Supporting information

Nonstoichiometric oxides as a continuous homologous series: linear free-energy relationship in oxygen exchange

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Appendix 1

The equilibrium exchange rate $\Re_0$ can be considered in terms of the transition state theory as

$$\Re_0 = k_0 \prod_i \alpha_i^{n_i} \exp\left(-\frac{G_{\mathrm{TS}}^0(\delta) - G_{\mathrm{r}}^0(\delta)}{RT} \right) \tag{S.1}$$

where α_i and n_i are activities and reaction orders of the rds reactants, k_0 is the rate of transformation of the transition state to the reaction products (usually proportional to kT/h), $G_{\mathrm{TS}}^0(\delta)$ and $G_{\mathrm{r}}^0(\delta)$ are standard Gibbs energies for the transition state and for the system of reactants in their ground states. The formulation given by eq S.1 assumes that a specific direction of the reaction is considered – the forward or the reverse (oxidation or reduction). The components in eq S.1 and their values will indeed depend on the direction selected. At the same time, as the equilibrium is considered, the resulting value of $\Re_0$ is independent of the reaction direction by the definition. Additionally, as the equilibrium state of an oxide having certain oxygen non-stoichiometry δ (the state of a δ-homologue) is fully defined by the pair of parameters δ and T (or equivalently by pO_2 and T), the dependence $\Re_0(\delta, T)$ (or $\Re_0(pO_2, T)$) does not depend on the selected reaction direction as well. It can be said more detailed that values of the mass action factor $\prod_i \alpha_i^{n_i}$ and standard Gibbs energies entering eq S.1 are unambiguous functions of (δ, T) or (pO_2, T) due to constraints caused by equilibrium, charge neutrality and conservation of crystallographic positions' ratios in the oxide phase.

The equation S.1 could be the way to determine Gibbs activation energy $G_{\mathrm{TS}}^0(\delta) - G_{\mathrm{r}}^0(\delta)$ but it would require knowledge of detailed mechanism of rds (that is the mass action product), which is unknown as a rule, and is rather a subject of study in most cases. A compromise could be the formal inclusion of the mass action coefficients into the activation factor of the reaction like the following

$$\Re_0 = k_0 \exp\left(-\frac{G^0_{\mathrm{TS}}(\delta) - G_{\mathrm{r}}(\delta)}{RT} \right), \tag{S.2}$$

with G_{r} to be Gibbs energy of the rds reactants' system at their current activities. This notation is totally independent of the selected reaction direction. This allows formulation of an apparent energetic value qualitatively analogues to Gibbs activation energy

$$\Delta G_a(\delta) = \Delta G^{\neq}(\delta) - RT\sum_i n_i \ln \alpha_i - RT \ln k_0 \tag{S.3}$$

The usage of such pseudo-activation energy instead of true Gibbs barrier given by $G^0_{\mathrm{TS}}(\delta) - G^0_{\mathrm{r}}(\delta)$ brings an advantage of easy analysis of possible LFER without knowledge of the detailed mechanism of rds. The term appearing in ΔG_a due to k_0 does not influence the desired LFER analysis as not contributing a dependence on δ (the same is true for any other possible constant coefficients of $\Re_0$, which may appear due to features of experimental techniques). A drawback is that BEP coefficient β in eq 2 obtained that way will contain additional contribution by the δ-parametric dependence of the mass action product in the equation S.1. This hindrance is not an insuperable one though as this additional contribution can be analyzed by providing and testing necessary hypotheses on the mechanism of rds. An example of a theoretic framework necessary for such analysis is suggested in [7].

Appendix 2

Experimental setup and theoretic background of the oxygen partial pressure relaxation technique

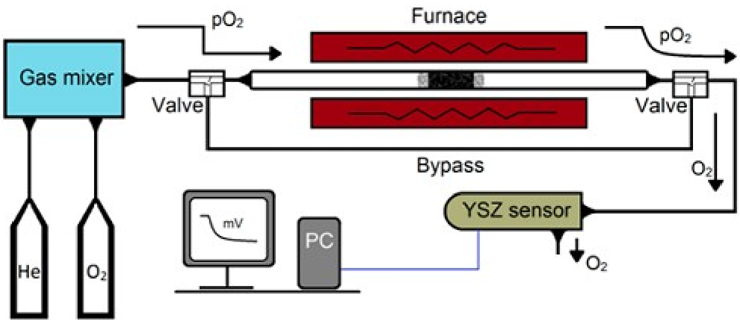


Figure 1S. Experimental installation for obtaining of the phase diagrams «*3-δ–log* pO_2 *-T*» by means of the quasi equilibrium oxygen release (QEOR) method and kinetic data by means of oxygen partial pressure r (OPPR) technique.

To accomplish the task of LFER analysis, we need to obtain two sets of data: equilibrium data (chemical potentials of δ-homologues) and kinetic data (relaxation data at different temperatures on oxygen exchange for oxide with a certain stoichiometry). Earlier [13, 15], we have developed an installation (Fig. 1S), which allows for continuous monitoring of pO_2 in continuous-flow fixed-bed reactor with MIEC oxide sample during the step-like change of oxygen partial pressure using YSZ oxygen sensor. The installation allowed obtaining both data sets [13, 32] while operating in different conditions. The installation is based on the CSTR type reactor made of quartz tube filled with quartz inserts in order to minimize the free volume V_r in which the oxide sample is placed. The section of the reactor tube including the gas line and the sample placement position is kept at regulated temperature. The gas switching/mixing equipment provides supplement of the reactor with the mixture of an inert sweep gas (usually He) with oxygen at regulated partial pressure. After holding the sample in the gas flow with a constant initial oxygen partial pressure (for a time necessary for the oxide stoichiometry equilibration) step like drop/rise (usually drop) of the oxygen partial pressure is triggered by the gas switching equipment. The drop/rise provokes the oxygen release/uptake from/on the oxide and corresponding change of the stoichiometry until the new equilibrium is reached with the lower/higher oxygen pressure. The process of relaxation is registered with the oxygen sensor installed in the gas line downstream to measure the dependence of pO_2 on time at the outlet of the reactor.

The evolution of pO_2 after the pressure drop/rise is defined by the mass balance equation describing the change of pO_2 in the reactor due to contributions provided by input and output gas flow $J_{\text{in/out}}$ and internal oxygen release/uptake by the oxide dQ/dt

$$W_r \frac{d\left(pO_2/p\right)}{dt} = J_{in}\left(pO_{2\text{in}}/p\right) - J_{out}\left(pO_2/p\right) - \frac{dQ}{dt} \tag{S.4}$$

W_r is is number of moles of gas in the free reaction volume at given temperature $V_r p/\left(RT\right)$, $pO_{2\text{in}}$ is the oxygen partial pressure in the input sweep gas flow, p is total gas pressure (1bar), Q is current number of oxygen moles in the oxide sample. The output sweep gas flow is defined by the overall mass balance $J_{\text{out}} = J_{in} - dQ/dt$. The solutions to the equation S.4 are used for analysis of $pO_2(t)$ dependencies obtained in two typical regimes of the setup (details of the solutions are described in [13, 14]). In the oxygen quasi-equilibrium release (QEOR) regime the input oxygen pressure is typically dropped from 1 bar to zero (oxygen flow is switched to He). Setting the gas flow to a sufficiently low level and using the sample with high specific surface area provide the conditions at which oxygen release from the oxide in the sample is able to restore pO_2 in the reactor's free volume to a value close to $pO_{2\mathrm{eq}}(Q)$ corresponding to equilibrium with the oxide with current oxygen stoichiometry. In this regime, the oxygen release rate dQ/dt is defined by oxygen removal from the reactor by the sweep gas flow. Thus, integration of the equation gives the approximation to $Q_{\mathrm{eq}}(t)$ dependence corresponding to the registered $pO_2(t)$

$$Q_{\mathrm{eq}}(t) = Q(0) + W_{\mathrm{r}} \ln\left(\frac{p - pO_2(t)}{p - pO_2(0)}\right) - J_{\mathrm{in}} \int_0^t \frac{pO_2(t')}{p - pO_2(t')} dt' \tag{S.5}$$

Recalculation of Q values to the oxygen non-stoichiometry parameter $3-\delta$ finally gives the equilibrium dependencies for "$\ln(pO_2)$–$3-\delta$–T" phase diagrams.

In the second regime, the oxygen partial pressure relaxation (OPPR), the oxygen partial pressure is dropped from the initial value corresponding to definite initial $3-\delta_i$ composition to the final value providing decrease of the stoichiometry by definite small $\Delta\delta \ll 1$ [13]. At this regime, high level of the sweep gas flow is used and the sample has lower surface area which provide that oxide appears in the non-equilibrium conditions in the sweep gas flow. The oxygen release rate dQ/dt is defined then by the oxygen exchange reaction with the oxide going in the conditions of small deviation from the equilibrium. The solution to the equation (S.4) can be obtained in the quasi-stationary approximation as

$$\frac{pO_2 - pO_2^f}{pO_2^i - pO_2^f} = A\exp(-k_{\mathrm{r}} t) \tag{S.6}$$

where pO^i_2 and pO^f_2 are the initial and final oxygen partial pressures, A is the amplitude of the pressure relaxation signal and k_{r} is the relaxation rate constant defined by

$$\frac{1}{k_r} = \frac{V}{Sk_\delta} + \frac{\Delta Q\left(p - pO_2^f\right)}{J_{\mathrm{in}}\Delta pO_2} \tag{S.7}$$

ΔQ is the total change of oxygen content in oxide after the relaxation, $\Delta pO_2 = pO^i_2 - pO^f_2$ is the oxygen partial pressure step in the relaxation [14], V and S are total volume and surface area of the oxide sample, k_δ is the oxygen surface exchange constant. The equilibrium exchange rate $\Re_0$ is then obtained according to the equation 3.

Appendix 3

Eq. 10 has the consequence; it allows to consider the equilibrium dependencies $\mu O_2^{oxide}(\delta)$ as information on electronic structure of oxide and to estimate the density of states (DOS) near the Fermi level [15]:

$$g(\varepsilon_F)=\frac{\partial[e^-]}{\partial\mu_e}\approx -8\left(\frac{\partial\mu O_2^{oxide}}{\partial\delta}\right)^{-1} \tag{4}$$

In particular, for the SCF perovskite, where the dependence of the oxygen nonstoichiometry (δ) from the partial oxygen pressure pO_2 (Fig. 1a) may be approximated by the ratio $\delta=\delta_0-\beta\ln pO_2$, the DOS is:

$$g(\varepsilon_F)\approx\frac{8\beta}{RT} \tag{5}$$

Since the slope β changes during the transition from P_1 to P_2 phase, it can be assumed that these phases have metal-like electronic structure with different density of states near the Fermi level.

Table 1S. Parameters β (the (slope of equilibrium dependence of *3-δ vs. log pO₂*) for SCF phases P_1 and P_2 .

T,°C	Parameter β for P_1 phase		Parameter β for P_2 phase	
800	-0,02472	1,4E-4	-0,02147	4,8E-5
840	-0,02758	1,9E-4	-0,02306	6,6E-5
860	-0,02678	1,3E-4	-0,02381	5,6E-5
900	-0,02572	7,2E-4	-0,0269	6,9E-5

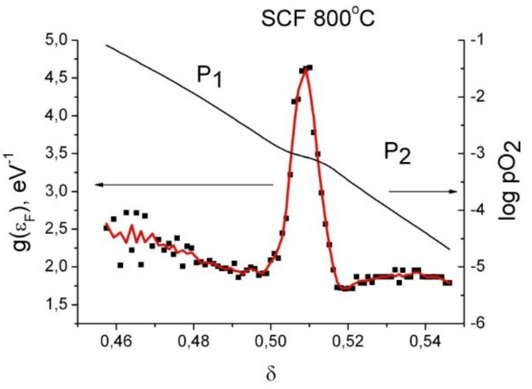


Fig. 3S. Density of states near the Fermi level and log pO_2 *vs.* oxygen nonstoichiometry for P_1 and P_2 phases of SCF

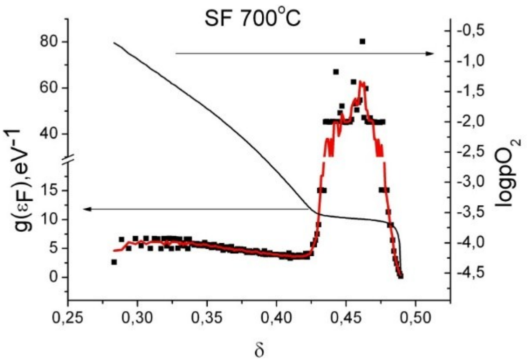
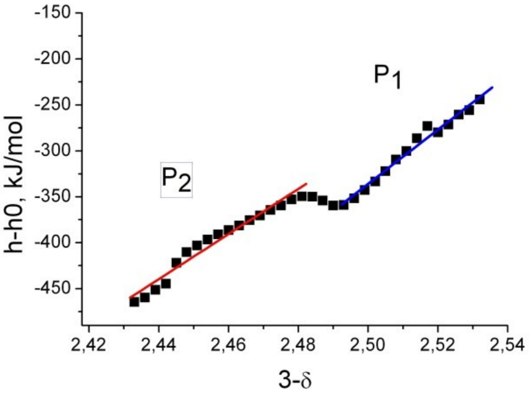


Fig. 4S. Density of states near the Fermi level and log pO_2 *vs.* oxygen nonstoichiometry for SF calculated using rigid band model

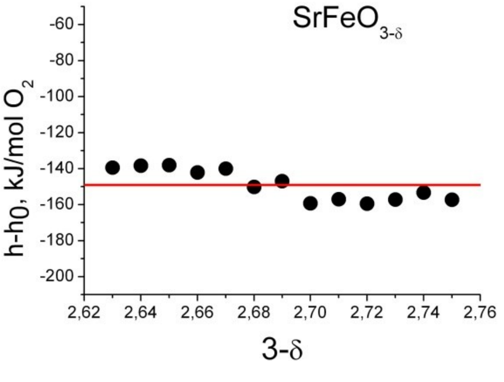
Appendix 4.

$SrCo_{0.8}Fe_{0.2}O_{3-\delta}$

$SrFeO_{3-\delta}$



a



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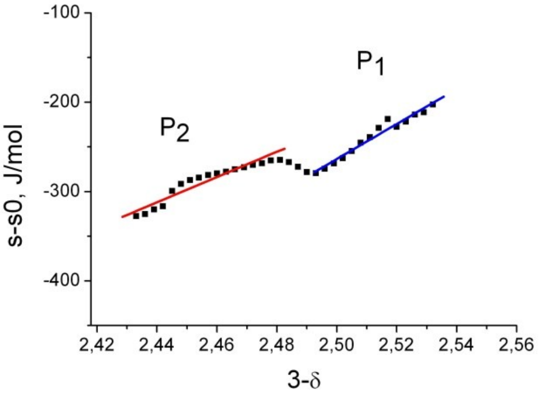
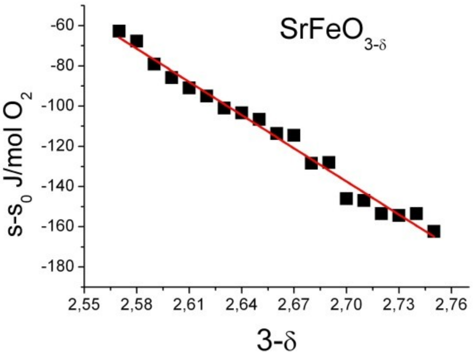


c



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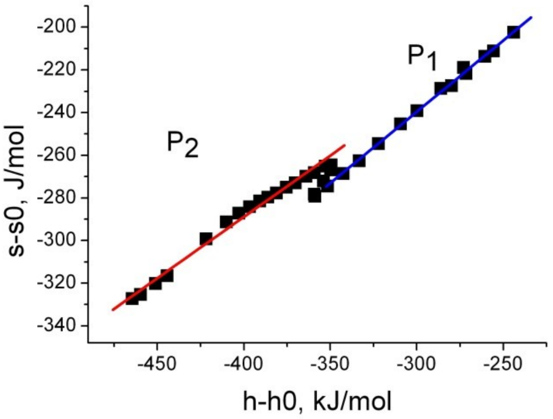

e

Fig. 6S. Dependencies of partial enthalpy ($h-h_0$) (a, b) and entropy ($s-s_0$) (c, d) on oxygen nonstoichiometry for SCF and SF perovskites calculated from the equilibrium data obtained using QEOR method. e – correlation of partial enthalpy and entropy for SCF