Since structural materials contain large amounts of alloying elements as well as decorated metal organic frameworks (MOF). The A New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan. N Yoji Sahara

C7-01 Invited
Computational modelling and simulation of materials for hydrogen storage
Sourav Pal
CSIR-National Chemical Laboratory, Dr Homi Bhabha Road, Pune 411008, India

In this talk, I will discuss results from our group in the area of computational modeling using density functional theory for reversible hydrogen storage materials. The reversible hydrogen storage is an important area in the context of renewable energy and the reversibility places important challenge. We have studied doped magnesium hydrides as well as decorated metal organic frameworks (MOF). The strategy of doping/ decoration in each of these two cases and the salient results for hydrogen storage will be presented. Specifically, fractional substitution of silicon and aluminium in magnesium hydride and light metal decoration of MOFs will be presented.

C7-02 Invited
Theoretical investigation of electronic structures and phase stability in structural materials
Ryoji Sahara
National Institute for Materials Science

Since structural materials contain large amounts of alloying elements to control the phase stability and microstructures, it is important to clarify the role of each element to be able to design alloys that use alloying elements in the most efficient way.

In the present study, the electronic structures and structural properties of body-centered cubic (bcc) Ti based alloys, face-centered cubic (fcc) Al and Fe based alloys were studied by first-principles calculations. To determine the effect of the concentration and atomic distribution of the alloying elements on the phase stability, ordered structure models and special quasirandom structure (SQS) models were used for emulating the solid solution state of the alloys. The alloying elements dependencies of the formation energies, the structural parameters, and density of states were analyzed. Furthermore, the valence band electronic structures were measured by hard X-ray photoelectron spectroscopy (HAXPES). It is clearly shown that the present model reproduces the experimental values well.


C7-03 Invited
Efficient Gas Selection and Storage Using Nanosise Cage Structures: A Theoretical Investigation on Hydrate Clathrate and Mackay Crystal Yosiyuki Kawazoe1, 2
New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan; 1Institute of Thermophysics, Siberian Branch, Russian Academy of Science, Novosibirsk, Russia

To realize sufficient energy storage and transfer with environmentally safety condition, it is important to select gas selection and storage materials in practical usages. Among them cleanest energy carrier is the gas hydrates, by which we can carry different types of gases starting from natural gas, methane, CO2, etc. We have studied gas hydrates using ab initio methods and thermodynamics to predict stable T-P phases. A number of studies have been made for gas storage in carbon nanostructures such as nanotube and graphene. Recently we have proposed a new set of 3D carbon cage structures, Mackay-like crystals, which contain large cages suitable for gas selection and storage. In the talk, I will present recent numerical results on these materials.

C7-04 Invited
 Tight-Binding Quantum Chemical Molecular Dynamics Simulation of Etching Process for Quantum Dots Solar Cells Hiroshi Ito1, Takuya Kuwahara, Yuji Higuchi, Nobuki Ozawa, and Momoji Kubo2
Graduate School of Engineering, Tohoku University / 6-6-11-703 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

A quantum dot solar cell (QDSC) has a high energy conversion efficiency and contributes greatly to a development of the renewable technology. In the manufacturing process of QDSC, plasma-etching has high expectations because it can be applied to fabrication of high density and unified quantum dots. However, plasma-etching has serious problems such as side-etching and deformation of holes. To resolve the problems and design an optimal etching, atomistic etching mechanisms should be investigated. In this study, we developed an original etching simulator based on tight-binding quantum chemical molecular dynamics [JPCC, 118 (2014) 21580], and performed SiO2 etching simulations by CF2 and CF4 radicals which are the dominant species in fluorocarbon plasma. In the simulations, irradiations of etchants cause chemical reactions on the SiO2 surface, and then Si-O bonds are dissociated. Moreover, CO, CO2, COF2, and SiF4 molecules, which are by-products in experiments, are generated. Furthermore, we observed that CF2 dissociates Si-O bonds more than CF4 in low energy because of its high chemical reactivity. Conversely, in high energy, CF4 promotes etching rapidly because a larger number of F atoms causes chemical reactions more than CF2. In conclusion, the SiO2 etching mechanisms are successfully revealed by our etching simulator.

C7-05 Invited
Thin-Film Growth Simulations of a-Si:H for Solar Cells using Density-Functional Tight-Binding Method Takuya Kuwahara1, Hiroshi Ito, Yuji Higuchi, Nobuki Ozawa, Momoji Kubo2
Graduate School of Engineering, Tohoku University / 6-6-11-703 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

Micromcrystalline and amorphous Si films have attention as promising materials for solar cells. Thin-film Si is usually prepared by plasma-enhanced chemical vapor deposition (PECVD). However, the growth mechanisms have not yet been revealed due to the complexity of surface reactions. It is therefore desired to understand the growth mechanisms on an atomic scale. Here, to reveal the growth mechanisms of thin-film Si in PECVD, we perform CVD simulations of thin-film Si using self-consistent-charge density-functional-tight-binding molecular dynamics (SCC-DFTB-MD) method.

We use our original SCC-DFTB-MD code. CVD processes are simulated by the continuous impingement of SiH4 radicals onto a Si(001):H surface. We reveal that the deposition of thin-film Si in PECVD consists of two chemical reactions. One is a H abstraction reaction. A SiH3 radical abstracts a H atom from a hydrogenated surface, and then a dangling bond (DB) is generated there. The other is an adsorption of a SiH2 radical on the DB generated by the H abstraction. We propose that the “abstraction-adsorption” mechanism explains the initial growth of thin-film Si in PECVD [1, 2].

C7-06 Invited
Monitoring Changes in Molecular Structures of D-π-A Dye for Novel Organic Dyes Development in DSSC: A Theoretical Investigation-Based on OD-3 Dye
Thi M. T. Nguyen1, Nguyen-Nguyen Pham-Tran2⁎⁎, Yoshiyuki Kawazoe3, Duc Nguyen-Manh4
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From experimental result, OD-3 organic dye has contributed to dye database for dye-sensitized solar cell (DSSC) with the power conversion efficiency is 5.82%. For further development of novel and efficient organic dye sensitizer based on OD-3, in this study, we use hybrid DFT and PCM-TD-DFT methods to investigate the effect of the functional groups to the electronic and optical properties of OD-3 dye by alteration of three moieties, electron donors, σ spacers and electron acceptors, according to the commonplace D-π-A model. Electronic structures and absorption spectra were analyzed to view the qualitative linkage between the experiment and theory on dye aggregation, dye regeneration, electron injection capability to semiconductors and the absorption responses to wavelengths. Alk-1-ene modified groups shown useful on preventing dye aggregation only. While π spacers showed their effectiveness in improving the absorption band from the initial OD-3 dye. A dye contained only cyano groups in acceptor segment showed its dramatic role in broadening maximum absorption wavelength.

C7-07 Invited
How to improve Hydrogen desorption temperature of Magnesium Hydride by going from bulk to nano-phase?
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2Theoretical Chemistry Section, Bhabha Atomic Research Centre, Mumbai-400085, India

In search of the right candidate material for hydrogen storage, bulk MgH2 show impressive gravimetric efficiencies (~7.7 wt %), cost effectiveness and abundant availability. However, its practical usage has been hindered because of its high desorption enthalpy (~0.8 eV H2 molecule), which results in an undesirable desorption temperature of 300°C at 1 bar H2. Nanostructuring (via ball milling) is expected to improve the desorption enthalpy as well as the desorption temperature due to the higher diffusivity of hydrogen and higher surface to volume ratios of the nanoclusters. Most of the earlier studies, however, have been focused on the adsorption of atomic hydrogen with Mg nanoclusters (forming MgHx, nanoclusters) for which the hydrogen desorption temperature gets only marginally reduced. Therefore, it is necessary to investigate the adsorption of hydrogen in molecular form with Mg nanoclusters. In this talk, we shall discuss our first principles density functional theory (DFT) based results on the structure, stability and desorption kinetics of H2 molecules adsorbed on neutral as well as charged Mg, nanoclusters. Some of the outstanding issues and challenges faced in exploiting nanostructured hydride complexes will be highlighted.

C7-08 Invited
First-Principles Molecular Dynamics Simulation on Hydrogen Generation Processes by Vibrationally-Excitation
Yuji Higuchi⁎⁎, Naoki Yokoyama, Nobuki Ozawa, Hiroo Yugami, Momoji Kubo

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Hydrogen production by steam reforming reaction of methane attracts much attention as a new energy resource. Recently, the vibrationally-excited method by the thermal radiation spectrum is employed to increase hydrogen generation [1]. To improve the method, the relevance of the chemical reaction dynamics is essential. Thus, we study the hydrogen generation processes by our developed first-principles molecular dynamics code “Violet” [2] at B3LYP/6-31g* level.

We calculate the collision process of a vibrationally-excited CH4 and a H2O molecules. At the collision, the hydrogen atom at the elongated C-H bond reacts with a hydrogen atom of the H2O molecule. Then, a hydrogen and methanol molecules are generated. Next, we also calculate the collision process in ground state and compare the difference. It is revealed that the excited state generates hydrogen molecules more easily than the ground state in various collision angles. We also report another hydrogen generation process from water molecules on silicon by using vibrationally-excitation and overview new energy harvesting.


C7-09 Invited
Decorating Graphene with Aromatic Structures via Coordination Bonds with Metal Atoms: Density Functional Theory Investigations
Hung M. Le1,⁎, Hajime Hira1,*, Yoshiyuki Kawazoe3, Duc Nguyen-Manh4
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The interesting coordination bonding features between graphene and transition-metal atoms have been intensively studied though numerous theoretical and experimental studies. In this work, we utilize metal atoms as potential bridging atoms for the attachments of various functional groups on the graphene surface, and perform first-principles modeling of such systems using density-functional-theory calculations. Those functional groups may be another graphene monolayer, benzene, naphthalene, or even buckminster fullerene (C60). We observe different bonding schemes in the investigated structures depending upon the ligand identity and bridging metal atoms in use. More importantly, different magnetic moments are observed, which highly depends on the bonding interaction. We suggest that the developed graphene-based structure might find interesting applications in chemical reaction catalysis, hydrogen storage, and spintronic devices.

C7-10 Invited
Virtual Fab for Design of Anode Materials of Li Ion Battery
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Owing to the rapid increase in computing power and successful development of the computation methodology, predicting capability of atomic level computer simulation has been significantly increased. Furthermore, combined with WEB 2.0 technology, web-based materials design platform is drawing much attention. The platform is expected to decrease the entrance barrier for non-theoretical researchers who want to utilize the massive computation tools for designing their materials. We are developing a Web 2.0 based virtual fab for Li ion battery materials composed of Anode Design Lab, Cathode Design Lab, Electrolyte Design Lab. We designed the web-based
working environment that can provide materials manipulating modules, computational experiment modules with extensive analysis modules. This platform will be combined with interatomic potential and materials informatics DBs. In the present talk, we will focus on the Anode Design Lab to demonstrate the concept of the virtual fab and address the issues for further development of robust virtual design environment.

C7-11 Invited
Theoretical and Experimental Study of Surfaces and Interfaces of Electrodes of Lithium-Ion Batteries
Shingo Tanaka, Mitsunori Kitta, Tomoki Akita, Yasushi Maeda and Masanori Kohyama*
UBIQEN, National Institute of Advanced Industrial Science and Technology

Lithium-ion batteries (LIBs) attract much attention as energy-storage devices for natural energy resources as well as those for electric vehicles. It is crucial to understand the phenomena at surfaces and interfaces of electrode materials in LIBs during Li insertion/extraction. Our research group is engaged in basic studies on such surfaces and interfaces by the collaboration among scanning transmission electron microscopy (STEM), scanning probe microscopy (SPM) and density-functional theory (DFT) calculations. In this talk, we present our recent approaches to the surfaces and interfaces of lithium titanate, Li_4Ti_5O_12 (LTO) as a high-performance anode, where negligible volume changes between pristine and Li-inserted (Li-LTO) phases lead to excellent durability and quick Li-insertion/extraction reactions. First, we show the detailed structural analysis of LTO surfaces by the SPM observation and DFT calculation [1]. Second, we show the detailed analysis of LTO/Li-LTO interfaces by the STEM observation and DFT calculation [2].


C7-12 Invited
Ab initio molecular dynamics study of degradation process at EC-Li_2O_2 interfaces
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Li-air batteries are one of the attracted candidates of the next-generation secondary batteries. Organic liquids are normally used as a solvent of electrolytes. However, it has been well known that some kinds of alkyl carbonates such as ethylene carbonate (EC) are not stable on Li_2O_2 that grows up on the cathode in the discharging process. In this presentation, we demonstrate electrochemical reactions of the EC molecules on Li_2O_2 substrate by ab initio molecular dynamics. We use OpenMX code based on density functional theory combined with effective screening medium method.

In our simulation, EC molecules adsorbed onto the peroxide (Li_2O_2) spontaneously without excess charge. Adsorbed EC molecule changes its structure form sp2-like to sp3-like one by forming a bond with oxygen of Li_2O_2. We find through the analysis of density of states that the adsorption is caused by the hybridization of sp2 orbital and surface states of the Li_2O_2. After adsorption, EC ring opens and sp2 structure is reconstructed with O atom at the adsorption site. Finally, the peroxide at adsorption site is decomposed and a carboxyl forms. We determine the product structure as O-(CH_2)_2OCOO-. This kind of alkyl carbonates was found in experiments.