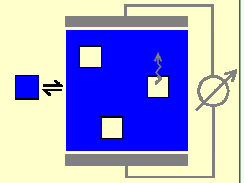




# Atomistic modelling of oxygen incorporation into (La,Sr)MnO<sub>3</sub> solid oxide fuel cell cathode

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## Introduction

\* SOFC cathode materials: typically mixed conducting perovskites

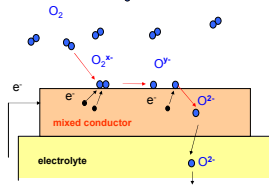
\* role of the electronic structure and ionic point defects?

\* reaction mechanism cannot be resolved from experiments alone

macroscopic kinetics: impedance spectroscopy, relaxation kinetics

microscopic investigations: XPS under in-situ conditions  
⇒ identify intermediates

ab-initio calculations: ⇒ energy of intermediates, height of barriers



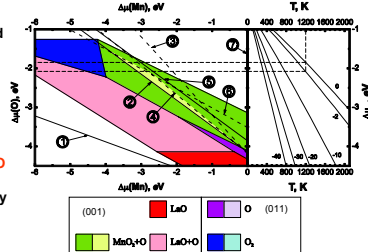
## LaMnO<sub>3</sub>: stable surface termination

We extended standard *ab initio* calculations by thermodynamic analysis at finite temperatures and external oxygen gas pressure.

The *ab initio* thermodynamic analysis clearly demonstrates that under the SOFC operation conditions (T= 1000-1200 K, oxygen pressure 0.01-0.2 bar) the cubic MnO<sub>2</sub> terminated surface with adsorbed O atoms is the most stable (the horizontal line). The alternative O (110) surface becomes stable only at very low gas pressures.

Mastrikov et al, Surf.Sci. 603, 326 (2009).

Mastrikov et al, J. Phys. Chem. V 114, 3017 (2010)



Calculated stability regions of LaMnO<sub>3</sub> surfaces with different terminations vs. the chemical potential variation for Mn and O atoms (determined by temperature and external oxygen pressure).

## Computational details

*Ab initio* DFT computer code VASP (plane wave basis) was used with GGA-Perdew Wang-91 exchange-correlation functional.

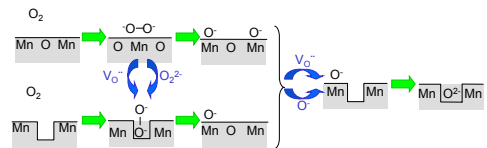
LaMnO<sub>3</sub> was treated in the form of 7- and 8-layer 2D slabs with MnO<sub>2</sub> (001) terminations in both cubic and orthorhombic phases. The surface supercell used corresponds typically to 12.5% surface coverage with V<sub>O</sub><sup>••</sup> or adsorbates.

The main properties calculated include the atomic and electronic structure, optimal adsorption sites, the effective (Bader) charges and electronic density redistribution, the binding and migration energies.

E. A. Kotomin, Y. A. Mastrikov, E. Heifets, J. Maier, Phys. Chem. Chem. Phys. 10 (2008) 4644

## Possible surface reaction pathways

Mastrikov et al, J. Phys. Chem C 114, 3017 (2010)

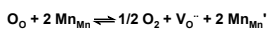


Three possible scenarios of oxygen incorporation into LSM cathode:

- O<sub>2</sub> adsorption and dissociation without vacancy
- O<sub>2</sub> adsorption without vacancy but dissociation with V<sub>O</sub><sup>••</sup> assistance
- O<sub>2</sub> adsorption directly into vacancy

## V<sub>O</sub><sup>••</sup> concentration and mobility at surface

oxygen vacancy formation enthalpies:



in bulk: +4.6 eV

in MnO<sub>2</sub>(001) surface layer: +3.2 eV

1.4 eV less endothermic

surface vacancy concentration:

-1.4 eV ⇒ factor of 10<sup>7</sup> @ 700°C

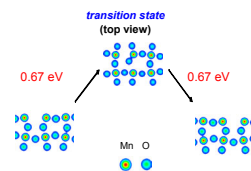
but: lower surface defect formation entropy

⇒ [V<sub>O</sub><sup>••</sup>] enhancement by about 10<sup>5</sup>

expt. bulk-[V<sub>O</sub><sup>••</sup>] in La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub> 700°C: 10<sup>-8</sup>

oxygen vacancy migration:

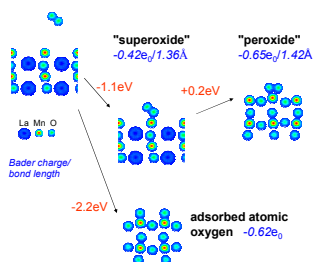
in the MnO<sub>2</sub> (001) surface layer: 0.67 eV  
⇒ 0.95 eV in bulk



surface layer vs. bulk: higher V<sub>O</sub><sup>••</sup> concentration and mobility

## Coverage with charged oxygen adsorbates

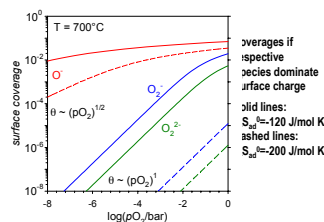
chemisorption enthalpies from DFT:



molecular and dissociative chemisorption is exothermic even on defect-free MnO<sub>2</sub>(001) surface

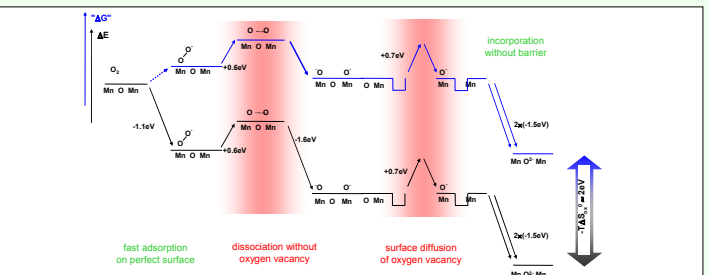
charged adsorbates: deviation from Langmuir

$$\text{O}_2^-, \text{O}_2^{2-}: \theta_{\text{O}_2^{\pm}} = K_{\text{O}_2^{\pm}} p_{\text{O}_2} \cdot e^{-\mu_{\text{O}_2^{\pm}}/kT}$$
$$\text{O}^-: \theta_{\text{O}^-} = K_{\text{O}^-} \sqrt{p_{\text{O}_2}} \cdot e^{-\mu_{\text{O}^-}/kT}$$

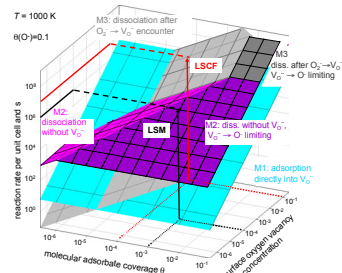


charged oxygen adsorbates ⇒ maximum coverage in % range

J. Fleig, R. Merkle, J. Maier, PCCP 9 (2007) 2713



Total energy (black) and Gibbs free energy (blue) profiles of the most probable oxygen incorporation mechanism. Possible rate determining steps are marked in red.



LSM:  
at low pO<sub>2</sub>, i.e. low O<sub>2</sub> coverage, the rate determining step changes to O<sub>2</sub> dissociation

LSCF:  
smaller oxidation enthalpy than LSM  
⇒ slightly lower adsorbate coverage  
⇒ much higher V<sub>O</sub><sup>••</sup> concentration

Dependence of the incorporation mechanism on the external conditions and material. DFT predicts higher rate for LSCF than for LSM, in agreement with experiments.

## Summary

\* MnO<sub>2</sub> (001) with adsorbed O is the most stable surface termination under SOFC conditions

\* surface segregation energy for V<sub>O</sub><sup>••</sup> is 1.4 eV

\* reduced migration barrier for V<sub>O</sub><sup>••</sup> in the surface layer (0.67 eV instead of 0.95 eV)

\* dissociation of peroxide without a V<sub>O</sub><sup>••</sup> as well as its migration has quite low energy barriers in contrast to the O<sup>-</sup> ion migration energy (2 eV)

\* the rate-determining step is either approach of vacancies to adsorbed O<sup>-</sup> ions, or peroxide ion dissociation at low oxygen pressure (red area in figure above)

\* incorporation of O<sup>-</sup> into V<sub>O</sub><sup>••</sup> occurs without barrier

We thank E. Heifets, Yu. Mastrikov, J. Fleig for a long-term collaboration and fruitful discussions.

## Transition states

