

Searching for fast oxygen exchange kinetics: (Bi,Sr)(Fe,Co)O_{3-δ} perovskites

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Our interest in the exchange reaction of oxygen between the gas phase and oxides is twofold: (i) to understand the mechanistic details of one of the "simplest" gas-solid reactions - which nevertheless exhibits an astonishing complexity in terms of reaction pathways, (ii) to use this knowledge for improving electrochemical devices which rely critically on a fast oxygen incorporation rate such as cathodes for solid oxide fuel cells (SOFC). In order to clarify the reaction mechanisms we combined various experimental techniques with phenomenological as well as ab-initio modelling. In addition to stability issues, SOFC cathode materials should allow for rapid oxygen incorporation on the whole electrode surface area, as well as quick ion transport through the electrode to the electrolyte. In the perovskites of interest the ionic conductivity is enabled by oxygen vacancies.

Investigating a whole class of mixed conducting perovskites showed that not so much the adsorption but rather ionization, dissociation and incorporation into vacancies are sluggish steps (red arrows in Fig. 1). In the typical cathode materials that show a high electronic conductivity it is the latter step that is limiting. Obviously for this step oxygen vacancies are crucial. We found that it is not only the concentrations of these defects that are important for the chemical kinetics, but also their mobilities since relevant adsorbed oxygen species are quite immobile and it is rather the vacancy that seeks O_{ads} than vice versa [1]. Hence it is - as for bulk transport - the conductivity, i.e. concentration × mobility, that needs to be optimized [2].

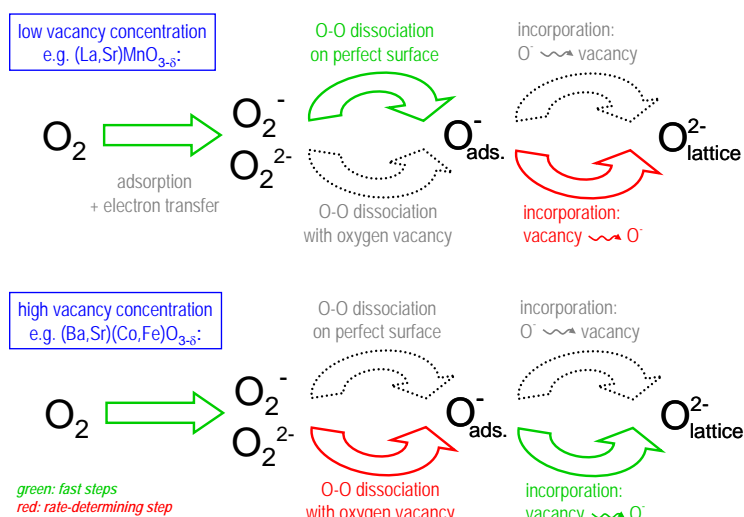


Figure 1: Scheme of possible reaction pathways for oxygen incorporation. Depending on the characteristics of the actual material, different branches are taken, and different steps are rate-determining.

The importance of both factors for the surface exchange rates is depicted in Fig. 2 which summarizes experimental results from several perovskite materials studied in our group. Moving from (La,Sr)MnO_{3-δ} to (La,Sr)(Co,Fe)O_{3-δ} perovskites it is mainly the strong increase of the oxygen vacancy concentration which accelerates the surface reaction by two orders of magnitude (the mobility remains constant). Going from (La,Sr)(Co,Fe)O_{3-δ} to (Ba,Sr)(Co,Fe)O_{3-δ} the increasing mobility of oxygen vacancies - as measured in separate diffusion experiments - makes the main contribution to the increase in reaction rate. (The origin of this increased vacancy mobility in (Ba,Sr)(Co,Fe)O_{3-δ} could be traced back to a combination of geometric and electronic factors by DFT calculations)[3].

While (Ba,Sr)(Co,Fe)O_{3-δ} perovskites exhibit fast oxygen exchange, their use as SOFC cathode is impeded by drawbacks such as carbonate formation, detrimental phase transformation and unwanted reactivity with the electrolyte materials. Taking the criterion of a high oxygen ion conductivity as a guideline, we turned to (Bi,Sr)(Fe,Co)O_{3-δ} [4] owing to a high concentration (due to Sr²⁺ acceptor

doping on the Bi^{3+} site) and mobility (due to the high polarizability of Bi^{3+}) of oxygen vacancies while avoiding Ba^{2+} which is largely responsible for the drawbacks of $(\text{Ba,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$.

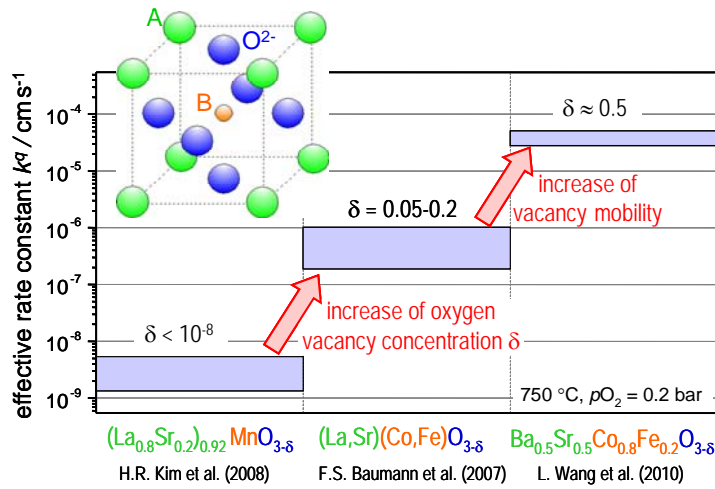


Figure 2: Effective rate constants for oxygen exchange between gas phase and several mixed-conducting perovskites with different concentrations and mobilities of oxygen vacancies.

At low to moderate Sr content $x \leq 0.5$ iron in $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ is present essentially in the 3+ oxidation state, only for high Sr concentration a significant fraction of Fe^{4+} is found. Thus the Sr acceptor dopants are largely compensated by a comparably high concentration of oxygen vacancies leading to ionic conductivity. The electronic conductivity in the range of 0.1-10 S/cm (depending on x , T , and $p\text{O}_2$) is lower than for $(\text{La,Sr})\text{FeO}_{3-\delta}$ or $(\text{La,Sr})\text{CoO}_{3-\delta}$ perovskites. In contrast to the Ba-containing perovskites, $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ does not form significant amounts of carbonates in air, it has a lower thermochemical expansion coefficient and it starts to react with the YSZ electrolyte only at temperatures higher than typical SOFC operation.

To allow for a reliable comparison of effective rate constants - unaffected by the hardly reproducible morphology of porous films - the $(\text{Bi,Sr})(\text{Fe,Co})\text{O}_{3-\delta}$ perovskites are prepared as dense films on YSZ single crystal substrates as oxygen ion conducting electrolyte by Pulsed Laser Deposition. The films with 150-450 nm thickness are polycrystalline with a lateral crystallite size of ≈ 100 nm. The effective rate constant k of oxygen exchange was determined by electrochemical impedance spectroscopy. The diameter R_s of the semicircle in the spectra (Fig. 3) yields the rate constant $k \propto (R_s)^{-1}$ at various temperatures and oxygen partial pressures ($p\text{O}_2$).

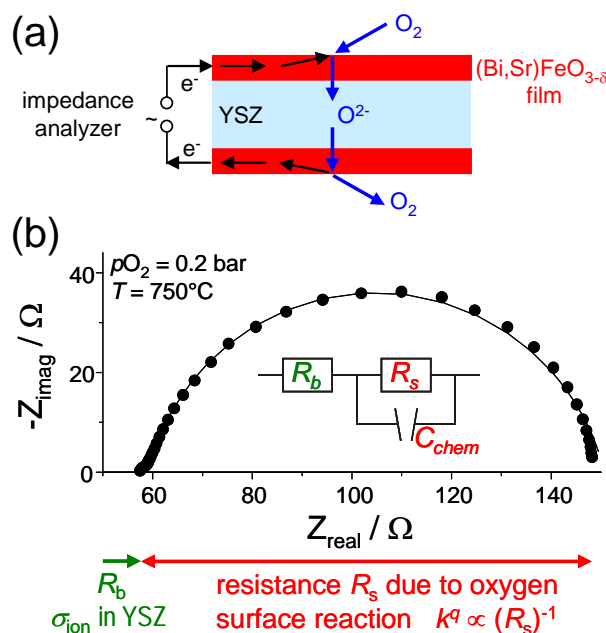


Figure 3: (a) Sketch of sample: YSZ coated on both sides with mixed conducting perovskite film. Applying an AC voltage leads to oxygen in- and exorporation on the perovskite surface. (b) Impedance spectrum of a $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ film on YSZ. The large semicircle corresponds to the resistance R_s caused by the oxygen exchange surface reaction, the axis intercept is related to the ionic conductivity of the YSZ electrolyte.

Within the series of $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ perovskites, the measured oxygen exchange rate increases with increasing Sr content (Fig. 4a). A partial substitution of Fe by Co strongly enhances the electronic conductivity and accelerates the oxygen exchange further. This is different from $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ perovskites studied previously [7] where the Co content has a minor effect, and thus the effective rate constants of $\text{Bi}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ are higher in particular for Co-containing compositions.

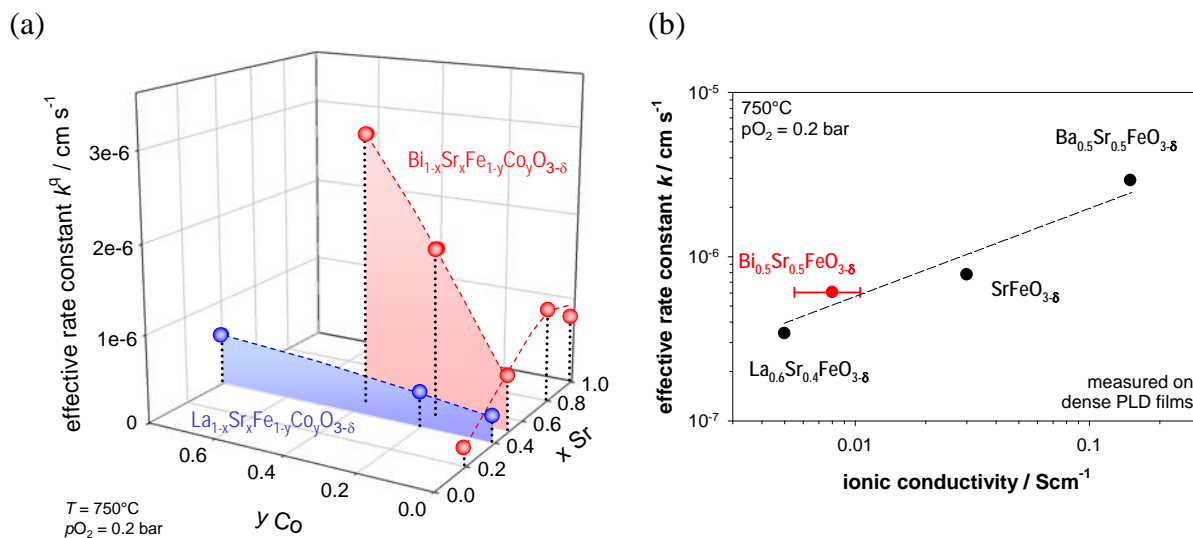


Figure 4: (a) Effective rate constant k for the surface oxygen exchange reaction of $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ [7] and $\text{Bi}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ perovskites. (b) Correlation of k with oxygen ion conductivity. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ and $\text{SrFeO}_{3-\delta}$: k and ionic conductivity from [1], $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$: k from [7], ionic conductivity from [1], $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$: k from the present study, ionic conductivity estimated from [5,6].

When the approach of a vacancy to an adsorbed oxygen species is rate-determining for the surface reaction, an increase of the ionic conductivity is expected to lead to a linear increase of the reaction rate. Fig. 4b shows that indeed a correlation between rate constant and ionic conductivity is found for the series of $(\text{La,Sr,Ba})\text{FeO}_{3-\delta}$ perovskites (the slope is slightly smaller than 1, as additional effects such as changes in the oxygen adsorption enthalpy influence the rate).

In short, we combined experimental techniques (in particular impedance spectroscopy) with phenomenological modelling (on the level of master equations) and DFT calculations to elucidate the mechanism of oxygen reduction and incorporation on mixed conducting perovskites. The interpretation resulted in a well-defined search strategy. As a result of a targeted research, we have been led to the $(\text{Bi,Sr})(\text{Fe,Co})\text{O}_{3-\delta}$ perovskites which indeed prove to be a promising electrocatalyst for high temperature fuel cells.

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