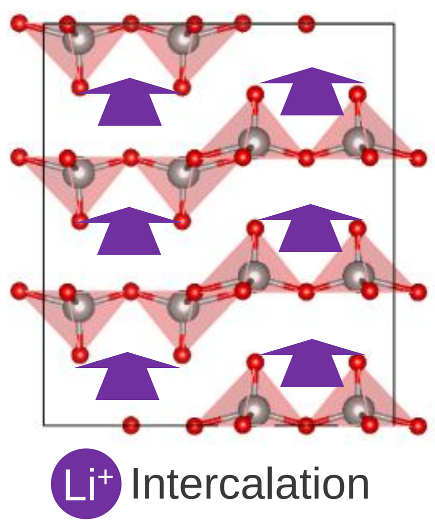
Effect of Sn Doping on Li Intercalation in V_2O_5 Cathodes of Li-Ion Batteries: A First-Principles Study

Lappawat Ngamwongwan[a], Ittipon Fongkaew[a], Sirichok Jungthawan[a], Anchalee Junkaew[b], Pussana Hirunsit[b], Suwit Suthirakun[c,*]

[a]School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand
[b]National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani, 12120, Thailand
[c]School of Chemistry, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand
*E-mail: suthirak@sut.ac.th

Introduction

V_2O_5 cathodes of Li-ion batteries



- Layered structures of V_2O_5 → accommodate Li^+
- It can be used as cathode materials.

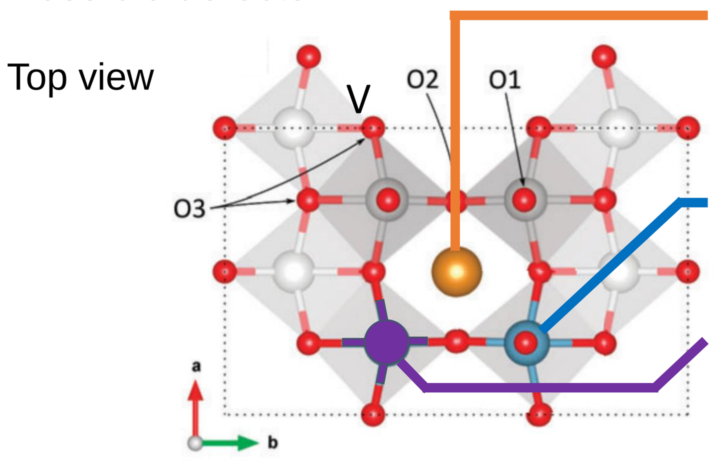
High theoretical capacity 442 mAh g^{-1} (commercial $LiCoO_2$: 272 mAh g^{-1})

Poor structural stability
Low electronic and ionic conductivity

Sn doping Exhibits better electrochemical performances
I) higher capacity II) faster kinetics III) better cyclability

The role of Sn doping is still unclear such as the defect site is still under debate.

Possible defects:



1. Sn interstitial
Y. N. Li, J. Phys. Chem. C 2013, 117, 23507
S. W. Le, Solid State Ion. 2019, 341, 115028
2. Sn substitution for V
L. D. Xing, J. Mater. Chem. A 2019, 7, 25993
3. Sn substitution for VO group
Z. Y. Li, Electrochim. Acta 2016, 222, 1831

Objective

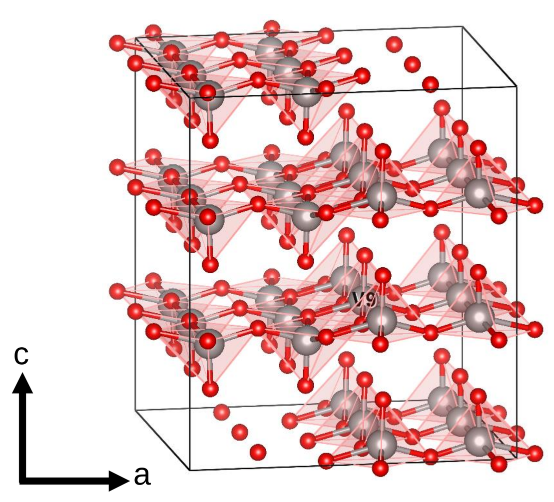
To explore the effect of Sn doping on the V_2O_5 electrode mainly defect/carrier formation and Li-electron transport based on atomistic model calculations.

Methodology

1. Create and optimize three possible Sn-related defects.
2. Calculate defect formation energy in experimental condition

$$E^f(X^q) = E_{tot}(X^q) - E_{tot}(\text{bulk}) - \sum_i n_i\mu_i + q(E_{vbm} + E_F) + E_{corr}$$

3. Estimate defect concentration
   Statistical model with charge neutrality
4. Identify the most dominant defects
5. Study charge carrier transport
   via electron polaron hopping
6. Study Li transport



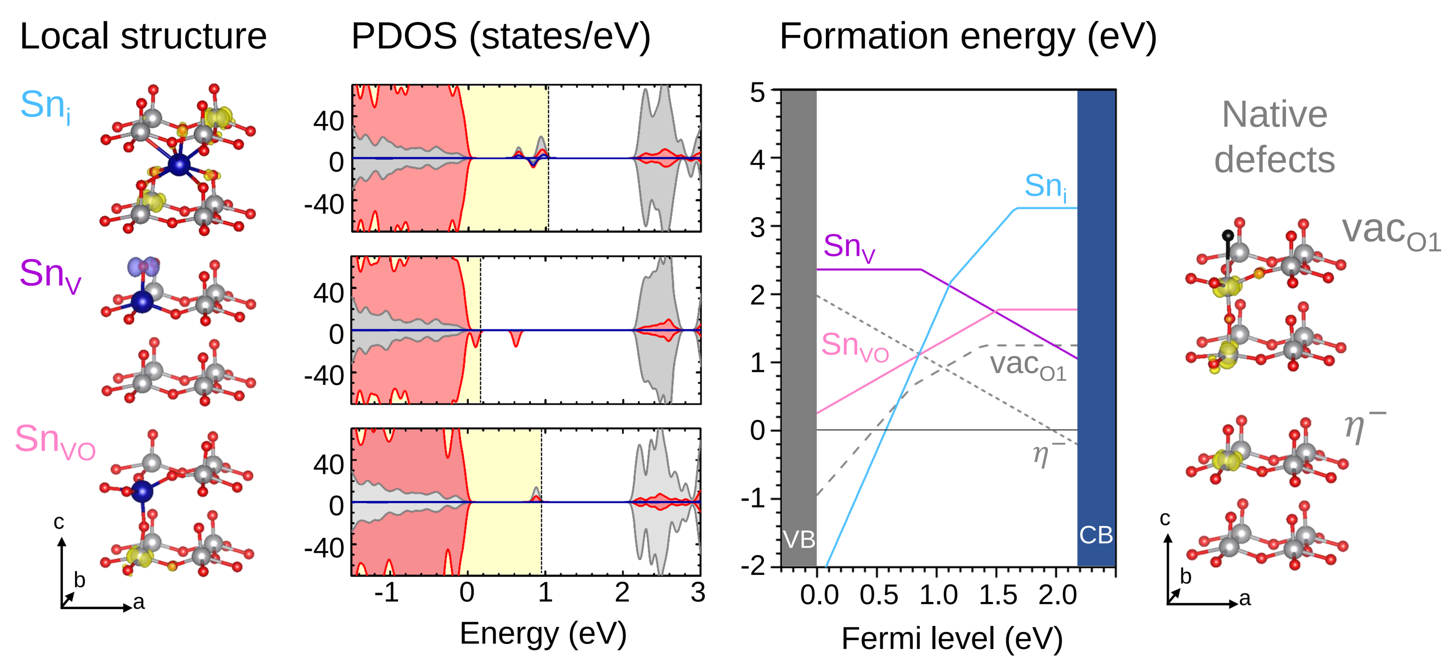
1x3x3 supercell
126 atoms with PBC

Computational details

- DFT calculations: VASP
- Spin-polarized PBE+U; $U_{3d}(V)$ = 3.5 eV
- Van der Waals correlation: optPBE-vdw
- Transport calculations: CINEB + LE methods

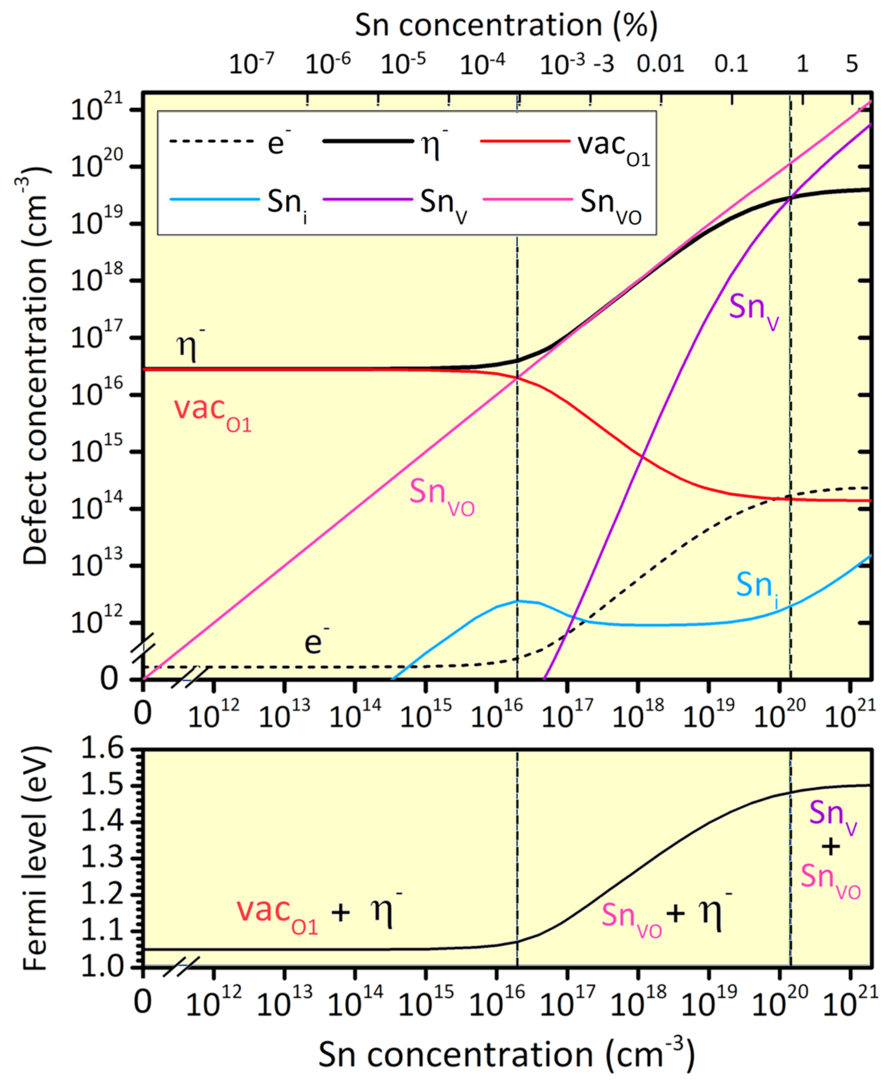
Results and discussion

Defect structures and their formation energies

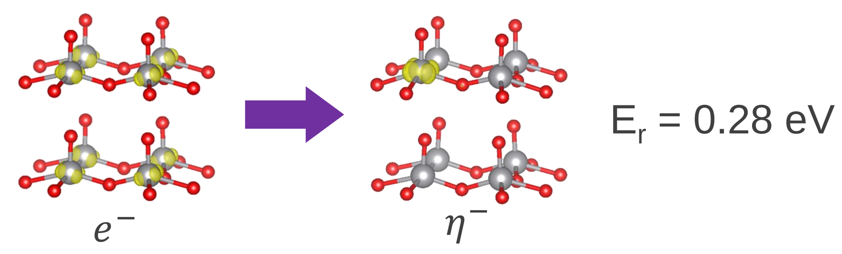


Results and discussion

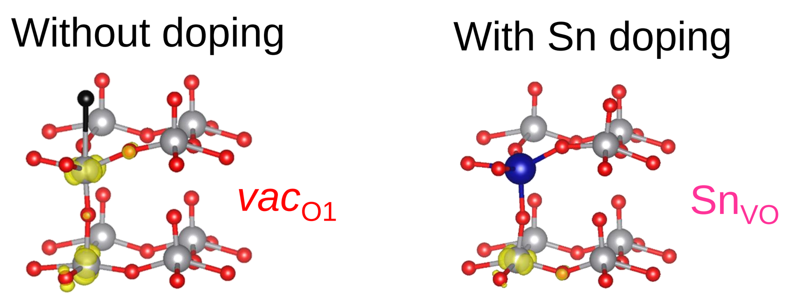
Defect concentrations under thermodynamic equilibrium



The electron prefers to localize as polaron (η^-) rather than free electron (e^-).



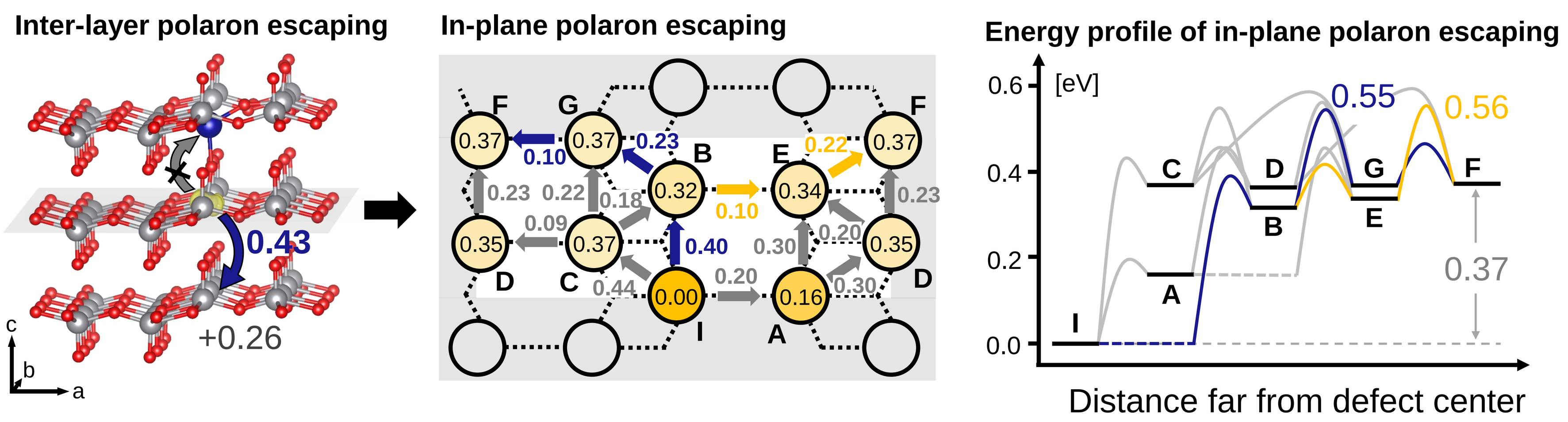
The η^- could act as charge carriers.

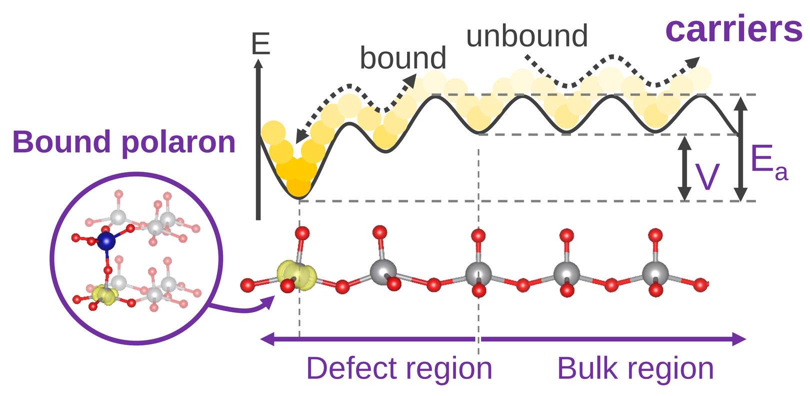


C_0 ~ 10^{16} cm^{-3} C_0 ~ 10^{19} - 10^{21} cm^{-3}

Both defects can provide η^- but they may be trapped at defect center.

Polaron trapping in Sn_{VO}

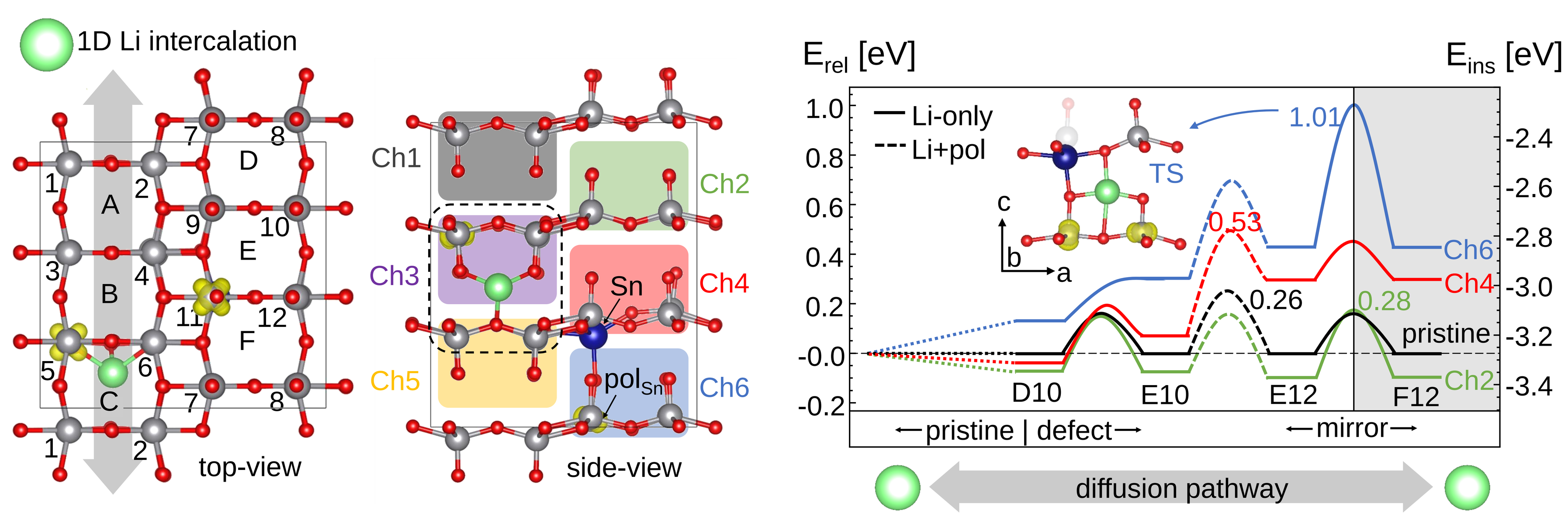




Systems	V (eV)	E_a (eV)	C_0 (cm^{-3})
Sn_{VO} (1%)	0.37	0.55	$1x10^{20}$
vac_{O1}	0.41	0.60	$3x10^{16}$
pristine	0.00	0.21	$4x10^{4}$

Polaron in Sn_{VO} is trapped by the potential (V) of 0.37 eV and the effective barrier (E_a) of escaping outward the defect center is 0.55 eV, which is slightly less than those in vac_{O1}.

Li-coupled polaron transport in Sn_{VO}



The Sn defect center could slow down Li-coupled polaron diffusion with effective barrier of 1.01 eV in Sn-channel and 0.55 eV in pol_{Sn} channel as compared to pristine V_2O_5 (0.26 eV).

Conclusions

- Sn dopant incorporates in the form of Sn_{VO}.
- The Sn_{VO} generates more bound polarons concentration as the Sn doping concentration increase. These polarons could be thermally activated and mobile as charge carrier of the system, resulting in improved electronic conductivity due to more numbers of charge carriers.
- The Sn_{VO} acts as a repulsion center and may not enhance Li-coupled polaron transport.

Acknowledgements

- Computational resources from Suranaree University of Technology and NSTDA Supercomputer Center
- Funding from Development and Promotion of Science and Technology Talents Project (DPST) and National Research Council of Thailand (NRCT)