by varying the Ba:Sr and Co:Fe ratios. The significant oxygen non-stoichiometry deviations ($0.3<\delta<0.8$ at $873<T<1173$ K) exhibited by the $Ba_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ perovskites, together with the variation of the structural characteristics are depending on temperature and oxygen partial pressure [9], [10], [11], [12], [13] leading to substantial variations in the electrochemical activity of electrodes.

As a SOFC cathode, the long-term stability of such a highly defective material under the operating conditions of an IT-SOFC is crucial. Most of the quaternary BSCF compounds exhibit cubic symmetry at 1273 K in air. Some of the BSCF compositions undergo a cubic to hexagonal transition at low temperatures as polymorphs of hexagonal symmetry in the BSCF system are expected regarding the symmetries of the end members in this system [14], [15]. Especially under reducing conditions ($<10^{-5}$ atm) the thermal treatment showed decomposition through a complex series of phase transitions due to ordering [5], [6]. Although the knowledge of the fundamental solid state chemistry in the BSCF materials, including the relation between defect structure and thermodynamic stability has increased during the years, the role of the energetic parameters as driving forces leading to materials with the greatest stability during operation is still needed.

In the BSCF series, the composition $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) has been of particular interest as it has a good oxygen permeation [1], [2], [16], [17], and low non-ohmic losses as IT-SOFC cathodes [3], [18], [19], [20]. However, even for this composition, the degradation of the permeability and of the oxygen ion conduction associated with the formation of less symmetrical non-cubic phases at 973–1173 K was already reported [1], [15], [21], [22]. By using transmission electron microscopy, Efimov [23] reported in the intermediate temperature range below 1123 K the decomposition of cubic BSCF5582 into a mixture of phases including a lamellar-shaped $Ba_xSr_{1-x}Co_{2-y}Fe_yO_{5-\delta}$ complex oxide in addition to hexagonal perovskite $Ba_{0.6}Sr_{0.4}CoO_{3-\delta}$. Searching for the phase stability and the decomposition pathway of cubic $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, P. Müller et al. [24], [25] reported that the crystallization of the hexagonal phase is limited to temperatures below 1103 K and the growth of plate-like regions with trigonal crystal structure was detected up to 1173 K annealing. The formation of secondary phases will have a negative impact on oxygen-ion conduction, by increasing the lattice stress and decreasing the oxygen vacancies mobility.

Compared with BSCF5582composition, the BSCF6482 – based cathode material has been reported by Zhao et al. [4] to exhibit better cell performance due to the relatively higher electrical conductivity at intermediate temperatures (873–1073 K). The values of activation energy for the conductivity found by Wei

et al. [8] and Yang et al. [15] are smaller for the composition with x=0.6 comparatively with the corresponding values obtained for x=0.5. Nevertheless, comparatively with BSCF5582, very little work was performed on the BSCF6482.

When varying the Ba/Sr ratio in $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (from x=0.2 to 0.8) a maximum in the partial molar free energy is obtained in the temperature range from 800 to 900K for 50mol% Ba, indicating the compositions with x=0.5 and y=0.2 to have the highest oxide ionic conductivity [26] and at 900K, the thermodynamic data suggest an increase of the oxygen vacancies concentration correlated with higher oxygen conductivity for the composition with 60mol% Ba, consistent with the analysis by Zhao et al. [4]. To our best knowledge, no other thermodynamic characterization of compounds in the BSCF system is available.

In the present paper, the thermodynamic properties of the $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF6482) material is characterized from room temperature to 1300K and the correlation between the thermodynamic parameters and the change in the oxygen nonstoichiometry is given.

Section snippets

Experimental

The powder specimens of $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ were synthesized by solid state reaction method which was previously described in detail [15], [26]. According to the X-ray diffraction (XRD), furnace quenched powders of $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ calcined at 1273K in air exhibit pure cubic perovskite structure [15], [26].

The morphology of the samples was analyzed by scanning electron microscopy (SEM) using a FEI Quanta 3D equipment. In order to evidence the surface features of the particles the…

Results and discussion

By using the experimental values of the electromotive force of the cell, the thermodynamic data represented by the relative partial molar free energies ($\Delta\bar{G}_{O_2}$), enthalpies ($\Delta\bar{H}_{O_2}$) and entropies ($\Delta\bar{S}_{O_2}$) of the oxygen dissolution in the perovskite phase, as well as the equilibrium partial pressures of oxygen have been calculated according to the known relationships [28], [30]. The partial molar free energies ($\Delta\bar{G}_{O_2}$) and the corresponding $\log p_{O_2}$ for the BSCF6482 sample are shown in Fig. 1. $\Delta\bar{G}_{O_2}$…

Conclusions

The energetic parameters obtained by a couple of measurements (EMF, TG, DSC, Drop Calorimetry) allow for the correlation of the thermodynamic stability with the defect structure in particular temperature ranges.

The thermodynamic data of oxygen dissolution have a strong dependence on the temperature, and show significant variations with respect to the oxygen stoichiometry change. These may explain the different behaviors in the different temperature regimes. The oxygen vacancy order also shows…

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