Novel oxygen partial pressure relaxation technique for study of oxygen exchange in nonstoichiometric oxides. The model of relaxation kinetics

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ABSTRACT

The development of the theoretical background of a new relaxation technique based on pO_2 monitoring at the outlet of the continuous-flow fixed-bed reactor is presented. The model describes the relaxation kinetics of oxygen exchange between the nonstoichiometric oxide and the gas phase in a case when surface reaction is the rate-limiting step. The model takes into account the feedback between the oxygen exchange rate and the oxygen partial pressure in the reactor: the rate is affected by oxygen released or uptaken by the sample. In the frame of material-gas feedback approach the influence of the sweep gas flow rate on the relaxation rate constant is shown. An analytical expression which allows determining correct value of the key material kinetic characteristic (surface exchange rate constant) from experimentally measured relaxation rate constant is derived. The proposed feedback approach has the versatility: the correction of the relaxation rate constant is necessary not only for the novel oxygen partial pressure relaxation method, but also for the other traditional relaxation techniques when oxides possess high oxygen exchange rate that does not allow to maintain constant oxygen partial pressure in the reactor even with high sweep gas flow rate.

1. Introduction

Nonstoichiometric oxides are characterized by high ionic and electronic conductivity at elevated temperatures, which is a prerequisite for their use as materials for solid oxide fuel cells, oxygen separation membranes, oxygen sensors etc. An important characteristic of such materials is the rate of oxygen exchange between the oxide and the gas phase. Among various methods of kinetic studies relaxation techniques are widely used to explore reactivity of nonstoichiometric oxides with respect to oxygen [1–15]. The techniques based on measurement of oxide composition respond to a fast change of oxygen activity in gas phase are aimed to determine material kinetic properties of oxides like the chemical surface exchange coefficient k_{chem} and chemical diffusion coefficient D_{chem}. Correct determination of the kinetic properties is crucial for understanding the mechanism of the oxygen exchange and the rate limiting factors in practical applications of such materials. There are several variants of the relaxation technique based on the rapid change of the oxygen partial pressure (pO_2) or isotope composition (O^{16}/O^{18}) in gas phase flowing through a reactor containing an oxide sample (the continuous flow reactor). The variation of oxygen content in the sample initiated by the oxygen pressure change is typically monitored using an appropriate secondary indicator such as

electrical conductivity, lattice volume, mass change, etc. [1–15]. It worth noting that k^* and D^* values evaluated from isotope exchange method differ from that obtained by the other above-mentioned techniques by thermodynamic factor [16,17]. Among these methods, the electrical conductivity relaxation (ECR) technique is the most common. However, along with undoubted merits in the ECR method powder samples cannot be used. Moreover, the ECR technique requires well-sintered samples few millimeters in size. For such samples, the bulk diffusion of oxygen ions may become the main limiting factor of the oxygen exchange which results in low reliability of the surface exchange rate constants k_{chem} determined from relaxation data [4]. The use of sintered samples with high open porosity facilitates the analysis of the relaxation data, because the influence of the bulk diffusion on the relaxation rate can be neglected [18–20].

However, one of the most serious problems ECR faced with while studying oxides exhibiting very high oxygen exchange rates arises when the amount of oxygen released or uptaken by oxide can be so high that the sweep gas flow rate (J_{in}) is not sufficient to retain constant pO_2 in the reactor in the course of relaxation [21–23]. The diffusion-kinetic Crank's model [24], which is used to determine values of k_{chem} and D_{chem} from the relaxation kinetic data relies on the assumption that pO_2 near the sample in the reactor reproduces the same step-like change

behavior as that introduced in the sweep gas flow entering the reactor inlet. The model requires that pO_2 in the reactor to remain constant equal to the final desired value after the step-like change of pO_2 at the inlet gas flow. Direct measurements of pO_2 in the sweep gas flow downstream the oxide samples shows that the pressure change does not follow this assumption until J_{in} as high as 1000 ml/min [21]. The traditional analysis of the relaxation data using Crank's model yielded values of k_{chem} and D_{chem} varied up to an order of magnitude depending on J_{in} [21]. It was concluded by Falkenstein et al. [21] that the kinetic parameters obtained from ECR experiments using Crank's model cannot be regarded as reliable even at high gas flow rates.

Careful analysis of the aforementioned problem made by Falkenstein et al. [21] and by Ji et al. [22,23] resulted in clear formulation of two limiting regimes of ECR relaxation experiments. In case of low J_{in} and high rate of oxygen exchange provided by an oxide sample (high reactivity, large specific surface area, elevated temperatures) the relaxation goes in the *gas-phase limited regime*: the relaxation is limited by the capacity of the gas flow to supply or remove oxygen to/from the oxide which is capable to maintain the equilibrium oxygen pressure corresponding to its current oxygen non-stoichiometry. Criteria of the gas-phase limiting regime were also analyzed in the earlier work by Starkov et al. [25], which made it possible to utilize the gas-phase limit for obtaining continuous pO_2-δ-T equilibrium diagrams [26]. On the contrary, in the material-kinetic limit, the relaxation rate is controlled by the surface exchange kinetics or by the bulk diffusion in oxide. It is the material-kinetic limit that should be ideally used in relaxation experiments to determine valid quantities of k_{chem} and D_{chem} whereas in the gas-phase controlled regime the relaxation rate is only determined by the thermodynamic properties of the oxide and the sweep gas flow rate. Unfortunately, to reach the material-kinetic limit in case of highly reactive oxides too high gas flow rates should be used [21] at which other experimental artifacts may rise uncontrollably.

It can be concluded that the better solution to the problem could be an advanced analysis of relaxation data obtained in the intermediate regime lying between the material-kinetic and the gas-phase limits. The desired analysis should allow accounting for the non-step-like pO_2 behavior in the reactor. Although a theory was already proposed considering an effect of non-instant pO_2 change [10,27] it corresponds to the qualitatively different problem formulation. The theory of flush time correction [27] considers cases when pO_2 changes non-step-like in the reactor because of two reasons: a finite time period necessary to flush the reactor volume with the new gas flow composition and due to possible non-step-like pO_2 change at the reactor inlet (for example, due to restrictions of a gas supply facility). On the whole, the flush time correction model [27] corresponds to a deconvolution problem because it considers a process going in the changing conditions of pO_2 controlled externally to the process. The currently considered problem corresponds to a case when pO_2 in the reactor changes non-step-like because of the very fast oxygen exchange reaction. As the pO_2 change affects back the rate of the reaction that causes the change we should consider the feedback problem. The relaxation going in the conditions lying between the material-kinetic and the gas-phase limits can be called the material-gas feedback regime. As the kinetics of the feedback regime is still completely defined by the same kinetic properties of the material and the gas phase, it should be possible to evaluate correct material kinetic properties by a proper analysis of the feedback problem.

To explore the relaxation in the feedback regime pO_2 monitoring is required. It should be noted that pO_2 in this case becomes the primary indicator of the reaction since the change of pO_2 in the reactor can be directly related to the change of oxygen stoichiometry of the oxide through the principle of mass conservation.

Recently we have reported the novel oxygen partial pressure relaxation (OPPR) technique, which implements the above idea by pO_2 monitoring on the outlet of the continuous-flow fixed-bed reactor [17]. The suggested method allows avoiding the limitations of ECR mentioned above. Other advantages of OPPR are:
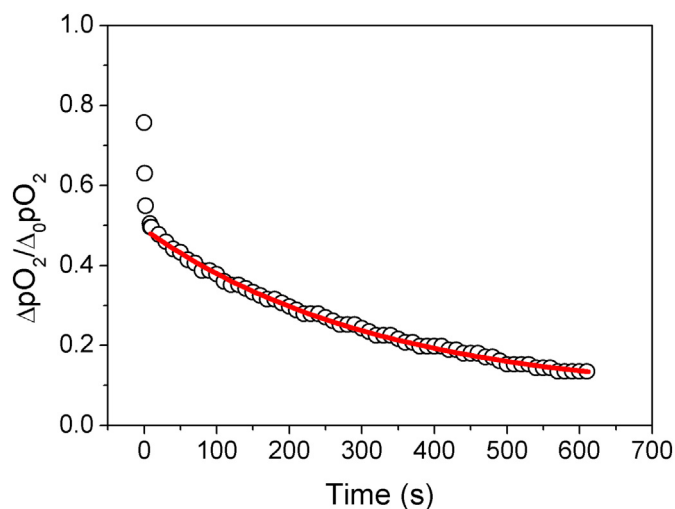

Fig. 1. Experimental data of the relaxation kinetics obtained by OPPR for SrFeO$_{3-\delta}$ sample: the time dependence of pO_2 at the outlet of the reactor (open circles) fitted by decaying exponential (red line). The oxygen partial pressure change is normalized to the total pO_2 step applied to initiate the relaxation. The volumetric sweep gas flow rate is 50 sccm, $T = 973$ K, $k_r = 2.1 \times 10^{-3}$ s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

– high sensitivity that allows to relaxation measurements towards lower temperatures and oxygen partial pressures,
– possibility to measure oxygen exchange rate for both bulk and powder samples.

Measurements using OPPR technique proved the significant influence of the oxide relaxation on the pO_2 behavior in the reactor. Fig. 1 shows an example of pO_2 change in a flow reactor with a SrFeO$_{3-\delta}$ sample after a step-like change in pO_2 at the inlet of the reactor (the relaxation curves with and without the sample in the reactor and their difference are shown in Supplementary information (SI) Figs. 1S, 2S). As can be seen, in the first stage, the drop of pO_2 occurs rapidly, and then a slow exponential decay begins, because the oxide intensively releases oxygen, approaching a new equilibrium state.

In this paper, we present the model describing the relaxation proceeding in the feedback regime and based on the explicit consideration of mass balance equation for oxygen in the continuous flow stirred-tank reactor. The model is not only necessary as the theoretical background of the OPPR technique but is supposed to give a solution of the problem emerging in ECR method when pO_2 changes in the reactor because of the fast oxygen exchange between nonstoichiometric oxide and gas phase. The proposed model demonstrates that pO_2 in the reactor does not change instantaneously, but depends on the relation between the gas flow rate and rate of oxygen release/uptake by the oxide. Consideration of the feedback phenomenon predicts the effect of the sweep gas flow rate on the measured relaxation rate constant k_r. For the purpose of illustration, some experimental data obtained by means of OPPR technique supporting the model are included.

2. The model

It is known that the rate of the oxygen exchange can be limited either by the surface reactions or by the bulk diffusion of oxygen ions. The mixed regime is realized when the oxygen exchange rate at the surface and bulk diffusion simultaneously influence the overall oxygen exchange. The rate limiting stage is determined by the ratio of the diffusion length L_d (characteristic size of reacting particles) to the characteristic thickness $L_c = D_{chem}/k_{chem}$ [28,29]. In this paper, we consider the case when the surface kinetics is the limiting factor, so the bulk diffusion of oxygen ions is fast and the concentration of oxygen in the sample is uniform at any time. This can be realized for powders or