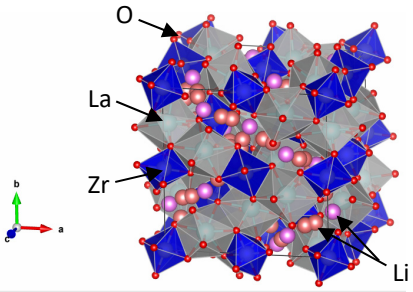
Estimation of stability of LLZO by ab-initio calculation (effect of the substituted element)

It's known that $Li_7La_3Zr_2O_{12}$ (LLZO) for all-solid LIB has various electrochemical properties like impedance and ion conductivity due to its dopants which involves in its surface reducibility. This is an example of considering why such differences appear among these elements by ab-initio calculation.

1. Previous experimental reports about effect of doped elements into LLZO



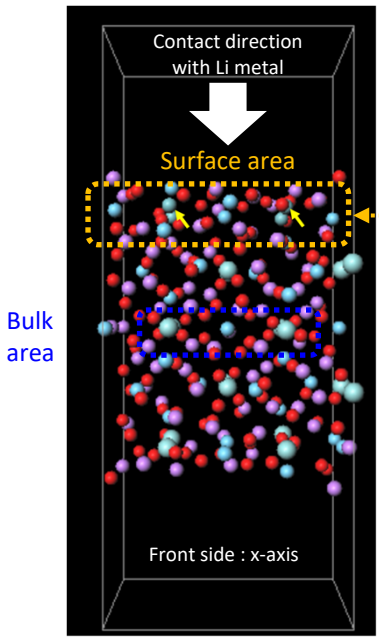
【cubic-LLZO】
Li (24d site● /96h site●) : substitution with Al, Ga
Zr (16a site●) : substitution with Ta, Nb

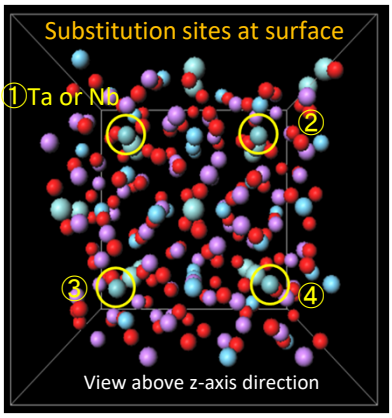
【previous reports by experimental analysis】
A cell with Nb-doped one had higher resistance. Its Nb and Zr were reduced more at surface to Li metal than Ta-doped one and Al-doped one.
(DOI:10.1002/aenm.201803440)

2. Thermodynamic stability and reducibility about LLZO by DFT calculation

Model: substituting Zr sites with Ta or Nb in LLZO (surface or bulk) by 20% referring to previous reports
※to estimate its thermodynamic stability by total energy and its reducibility by density of states (DOS)

Thermodynamic stability



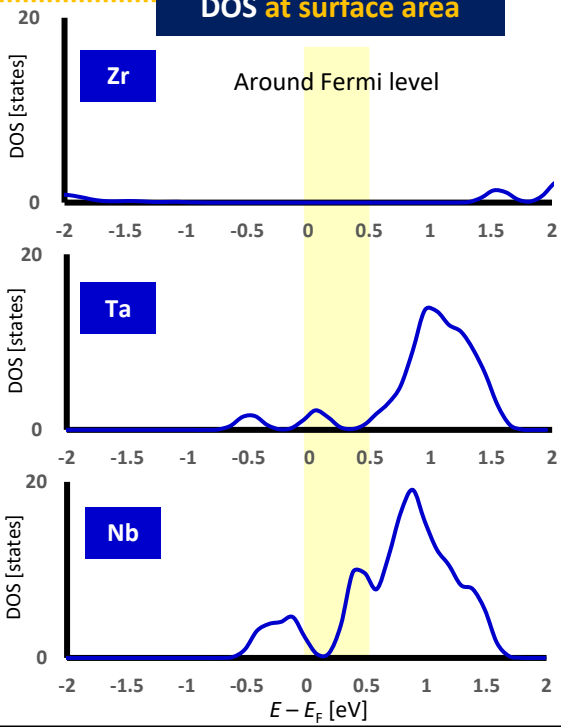


Higher ⊿E means that dopant is more stable around surface by following difference in total energy between surface and bulk.

⊿E=E(bulk)-E(surface)
⊿E(Ta) : 0.19 eV < ⊿E(Nb): 2.2 eV

- Ta : Not big difference between bulk and surface
- Nb : More stable at surface than in bulk

DOS at surface area



Integrated DOS values in 0-0.5 eV(unoccupied orbitals)
Zr:0 < Ta: 0.49 < Nb:2.0

Nb seems to be reduced easier because it prefers to exist around surface and its orbitals occupy around Fermi level.

DFT is useful to predict or analyze trends of thermodynamic stability and reducibility about crystal solid electrolyte to Li metal before and/or after experiments .

Toray Research Center, Inc.