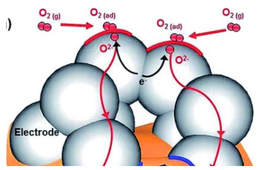
Engineering the Surface of Perovskite Catalysts with Metal Oxide Promoters

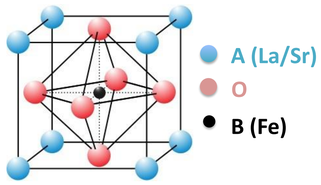
Yuan Cheng, Liang Zhang, Aleksandra Vojvodic, John M. Vohs , and Raymond J. Gorte

University of Pennsylvania, Department of Chemical and Biomolecular Engineering, Philadelphia PA

Perovskite Cathodes in SOFCs



Kim, J. H., & Manthiram, A. (2015). Layered $LnBaCo_2O_{5+\delta}$ perovskite cathodes for solid oxide fuel cells: an overview and perspective. *Journal of Materials Chemistry A*, *3*(48), 24195-24210.

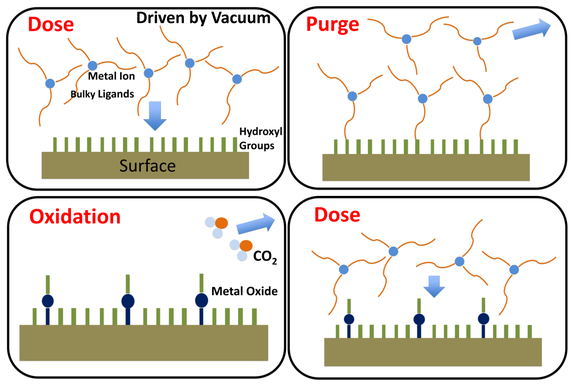


http://www.cei.washington.edu/education/science-of-solar/perovskite-solar-cell/

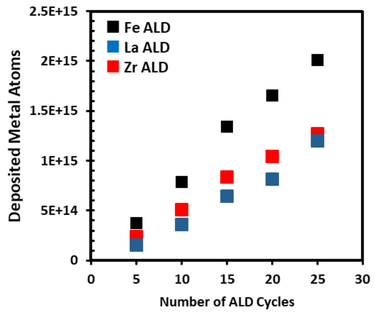
- Solid Oxide Fuel Cells (SOFCs) are high-temperature electricity generating devices
- Oxygen reduction happens at the cathode side
- $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ *(LSF)* is one of the most commonly used perovskite phase (ABO_3) cathodes

Atomic Layer Deposition (ALD)

- ALD is a self-limited, film-growth method
- Changes only the surface composition but not the surface area



Linear ALD Growth Curve

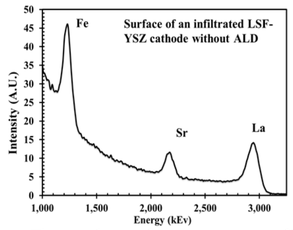


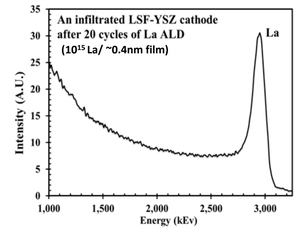
Typical Growth Rate Calculated from gravimetric measurement:

La	4.8×10^{13} metal atoms cm^{-2} $cycle^{-1}$	$La(THMD)_3$
Zr	5.1×10^{13} metal atoms cm^{-2} $cycle^{-1}$	$Zr(THMD)_3$
Fe	8.1×10^{13} metal atoms cm^{-2} $cycle^{-1}$	Ferrocene

*1 monolayer is considered to have ~10^{15} atoms

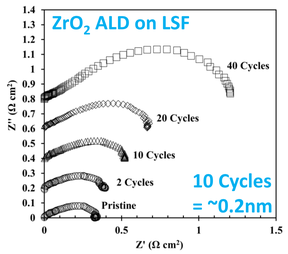
Surface Study with Low Energy Ion Scattering (LEIS)

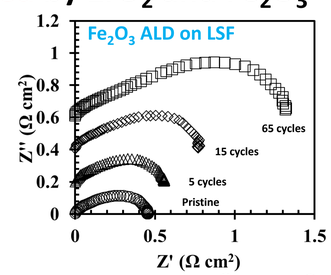


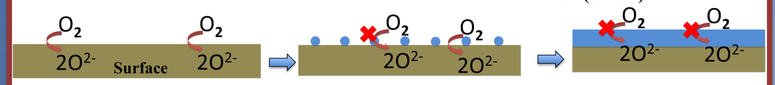


- The surface of the porous scaffold has been uniformly covered with La_2O_3 after 20 ALD cycles
- In a separate study, 5 cycles of La ALD was not enough to cover the whole sample surface
- Combined with gravimetric measurement: One monolayer coverage of La_2O_3 is approximated achieved around 10 ALD cycles

Surface Reaction Blocked by ZrO_2 and Fe_2O_3



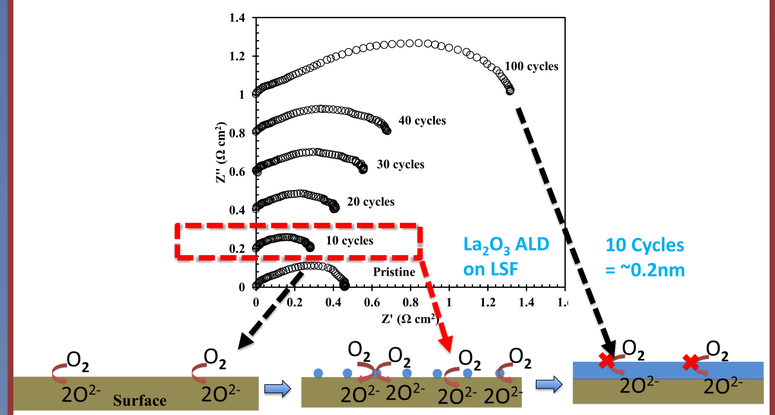




Pristine surface | Submonolayer coverage | > 1 monolayer

- Surface kinetics slows as coverage increases

Surface Reaction Promoted by La_2O_3



Pristine surface | Submonolayer coverage | ~ 2 nm film

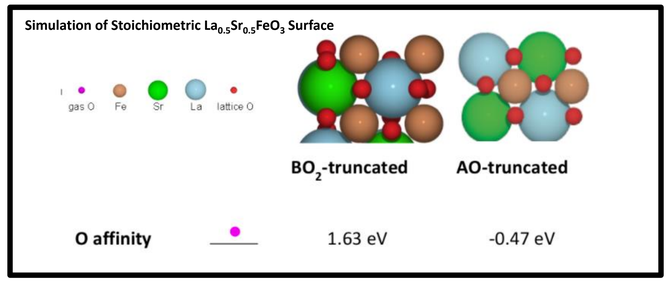
Surface Kinetics Promoted✓

Surface Modification with Different Metal Oxides

Metal Elements of Deposited Metal Oxide		Change in Surface Resistance After 5 cycles
A-Site Element	La	-43%
	Pr	-52%
	Sr	-53%
	Ca	-47%
Non-A-Site Element	Mn	72%
	Fe	28%
	Zr	24%

- Surface modification with A-site metal oxides (AO) are effective, but not with other metal oxides

AO Has Larger Oxygen Affinity



- Having atoms of AOs on BO_2 surface introduces more oxygen affinity to the surface, thus promoted surface reaction rate
- However, stacking AOs on perovskite surface will eventually block oxygen ion transportation pathways, leading to low surface kinetics

Acknowledgement

- Vojvodic research group (U. Penn.)
- Dr. Steve McIntosh (Lehigh)
- Julian Paige and Danny Sun
- DOE-NETL Funding, Grant DE-FE0023317