

## Functional Thin Films and Surfaces

### Room Pacific D - Session C3-1-ThM

#### Thin Films for Energy Storage and Conversion I

**Moderators:** Clio Azina, RWTH Aachen University, Germany, Tushar Shimpi, Colorado State University, USA

8:00am C3-1-ThM-1 **Designing Optimal Environments for Surface Catalytic Reactions in Perovskite Oxide Electrodes**, L. Martin, Abel Fernandez ([abel\\_fernandez@berkeley.edu](mailto:abel_fernandez@berkeley.edu)), University of California, Berkeley, USA

INVITED

Solid-gas interactions at electrode surfaces determine the efficiency of solid-oxide fuel cells and electrolyzers. Of particular relevance are the local chemistry and electronic structure at the exposed electrode surface. Using epitaxial thin films as model systems, we studied the evolution of surface chemistry and electronic structure in perovskite electrodes with different surface orientations and epitaxial strain states. First, synthesizing  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  films on  $\text{SrTiO}_3$  (001)-, (110)-, and (111)-oriented substrates wherein the surface orientation of the film is set by the substrates. Electrochemical impedance spectroscopy and electrical conductivity relaxation measurements reveal a strong surface-orientation dependency of the gas-exchange kinetics, wherein (111)-oriented surfaces exhibit an activity >3-times higher as compared to (001)-oriented surfaces. First-principles calculations suggest that the formation energy of vacancies and adsorption at the various surfaces is different and influenced by the surface polarity. Finally, synchrotron-based, ambient-pressure X-ray spectroscopies reveal distinct electronic changes and surface chemistry among the different surface orientations. Taken together, thin-film epitaxy provides an efficient approach to control and understand the electrode reactivity ultimately demonstrating that the (111)-surface exhibits a high density of active surface sites which leads to higher activity.<sup>1</sup> Outside of surface chemistry, manipulation of the surface electronic structure via epitaxial strain presents another route toward enhancing surface reaction rates. Combining high-temperature electrical-conductivity-relaxation studies and synchrotron-based X-ray absorption spectroscopy studies of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{-3}$  thin films under varying degrees of epitaxial strain reveals a strong correlation between orbital structure and catalysis rates. In both systems, films under biaxial tensile strain exhibit the fastest reaction kinetics, in agreement with previous reports. Films under tensile biaxial strain also possess the lowest electron occupation in the  $d^2$  orbitals, suggesting the orbital occupation plays an important role in determining the electrocatalytic properties of perovskite cathodes.<sup>2</sup>

1. R. Gao *et al.* *Adv. Mater.* 33, 2100977 (2021).

2. A. Fernandez *et al.* *Adv. Energy Mater.* 2102175 (2021).

8:40am C3-1-ThM-3 **Halide Perovskites: Advanced Photovoltaic Materials Empowered by a Unique Bonding Mechanism**, Matthias Wuttig

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Outstanding photovoltaic (PV) materials combine a set of advantageous properties including large optical absorption and high charge carrier mobility, facilitated by small effective masses. Halide perovskites ( $\text{ABX}_3$ , where X = I, Br or Cl) are among the most promising PV materials. Their opto-electronic properties are governed by the B-X bond, which is responsible for the pronounced optical absorption and the small effective masses of the charge carriers. These properties are frequently attributed to the  $ns^2$  configuration of the B atom, i.e. Pb 6s<sup>2</sup> or Sn 5s<sup>2</sup> ('lone-pair') states. Our analysis of the PV properties in conjunction with a quantum-chemical bond analysis reveals a different scenario. The B-X bond differs significantly from ionic, metallic or conventional 2c-2e covalent bonds. Instead it is better regarded as metavalent, since it shares about one p-electron between adjacent atoms. The resulting s-bond, formally a 2c-1e bond, is half-filled, causing pronounced optical absorption. Electron transfer between B and X atoms as well as lattice distortions open a moderate band gap resulting in charge carriers with small effective masses. Hence metavalent bonding explains favorable PV properties of halide perovskites, as summarized in a map for different bond types, which provides a blueprint to design PV materials.

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*Halide perovskites: third generation photovoltaic materials empowered by an unconventional bonding mechanism*

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