

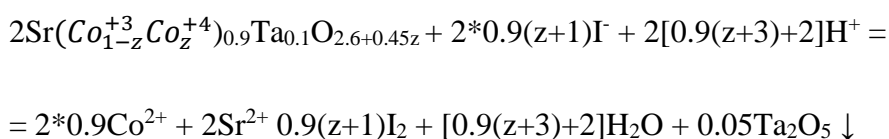
The Brønsted-Evans-Polanyi Relationship in Oxygen Exchange of Fuel Cell Cathode Material
 $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}$ with Gas Phase†

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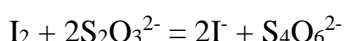
Supporting Information

Determination of oxygen stoichiometry

The oxygen content in the initial oxide was determined by iodometric titration. For this, a weighed quantity of the substance of 30-50 mg was placed in a measuring flask and dissolved in 20 ml of 0.7M hydrochloric acid in the presence of 1.5g KI. It should be kept in mind that tantalum oxide does not dissolve in hydrochloric acid and precipitates. The reaction equation can be written as:



During the reaction, an elementary iodine is formed, the solution is colored brown. The released iodine was titrated with a solution of sodium thiosulfate before staining the solution in a straw-yellow color. The reduction reaction of iodine:



After this, a few drops of starch solution are added, forming a bright purple complex with the remaining iodine. The equivalence point is fixed at the moment of the complete decoloration of the solution. 2 mol of thiosulfate is used for 1 mol of iodine, which corresponds to 2 mol of cobaltite. Based on this, we can write the following equation, from which z can be determined:

$$C_t V_t = 0.9 \frac{m_s}{M_s} (z+1)$$

where M_s is the molar mass of the test substance, $M_s = M_{\text{SCTO}_{2.6}} + 0.45 \cdot z \cdot M_{\text{O}}$, M_{O} is the molar mass of an oxygen atom, $M_{\text{SCTO}_{2.6}}$ is the molar mass of $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{2.6}$, C_t is the molar

concentration of titrant, V_t is the volume of the titrant, m_s is the mass of the test substance, z is the amount of cobalt in the oxidation state +4.

Thermogravimetric analysis

To conduct thermogravimetric measurements, the STA 449c derivatograph (NETZSCH, Germany) was used in dynamic mode while heating the sample in He/O₂ mixture ($pO_2=0.1$ atm) up to 1000°C at the speed of 10°C/min.

Since the change in the oxide mass is associated only with the release of oxygen/absorption, the relative change in the oxygen nonstoichiometry was determined from the data on the change in mass (Fig. S1):

$$3 - \delta_i = \frac{m_i}{m_0} M_{SCTO_{3-\delta_0}} - \frac{M_{SCTO_3}}{M_O}$$

where m_0 and m_i are the initial mass of the sample and its mass at temperature T_i , respectively, $3 - \delta_0$ is the initial oxygen content, the value of which was determined using iodometric titration, M_X are molar masses of corresponding substances defined by indexes.

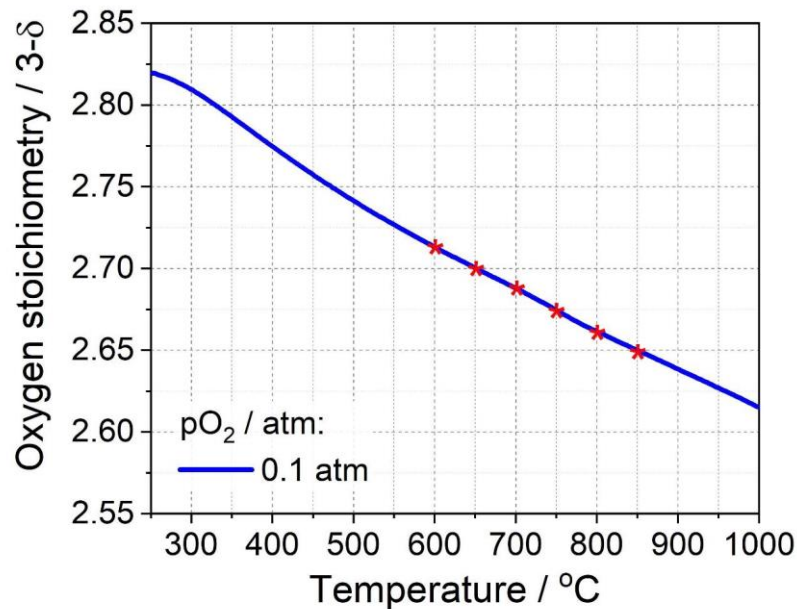


Figure S1. Temperature dependence of oxygen stoichiometry in SrCo_{0.9}Ta_{0.1}O_{3-δ} (SCT10) at $pO_2=0.1$ atm.

The obtained equilibrium data (Fig. S1) was used as fixed points in the continuous equilibrium diagrams obtained by the method of quasi-equilibrium oxygen release (QEOR) [1].

The study of the oxygen release in quasi-equilibrium mode

The method is implemented on the installation schematically shown in Fig. S2.

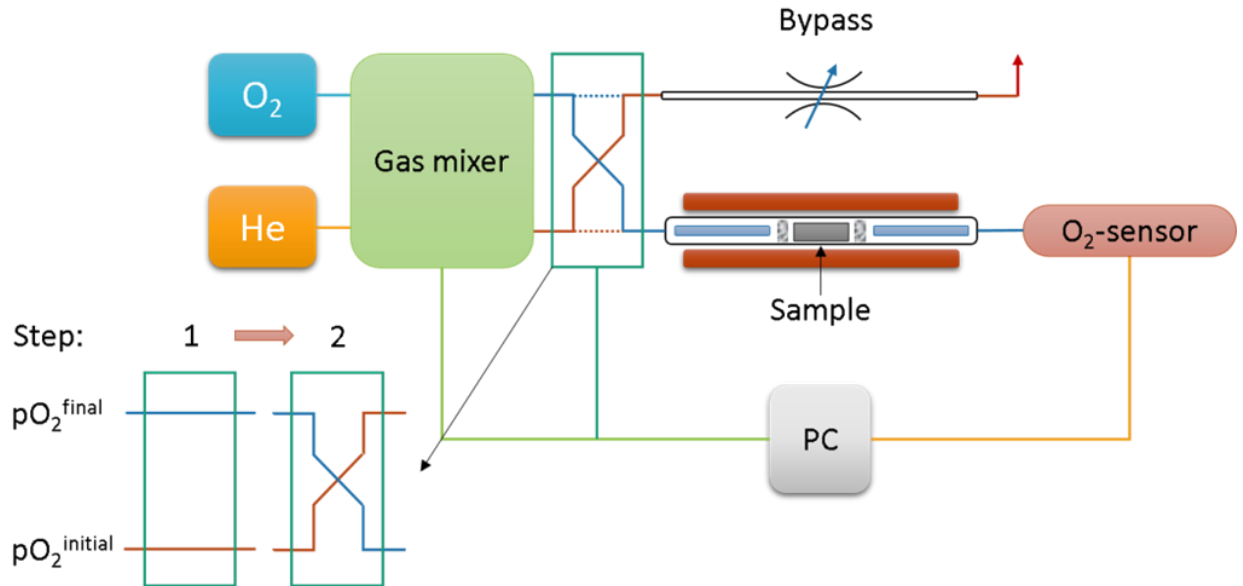


Figure S2. Schematic diagram of the installation used in QEOR and OPPR methods.

The changes in the oxygen's partial pressure at the outlet of the tubular flow reactor occurs as a result of rapid switching of the oxygen content in the incoming He/O₂ gas mixture. Registration of these changes allows the direct measuring of the amount of oxygen released or absorbed by the sample in the reactor. Mass balance equation for an ideal mixing reactor [1]:

$$\frac{V_r}{RT} \frac{dpO_2}{dt} = J(pO_{2in} - pO_2) - \frac{dQ}{dt}(1 - pO_2) \quad (S1)$$

where V_r is the free volume of the reactor, pO_2 and pO_{2in} are the current oxygen pressure in the reactor and in the input stream (normalized to the total gas pressure, 1atm), J (mol/sec) is the input flow of the gas mixture, Q (mol) is the total content of molecular oxygen in the sample.

This equation relates the rate of oxygen release/absorption by the sample dQ/dt to the measured dependence of the partial oxygen pressure at the time $pO_2(t)$. Integration of dQ/dt allows the determining of the current oxygen content in the sample $Q(t)$ and, accordingly, the degree of nonstoichiometry $\delta(t)$ at a known pO_2 .

Depending on the experimental conditions, relaxation of the sample's composition to equilibrium with the gas mixture in the incoming flow occurs either in a non-equilibrium or quasi-equilibrium mode [1-3]. The use of high gas flow rates J and porous samples with a high specific surface leads to a non-equilibrium relaxation mode, when the oxygen exchange rate is insufficient to maintain the equilibrium oxygen pressure over the sample in a reactor purged with a gas with a different composition. This mode is used to obtain the kinetic characteristics of the surface oxygen exchange. By lowering the flow rate J and using the powder sample of oxide with a high surface, it is possible to achieve quasi-equilibrium conditions of the reaction, when the oxide manages to bring the composition of the purged gas to an equilibrium value corresponding to the current composition of the oxide. The achievement of a quasi-equilibrium mode is confirmed by the fact that the $pO_2(t)$ dependences obtained at different flow rates coincide with each other after the affine time transformation $t \rightarrow t*J$. In this case, the dependence $\delta(pO_2)$, obtained as a result of two parametric dependencies $\delta(t)$ and $pO_2(t)$, asymptotically approaches the limit function corresponding to the equilibrium between oxide and oxygen at a different pO_2 . Relative changes in δ , initially obtained by integrating the dQ/dt dependencies, are converted to absolute values using reference data on the oxygen content in the oxide obtained from iodometry and the results of TG experiments. As a result, the described method allows the obtaining of continuous (step by δ is less than 0.001) equilibrium isotherms " $\lg pO_2 - 3-\delta$."

Kinetic measurements of oxygen exchange

To implement the kinetic measurements of oxygen exchange with the SCT10 oxide by the method of oxygen partial pressure relaxation (OPPR) [3], the above-described installation (Fig. S2) was used, operating under non-equilibrium conditions. For this purpose, a porous cylindrical oxide sample (table S1) and a gas mixture flow of 200 ml/min were used.

Table S1. Parameters of a porous cylindrical sample

Composition	Weight, g	Cylinder diameter, mm	Cylinder height, mm	Relative porosity, %
$SrCo_{0.9}Ta_{0.1}O_{3-\delta}$	0.7514(1)	4.02(2)	13.65(2)	24(1)

Before the start of each measurement stage, the sample was kept in the gas flow of a given composition until equilibrium was reached, as determined by the achievement of a stationary oxygen sensor's signal. After that, a software-controlled switching of the gas composition at the reactor inlet was performed and a signal of oxygen pressure relaxation at the reactor outlet was

recorded. Switching the composition of the He/O₂ gas mixture was performed in steps, up and down, between neighboring compositions in a row 0.1%-0.2%-0.3%-0.5%-0.7%-1%-1.5%-2% O₂ in He, at temperatures varying from 600°C to 900°C. The speed of the flow switching system allows the changing of the oxygen partial pressure in an empty reactor within 2-3 seconds which, in turn, allows the reliable recording of the kinetics of oxygen pressure relaxation in the presence of a sample, typically taking several hundred seconds. The total number of recorded and analyzed kinetic dependencies was 70.

The obtained kinetic curves were analyzed using a previously developed theoretical model [4]. The model describes the oxygen exchange kinetics in the mode of the surface reaction control, which is applicable for the oxide particles size not exceeding L_c , characteristic particle size above which the process is controlled by bulk diffusion [5, 6]. The change in the concentration of oxygen $\Delta c(t)=c(t)-c(t=0)$ in particles of the size D follows the equation 2:

$$\frac{d\Delta c(D,t)}{dt} = \frac{6}{D} k_{\delta} (\Delta c_e(t) - \Delta c(D,t)) \quad (\text{S2})$$

where $\Delta c_e(t) = c_e(t) - c(t=0)$ corresponds to the effective equilibrium oxygen concentration in oxide, changing with the current $pO_2(t)$ in the reactor. The characteristic feature of the model, in contrast to the standard relaxation models, is that it explicitly takes into account the dependence of the oxygen exchange rate constant on the nonstoichiometry of the oxide δ , which changes during the relaxation of the sample to a new equilibrium. This is specified by the power dependence of the surface exchange rate constant on the equilibrium oxygen pressure pO_2^{eq} at a given δ :

$$k_{\delta}(p_e) = k_0 (pO_2^{\text{eq}})^n \quad (\text{S3})$$

Such the power dependence of k_{δ} on p_e is often observed in studies as an empiric rule [7]. Taking into account the goal set in the work, it can be noted that the use of this power-law dependence in the analysis of experimental kinetics automatically solves the problem of determining the Brønsted coefficient for the considered continuous series of δ -homologues.

With small changes in stoichiometry, the oxygen concentration changes approximately linearly with the logarithm of the equilibrium pressure. Thus, the equilibrium pressure pO_2^{eq} can be coupled with Δc according to the approximate expression

$$\ln\left(\frac{pO_2^{eq}}{pO_2(t=0)}\right) = \gamma\Delta c$$

$$\gamma = \left(\frac{d \ln(pO_2)}{d\Delta c}\right)_{eq}$$
(S4)

where γ is local derivative of the equilibrium dependence. Accordingly, the current equilibrium concentration $\Delta c_e(t)$ can be expressed from $pO_2(t)$ as

$$\Delta c_e(t) = \frac{1}{\gamma} \ln\left(\frac{pO_2(t)}{pO_2(0)}\right)$$
(S5)

When determining the total flow of oxygen from the sample, the particle size distribution $F(D)$ is taken into account:

$$Q(t) - Q_{ini} = V \int_{D_{min}}^{D_{max}} F(D) \Delta c(D, t) dD$$
(S6)

where V is the total volume of the oxide sample. Differential equation (S2) forms a system with equation (S6) and the mass balance equation in reactor (S1), numerical solution of which allows the obtaining of the dependence of $pO_2(t)$ in the reactor with the given parameters k_0 , n , γ and a known distribution $F(D)$. To perform a comparison with the experimental oxygen pressure relaxation curve, a convolution of the calculated $pO_2(t)$ dependence with the response function of the experimental setup is used, which is determined as the exponential fit of the pressure relaxation curve in an empty reactor (Fig. S3a).

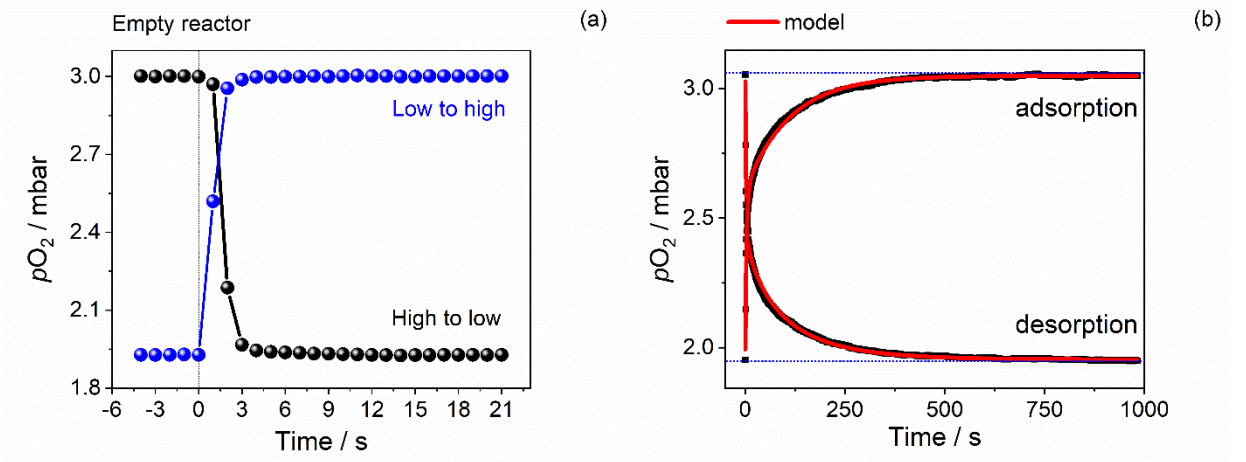


Figure S3. An example of the kinetics of switching the gas composition in an empty reactor at a gas flow rate of 200 ml/min (a) and the kinetics of oxygen partial pressure relaxation in SCT10 with the same switching of the gas composition and $T=600$ °C (b). The solid line on the right graph is the calculated model kinetic curve.

To determine the parameters of the model k_0 , n and γ a joint nonlinear least-squares optimization was performed for a data set corresponding to all the variants of gas composition switching at the same temperature. The result is a set of temperature dependencies $k_0(T)$, $n(T)$ and $\gamma(T)$, from which the values of the oxygen exchange rate constant $k_\delta(pO_2^{eq}) = k_0(pO_2^{eq})^n$ and the equilibrium exchange rate $R_0(pO_2^{eq}) = k_0(pO_2^{eq})^n/\gamma$ are calculated and then to $k_\delta(\delta)$ and $R_0(\delta)$ using equilibrium diagrams.

Reference

- [1] I. Starkov, S. Bychkov, A. Matvienko, A. Nemudry, Oxygen release technique as a method for the determination of " δ - pO_2 - T " diagrams for MIEC oxides, *Phys. Chem. Chem. Phys.* 16 (2014) 5527-5535
- [2] I.A. Starkov, S.F. Bychkov, S.A. Chizhik, A.P. Nemudry, Oxygen Release from Grossly Nonstoichiometric $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ Perovskite in Isostoichiometric Mode, *Chem. Mater.* 26 (2014) 2113-2120
- [3] S.F. Bychkov, I.I. Gainutdinov, S.A. Chizhik, A.P. Nemudry, Novel oxygen partial pressure relaxation technique for study of oxygen exchange in nonstoichiometric oxides. The model of relaxation kinetics, *Solid State Ionics* 320 (2018) 297-304
- [4] S.A. Chizhik, S.F. Bychkov, M.P. Popov, A.P. Nemudry, Brønsted-Evans-Polanyi relationship in oxygen exchange of non-stoichiometric oxides with gas phase, *Chem. Eng. J.* 371 (2019) 319-326
- [5] F. Viani, V. Dovì, F. Gesmundo, A method of analysis of the relaxation data for evaluation of the chemical diffusion coefficient in the case of partial rate control by surface reaction, *Oxid. Met.* 21 (1984) 309-327

[6] H.J.M. Bouwmeester, H. Kruidhof, A.J. Burggraaf, Importance of the surface exchange kinetics as rate limiting step in oxygen permeation through mixed-conducting oxides, *Solid State Ionics* 72 (1994) 185-194

[7] J. Yoo, A. Verma, S. Wang, A.J. Jacobson, Oxygen Transport Kinetics in $\text{SrFeO}_{3-\delta}$, $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$, and $\text{La}_{0.2}\text{Sr}_{0.8}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Measured by Electrical Conductivity Relaxation, *J. Electrochem. Soc.* 152 (2005) A497