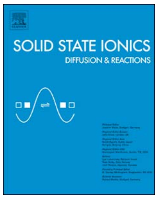
Solid State Ionics 309 (2017) 48–57

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



Defect chemistry and transport properties of $SrCo_{1-x}Ta_xO_{2.5+\delta}$ as a promising oxygen electrocatalyst for reversible solid oxide fuel cells

Xinfang Jin, Jie Wang, Kevin Huang*

Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29201, USA

ARTICLE INFO

Keywords:
Oxygen interstitials
Large polarons
Small polarons
Oxygen stoichiometry
Hole mobility

ABSTRACT

In this study, we report on thermodynamic and transport properties of $SrCo_{1-x}Ta_xO_{2.5+\delta}$ (SCT) derived from a defect chemistry model encompassing oxygen interstitials as the ionic point defect and holes/excess electrons as the electronic point defects. The results show that SCT can be reasonably modelled as a large-polaron itinerant hole-conductor with a constant mobility at high oxygen stoichiometry (2.5 + δ). At low oxygen stoichiometry, electronic carriers tend to be localized small-polarons with a trapping center at $Ta_{Co}^{\cdot\cdot}$. With the established defect model, a complete picture of electron hole concentration $p = p(T, Po_2)$, excess electron concentration $n = n(T, Po_2)$ and oxygen nonstoichiometry $\delta = \delta(T, Po_2)$ is mapped out, from which $p = p(T)$ under a constant δ is derived. The latter further reveals the true activation energy for hole-conduction under a constant δ and yields thermodynamic data for the oxygen incorporation reaction creating oxygen interstitials. These fundamental data are also compared with $SrCo_{1-x}Nb_xO_{2.5+\delta}$ (SCN), suggesting that SCT is a better hole-conductor with higher hole concentration for oxygen electrocatalysis.

1. Introduction

As a critical performance-limiting component of intermediate-temperature reversible solid oxide fuel cells (IT-RSOFCs) [1–4], the research on bifunctional oxygen electrode materials has attracted much attention in recent decades. A key performance metrics for a good bifunctional oxygen electrode material is the fast concurrent oxide-ion and electron transport. Over years' effort, researchers have identified a broad range of cobalt-containing complex oxides exhibiting high mixed oxide-ion and electronic conductivity, an exemplary group of which includes perovskites $La_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$ (LSCF) [5–12], $Sm_xSr_{1-x}CoO_{3-\delta}$ (SSCo) [13–15], $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$ (BSCF) [16] and layered/cation ordered $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Nd, Sm and Gd) [17–20].

A very recent development of bifunctional mixed conducting oxygen electrode materials has suggested that donor-doped $SrCoO_3$ is a promising class of candidate materials with a balanced catalytic activity and chemical stability [21–33]. Pure $SrCoO_3$ (SCO) is a 3C-type primitive cubic structured perovskite. However, it can easily lose one-sixth of its lattice oxygen at elevated temperatures, transforming itself into a brownmillerite phase $SrCoO_{2.5}$ with long-range ordering of oxygen vacancies. Experiments have also shown that those ordered oxygen vacancies in brownmillerite are oxygen-intercalatable [34–39], which implies that oxygen interstitials can be viewed as a type of ionic point defect in the framework of brownmillerite structure. Based on this consideration, we have recently proposed a defect chemistry model using brownmillerite as a reference framework and encompassing oxygen interstitials as the ionic point defect, itinerant-to-localized holes and localized excess electrons as the electronic point defects to interpret the transport properties of Nb-doped SCO (SCN) with satisfactory results [40].

In this work, we further apply the developed defect chemistry model to Ta-doped SCO (SCT) system, a rivalry system to SCN, for transport properties. In particular, we compare the obtained transport properties of SCT with SCN systems to gain insights into how the fundamental covalent bonding and electronic structure affect the oxygen stoichiometry and transport of electrons and oxide-ions. The SCN and SCT systems provide a unique opportunity for this study because Nb^{5+} and Ta^{5+} in VI-coordination have identical ionic radii (0.64 Å), by which the effect of size-induced lattice distortion can be neglected, allowing ones to assess the correlation between electronic structure and transport properties without "size" effect.

2. Description of defect chemistry model

2.1. Introduction of oxygen interstitials into donor-doped SCO

According to the defect chemistry model developed for the donor-

---

* Corresponding author.
E-mail address: huang46@cec.sc.edu (K. Huang).

http://dx.doi.org/10.1016/j.ssi.2017.07.001
Received 11 April 2017; Received in revised form 13 May 2017; Accepted 2 July 2017

doped SCN system [40], a perfect brownmillerite (BM) structure is viewed as the reference framework, within which oxygen interstitials are considered over cation vacancies (based on energetics [41]) as the ionic point defect to charge compensate the positively charged dopant, while electron holes/excess electrons are taken as the electronic point defects. Therefore, the oxygen stoichiometry of SCT can be viewed as 2.5 + δ, with δ representing the concentration of oxygen interstitials introduced by donor-doping and occupied on the previously vacant but ordered oxygen vacancy sites in the original BM structure where the formal oxidation state of Co-ions is 3 +. With the Kröger-Vink notation, the negatively charged oxygen interstitials (${O_I}^{''}$) are treated as a charge-balancing point defect to the positively charged donor dopants (${Ta_{Co}}^{\cdot\cdot}$) and electron holes (${Co_{Co}}^{\cdot}$). The equilibrium between oxygen interstitials ${O_I}^{''}$ and vacancies ${V_O}^{\cdot\cdot}$ is intrinsically governed by anion Frenkel defect reaction:

$$V_I^X + O_O^X \rightleftarrows O_I^{\prime\,\prime} + V_O^{\bullet\bullet} \tag{1}$$

where ${V_I}^X$ and ${O_O}^X$ represent the oxygen interstitials and regular sites, respectively. If an ideal perovskite structure is chosen as the reference framework, oxygen vacancies will be considered point ionic defects. The Appendix details the discussion on the defect model using two difference reference frameworks.

2.2. The defect reactions

The defect chemistry of $SrCo_{0.9}Ta_{0.1}O_{2.5+\delta}$ is examined under a perfect BM reference framework $SrCoO_{2.5}$, in which the formal oxidation-state of Co-ions is 3 +. The oxygen interstitials ${O_I}^{''}$, electron holes ${Co_{Co}}^{\cdot} = Co^{4+}$ and excess electrons ${Co_{Co}}^{'} = Co^{2+}$ are the predominant point defect species according to Kröger-Vink notations. Assuming that these defects are randomly distributed across the lattice and non-interacting, the Ta_2O_5-doping reaction in SCO can be expressed by:

$$Ta_2O_5 \xrightarrow{Co_2O_3} 2Ta_{Co}^{\cdot\cdot} + 2O_I^{\prime\prime} + 3O_O^X \tag{2}$$

Here the positively charged dopant ${Ta_{Co}}^{\cdot\cdot}$ is charge-compensated by the negatively charged oxygen interstitial ${O_I}^{''}$. Also, Ta^{5+} has a fixed oxidation state under the generally oxidizing atmospheres of this study [40,42].

The oxygen incorporation reaction can then be written by:

$$\frac{1}{2}O_2(g) + 2Co_{Co}^X + V_I^X \rightleftarrows O_I^{\prime\prime} + 2Co_{Co}^{\bullet} \tag{3}$$

where ${O_I}^{''}$ is created by $1/2O_2$ occupying the vacant oxygen site ${V_I}^X$ in the BM, while oxidizing lattice $Co^{3+} = {Co_{Co}}^X$ into $Co^{4+} = {Co_{Co}}^{\cdot}$; the latter is the electron holes predominantly responsible for the conductivity of the material. Applying the mass-action law with the assumption that the activity of each species is the same as its concentration, the equilibrium constant K_{ox} of reaction (3) can be written as:

$$K_{ox} = \frac{[O_I^{\prime\prime}][Co_{Co}^{\bullet}]^2}{Po_2^{0.5}[Co_{Co}^X]^2[V_I^X]} \tag{4}$$

The excess electron ${Co_{Co}}^{'}$ is produced at high temperatures and low partial pressures of oxygen through Co-ions charge-disproportionation reaction:

$$2Co_{Co}^X \rightleftharpoons Co_{Co}^{\bullet} + Co_{Co}^{\prime} \tag{5}$$

The equilibrium constant K_{dsp} of Eq. (5) under the same assumption as Eq. (4) is given by:

$$K_{dsp} = \frac{[Co_{Co}^{\bullet}]\bullet[Co_{Co}^{\prime}]}{[Co_{Co}^X]^2} \tag{6}$$

In addition, the electroneutrality and site conservations need to be maintained across the lattice:

$$2[Ta_{Co}^{\bullet\bullet}] + [Co_{Co}^{\bullet}] = 2[O_I^{\prime\prime}] + [Co_{Co}^{\prime}] \tag{7}$$

$$[Co_{Co}^X] + [Co_{Co}^{\bullet}] + [Co_{Co}^{\prime}] + [Ta_{Co}^{\bullet\bullet}] = 1 \tag{8}$$

$$[V_I^X] + [O_I^{\prime\prime}] = 0.5 \tag{9}$$

For *p*-type electronic conductors, the electron holes dominate the total conductivity. In this case, the conductivity of ${Co_{Co}}^{\cdot}$ determines the conductivity of the material. The electrical conductivity of holes is expressed by:

$$\sigma = \frac{[Co_{Co}^{\bullet}]F\mu}{N_A \times a^3} \tag{10}$$

where, F is the Faraday constant = 96485C/mol; ($\frac{[Co_{Co}^{\bullet}]}{N_A \times a^3}$) is the concentration of holes; μ ($m^2/V/s$) is the mobility of holes; N_A is the Avogadro constant, 6.02×10^{23} (mol^{-1}); a is the lattice constant of a pseudo-cubic SCT (with 10 mol% Ta doping, $a = 3.90$ Å). According to the earlier studies [34,43], Co-3d orbital and O-2p orbital tend to hybridize strongly in the SCO systems, generating a wide conduction band. The mean-free-path between hole scattering event is short to give a weak temperature dependence of mobility $\mu = e\tau/m^*$ [44], where e is the charge of the charge carrier; τ and m* are collision time and effective mass of the charge-carrier, respectively. Therefore, we have assumed in this study that the hole-mobility μ is a T-independent constant and the observed decrease in hole-conductivity with increasing temperature under a constant Po_2 (see later Fig. 3) mainly arises from the decrease in hole-concentration induced by the loss of interstitial oxygens and therefore holes.

The analytic solutions for $n = [{Co_{Co}}^{'}]$, $[{Co_{Co}}^X]$, $\delta = [{O_I}^{''}]$ and $[{V_I}^X]$ as a function of $p = [{Co_{Co}}^{\cdot}]$, K_{ox} and K_{dsp} can be obtained by Eqs. (4), (6)–(9). Details on the deduction are available in Appendix A as well as our previous publication [40]. The electrical conductivity of the material $\sigma = \sigma(T, Po_2)$ is correlated to $p = [{Co_{Co}}^{\cdot}]$ by Eq. (10). Using the experimental $\sigma = \sigma(T, Po_2)$ as the objective function, the dependence of n, δ and p on T and Po_2 with only two adjustable parameters K_{ox} and K_{dsp} can then be attained through nonlinear regression as described in Section 5.

3. Experimental methods

3.1. Sample synthesis

The composition of $SrCo_{0.9}Ta_{0.1}O_{2.5+\delta}$ (SCT10) was selected for this study and synthesized *via* conventional solid-state reaction method by using high purity $SrCO_3$ (≥ 99.9%, Alfa Aesar), Co_3O_4 (≥ 99.7%, Alfa Aesar) and Ta_2O_5 (≥ 99.9%, Alfa Aesar) as the starting materials. Required amounts of the starting materials were weighted, mixed and calcined in air at 1000 °C for 10 h. The as-calcined powders were then crushed and ball-milled, followed by further sintering in air at 1200 °C for 10 h. Ball-milling and calcination were conducted three times to obtain phase-pure SCT10 powders. Then, the as-prepared ball-milled SCT10 powders were pressed into bars with a dimension of 45 mm × 6 mm × 4 mm and finally sintered in air at 1200 °C for 10 h to achieve a dense microstructure for electrical conductivity measurement.

3.2. Phase examination

The XRD (HT-XRD) data was collected at 500 °C on an X-ray diffractometer (X1 Theta-Theta, Scintag, USA) equipped with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). The scan was performed at a rate of $1^{\circ}\cdot min^{-1}$ from $2\theta = 10$–80°. Under the testing temperature, the sample was held for 3 h to ensure phase equilibrium.

3.3. Electrical conductivity measurement

The total conductivity of sintered bar samples were measured as a function of T and Po_2 by using a standard four-terminal method with