

Mechanistic insight into oxygen exchange on mixed conducting oxides from experiments and theory

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The oxygen incorporation surface reaction into mixed conducting oxides is important for adjusting the oxygen stoichiometry of a material (and thus its electrical, optical, magnetic properties etc.) as well as for oxidation catalysis and (electro)chemical devices such as fuel cells, permeation membranes and sensors [1]. Nevertheless, a detailed mechanistic understanding in terms of reaction pathways and rate-determining steps is difficult to achieve.

Effective rate constants k^q for the oxygen incorporation reaction were determined by impedance spectroscopy on PLD-deposited thin-film microelectrodes on YSZ substrates. This method allows us to measure k^q values for different materials [2] without interference from different morphologies that could arise when studying porous films. The comparison of k^q for (La,Sr)MnO_{3±d}, (La,Sr)(Co,Fe)O_{3-d} and (Ba,Sr)(Co,Fe)O_{3-d} perovskites and the correlation with vacancy diffusion coefficients suggests that not only the concentration of oxygen vacancies but also their mobility plays a crucial role in oxygen exchange kinetics [3].

For the mechanistic understanding, ab-initio DFT calculations are a valuable tool which supplies information difficult to obtain from experiments, e.g. adsorption enthalpies, energies of intermediates, and reaction barriers. In combination with experimental data this allowed us to suggest a reaction mechanism for oxygen incorporation into (La,Sr)MnO_{3±d} [4].

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