

FIRST PRINCIPLES MODELING OF OXYGEN INCORPORATION INTO OXYGEN PERMEATION MEMBRANES AND SOFC CATHODES

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Currently, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_{3-d}$ (BSCF) shows the best oxygen exchange kinetics among mixed conducting perovskites (despite other drawbacks) and is a candidate for permeation membranes and solid oxide fuel cell (SOFC) cathodes [1]. As it is well established now, the two key factors, which control the oxygen reduction, are the high oxygen vacancy (V_o) concentration at the cathode surface and the high vacancy mobility.

In this talk, we discuss calculated from first principles the atomic and electronic structure of oxygen vacancies, their formation and migration energies in the bulk and in the surface layer, the defect-induced electronic density redistribution, and dependence of defect properties on the chemical composition of the BSCF (Fe/Co ratio) [2,3]. Additionally, the adsorption energies of an oxygen molecule and an O atom were obtained. Our calculations confirm that the O-vacancy formation and, in particular, migration energies in BSCF are considerably smaller than in similar LSM and LSCF perovskites [2,3] which explains its good performance. The gradual increase of these energies with an increase of the iron content is explained by analysis of the relevant density of the states.

We predict that in both $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF) and BSCF perovskites the dissociation of surface peroxide or superoxide ion occurs with assistance of V_o , their encounter being the *rate-determining step*. The estimated reaction rate for this mechanism is significantly higher than in other perovskites, in good agreement with the experimental observations.

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