6. Computational Design of Energy-related Materials

Contents

- 6.1 Atomistic Simulation Methods for Energy Materials
- 6.2 ab initio design of photovoltaic materials
- 6.3 Solid Ion Conductors for Fuel Cells
 - 6.3a Proton transport through perovskite oxides (ABO3)
 - 6.3b Oxide-ion transport through apatite silicates
 - 6.3c Cathode Materials for Lithium Batteries
- 6.4 Water splitting with Photocatalysis and Hydrogen Storage Materials
- 6.5 Thermoelectric Materials

6.1 Atomistic Simulation Methods for Energy Materials

Shell model (GLUP), MD (DL_POLY), ab initio DFT (VASP, CASTEP) Typical option for first-principles calculation: (1) Calculations are carried out using supercells composed of about 16 chemical units; (2) Nuclear motions are assumed to be separable from the electronic motions within the Born-Oppenheimer approximation and are treated classically; (3) Electronic effects are treated within density functional theory (DFT) using the local density approximation (LDA or GGA) form of the exchange-correlation functional. These calculations give us the total energies corresponding to the electronic ground state $E({R_a})$ corresponding to the nuclear coordinates { R_a } and with corresponding self-consistent electron density

 $\rho(\mathbf{r}, {\mathbf{R}_{\alpha}})$; (4) Meta-stable configurations are determined by minimizing the total energies

and converging the forces $\left| \nabla_{\alpha} E(\{\mathbf{R}_{\alpha}\}) \right| < 0.01 \, eV/A$; (5) Migration energies E_m between

adjacent metal-stable configurations are determined using the Nudged Elastic Band method within an estimated error of ± 0.05 eV.



6.2 Ab initio modeling of semiconductors for photovoltaics

Solar cells are devices which convert solar energy into electricity, either directly via the photovoltaic effect, or via the intermediate of heat or chemical energy. The ideal solar energy

cell is required to have a band gap in the visible light region as well as to have high absorption in the visible region. CIS has a band gap of 1.04 eV, which is smaller than the ideal value of the solar cell absorber at 1.40 eV. Therefore, the solid solutions such as $CuIn_{1-x}Ga_xSe_2$ (CIGS) alloy were studied to develop a new material with the ideal bandgap.

The effect of the Ga doping to CuInSe₂ can be observed to change the band gap

$$E_q(x) = (1 - x)E_q(CIS) + xE_q(CGS) - bx(1 - x)$$

with b=0.21. CIS exhibits a direct band gap at Γ point, which indicates that photon energy is directly converted into the creation of electron/hole pairs in the semiconductor materials. This is preferable to the material that exhibits an indirect band gap, where there is some energy loss due to the creation of phonons. The fundamental absorption of CIS corresponds to a strong absorption region which is in order of 10^5 cm⁻¹ to 10^6 cm⁻¹. The interband absorption coefficient is up to 8×10^5 cm⁻¹ in the energy range where we are interested in.

Interface control and doping control are two limiting factors for the technological progress of chalcogenide thin film solar cells. To circumvent the issues, there are attempts to integrate *ab initio* calculations to complete modeling of the device characteristics. The benefit of such methods has been especially important as chalcopyrites are a very complex class of semiconductors, in which the interpretation of experiments is far from straightforward. The role of point defects in the electronic properties of chalcopyrites has been recognized. The control of doping is important because the interplay of extrinsic and intrinsic doping in chalcogenide semiconductors and the tendency to self-compensation make this difficult to achieve.

Band structures

The effective mass of the perfect chalcopyrite have been checked and are in good agreement with experimental measurements: the electron mass is $m_e = 0.089$ (exp. 0.092) and the hole mass is $m_{hh} = 0.69$ (exp. 0.71). They are determined from the curvature of the valence and conduction bands at the Γ -point from a band structure calculation.

Defect formation energies

Chalcopyrite-type CIS has various kinds of defects such as vacancies, interstitials and defect pairs. The CIS thin film for solar cells exhibits p-type electronic conductivity attributed to the native point defects. In the calculation of total energy for the supercells with and without a vacancy, the 2x2x2 k-point mesh generated by the Monkhorst–Pack scheme was employed for numerical integrations over the Brillouin zone.

The formation energy of point defects was calculated from the difference of total energy between perfect crystal and imperfect crystal. The total energy of the perfect crystal was

calculated using the chalcopyrite-type unit cell ($I\overline{4}2d$). Calculations for imperfect crystal was

performed using the supercell with 64 atoms. To simulate infinitely dilute defect concentration, lattice constants of the imperfect crystal supercell were fixed at the optimized values of the perfect crystal. Atomic arrangements around a vacancy were optimized allowing relaxation of the first- and second- nearest neighbor atoms.

The formation energy of a neutral vacancy in a compound depends on the atomic chemical potentials in the system. The formation energies of Cu, X (In, Ga, Al) and Se vacancies can be, respectively, presented by

$$\begin{split} E_f(V_{Cu}) &= E_t^V[Cu_{n-1}X_nSe_{2n}] - E_t[Cu_nX_nSe_{2n}] + \mu_{Cu} \,, \\ E_f(V_X) &= E_t^V[Cu_nX_{n-1}Se_{2n}] - E_t[Cu_nX_nSe_{2n}] + \mu_X \,, \\ E_f(V_{Se}) &= E_t^V[Cu_nX_nSe_{2n-1}] - E_t[Cu_nX_nSe_{2n}] + \mu_{Se} \,, \end{split}$$

where E_t^V is the total energy of the supercell with a defect and E_t is the total energy of the perfect chalcopyrite-type crystal. The symbol μ is the chemical potential of the constituent elements (Cu, In/Ga/Al and Se) and n=16. The chemical potential μ changes depending on the chemical environment of the system.

The chemical potentials of Cu, X and Se should be correlated with each other to satisfy





$$\mu_{Cu} + \mu_X + 2\mu_{Se} = \mu_{CuXSe_2(bulk)}$$
. Chemical

potentials for the bulk substances were obtained as the total energies per unit formula by separate calculations. Chemical potentials of the constituent elements (Cu, X(In, Ga, Al) and Se) can be estimated with:

Cu - rich	Cu - poor
$\mu_{Cu} = [\mu_{Cu_2Se(bulk)} - 2\mu_{Se(bulk)}] \big/ 2$	$\mu_{Cu} = [2\mu_{CuXSe_2(bulk)} - \mu_{X_2Se_3(bulk)} - \mu_{Se(bulk)}] / 2$
$\mu_X = \left[2\mu_{CuXSe_2(bulk)} - \mu_{Cu_2Se(bulk)} - 3\mu_{Se(bulk)}\right] / 2$	$\mu_X = [\mu_{X_2Se_3(bulk)} - 3\mu_{Se(bulk)}]/2$
$\mu_{Se} = \mu_{Se_2(bulk)}$	$\mu_{Se} = \mu_{Se(bulk)}$

The formation energy of Cu vacancy under the Cu-rich conditions such as point 1, 2 and 5 is larger than those under the Cu-poor condition. The formation energy of Cu vacancy at Cu-poor point 3 at which CIS coexists with In_2Se_3 and Se is the lowest value of -0.8 eV.

Under Cu-poor condition (point 3), the formation energy of Cu vacancy in CIS is smaller than those in CGS and CAS. The formation energy of In vacancy in CIS is larger than that of Ga vacancy in CGS and that of Al vacancy in CAS. The formation energy of Se vacancy in



CIS is smaller than those in CGS and CAS as well as the tendency under the Cu-rich condition.

The formation energy of $(2V_{Cu} + In_{Cu})$ pair in CIS greatly depends on the chemical potentials of the constituent elements. The formation

energy of ($2V_{Cu} + In_{Cu}$) under Cu-poor condition



that $(2V_{Cu} + In_{Cu})$ defect pair easily generates in CIS under the

is much lower than that under Cu-rich condition. This means

Cu-poor condition.

Defect energies were computed for single defects as well as for pairs of intrinsic defects, and for different supercell sizes so as to evaluate the defect-defect interaction (see table I for some representative results). Doping by foreign elements was also considered (see table II), some of which are likely to occur even

without intentional incorporation, because of the natural presence of the elements during the process. Note that for some defects strongly coupled to conduction band states, there is a strong uncertainty as to the formation energy, as some components of its electronic energy is unreliable.

Table I: Intrinsic point defect energies (in eV) in CuInSe₂ with various cell size GGA calculations (defect formation energies are references to the following chemical potentials: $\mu_{Cu} = \mu_{III} = 0$ eV).

	V _{Cu}	V _{In}	\mathbf{V}_{Se}	Cu _i O	Cu _i T	Se _i O	Se _i T	In _i O	In _i T	Cu _{In}	In _{Cu}	Cu _{Se}	Se _{Cu}	In _{Se}	Se _{In}
16 at.	0,69	2,61	1,83	2,80	2,67	2,33	2,45	6,02	5,66	1,26	3,48	2,51	4,41	2,85	2,76
32 at.	0,46	2,26	1,93	2,65	2,79	2,21	2,41	5,97	5,57	1,11	3,28	2,58	4,36	2,97	2,67
64 at.	0,38	2,24	1,94	2,66	2,76	2,11	2,29	5,90	5,43	1,12	3,14	2,98	4,50	3,16	2,90

Table II: Formation energies of $Cu(In_{0.5}Fe_{0.5})Se_2$ and Zn defects ($\mu_{Cu} = \mu_{In} = 0$ eV, $\mu_{Fe} = \mu_{Zn} = 0$ eV). A band gap correction of 1 eV is applied to the Zn_{Cu} antisite formation energy. The formation energy without correction is in parenthesis.

	Fe _{in}	Zn _{Cu}	Zn _{In}	Zn _{Cu} +Zn _{In}
Reference	CulnSe ₂ – CuFeSe ₂	Zn, Cu pure	Zn, In pure	CulnSe ₂ – ZnSe
GGA (eV)	~ 0	0.98 (-0.02)	0.06	0.02

6.3 Solid Oxide Fuel Cells

Fuel cell is a device which can directly convert fuel such as H_2 into electricity. It provides the function by integrating four core components into a cooperative working module:

(1) Anode: The anode is designed to conduct electrons from hydrogen ions, which are formed by catalyst, to the external motor drive.



(2) Cathode: The cathode then distributes the electrons back from circuit to combine with oxygen ions and hydrogen ions to form water molecules.
(3) PEM: The proton exchange membrane (PEM) allows conduction of protons from anode to cathode, while blocks the electrons from moving across the membrane. To function properly, the material of

PEM must be hydrated.

(4) Catalysts: The catalysts lying at the interfaces between the anode/cathode and PEM allow reaction of oxygen and hydrogen, generally made from platinum nanoparticles on a carbon support. Catalyst ionizes hydrogen molecule.

A Solid Oxide Fuel Cell is a device which converts chemical energy to electricity and consists solely of solid ceramic components. A better understanding of <u>the structure and dynamics of</u> <u>the electrochemically active cathode surfaces</u> and of <u>electrocatalytic pathways</u> involving coupled electron- and oxygen transfer processes is of paramount importance in predicting their electrochemical/catalytic performance for oxygen reduction and transport in SOFCs. Lithium grand potential phase diagrams represent the phase equilibria of a lithium compound that is open to lithium, which is relevant when the solid electrolyte is in contact with a reservoir of lithium. Calculate the lithium grand potential phase diagrams of the lithium compound system at various lithium chemical potentials of interest.

	Cathode	Old technology:	Store Li ⁺
	materials	LiCoO ₂ ,	ions and
HYDROGEN CONTROL OF CO		LiNiO ₂ ,LiMn ₂ O ₄	electrons in
Flow		New technology:	discharge
		LiFePO ₄	mode
Heat 85° C	and and	Barium/ Strontium	
21 0 0 0		Ferrate/ Cobaltate	
Catalysts G &		(BSCF:	
Unused H20 Air and United Unit		Ba _{0.5} Sr _{0.5} Fe _{0.2} Co _{0.8} O ₃):	
Anode Cathode emissions		(1) What is the rate of	
		oxygen migration?	
		(calculate the vacancy	

	migration energetics)	
	(2) What are the active	
	sites for the oxygen	
	reduction reaction at	
	the cathode's surface?	
Electrolyte	Liquid solvent, gel,	Transport
materials	polymer, LiPF ₆ , and	Li ⁺ ions
	LiClO ₄	Exclude
	Solid: LiPON,	electrons
	γ -Li ₃ PO ₄ , and	
	$Li_{10}GeP_2S_{12}$ (LGPS)	
Anode	Li-Al alloy	Provide
materials	Li intercalated graphite	source of
	Metal Li	Li ⁺ ions;
		Make
		stable
		interface
		and
		electrons in
		discharge
		mode.

Model construction

- •
- Started with ideal γ -Li₃PO₄ crystal Constructed an ideal surface plane, assuming charge neutrality and keep all PO₄ bonds. •
- Relax surface in vacuum •
- Deposit a few layers of Li between electrolyte surface and vacuum •
- Relax the structure ٠



The resulting $Li-Li_3PO_4$ interface along the *c*-direction.



 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ ($\delta = 0.5$) supercell ground state structure. Four oxygen vacancies are denoted as V_o. The positions of oxygen atoms in vacancy free lattice are labeled as O_x to demonstrate oxygen atoms displacement upon oxygen vacancies formation.

The perovskite remains cubic throughout the fuel cell operation temperature range, leading to a picture of vacancy migration in a cubic cross sections. The oxygen vacancy can move by the following pathway





In order to calculate vacancy migration energy we took the difference between the ground state and the transition state. By mapping first principles calculations with different local-cation arrangements and applying these results in kinetic Monte Carlo simulations, we can properly sample a large number of local environments in a statistically meaningful

manner.

Proton transport through perovskite oxides (AMO₃)



Oxide-ion transport through apatite silicates ($M_{10}(SiO_4)_6O_2$ and LaBaGaO₄)



Cathode Materials for Lithium Batteries (defects and ion transport in LiFePO₄)



Water splitting with Photocatalysis and hydrogen storage materials A

Thermoelectric Materials A