Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental information

for

“*Ab initio* and Empirical Defect Modeling of $LaMnO_{3\pm\delta}$ for Solid Oxide Fuel Cell Cathodes”

Yueh-Lin Lee[1] and Dane Morgan[1]

[1] Department of Materials Science and Engineering, University of Wisconsin–Madison,
Madison, Wisconsin 53706,

E-mail: ddmorgan@wisc.edu

I. Static Calculations of Normalized E(C_{defect}) vs. C_{defect} Using Ideal (Non-distorted) Perovskite Supercells

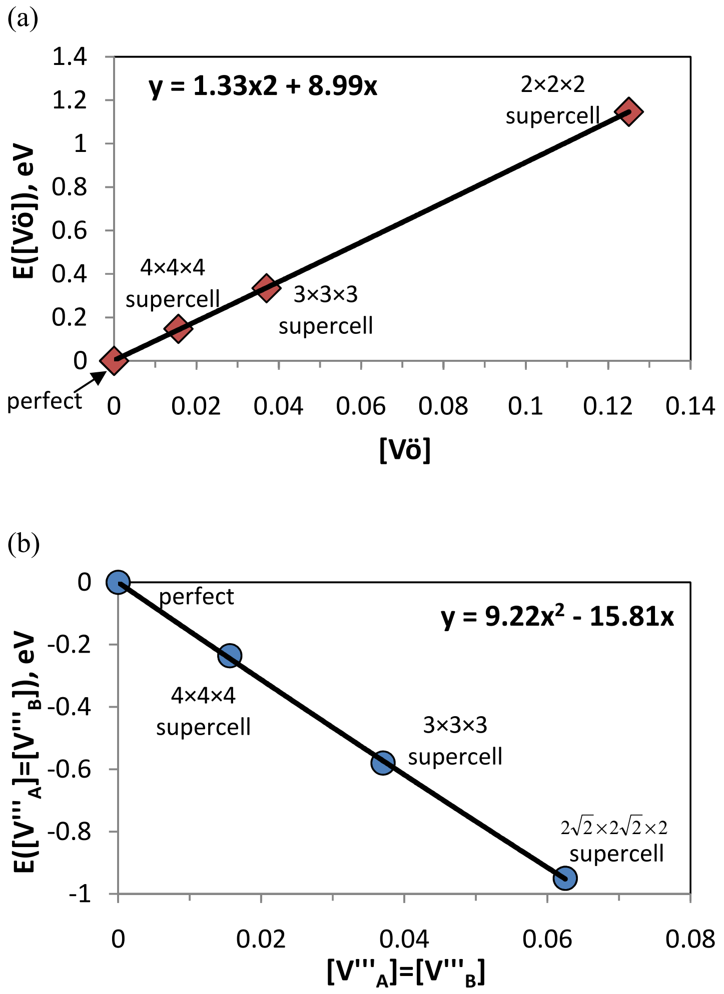

Figure S1. Quadratic fittings of *ab initio* total energies (normalized as per Mn and referenced to the perfect bulk) vs. defect concentration obtained from static calculations using ideal (non-distorted) perovskite supercells without relaxation with various supercell sizes for (a) oxygen vacancy formation reaction (*i.e.* Eqn. (1) of the main article) and (b) cation vacancy formation reaction (*i.e.* Eqn. (2) of the main article).

Following Eqn. (9) of the main article these calculations yield $I_{red} = 2.66$, $I_{ox} = 18.44$ for the unrelaxed cells, quite close to the values from the fully relaxed cells (Table 2 of the main article).

II. Method for Solving the LaMnO$_{3\pm\delta}$ Defect Model

The following describes the sequential approach for solving the LaMnO$_{3\pm\delta}$ model adapted from Poulsen's work[1].

1. Variables and equations to be solved in the LMO defect model

Based on site and mass balance, the defect species in LMO can be reduced to four independent variables. It is noted that the assumed cation vacancy formation reaction does not allow different A-site and B site concentration. One can further refine the model by splitting the cation vacancy formation reaction into separate oxide precipitation reactions such as formation of La and Mn binary oxides. Here, we use

the combined cation vacancy formation reaction as an approximation and fix the La/Mn ratio to be 1. The four independent variable we will use are shown in Table 3 of the main article and are $[V_A''']$, $[Mn_B^\bullet]$, $[Mn_B']$, and $[V_O^{\bullet\bullet}]$. These independent variables can be solved for by incorporating the constraints of 3 defect reactions and the principle of charge neutrality, as expressed by the following equations:

(a) Oxygen vacancy formation reaction:

$$K_{red} = \exp(-\frac{\Delta G_{red}^{*}}{k_b \cdot T}) = \exp(-\frac{\Delta\varepsilon_{red}([V_O^{\bullet\bullet}]) + \Delta G_{red}^{vib}(T)}{k_b \cdot T})$$
$$= \exp(-\frac{(E_{red} + I_{red} \cdot [V_O^{\bullet\bullet}]) + \Delta G_{red}^{vib}(T)}{k_b \cdot T}) = \frac{[Mn_B']^2 \cdot [V_O^{\bullet\bullet}] \cdot P(O_2)^{1/2}}{[Mn_B^x]^2 \cdot [O_O^x]} \quad \text{........(S.1)}$$

(b) Cation vacancy formation reaction:

$$K_{ox} = \exp(-\frac{\Delta G_{ox}^{*}}{k_b \cdot T}) = \exp(-\frac{\Delta\varepsilon_{ox}([V_A'''] + [V_B''']) + \Delta G_{ox}^{vib}(T)}{k_b \cdot T})$$
$$= \exp(-\frac{E_{Ox} + I_{Ox} \cdot ([V_A'''] + [V_B''']) + \Delta G_{ox}^{vib}(T)}{k_b \cdot T}) = \frac{[Mn_B^\bullet]^6 \cdot [V_A'''] \cdot [V_B'''] \cdot [O_O^x]^3}{[Mn_B^x]^6 \cdot P(O_2)^{3/2}} \quad \text{...(S.2)}$$

(c) Charge disproportionation reaction:

The equilibrium constant of the charge disproportion reaction (Eqn.(3)) can be expressed as:

$$K_{chg\_disp} = \exp(-\frac{\Delta G^{*}_{chg\_disp}}{k_b \cdot T}) = \exp(-\frac{\Delta \varepsilon_{chg\_disp}}{k_b \cdot T}) = \frac{[Mn_B^{\bullet}]\cdot[Mn_B^{'}]}{[Mn_B^{x}]^2} \text{........(S .3)}$$

all term in the above equations (Eqns. (S.1) - (S.3)) have been defined in the main article.

(d) Charge neutrality:

$$3\cdot[V_A^{'''}]+3\cdot[V_B^{'''}]+[Mn_B^{'}]+[Sr_A']=2\cdot[V_O^{\bullet\bullet}]+[Mn_B^{\bullet}] \text{ .... (S.4)}$$

For undoped LMO, $[Sr_A']$ is set as 0.

2. Sequential approach to solve the coupled nonlinear equations

Following Poulsen's sequential approach[1], a series of physically possible $[V_O^{\bullet\bullet}]$ values are set to solve for the variables of $[V_A^{'''}]$, $[Mn_B^{\bullet}]$, and $[Mn_B']$ along with the corresponding P(O_2). The first nonlinear equation to be solved as in Poulsen's LMO defect model[1] is via the constraint of the equilibrium constant of the Schottky reaction, which can be obtained from linear combination of the assumed defect reactions (*i.e.*, Schottky reaction = 3×Eqn.(1) + Eqn.(2) – 6×Eqn.(3), where Eqns. (1)~(3) have been defined in the main article, i.e. Eqn.(1) = Oxygen vacancy formation reaction: $2\cdot Mn_B^x + O_O^x \leftrightarrow 2\cdot Mn_B' + V_O^{\bullet\bullet} + \frac{1}{2}\cdot O_2(gas)$; Eqn.(2) = Cation vacancy formation reaction: $6\cdot Mn_B^x + \frac{3}{2}O_2(gas) \leftrightarrow 6\cdot Mn_B^{\bullet} + V_A^{'''} + V_B^{'''} + 3\cdot O_O^x$; Eqn.(3) = Charge disproportionation reaction: $2\cdot Mn_B^x \leftrightarrow Mn_B^{\bullet} + Mn_B'$). Therefore, the constraint of Schottky reaction with its equilibrium constant can be written as:

$$K_{Schottky} = \frac{(K_{red})^3\cdot K_{ox}}{(K_{chg\_disp})^6} = [V_A^{'''}]\cdot[V_B^{'''}]\cdot[V_O^{\bullet\bullet}]^3 \text{ .... (S.5)}$$

Since the cation vacancy formation reaction does not allow varying A/B ratio, with a given $[V_O^{\bullet\bullet}]$ and applying the inherent constraint of $[V_A^{'''}]=[V_B^{'''}]$, Eqn. (S.5) can be rearranged as:

$$\frac{(K_{red})^3\cdot K_{ox}}{(K_{chg\_disp})^6}=[V_A^{'''}]^2\cdot[V_O^{\bullet\bullet}]^3=\frac{(K_{red})^3}{(K_{chg\_disp})^6\cdot[V_O^{\bullet\bullet}]^3}\cdot K_{ox}=[V_A^{'''}]^2\Rightarrow$$

$$\Rightarrow\frac{(K_{red})^3}{(K_{chg\_disp})^6\cdot[V_O^{\bullet\bullet}]^3}\cdot\exp\left(\frac{\left\{\begin{array}{l}-E_{Ox}-I_{Ox}\cdot 2\cdot[V_A^{'''}]\\+3\cdot\left[\begin{array}{l}\frac{1}{2}(H_{O_2}^{NIST}-T\cdot S_{O_2}^{NIST})\\-(G_{vib}(O_{solid}^{2-})-H_{vib}^{0}(O_{solid}^{2-}))\end{array}\right]\end{array}\right\}}{k_b\cdot T}\right)=[V_A^{'''}]^2$$

$$\Rightarrow\alpha=[V_A^{'''}]^2\exp(2\cdot\beta\cdot[V_A^{'''}])=\left\{[V_A^{'''}]\cdot\exp(\beta\cdot[V_A^{'''}])\right\}^2\text{............}(S.6)$$

where

$$\alpha=\left\{\frac{(K_{red})^3}{(K_{chg\_disp})^6\cdot[V_O^{\bullet\bullet}]^3}\cdot\exp\left(\frac{-E_{Ox}+3\cdot\left[\begin{array}{l}\frac{1}{2}(H_{O_2}^{NIST}-T\cdot S_{O_2}^{NIST})\\-(G_{vib}(O_{solid}^{2-})-H_{vib}^{0}(O_{solid}^{2-}))\end{array}\right]}{k_b\cdot T}\right)\right\}\text{.............}(S.7)$$

and $\beta=\dfrac{I_{Ox}}{k_b\cdot T}$.

The value of α at a given T and $[V_O^{\bullet\bullet}]$ can be directly calculated using the values of K_{red} and K_{chg_disp} from Eqn. (S.1) and Eqn. (S.3) along with the derivation of $\Delta G^{*}_{defect\ \ form}(c_{defect},T)$ discussed in the main article. Taking the positive square root of Eqn. (S.4) for the solution of positive concentration, the equation is then in the form of Lambert W function ($z=W(z)\cdot\exp(W(z))$)^2:

$$\alpha^{1/2}=\frac{1}{\beta}\{\beta\cdot[V_A^{'''}]\cdot\exp(\beta\cdot[V_A^{'''}])\}\Rightarrow\alpha^{1/2}\cdot\beta=(\beta\cdot[V_A^{'''}])\cdot\exp(\beta\cdot[V_A^{'''}])\quad\text{........}(S.7)$$

where $z = \alpha^{1/2} \cdot \beta$ and $W(z) = \beta \cdot [V_A''']$. Therefore, the solution for $[V_A''']$ is:

$$[V_A'''] = \frac{1}{\beta} \cdot W_0(\alpha^{1/2} \cdot \beta)\text{........(S.8)}$$

where W_0 is the *0th* branch of the Lambert *W* function, which must be used to give a real number solution (instead of the complex solutions associated with other branches).

With the derivation of the solution for $[V_A''']$, one can then follow the procedures in Poulsen's work[1] (mainly Eqn. (15) – Eqn.(17) in Ref. 1) to obtain the other two independent variables, $[Mn_B^{\bullet}]$ and $[Mn_B']$, and then further extract the complete solution, including the corresponding $P(O_2)$.

III. Refitted $LaMnO_3$ Nonstoichiometry vs. P(O_2) with Adjusted Defect Energetics

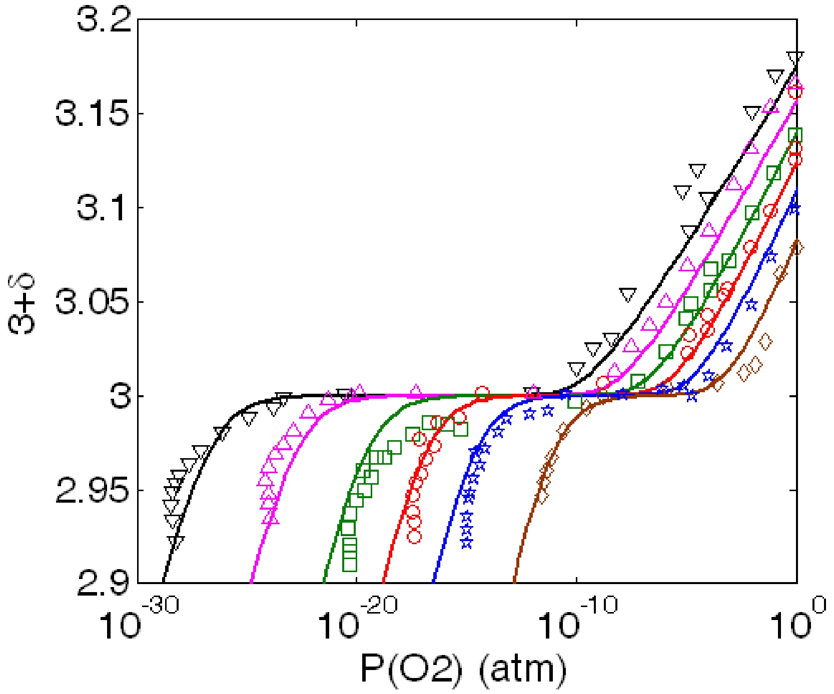

Figure S2. $LaMnO_3$ oxygen nonstoichiometry vs. P(O_2) based on the defect model in this work with the *ab initio* defect energetics (solid lines) the same as shown in Table 2 of the main article except for the value I_{red}, which is adjusted from 2.54 eV to 0.8 eV for fitting to the experimental data (the same data as in Fig. 6 and Fig. 10 of the main article).

References

1. F. W. Poulsen, *Solid State Ionics*, 2000, **129**, 145-162.
2. R. M. Corless, G. H. Gonnet, D. E. G. Hare, D. J. Jeffrey and D. E. Knuth, *Adv. Comput. Math.*, 1996, **5**, 329-359.