High Conductivity Oxides for Solid Oxide Fuel Cells

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How do Solid Oxide Fuel Cells Work?

Porous cathode reduces $O_2$ from flowing air, currently $LaMnO_3$, $La_{1-x}Sr_xMnO_3$

Reduced $O^{2-}$ conducts through ionic conducting electrolyte, currently yttria-stabilized-zirconia (YSZ)

Fuel is oxidized at anode, releasing electrons to circuit, currently Ni-YSZ

Operating Temps: 650-800°C
SOFCs will solve the energy crisis

- Stand-alone chemical-to-electrical efficiency between 45-65%, twice that of internal combustion engines
- Can be used in combined heat power applications for higher efficiency ~75%
- Facilitate the transition from fossil fuel economy to hydrogen based economy
SOFCs still face obstacles

- Electrodes must be porous to make up for poor conductivity, reactions happen at triple phase boundary
- Electrodes must be chemically compatible at electrode/electrolyte interface
- Electrodes sinter at high temperature, ruin porosity
- Need matching CTE for mechanical durability

Interconnect must be stable at high temperature, as well oxidizing and reducing environments

To lower operating temperature, need better electrolyte
High-temperature Bi$_2$O$_3$ (>730°C) has potential as new electrolyte, higher conductivity than currently used YSZ electrolyte.

- Naturally occurring mineral *bismite*
- Complicated monoclinic structure
- Exhibits no ionic conductivity

- Defect fluorite structure with 25% of anion sites vacant
- High ionic conductivity due to large concentration of vacancies
- Bi$^{3+}$ in a fluorite lattice
Isovalent lanthanide-doping stabilizes the $\delta$-$\text{Bi}_2\text{O}_3$ structure to lower temperature (~500°C)

- Larger cationic radii destabilizes cubic structure at lower temperatures (similar to Bi$^{3+}$)
Oxygen vacancy ordering below 600°C decreases conductivity

- Oxygen vacancies order along body diagonal, <111>, across octahedral sites, and <110> next to Bi cations due to lone pair, high polarizability
- Higher concentrations of dopant increasing aging effect

Vacancy ordering is accompanied by oxygen anion positional ordering in 32f interstitial sites

- In ordered structure oxygen ions have high occupancy of 32f interstitial sites along <111> direction towards empty octahedral site (center of unit cell)
- Observed in TEM diffraction, neutron diffraction
Ion conduction occurs through empty octahedral site, limited by interstitial occupancy and anion ordering.

- Disordered structure has more jump directions, 8c site is unstable, interstitials can only jump to octahedral site.
- Occupation of interstitial sites decreases activation energy.

Oxygen sublattice ordering is limited by polarizability of cations

- Larger atomic radius implies higher polarizability, Bi$^{3+}$ has lone pair, destabilizes <111> ordering of vacancies
- Dy has lowest occupancy of 32f sites, maintains disorder after annealing at 500°C
- Lower concentration of dopant cations allows for structure more similar to δ-Bi$_2$O$_3$, higher conductivities

Use of two dopants allows for lower dopant concentration, higher conductivities

Conclusions

• $\delta$-Bi$_2$O$_3$ promises very high conductivities, need to stabilize the high temperature structure below transformation temperature

• Structure experiences anion vacancy ordering at low temperatures, which can be limited by a low concentration of large radii dopant

• Double-doping allows for reduced concentration of dopant necessary to stabilize cubic structure

• Highest conductivity of ceramic electrolyte achieved with Dy$_{0.08}$W$_{0.04}$Bi$_{0.88}$O$_{1.56}$