Understanding catalytic properties of $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ for the air electrode of Protonic Ceramic Electrolysis Cell using Density Functional Theory calculations

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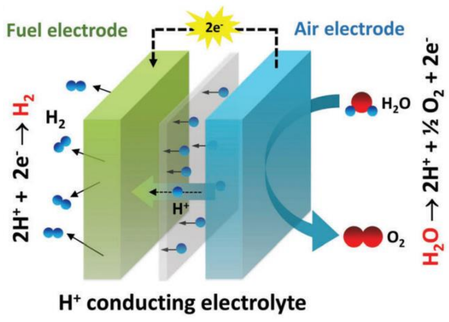
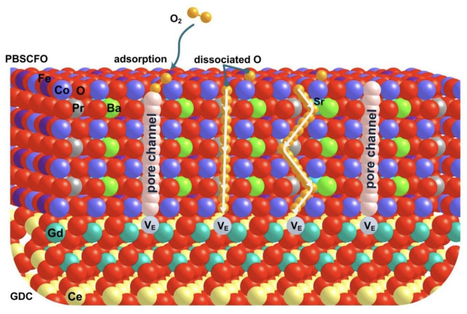
Abstract

$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$(PBSCFO) is a widely used air electrode material for protonic ceramic electrolysis cells (PCEC). However, the detailed reaction mechanism for the oxygen evolution reaction (OER) via proton and oxygen anion conductions is not well known. In this study, we employ periodic density functional theory (DFT) calculations to identify the detailed reaction mechanism, and investigate the effect of the oxygen vacancy concentration on ion conductivities and OER activities of the PBSCFO material.

Introduction





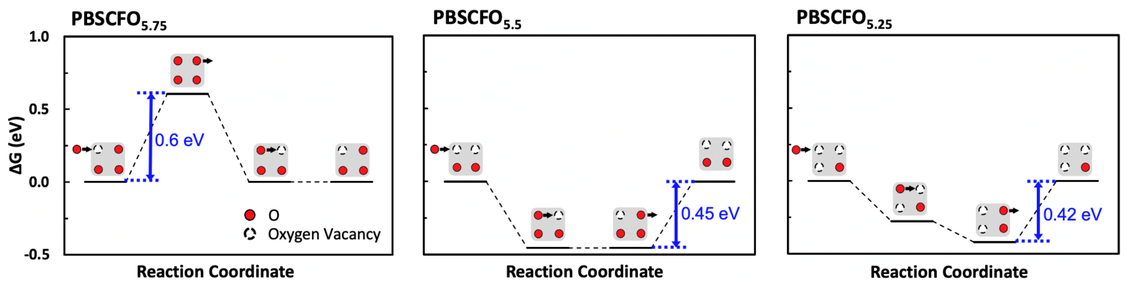
- Air electrode for PCEC should show high ion conductivity and OER activity for overall cell performance.
- PBSCFO is known to naturally form oxygen vacancies which influence oxygen ion conductivity.

Computational Methods

- VASP software package
- Spin-polarization method
- RPBE functional (GGA)
- Energy cutoff of 500 eV
- EDIFF of 1×10^{-4} eV
- 4×4×1 Monkhorst-Pack *k*-point mesh

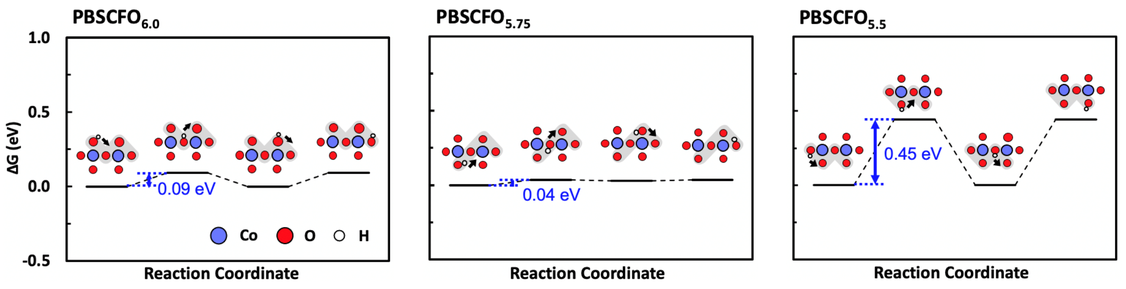
Ion Conductivity

Oxygen Anion Conductivity



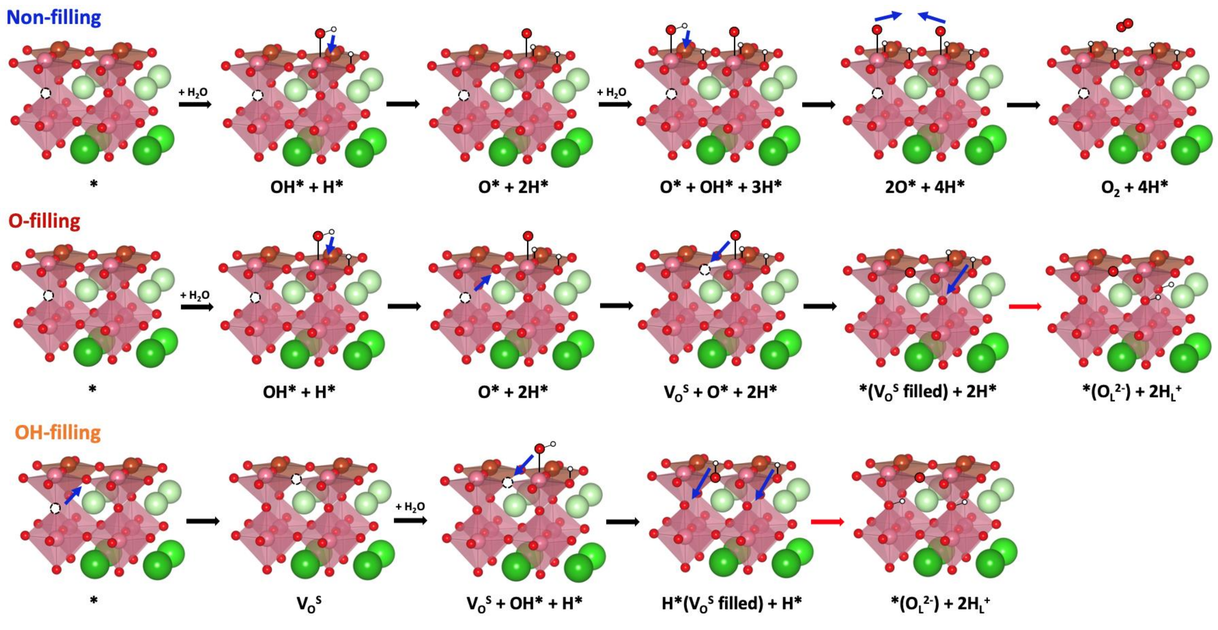
- PBSCFO with more V_O ($PBSCFO_{5.5}$) shows better oxygen ion conductivity.
- Oxygen vacancy is effective for oxygen ion conduction.

Proton Conductivity

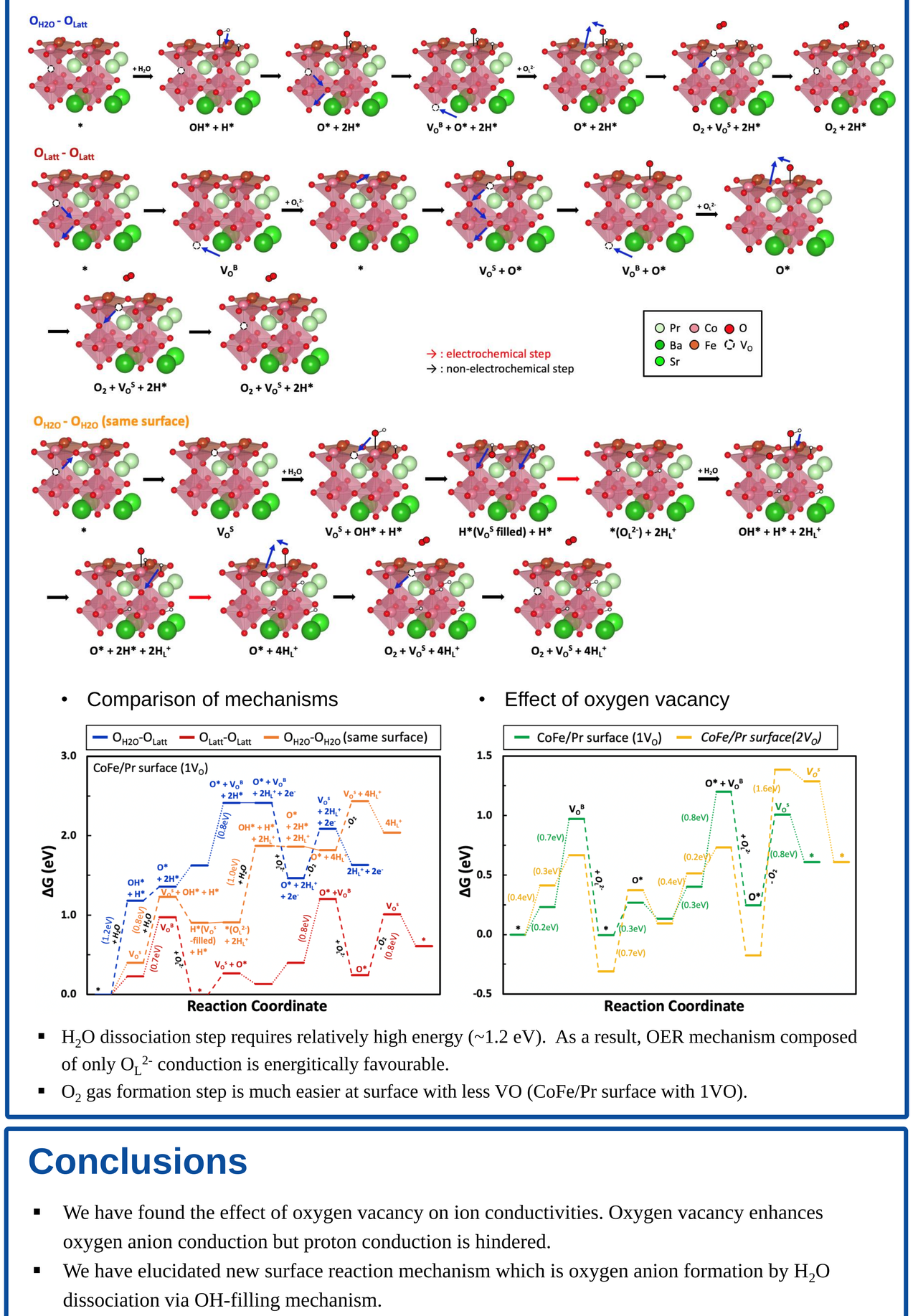


- Proton conductivity suddenly decrease with $2V_O$ ($PBSCFO_{5.5}$).
- This is a consequence of relatively low H^+ adsorption energy of O site which is adjacent to all $2V_O$.

Oxygen Anion Formation



Oxygen Gas Evolution Mechanism



- Comparison of mechanisms

- Effect of oxygen vacancy

- H_2O dissociation step requires relatively high energy (~1.2 eV). As a result, OER mechanism composed of only O_L^{2-} conduction is energitically favourable.
- O_2 gas formation step is much easier at surface with less VO (CoFe/Pr surface with 1VO).

Conclusions

- We have found the effect of oxygen vacancy on ion conductivities. Oxygen vacancy enhances oxygen anion conduction but proton conduction is hindered.
- We have elucidated new surface reaction mechanism which is oxygen anion formation by H_2O dissociation via OH-filling mechanism.
- These oxygen anions participate in OER mechanism while conducting inside the PBSCF. With participation of oxygen anion inside, oxygen formed at the surface actually comes from lattice oxygen as H_2O dissociation is energetically unfavorable. As a result, at the surface of PBSCF, OER is proceeded with consistently exchanging oxygen between the lattice and provided steam.