



# Thermodynamic quantities and defect equilibrium in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$

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## ABSTRACT

In order to elucidate the relation between thermodynamic quantities, the defect structure, and the defect equilibrium in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ , statistical thermodynamic calculation is carried out and calculated results are compared to those obtained from experimental data. Partial molar enthalpy of oxygen and partial molar entropy of oxygen are obtained from  $\delta-P(\text{O}_2)-T$  relation by using Gibbs–Helmholtz equation. Statistical thermodynamic model is derived from defect equilibrium models proposed before by authors, localized electron model and delocalized electron model which could well explain the variation of oxygen content of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ . Although assumed defect species and their equilibrium are different, the results of thermodynamic calculation by localized electron model and delocalized electron model show minor difference. Calculated results by the both models agree with the thermodynamic quantities obtained from oxygen nonstoichiometry of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ .

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## 1. Introduction

Because of high mixed conductivities of oxide ions and electrons and high catalytic activity, Ni based  $\text{K}_2\text{NiF}_4$  type oxides are expected as the component of electrochemical devices such as a cathode material for solid oxide fuel cells [1], an oxygen permeation membrane [2], a catalyst for the reforming of hydrocarbons [2,3]. Earlier works revealed that  $\text{La}_2\text{NiO}_{4+\delta}$  shows large oxygen excess composition [4–6]. Jorgensen et al. carried out the neutron diffraction measurement, and elucidated that the interstitial oxygen exists at the center of La tetrahedron in  $\text{La}_2\text{NiO}_{4+\delta}$  [7]. Since interstitial oxygen becomes a major ionic carrier and holes are simultaneously generated to retain charge neutrality, interstitial oxygen formation significantly affects the electrochemical properties of  $\text{K}_2\text{NiF}_4$  type oxides. Therefore, it is essential to elucidate how oxygen nonstoichiometry emerges in  $\text{K}_2\text{NiF}_4$  type oxides.

In the previous work, we reported oxygen nonstoichiometry and defect equilibrium in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  ( $x = 0, 0.1, 0.2, 0.3, 0.4$ ) as a function of  $P(\text{O}_2)$ ,  $T$ , and Sr content,  $x$  [8].  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  shows oxygen excess and oxygen deficiency depending on  $P(\text{O}_2)$ ,  $T$ , and  $x$ . In order to elucidate how oxygen nonstoichiometry emerges, two defect equilibrium models were proposed under the assumption that the defects are randomly distributed. One is localized electron model and the other is delocalized electron model. Although electronic state is completely different, both defect equilibrium models can well explain oxygen nonstoichiometric behavior. This indicates that the electronic state of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is intermediate between the localized state and the

itinerant state [8]. There are only limited reports about the nonstoichiometric compounds which show metallic band conduction.  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  and  $\text{Ag}_2\text{S}$  were treated as the itinerant electron system [9,10]. Kanai et al. reported that the electronic state of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$  transits from the metallic state to the localized state depending on the Cu mean valence at 1073–1273 K [11]. Mizusaki et al. have clearly shown the relationship between defect equilibrium and thermodynamic quantities of  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ , which is a typical localized electron system [12,13].

In this paper, we clarify the relation between the thermodynamic quantities, the defect structure, and the defect equilibrium in the  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ . Two statistical thermodynamic models are derived from localized electron model and delocalized electron model. Then, the thermodynamic quantities calculated from the statistical thermodynamic model are compared to those obtained from nonstoichiometric data of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ .

## 2. Partial molar enthalpy and entropy of oxygen

The  $P(\text{O}_2)$  is related to the oxygen chemical potential in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ,  $\mu_{\text{O}}$ , by the equation

$$\mu_{\text{O}} - \mu_{\text{O}}^{\circ} = \frac{RT}{2} \ln P(\text{O}_2) \quad (1)$$

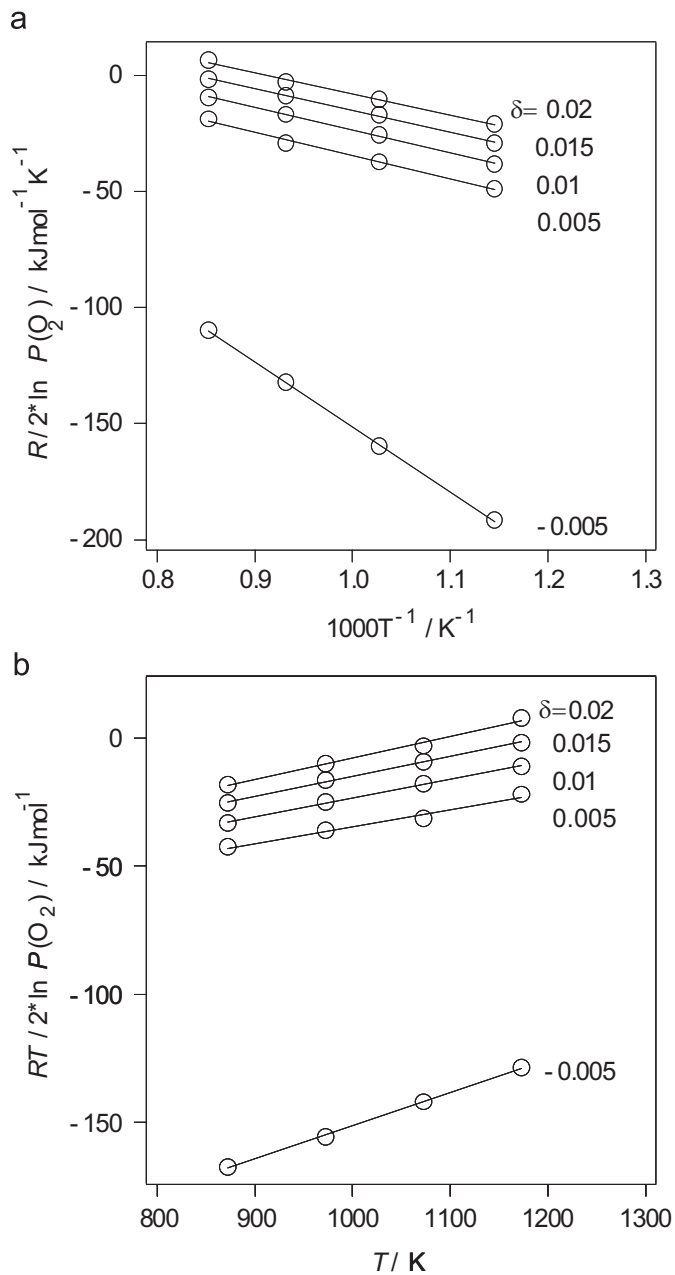
where  $R$  and  $T$  are the gas constant and the temperature, respectively. Superscript  $\circ$  denotes the standard state, equilibrium state with 1 bar  $\text{O}_2$ . From the Gibbs–Helmholtz equation, we obtain

$$h_{\text{O}} - h_{\text{O}}^{\circ} = \frac{\partial}{\partial(1/T)} \left( \frac{R}{2} \ln P(\text{O}_2) \right) \quad (2)$$

$$s_{\text{O}} - s_{\text{O}}^{\circ} = - \frac{\partial}{\partial T} \left( \frac{RT}{2} \ln P(\text{O}_2) \right) \quad (3)$$

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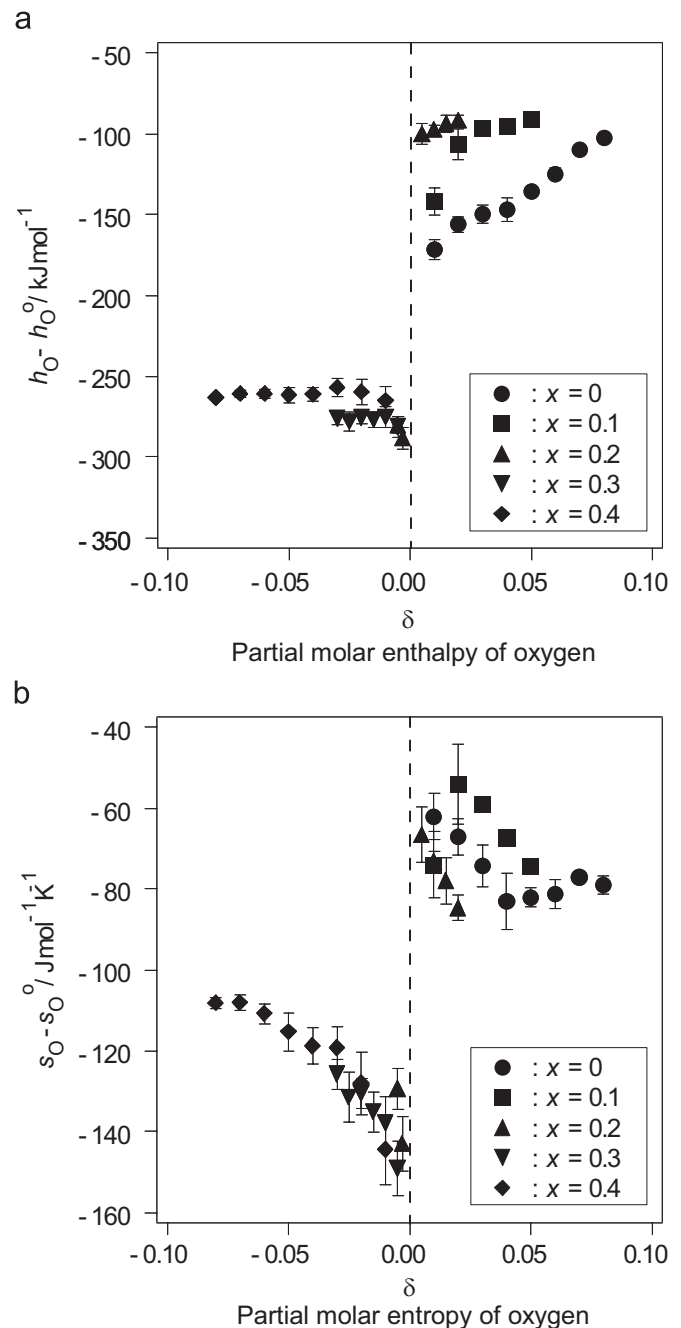
E-mail address: [t-naka@mail.tagen.tohoku.ac.jp](mailto:t-naka@mail.tagen.tohoku.ac.jp) (T. Nakamura).



**Fig. 1.** The relationship between  $R/2 \ln P(\text{O}_2)$  and  $1/T$  (a) and  $RT/2 \ln P(\text{O}_2)$  and  $T$  (b) of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$  at selected oxygen content.

where  $h_{\text{O}} - h_{\text{O}}^{\circ}$  and  $s_{\text{O}} - s_{\text{O}}^{\circ}$  are the partial molar enthalpy of oxygen, and the partial molar entropy of oxygen, respectively. Fig. 1 shows  $R/2 \ln P(\text{O}_2)$  vs.  $1/T$  plots and  $RT \ln P(\text{O}_2)$  vs.  $T$  plots of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$  at each oxygen content. The plots are obtained from the oxygen nonstoichiometric data of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  [8]. Linear plots in Fig. 1 indicate that  $h_{\text{O}} - h_{\text{O}}^{\circ}$  and  $s_{\text{O}} - s_{\text{O}}^{\circ}$  are essentially independent of temperature.

Fig. 2 shows  $h_{\text{O}} - h_{\text{O}}^{\circ}$  and  $s_{\text{O}} - s_{\text{O}}^{\circ}$  of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  as a function of  $\delta$  and  $x$ . In the calculation, oxygen nonstoichiometric data in Ref. [8] is used. The abrupt change of thermodynamic quantities at  $\delta = 0$  indicates that the oxygen defect structure changes suddenly at the stoichiometric composition. The value of  $h_{\text{O}} - h_{\text{O}}^{\circ}$  approaches zero as  $\delta$  increases in the oxygen excess region, while they are almost independent of  $\delta$  in the oxygen deficient region. This means that the system is like an ideal solution in the oxygen deficient region and deviate from ideal-solution-like state in the oxygen excess region. In the oxygen deficient region, the



**Fig. 2.** Partial molar enthalpy of oxygen (a) and partial molar entropy of oxygen (b).

variation of the interaction among quasi-chemical species is negligibly small, while that becomes significant in oxygen excess region. The change of  $h_{\text{O}} - h_{\text{O}}^{\circ}$  in oxygen excess region was caused by the defect species, interstitial oxygen, in the system. The enthalpy change was introduced in the defect equilibrium analysis as a regular solution approximation for the interstitial oxygen formation reaction [8]. At given oxygen content,  $h_{\text{O}} - h_{\text{O}}^{\circ}$  approaches zero as the Sr content increases in both oxygen excess and oxygen deficient regions. Regular-solution-like state holds for Sr distribution as well as the interstitial oxygen formation.

### 3. Defect equilibrium model for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$

In this section, two defect equilibrium models of our preceding work are briefly outlined [8]. One is the defect equilibrium with

localized electron (3.1) and the other is the defect equilibrium with delocalized electron (3.2).

### 3.1. Defect equilibrium with localized electron

Defect equilibrium model with localized electron is constructed by considering the equilibrium among  $\text{Sr}'_{\text{La}}$ ,  $\text{O}'_i$ ,  $\text{V}_{\text{O}}^{\bullet\bullet}$ ,  $\text{Ni}^{\times}_{\text{Ni}}$ , and  $\text{Ni}^{\bullet}_{\text{Ni}}$ . Defect species are expressed by the Kröger–Vink notation [14]. The incorporation of oxygen into the interstitial site, and the oxygen vacancy formation are expressed as



The exchange of interstitial oxygen and oxygen sublattice is expressed by the Frenkel defect formation



The standard Gibbs free energy change for reactions (4)–(6) are

$$\Delta G_{i,\text{loc}}^{\circ} = -RT \ln \frac{[\text{O}'_i][\text{Ni}^{\bullet}_{\text{Ni}}]^2}{P(\text{O}_2)^{1/2}[\text{V}_i^{\times}][\text{Ni}^{\times}_{\text{Ni}}]^2} - RT \ln \frac{\gamma_{\text{O}'_i} \gamma_{\text{Ni}^{\bullet}_{\text{Ni}}}^2}{\gamma_{\text{Ni}^{\times}_{\text{Ni}}}^2} \quad (7)$$

$$\Delta G_{v,\text{loc}}^{\circ} = -RT \ln \frac{P(\text{O}_2)^{1/2}[\text{V}_0^{\bullet\bullet}][\text{Ni}^{\times}_{\text{Ni}}]^2}{[\text{O}_0^{\times}][\text{Ni}^{\bullet}_{\text{Ni}}]^2} - RT \ln \frac{\gamma_{\text{V}_0^{\bullet\bullet}} \gamma_{\text{Ni}^{\times}_{\text{Ni}}}^2}{\gamma_{\text{O}_0^{\times}} \gamma_{\text{Ni}^{\bullet}_{\text{Ni}}}^2} \quad (8)$$

$$\Delta G_{f,\text{loc}}^{\circ} = -RT \ln \frac{[\text{O}'_i][\text{V}_0^{\bullet\bullet}]}{[\text{O}_0^{\times}][\text{V}_i^{\times}]} - RT \ln \frac{\gamma_{\text{O}'_i} \gamma_{\text{V}_0^{\bullet\bullet}}}{\gamma_{\text{O}_0^{\times}} \gamma_{\text{V}_i^{\times}}} \quad (9)$$

where  $\gamma$  is the activity coefficient for quasi-chemical species and the subscript  $i$  denotes quasi-chemical species. The relationship between Gibbs free energy changes of reactions (4)–(6) is expressed by

$$\Delta G_{f,\text{loc}}^{\circ} = \Delta G_{i,\text{loc}}^{\circ} + \Delta G_{v,\text{loc}}^{\circ} \quad (10)$$

The amount of oxygen nonstoichiometry,  $\delta$ , is expressed by

$$[\text{O}'_i] - [\text{V}_0^{\bullet\bullet}] = \delta \quad (11)$$

The ratio of the anion and cation is balanced by

$$[\text{Sr}'_{\text{La}}] + [\text{La}^{\times}_{\text{La}}] = 2 \quad (12)$$

$$[\text{Ni}^{\times}_{\text{Ni}}] + [\text{Ni}^{\bullet}_{\text{Ni}}] = 1 \quad (13)$$

$$[\text{O}_0^{\times}] + [\text{V}_0^{\bullet\bullet}] = 4 \quad (14)$$

$$[\text{O}'_i] + [\text{V}_i^{\times}] = 2 \quad (15)$$

Because interstitial oxygen exists at the center of La tetrahedron, the structural limit for the maximum oxygen excess is 2 as expressed in Eq. (15) [7,15]. The charge neutrality is maintained by the equation

$$[\text{Sr}'_{\text{La}}] + 2[\text{O}'_i] = [\text{Ni}^{\bullet}_{\text{Ni}}] + 2[\text{V}_0^{\bullet\bullet}] \quad (16)$$

As mentioned previously, the system behaves like an ideal solution in the oxygen deficient region, while it deviates from the ideal-solution-like state in the oxygen excess region. An ideal solution approximation is applied to the reactions (5) and (6), i.e. the interaction between randomly distributed quasi-chemical species is negligible. The products of the activity coefficients in Eqs. (8) and (9) are considered as unity. A regular solution approximation is applied to the reaction (4) with an excess enthalpy change. As a first approximation, we assume that the relation between  $h_{\text{O}} - h_{\text{O}}^{\circ}$  and  $[\text{O}'_i]$  is linear. Then, excess enthalpy

change is expressed by

$$\Delta H_{\text{ex,loc}} = -RT \ln \left( \frac{\gamma_{\text{O}'_i} \gamma_{\text{Ni}^{\bullet}_{\text{Ni}}}^2}{\gamma_{\text{Ni}^{\times}_{\text{Ni}}}^2} \right) = a[\text{O}'_i] \quad (17)$$

where  $a$  is a constant which is independent of  $\delta$  and  $T$  for given constraints. This approximation provides good fitting results [8]. From Eqs. (7), (9), (11)–(17), the relation between  $\delta$  and  $P(\text{O}_2)$  can be obtained with the fitting parameters,  $\Delta G_{i,\text{loc}}^{\circ}$ ,  $a$ , and  $\Delta G_{f,\text{loc}}^{\circ}$ .

### 3.2. Defect equilibrium with delocalized electron

Defect equilibrium model with itinerant electron is constructed by considering the defect equilibrium among  $\text{Sr}'_{\text{La}}$ ,  $\text{O}'_i$ ,  $\text{V}_0^{\bullet\bullet}$ , and free hole in the valence band,  $\text{h}^{\bullet}$ . Here, we consider the metal like band conduction as suggested by Goodenough et al. [16,17]. The equilibrium between the sample and surrounding gas is expressed by the equations



The exchange of the interstitial and oxygen sublattice is represented by Eq. (6). Since  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is a two dimensional conductor, density of state is independent of energy level of electron [18]. Then, the chemical potential of hole,  $\mu_{\text{h}^{\bullet}}$ , can be expressed by using the analytical solution of the integration of Fermi–Dirac distribution function [8]. That is

$$\mu_{\text{h}^{\bullet}} = \mu_{\text{h}^{\bullet}}^{\circ} + RT \ln \left\{ \exp \left( \frac{N_{\text{A}}}{D_{\text{V}} V_{\text{m}}} [\text{h}^{\bullet}] \right) - 1 \right\} \quad (20)$$

where  $\mu_{\text{h}^{\bullet}}^{\circ}$ ,  $D_{\text{V}}$ ,  $N_{\text{A}}$ , and  $V_{\text{m}}$  are the  $\mu_{\text{h}^{\bullet}}$  in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  in equilibrium with 1 bar  $\text{O}_2$ , the density of state in the valence band, the Avogadro's constant, and the molar volume, respectively. The standard Gibbs free energy change for the reactions (18), (19) and (6) are

$$\Delta G_{i,\text{del}}^{\circ} = -RT \ln \frac{[\text{O}'_i]}{P(\text{O}_2)^{1/2}[\text{V}_i^{\times}]} - RT \ln \gamma_{\text{O}'_i} - 2RT \ln \left\{ \exp \left( \frac{N_{\text{A}}}{D_{\text{V}} V_{\text{m}}} [\text{h}^{\bullet}] \right) - 1 \right\} \quad (21)$$

$$\Delta G_{v,\text{del}}^{\circ} = -RT \ln \frac{P(\text{O}_2)^{1/2}[\text{V}_0^{\bullet\bullet}]}{[\text{O}_0^{\times}]} - RT \ln \frac{\gamma_{\text{V}_0^{\bullet\bullet}}}{\gamma_{\text{O}_0^{\times}}} + 2RT \ln \left\{ \exp \left( \frac{N_{\text{A}}}{D_{\text{V}} V_{\text{m}}} [\text{h}^{\bullet}] \right) - 1 \right\} \quad (22)$$

and

$$\Delta G_{f,\text{del}}^{\circ} = -RT \ln \frac{[\text{O}'_i][\text{V}_0^{\bullet\bullet}]}{[\text{O}_0^{\times}][\text{V}_i^{\times}]} - RT \ln \frac{\gamma_{\text{O}'_i} \gamma_{\text{V}_0^{\bullet\bullet}}}{\gamma_{\text{O}_0^{\times}} \gamma_{\text{V}_i^{\times}}} \quad (23)$$

respectively. Charge neutrality for delocalized electron system is maintained by

$$[\text{Sr}'_{\text{La}}] + 2[\text{O}'_i] = [\text{h}^{\bullet}] + 2[\text{V}_0^{\bullet\bullet}] \quad (24)$$

Similar to the localized electron model, an ideal solution approximation is applied to the reactions (6) and (19) and a regular solution approximation is applied to the reaction (18) by the equation

$$\Delta H_{\text{ex,del}} = -RT \ln \gamma_{\text{O}'_i} = b[\text{O}'_i] \quad (25)$$

where  $b$  is a constant which is independent of  $\delta$  and  $T$ . From Eqs. (11), (12), (14), (15), (21), and (23)–(25), the relation between  $\delta$  and  $P(\text{O}_2)$  can be obtained with the fitting parameters,  $\Delta G_{i,\text{del}}^{\circ}$ ,  $\Delta G_{f,\text{del}}^{\circ}$ , and  $D_{\text{V}}$ .

#### 4. Statistical thermodynamic model for $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$

##### 4.1. Statistical thermodynamic model with localized electron

The statistical thermodynamic model is formulated from the Gibbs free energy of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ,  $G$ . When electron is localized,  $G$  is expressed by

$$G = G^\circ + \sum_i x_i \mu_i = G^\circ + \sum_i x_i \mu_i^\circ + \sum_i x_i RT \ln \gamma_i x_i \quad (26)$$

where  $x$ , and  $\mu$  represents the molar fraction and the chemical potential, respectively. The oxygen chemical potential in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is the differentiation of  $G$  with the number of moles of oxygen,  $4+\delta$ . Then,  $\mu_{\text{O}}$  can be calculated by

$$\mu_{\text{O}} = \frac{\partial G}{\partial(4+\delta)} = \frac{\partial G}{\partial \delta} = \sum_i \frac{\partial x_i}{\partial \delta} \mu_i^\circ + \sum_i RT \frac{\partial x_i}{\partial \delta} \ln \gamma_i + \frac{\partial}{\partial \delta} \sum_i RT x_i \ln x_i \quad (27)$$

here, we assume that  $\mu^\circ$  and  $\gamma$  of quasi-chemical species are independent of  $\delta$ .

Statistical thermodynamic model with localized electron is derived by combining Eqs. (11)–(17) and (27). The configurational entropy of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  with localized electron,  $S(\text{conf})_{\text{loc}}$ , can be calculated by

$$S(\text{conf})_{\text{loc}} = k \left[ \ln \left( \frac{(2N_A)!}{([\text{Sr}'_{\text{La}}]N_A)!([\text{La}^x_{\text{La}}]N_A)!} \right) + \ln \left( \frac{N_A!}{([\text{Ni}^\times_{\text{Ni}}]N_A)!([\text{Ni}^\bullet_{\text{Ni}}]N_A)!} \right) + \ln \left( \frac{(4N_A)!}{([\text{V}^\bullet_{\text{O}}]N_A)!([\text{O}^\times]N_A)!} \right) + \ln \left( \frac{(2N_A)!}{([\text{O}'_i]N_A)!([\text{V}^\times_i]N_A)!} \right) \right] \quad (28)$$

where  $k$  is the Boltzmann constant. The partial molar entropy due to configurational entropy,  $s_{\text{O}}(\text{conf})_{\text{loc}}$ , is obtained by the differentiation of  $S(\text{conf})_{\text{loc}}$  with respect to  $\delta$

$$s_{\text{O}}(\text{conf})_{\text{loc}} = \frac{\partial S(\text{conf})_{\text{loc}}}{\partial \delta} = k \frac{\partial}{\partial \delta} \left[ \ln \left( \frac{(2N_A)!}{([\text{Sr}'_{\text{La}}]N_A)!([\text{La}^x_{\text{La}}]N_A)!} \right) + \ln \left( \frac{N_A!}{([\text{Ni}^\times_{\text{Ni}}]N_A)!([\text{Ni}^\bullet_{\text{Ni}}]N_A)!} \right) + \ln \left( \frac{(4N_A)!}{([\text{V}^\bullet_{\text{O}}]N_A)!([\text{O}^\times]N_A)!} \right) + \ln \left( \frac{(2N_A)!}{([\text{O}'_i]N_A)!([\text{V}^\times_i]N_A)!} \right) \right] \quad (29)$$

From the Stirling's approximation and the relation of  $R = kN_A$ , we obtain

$$s_{\text{O}}(\text{conf})_{\text{loc}} = -R \frac{\partial}{\partial \delta} \{ [\text{Sr}'_{\text{La}}] \ln [\text{Sr}'_{\text{La}}] + [\text{La}^x_{\text{La}}] \ln [\text{La}^x_{\text{La}}] + [\text{Ni}^\times_{\text{Ni}}] \ln [\text{Ni}^\times_{\text{Ni}}] + [\text{Ni}^\bullet_{\text{Ni}}] \ln [\text{Ni}^\bullet_{\text{Ni}}] + [\text{O}^\times] \ln [\text{O}^\times] + [\text{V}^\bullet_{\text{O}}] \ln [\text{V}^\bullet_{\text{O}}] + [\text{O}'_i] \ln [\text{O}'_i] + [\text{V}^\times_i] \ln [\text{V}^\times_i] \} \quad (30)$$

Eq. (30) is exactly the same as the third term in the right side of the Eq. (27). From Eqs. (11)–(16)  $s_{\text{O}}(\text{conf})_{\text{loc}}$  is simplified to

$$s_{\text{O}}(\text{conf})_{\text{loc}} = R \left[ (\ln [\text{V}^\times_i] - \ln [\text{O}'_i]) \frac{\partial [\text{O}'_i]}{\partial \delta} + (\ln [\text{O}^\times] - \ln [\text{V}^\bullet_{\text{O}}]) \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} + 2 \ln \left( \frac{1 - [\text{Sr}'_{\text{La}}] - 2\delta}{[\text{Sr}'_{\text{La}}] + 2\delta} \right) \right] \quad (31)$$

The value of  $s_{\text{O}}(\text{conf})_{\text{loc}}$  can be calculated by Eq. (31) with the defect concentration and the value of  $\partial [\text{O}'_i] / \partial \delta$  and  $\partial [\text{V}^\bullet_{\text{O}}] / \partial \delta$ .

The relationship between statistical thermodynamic model and defect equilibrium model is derived as follows. From Eqs. (11)–(17), (27), and (30), the formula for  $\mu_{\text{O}} - \mu_{\text{O}}^\circ$  can be

simplified to

$$\begin{aligned} \mu_{\text{O}} - \mu_{\text{O}}^\circ &= \frac{\partial [\text{O}'_i]}{\partial \delta} (\mu_{\text{O}'_i}^\circ + 2\mu_{\text{Ni}^\bullet_{\text{Ni}}}^\circ - \mu_{\text{V}^\times_i}^\circ - 2\mu_{\text{Ni}^\times_{\text{Ni}}}^\circ) \\ &+ \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} (\mu_{\text{V}^\bullet_{\text{O}}}^\circ + 2\mu_{\text{Ni}^\times_{\text{Ni}}}^\circ - \mu_{\text{O}^\times}^\circ - 2\mu_{\text{Ni}^\bullet_{\text{Ni}}}^\circ) \\ &+ \frac{\partial [\text{O}'_i]}{\partial \delta} RT \ln \frac{\gamma_{\text{O}'_i} \gamma_{\text{Ni}^\times_{\text{Ni}}}^2}{\gamma_{\text{Ni}^\bullet_{\text{Ni}}}^2} + \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} RT \ln \frac{\gamma_{\text{V}^\bullet_{\text{O}}} \gamma_{\text{Ni}^\times_{\text{Ni}}}^2}{\gamma_{\text{O}^\times} \gamma_{\text{Ni}^\bullet_{\text{Ni}}}^2} \\ &- T s_{\text{O}}(\text{conf})_{\text{loc}} - \mu_{\text{O}}^\circ \end{aligned} \quad (32)$$

The chemical potential of 1 bar oxygen gas,  $\mu_{\text{O}_2, \text{gas}}^\circ$ , is related to  $\mu_{\text{O}}^\circ$  by the equation

$$\mu_{\text{O}_2, \text{gas}}^\circ = 2\mu_{\text{O}}^\circ \quad (33)$$

The Gibbs free energy changes for the reactions (4) and (5) are expressed by chemical potential of quasi-chemical species by

$$\Delta G_{\text{I}, \text{loc}}^\circ = \mu_{\text{O}'_i}^\circ + 2\mu_{\text{Ni}^\bullet_{\text{Ni}}}^\circ - \mu_{\text{V}^\times_i}^\circ - 2\mu_{\text{Ni}^\times_{\text{Ni}}}^\circ - 1/2\mu_{\text{O}_2, \text{gas}}^\circ \quad (34)$$

$$\Delta G_{\text{V}, \text{loc}}^\circ = \frac{1}{2}\mu_{\text{O}_2, \text{gas}}^\circ + \mu_{\text{V}^\bullet_{\text{O}}}^\circ + 2\mu_{\text{Ni}^\times_{\text{Ni}}}^\circ - \mu_{\text{O}^\times}^\circ - 2\mu_{\text{Ni}^\bullet_{\text{Ni}}}^\circ \quad (35)$$

Using Eqs. (32)–(35) and the differentiation of Eq. (11) with  $\delta$ , we obtain the partial molar quantities

$$\mu_{\text{O}} - \mu_{\text{O}}^\circ = \frac{\partial [\text{O}'_i]}{\partial \delta} (\Delta G_{\text{I}, \text{loc}}^\circ - \Delta H_{\text{ex}, \text{loc}}) + \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} \Delta G_{\text{V}, \text{loc}}^\circ - T s_{\text{O}}(\text{conf})_{\text{loc}} \quad (36)$$

$$h_{\text{O}} - h_{\text{O}}^\circ = \frac{\partial [\text{O}'_i]}{\partial \delta} (\Delta H_{\text{I}, \text{loc}}^\circ - \Delta H_{\text{ex}, \text{loc}}) + \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} \Delta H_{\text{V}, \text{loc}}^\circ \quad (37)$$

$$s_{\text{O}} - s_{\text{O}}^\circ = \frac{\partial [\text{O}'_i]}{\partial \delta} \Delta S_{\text{I}, \text{loc}}^\circ + \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} \Delta S_{\text{V}, \text{loc}}^\circ + s_{\text{O}}(\text{conf})_{\text{loc}} \quad (38)$$

Eqs. (36)–(38) gives the relationship between partial molar quantities and the fitting parameters determined by the defect chemical analysis with localized electron model.

##### 4.2. Statistical thermodynamic model with delocalized electron

Statistical thermodynamic model with itinerant electron is derived by combining Eqs. (11), (12), (14), (15), and, (21)–(25). When electron is itinerant, the Gibbs free energy of the system is expressed by

$$G = G^\circ + \sum_i x_i \mu_i = G^\circ + \sum_i x_i \mu_i^\circ + \sum_i x_i RT \ln \gamma_i x_i + [h^\bullet] \mu_{h^\bullet}^\circ + [h^\bullet] RT \ln \left\{ \exp \left( \frac{N_A}{D_V V_m} [h^\bullet] \right) - 1 \right\} \quad (39)$$

Unlike quasi-chemical species, free hole in the valence band is uncountable for the configurational entropy. The configurational entropy with delocalized electron,  $s_{\text{O}}(\text{conf})_{\text{del}}$ , can be expressed by

$$s_{\text{O}}(\text{conf})_{\text{del}} = -R \frac{\partial}{\partial \delta} \{ [\text{Sr}'_{\text{La}}] \ln [\text{Sr}'_{\text{La}}] + [\text{La}^x_{\text{La}}] \ln [\text{La}^x_{\text{La}}] + [\text{Ni}^\times_{\text{Ni}}] \ln [\text{Ni}^\times_{\text{Ni}}] + [\text{O}^\times] \ln [\text{O}^\times] + [\text{V}^\bullet_{\text{O}}] \ln [\text{V}^\bullet_{\text{O}}] + [\text{O}'_i] \ln [\text{O}'_i] + [\text{V}^\times_i] \ln [\text{V}^\times_i] \} \quad (40)$$

The value of  $s_{\text{O}}(\text{conf})_{\text{del}}$  can be calculated from the defect concentrations by the equation

$$s_{\text{O}}(\text{conf})_{\text{del}} = R \left[ (\ln [\text{V}^\times_i] - \ln [\text{O}'_i]) \frac{\partial [\text{O}'_i]}{\partial \delta} + (\ln [\text{O}^\times] - \ln [\text{V}^\bullet_{\text{O}}]) \frac{\partial [\text{V}^\bullet_{\text{O}}]}{\partial \delta} \right] \quad (41)$$

The relationship between statistical thermodynamic model and defect equilibrium model is shown in the following part. The formula for  $\mu_{\text{O}} - \mu_{\text{O}}^\circ$  is derived from Eqs. (11), (12), (14), (15),

**Table 1**

Values of the fitting parameters for the statistical thermodynamic models determined by the defect chemical analysis [8]: (a) fitting parameters for the statistical thermodynamic model with localized electron,  $\Delta H_{f,loc}^\circ$ ,  $\Delta S_{f,loc}^\circ$ , and  $a$ . The value of  $a$  for  $x = 0, 0.1$ , and  $0.4$  were determined by the extrapolation and (b) fitting parameters for the statistical thermodynamic model with delocalized electron,  $\Delta H_{f,del}^\circ$ ,  $\Delta S_{f,del}^\circ$ , and  $b$ . The value of  $b$  for  $x = 0, 0.1$ , and  $0.4$  were determined by the extrapolation.

$x$	$\Delta H_{f,loc}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_{f,loc}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{f,loc}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_{f,loc}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$a$ (J mol <sup>-2</sup> )
(a)					
0	-157 ± 2.6	-145 ± 2.6	167 ± 1.5	-24 ± 1.4	(-5.5 × 10 <sup>5</sup> )
0.1	-125 ± 5.4	-129 ± 5.2	177 ± 4.9	-27 ± 4.8	(-6.7 × 10 <sup>5</sup> )
0.2	-104 ± 1.5	-138 ± 1.4	189 ± 2.7	-29 ± 2.6	-7.4 ± 0.2 × 10 <sup>5</sup>
0.3	-75 ± 6.1	-140 ± 5.9	199 ± 4.4	-34 ± 4.2	-8.4 ± 0.4 × 10 <sup>5</sup>
0.4	-63 ± 1.9	-143 ± 1.8	197 ± 4.9	-48 ± 4.8	(-9.3 × 10 <sup>5</sup> )
(b)					
$x$	$\Delta H_{f,del}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_{f,del}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{f,del}^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_{f,del}^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$b$ (J mol <sup>-2</sup> )
0	-144 ± 1.8	-117 ± 1.7	167 ± 1.5	-24 ± 1.4	(-5.4 × 10 <sup>5</sup> )
0.1	-119 ± 3.6	-106 ± 3.5	171 ± 4.4	-34 ± 4.2	(-6.8 × 10 <sup>5</sup> )
0.2	-99 ± 1.1	-116 ± 1.0	186 ± 2.7	-30 ± 2.6	-7.9 ± 0.2 × 10 <sup>5</sup>
0.3	-71 ± 1.6	-123 ± 1.6	200 ± 3.3	-41 ± 3.2	-9.5 ± 0.3 × 10 <sup>5</sup>
0.4	-46 ± 1.7	-112 ± 1.6	211 ± 4.4	-40 ± 4.2	(-1.1 × 10 <sup>6</sup> )

(21)–(25), (39), (40), and the differentiation of Eq. (11) with  $\delta$ . That is

$$\begin{aligned} \mu_{\text{O}} - \mu_{\text{O}}^\circ &= \frac{\partial[\text{O}_i^\bullet]}{\partial\delta} \left( \mu_{\text{O}_i^\bullet}^\circ + 2\mu_{\text{h}^\bullet}^\circ - \mu_{\text{V}_i^\bullet}^\circ - \frac{1}{2}\mu_{\text{O}_2,\text{gas}}^\circ \right) \\ &+ \frac{\partial[\text{V}_{\text{O}}^{\bullet\bullet}]}{\partial\delta} \left( \mu_{\text{V}_{\text{O}}^{\bullet\bullet}}^\circ - \mu_{\text{O}_\circ}^\circ - 2\mu_{\text{h}^\bullet}^\circ + \frac{1}{2}\mu_{\text{O}_2,\text{gas}}^\circ \right) \\ &+ \frac{\partial[\text{O}_i^\bullet]}{\partial\delta} RT \ln \gamma_{\text{O}_i^\bullet} + \frac{\partial[\text{V}_{\text{O}}^{\bullet\bullet}]}{\partial\delta} RT \ln \frac{\gamma_{\text{V}_{\text{O}}^{\bullet\bullet}}}{\gamma_{\text{O}_\circ}^\circ} \\ &- T \left( s_{\text{O}}(\text{conf})_{\text{del}} - 2R \ln \left\{ \exp(N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}) - 1 \right\} \right. \\ &\left. - \frac{2RN_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}}{1 - \exp(-N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}})} \right) \end{aligned} \quad (42)$$

The Gibbs free energy change for the reactions (18) and (19) are

$$\Delta G_{\text{I,del}}^\circ = \mu_{\text{O}_i^\bullet}^\circ + 2\mu_{\text{h}^\bullet}^\circ - \mu_{\text{V}_i^\bullet}^\circ - 1/2\mu_{\text{O}_2,\text{gas}}^\circ \quad (43)$$

$$\Delta G_{\text{V,del}}^\circ = \frac{1}{2}\mu_{\text{O}_2,\text{gas}}^\circ + \mu_{\text{V}_{\text{O}}^{\bullet\bullet}}^\circ - \mu_{\text{O}_\circ}^\circ - 2\mu_{\text{h}^\bullet}^\circ \quad (44)$$

Using Eqs (42)–(44), one can obtain the partial molar quantities

$$\begin{aligned} \mu_{\text{O}} - \mu_{\text{O}}^\circ &= \frac{\partial[\text{O}_i^\bullet]}{\partial\delta} (\Delta G_{\text{I,del}}^\circ - \Delta H_{\text{ex,del}}) + \frac{\partial[\text{V}_{\text{O}}^{\bullet\bullet}]}{\partial\delta} \Delta G_{\text{V,del}}^\circ \\ &- T \left( s_{\text{O}}(\text{conf})_{\text{del}} - 2R \ln \left\{ \exp(N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}) - 1 \right\} \right. \\ &\left. - \frac{2RN_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}}{1 - \exp(-N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}})} \right) \end{aligned} \quad (45)$$

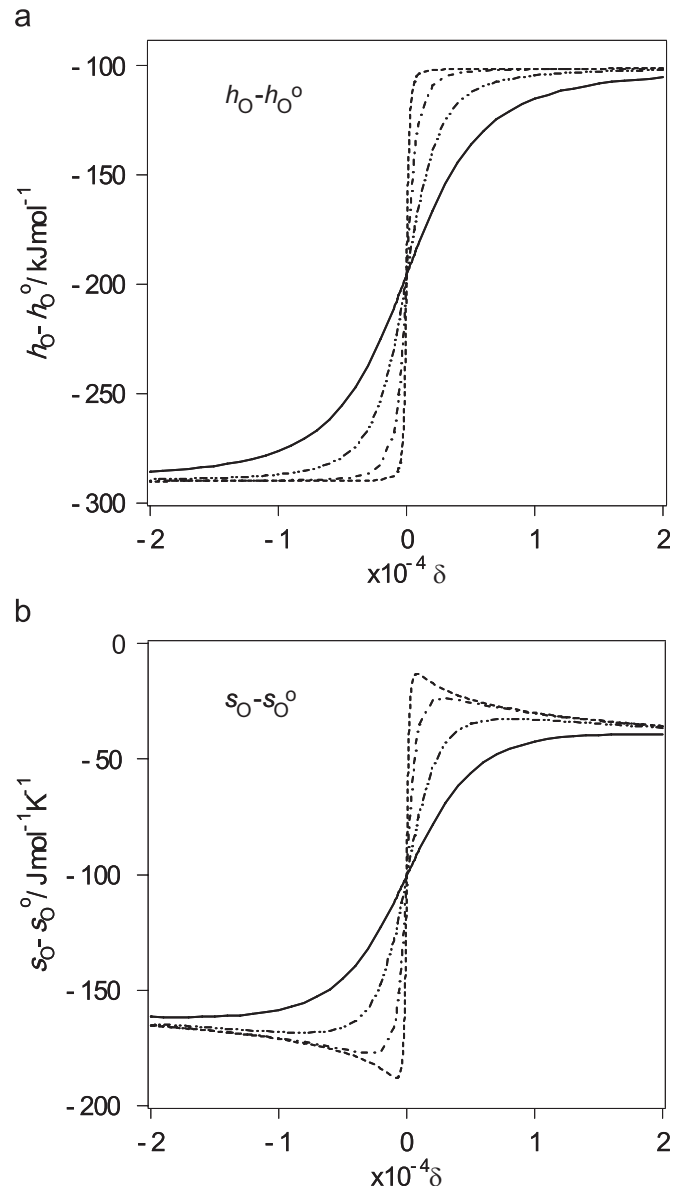
$$h_{\text{O}} - h_{\text{O}}^\circ = \frac{\partial[\text{O}_i^\bullet]}{\partial\delta} (\Delta H_{\text{I,del}}^\circ - \Delta H_{\text{ex,del}}) + \frac{\partial[\text{V}_{\text{O}}^{\bullet\bullet}]}{\partial\delta} \Delta H_{\text{V,del}}^\circ \quad (46)$$

$$\begin{aligned} s_{\text{O}} - s_{\text{O}}^\circ &= \frac{\partial[\text{O}_i^\bullet]}{\partial\delta} \Delta S_{\text{I,del}}^\circ + \frac{\partial[\text{V}_{\text{O}}^{\bullet\bullet}]}{\partial\delta} \Delta S_{\text{V,del}}^\circ + s_{\text{O}}(\text{conf})_{\text{del}} \\ &- 2R \ln \left\{ \exp(N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}) - 1 \right\} \\ &- \frac{2RN_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}}}{1 - \exp(-N_{\text{A}}[\text{h}^\bullet]/D_{\text{V}}V_{\text{m}})} \end{aligned} \quad (47)$$

Eqs. (45)–(47) gives the relation between partial molar quantities and the fitting parameters determined by the defect chemical analysis with delocalized electron model.

## 5. Partial molar quantities calculated from the statistical thermodynamic model

The parameters,  $\Delta G_{\text{I,loc}}^\circ$ ,  $\Delta G_{\text{f,loc}}^\circ$ ,  $a$ ,  $\Delta G_{\text{I,del}}^\circ$ ,  $\Delta G_{\text{f,del}}^\circ$ ,  $b$ , and  $D_{\text{V}}$ , were determined in the defect chemical analysis on the oxygen nonstoichiometry of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  [8]. Obtained  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and the constants,  $a$  and  $b$ , are summarized in Table 1. In the delocalized electron model, best fitted results were obtained



**Fig. 3.** Temperature dependence of  $h_{\text{O}} - h_{\text{O}}^\circ$  and  $s_{\text{O}} - s_{\text{O}}^\circ$  calculated by Eqs. (37) and (38). Solid line (1173 K), dashed-two dotted line (1073 K), dashed-dotted line (973 K), and dashed line (873 K).

when  $D_V$  is equal to  $4.2 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$  which is slightly larger than that of  $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$  [19]. The value of  $D_V$  is also used in the statistical thermodynamic analysis.

To calculate the partial molar quantities, the value of  $\partial[\text{O}_i^{\prime\prime}]/\partial\delta$  and  $\partial[\text{V}_\text{O}^{\bullet\bullet}]/\partial\delta$  is required. The equilibrium constant for the equilibrium reaction (6) is expressed by

$$K_f = \exp\left(-\frac{\Delta G_f^\circ}{RT}\right) = \frac{[\text{O}_i^{\prime\prime}][\text{V}_\text{O}^{\bullet\bullet}]\gamma_{\text{O}_i^{\prime\prime}}\gamma_{\text{V}_\text{O}^{\bullet\bullet}}}{[\text{O}_\text{O}^{\times}][\text{V}_\text{I}^{\times}]\gamma_{\text{O}_\text{O}^{\times}}\gamma_{\text{V}_\text{I}^{\times}}} \quad (48)$$

Here, the products of activity coefficients are considered to be unity because an ideal solution approximation is applied for reaction (6). From the differentiation of Eqs. (11) and (48) with respect to  $\delta$ , the value of  $\partial[\text{O}_i^{\prime\prime}]/\partial\delta$  and  $\partial[\text{V}_\text{O}^{\bullet\bullet}]/\partial\delta$  can be calculated

from defect concentration by the equation

$$\frac{\partial[\text{O}_i^{\prime\prime}]}{\partial\delta} = \frac{[\text{O}_i^{\prime\prime}] + K_f[\text{V}_\text{I}^{\times}]}{[\text{V}_\text{O}^{\bullet\bullet}] + K_f[\text{O}_\text{O}^{\times}] + [\text{O}_i^{\prime\prime}] + K_f[\text{V}_\text{I}^{\times}]} \quad (49)$$

$$\frac{\partial[\text{V}_\text{O}^{\bullet\bullet}]}{\partial\delta} = -\frac{[\text{V}_\text{O}^{\bullet\bullet}] + K_f[\text{O}_\text{O}^{\times}]}{[\text{V}_\text{O}^{\bullet\bullet}] + K_f[\text{O}_\text{O}^{\times}] + [\text{O}_i^{\prime\prime}] + K_f[\text{V}_\text{I}^{\times}]} \quad (50)$$

From Eqs. (31), (36), (41), (45), (49), (50), and the parameters in Table 1, the thermodynamic quantities are calculated by using the statistical thermodynamic model. Fig. 3 shows thermodynamic quantities of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$  at 873–1173 K calculated by Eqs. (37), and (38) (localized electron model). The figure is focused near the stoichiometric oxygen content,  $\delta = 0$ . As temperature decreases,

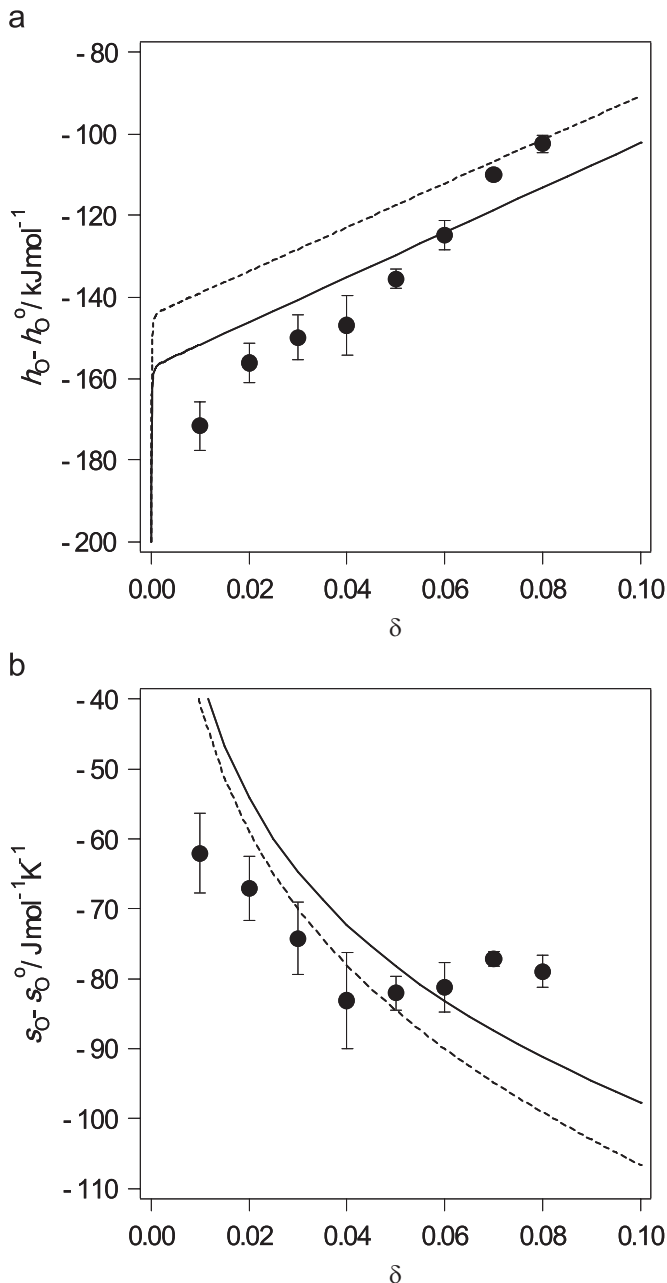


Fig. 4. Partial molar enthalpy and entropy of oxygen for  $\text{La}_2\text{NiO}_{4+\delta}$ . Solid lines are calculated by Eqs. (37) and (38) (localized electron model) and dashed lines are calculated by Eqs. (46) and (47) (delocalized electron model).

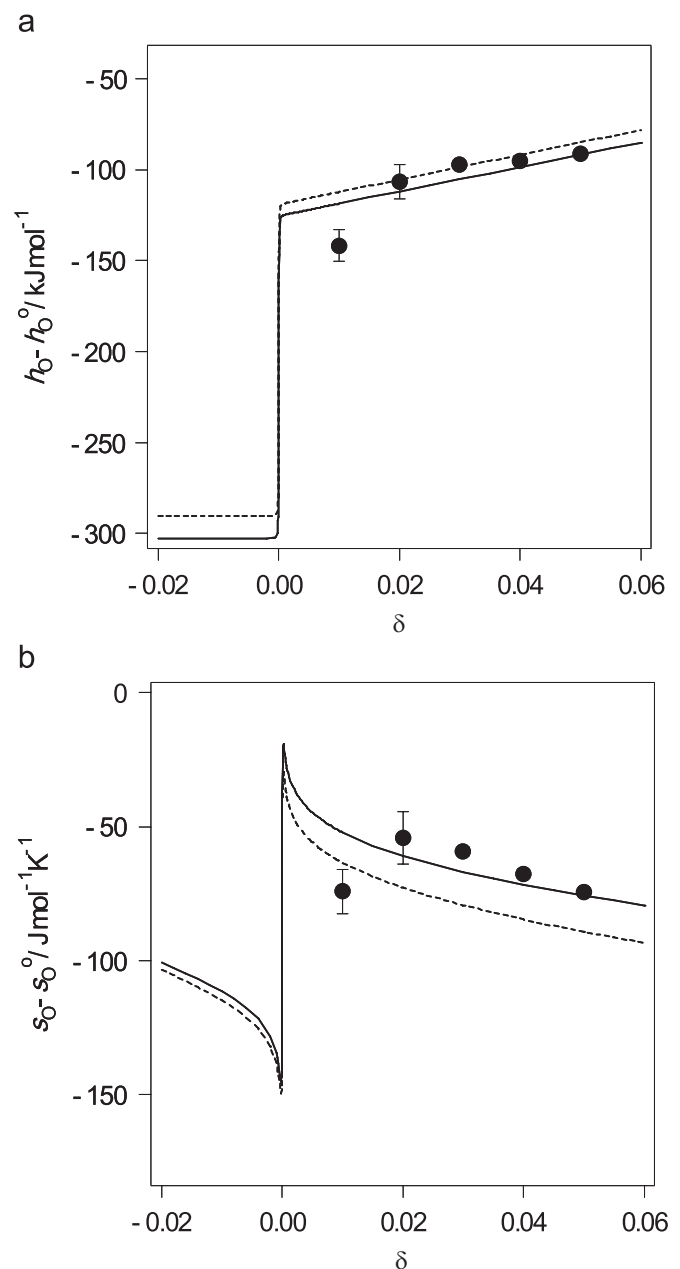


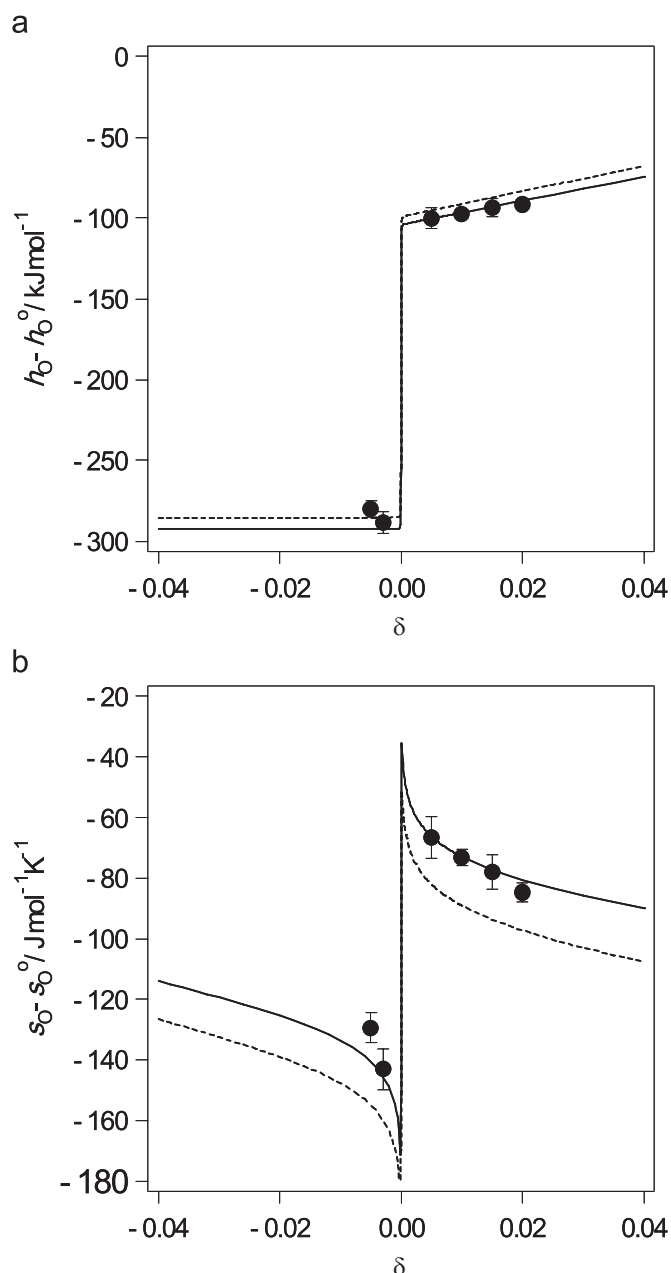
Fig. 5. Partial molar enthalpy and entropy of oxygen for  $\text{La}_{1.9}\text{Sr}_{0.1}\text{NiO}_{4+\delta}$ . Solid lines are calculated by Eqs. (37) and (38) (localized electron model) and dashed lines are calculated by Eqs. (46) and (47) (delocalized electron model).

the change of  $h_{\text{O}} - h_{\text{O}}^{\circ}$  and  $s_{\text{O}} - s_{\text{O}}^{\circ}$  near the stoichiometric oxygen content becomes more drastic. This behavior reflects the temperature dependence of  $K_f$ . The value of  $K_f$  becomes smaller as temperature decreases. The small difference between calculated curves at different temperature appears only within very narrow range of  $\delta$ . Calculated curves at different temperature are almost the same. This is because the values of  $K_f$  for  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  are extremely small, which are in the range of  $10^{-14}$ – $10^{-8}$ . It is confirmed that calculated curves by Eqs. (46) and (47) (delocalized electron model) also show minor difference against temperature. Because the variation of calculated curves with temperature is very small, only the calculated curve at 1073 K is shown in the following discussion.

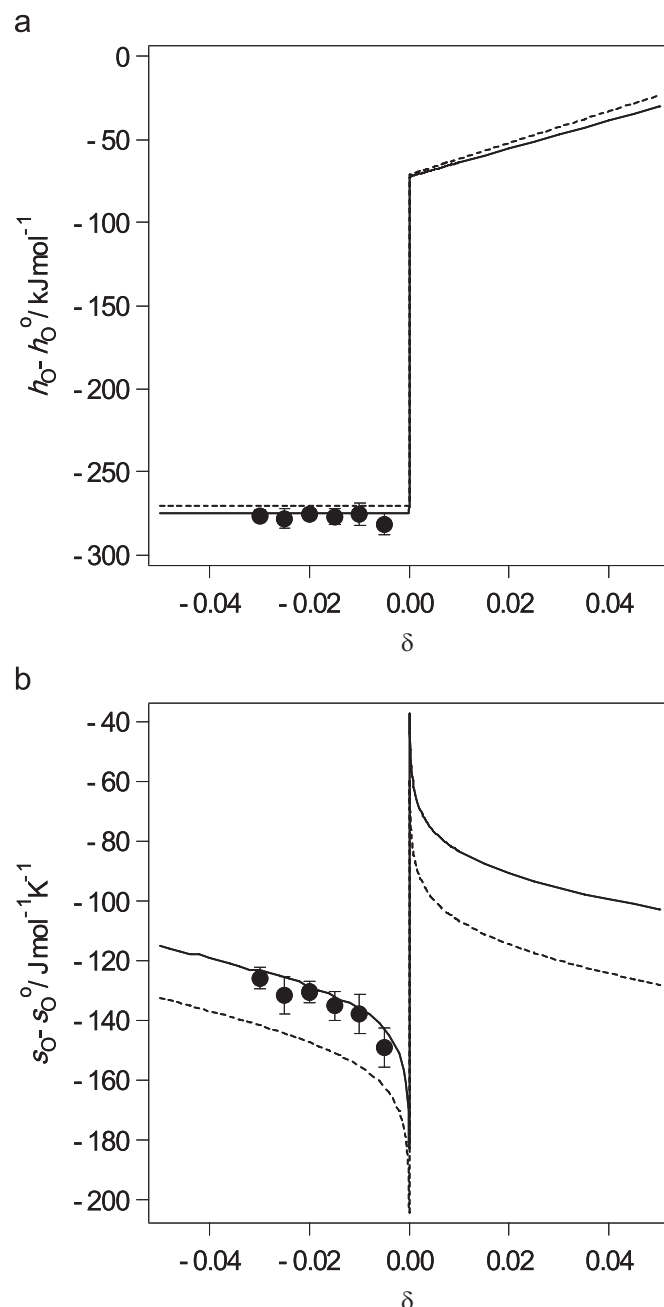
Figs. 4–8 show the partial molar quantities of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  obtained from  $\delta$ - $P(\text{O}_2)$ - $T$  relation and those calculated from

statistical thermodynamic models. Statistical thermodynamic models proposed here can quantitatively explain the dependence of  $h_{\text{O}} - h_{\text{O}}^{\circ}$  on  $\delta$ . In the case of  $s_{\text{O}} - s_{\text{O}}^{\circ}$ , localized electron model show better agreement than the delocalized electron model. Calculated results of delocalized electron model are smaller than  $s_{\text{O}} - s_{\text{O}}^{\circ}$  obtained from the nonstoichiometric data. Goodenough et al. suggested the coexistence of localized and itinerant electron in  $\text{La}_2\text{NiO}_{4+\delta}$  [16,17]. The contribution of the coexistent state of electron is not considered in this study. This may cause the deviation between calculated results and  $s_{\text{O}} - s_{\text{O}}^{\circ}$  obtained from the  $T$ - $\delta$ - $P(\text{O}_2)$  relationship.

The relationship between the thermodynamic quantities, the defect structure, and the defect equilibrium of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is clearly shown by using the statistical thermodynamic models and defect equilibrium models. As shown in our pervious and this

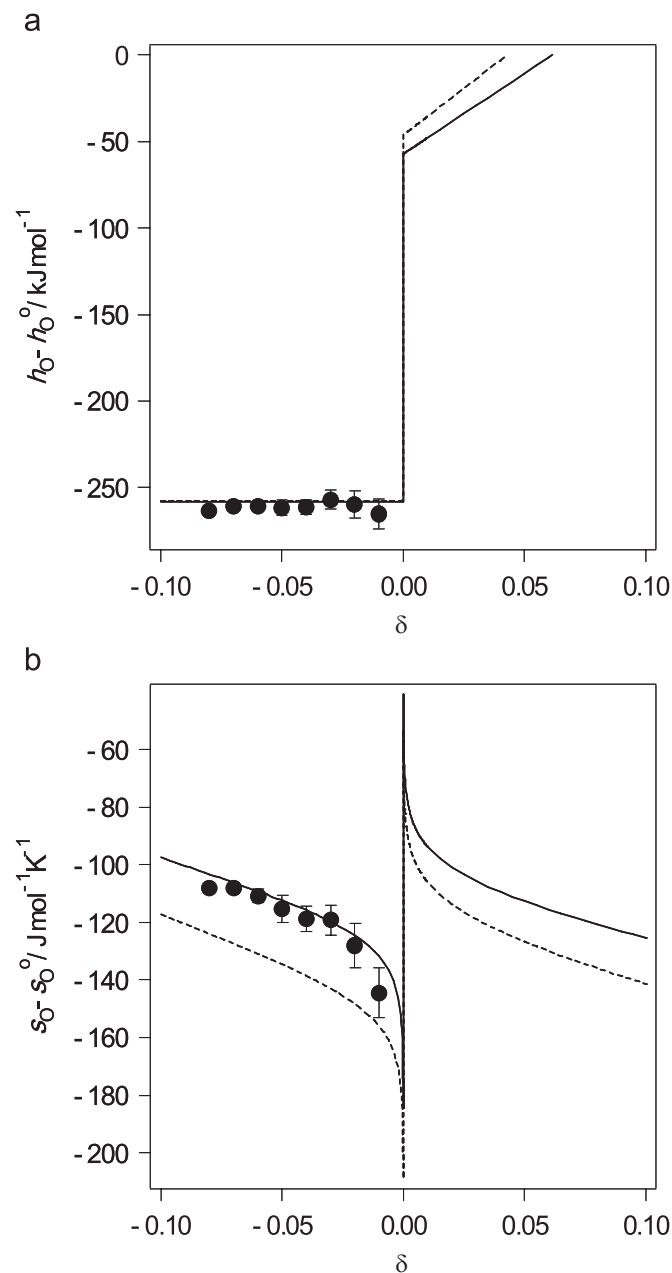


**Fig. 6.** Partial molar enthalpy and entropy of oxygen for  $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_{4+\delta}$ . Solid lines are calculated by Eqs. (37) and (38) (localized electron model) and dashed lines are calculated by Eqs. (46) and (47) (delocalized electron model).



**Fig. 7.** Partial molar enthalpy and entropy of oxygen for  $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_{4+\delta}$ . Solid lines are calculated by Eqs. (37) and (38) (localized electron model) and dashed lines are calculated by Eqs. (46) and (47) (delocalized electron model).





**Fig. 8.** Partial molar enthalpy and entropy of oxygen for  $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_{4+\delta}$ . Solid lines are calculated by Eqs. (37) and (38) (localized electron model) and dashed lines are calculated by Eqs. (46) and (47) (delocalized electron model).

works, both localized electron model and delocalized electron model can explain thermodynamic quantities of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  as well as the oxygen nonstoichiometric behavior at temperature range between 873–1173 K. This means that the electronic state of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  cannot be determined from the defect chemical and the statistical thermodynamic analyses. So far, the electronic state of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is controversial. Goodenough et al. proposed the coexistent state of localized and itinerant electron [16,17]. The coexistence state is established by itinerant  $d_{x^2-y^2}$  electron occupying  $\sigma_{x^2-y^2}$  band and localized  $d_{z^2}$  electron. On the other hand, some researchers suggest that the conduction mechanism is small polaron or diffusive-type charge transport [20–23]. In both cases, the hypothesis is derived mainly from the qualitative discussion. Further investigations are needed to

understand the electronic state and the conduction mechanism of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ .

## 6. Conclusions

Statistical thermodynamic models are constructed based on the defect equilibrium models, localized electron model and delocalized electron model. The relationship between thermodynamic quantities and the defect equilibrium in  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  is well expressed through the Gibbs free energy change of the equilibrium among defect species. Calculated results by the statistical thermodynamic models are compared to partial molar enthalpy of oxygen and partial molar entropy of oxygen determined from  $\delta$ - $P(\text{O}_2)$ - $T$  relation of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ . No significant difference between the localized electron models and the delocalized electron model is confirmed. Thermodynamic quantities calculated by the statistical thermodynamic model show good agreement with those determined from the oxygen nonstoichiometric data.

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