Mechanism for the enhancement of the oxygen diffusivity by cation substitution in La$_{2-x}$Sr$_x$CuO$_4$

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Derivation of $P(\alpha, t)$

We assume there are n hopping paths and per unit attempt time δt, there is probability p_α for a vacancy to hop to paths α. If the hopping to each path is independent, the probability $P(k)$ that the first hopping happens at the k-th trial follows the geometric distribution

$$P(k) = \Big(\prod_{\alpha=1}^{n}(1 - p_\alpha)\Big)^{(k-1)}\Big(1 - \prod_{\alpha=1}^{n}(1 - p_\alpha)\Big). \tag{1}$$

Equation (1) does not exclude the probability that more than one hopping occurs during a single try, which is clearly unphysical. To avoid this problem, we extend the domain of P from integer variable k to continuous variable t and defines $\frac{p_\alpha}{\delta t} \equiv \overline{p_\alpha}$. By $\delta t \to 0$, we can make the probability of unphysical simultaneous hopping during δt approaches zero. The probability $P(t)$ that the first hopping happens at time t now becomes

$$P(t) = N\Big(\prod_{\alpha=1}^{n}(1 - \overline{p_\alpha}\delta t)\Big)^{\frac{t}{\delta t} - 1}\Big(1 - \prod_{\alpha=1}^{n}(1 - \overline{p_\alpha}\delta t)\Big), \tag{2}$$

where

$$N = \frac{\log\Big(\prod_{\alpha=1}^{n}(1 - \overline{p_\alpha}\delta t)\Big)}{\Big(\prod_{\alpha=1}^{n}(1 - \overline{p_\alpha}\delta t) - 1\Big)\delta t} \tag{3}$$

is a normalization factor for $P(t)$ to satisfy $\int_{\delta t}^{\infty} P(t)\, dt = 1$. By taking a limit $\delta t \to 0$, we can obtain Eq. (2) of main manuscript. Because each hopping is independent, the joint probability $P(\alpha, t)$ is simply the probability p_α-weighted partition of $P(t)$ and Eq. (1) of main manuscript holds.

Equilibrium concentrations of charge states of oxygen vacancies

The equilibrium concentrations of each charge states of oxygen vacancy can be derived from the following four relations.

$$k_1[\mathrm{V_O}][\mathrm{h}^\bullet] = k_1'[\mathrm{V_O^\bullet}] \tag{4}$$

$$k_2[\mathrm{V_O^\bullet}][\mathrm{h^\bullet}] = k_2'[\mathrm{V_O^{\bullet\bullet}}] \tag{5}$$

$$[\mathrm{V_O}] + [\mathrm{V_O^\bullet}] + [\mathrm{V_O^{\bullet\bullet}}] = [\mathrm{V_O^{tot}}] \tag{6}$$

$$[\mathrm{h^\bullet}] + [\mathrm{V_O^\bullet}] + 2[\mathrm{V_O^{\bullet\bullet}}] = [\mathrm{Sr}], \tag{7}$$

where $k_i(i = 1, 2)$ are the reaction rate constants of Eq. (5) given by

$$\frac{k_{1(2)}}{k_{1(2)}'} = \exp\left(-\frac{\Delta E_{1(2)}}{k_B T}\right). \tag{8}$$

Equations (6) and (7) are the conservation relations of oxygen vacancies and charge, respectively. For given $[\mathrm{V_O^{tot}}]$ and $[\mathrm{Sr}]$, $[\mathrm{V_O}]$, $[\mathrm{V_O^\bullet}]$, $[\mathrm{V_O^{\bullet\bullet}}]$, and $[\mathrm{h^\bullet}]$ can be obtained by solving a cubic equation derived from the four equations above. Due to the large reaction energy ΔE_1 and ΔE_2, $[\mathrm{h^\bullet}]$ is much smaller than the concentrations of oxygen vacancies, and in this case, we can express the vacancy concentrations in terms of $[\mathrm{Sr}]/[\mathrm{V_O^{tot}}]$.