Designing the electronic structure and reactivity of metal oxides through strain, d-band filling and oxidation state

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Why do we need to control metal oxide reactivity?

• Applications of oxides
  – Catalysis
  – Energy
  – Electronics
  – Thermal barrier coatings
  – Corrosion resistant coatings
  – Paints
  – Personal products

• In some applications we want reactivity, in others we do not

• How do we design materials that do what we want?
Understanding the reactivity of \(d\)-metals

- **Au** - Noble metals
  - Very weak bonding

- **Ni, Pt**, transition metals
  - Strong bonding

- \(d\)-band properties dominate the trends in adsorption behavior
- Changing \(d\)-band properties changes adsorption behavior
Alloying leads to combinations of strain and ligand effects

Straining metal films leads to changes in $d$-band width

“Ligand” effects lead to changes in $d$-band width

We are at a stage where we know a lot about metals and their reactivity. So far, nothing like this exists for metal oxides.


Why metal oxides are harder than metals

- Many more different crystal structures and stoichiometries
- Many different defect and oxidation states that can be determined by the environment
- More complex bonding – Covalent and ionic
- Different adsorption mechanisms

Are there simple concepts in oxide reactivity that are analogous to metals?
- Can strain be used to control reactivity?
- What electronic structure features dominate trends in reactivity?
Part I – Reactivity of supported thin oxide films

- The conductivity of thin oxide films varies in reactive environments (gas sensors)
- Conductivity is related to concentration of oxygen vacancies
- Sensitive probe to surface reactivity
- Focus here on La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSM) films
  - Perovskite used in solid oxide fuel cells, catalysis

Thin films synthesized by pulsed laser deposition

$g(t) = \frac{(\sigma_t - \sigma_{\text{initial}})}{(\sigma_{\text{final}} - \sigma_{\text{initial}})} = 1 - \exp\left(-\frac{t}{\tau}\right) = 1 - \exp\left(-\frac{k_{\text{chem}}}{L}t\right)$

Heteroepitaxial growth of oxides to introduce strain

- Film
  - $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) $a=3.876$ Å
- Single crystal substrates
  - $\text{SrTiO}_3$ (100) $a=3.905$ Å
    (heteroepitaxial growth leads to tensile strain)
  - $\text{NdGaO}_3$ (110) $a=3.864$ Å
    (heteroepitaxial growth leads to compressive strain)
- Grow films with varying thickness
  - Films are smooth and polycrystalline
Characterizing the strain in thin films

- XRD rocking curves characterize the lattice parameters of the films
- FWHM of rocking peaks related to defect density
- Thin films (50 nm) are epitaxial and fully strained at the substrate lattice constant
- Thick films relax by defect formation
Strain has a big impact on reactivity

- Tensile strained films have larger $k_{chem}$ (higher O2 exchange rate) than compressively strained films
- Order of magnitude difference!

The question is: how do we understand why?
1. Are vacancies easier to form under strain?
2. Is adsorption more favorable under strain?
3. Is this unique to LSM? How would changing the composition affect reactivity?
Part II – Computational investigations of oxide reactivity

• Trends in properties of cubic $3d$-perovskites
  – Composition
    • $B = \text{Sc through Cu}$
    • $\text{LaBO}_3 (B^{+3})$
    • $\text{SrBO}_3 (B^{+4})$
  – Strain
    • At lattice constants of ±5%, ±2.5% and DFT equilibrium volumes
  – Electronic structure
    • Properties of the atom-projected $d$-band density of states
  – Reactivity
    • Dissociative adsorption energy
    • Surface oxygen vacancy energy

• DACAPPO (DFT/US-PP/planewaves)
  – No hybrid functionals or DFT+U, no spin-polarization
Oxide reactivity with oxygen

- Adsorption and vacancy formation energies are reactivity prototypes.
- We anticipate that trends in these prototype reactions will be representative of other types of reactivity.

\[
\begin{align*}
\text{Clean slab} & \quad \text{Reactive surface} \\
\text{slab} + \frac{1}{2} \text{O}_2 & \rightarrow \text{slab} + \text{O}^* \\
\Delta E_{\text{ads}} (eV) & = E_{\text{slab}+O} - E_{\text{slab}} - \frac{1}{2}E_{\text{O}_2} \\
\text{slab} & \rightarrow \text{slab} + \text{vac} + \frac{1}{2} \text{O}_2 \\
\Delta E_{\text{vac}} & = E_{\text{slab}+\text{vac}} + \frac{1}{2}E_{\text{O}_2} - E_{\text{slab}}
\end{align*}
\]
Perovskite electronic structure evolution with strain

- Strong hybridization between B atom $d$-orbitals and O $s,p$ orbitals
- Convergence of bands occurs as the B-atom $d$-band filling increases
- Tensile strain causes band narrowing
$d$-band widths of $B$ atom in strained perovskites

$$w_d \propto \frac{r_d^{2/3}}{d^{2/7}}$$

– $d$-$s/p$ orbital coupling

• The strain dependence of the bulk $d$-band width depends on the size of the $B$ atom
Pseudo-rectangular band model for perovskite $d$-band

- The ABO$_3$ series shows a $w_d/\varepsilon_d$ correlation consistent with a rectangular band model
- Nearly constant $d$-band filling observed
- This is the same behavior as observed in metals

Electronic structure-reactivity correlations of adsorption energy

- For most perovskites the adsorption energy is related to the $d$-band center of the $B$-atom
- Higher oxidation states tend to have weaker adsorption energies
- LaScO$_3$ and SrTiO$_3$ are different
  - Probably an error in the pseudopotentials which do not have semicore states
Chemical correlations in reactivity

- Adsorption is strongest on materials where oxygen vacancies are hard to make.
- Correlated properties make it difficult to identify key factor(s) in reactivity.
- We know other correlations also exist.
Correlations can limit performance
Example: oxygen evolution on oxides

\[
2H_2O \rightarrow HO^* + H_2O + H^+ + e^- \\
HO^* + H_2O + H^+ + e^- \rightarrow O^* + H_2O + 2H^+ + 2e^- \\
O^* + H_2O + 2H^+ + 2e^- \rightarrow HOO^* + 3H^+ + 3e^- \\
HOO^* + 3H^+ + 3e^- \rightarrow O_2 + 4H^+ + 4e^- \\
2H_2O \rightarrow 4(H^+ + e^-) + O_2
\]

• Correlations in reaction energies lead to limits in reactivity

Conclusions

• The bulk electronic structure of perovskite $B$-atoms is reasonably modeled as a rectangular band

• $d$-band filling is the dominant factor in determining reactivity, followed by oxidation state

• The oxygen adsorption energy and vacancy formation energies are correlated in this class of perovskites

• Correlations limit degrees of freedom for materials design

• The outlook for systematically understanding oxide reactivity is very bright!