A New Defect Chemistry Model for Nb-doped $\text{SrCoO}_{2.5+\delta}$: The Role of Oxygen Interstitials and Delocalized-to-Localized Electron Holes

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Abstract

A new defect chemistry model featuring oxygen interstitials (O_I'') and delocalized-to-localized d -electron holes ($Co_{Co}^{\bullet}$) as point defects is demonstrated under a perfect Brownmillerite $\text{SrCoO}_{2.5}$ reference framework to elucidate transport properties of Nb-doped $\text{SrCoO}_{2.5+\delta}$ (SCN) system over a range of partial pressure of oxygen (P_{O_2}) and temperature (T). With this new defect chemistry model, the electronic conductivity behaviors with T and P_{O_2} can be well interpreted by the change in concentration of d -electron holes migrating with a constant mobility. The important concentration contours of electron holes, excess electrons and oxygen interstitials are mapped out on the T - P_{O_2} domain, from which hole-concentration and conductivity under iso-stoichiometry are reconstructed. The partial/integral molar thermodynamic properties and thermodynamic factor of the SCN solid solution are also determined. A transitional delocalized-to-localized hole-transport mechanism with decreasing oxygen stoichiometry is discussed based on $p=p(T)$ obtained under constant oxygen stoichiometry.

Keywords: defect chemistry; oxygen interstitials; delocalized and localized holes; oxygen stoichiometry; hole mobility

I. Introduction

Reversible bifunctional oxygen electrodes are a class of critical functional materials for regenerative solid oxide fuel cells (RSOFCs). As the development of RSOFCs is shifting towards intermediate-temperature range (500-700 °C)^{1, 2}, bifunctional oxygen electrodes with high intrinsic electrocatalytic activity become more demanding. Recently, $\text{SrCoO}_{3-\delta}$ based materials emerge as a promising bifunctional oxygen electrode for intermediate-temperature RSOFCs due to its unique reversible oxygen storage and release capability^{3, 4}.

Pure $\text{SrCoO}_{3-\delta}$ (denoted as SCO hereinafter) is an oxygen-deficient cubic structured perovskite oxide with excellent ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) activities^{5, 6}. However, this material is only stable under a high partial pressure of oxygen (>15MPa)^{7, 8} or in the presence of an extremely oxidizing agent such as Br ⁹⁻¹¹. Under a typical RSOFC operating condition, *e.g.* ambient pressure and 500-700 °C, SCO readily decomposes into the more stable brownmillerite phase $\text{SrCoO}_{2.5}$ (denoted as BM hereinafter) by losing one-sixth of its lattice oxygen, rendering oxygen vacancies into an ordered state. Compared to SCO, BM is electrically less conductive and catalytically less active to either ORR or OER because of immobile ordered oxygen-vacancies at lower temperatures^{4, 12}.

To leverage the high ORR/OER activity in cubic-structured SCO for practical RSOFC applications without invoking unwanted BM phase, SCO's propensity to lose significant lattice oxygen at elevated temperatures must be alleviated. A common alleviation strategy is to chemically supply oxygen into the oxygen lattice by doping with higher oxidation-state metal-oxides (or known as “donor doping” or “electron doping”). Such a “donor-

doping” strategy has been proven very effective in stopping the BM formation as demonstrated in systems where the Co-site is substituted by Nb-, Ta-, Fe- and Sb¹³⁻²⁰ and Sr-site by Y and La²¹⁻²⁴.

While a variety of donor dopants for the SCO system has been investigated for years, an in-depth fundamental understanding of their bulk defect structures and charge transport properties are still lagging. In theory, a good understanding of transport behaviour in nonstoichiometric oxides depends critically upon the knowledge of concentrations of charge carriers and oxygen nonstoichiometry. Traditionally, this set of knowledge is acquired by either Thermogravimetric Analysis (TGA)²⁵ or Oxygen Coulometric Titration (OCT)^{20, 26, 27}. By combining the obtained oxygen nonstoichiometry with a transport property descriptor such as electrical conductivity or thermopower (Seebeck coefficient)^{23, 28}, the concentrations of charge carriers as well as important thermodynamic properties of the solid solution can be determined.

In the present work, we use Nb-doped SCO (denoted as SCN) as a model system to show that with the help of a proper defect chemistry model based on $\text{SrCoO}_{2.5+\delta}$, electrical conductivity is the only raw data needed to derive concentrations of electron charge carriers and oxygen nonstoichiometry of nonstoichiometric oxides. We also show that the electron-hole transport in SCN exhibits a gradual transition from delocalized (or itinerant) holes at high oxygen stoichiometry to localized holes at low oxygen stoichiometry. The partial and integral thermodynamic properties as well as thermodynamic factor of the SCN solid solution are also determined. To the best of our knowledge, this is the first work defining a defect chemistry model for the SCO-based systems under a BM reference framework and considering oxygen interstitials as the ionic point defect. The results presented offer new insights into the defect

structure/chemistry and electron transport properties in the SCO-based materials that are considered a promising bifunctional oxygen electrode for fuel cells and battery applications.

II. Defect Chemistry Model Description

2.1 The rationale for the new defect chemistry model

The new defect chemistry model for the SCN systems is constructed upon a perfect BM structure as the reference framework, oxygen interstitials as the ionic point defect and constant-mobility electron holes as the electronic point defect. Within the BM reference framework, the oxygen stoichiometry of SCN can be viewed as $2.5+\delta$, where δ represents 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 ($Nb_{Co}^{\bullet\bullet}$) and electron holes ($Co_{Co}^{\bullet}$).

The rationale for selecting BM as the defect reference framework is the structural feature of the BM phase and prior studies. The brownmillerite $ABO_{2.5}$ structure is a derivative of cubic perovskite by the removal of one-sixth of the oxide-ions in continuous rows, creating a structure that consists of layers of parallel chains of corner-sharing BO_4 tetrahedra alternating with layers of corner-sharing BO_6 octahedra^{3, 4}. This creates 1D “channels” of oxygen vacancies, which are thought to play a role in the transport of oxide-ions through the structure. Mitra *et al* predicted from DFT calculations that oxygen-interstitial migration within this 1D ordered oxygen vacancy channel needs to overcome

an energy barrier as low as 0.62 eV¹². Furthermore, these ordered oxygen vacancies have also been considered as good candidates for anion intercalation such as O²⁻ and F⁻ with a full occupation of the vacant sites to yield a simple perovskite structure²⁹⁻³¹. Aukett *et al* further confirmed by Lorentzian broadening of the quasielastic neutron scattering spectrum that induced rotations of BO₄ by higher temperatures are a precondition for moving oxide-ion into tetrahedral layers from the octahedral layers^{32,33}, creating oxide-ion conduction pathways and activating long-range diffusion at the interface between layers; the latter is thought to be the driving force for oxygen vacancies disorder and isotropic oxygen diffusion. More recently, Lu *et al* demonstrated a reversible conversion from BM to SCO phase after a sufficient amount of oxygen is electrochemically injected into the lattice of BM without changing the surrounding atmosphere³⁴. Based on these prior studies, it is, therefore, reasonable to conceive that the ordered oxygen vacancies in the BM phase are excellent sites for oxygen intercalation, forming oxygen interstitials as the ionic point defect.

It is to be noted that the development of defect chemistry model for SCN is scarce in the literature, the only one of which by Zhou *et al*¹⁵ considers SrCoO_{3-δ} as the reference framework and oxygen vacancies as an ionic point defect, but contains a wrong description of point-defect (Sr'_{Sr}) to charge balance oxygen vacancies. No specific reason was given in their original paper why (Sr'_{Sr}) was chosen as a point defect.

2.2 Structural illustration of oxygen interstitials in donor-doped SCO

The ordered oxygen vacancies in BM are schematically shown in Fig.1 (a) as black squares within the tetrahedral layer alternating with the octahedral layer. After donor

doping, the introduced extra oxide-ions occupy some of those ordered oxygen vacancy sites, forming octahedra within the original tetrahedral layer as shown in Fig.1 (b). As more and more tetrahedra are converted to octahedra by donor doping, the structure is gradually transformed from orthorhombic brownmillerite into a primitive cubic perovskite shown in Fig.1 (c). The oxygen partially filled BM, Fig.1 (b), can, therefore, be viewed as a transitional structure towards an ideal cubic perovskite.

From the perspective of structural stability, Nb^{5+} substitution for low-spin Co(III) in SCO is also preferred since Nb^{5+} is much more stable than low-spin Co(III) in tetrahedral and five-fold coordination. In addition, the Nb^{5+} would attract interstitial oxygen to the BM empty channels to become five-fold coordinated.

In the following, based on the defect model described above, we first demonstrate the analytic solutions for T- and Po_2 -dependent concentrations of point-defects including oxygen interstitials, electron holes and excess electrons. We then map out the concentration contours of these point defects under the T- Po_2 domain, reconstruct $p=p(\text{T})|_\delta$ and $\sigma=\sigma(\text{T})|_\delta$ under a constant oxygen nonstoichiometry, calculate important partial/integral thermodynamic properties and ultimately gain a better understanding of the defect structures/reactions and electron transport in the SCN system.

2.3 Defect reactions

Under a perfect BM reference framework, the formal oxidation-state of Co-ions in $\text{SrCoO}_{2.5}$ is 3+. Thus, the Nb_2O_5 -doping reaction in SCO can be expressed by:

Here we consider oxygen interstitial O_I'' (Kröger-Vink notations) as the negatively charged ionic point defect to compensate the positively charged dopant $Nb_{Co}^{\bullet\bullet}$ (Kröger-Vink notations). We also consider that Nb^{5+} has a fixed oxidation state under the generally oxidizing atmospheres of this study, which is also assumed by Usiskin et al's work ²⁵. The chemical equilibrium between O_2 in the surrounding atmosphere and the donor-doped $SrCoO_{2.5+\delta}$ can then be represented by:

where O_I'' is created by $1/2O_2$ occupying the vacant oxygen site $V_I^{\times}$ (Kröger-Vink notations) in the BM, while oxidizing lattice Co^{3+} ($Co_{Co}^{\times}$, Kröger-Vink notations) into Co^{4+} ($= Co_{Co}^{\bullet}$, Kröger-Vink notations); the latter is the electron holes predominantly responsible for conductivity of the material. Application of mass action law to eq. (2) yields the equilibrium constant K_{ox} :

$$K_{ox} = \frac{[O_I''] [Co_{Co}^{\bullet}]^2}{P_{O_2}^{0.5} [Co_{Co}^{\times}]^2 [V_I^{\times}]} \quad (3)$$

Since the donor-doping (or electron-doping) elevates the Fermi level, another important reaction that is prone to occur at high temperatures and low P_{O_2} is the Co disproportionation reaction:

where, Co_{Co}' represents Co^{2+} ions (Kröger-Vink notations). The equilibrium constant K_{dsp} of eq. (4) is written by:

$$K_{dsp} = \frac{[Co\dot{Co}][Co'_{Co}]}{[Co^{\times}_{Co}]^2} \quad (5)$$

For all the charged point defects considered in this model, the following electro-neutrality condition must be fulfilled:

$$2[Nb\ddot{Co}] + [Co\dot{Co}] = 2[O''_I] + [Co'_{Co}] \quad (6)$$

The site conservation for oxygen and cobalt lattices are:

$$[Co^{\times}_{Co}] + [Co\dot{Co}] + [Co'_{Co}] + [Nb\ddot{Co}] = 1 \quad (7)$$

$$[V_I^{\times}] + [O''_I] = 0.5 \quad (8)$$

Since the electron holes dominate the conductivity of the material, we assume that the total conductivity equals the conductivity of the electron holes, which is expressed as a product of charge (F: Faraday constant= 96485C/mol), concentration ($\frac{[Co\dot{Co}]}{N_A \times a^3}$) and mobility of the holes (μ , m²/V/s):

$$\sigma = \frac{[Co\dot{Co}]F\mu}{N_A \times a^3} \quad (9)$$

where, N_A is the Avogadro constant, 6.02×10^{23} (mol⁻¹); a is the lattice constant of a pseudo-cubic SCN (with 10mol%Nb doping) is 3.90 Å³⁵. According to prior studies, Co-3d orbital and O-2p orbital tend to hybridize strongly in SCO systems^{21, 32}, producing a broad conduction band. The mean-free-path between hole scattering event is short to give a weak temperature dependence of mobility $\mu = e\tau/m^*$ ³⁶, where e is the charge of the charge carrier; τ and m^* are collision time and effective mass of the charge-carrier, respectively. We here assume that the hole-mobility μ is a T-independent constant, and

the observed decrease in hole-conductivity with increasing temperature under a constant P_{O_2} (see later Fig. 3), therefore, primarily arise from the decrease in hole-concentration induced by the loss of interstitial oxygens.

Solving eqs. (3), (5)-(8) leads to analytic expressions of $n = [Co'_{Co}]$, $[Co^x_{Co}]$, $\delta = [O''_I]$ and $[V_I^x]$ as a function of $p = [Co\dot{Co}]$, K_{ox} and K_{dsp} . Details about the deduction process can be found in the Appendix-A of Supporting Information (SI). The final analytic solution of $\sigma = \sigma(T, P_{O_2})$ can then be established through eq. (9). With the experimental $\sigma = \sigma(T, P_{O_2})$, the dependence of n , δ and p on T and P_{O_2} with only two adjustable parameters K_{ox} and K_{dsp} can then be attained through nonlinear regression described below.

III. Experimental Methods

3.1 Sample synthesis

The $SrCo_{0.9}Nb_{0.1}O_{2.5+\delta}$ (denoted as SCN10) sample was selected as the model system and synthesized via a conventional solid-state reaction method. First, the stoichiometric amount of the starting materials $SrCO_3$ ($\geq 99.9\%$, Aldrich), Co_3O_4 (99.7%, Alfa Aesar) and Nb_2O_5 (99.9%, Alfa Aesar) was intimately mixed, pelletized and calcined in air at 1000 °C for 10 h. The as-calcined pellets were then broken up and ball-milled into submicron powders, followed by pressing into bars with a dimension of 45 mm $\times$ 6 mm $\times$ 4 mm and finally sintering in air at 1200 °C for 10 hours to achieve a dense microstructure for phase examination and electrical conductivity measurement.

3.2 Phase examination

The phase composition of synthesized samples was examined by powder X-ray diffraction (PXRD) with a D/max-A (Rigaku, Japan) X-ray diffractometer operated with Cu K α radiation ($\lambda=1.5418$ Å). The scan was performed at a rate of 5° min^{-1} and a step size of 0.02° from $2\theta=10$ – 110° . Rietveld refinements of the collected XRD patterns were performed using GSAS/ EXPGUI software to determine phase composition and crystallographic parameters of SCN10.

3.3 Electrical conductivity measurement

The total conductivity of sintered bar samples were measured as a function of T and P_{O_2} using a standard four-probe method. The E-I testing module in the CorrWare software within a Solartron 1287/1260 electrochemical workstation system was employed to obtain voltage difference across the sample under a controlled current I, from which the resistance R of the sample can be obtained by $(\Delta V - V_{\text{bckgr}})/I$, where ΔV and V_{bckgr} are the voltage drops across the sample at a given I and background voltage at $I=0$, respectively. With the known length L and cross-sectional area A of the sample, the conductivity σ can then be calculated out by $\sigma=L/(R \cdot A)$.

The temperature of interest for this study ranged from 300 to 700 °C in a step of 50 °C. No higher than 700 °C was pursued in this study because of the concerns over the stability of SCN10 above 700 °C according to our previous study³⁵ as well as another study²⁵. In the meanwhile, P_{O_2} was varied only in the range of 0.001-1 atm in a total of 12 steps at each temperature. No conductivity was measured below $P_{O_2}=10^{-3}$ atm due to the consideration that SCN is intended for an oxygen-electrode working under oxidizing

atmospheres. To ensure a full gas-solid equilibrium, the samples were held at a given temperature and P_{O_2} for a sufficiently long time. It is worth mentioning that at low temperatures and low P_{O_2} , the equilibrium time can take up to 15-20 hours. An isothermal conductivity vs P_{O_2} measurement was typically started from pure O_2 toward low P_{O_2} , after which the measurement was retaken in pure O_2 to check whether the same conductivity can be obtained as before. This simple verification can help determine whether the original phase of the sample has been retained after being exposed to low P_{O_2} and high temperatures for a long period of time.

IV. Structural Examination and Electrical Conductivity

4.1 Phase composition

The XRD pattern of SCN10 collected over $2\theta=10-110^\circ$ at room temperature is shown in Fig. 2, where the refinement results using Pm3m (cubic) and P4/mmm (tetragonal) as the crystal-structure models are also overlaid. In the proposed mixed two-phase model, Nb was fixed at Co1 (1a: (0,0,0)) position. The refinement shows in general a good agreement between the calculated and observed profiles ($R_{wp}=1.58\%$; $R_p=1.17\%$, $\chi^2=4.801$), which suggests that the synthesized SCN10 contains a mixed tetragonal and cubic phase at room temperature. The ratio between tetragonal and cubic phase is ~85:15 (mole %). The refined lattice parameters are $a \times b \times c = 3.8742\text{\AA}(3) \times 3.8742\text{\AA}(3) \times 7.7868\text{\AA}(1)$ for the tetragonal phase and $a \times b \times c = 3.9002\text{\AA}(6) \times 3.9002\text{\AA}(6) \times 3.9002\text{\AA}(6)$ for the cubic phase. Evidently, the tetragonal phase has a superlattice structure with a $2 \times$ elongation along c-axis of the cubic structure. This observation is

consistent with early studies on the crystal structures of SCO systems represented by a homologous series of $\text{Sr}_n\text{Co}_n\text{O}_{3n-1}$. For oxygen stoichiometry $(3n-1)/n$ at 2.50^{37, 38}, 2.75³⁸⁻⁴⁰, 2.80⁴⁰, 2.87³⁹, 2.96³⁹ and 3.00³⁹, the corresponding n values are 2, 4, 5, 8, 32 and ∞ , respectively. At each n value, a superlattice structure featured by the ordered oxygen vacancies is observed. For example, for $n = 3$ phase with a stoichiometry of $\text{SrCoO}_{2.68}$, a superlattice structure is found in a tetragonal (t) unit cell with lattice parameters of $a_t \times b_t \times c_t = a_c \times a_c \times 4a_c$ ⁴⁰.

At elevated temperatures, e.g. $>300^\circ\text{C}$, these oxygen-ordered superlattice structures tend to transform into a single-phase oxygen-disordered perovskite pseudo-cubic unit cell as revealed by our early high-temperature XRD examination³⁵. Figure 2 (b) and (c) further show high-temperature XRD patterns of SCN10. It is evident that the oxygen-ordered tetragonal superstructure diminishes above 400°C , suggesting that an order-to-disorder transition of oxygen has taken place, resulting in a single phase composition. The single-phase at elevated temperatures is the prerequisite for the proposed defect chemistry model that is only valid for single homogeneous phase composition of a material. This single-phase precondition has also been ascertained by limiting the temperature to $\leq 700^\circ\text{C}$ and partial pressure of oxygen above 10^{-3} atm, where a single-phase composition exists in SCN system.

4.2 Electrical conductivity

The original electrical conductivity of SCN10 sample is shown in Fig. 3 on a time-scale for all Po_2 and temperatures studied. The results clearly show that the conductivity increases with Po_2 , inferring that p -type electron holes are the predominant charge carriers. On the other hand, Fig. 4 shows that the conductivity is not thermally activated,

decreasing with temperature at a given P_{O_2} , which suggests that electron-holes may not be completely localized small polarons as commonly perceived.

In a later discussion, we show that electron holes for the SCN10 system virtually exhibit a transition from delocalized (or itinerant) to localized holes with increasing temperature. The decrease of conductivity with temperature under a constant P_{O_2} shown in Fig.4 arises mainly from decrease in electron-hole concentration induced by the loss of interstitial oxygens. It is also noted from Fig. 4 that the lower the T and P_{O_2} , the longer the measurement will take to reach a true gas-solid equilibrium.

V. Modeling Results and Discussion

The nonlinear regression of (A-9) in the ESI in conjunction with eq. (9) was carried out by Matlab LSQNONLIN. To ensure high fidelity of the modeling results, the following sum of squares (Objective function, Obj) is used for the best fitting:

$$Obj = \sum_{n=1}^N (\log p_{O_2,m,n} - \log p_{O_2,exp,n})^2 \quad (10)$$

Here, P_{O_2} represents the partial pressure of oxygen; the subscripts m and exp represent model and experiment, respectively; N is the number of conductivity data points collected over a range of P_{O_2} .

5.1 Modelled vs experimental hole-conductivity

With the established defect model, Fig. 5 shows the comparison between modelled and experimental data attained in $P_{O_2}=10^{-3}$ to 1 atm and $T=300-700^\circ\text{C}$. It is reemphasized here

that the low-spin d -holes in the SCO systems are assumed to transport across Co-O-Co lattices with a constant mobility. In fact, we first treated the mobility as an adjustable parameter in the fitting process and found out that it only varied within a small range of 0.5-0.9 cm²/V/s for all temperatures (300-700 °C). For convenience, we take $\mu = 0.70$ cm²/V/s as an averaged constant for the fittings shown in Fig. 5. The good agreement between the experimental and modelled values shown in Fig. 5 suggests a good fidelity of the defect model that includes oxygen interstitials and constant-mobility d -holes as point defects in the SCO system.

To support further the SrCoO_{2.5+ δ} defect model, we also performed a similar mathematical treatment with an oxygen-deficient perovskite SrCoO_{3- δ} as the reference framework and oxygen vacancies as ionic point defect. Detailed results can be found in Appendix-B of the ESI. A general conclusion is that with the SrCoO_{3- δ} defect model, the trending of K_{dsp} with temperature is completely wrong, suggesting inappropriateness of the model. If the SrCoO_{3- δ} defect model is adopted for SCN systems, additional oxygen nonstoichiometry δ might also be needed as a part of the raw data set.

5.2 K_{ox} and K_{dsp} vs 1000/T

The plot of the obtained equilibrium constant K_{ox} in logarithmic scale vs 1000/T is shown in Fig. 6, where excellent linear relationship is observed with very small error bars. In addition, it indicates that K_{ox} decreases with T, implying that lower temperatures favour the defect reaction (2) and the production of delocalized low-spin d -electron holes. Conversely, at higher temperatures the reverse of the reaction (2) will take place,

releasing interstitial oxygens into the atmosphere and consuming low-spin d -holes, which is consistent with the TGA results^{25, 35}.

From Fig. 6, the standard Gibbs free energy ΔG_{ox}^0 of the reactions (2) can be calculated by:

$$\Delta G_{ox}^0 = \Delta H_{ox}^0 - T\Delta S_{ox}^0 = -RT\ln K_{ox} \quad (11)$$

Assuming that enthalpy ΔH_{ox}^0 and entropy ΔS_{ox}^0 are T-independent, they can be then obtained from the slope and intercept of the line, yielding $\Delta H_{ox}^0 = -57$ kJ/mol and $\Delta S_{ox}^0 = -95$ J/mol/K over the entire temperature range studied. The negative value of ΔH_{ox}^0 suggests that lower temperature favors the reaction (2).

Similarly, the obtained equilibrium constant K_{dsp} of the cobalt-ion disproportionation reaction (4) is plotted against $1000/T$ in Fig. 7. Different from Fig. 6, Fig.7 only shows a linear relationship between K_{dsp} in logarithmic scale and $1000/T$ above 550 °C, below which K_{dsp} is several orders of magnitude lower and scattered. Considering the fact that generation of excess electrons (Co'_{Co}) is more favorable at higher temperatures, the trending observed in Fig. 7 is thus reasonable. The extremely low concentration of excess electrons (Co'_{Co}) at <550 °C is likely to be the reason for the large data scattering observed.

From Fig. 7, the standard Gibbs free energy ΔG_{dsp}^0 of the reactions (4) at ≥ 550 °C is calculated by:

$$\Delta G_{dsp}^0 = \Delta H_{dsp}^0 - T\Delta S_{dsp}^0 = -RT\ln K_{dsp} \quad (12)$$

Assuming that enthalpy ΔH_{dsp}^0 and entropy ΔS_{dsp}^0 are T-independent, they can be then obtained from the slope and intercept of the line ≥ 550 °C, yielding $\Delta H_{dsp}^0 = 50$ kJ/mol and $\Delta S_{dsp}^0 = 15.3$ J/mol/K. The positive value of ΔH_{dsp}^0 also suggests that higher temperature favors the reaction (4).

5.3 p , n and δ contours on the T- Po_2 domain

With the obtained K_{ox} and K_{dsp} , the molar fractions of d -hole (p) and excess-electron (n) as well as oxygen nonstoichiometry (δ) can be calculated out as a function of Po_2 and T using eqs. (9), (A-2), (A-6) and (A-7) in the ESI; the results of concentration contours on the T- Po_2 domain are shown in Fig. 8. The p in Fig. 8 (a) varies in the range of 0.079-0.391 and decreases dramatically with decreasing Po_2 or increasing temperature. Such a trend is consistent with the measured electrical conductivity shown in Fig. 4.

Similarly, the molar fraction contour of excess-electron n is shown in Fig.8 (b). At high T (e.g. 700 °C) and low Po_2 (10^{-3} atm), n can be as high as 0.14. However, at lower T (e.g. ≤ 500 °C) excess electrons are almost non-existent regardless of Po_2 . It is to be shown later that excess electrons are mostly immobile and trapped at dopant $\text{Nb}_{\text{Co}}^{\bullet\bullet}$, which makes SCN a p -type conductor. This is consistent with the conductivity data shown in Fig. 3.

The oxygen nonstoichiometry δ (or the concentration of oxygen-interstitial) contour is also calculated and plotted in Fig. 8 (c). Because of the charge neutrality requirement, δ is essentially the combination of p and n shown in Fig. 8 (a) and (b). It varies from 0.0711 to 0.288 in the range of $0.001 \text{ atm} \leq p_{\text{O}_2} \leq 1 \text{ atm}$ and $300 \text{ °C} \leq T \leq 700 \text{ °C}$. The lower the

temperature and the higher the oxygen partial pressure, the higher the oxygen nonstoichiometry δ .

Comparing the oxygen nonstoichiometry δ obtained in this study with those experimentally measured from TGA by Usiskin et al.²⁵, an excellent agreement has been observed. For example, in the temperature range of 500°C to 700°C, Usiskin *et al* reported $3-\delta$ in the range of 2.57 to 2.70, which corresponds well to $2.5+\delta$ with $\delta=0.07$ to 0.20 shown in Fig. 8 (c).

5.4 Thermodynamic properties

A replotted isotherm of δ vs P_{O_2} from Fig. 8 (c) is shown in Fig. 9, from which a second-order polynomial fitting is performed to produce the following analytic expression for $\delta=\delta(T, P_{O_2})$:

$$2.5 + \delta = 2.2034 + 0.00836 \ln p_{O_2} + 0.52127 \times \frac{1000}{T} + 4.60926 \times 10^{-4} \times (\ln p_{O_2})^2 - 0.09848 \times \left(\frac{1000}{T}\right)^2 + 0.00629 \times \ln p_{O_2} \times \frac{1000}{T} \quad (13)$$

The corresponding average oxidation-state of Co-ions calculated from the assumption of Sr^{2+} , Nb^{5+} , and O^{2-} is displayed on the right y-axis. It is evident that the oxygen stoichiometry has been raised from 2.50 to 2.60 at 3+ formal Co-oxidation state by the Nb-doping. On the other hand, the original formal oxidation state of Co-ions at oxygen stoichiometry 2.5 has been lowered from 3+ to 2.8+ by the Nb-doping, reflecting the nature of electron donation from Nb^{5+} .

As discussed in early studies^{25, 40, 41}, the partial molar chemical potential of oxygen dissolved in the SCN10 solid solution, $\Delta\overline{\mu}_O$, can be linked to the equilibrium P_{O_2} in the gas phase by:

$$\Delta\overline{\mu}_O = \frac{RT}{2} \ln p_{O_2} \quad (14)$$

Since $\Delta\overline{\mu}_O = \Delta\overline{h}_O - T\Delta\overline{s}_O$, eq. (14) can be rewritten into,

$$\frac{R}{2} \ln p_{O_2} = \frac{\Delta\overline{h}_O}{T} - \Delta\overline{s}_O \quad (15)$$

where $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ are the partial molar enthalpy and entropy of oxygen interstitials in SCN10, respectively; R is the gas constant. Therefore, under a given oxygen nonstoichiometry δ , a plot of $(0.5R\ln p_{O_2})|_\delta - 1/T$ yields $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ as the slope and the negative intercept of the line, respectively.

Fig. 10 (a) shows the $(0.5R\ln p_{O_2})|_\delta - 1000/T$ plots at five δ values produced from eq. (13). Subsequently, $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ are obtained from the slope and the negative intercept of the line at each δ and plotted in Fig. 10 (b) as a function of δ . As δ increases, both $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ increase monotonically. The magnitude of $\Delta\overline{h}_O$ ranges from -98 to -51 kJ/mol-O, while $\Delta\overline{s}_O$ varies from -95 to -73 J/mol-O/K. These values are in good agreement with those obtained by Usiskin et al ²⁵ with TGA method. The sensitive variations of $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ with δ suggest a strong non-ideal solution behaviour for the SCN10 system, which could be attributed to the high concentration of oxygen interstitial in the material.

From a thermodynamic perspective, the obtained partial molar thermodynamic $\Delta\overline{h}_O$ and $\Delta\overline{s}_O$ are interrelated to the integral thermodynamic ΔH_{ox}^0 and ΔS_{ox}^0 in eqs. (11) and (12).

The linking equations between them are:

$$\Delta\overline{h}_O = \frac{\partial [Co'_{Co}]}{\partial \delta} \Delta H_{dsp}^0 + \Delta H_{ox}^0 \quad (16)$$

$$\Delta\overline{S}_0 = \frac{\partial[Co'_{Co}]}{\partial\delta} \Delta S_{dsp}^0 + \Delta S_{ox}^0 + s_0(conf) \quad (17)$$

The details about the deduction process of the above equations are given in Appendix-C of the SI. To verify the validity of eqs. (16) and (17), we independently calculated $\Delta\overline{h}_O$ and $\Delta\overline{S}_O$ using eqs. (16) and (17) and plot the values against those shown in Fig. 10 (b), which were calculated from experimental data; the results are shown in Fig. 11. Evidently, the experimentally obtained $\Delta\overline{h}_O$ and $\Delta\overline{S}_O$ are in good agreement with the theoretical ones, further confirming the correctness of eqs. (16) and (17). Note that only higher temperature data were compared in Fig. 11 to avoid large errors in ΔH_{dsp}^0 and ΔS_{dsp}^0 at low temperatures due to the extremely low concentration $[Co'_{Co}]$ of excess electrons.

5.5 $p=p(T)|_\delta$ under constant oxygen stoichiometry

Thermodynamically speaking, electron transport of a nonstoichiometric oxide should be represented under a constant oxygen stoichiometry. With the modelled data shown in Fig. 8, we are able to reconstruct hole concentration as a function of T under a constant δ . Fig. 12(a) shows Arrhenius format of p -T relationship. First, it is shown that p increases with T under a constant δ , becoming thermally activated; this is the opposite to what was observed under a constant P_{O_2} shown in Fig.3. It is understandable from the charge neutrality equation (eq. (7)) $2x+p=2\delta+n$ that p is proportional to n under a constant δ and $x=[Nb_{Co}^{\bullet\bullet}]$. Since n increases with T, so does p . Second, it is observed that p also increases with δ at a given T. This is also understandable in that the hybridization of Co-3d (Co-3d_{xy} and Co-3d_{xz}) and O-2p orbitals under octahedral coordination become

stronger at higher oxygen stoichiometry ⁴¹, thus producing more holes with O-2p ligand character. Third, Fig. 12(b) shows that the activation energy ΔE_a for the hole-production decreases from 0.20 eV to 0.06 eV as δ increases from 0.116 to 0.249. This result is in good agreement with Fig. 9 of Ref. ²⁵ reported by Usiskin *et al.* As aforementioned, at high oxygen stoichiometry, Co-3d orbital hybridizes heavily with O-2p orbital, broadening the conduction band and producing delocalized (or even itinerant holes) large-polarons with very low activation energy. In contrast, at low oxygen stoichiometry, the hybridization between Co-3d orbital and O-2p orbital becomes weaker, particularly with excess electrons trapped on the dopant $\text{Nb}_{\text{Co}}^{\bullet\bullet}$, forming a relatively narrow band and producing localized small-polarons. Similar observations has also been reported by Mitberg *et al* ²³, Usiskin *et al* ²⁵ and Karvonen *et al* ⁴¹. Since it has been previously suggested that electron transport with $\Delta E_a > 0.1$ eV can be characterized by small-polaron conduction, whereas by a large-polaron conduction when $\Delta E_a \leq 0.1$ eV ⁴², we can then conclude that electron holes in SCN system are gradually transitioning from delocalized large-polarons at high oxygen stoichiometry to localized small-polarons at low oxygen stoichiometry.

5.6 $\sigma=\sigma(T)|_{\delta}$ under constant oxygen stoichiometry and $\sigma=\sigma(\delta)$ isotherms

The varying trend of σ with T is the same as p with T since σ is directly proportional to p for constant-mobility holes. Fig. 13 (a) indeed shows an almost identical plot to Fig. 12 (a) with the same activation energy. In the meanwhile, Fig. 13 (b) shows the changes of σ with oxygen stoichiometry $2.5+\delta$. Again, we observe that σ is nearly independent of T at ≤ 500 °C, where $(2.5+\delta) \geq 2.7$, reflecting the behaviour of delocalized holes with a broad

conduction band. Only at $T \geq 550$ °C where $2.5 + \delta < 2.7$, does σ start to diverge for different temperatures, exhibiting a localized small-polaron behaviour. The fact that excess electrons are essentially trapped on the dopant $\text{Nb}_{\text{Co}}^{\bullet\bullet}$ and heavily polarize the Co-O-Co lattice is likely the reason for the small-polaron conduction.

5.7 Thermodynamic factor A

Even though the ionic conductivity contributes a small fraction to the total conductivity of a mixed conductor, it does play a crucial role in the ORR catalysis. The thermodynamic factor is a useful term to gauge the enhancement of ionic conduction by fast moving electron holes in mixed conductors⁴³. From the data obtained in Fig. 9, we attempt to calculate the isothermal thermodynamic factor A related to oxygen interstitials using the following equation:

$$A = \frac{1}{2} \left[\frac{\partial(\ln P_{\text{O}_2})}{\partial \ln x_{\text{O}}} \right]_T \quad (18)$$

where, $x_{\text{O}} = \delta / (2.5 + \delta)$ is the molar fraction of oxygen interstitials in the BM. More information is given in Appendix-D of the SI. The A value is known to be the ratio of chemical diffusion coefficient D_{c} to self-diffusion coefficient D_{s} , *i.e.* $D_{\text{c}} = A * D_{\text{s}}$ ⁴⁴. It can be interpreted kinetically as the generation of internal electric field by two charge carriers with different mobilities. If one charge carrier such as electron holes has a significantly higher mobility than the other charge carrier such as oxygen-interstitials, the local charge neutrality would require a slow-down of the fast moving electron holes and speed-up of the slow moving oxygen-interstitials, exhibiting the “drag-pull” effect⁴⁴. Fig. 14 (a) is a reformatted plot of Fig. 9 in the temperature range of 500-700 °C. The calculated

thermodynamic factor A is shown in Fig. 14 (b) as a function of P_{O_2} . Few important information can be gathered from Fig. 14 (b). First, $A > 1$ implies that the chemical diffusion coefficient of oxygen-interstitial is higher than the self-diffusion coefficient, inferring that the presence of electronic conduction indeed enhances the diffusion of oxygen. This is consistent with the observations in other Co-containing perovskite oxide systems⁴⁵⁻⁴⁷. Second, it appears that there is a trending change between A and P_{O_2} at 550 °C, an onset temperature that the concentration of excess electrons n changes in orders of magnitudes (see Fig. 8). The more excess electrons at higher T and lower P_{O_2} trapped on the dopant $Nb_{Co}^{\bullet\bullet}$ polarize the Co-O-Co lattice, thus inducing localized small polarons with lowered p -conductivity and oxygen ionic conductivity, ultimately decreasing the chemical diffusion coefficient of oxygen and A value. At $T < 550$ °C, the number of excess electrons are negligible and electron-holes are delocalized with high conductivity, thus leading to a higher oxygen ionic conductivity and a higher A value.

VI. Conclusions

In summary, a unique defect chemistry model featuring oxygen interstitials and delocalized-to-localized d -electron holes as the point defects is demonstrated under a Brownmillerite reference framework to elucidate the electrical conductivity behaviour observed in the SCN solid solution. The variations of electronic conductivity with T and P_{O_2} are assumed to arise primarily from change in concentration of d -holes with a constant-mobility. Following the new defect model, the equilibrium constant $\log K_{ox}$ for the oxygen-interstitial formation reaction is found to follow an excellent linear

relationship with $1/T$, while the equilibrium constant $\log K_{\text{dsp}}$ for the Co-ion disproportionation reaction follows a linear relationship with $1/T$ at ≥ 550 °C. Furthermore, concentration contours of $p=p(T, \text{Po}_2)$, $n=n(T, \text{Po}_2)$ and $\delta=\delta(T, \text{Po}_2)$ are mapped out over a range of Po_2 and T , from which the hole concentration (and conductivity) *vs* T was reconstructed under a constant oxygen-stoichiometry, revealing that electron holes essentially transit from delocalized (or itinerant) large-polarons at high oxygen stoichiometry (low temperatures and high Po_2) toward localized small-polarons at low oxygen stoichiometry (higher temperatures and low Po_2). The partial, integral molar thermodynamic properties and thermodynamic factor of the oxygen-interstitial dissolution process are also evaluated and found in good agreement with the literature data obtained from TGA method. Overall, this study demonstrates that with the help of a good defect chemistry model only electrical conductivity data are needed to derive reliable and quality thermodynamic and transport properties of nonstoichiometric oxides.

Acknowledgements

The information, data or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award number DE-AR0000492.

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Figure Caption

Fig. 1 Introduction of oxygen interstitial into an ideal BM structure (a), producing a transitional pseudo-cubic structure (b) and a terminal ideal primitive perovskite structure (c).

Fig. 2 (a) XRD pattern and Rietveld refinement of SCN10. Measured data: cross symbols; calculated: continuous line; (b) high-temperature (HT) XRD patterns; (c) blow-up of HT-XRD in $2\theta=35-50^\circ$.

Fig. 3 Electrical conductivity evolution with time at different Po_2 and temperature T; (a) 300-450 °C; (b) 500-700 °C.

Fig. 4 The conductivity (σ) measured as a function of temperature (T) under different Po_2 .

Fig. 5 Electrical conductivity of SCN10 vs Po_2 under different T. Solid line: modelled data; solid circle: experimental data.

Fig. 6 Plot of $\ln K_{ox}$ vs $1000/T$. The error bars shown in magenta colour corresponds to 95% confidence level.

Fig. 7 Plot of K_{dsp} vs $1000/T$. The error bars shown in magenta colour corresponds to 95% confidence level.

Fig. 8 Calculated molar fraction contours of (a) d -electron p ; (b) excess-electron n and (c) oxygen nonstoichiometry δ on a T- Po_2 domain

Fig. 9 Calculated oxygen stoichiometry $2.5+\delta$ vs Po_2 isotherms.

Fig. 10 (a) $(\frac{R}{2} \ln p_{O_2})|_\delta$ vs $\frac{1000}{T}$ under a constant δ ; (b) $\Delta \bar{h}_O$ and $\Delta \bar{s}_O$ vs δ .

Fig. 11 Comparison of partial molar enthalpy (a) and entropy (b) from Fig.10 with those calculated from eqs. (16) and (17).

Fig. 12 (a) $(\log p)|_\delta$ vs $1/T$ under iso-stoichiometric condition; (b) activation energy vs oxygen stoichiometry ($2.5+\delta$)

Fig. 13 (a) $(\log \sigma T)|_\delta$ vs $1/T$ under iso-stoichiometry; (b) $\log \sigma$ vs $2.5+\delta$ isotherms

Fig. 14 (a) $\ln \text{Po}_2$ vs $\ln x_o$; (b) thermodynamic factor as a function of Po_2

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Fig. 9 Calculated oxygen stoichiometry $2.5 + \delta$ vs P_{O_2} isotherms.

Fig. 10 (a)

(a) $(\frac{R}{2} \ln p_{O_2})|_{\delta}$ vs $\frac{1000}{T}$ under a constant δ ; (b) $\Delta \bar{h}_O$ and $\Delta \bar{S}_O$ vs δ .

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Fig. 14 (a) $\ln P_{O_2}$ vs $\ln x_O$; (b) thermodynamic factor as a function of P_{O_2}

Graphical Abstract Legend

Introduction of oxygen interstitials into an ideal BM structure (a), producing a transitional pseudo-cubic structure (b) and a terminal ideal primitive perovskite structure (c).

Graphical Abstract