Engineering the Surface of Perovskite Catalysts with Metal Oxide Promoters

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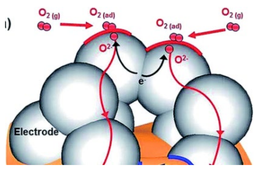
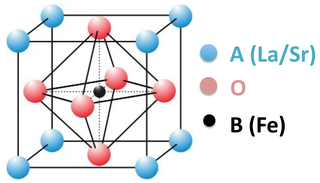
Perovskite Cathodes in SOFCs



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.

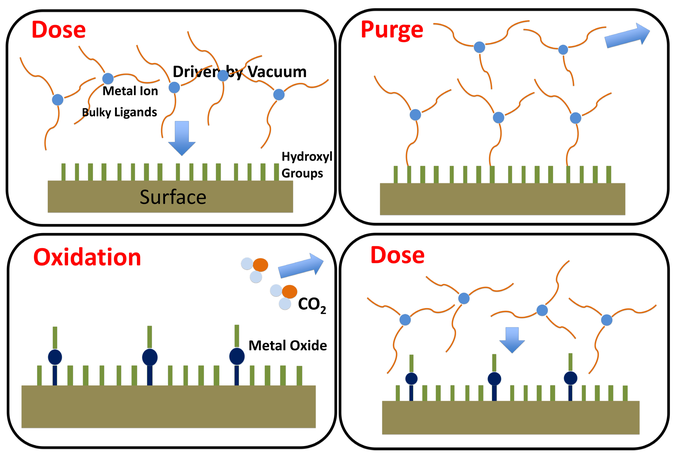


http://www.cei.washington.edu/education/science-of-solar/perovskite-solar-cell/

- 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

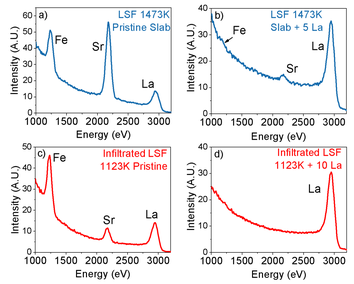


ALD Growth Rate

Element	Precursor	Assumed Metal Oxide Composition	Growth Rate Per Cycle (metal atoms cm^{-2})
La	$La(TMHD)_3$	La_2O_3	$4.8 \cdot 10^{13}$
Pr	$Pr(TMHD)_3$	Pr_2O_3	$5.4 \cdot 10^{13}$
Sr	$Sr(TMHD)_2$	SrO	$5.3 \cdot 10^{13}$
Ca	$Ca(TMHD)_2$	CaO	$6.9 \cdot 10^{13}$
Mn	Mn(TMHD)3	Mn_2O_3	$5.1 \cdot 10^{13}$
Zr*	$Zr(TMHD)_4$	ZrO_2	$5.1 \cdot 10^{13}$
Fe*	Ferrocene	Fe_2O_3	$8.4 \cdot 10^{13}$

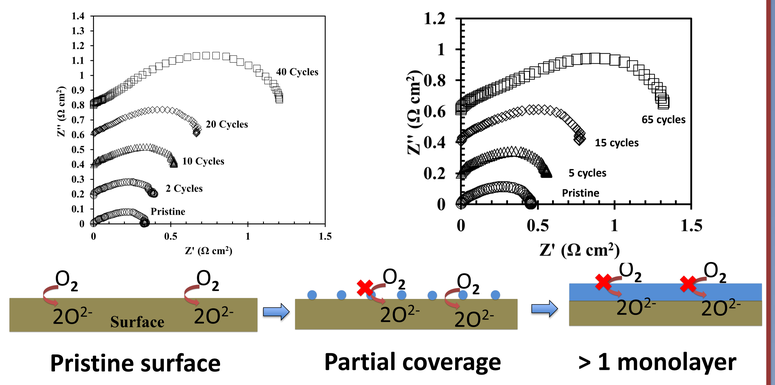
- Growth rate differ with ligand size
- Approximately, 10 ALD cycles ~ 1 monolayer coverage

LSF Surface Study with LEIS



- Pristine surface composition is affected by preparation temperature
- ALL three metal elements are on the surface
- 5 ALD cycles cannot cover surface
- 10 ALD uniformly cover all the surface

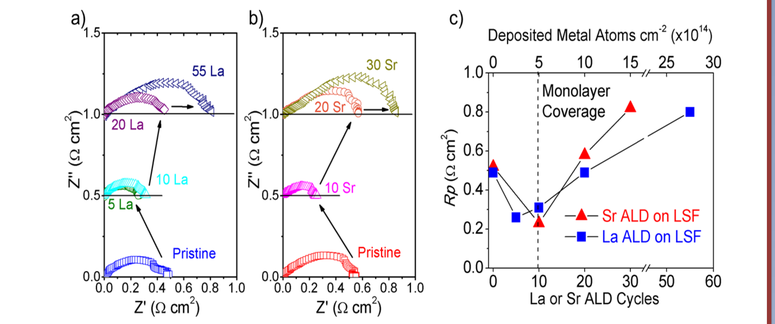
LSF Surface Reaction Blocked by ZrO_2 and Fe_2O_3



Pristine surface — Partial coverage — > 1 monolayer

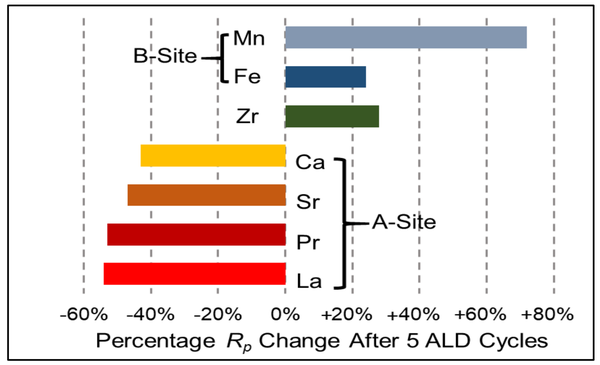
- Surface kinetics slows as coverage increases

LSF Surface Reaction Promoted with La_2O_3 and SrO



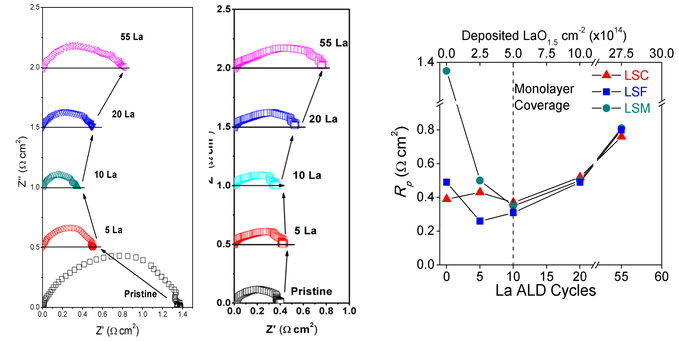
Pristine surface — Partial coverage, Surface Kinetics Promoted✓ — ~ 2 nm film

LSF Surface Modification with Different Metal Oxides



- Surface modification with A-site metal oxides (AO) are effective, but not with B-Site Oxides (BO_2) or inert oxides

Different Effects on LSM and LSCo



- Surface modification of La_2O_3 made LSM significantly better, but not LSCo
- LSCo is much easier to reduce -- has much more surface vacancies than LSM
- Surface improvement effect via ALD is due to an increment in surface vacancies

Acknowledgement

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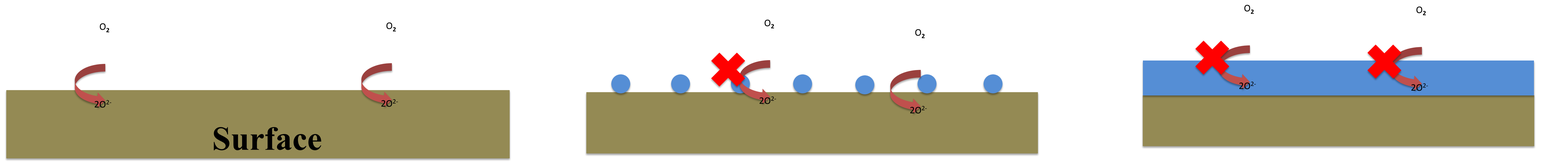
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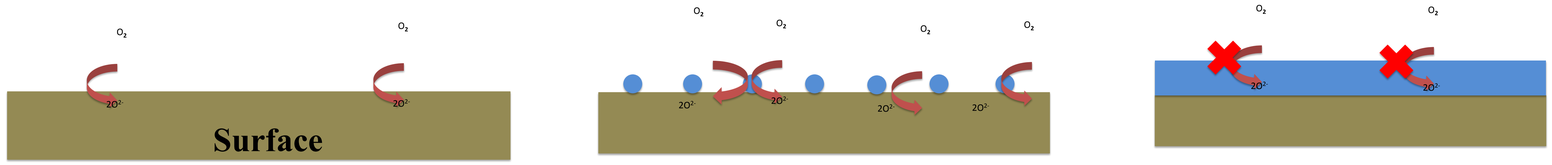
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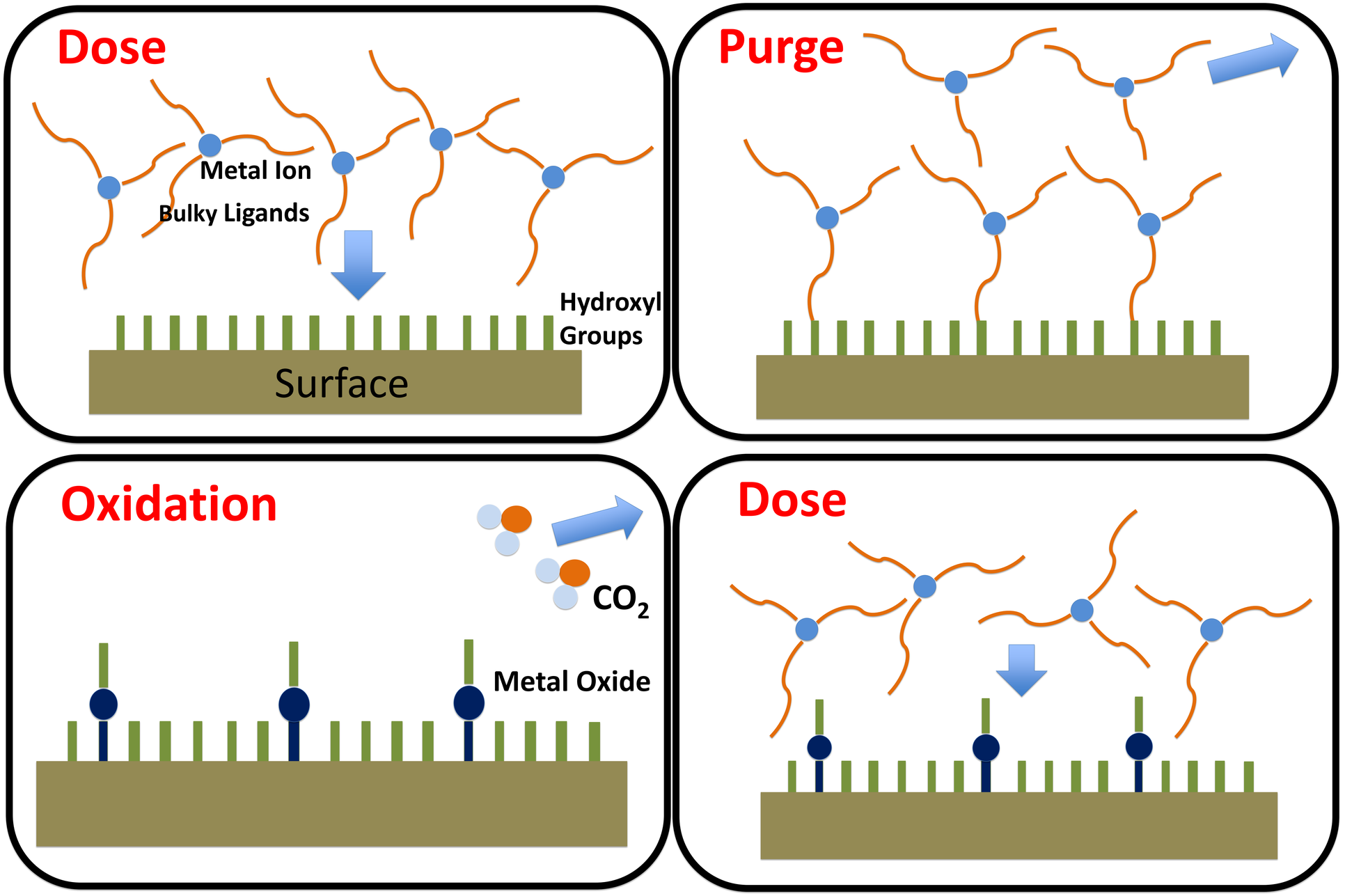
Dose
Metal Ion
Bulky Ligands
Hydroxyl
Groups
Surface
Purge
Oxidation
CO_2
Metal Oxide
Dose