Supplementary information for

Oxygen surface exchange kinetics of $SrTi_{1-x}Fe_xO_{3-\delta}$ mixed conducting oxides

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S1 Theory of oxygen isotopic exchange

In this supplementary information, the theory of oxygen isotopic exchange on solid oxides is presented. The equations provided are adapted to conditions encountered in the ^{18}O-^{16}O pulse isotopic exchange (PIE) experiments, thereby following the more general treatment given earlier by den Otter et $al..$[1]

The PIE experiments are supposed to be carried out under isothermal and iso-pO_2 conditions, and under conditions that negligible accumulation of ^{18}O occurs at the oxide surface. The latter implies that the exchange time must be smaller than the time constant $\tau = D^* / k_s^2$, where D^* is the oxygen tracer diffusivity, and k_s the surface exchange coefficient. The latter is calculated from $k_s = \Re_0 / c_o$, where $\Re_0$ is the rate of oxygen exchange, and c_o the concentration of oxide ions in the solid oxide. The time constant τ dictates how fast ^{18}O piles up at the surface.[2] In the PIE experiments, the actual exchange time corresponds to the duration of a pulse. The number of ^{18}O atoms in the gas phase pulse is maintained substantially smaller than the number of oxide ions in the oxide, preventing significant accumulation of ^{18}O in the oxide.

The expectation values to find ^{18}O-labeled oxygen in the O_2 molecule after an exchange act are

$$\begin{aligned}
\alpha_1 &= p_1 f_b^* + (1 - p_1) f_g^* \\
\alpha_2 &= p_2 f_b^* + (1 - p_2) f_g^*
\end{aligned} \tag{S.1}$$

where p_1 and p_2 designate the probabilities of both atoms for exchange with lattice oxygen, and f_g^* and f_b^* are the ^{18}O-fractions in the gas phase and oxide, respectively. The differential equations describing the time dependence of x, y, and z, denoting the gas phase fractions of $^{36}O_2$, $^{34}O_2$, and $^{32}O_2$, respectively, in a volume element, traversing through the reactor can be written as

$$\begin{aligned}
n \cdot \frac{\partial x}{\partial t} &= S \cdot \Re_a \left[-x + (\alpha_1 \cdot \alpha_2) \right] \\
n \cdot \frac{\partial y}{\partial t} &= S \cdot \Re_a \left[-y + (\alpha_1 (1 - \alpha_2) + \alpha_2 (1 - \alpha_1)) \right] \\
n \cdot \frac{\partial z}{\partial t} &= S \cdot \Re_a \left[-z + ((1 - \alpha_1)(1 - \alpha_2)) \right]
\end{aligned} \tag{S.2}$$

where n (mol O) denotes the number of O atoms in the gas phase of a volume element (which is twice the number of O_2 molecules), $\Re_a$ (mol O m^{-2} s^{-1}) the rate of adsorption, and S the oxide surface area. Quantities n and S are normalized over the entire volume of the reactor. Since in the PIE experiments, $f_b^* \approx 0$, eqn (S.2) can be rewritten as

[1] M. W. den Otter, B. A. Boukamp and H. J. M. Bouwmeester, *Solid State Ionics*, 2001, **139**, 89.
[2] P. Fielitz and G. Borchardt, *Solid State Ionics*, 2001, **144**, 71.

$$n \cdot \frac{\partial x}{\partial t} = S \cdot \Re_a \left[-x + f_g^{*2} \cdot (1 - p_1)(1 - p_2) \right]$$

$$n \cdot \frac{\partial y}{\partial t} = S \cdot \Re_a \left[-y + f_g^{*2} \cdot \left((1 - p_1) p_2 + p_1 (1 - p_2) \right) \right] \qquad \text{(S.3)}$$

$$n \cdot \frac{\partial z}{\partial t} = S \cdot \Re_a \left[-z + f_g^{*2} \cdot (p_1 p_2) \right]$$

The ^{18}O-fraction in the gas phase can be calculated from

$$f_g^* = x + \frac{1}{2} y \qquad \text{(S.4)}$$

Hence, its time dependence follows from the first order linear differential equation,

$$n \cdot \frac{\partial f_g^*}{\partial t} = -S \cdot \left(\frac{1}{2} (p_1 + p_2) \cdot \Re_a \right) \cdot f_g^* \qquad \text{(S.5)}$$

which is in accord with McKay's law for isotopic exchange reactions.[3] Integration with respect to time yields

$$f_g^*(t) = f_{g,i}^* \cdot exp\left(-\frac{t}{\tau_0} \right) \qquad \text{(S.6)}$$

where

$$\tau_0 = \frac{n}{\Re_0 S} \qquad \text{(S.7)}$$

Hence, the overall ^{18}O-^{16}O exchange rate $\Re_0$ is given by

$$\Re_0 = \frac{1}{2} (p_1 + p_2) \cdot \Re_a \qquad \text{(S.8)}$$

eqn (S.6) is equivalent to eqn (1) for $t = \tau_r$, where τ_r is the time of residence in the reactor.

So far the two oxygen atoms in the gaseous O_2 molecule are considered to have independent probabilities (p_1, p_2) for exchange with lattice oxygen, *i.e.*, not determined by the pathway for oxygen exchange. In the isotopic exchange theory developed by Klier *et al.*,[4] and independently by Boreskov and Muzykantov,[5] the exchange is described by three parallel one-step mechanisms. In the theory developed by these authors, it is conceived that the O_2 molecule may exchange either one or both atoms with lattice oxygen (referred to as hetero exchange) at a rate R^1 and R^2 respectively, or, without

[3] H. A. C. McKay, *Nature*, 1938, **142**, 997.
[4] K. Klier, J. Nováková and P. Jíru, *J. Catal.*, 1963, **2**, 479.
[5] G. Boreskov and V. Muzykantov, *Ann. Ny. Acad. Sci.*, 1973, **213**, 137.

the involvement of lattice oxygen, *i.e.*, only with oxygen atoms from the gas phase (referred to as homo exchange), at a rate R^0. The stochastic theory developed by the above cited authors is mathematically consistent with the present theory. Its relationship becomes more clear if we write the rates associated with each of the one-step mechanisms as

$$
\begin{aligned}
R^0 &= \mathfrak{R}_a \left[(1-p_1) \cdot (1-p_2) \right] \\
R^1 &= \mathfrak{R}_a \left[p_1 (1-p_2) + (1-p_1) p_2 \right] \\
R^2 &= \mathfrak{R}_a \left[p_1 p_2 \right]
\end{aligned}
\tag{S.9}
$$

noting that

$$
\mathfrak{R}_a = R^0 + R^1 + R^2
\tag{S.10}
$$

When $(p_1, p_2) = (0,0)$, $(p_1, p_2) = (1,0)$ or $(0,1)$, or $(p_1, p_2) = (1,1)$, either mechanism R^0, R^1 or R^2 occurs exclusively. When both p_1 and p_2 depart from 0 or 1, all three one-step mechanisms will occur simultaneously. The charm of the theory developed by den Otter *et al.*,[1] in which the parameter set $(\mathfrak{R}_a, p_1, p_2)$ is used, rather than (R^0, R^1, R^2), is that mechanistic models for the oxygen isotopic exchange are easily implemented.

In the following, we exclude *i)* mutual exchange of oxygen between O_2 molecules in the gas phase, and *ii)* possible swapping out of one of the oxygen atoms of the O_2 molecule for another oxygen during hypothetical formation of a three-atom complex between a gas phase O_2 molecule and an adsorbed O adatom, or of any other multi-atom complex between O_2 molecules and adsorbed species. Analysis of the mechanistic pathways, and associated statistics, shows that the exchange of oxygen between the gas phase and oxide can be described to proceed via two reversible two-step mechanisms, following dissociative adsorption of oxygen.

In the first of these mechanisms, both O-adatoms, O_{ad}, formed after homolytic dissociative adsorption of O_2, have equal probability (*i.e.*, $p_1 = p_2 = p$) to be converted into lattice oxygen,

$$
O_2^* \underset{\overrightarrow{\mathfrak{R}_a}}{\overset{\overleftarrow{\mathfrak{R}_a}}{\rightleftharpoons}} 2O_{ad}^*
$$

$$
O_{ad}^* \underset{\overrightarrow{\mathfrak{R}_i}}{\overset{\overleftarrow{\mathfrak{R}_i}}{\rightleftharpoons}} O_{lattice}
\tag{4}
$$

The incorporation of O_{ad} into the oxide lattice is bounded by rates $\mathfrak{R}_a$ and $\mathfrak{R}_i$. It is easily verified that

$$
\mathfrak{R}_0 = \mathfrak{R}_a \cdot p = \frac{\mathfrak{R}_a \mathfrak{R}_i}{\mathfrak{R}_a + \mathfrak{R}_i}
\tag{S.11}
$$

and, by substitution of $p_1 = p_2 = p$ into eqn (S.9),
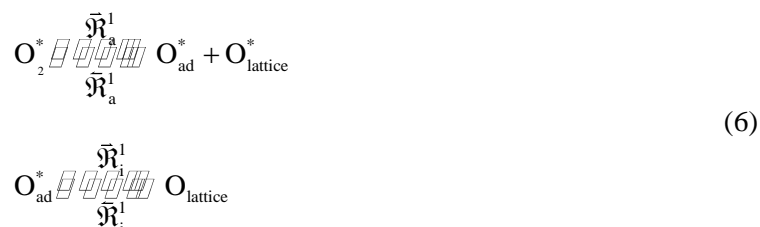
$$
\begin{aligned}
R^0 &= \mathfrak{R}_a \cdot (1-p)^2 \\
R^1 &= \mathfrak{R}_a \cdot 2p(1-p) \\
R^2 &= \mathfrak{R}_a \cdot p^2
\end{aligned}
\tag{S.12}
$$

It follows that by adopting scheme (4) as the mechanism for isotopic exchange, the rates R_0, R_1, and R_2 are subject to constraint $R^1 = \sqrt{4R^0 R^2}$. Substitution of eqn (S.6) in eqn (S.3), followed by integration over the time of residence yields

$$
x = \left(\frac{(1-p)}{(1-2p)^{\frac{1}{2}}} \cdot f^*_{g,i} \right)^2 \cdot \exp(-\frac{t}{\tau_0}) + \left(x_i - \left(\frac{(1-p)}{(1-2p)^{\frac{1}{2}}} \cdot f^*_{g,i} \right)^2 \right) \cdot \exp(-\frac{t}{p\tau_0})
\tag{S.13}
$$

where $x_i = x(0)$ denotes the fraction x in the inlet pulse. Eqn (S.13) can be used to calculate p from the value of x in the pulse at the exit of the reactor. Explicit expressions for y and z follow from the use of equations (S.4) and $x + y + z = 1$.

In the second of these mechanisms, one oxygen atom is immediately incorporated ($p_1 = 1$) upon adsorption, the other is an oxygen adatom, O_{ad}, migrating over the surface until it either recombines with lattice oxygen and desorbs as an oxygen molecule or is incorporated (with probability $p_2 = p'$) into the oxide lattice,

$$
\begin{aligned}
O_2^* &\; \underset{\tilde{\mathfrak{R}}_a^1}{\overset{\bar{\mathfrak{R}}_a^1}{\rightleftharpoons}} \; O_{ad}^* + O_{lattice}^* \\[2mm]
O_{ad}^* &\; \underset{\tilde{\mathfrak{R}}_i^1}{\overset{\bar{\mathfrak{R}}_i^1}{\rightleftharpoons}} \; O_{lattice}
\end{aligned}
\tag{6}
$$

where the superscripts in $\mathfrak{R}_a^1$ and $\mathfrak{R}_i^1$ have been adapted (to designate that in this model one oxygen atom is immediately incorporated upon adsorption). It follows that

$$
\mathfrak{R}_0 = \frac{1}{2}\mathfrak{R}_a^1 \cdot (1+p') = \frac{1}{2}\mathfrak{R}_a^1 \cdot \left(1 + \frac{\mathfrak{R}_i^1}{\frac{1}{2}\mathfrak{R}_a^1 + \mathfrak{R}_i^1} \right)
\tag{S.14}
$$

and, by substitution of $p_1 = 1; p_2 = p$ into eqn (S.9),

$$R^0 = 0$$
$$R^1 = \mathfrak{R}_a^1 \cdot p'$$
$$R^2 = \mathfrak{R}_a^1 \cdot \left(1 - p'\right)$$

(S.15)

Making the appropriate substitutions, one may derive from eqn (S.3),

$$x = x_i \cdot \exp\left(-\frac{2}{(1+p')} \cdot \frac{t}{\tau_0}\right)$$

(S.16)

which can be used to evaluate p' from the fraction x in the exit pulse. Both mechanisms (4) and (6) converge into a one-step R^2-mechanism if both oxygen atoms in the O_2 molecule have a probability of unity for incorporation into the oxide lattice. It is further noted that both steps in schemes (4) and (6) may involve a consecutive set of elementary reactions. Finally, it is stressed that PIE measurements alone cannot discriminate between the validity of two-step schemes (4) and (6). To this end, the isotopic equilibration between gas phase and oxide needs to be monitored as a function of time. Proper account needs to be taken in such experiments when the isotopic equilibration is partly governed by diffusion of ^{18}O in the oxide.[6]

S2 Data for alternative two-step exchange mechanism

Table S1 Power law exponents of the pO_2 dependencies of the rates of oxygen dissociative adsorption ($\mathfrak{R}_a^1$), and oxygen incorporation ($\mathfrak{R}_i^1$) for STO, STF35, and STF50 at different temperatures. Values for $\mathfrak{R}_a^1$ and $\mathfrak{R}_i^1$ were calculated on the basis of two-step exchange scheme (6) for modeling the data from PIE measurements. Standard errors are given in parentheses and refer to the least significant decimals.

	$T\,(^{\circ}C)$	$\mathfrak{R}_a^1$	$\mathfrak{R}_i^1$
STO	900	0.65 (8)	-
STF35	350	0.72 (9)	-0.29 (3)
	400	0.66 (6)	-0.84 (6)
STF50	400	0.8 (1)	0.1 (2)
	450	0.8 (1)	-0.2 (2)

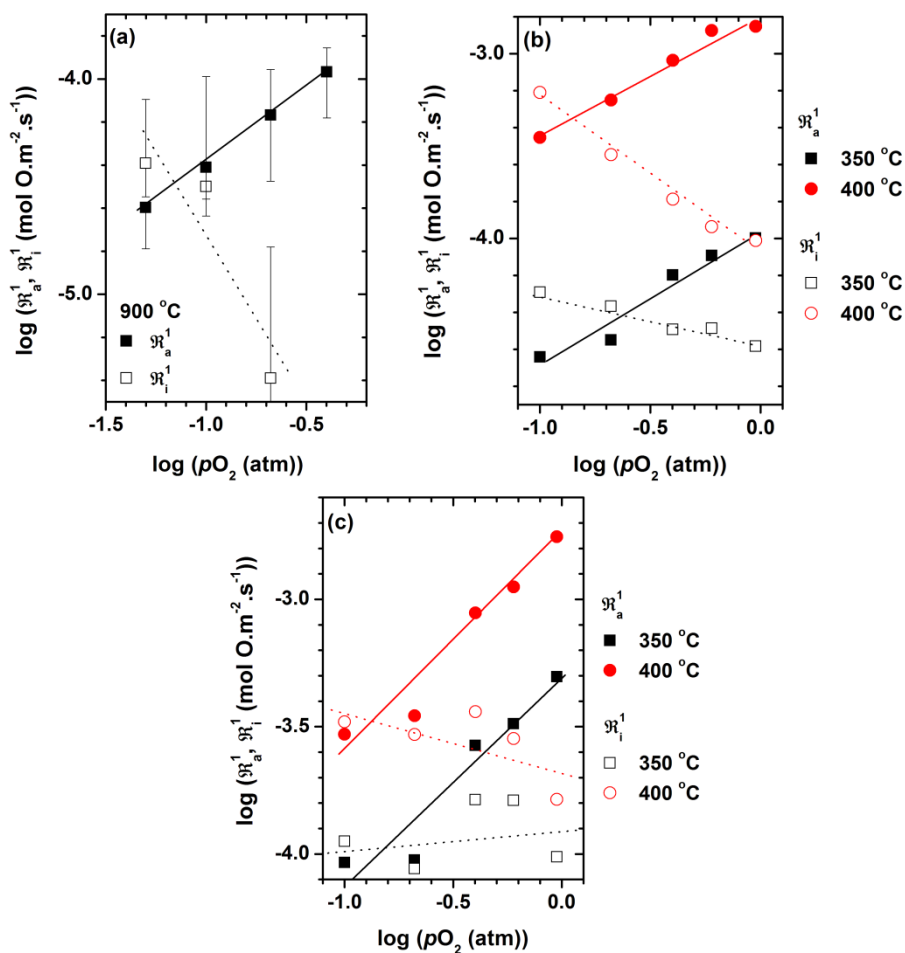[6] K. Klier and E. Kucera, *J. Phys. Chem. Solids*, 1966, **27**, 1087.

Figure S1 Oxygen partial pressure dependence of the rates of oxygen dissociative adsorption ($\mathfrak{R}_a^1$) and oxygen incorporation ($\mathfrak{R}_i^1$) rate for selected $SrTi_{1-x}Fe_xO_{3-\delta}$ compositions: (a) STO, (b) STF35, and (c) STF50. Calculations were performed on the basis of two-step exchange scheme (6) for modeling the data from PIE measurements. See main text.