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Isothermal transport properties and majority-type defects of BaCo$_{0.70}$Fe$_{0.22}$Nb$_{0.08}$O$_{3-\delta}$

Taewon Lee[a], Deok-Yong Cho[b], Hyung-Soon Kwon[a], and Han-Ill Yoo[a*]

[a] Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

[b] Department of Physics, Chonbuk National University, Jeonju 561-756, Korea

Abstract

(Ba,Sr)(Co,Fe)O$_{3-\delta}$ based mixed conducting oxides, e.g. (Ba$_{0.5}$Sr$_{0.5}$)(Co$_{1-x}$Fe$_x$)O$_{3-\delta}$ and Ba(Co$_{0.7}$Fe$_{0.3-x}$Nb$_x$)O$_{3-\delta}$ are promising candidates for oxygen permeable membranes and SOFC cathodes due to their excellent ambipolar conductivities. Despite these excellent properties, however, their mass/charge transport properties have not been fully characterized and hence, their defect structure remains not clearly elucidated. Up until now, the majority types of ionic and electronic defects have been regarded as oxygen vacancies and localized holes. Holes, whether localized or not, are acceptable as majority electronic carriers on the basis of the as-measured total conductivity, which is essentially electronic, and electronic thermopower. On the other hand, the proposal of oxygen vacancies as majority ionic carriers lacks solid evidences. In this work, we document all the isothermal transport properties of Ba(Co$_{0.70}$Fe$_{0.22}$Nb$_{0.08}$)O$_{3-\delta}$ in terms of a 2×2 Onsager transport coefficient matrix and its steady-state electronic thermopower against oxygen activity at elevated temperatures, and determine the valences of Co and Fe via soft X-ray absorption spectroscopy. It turns out that the ionic and electronic defects in majority should be oxygen interstitials and at least two kinds of holes, one free and the other trapped. Furthermore, the lattice molecule should be Ba(Co$_{0.7}$Fe$_{0.3-x}$Nb$_x$)O$_{2+\delta}$, not Ba(Co$_{0.7}$Fe$_{0.3-x}$Nb$_x$)O$_{3-\delta}$, to be consistent with all the results observed.

Keywords: BaCo$_{0.70}$Fe$_{0.22}$Nb$_{0.08}$O$_{3-\delta}$, Defect types, Onsager matrix, Ionic/electronic conductivity, Thermopower, Ion-blocking method, X-ray absorption spectroscopy, Charge of transport

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* Corresponding author. Tel.: +82 2 8807163
E-mail address: hiyoo@snu.ac.kr (H.-I. Yoo)

1. Introduction

(Ba,Sr)(Co,Fe)$O_{3-\delta}$ -based mixed conductors, e.g. $(Ba_{0.5}Sr_{0.5})(Co_{1-x}Fe_x)O_{3-\delta}$[1-6] and $Ba(Co_{0.7}Fe_{0.3-x}Nb_x)O_{3-\delta}$[7,8] have been attracting wide attention as promising materials for the oxygen separation membrane and SOFC cathode primarily due to their excellent ambipolar conductivities. Despite these promises, however, their mass/charge transport properties have not been fully characterized and their defect structure remains still not clearly elucidated.

Up until now, oxygen vacancies ($V_O^{\bullet\bullet}$) and holes ($h^\bullet$) have been believed to be the majority disorder types in these systems.[2-8] Holes, whether localized or not, are acceptable as the majority type of electronic carriers or disorders because the total conductivities as measured on these systems, that are essentially electronic, always increase with increasing oxygen activity at fixed temperatures[3,6,7] and the sign of electronic thermopower is always consistent with the p-type carriers[6]. Oxygen vacancies as the majority type of ionic carriers or disorders, on the other hand, lack experimental evidences. The only circumstantial evidence available is that the oxygen contents of these oxides are always found to be smaller than 3 per lattice molecule with reference to the ideal perovskite lattice molecule $A^{2+}B^{4+}O_3$, or (Ba,Sr)(Co,Fe)$O_{3-\delta}$.[2,3,5,8] Furthermore, if these $V_O^{\bullet\bullet}$ and $h^\bullet$ were the case indeed, there would have to be effectively negatively charged defects, e.g., acceptor impurities, A_C' for charge compensation such that

$$\left[A_C'\right]=2\left[V_O^{\bullet\bullet}\right]+p+\sum\left[M_B^\bullet\right] \tag{1}$$

where [   ] stands for the concentration of the species therein, $p \equiv [h^\bullet]$, and $M_B^\bullet$ for the possible trapped (or localized) holes on multivalent B-site cations (Co,Fe). The identity of A_C' , however, has never been questioned thus far.

One well established method to identify the majority types of ionic and electronic defects or carriers is to measure the partial ionic and electronic conductivity against oxygen activity at fixed temperatures. If oxygen vacancies are the majority ionic defects, the partial ionic conductivity will have to decrease with increasing oxygen activity as long as their mobility remains independent of their concentration as is generally the case; If holes are in the majority, the electronic partial conductivity also has to increase with increasing oxygen activity. Another way to identify the majority disorder types is to observe the partial ionic and electronic thermopower in

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the steady sate because each thermopower is to be determined mostly by the partial molar entropy of the

majority carrier with a characteristic sign corresponding to the effective charge of the carrier[9] and hence, its sign

first indicates the identity of each majority type carriers.

In this work, we will first establish the isothermal Onsager-transport-coefficient-matrix, the most succinct

representation of all the isothermal mass/charge transport properties of a mixed conductor[10], for the system of

$BaCo_{0.70}Fe_{0.22}Nb_{0.08}O_{3-\delta}$ (BCFN) in the oxygen activity range of $-9.5 \leq \log a_{O_2} \leq -1$ at 750, 850, and 950 $^{\circ}C$,

respectively, by the ion-blocking polarization method[11]. The steady-state electronic thermopower is then

measured at the same thermodynamic states. Furthermore, the valences of B-site variable-valence cations Co

and Fe are determined by soft X-ray absorption spectroscopy (XAS) on the specimens quenched at different

thermodynamic states. We will thereby identify the majority types of ionic and electronic carriers and propose

the reference stoichiometric composition of the BCFN systems.

2. Theoretical background

2.1. Isothermal Onsager matrix

For the mixed conductor compound of present interest, BCFN, the mobile charged components are no doubt

holes h^+ (=h) and oxide ions O^{2-}(=i) for all the cations are practically immobile. Letting J_k and $\nabla\eta_k$ denote the

flux and electrochemical potential gradient, respectively, of the k(=i,h)-type charged component, all the

isothermal mass/charge transport properties of the present system may then be succinctly condensed into or

documented by a 2×2 Onsager transport coefficient matrix L such that[10-12]

$$\begin{pmatrix} J_i \\ J_h \end{pmatrix} = -\begin{pmatrix} L_{ii} & L_{ih} \\ L_{hi} & L_{hh} \end{pmatrix}\begin{pmatrix} \nabla\eta_i \\ \nabla\eta_h \end{pmatrix},$$

(2)

where, due to Onsager[13,14],

$$L_{ih}=L_{hi}.$$

(3)

The L-matrix, thus, involves only 3 independent coefficients, which may easily be evaluated simply by

measuring the three different transport properties, e.g., the total electrical conductivity (σ), the (electronic)

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conductivity with ion-transfer suppressed (σ'_e), and the ionic charge-of-transport (α^*_i) as[11,15,16]

$$\sigma = F^2 \left[2L_{ii} \left(2 - \frac{L_{ih}}{L_{ii}} \right) + L_{hh} \left(1 - 2\frac{L_{ih}}{L_{hh}} \right) \right]; \quad \sigma'_e = F^2 L_{hh} \left(1 - \frac{L^2_{ih}}{L_{ii}L_{hh}} \right); \quad \alpha^*_i = \frac{L_{ih}}{L_{ii}}, \tag{4}$$

where F denotes the Faraday constant.

It is noted[17] that

$$L_{kk} = [k]B_k = \sum_d [d]B_d \tag{5}$$

where [k] and B_k represent the concentration of the k-type mobile charged component and its mechanical mobility at infinite dilution, respectively, and [d] and B_d the corresponding quantities of the d-type defects responsible for the charged component mobility B_k. For k=i(O^{2-}), "d" can be interstitials O''_I (d=I) and vacancies $V^{\bullet\bullet}_O$ (d=V), and for k=h, electrons e' (d=n), holes $h^\bullet$ (d=p), and trapped ones, e.g., $M^\bullet_B$, if any. By measuring L_{kk} against oxygen activity at given temperatures, thus, one can identify the majority types of ionic and electronic defects by observing whether L_{kk} increases or decreases with increasing oxygen activity.

2.2. Electronic thermopower

The electronic thermopower θ_h is generally defined as†[9]

$$\theta_h \equiv \frac{1}{F} \left(\frac{\nabla \eta_h}{\nabla T} \right). \tag{6}$$

According to irreversible thermodynamics,[9,18] the electronic thermopower at the steady state or Soret

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† It is noted that here we employ the Wagner sign convention on thermopower[9] as defined in eqn (6), viz., + for electrons and – for holes. From the electrochemistry and thermodynamics view point, this is more logical and consistent in dealing with the ionic and electronic thermopowers of a mixed conductor.

equilibrium is determined by the sum ($\overline{\overline{S}}_d$) of the partial molar entropy $\overline{S}_d$ and entropy-of-transport S_d^* of

holes as defects (d=p) if p-type (p>>n), and by that of electrons as defects (d=n) if n-type (n>>p)‡ or

$$\theta_h^{st} = \begin{cases} -\dfrac{1}{F}\left(\overline{s}_p + s_P^*\right) & \text{if } p>>n \\ +\dfrac{1}{F}\left(\overline{s}_n + s_n^*\right) & \text{if } n>>p \end{cases} \tag{7}$$

In the ideal dilute solution regime of electronic defects, the partial molar entropy of defects of kind d(=n, p,

trapped ones) is written in terms of their concentration [d] as[9]

$$\overline{S}_d = S_d^0 - R \ln[d] \tag{8}$$

where S_d^0 stands for the standard molar entropy of defects of kind d. In any case, $\overline{\overline{S}}_d = \overline{S}_d + S_d^* > 0$ in general,

thus, the sign of the steady state electronic thermopower θ_h^{st} already indicates the identity of the electronic

defects in majority.

3. Experimental

3.1. Ion-blocking cell

The specimen, $BaCo_{0.70}Fe_{0.22}Nb_{0.08}O_{3-\delta}$ (BCFN) was prepared to have a relative density of ca. 96% and a mean

grain size of 16±5 μm, via a conventional solid state reaction route, as detailed earlier.[11]   The   ion-blocking

cell was constructed, as illustrated in Fig. 1, with a parallelepiped BCFN specimen, measuring the cross

sectional area A=41.79±0.05 mm^2 and overall length L=12.540±0.005 mm, equipped with a pair of electronic

probes (EP), Pt-wires (#1 at x=x_ and #2 at x=x_+), and a pair of ionic probes (IP), galvanic cells $YSZ\,|\,Pt, a_{O_2}^{ref}$

(#3 at x=x_ and #4 at x=x_+) that are symmetrically implanted at a distance $\ell\,(=x_+-x_-)$ apart in the reference

oxygen activity ($a_{O_2}^{ref}$) atmosphere.

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‡ Here, $n \equiv [e'](p \equiv [h^\bullet])$, not to be confused with the subscript "n(p)" to denote $e'(h^\bullet)$ as defects.

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(Fig. 1)

For the experimental details, the reader is referred to Ref. 11. The only difference from the earlier study[11] is that for the purpose of applying temperature gradients across the specimen to measure θ_h^{st}, we have additionally attached a local heater, an alumina disk (13 mm diameter × 1 mm thickness) with 0.2 mm diameter Pt-resistance wires embedded, at the opposite side of the YSZ, and attached an S-type thermocouple at each of the inner probes (#1-4) to measure local temperatures. The cell was then hermetically sealed with a glass as before [11]. When a current is passed between the electrodes #5 and #6, the cell turns symmetrically ion-blocking unlike the earlier asymmetric configuration[11], because the alumina disk (=heater) at the top and the YSZ disk at the bottom of the specimen both mechanically block the solid/gas oxygen exchange. The initial thermodynamic state of the system with respect to oxygen nonstoichiometry δ was adjusted by coulometric titration through the electrolyte YSZ.

3.2. Isothermal, ion-blocking measurements

Ion-blocking polarization and subsequent depolarization were carried out by switching on a constant current I and off between the electrode #5 to #6, while monitoring the open-circuit-voltages (OCV), U between the pair of IPs (with reference to #3), V between the pair of EPs (with reference to #1), u_+ between EP #2 and IP #4 (with reference to the latter) at the position $x_+[=(L+\ell)/2]$, and u_- between EP #1 and IP #3 (with reference to the latter) at the position $x_-[=(L-\ell)/2]$. The procedure was repeated by changing the current direction: the positive direction of the current (I>0) was defined to be from Pt-electrode #5 to #6 (i.e., x>0 direction).

The information content of each OCV is all listed in Table 1, where $\Delta\eta_k$ denotes the difference of η_k (k=i,h) across ℓ (=x_+-x_-), and $\mu_O(x)$ the oxygen chemical potential at the position x(=x_+ or x_-).

Table 1 Information contents of the OCVs monitored in the present galvanostatic chemical polarization under the symmetric ion blocking condition. Here, $\mu_{O_2}^{ref} (= \mu_{O_2}^o + RT \ln a_{O_2}^{ref})$ denotes the oxygen chemical potential in the surrounding.

OCV	Information content
U	$-\dfrac{\Delta \eta_i}{2F} \approx -\dfrac{\ell \nabla \eta_i}{2F}$
V	$\dfrac{\Delta \eta_h}{F} \approx \dfrac{\ell \nabla \eta_h}{F}$
u_+	$\dfrac{1}{2F}\left[\mu_O(x_+) - \dfrac{1}{2}\mu_{O_2}^{ref} \right]$
u_-	$\dfrac{1}{2F}\left[\mu_O(x_-) - \dfrac{1}{2}\mu_{O_2}^{ref} \right]$

As shown in the table, by using the pairs of IPs and EPs arranged as illustrated in Fig. 1, one can measure all the driving forces and even local oxygen activity values as well. The three isothermal transport properties in eqn (4) were thus determined, via eqn (2), as[11,15]

$$\sigma = -\frac{I/A}{V_0/\ell} \quad ; \quad \alpha_i^* = -\left(\frac{\nabla \eta_i}{\nabla \eta_e}\right)_{J_i=0} = \left(\frac{2U}{V}\right)_{J_i=0} ; \quad \sigma_e' = -\frac{\ell}{A}\left(\frac{I}{V}\right)_{J_i=0} \tag{9}$$

where V_0 is the initial voltage jump between the pair of EPs upon switching on I at t=0 or the initial voltage drop upon switching off I at the steady state (t→∞ or $t' = 0$), and the subscript J_i=0 means the steady state or t→∞ with I on. One may further determine the chemical diffusion coefficient from the transient V(t) or U(t) by using their analytic solutions[15], but that is out of the scope of the present paper. In the present operation, the current level was chosen in such a way that $|u_+| \approx |-u_-| <$ 3 mV or the oxygen activity is varied across ℓ only in the range $\left| \log\left(a_{O_2} / a_{O_2}^{ref}\right) \right| < 0.05$, thus one may assign the resulted transport properties to the thermodynamic state $a_{O_2}^{ref}$ of the system BCFN.

3.3. Non-isothermal, thermopower measurements

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The specimen was first fully equilibrated by short-circuiting the YSZ electrolyte in a prefixed $a_{O_2}^{ref}$ atmosphere at a prefixed uniform temperature, and then the local heater was switched on while monitoring the temperatures at the positions x_- and x_+, $T_1(t)$ and $T_2(t)$, respectively, against time t by using the thermocouples located at the respective positions, and V(t) between EP #1 and #2 respectively at the same positions, see Fig. 1.

The present thermocell has the configuration of phases and temperatures,

$$\begin{array}{cccc} Pt(\#1) & | \ BCFN \ | & Pt(\#2) \\ T_o & T_1 & T_2 & T_o \end{array} \tag{I}$$

The OCV of the cell, V as measured at the common temperature T_o should, thus, be written as

$$V = \frac{\Delta\eta_h}{F} - \int_{T_1}^{T_2} \theta^{(Pt)} dT \tag{10}$$

where $\theta^{(Pt)}$ stands for the absolute thermopower of Pt-leads that is well documented.[19] By correcting against $\theta^{(Pt)}$ according to eqn (10), $\Delta\eta_h(t)$ was obtained for given $\Delta T(t)[=T_2(t)-T_1(t)]$. The temperature differences applied were kept less than 7 K at maximum at a pre-fixed mean temperature. The steady state thermopower θ_h^{st} was finally evaluated as the best-fitted value for the slope of $\Delta\eta_h/F$ vs. ΔT at the steady state or

$$\theta_h^{st} = \lim_{t\to\infty} \frac{1}{F}\left(\frac{\Delta\eta_h(t)}{\Delta T(t)} \right). \tag{11}$$

3.4. X-ray absorption spectroscopy

In order to identify the chemical states of multi-valent Fe and Co ions, soft x-ray absorption spectroscopy (XAS) was performed on the BCFN specimens with the defect structure frozen-in at different thermodynamic states. The parallelepiped specimens, measuring ca. $5\times5\times3$ mm^3 cut out of the as-sintered pellet, were first equilibrated in three different oxygen activity atmospheres ($\log a_{O_2}$ =-0.998±0.002, -1.794±0.002, and -4.112±0.013) at three different temperatures (750, 850, and 950 °C), and subsequently quenched to ca. -80 °C. Afterwards, the surface of each quenched specimen was ground off to a thickness of 0.5~1.0 mm in order to eliminate the possible

diffusion effect during quenching. (The diffusion distance during quenching was expected to be $4\sqrt{\widetilde{D}_O t} < 0.7$

mm, by taking the time elapse during quenching $t \le 0.3$ s and the upper bound of oxygen chemical diffusivity

$\widetilde{D}_O < 10^{-3}$ cm^2/s on the basis of the ion-blocking polarization kinetics.) The specimens may, thus, be safely

regarded as being frozen-in at the equilibrium defect structure corresponding to each thermodynamic condition

of temperature and oxygen activity. For experimental details for quenching, see Ref. 20.

The XAS measurement was done at the Beam Line 2A in the Pohang Light Source, Pohang, Korea, using

the total electron yield (TEY) mode. The sample chamber was baked at 120 ^{o}C for 6 hours to get ultrahigh

vacuum (UHV; $\sim 10^{-9}$ Torr) for the soft XAS measurement. We used linear beam polarization with incident x-

rays perpendicular to the plane of a specimen. It is generally known that the probing depth of the TEY mode in

soft XAS is approximately 10 nm, which is much larger than those (~ 2 nm) of other surface-sensitive techniques

such as x-ray photoelectron spectroscopy or Auger electron spectroscopy. Therefore, the XAS spectra may be

regarded as reflecting the electronic structure of the bulk BCFN, which is essentially free from the effect of

surface reaction under UHV condition considering the temperature dependence of the surface oxygen exchange

reaction and diffusion kinetics. The overall energy resolution was 0.1 eV.

4. Results and Discussions

4.1. Isothermal Onsager matrix

Fig. 2 shows the temporal variations of the OCVs, $u_+(t)$, $u_-(t)$, $U(t)$, and $V(t)$ upon polarization in one direction

($I<0$) followed by de-polarization ($I=0$), and upon repetition in the opposite direction ($I>0$). It is noted in Fig.

2(a) that $u_+(t)$ and $u_-(t)$, the measure of $\mu_O(x)$ at $x=x_+$ and x_-, respectively, are almost anti-symmetric or $u_+(t) \approx -u_-$

(t). This means that all the transport properties involved indeed remain almost constant under the small enough

driving forces employed in the present study (V, $U < 10$ mV) as designed. The corresponding $U(t)$ and $V(t)$ are

in perfect agreement with what have been repeatedly observed upon galvanostatic polarization/depolarization

under the ion-blocking condition[11,12].

(Fig. 2)

The three different transport properties σ, σ'_e, and α_i^* are subsequently evaluated, according to eqn (9), from

Fig. 2(b) and summarized in Fig. 3 and Fig. 4.

(Fig. 3)   (Fig. 4)

It should be mentioned that the total conductivity σ was evaluated, via eqn (9), by using the instantaneous voltage changes V_0 at the moments of current-on and -off. Strictly speaking, the former corresponds to the uniform oxygen chemical potential or $u_+=u_-=0$, while the latter to a mean oxygen chemical potential at steady state, $\bar{\mu}_O = 2F\left(\dfrac{u_+ + u_-}{2}\right) + \dfrac{1}{2}\mu_{O_2}^{ref}$ with $u_++u_-\approx0$. These two, of course, have turned out to be the same within experimental error as designed. Furthermore, such σ is in agreement within 10 % with σ^{ref}, the total electrical conductivity as measured independently on the different specimen of the same composition via dc 4-probe method[11]. The ionic charge-of-transport, the measure of electron-ion interference effect[16], takes a value in the range of $0.19\leq \alpha_i^* \leq0.32$, also in agreement with the earlier report[11].

Via eqn (4) from these σ, σ_e', and α_i^*, the Onsager transport coefficients L_{ii}, L_{hh} and $L_{ih}(=L_{hi})$ are all evaluated across the entire range of the phase stability and documented in Fig. 5. It is seen that the earlier results, only in the limited range[11], are in acceptable agreement.

(Fig. 5)

Once the isothermal Onsager matrix is given as now, one can then calculate all the isothermal mass/charge transport properties (with the aid of the thermodynamic factor for the case of $\widetilde{D}_O$).[10,21] For example, the partial ionic and electronic conductivities§, σ_i and σ_h, respectively, as measured in the reversible electrode condition, thus, at the uniform composition, may be calculated as[11,15]

$$\sigma_i = 4F^2L_{ii}\left(1-\frac{L_{ih}}{2L_{ii}}\right) \quad ; \quad \sigma_h = F^2L_{hh}\left(1-2\frac{L_{ih}}{L_{hh}}\right). \tag{12}$$

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§ Note that if $\alpha_i^* \neq 0$, $\sigma_h \neq \sigma_h'$ and likewise, $\sigma_i \neq \sigma_i'$.[16,22]

The results are as shown in Fig. 6.

(Fig. 6)

It is noted that L_{ii} or σ_i and L_{hh} or σ_h are all increasing with increasing oxygen activity: the former rather monotonically, but the latter rather nonmonotonically with an inflection approximately in the middle.

4.2. Steady-state electronic thermopower

When the heater is on with a preset power (see Fig. 1), $\Delta T(=T_2 - T_1)$ and induced V develop against time as shown in Fig. 7(a) and (b), respectively. Such V(t) is then corrected against the thermovoltage of the Pt-lead wires according to eqn (10), resulting in $\Delta\eta_h[=\eta_h(T_2) - \eta_h(T_1)]$ as shown in Fig. 7(c). One can see that all the signals eventually achieve the steady state value. Such operation was repeated at different steady-state $\Delta T's$ to have a steady state data set $\{\Delta T, \Delta\eta_h\}$ as shown in Fig. 8. The slopes of these plots finally give the steady state thermopowers, which are all collected in Fig. 9.

(Fig. 7),

(Fig. 8),

(Fig. 9)

It is noted that the electronic thermopower has negative sign all the way across the entire range and apparently show a hump at each temperature.

4.3. Chemical states of Co and Fe

Fig. 10 shows the Co L_3-edge XAS spectra of the specimens frozen-in at (a) $\log a_{O_2}$ =-0.998±0.002, (b) $\log a_{O_2}$ =-1.794±0.002, and (c) $\log a_{O_2}$ =-4.112±0.013, respectively. It is well known[23] that the sharp and strong absorption at ~785 eV is attributed to the Ba M_5-edge absorption (Ba $3d_{5/2} \rightarrow p$), indicating that the valence of Ba ions is fixed at +2 irrespective of defect structures frozen-in. The features at 778 ~ 783 eV are the signals from the Co L_3-edge absorption: Many peaks here are due to electron correlation effects in the Co d shell[24]. For the identification of those multiplets, the spectra of CoO and Co_3O_4 powders, taken from Ref. 25, are included

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in Fig. 10(a). In the case of rocksalt-structure CoO, a Co^{2+} ion with 7 d-electrons is coordinated by an oxygen octahedron.[24] The many-body Coulomb interactions between the 7 d-electrons as well as with the $2p_{3/2}$ core holes result in a complicated peak split as exhibited in the spectrum of CoO. Meanwhile, in the case of Co_3O_4 spinel, 1/3 of the Co ions are divalent with tetrahedral coordination while the rest 2/3 are trivalent with octahedral coordination.[26] Therefore, two peaks (for Co^{2+} and Co^{3+}) should largely appear in the spectrum of Co_3O_4.

The Co-spectra of the sample frozen-in in the most oxidizing atmosphere ($\log a_{O_2}$ =-0.998±0.002) evolve the most actively with temperature, see Fig. 10(a). At 750 °C, the spectrum appears rather like that of Co_3O_4, suggesting the abundance of Co^{3+} ions: By fitting the as-measured spectra as superposition of those of CoO and Co_3O_4, the concentration ratio $[Co^{2+}]/[Co^{3+}]$ is roughly estimated to be 35/65. As the temperature increases, however, the spectrum grows more similar to that of CoO, suggesting the gradual prevalence of Co^{2+} ions. The signatures of Co^{2+} are indicated by arrows in Fig. 10(a). The $[Co^{2+}]/[Co^{3+}]$ ratio is then roughly estimated to be ca. 65/35 at both 850 and 950 °C. This demonstrates unambiguously that Co^{2+} becomes more and more prevailing with increasing temperature at a fixed oxygen activity, in accord with the general trend of reduction of an oxide. Meanwhile, for the case of the specimens frozen-in in more reducing atmospheres ($\log a_{O_2}$ =-1.794±0.002 and -4.112±0.013), such spectral evolution with temperature has become much attenuated, see Figs. 10(b) and (c). All the spectra there are more similar to that of CoO, suggesting the dominance of Co^{2+} with decreasing a_{O_2}. We may therefore conclude that (i) Co ions have valences of either +2 or +3, but not +4, and (ii) $[Co^{2+}]$ tends to increase with increasing temperature and decreasing oxygen activity in agreement with the general tendency of oxide reduction. The overwhelming existence of Co^{2+} ions strongly suggests the stability of a highly oxygen-deficient perovskite phase $A^{2+}B^{2+}O_2$.

(Fig. 10)

Fig. 11 shows the Fe L_3-edge XAS spectra of the specimens frozen-in in the same oxygen activity atmospheres as above, viz., (a) $\log a_{O_2}$ = -0.998±0.002, (b) $\log a_{O_2}$ = -1.794±0.002 and (c) $\log a_{O_2}$ = -4.112±0.013. Contrary to the case of the Co L_3-edge XAS, the Fe L_3-edge spectra are very similar to each other. For comparison purpose, the spectra of "FeO" and α-Fe_2O_3 (taken from Ref. 25) are added in Fig. 11(c). All the

spectra are almost like that of Fe_2O_3, indicating the dominance of Fe^{3+}. At the highest temperature 950 ^oC in the most reducing atmosphere ($\log a_{O_2}$ =-4.112±0.013), however, there start to appear the features of Fe^{2+} (similar to "FeO") as indicated by the arrows, but $[Fe^{2+}]/[Fe3+]\leq 0.1$. One can, thus, conclude that Fe ions remain mostly trivalent in all cases.

(Fig. 11)

The present findings are consistent with the literature. Yi et al.[27] reported that the valences of Co are +2 and +3, and an average valence of Fe is about +3.1 at 900 ^oC in $BaCo_{1-x-y}Fe_xNb_yO_{3-\delta}$ systems. Harvey et al.[28] also reported that Co has the valence of +2 and +3 while Fe has nearly unchanged valence of +3 at the temperature ranging from 300 to 1223 K in $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ systems.

4.4. Ionic defects in majority

We have observed in Fig. 5 that L_{ii} of the present system increases with oxygen activity. For better resolution, we replot, notwithstanding the redundancy, L_{ii} in Fig. 12. It unambiguously increases monotonically even though the increasing rate is small. Recalling eqn (5) and the fact that the mechanical mobility of a type of carriers at infinite dilution is constant, this fact no doubt indicates the ionic carrier concentration is increasing as oxygen activity increases. It is, therefore, unavoidable to conclude that the ionic carriers of the present system should be oxygen interstitials (O_I''), not vacancies ($V_O^{\bullet\bullet}$), across the entire ranges of thermodynamic variables examined.

(Fig. 12)

4.5. Electronic defects in majority

It is reminded that L_{hh} also increases with increasing oxygen activity (Fig. 5). For a better resolution, we re-plot, despite the redundancy, L_{hh} in Fig. 13 together with its first derivative ($\partial \log L_{hh} / \partial \log a_{O_2}$) at, e.g., 950 ^oC. Furthermore, the sign of the steady state electronic thermopower is negative (Fig. 9) all the way. These two facts clearly indicate that the electronic carriers are positively charged or p-type carriers. The possible carriers in the present system involving multivalent cations on B-sites (M_B) may be delocalized holes ($h^\bullet$) and localized holes

13

($M_B^{\bullet}$, $M_B^{\bullet\bullet}$, and the like).

It is emphasized that L_{hh} exhibits an inflection at each temperature, where the local slope becomes minimum, see Fig. 13. This suggests that there are at least two kinds of p-type carriers, one dominating before the inflection and the other after the inflection.

(Fig. 13)

This scenario is strongly supported by the presence of a hump upon each thermopower isotherm, see Fig. 9. When there are two types of electronic carriers, say, electrons and holes, for example, the electronic thermopower is given by the fractional sum of the two contributions or[9,18,30]

$$\theta_h = \sum_{d=n,p} \left(\frac{\sigma_d \theta_d}{\sum_d \sigma_d} \right) \tag{13}$$

where σ_d is the partial electrical conductivity due to the d-kind electronic defects. As $n \propto p^{-1} \propto \ln a_{O_2}^{-m}$ with the oxygen exponent m>0, in the mixed conducting region of oxygen activity, substitution of eqn (7), (8) into eqn (13) renders the electronic thermopower to vary against oxygen activity as shown schematically in Fig. 14(a) and this is actually what have been repeatedly observed on the systems of e.g., PbS[31], Gd-doped CeO$_2$[32,33], and BaTiO$_3$[18,34]. Now, if there are two kinds of p-type carriers, say, d=p$_1$ and p$_2$, then one may easily expect that the electronic thermopower will vary, while keeping the same sign(<0), as shown in Fig. 14(b)¶ again due to eqn (7), (8) and (13). This is actually what is seen in Fig. 9. These two possible kinds for the system in question are highly likely free holes ($h^{\bullet}$) and trapped holes ($M_B^{\bullet}$).

(Fig. 14)

¶ In this case, the oxygen exponents for [p$_1$] and [p$_2$] may differ from each other, thus, θ_{p1} and θ_{p2} appear to have different slopes in this figure.

4.6. Stoichiometric composition

We have come to know about the present system BCFN that A-site cation Ba has the fixed valence of +2, B-site cations M(=Co and Fe) have only two charge states, M^{2+} and M^{3+}, the ionic defects in majority are oxygen interstitials O_I'', the electronic defects are at least of two kinds, itinerant holes $h^\bullet$ and trapped holes $M_B^\bullet \left[\equiv \left(M_B^x, h^\bullet \right)^\bullet \right]$. Oxygen interstitials suggest the present system must be hyperstoichiometric or with an oxygen excess over the stoichiometric composition, but the conventionally accepted, stoichiometric lattice molecule $BaCo_{0.70}Fe_{0.22}Nb_{0.08}O_3$ would be by no means hyperstoichiometric, but always hypostoichiometric for the ideal perovskite lattice $Ba^{2+}B^{4+}O_3$ does not allow O_I'' becasue it is energetically too expensive[35]. Furthermore, there can be no trapped holes $M_B^\bullet (= Co_B^{5+}, Fe_B^{5+})$. What should then be the stoichiometric lattice molecule in order to be consistent with all of the present findings?

One may then consider $Ba^{2+}B^{3+}O_{2.5}$ like an end member of the solution $SrTi_{1-x}Fe_xO_{3-x/2}$ with O_I'', $Sr^{2+}Fe^{3+}O_{2.5+\delta}$[36]. For the trapped holes, there should be M_B^{4+}, but we have failed to see any, thus this possibility should be ruled out. The only remaining possibility will then be $Ba^{2+} \left(Co_{1-x}^{2+} Fe_x^{2+} \right) O_2$. The structurally empty O-sites (1 per lattice molecule) in the virtual perovskite structure ABO_3 are now considered to be the interstitial sites for O_I'', and $M_B^\bullet (= Co_B^{3+}, Fe_B^{3+})$ to be the trapped holes, thus, satisfying all the experimental findings. The charge neutrality may then be written as

$$[O_I''] = \frac{3}{2}\left[Nb_B^{\bullet\bullet\bullet} \right] + \frac{1}{2}\left[h^\bullet \right] + \frac{1}{2} \sum_{M=Co,Fe} \left[M_B^\bullet \right]. \tag{14}$$

Here, the valence charge of Nb is regarded as +5.[27] Thence, the reference stoichiometric lattice molecule of the present system should be written as

$$Ba \left(Co_{0.70} Fe_{0.22} Nb_{0.08} \right) O_{2.12}. \tag{15}$$

Of course, the defect structure can be completely explained on the basis of this stoichiometric composition, which will the subject of a forthcoming paper. It should, however, be mentioned that this is only a proposal to

explain the defect structure at this stage and obviously more elaborate structural study should be followed to confirm the proposal, eqn (15).

5. Summary and Conclusions

We have established completely the isothermal Onsager transport coefficient matrix for the system of nominal composition $Ba(Co_{0.70}Fe_{0.22}Nb_{0.08})O_{3-\delta}$, a best oxygen separation membrane material, in its entire stability range at elevated temperatures of practical interest. All the isothermal transport properties of the system, including the ambipolar conductivity can now be derived from this matrix.

The partial ionic conductivity at infinite dilution, as derived against oxygen activity, indicates that the majority ionic defects are oxygen interstitials, contrary to the conventional lattice molecule representation $Ba(Co_{0.70}Fe_{0.22}Nb_{0.08})O_{3-\delta}$. The partial electronic conductivity at infinite dilution as derived and the steady state electronic thermopower as measured against oxygen activity indicates that the electronic defects in majority are p-type carriers of at least two kinds, viz., itinerant and trapped holes. XAS study has shown that the multi-valent Co and Fe take +2 and +3 depending on the thermodynamic states with Ba fixed at +2. In order to be consistent with all these findings, the lattice molecule should be $A^{2+}B^{2+}O_2$-based $Ba(Co_{0.70}Fe_{0.22}Nb_{0.08})O_{2.12+\delta}$.

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Figure Captions

Fig. 1   Schematic of the as-constructed cell with the lateral surface hermatically sealed with a glass for the. ●●● , local heater; ▬ , porous Pt-paste; ▬▬▬ , Pt gauze; ▬▬ , Pt-wire; ▬▬ , Pt/Rh-wire; 1 & 2, electronic probes; 3 & 4, ionic probes; 5 & 6, current leads; L, total length of the specimen; ℓ , inter-probe distance; $a_{O_2}^{ref}$, reference oxygen activity.

Fig. 2   Typical temporal variations of (a) u_+, u_- and (b) U, V upon repeated polarizations (I=-25 mA and 25 mA) and subsequent depolarization (I=0) at 850 ^{o}C in the ambient of $\log a_{O_2}^{ref} = -3.442 \pm 0.003$.

Fig. 3   Total conductivities as determined by the 4-probe dc method (σ^{ref})[11], from the instantaneous voltage jump/drop upon polarization/depolarization (σ) and the (electronic) conductivity with ionic transfer suppressed (σ_e') vs. oxygen activity at (a) 950, (b) 850, and (c) 750 ^{o}C.

Fig. 4   Ionic charge-of- transport, α_i^* vs. oxygen activity at (a) 950, (b) 850 ,and (c) 750 ^{o}C. Circle, as-measured in this work; triangle, as- reported in previous work[11].

Fig. 5   Isothermal Onsager transport coefficients L_{mn}(m,n=i,h) vs. oxygen activity of $BaCo_{0.7}Fe_{0.22}Nb_{0.08}O_{3-\delta}$ at (a) 950, (b) 850, and (c) 750 ^{o}C. Closed symbols, as-measured in this work; open symbols, as-reported in earlier work[11].

Fig. 6   Ionic (σ_{ion}) and electronic (σ_{el}) conductivities in the reversible electrode condition vs. oxygen activity of $BaCo_{0.7}Fe_{0.22}Nb_{0.08}O_{3-\delta}$ at 950, 850, and 750 ^{o}C.

Fig. 7   Typical temporal variations of (a) ΔT, (b) V, and (c) $\Delta \eta_h / F$ corrected by using eqn (10) during heating (heater-on) and subsequent cooling (heater-off) at 850 ^{o}C in $\log a_{O_2} = \log a_{O_2}^{ref} = -3.442 \pm 0.003$. Where $\Delta T = T_1 - T_2$.

Fig. 8 $\Delta\eta_{lh}/F$ obtained at the steady state vs. steady state ΔT at 850 ^{o}C in $\log a_{O_2} = \log a_{O_2}^{ref} = -3.442 \pm 0.003$. Symbol, as-measured values; solid line, best-fitted the slope of which is the steady state electronic thermopower (θ_h^{st}).

Fig. 9 Steady-state electronic thermopower vs. oxygen activity at 950, 850, and 750 ^{o}C. Note the sign $\theta_h^{st} < 0$ and a hump on each isotherm.

Fig. 10 Co L_3-edge XAS spectra of BCFN with their defect structures frozen-in at the 950, 850, and 750 ^{o}C, respectively, in the surrounding of $\log a_{O_2}$ =-0.998±0.002 (a), $\log a_{O_2}$ =-1.794±0.002 (b) and $\log a_{O_2}$ =-4.112±0.013 (c), respectively, and those of CoO and Co_3O_4 powders[25] for comparison. Note a clear evolution of the Co^{2+}-signatures (arrows) out of Co^{3+} with increasing temperature and decreasing oxygen activity and no other species than Co^{2+} and Co^{3+}.

Fig. 11 Fe L_3-edge XAS spectra of BCFN with their defect structures frozen-in at the 950, 850, and 750 ^{o}C, respectively, in the surrounding of $\log a_{O_2}$ =-0.998±0.002 (a), $\log a_{O_2}$ =-1.794±0.002 (b) and $\log a_{O_2}$ =-4.112±0.013 (c), respectively, and those of "FeO" and α-Fe_2O_3 powders[25] for comparison. Note that Fe ions remain mostly trivalent for all the samples.

Fig. 12 Direct Onsager coefficient for oxygen ion (L_{ii}) vs. oxygen activity at 950, 850, and 750 ^{o}C. Note that L_{ii} increases monotonically with increasing oxygen activity.

Fig. 13 Direct Onsager coefficient for holes (L_{hh}) and its first derivative vs. oxygen activity at 950 ^{o}C.[29] Note that L_{hh} increases with oxygen activity, but exhibiting an inflection at each temperature.

Fig. 14 Expected steady-state electronic thermopower vs. oxygen activity (a) for an electron (n)–hole (p) mixed conductor and (b) for a p-type conductor but with two different kinds p_1, p_2. θ_k and σ_k denote the partial thermopower and conductivity, respectively, of electronic carriers of type k(=n,p,p_1,p_2).

20

Table Caption

Table 1 Information contents of the OCVs monitored in the present galvanostatic chemical polarization under the symmetric ion blocking condition. Here, $\mu_{O_2}^{ref}(= \mu_{O_2}^{o} + RT \ln a_{O_2}^{ref})$ denotes the oxygen chemical potential in the surrounding.