The 1st International Symposium “HYDROGENOMICS” combined with the 14th International Symposium “Hydrogen & Energy” follows the 13th one that took place on January 20th - 25th, 2019, in GYEONG WON JAE AMBASSADOR, Incheon, South Korea with more than 60 participants. It serves as an information platform of the fundamental science and technology and the frontiers of research on hydrogen and energy.

The symposium consists top level keynote, invited, and contributed talks studying “HYDROGENOMICS” and the key properties of the hydrogen cycle, i.e. the hydrogen production, hydrogen storage, hydrogen combustion, and fuel cells. Furthermore, contributions on the batteries, synthetic fuels, and related functional materials are very welcome. Early stage and experienced researchers present their newest results also on posters.

The symposium will take place in The Hotel Monterey Edelhof Sapporo, Hokkaido, Japan; The number of participants is limited to 80.

5(Sun.) – 10(Fri.) January, 2020

The Hotel Monterey Edelhof Sapporo:
Nishi 1-1, Kita 2 Jyo, Chuo-ku, Sapporo,
Hokkaido, 060-0002, Japan
PHONE: +81-11-242-7111
URL: https://www.hotelmonterey.co.jp/en/edelhof/
ACKNOWLEDGEMENT

MEXT Grant-in-Aid for Scientific Research on Innovative “Hydrogenomics”

THE KAJIMA FOUNDATION

東京工業大学
Tokyo Institute of Technology

WPI Advanced Institute for Materials Research (WPI-AIMR)
1st INT’L SYMPOSIUM
Hydrogenomics
combined with
14th INT’L SYMPOSIUM
HYDROGEN & ENERGY
January 5th -10th, 2020
Hotel Monterey Edelhof Sapporo, SAPPORO, JAPAN

ORGANIZERS
Shin-ichi ORIMO, Tohoku University
Taro HITOSUGI, Tokyo Institute of Technology
Katsuyuki FUKUTANI, University of Tokyo
Andreas ZÜTTEL, EPFL, Switzerland

KEYNOTE and INVITED SPEAKERS
Keynote
Andreas ZÜTTEL, EPFL, Switzerland
Hans-Joachim FREUND, MPI-Berlin, Germany
Anibal Javier (Timmy) RAMIREZ-CUESTA
Oak Ridge National Laboratory, USA
Masaru TSUKADA, Univ. Tokyo, Japan

Invited
Ryotaro ARITA, Marcello BARICCO, Craig BUCKLEY,
Martin DORNHEIM, Jianping GUO, Ikutaro HAMADA,
Bjørn HAUBACK, Michael HIRSCHER, Craig JENSEN,
Genki KOBAYASHI, Michel LATROCHE, Katsutoshi
NAGAOKA, Chikashi NISHIMURA, Minoru OSADA,
Astrid PUNDT, Hiroyuki SAITO, Katsuya SHIMIZU,
Petra SZILÁGYI, Min ZHU (in alphabet order)

SUBJECTS
• Hydrogenomics*
• Hydrogen Production
• Hydrogen Storage
• Hydrogen Combustion
• Theory and Modeling
• Fuel Cells
• Batteries
• Synthetic Fuels
• Functional Mater.
*Hydrogen Densification, Localization, Migration, Activation,
and Advanced Measurement/Simulation, to fully utilize the
diverse functionalities of hydrogen in materials

CONFEREE FEE
¥50,000; incl., Welcome Reception, Lunch, Dinner, Conference Dinner, Coffee Breaks, Social Event

TIMELINE
Registration: August 31 2019
(Limited 80 Persons)
Abstract: October 11, 2019

LOCATION
Hotel Monterey Edelhof Sapporo
Nishi 1-1, Kita 2 Jyo, Chuo-ku,
Sapporo, Hokkaido, 060-0002, Japan
+81-11-242-7111
https://www.hotelmonterey.co.jp/en/edelhof/

Dec. 9, 2019
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Abstracts

Sunday
The Hotel Monterey Edelhof Sapporo
05.01.2020
15:00  Registration
17:00  Welcome Reception at The Hotel Monterey Edelhof Sapporo
19:00  End

Monday
The Hotel Monterey Edelhof Sapporo
06.01.2020
09:00  Opening: Shin-ichi ORIMO
       HYDROGENOMICS: CREATION OF INNOVATIVE MATERIALS, DEVICES, AND
       REACTION PROCESSES USING HIGHER-ORDER HYDROGEN FUNCTIONS
Coffee Break
10:30  Chair: Shin-ichi ORIMO
       K01: Andreas ZÜTTEL
       200 YEARS AFTER INDUSTRIALISATION THE TRANSITION TO RENEWABLE
       ENERGY
       11:10  I01: Michael HIRSCHER
       HYDROGEN STORAGE IN NANOPOROUS MATERIALS: STATUS AND FUTURE
       CONCEPTS

       13:30  Chair: Michael HIRSCHER
       I02: Min ZHU
       MG BASED AMORPHOUS FOR HYDROGEN AND ELECTRIC STORAGE
       14:00  C01: Kenichi OYAIZU
       REVERSIBLE HYDROGEN STORAGE WITH ORGANIC POLYMERS
       14:20  C02: Joseph TEPROVICH
       ENHANCED ELECTROCHEMICAL PROPERTIES OF HYDROGEN STORAGE
       MATERIALS
       14:40  C03: Toyoto SATO
       HYDROGEN STORAGE PROPERTIES AND CRYSTAL STRUCTURAL
       INVESTIGATIONS ON MG CONTAINING ALLOYS
Coffee Break
15:20  Chair: Min ZHU
IO3: Craig BUCKLEY
Thermal Battery Development for Concentrated Solar Power Systems

15:50  IO4: Chikashi NISHIMURA
NEW DEVICE FOR HYDROGEN SEPARATION FROM DECOMPOSED GAS OF ENERGY CARRIERS, NH₃ AND MCH, USING FLAT VANADIUM ALLOYS MEMBRANES

18:00  Poster Session
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STRUCTURAL AND DYNAMICAL STUDY ON PdPt HYDRIDE NANOPARTICLES

P02: Elvis ARGUELLES
H₂ Nuclear Spin Conversion on Metal Surfaces: Physisorption vs. Molecular Chemisorption

P03: Ho-Chol CHANG
PHOTOCHEMICAL HYDROGEN EVOLUTION FROM MOLECULAR IRON COMPLEXES WITH PHENYLENEDIAMINES

P04: Ken-Ichi FUJITA
DEVELOPMENT OF EFFICIENT SYSTEMS FOR HYDROGEN PRODUCTION BASED ON CATALYTIC ACTIVITY OF IRIDIUM COMPLEXES IN DEHYDROGENATIVE REACTIONS

P05: Jun HARUYAMA
FIRST PRINCIPLES STUDY OF HYDRIDE ION CONDUCTOR

P06: Yoshiki HIGUCHI
NEW ASSAY METHOD FOR THE ENZYMES REACTING WITH GASEOUS SUBSTRATES BY RAMAN SPECTROSCOPY

P07: Taro HITOSUGI
Epitaxial growth of Ca₂NH thin films using reactive magnetron sputtering

P08: Soshi IIMURA
H⁺ ION CONDUCTION AND ANHARMONIC VIBRATION IN OXYGEN-DOPED LANTHANUM HYDRIDE

P09: Munehiro INUKAI
GLASS-PHASE COORDINATION POLYMER DISPLAYING PROTON CONDUCTIVITY AND GUEST-ACCESSIBLE POROSITY

P10: Takayoshi ISHIMOTO
THEORETICAL STUDY OF H/D ISOTOPE EFFECT WITH METAL BY USING COMBINED PLANE WAVE AND LOCALIZED BASIS SET APPROACH
P11: Yuki KANAZAWA
DEVELOPMENT OF POWDER NEUTRON HOLOGRAPHY FOR INVESTIGATION OF HYDRIDES

P12: Hiroyuki KATO
ATTEMPT TO CONTROL H⁺ TRANSFER IN MOLECULAR BILAYERS FOR A FUTURE HYDROGENOMIC DEVICE

P13: Kazuaki KISU
ALL SOLID-STATE BATTERIES USING LIBH₄-BASED SOLID ELECTROLYTE AND LITHIUM METAL ELECTRODE

P14: Masaaki KITANO
LANTHANUM OXYHYDRIDES SUPPORTED RUTHENIUM CATALYST FOR AMMONIA SYNTHESIS

P15: Youngdon KO
EFFETS OF Ni-CONTAINING POROUS CARBON SHEETS (Ni-PCS) ON THE DEHYDROGENATION PROPERTIES OF Mg(AlH₄)₂

P16: Takahiro KONDO
CARBON DOPING OF HYDROGEN BORIDE SHEET REDUCES H₂ RELEASE TEMPERATURE

P17: Akihiko MACHIDA
LOCAL STRUCTURE STUDY OF METAL–HYDROGEN SYSEMS BY X-RAY TOTAL SCATTERING

P18: Mitsuhiko MAESATO
LOW TEMPERATURE HYDROGEN ION BEAM IRRADIATION FOR EXPLORING EXOTIC PHYSICAL PROPERTIES

P19: Hiroki MIYAOKA
ANALYSIS OF AMMONIA ABSORPTION STATE OF METAL BOROHYDRIDE

P20: Naoya MIYAUCHI
LOCAL DIFFUSION COEFFICIENT OF DEUTERIUM PERMEATING THROUGH STAINLESS STEEL MEMBRANE

P21: Hatsumi MORI
ANHYDROUS PROTON CONDUCTIVITY OF IMIDAZOLIUM HYDROGEN DICARBOXYLATES

P22: Masakazu MORIMOTO
ADVANCED MOLECULAR MATERIALS BASED ON PHOTOCHROMIC DIARYLETHENES BEARING HYDROGEN-FUNCTIONAL UNITS

P23: Shin MURAKAMI
HIGH-PRESSURE AND HIGH-TEMPERATURE SYNTHESIS OF NOVEL Al-TM (TM=ZR, HF) HYDRIDES

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<td>Chair: Jianping GUO</td>
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<td>C06: Ken-ichi FUKUI</td>
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<td>C08: Motoyuki SHIGA</td>
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P24: Akinobu NAKADA
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P25: Yuki NAKAGAWA
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P26: Masashi NAKAMURA
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P27: Takashi NAKAMURA
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P28: Masayuki OCHI
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P29: Kenji OHYOYAMA
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P30: Kouki OKA
Poly(dihydroxybenzoquinone): Its High-density and Robust Charge Storage Capability in Rechargeable Acidic Polymer-air Batteries

P31: Toyoto SATO
HYDROGEN STORAGE PROPERTIES AND CRYSTAL STRUCTURAL INVESTIGATIONS ON Mg CONTAINING ALLOYS

P32: Ryuhei SATO
CRYSTAL STRUCTURE PREDICTION OF Li(CB₉H₁₀) BY XRD-ASSISTED MOLECULAR DYNAMIC SIMULATION

P33: Yasuteru SHIGETA
THEORETICAL ANALYSIS ON STRUCTURES OF RESTING OXIDIZED STATES OF [NIFE] HYDROGENASE

P34: Keita SHINZATO
HYDROGENATION PROPERTIES OF TITANIUM WITH SURFACE MODIFICATION BY CARBON

P35: Masanori TACHIKAWA
DEVELOPMENT OF MULTICOMPONENT QUANTUM CHEMISTRY METHODS FOR ACCURATE PREDICTION AND ELUCIDATION OF HYDROGEN-FUNCTIONAL MECHANISM

P36: Hidekazu TANAKA
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P37: Bo THOMSEN
CALCULATING THE pKW OF SUBCRITICAL AND SUPERCRITICAL H₂O AND D₂O

P38: Hayato TSURUGI
HYDROSILYLATION OF BENZOPHENONE DERIVATIVES CATALYZED BY RARE-EARTH METAL COMPLEXES: IMPORTANCE OF AGOSTIC INTERACTION BETWEEN RARE-EARTH METALS AND HYDROSILANE

P39: Noritaka USAMI
ROLE OF HYDROGENS AROUND HETEROINTERFACES IN IMPROVING PASSIVATION PERFORMANCE OF SOLAR CELLS

P40: Teppei YAMADA
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P41: Takayoshi YAMAMOTO
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P42: Yoshiyuki YAMAMOTO
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P43: Osamu YAMAMURO
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P44: Miho YAMAUCHI
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P45: Heena YANG
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20:00 End
Wednesday  The Hotel Monterey Edelhof Sapporo  
08.01.2020

09:00  Chair: Katsuyuki FUKUTANI

K03: Masaru TSUKADA  
QUANTUM TRANSITION OF HYDROGEN/ELECTRONS IN SOLID AND SURFACES -Some theoretical aspects-

09:40  I10: Katsuya SHIMIZU  
SYSTHESIS OF SUPERHYDRIDES UNDER HIGH PRESSURE

Coffee Break

10:30  I11: Ryotaro ARITA  
QUANTUM CRYSTAL STRUCTURE IN THE 250 K SUPERCONDUCTING LANTHANUM HYDRIDE

11:00  Network Meeting

Social Event

Attendant: Miki HINO and Yasuko ITO

12:00  Bus leaves for Social Event

Lunch in the bus

13:00  Otaru Canal Day Cruise and sightseeing in Otaru

16:30  Departure from Otaru

18:00  Dinner at The Sapporo Beer Garden

20:00  Bus return to The Hotel Monterey Edelhof Sapporo

Thursday  The Hotel Monterey Edelhof Sapporo  
09.01.2020

09:00  Chair: Taro HITOSUGI

K04: A. J. Timmy RAMIREZ-CUESTA  
VIOLATION OF THE SWITENDICK CRITERION IN METAL HYDRIDES EVIDENCED BY INELASTIC NEUTRON SCATTERING

09:40  I12: Petra SZILÁGYI  
METAL-ORGANIC FRAMEWORKS FOR THE HYDROGEN ECONOMY

Coffee Break

10:30  Chair: Petra SZILÁGYI

I13: Astrid PUNDT  
Phase transitions and ultra-high mechanical stress in Nb-H thin films
11:00  C09: Saya AJITO
A NEW TECHNIQUE FOR VISUALIZATION OF HYDROGEN PERMEATED
THROUGH PURE IRON USING AN IRIDIUM COMPLEX

11:20  C10: Loris LOMBARDO
COMPLEX HYDRIDES FOR CO\textsubscript{2} CAPTURE AND TRANSFORMATION

13:30  \textit{Chair: Astrid PUNDT}
I14: Bjørn C. HAUBACK
MULTIFUNCTIONAL METAL HYDRIDES

14:00  C11: Toshiya OTOMO
STRUCTURAL STUDY OF HYDRIDES BY A HIGH INTENSITY TOTAL
SCATTERING INSTRUMENT, NOVA

14:20  C12: Yoshinori OHMASA
STRUCTURE AND DYNAMICS OF HYDROGEN CLUSTER MATERIAL Li\textsubscript{6}NbH\textsubscript{11}

14:40  C13: Terry HUMPHRIES
RECENT DEVELOPMENTS IN HIGH TEMPERATURE METAL HYDRIDES FOR
THERMAL BATTERY APPLICATIONS

Coffee Break

15:20  \textit{Chair: Bjørn C. HAUBACK}
I15: Martin DORNHEIM
NOVEL METAL HYDRIDES DISCOVERY AND APPLICATION

15:50  I16: Michel LATROCHE
HYDRIDE-BASED SOLID STATE LI-ION BATTERIES FOR ENERGY STORAGE

18:00  Conference Dinner at The Hotel Monterey Edelhof Sapporo
\textit{Chair: Andreas ZÜTTEL and Yasuko ITO}

20:00  End

\textbf{Friday}  \textbf{The Hotel Monterey Edelhof Sapporo}
\textbf{10.01.2020}

09:00  \textit{Chair: Osamu YAMAMURO}
I17: Hiroyuki SAIETO
HIGH-PRESSURE SYNGHESIS OF NOVEL ALUMINUM-BASED HYDRIDES
USING SYNCHROTRON RADIATION X-RAYS

09:30  I18: Genki KOBAYASHI
MATERIAL DEVELOPMENT OF H\textsuperscript{-} CONDUCTIVE OXYHYDRIDES
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| 10:00 | I19: Ikutaro HAMADA
HETEROGENEOUS CATALYTIC REACTIONS FROM VAN DER WAALS DENSITY FUNCTIONAL |
| 10:30 | Closing: Shin-ichi ORIMO                                           |

**Science of Hydrogen & Energy Award**

**List of Participants**

**Information**

**Notes**
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### Registration

- Chair: Michael HIRSCHER
- Chair: Craig M. JENSEN
- Chair: Bjørn C. HAUBACK

### Welcome Reception

- Chair: Michael HIRSCHER
- Chair: Hans-Joachim FREUND
- Chair: Andreas ZÜTTEL

### Dinner

- Chair: Michael HIRSCHER
- Chair: Craig M. JENSEN
- Chair: Bjørn C. HAUBACK

### Conference Dinner

- Chair: Andreas ZÜTTEL
- Chair: Yasuo ITO

### Social Event

- Chair: Andreas ZÜTTEL
- Chair: Yasuo ITO

### Light Meal

- Chair: Michael HIRSCHER
- Chair: Hans-Joachim FREUND
- Chair: Andreas ZÜTTEL

### Poster

- Keynote: 4 Persons
- Invited: 19 Persons
- Contributed: 18 Persons
- Poster: 45 Persons
ABSTRACTS
HYDROGENOMICS:
CREATION OF INNOVATIVE MATERIALS, DEVICES, AND REACTION PROCESSES USING HIGHER-ORDER HYDROGEN FUNCTIONS

Shin-ichi ORIMO1

1 WPI-AIMR / Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Hydrogen in materials exhibits a wide range of concentration, high mobility, quantum nature, and superior chemical reactivity. All these features of hydrogen originate from its bonding and size flexibilities. The purpose of an MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan) project is to develop a new materials science of hydrogen / hydrides (hereafter referred to as "HYDROGENOMIC", i.e., hydrogen-omics) as a guideline to “fully utilize” the diverse functionalities of hydrogen in materials.

The MEXT 5-years large-scale project will focus on the four most important functionalities of hydrogen originated from its bonding and size flexibilities (hereafter, referred to as "hydrogen functions"); i.e., “high densification ability (#1)”, “interfacial localizability (#2)”, “fast migration ability (#3)” and “high activation ability (#4)”.

Then the project will merge them to induce unprecedented “higher-order hydrogen functions (synergistic effect between its individual hydrogen functions)” with the support of “advanced analysis and simulation techniques (#5)”, which will also be developed within this project to capture the hydrogen functions more accurately (Fig. 1).

Synergetic Effects betw. Individual Functions

Promotion

#1 Densification

#2 Localization

#3 Migration

#4 Activation

Measurement/Simulation

Fig. 1 Basic concept of MEXT, Grant-in-Aid for Scientific Research on Innovative Areas, “HYDROGENOMICS: Creation of innovative materials, devices, and reaction processes using higher-order hydrogen functions”

Shin-ichi ORIMO received his Ph.D. in 1995. He was a JSPS research fellow, a research associate in Hiroshima University, and a guest researcher in Max-Planck Institute for Metal Research awarded by Alexander von Humboldt Fellowship and MEXT Fellowship. He worked as the Special Advisor to the University President, and is currently Director of WPI-AIMR, and Head of Section of Institute of Materials Research (IMR), Tohoku University. The related research was recently awarded by “Metals Meritorious Award (Japanese Institute of Metals, 2011), “The Commendation for Science and Technology (The Minister of MEXT, 2012)”, “Hydrogen & Energy Award (2015)”, and so on.

http://www.hydrogen.imr.tohoku.ac.jp/

Corresponding author: Shin-ichi ORIMO, Email: orimo@imr.tohoku.ac.jp, Tel. (+81)22-215-2093.
200 YEARS AFTER INDUSTRIALISATION THE TRANSITION TO RENEWABLE ENERGY

Andreas ZÜTTEL*1,2, Heena YANG1,2, Loris LOMBARDO1,2, Youngdon KO1,2

Introduction

The intermittence of renewable energy as well as the mobile applications require massive storage. The gravimetric and volumetric energy density determine the range in mobile applications and the quantity of material needed in general. Beside the size of the storage the cost and the scarcity of the storage material are crucial parameters for the global distribution of energy storage.

Analysis

The end use and primary energy demand was analysed in detail on the example of Switzerland with the goal to determine the requirements of renewable energy converters and energy storage. The technical challenges are complemented with an economic analysis and the feasibility is discussed.

Results and Discussion

The comparison of the energy intensity for renewable energy conversion and population density is a direct measurement of the potential to use renewable energy. The energy storage depends very much on the technology and therefore on the achievements in capturing CO₂ and the control of the CO₂ reduction reaction for the storage of hydrogen in synthetic hydrocarbons.

The Swiss energy demand is only 0.03 TW as compared to the world energy demand of 18 TW. However, the example shows the feasibility and the market opportunities for the future. Even Switzerland is a wealthy country it is a representative example because the energy demand and the wealth are directly connected. The major investment is for the energy storage (seasonal and mobility) rather than for the energy conversion. However, the success of the mineral water business in Switzerland demonstrates the enormous value of storage. Even water is available in large quantities to everybody everywhere, in most cases drinking water quality, it is a business to sell water in plastic bottles for up to 15 CHF/litre. This is not peculiar for Switzerland e.g. French and Italian companies are selling bottled water in Japan. Therefore, energy storage is not only a cost or required investment but a great business opportunity.

References


Andreas ZÜTTEL

Born 22. 8. 1963 in Bern, Switzerland. 1985 Engineering Degree in Chemistry, Burgdorf, Switzerland. 1990 Diploma in Physics from the University of Fribourg (UniFR), Switzerland. 1993 Dr. rer. nat. from the science faculty UniFR. 1994 Post Doc with AT&T Bell Labs in Murray Hill, New Jersey, USA. 1997 Lecturer at the Physics Department UniFR. 2003 External professor at the Vrije Universiteit Amsterdam, Netherlands. 2004 Habilitation in experimental physics at the science faculty UniFR. President of the Swiss Hydrogen Association „HYDROPOLE“. 2006 Head of the section “Hydrogen & Energy” at EMPA and Prof. tit. in the Physics department UniFR. 2009 Guest Professor at IMR, Tohoku University in Sendai, Japan. 2012 Visiting Professor at Delft Technical University, The Netherlands, 2014 Full Professor for Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

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HYDROGEN STORAGE IN NANOPOROUS MATERIALS: STATUS AND FUTURE CONCEPTS

Michael Hirscher
Max Planck Institute for Intelligent Systems, Stuttgart, Germany

Hydrogen storage in nanoporous materials has been attracting a great deal of attention in recent years, as high gravimetric H2 capacities can be achieved at 77 K using materials with particularly high surface areas. Cryogenic storage by physisorption of hydrogen molecules will safely operate at low pressures, is fully reversible and possesses fast kinetics.

Introduction
The change from a fossil fuel-based energy economy to one based on renewable energy sources requires an easy and reliable method of storing energy, since renewables have daily and seasonal fluctuations. Chemical storage seems to be the best solution, and here hydrogen has gained major importance as an energy carrier. A large-scale Power-to-Hydrogen infrastructure can supplied hydrogen to the transport sector or back by Hydrogen-to-Power. Besides, large, long-term storage in geological cavities, stores of medium size are needed, which are safe, reversible, consuming low energy, and possessing quick response times. Here, cryo-adsorption of hydrogen in porous materials could be an attractive option.

Results and Discussion
The development of metal-organic frameworks (MOFs) with extremely high specific surface areas has pushed this field resulting in very high gravimetric storage densities at cryogenic temperatures [1]. Recently, an empirical relation between the volumetric and gravimetric hydrogen density has been obtained by predicting theoretically the hydrogen uptake of 4000 MOFs [2]. Experimental data of the gravimetric and volumetric hydrogen uptake have been analysed for many MOFs and correlated to the framework structures [3]. The gravimetric absolute uptake shows a linear correlation with the specific surface area (Chahine’s rule) [1,3]. A linear relation is found for the volumetric absolute hydrogen uptake as a function of the volumetric surface area, yielding the same hydrogen surface density as in Chahine’s rule [4]. The specific total volume occupied by a porous material, i.e. the inverse of its packing or single crystal density, as a function of its specific surface area yields a linear relationship, which is in good agreement with results on compacted MOF-177 [5]. A phenomenological model is developed for the volumetric absolute uptake as a function of the gravimetric absolute uptake [4]. Many MOFs follow this relation, but interpenetrated frameworks show a deviation and generally higher volumetric hydrogen uptakes [6]. Additionally, for technical applications the key parameter is the usable capacity, which is the amount of hydrogen that can be delivered between the maximum tank pressure and the back pressure required by the end-user [7]. Finally, this presentation will give a short overview on future concepts for improving hydrogen storage in nanoporous materials [8].

References
MG BASED AMORPHOUS FOR HYDROGEN AND ELECTRIC STORAGE

J.L. Huang¹, H.J. Lin², L.J. Huang¹, M. Zhu¹

1 School of Mater. Sci. Eng. South China Univ of Tech & Key Lab for Adv Energy Storage Mater of Guangdong Province, 2 Inst of Adv Wear & Corrosion Resistant and Functional Mater, Jinan Univ, Guangzhou, China

Abstract: The amorphous Mg-based alloys are investigated to improve their hydrogen storage and electric storage performance. It has been found that the amorphous phase can absorb large quantities of H with appropriate composition and a phase separation may occur, which influences hydrogen absorption kinetics. The electrochemical capacity of milled Mg-Ni is determined by the hydrogen desorption from its amorphous phase and the crystallization of amorphous is also a key reason for the electrochemical capacity decay.

Introduction

Mg-based alloys have high hydrogen storage capacity but suffer from high working temperature, which is related to the strong bonding of Mg-H. Amorphous phase has disordered atom structure and may lead to Mg-H interaction different to that in crystal MgH₂. Thus, Mg-based amorphous alloys have been developed for H storage with the aim of tuning the Mg-H interaction [1,2]. In addition, ball milled Mg-Ni based alloy exhibits very high electrochemical capacity as anode for Ni-MH battery. However, it suffers from poor cyclic stability, which was attributed to corrosion of Mg in alkali electrolyte but not substantially overcome by improving their corrosion resistance. Thus, the dependence of electrochemical performance on structure has been examined for Mg-Ni based amorphous, and the crystallization of amorphous phase has been found to play a key role for that [3,4].

Experimental

The Mg-Ni-RE-TM (RE: rare earth, TM: transition metal) alloys were prepared by induction melting and melt spinning under Ar atmosphere with commercial Mg, Ce, Ni and Cu ingots (99.9% purity) as raw materials. The Mg-Ni based amorphous was prepared by mechanical alloying Mg₂Ni with Ni powder by planetary milling. XRD, TEM, TGA and DSC were used to characterize the microstructure. Hydrogen storage properties and electrochemical properties were measured by PC isothermal, TG-MS and a tri-electrode cell.

Results and Discussion

Based on affinity to H, atomic size and glass forming ability, a series Mg-RE-Ni-TM alloys are designed and a hydrogen absorption capacity of more than 5 wt% is obtained as shown in Fig. 1, which is a little bit higher than the crystalline alloy of the same composition, and the hydrogen absorption results in phase separation at certain composition range. This phase separation accelerates the hydrogen absorption kinetics. However, the hydrogen desorption temperature is still high and the amorphous crystallizes to multi-phase during desorption process. By adding the element, such as Cu, to reduce the affinity to H, hydrogen desorption temperature can be modified as shown in Fig. 1.

With respect to electrochemical performance of Mg-Ni amorphous, it has been found that the amorphous phase crystallized gradually in the charge/discharge cycling and the capacity is proportional to the amount of amorphous and the fully crystallized sample could not deliver capacity. By adding Ti, the stability amorphous increased and the capacity decay improved.

Fig. 1: a) Hydrogenation kinetics of Mg₈₀Ce₁₀Ni₁₀/MG, b) TG curves of Mg-Ce-Ni-X (X= Ti, Co, Cu, Zn, Ag) MGs. Inserts show the HAADF-STEM image of amorphous alloys and hydrides, and the mixing enthalpy of X-H pairs.

References


Short CV: Received his Ph.D from Dalian University of Technology in 1988 and was a Humboldt Research Fellow in Technical University of Berlin. He is now professor and vice president of South China University of Technology. He has been dedicated to the research and development of advanced hydrogen storage materials and battery materials, with emphasis on high-performance metallic energy storage materials based on the multi-phase multi-scale structure, to boost the massive utilization of renewable energy source. Also, he invented a unique plasma milling technique for efficient powder materials preparation. He has authored and co-authored over 300 academic papers and published over 30 patents.

Corresponding author: Min Zhu, memzhu@scut.edu.cn, Tel. +86-20-87113924
REVERSIBLE HYDROGEN STORAGE WITH ORGANIC POLYMERS

Kenichi Oyaizu

Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan

Abstract
Organic compounds capable of reversibly reacting with H₂ to yield hydrogenated products have been studied as hydrogen carriers. However, these compounds often suffer from safety issues and are usually hydrogenated only at high H₂ pressure and/or temperature. We have found that the hydrogenation/dehydrogenation cycle is accomplished at moderate conditions with ketone/alcohol-containing polymers that can even be molded into a plastic sheet. All of the ketone groups in the polymer were hydrogenated by simply placing the sheet at room temperature under 1 atm of H₂ in the presence of an iridium catalyst, which then underwent H₂ release upon warming above 60 °C. The easy handling and moldable nature of the polymers indicate the feasibility of applying the materials as pocketable hydrogen carriers.

Introduction
Redox-active polymers with electrochemical reversibility and rapid reaction rates are employed to develop organic electrode-active materials, based on their self-exchange reactions in polymer layers [1]. Negative charging of the electroneutral redox polymers result in a significant increase in basicity to allow hydrogenation of each redox-active site in the polymer. Since most of the hydrogenated products are no longer redox-active, aprotic battery electrolytes are employed to avoid the hydrogenation.

Organic compounds that undergo hydrogenation, such as toluene to yield methylcyclohexane, have been studied as hydrogen storage materials. However, the hydrogenation with H₂ usually proceed via a highly energy consuming process. We anticipated that electrolytic hydrogenation of the redox-active molecules would provide a much simpler process, and found that ketone-containing polymers stored H₂ via the electrolytic process in H₂O at room temperature. The resulting alcohol polymer evolved H₂ by warming under mild conditions with an iridium catalyst [2]. Here we report that some of the relevant polymers represent an intriguing aspect of a non-electrolytic process, allowing the hydrogenation by simply reacting with H₂ gas.

Experimental
Polymers in Fig. 1 were prepared by radical polymerization of corresponding monomers, or by crosslinking of bis (diethylamino)fluorenone and tri(bromomethyl)benzene.

Results and Discussion
Polymers functionalized with fluorenone, quinoxalines and methylpyrazine (Fig. 1) demonstrated the reversible H₂ storage, according to the temperature. A high mass density of ca. 5 wt% was accomplished with the compact unit structure of the methylpyrazine-containing polymer. A temperature to dominate the equilibrium, R + (n/2)H₂ ⇄ RHₙ, is given by ΔrH /ΔrS, where ΔrH and ΔrS are the enthalpy and entropy changes for the hydrogenation. These functional groups are characterized by small ΔrH (for example, ca. -50 kJ/mol for fluorenone) compared to toluene (ca. -200 kJ/mol), resulting in the moderate critical temperature. Preliminary calculation supported that the fluorenone polymer was hydrogenated with H₂ at room temperature, but the reverse reaction proceeded above 60 °C to release H₂.

The results also gave insight into the nature of the reversible storage of H₂ where the bistability of the hydrogenated and dehydrogenated states seemed to be responsible, which was reminiscent of the electrochemical bistability required for the storage of charge in organic electrode-active materials.

Fig. 1 Polymers for H₂ storage, shown in the order of the approximate reduction potentials in V vs. Ag/AgCl, along with the mass storage density in wt%.

References


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ENHANCED ELECTROCHEMICAL PROPERTIES OF HYDROGEN STORAGE MATERIALS

Joseph A. Teprovich Jr1, Matthew Green1, Miguel Orozco1, Paulo Simon1, Jovy Santos1, Christopher Babasi1, Patrick A. Ward2, Ragaiy Zidan2, Puru Jena3

1 California State University Northridge, 18111 Nordhoff St, Northridge, CA 91330, USA
2 Savannah River National Laboratory, Aiken, SC 29803, USA
3 Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, USA

This talk will focus on: (1) the utilization of hydrogenated fullerenes (i.e. C_{60}H_{x}) as high capacity lithium intercalation anodes and (2) boron based clusters as solid-state electrolytes for lithium ion batteries. We have recently demonstrated that the quantity of chemisorbed hydrogen on C_{60} can be utilized to modulate the electrochemical properties of C_{60}. The attachment of chemisorbed hydrogen on C_{60} enables the reversible lithiation of the material for 2,000 cycles and an electrochemical capacity higher than that of the commonly utilized graphite electrode (588 mAh/g vs. 372 mAh/g). We have also investigated the use of LiBH_{4} and Li_{2}B_{12}H_{12} based electrolytes. The destabilization of the LiBH_{4} salt by the addition of C_{60} and partial dehydrogenation of the material enables the nanocomposite to be utilized as a solid-state electrolyte well below the orthorhombic to hexagonal phase transition temperature of LiBH_{4} (~115°C). We have also shown that the ionic conductivity of LiBH_{4} can be enhanced by high-energy milling with 1 mS/cm ionic conductivity achieved at ~55°C. Current work is focused on evaluating the ionic conductivity of Li_{2}B_{12}H_{12} based composite materials to simultaneously achieve high ionic conductivity at or below room temperature and reducing the thickness of solid-state electrolyte.

Introduction

There is a need to develop higher gravimetric and volumetric energy density batteries to power the next generation of consumer electronics and automobiles of the future. To achieve this goal there needs to be major advancements in the anode and the electrolyte used in batteries. Metal hydride based materials can potentially fill this void and advance utilization in commercially available electrochemical systems.

Experimental / Computational

C_{60}H_{x} was prepared by direct hydrogenation for 6-72 hours at 100 bar H_{2} and 350°C for different hydrogenation times. Electrochemical cycling was performed with LiPF_{6} in EC/DMC. Li_{2}B_{12}H_{12} was synthesized by an all-solid state route. The electrolyte was infused into the matrix via appropriate solvent. Cycling was performed at the indicated rates and temperatures.

Results and Discussion

A systematic experimental and theoretical analysis of a series of C_{60}H_{x} materials determined that they have the potential to be utilized as high capacity anodes for lithium ion batteries. It was determined that C_{60} with an average of 2.5 w.% hydrogen is optimal for this application. A reversible capacity of 588 mAh/g was achieved for this anode (Fig. 1).

On-going work with Li_{2}B_{12}H_{12} has shown it to be an effective and stable solid-state electrolyte for batteries. We have recently found that it is possible to incorporate this electrolyte into a matrix that enables it to utilized at room temperature at high cycling rates (up to 10°C) with good capacity retention (Fig. 2). Additional, cycling tests showed that this electrolyte can also operate below room temperature and is compatible with LTO anodes and TiS_{2} cathodes.

References


Joseph received his Ph.D in Chemistry from Lehigh University in 2008. He worked at Savannah River National Laboratory as a post-doctoral research scientist from 2009-2011 and was a staff scientist from 2011-2017. In 2017, he became a professor at California State University Northridge in the Department of Chemistry & Biochemistry. He has numerous publications and patents regarding the use of metal hydrides in a variety of energy storage applications and presented this research at a variety of national and international conferences. This research includes the synthesis of alanate (AlH_{3}) for portable power systems, boron based hydrides for solid ionic conductors, alanate for use as high capacity anode materials, metal intercalated carbon nanocomposites for hydrogen storage, and metal hydride based thermal energy storage systems for concentrating solar power.

Corresponding author: Joseph Teprovich, joseph.teprovich@csun.edu, +1 570-578-7842.
HYDROGEN STORAGE PROPERTIES AND CRYSTAL STRUCTURAL INVESTIGATIONS ON MG CONTAINING ALLOYS

Toyoto Sato¹, Tomohiro Mochizuki², Kazutaka Ikeda², Toshiya Otomo², Heena Yang³, Wen Luo³, Andreas Züttel³, Shigeyuki Takagi⁴, Tatsuo Kono⁴, Shin-ichi Orimo¹, ⁴

¹Institute for Materials Research, Tohoku University, Japan, ²Institute of Materials Structure Science, High Energy Accelerator Research Organization, KEK, Japan, ³Swiss Federal Institute of Technology in Lausanne, Switzerland, ⁴WPI-Advanced Institute for Materials Research (AIMR), Tohoku University, Japan

Mg containing alloys, Y(2–x)MgNi₄, with an FCC crystal structure were synthesized by heat-treatment at ≤ 1123 K of powder mixtures of (2–x)YNi₂ + xMgNi₂ (x: 0.6, 0.8, 1.0 and 1.2). Their hydrogen storage properties were investigated at 323 K, and reversible hydrogen absorption and desorption reactions were observed. Crystal structure of hydrogen absorbed phase of YMgNi₄ (x = 1.0) was studied by neutron diffraction, of which pattern was reproduced by an orthorhombic crystal structure with a = 5.0280(3) Å, b = 5.3827(4) Å and c = 7.2718(31) Å.

Introduction

Magnesium (Mg) is an abundant and light element and has a good reactivity with hydrogen. Therefore, Mg or Mg containing alloys are expected to be a promising material for hydrogen storage. In particular, REMgNi₂ (RE: rare-earth metals) with a similar crystal structure with the C15 Laves phase alloy exhibits reversible hydrogen absorption and desorption reactions at room temperature [1–3]. Even though Y is the lightest element in the RE, hydrogen mass density of YMgNi₄ is almost the same with the other REMgNi₂. To improve the hydrogen capacity of YMgNi₄, we have attempted to synthesize Y(2–x)MgNi₄ with systematically changed molar ratios of Y and Mg and investigate their hydrogen storage properties. In addition, we have clarified crystal structures of YMgNi₄, which is a basis of this study, in the hydrogen absorption reaction by neutron diffraction.

Experimental / Computational

The samples were synthesized from heat-treatment at ≤ 1123 K of powder mixtures of YNi₂ and MgNi₂ with 2–x : x in molar ratios (x: 0.6, 0.8, 1.0 and 1.2). The hydrogen storage properties on the samples were studied by pressure–composition–temperature measurements (so-called the PCT measurement) at 323 K. Crystal structure of hydrogen absorbed YMgNi₄ (x = 1.0) were determined from neutron diffraction under 5 MPa of deuterium gas pressure studied by NOVA at MLF, J–PARC.

Results and Discussion

After the syntheses, all samples were characterized by X–ray diffraction, in which major Bragg peaks were indexed by an FCC unit cell. In the x = 1.0, the unit cell parameter was close to previous results of YMgNi₄ reported by Aono et al. and Shtender et al. This indicated that YMgNi₄ was synthesized from YNi₂ and MgNi₂. Furthermore, the unit cell parameters (Table 1) were increasing with decreasing amount of Mg. This suggested that excess Mg atoms (x > 1.0) are located in Y atomic sites and excess Y atoms (x < 1.0) are located in Mg atomic sites. From the PCT measurements, reversible hydrogen absorption and desorption reactions at 323 K were observed.

Table 1 Unit cell parameters of (2–x)YNi₂ + xMgNi₂

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This work was supported by JSPS KAKENHI (JP18H05513 and JP18H05518) and JST SICORP (JPMJSC 1802). The neutron diffraction experiment was performed by NOVA, J–PARC (2019A0068).

References


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Thermal Battery Development for Concentrated Solar Power Systems

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Solar energy is the most abundant renewable energy resource and therefore logically represents the most important renewable energy resource for the future. The International Energy Agency (IEA) roadmap for solar energy set a target of ≈22% of global electricity production from solar energy by 2050, with 50% being produced from concentrating solar thermal (CST) power systems. Achieving this target will be possible only if the costs of producing electricity from solar energy are significantly reduced and cost effective energy storage technologies can be developed.

A major challenge is to achieve continuous, low-variability power generation from renewable energy sources, for stand-alone applications or for integration with domestic power grids. Solar mirror collection fields can collect thermal energy during the day and run a heat engine to convert it into electricity, but cannot provide power at night. However, if some of the heat is used to remove hydrogen from a metal hydride, the reverse reaction where hydrogen absorbs back into the material. Craig has published 1.

References

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NEW DEVICE FOR HYDROGEN SEPARATION FROM DECOMPOSED GAS OF ENERGY CARRIERS, NH$_3$ AND MCH, USING FLAT VANADIUM ALLOYS MEMBRANES

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Abstract: Hydrogen permeation performance of our device using flat vanadium membranes to separate highly pure hydrogen from a gas mixture of hydrogen and nitrogen will be presented. We have achieved the hydrogen permeation flow rate over 9 L/min at 623 K, using a newly designed multi-membrane device. Effects of hydrogen on mechanical properties of vanadium alloy will be also shown.

Introduction
Recently, there is a growing interest to develop new hydrogen permeable membranes which can substitute current palladium alloy membranes to reduce the cost. Group 5 elements, having BCC crystal structure, are good candidates for new membrane materials. Especially among them, vanadium has been recognized as promising element because of its high diffusivity and fair solubility of hydrogen. In this work, a new device using vanadium-iron alloy membranes were developed and hydrogen permeation performance was tested.

Experimental
Round-shaped sheets of V-10Fe alloy with about 100mm diameter and 0.1mm thick were cut from cold-rolled sheet and annealed, and then 100nm thick catalytic layers of Pd-25Ag alloy were deposited on both sides of the V-10Fe sheets, which gave hydrogen separation membranes. Hydrogen permeation tests were performed from a gas mixture of 75% H$_2$ + 25% N$_2$, at 623 K.

Results and Discussion
Four membranes of V-10Fe were equipped to give a hydrogen separation device [1]. Figure 1 shows an appearance of the device. When we applied 0.53 MPa of the gas mixture, 75% H$_2$ + 25% N$_2$, at 623 K, the hydrogen flow rate of 9.3 L/min. (=540 L/hr.) was achieved at a separation efficiency of 80%. The hydrogen flow rate, 540 L/hr. overpasses the flow rate necessary for operation of the ENE-FARM for home usage, 500 L/Hr. We believe that our device is promising to extract pure hydrogen gas from decomposed gas of energy carriers, ammonia and also methyl cyclohexane.

Effects of hydrogen on mechanical properties of V-10Fe and also, effects of trace amounts of ammonia and methylcyclohexane (MCH) on hydrogen permeation performance will also be shown.

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References

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STRUCTURAL AND DYNAMICAL STUDY ON PdPt HYDRIDE NANOPISTLES

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The nanometer-sized metals attract much attention since their physical and chemical properties are substantially different from those of bulk metals. The phase-separated nanoparticles of Pd-core and Pt-shell are mixed to be solid solution alloy by repeating hydrogen absorption/desorption processes at 373 K. To investigate the positions and diffusion dynamics of hydrogen atoms in PdPt nanoparticles, we measured the neutron powder diffraction (NPD) and quasielastic neutron scattering (QENS), respectively. Our QENS study suggested that the insertion of Pt atoms to Pd fcc lattice may deform the potential energy surfaces of the hydride sites and enhance the diffusion of hydrogen atoms.

Introduction
The nanometer-sized metals attract much attention since their physical and chemical properties are substantially different from those of bulk metals. Kobayashi et al. found that the phase-separated nanoparticles of Pd-core and Pt-shell are mixed to be solid solution alloy by repeating hydrogen absorption/desorption processes at 373 K [1]. In this study, we have investigated the positions and diffusion dynamics of hydrogen atoms in solid solution PdPt nanoparticles by means of neutron powder diffraction (NPD) and quasielastic neutron scattering (QENS), respectively.

Experimental
The mean diameter of nanoparticles was determined to be 5.0 nm from TEM images. The NPD patterns of Pd₀.₈P₀.₂H₀.₄7 separated nanoparticles were measured on NOVA at J-PARC. The QENS experiments of Pd₀.₈P₀.₂H₀.₄7 nanoparticles were performed on Pelican and Emu at ACNS, ANSTO. Neutron scattering is a powerful tool to explore the position and dynamics of hydrogen atoms in an atomic scale owing to the large coherent and incoherent scattering cross sections of hydrogen atoms.

Results and Discussion
The Rietveld and atomic pair distribution function (PDF) analyses for the NPD patterns [2] revealed that D atoms are located at the interstitial octahedral (O) and tetrahedral (T) sites of an fcc lattice, as schematically shown in the inset of Fig. 1. Interestingly, 47% of D atoms occupy the T sites even at 300 K, which is larger than that for Pd₀.₃6 nanoparticles (31%). Figure 1 shows the Arrhenius plot of the relaxation times (τ) for Pd₀.₈P₀.₂H₀.₄7 nanoparticles together with τ for PdH₀.₄7 nanoparticles obtained in our previous QENS experiments [3]. The slow and fast relaxation processes correspond to the hydrogen motions in the interior and subsurface regions of nanoparticle, respectively. The τ and the activation energy of Pd₀.₈P₀.₂H₀.₄7 nanoparticles are smaller than those for PdH₀.₄7 nanoparticles. It should be noted that the fast relaxation time is almost temperature independent below 250 K, suggesting tunneling processes. Thus, the substitution of Pt atoms may deform the potential energy surfaces and enhance the diffusion of hydrogen atoms.

Fig. 1: Arrhenius plot of the relaxation times for Pd₀.₈P₀.₂H₀.₄7 and PdH₀.₄7 nanoparticles.

References

Hiroshi Akiba studied physics at the Toho University and received his Ph. D. in 2012 with studies on the organic metals with a magnetic anion. He became a JST-CREST project researcher at the University of Tokyo in 2012. Currently, he is a research associate at the University of Tokyo. His present research interests are in the physical properties of metal hydrides and their nanoparticles. These are investigated by means of adiabatic calorimetry and neutron scattering.

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H$_2$ Nuclear Spin Conversion on Metal Surfaces: Physisorption vs. Molecular Chemisorption

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We investigate theoretically the ortho-para (o-p) conversion of H$_2$ in two adsorption states on metal surfaces: physisorption and molecular chemisorption. These two distinct states are prototypically represented by H$_2$/Ag(111) and H$_2$/Pd(210) for physisorbed and MC, respectively, and revisited by means of first principles calculations based on density functional theory (DFT). The ortho-para (o-p) conversion probability is evaluated by means of 2$^\text{nd}$ order perturbation theory. We found that the o-p conversion time on Ag(111) is longer than on Pd(210), reflecting a strong dependence on the adsorption state.

Introduction
It has been known that physisorbed hydrogen undergoes ortho-para (o-p) conversion in the order of minutes on non-magnetic metal surfaces such as Ag(111)[1]. This has been described by the virtual surface-molecule electron transfer and the hyperfine Fermi contact interaction within second order perturbation theory. Recent experiments have shown that on relatively open surfaces such as Cu(510)[2] and Pd(210)[3], H$_2$ is in the so-called molecularly chemisorbed state and behaves as a 2-dimensional quantum rotor, while the o-p conversion rate is 1 order magnitude faster than on flat surfaces. In this work we compare the adsorption state dependence of the hydrogen o-p conversion rate by means of model and first principles calculations.

Computational
The adsorption states on two representative metal surfaces are investigated by constructing an adsorption potential energy surface (PES). DFT calculations are performed using PBE-GGA, with a 500 eV plane wave cutoff energy, and 9x9x1 kpoints for Brillouin zone integration. PES is constructed by performing total energy calculations at different surface-molecule distances and orientations. From DFT, we obtain the equilibrium adsorption distance, bond length and electronic properties of surface and molecule complex which are used as parameters in the model calculations. To calculate the o-p conversion time, we considered a two-step process[1] in which perturbation is composed of Coulomb and Hyperfine Fermi-contact Hamiltonians, describing the virtual surface-molecule electron transfer and electron and nuclear spin interactions. The o-p conversion probability is calculated by Fermi’s golden rule and the conversion time is obtained subsequently.

Results and Discussion
Figure 1 shows the adsorption potential energy profiles for H$_2$/Ag(111) and H$_2$/Pd(210) systems. On Ag(111), H$_2$ is weakly physisorbed with an adsorption energy of around 6 meV. This is in contrast with case on Pd(210) in which the molecule adsorption is characterised by shorter adsorption height and stronger binding energy of around 300 meV. This difference in adsorption states can be ascribed to the position of the d-band centres of metal surfaces with respect to the Fermi level. Pd(210) d bands are narrower and shifted closer to EF than Ag(111), indicating higher reactivity. Our derived expression of the nuclear spin transition probability depends on several parameters that can be directly obtained from the above first principles calculations. We found that the transition rate depends on the Fermi level-density of states and work functions of the isolated substrates, the adsorption height, bond length, surface wave function decay parameter and the anti-binding level of adsorbed H$_2$. Furthermore, since the electron hopping parameter strongly depends on the adsorption height, the matrix element of the electron contribution in the transition probability of H$_2$/Pd(210) is larger than that of H$_2$/Ag(111). Using these parameters we found that o-p conversion on Pd(210) is faster than on Ag(111). Our results show that the conversion rate can be directly correlated to the chemical nature of adsorption on metal surfaces.

References

Fig. 1 Adsorption potential energy profile of H$_2$ on Ag(111) and Pd(210).

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PHOTOCHEMICAL HYDROGEN EVOLUTION FROM MOLECULAR IRON COMPLEXES WITH PHENYLENEDIAMINES

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This paper reports systematic studies on the iron complexes bearing o-phenylenediamines (opdas) and o-benziquinodiamines (bqdis) resulted by the stepwise two-electrons and two-protons transfer processes. Based on the fact that Fe[6(opda)]3(CIO4)2 ([6R]CIO4)3 demonstrates photochemical hydrogen evolution (HER), a suggestive mechanism for the HER will be discussed.

Introduction

Dihydrogen represents an attractive prospective energy carrier with minimal environmental impact. Due to the difficulties associated with the storage and transportation of dihydrogen gas, the development of safe and convenient hydrogen-storage materials is essential.

In 2013, we have reported a high-spin (hs) FeII complex containing o-phenylenediamine (opda) ligands, hs-[FeII(opda)3][CIO4]2 ([6R]CIO4)2), which exhibited photochemical HER (PHER) activity in THF under irradiation with UV light at room temperature. Furthermore, [6R]CIO42 is able to accept six electrons and six protons to afford low-spin (ls) [FeII(bqdi)]2(CIO4)2 (bqdi: o-benzquinodimine) ([6O]CIO4)2 upon aerobic oxidation. In the PHER, the opda ligand acts as an electron/proton pool for the photochemical generation of hydrogen, and the amount of evolved hydrogen is enhanced remarkably by the coexistence of an electron and proton donor such as hydroquinone, which is indicative of a catalytic photochemical generation of hydrogen.

Here we report the stepwise chemical reduction of [6O]PF62 and the isolation of the corresponding series of PLMV complexes, i.e., ls-[FeII(bqdi)(opda)]PF62 ([2R]PF62) and ls-[FeII(bqdi)(opda)]PF62 ([4R]PF62) (Scheme 1). The detailed structural and spectroscopic characterization both in the solid state and in solution revealed the properties of the PLMV complexes, together with those of [6R]CIO42 and [6O]PF62. These combined results suggested characteristic electron systems, wherein π- and d-electrons are strongly correlated.

Results and Discussion

The partially reduced and protonated complexes [2R]PF62 and [4R]PF62 were synthesized and fully characterized both in the solid state and in solution as intermediates of the proton-coupled multi-electron-transfer processes between [6R] and [6O]. Our findings offer important molecular insight into the injection of multiple proton-coupled electrons into the fully oxidized form, [6O], to afford the reduced complexes [2R], [4R], and [6R], which display photochemical HER activity, for the design of photo-driven molecular hydrogen-storage-evolution systems.

Scheme 1 Six-electron- and six-proton-transfer processes in ls-[FeII(bqdi)]2[6O]hs[FeII(opda)]2[4R].

References


Ho-Chol Chang was born in Kyoto, Japan in 1973. He studied chemistry and received his B.S. from Korea University in Tokyo, Japan (1995). He then received his M.S. from Tokyo Metropolitan University (1998) and earned his Ph.D. under the supervision of Professor S. Kitagawa of Kyoto University (2001). He became an assistant professor in the Department of Synthetic Chemistry and Biological Chemistry at Kyoto University in 2001, working in the research group of Professor S. Kitagawa. He was also a research member of the PRESTO project of the Japan Science and Technology Agency (JST) in 2002–2006. He becomes an associate professor of chemistry at Hokkaido University in 2008. From 2013, he is a full professor at Chuo University, Japan, where his group’s interests are centered on rational construction and dynamic control of electronically labile molecular assemblies in solid, liquid (solution), and liquid-crystalline phases.

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DEVELOPMENT OF EFFICIENT SYSTEMS FOR HYDROGEN PRODUCTION BASED ON CATALYTIC ACTIVITY OF IRIDIUM COMPLEXES IN DEHYDROGENATIVE REACTIONS

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Abstract
An efficient catalytic system for the production of hydrogen from a methanol-water solution has been developed using a new anionic iridium complex bearing a functional bipyridonate ligand as a catalyst. Additionally, we have also developed an efficient system for the synthesis of acetic acid via dehydrogenation of an ethanol-water solution using a new iridium catalyst bearing a functional bipyridonate ligand with N,N-dimethylamino substituents.

Introduction
Hydrogen is attracting considerable attention as an alternative energy source to fossil fuels. To work toward a “hydrogen economy” it is highly important to develop an efficient and practical method for the production of hydrogen from renewable and easy-to-handle resources. Therefore, the development of an efficient, safe, and sustainable hydrogen production method is required. During the course of our studies on the catalytic activity of iridium complexes, we have previously reported the dehydrogenative oxidation of alcohols catalyzed by iridium complexes 1 and 2 bearing functional bipyridine and bipyridonate ligands, respectively.1,2 On the basis of these investigations, we have succeeded in developing efficient systems for hydrogen production.

Results and Discussion
First, we have succeeded in developing effective hydrogen production from aqueous methanol under mild conditions (under reflux at 88 °C in dilute basic solution) and without an additional organic solvent by the employment of the water-soluble anionic iridium catalyst 3 bearing a bipyridonate-type functional ligand [Equation (1)].3

\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \xrightarrow{\text{catalyst 3 (0.5 mol\%) NaOH (0.5 mol\%)}} 3 \text{H}_2 + \text{CO}_2 & (1)
\end{align*}
\]

Furthermore, closely recently, we have also developed an efficient system for the synthesis of acetic acid with concomitant production of hydrogen from ethanol-water solution using a new iridium catalyst 4 [Equation (2)].4 It should be noted that the present system achieved selective production of acetic acid from sustainable resources (ethanol and water) without the use of any oxidant.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} & \xrightarrow{\text{catalyst 4 (0.25 mol\%) NaOH (1.2 equiv.)}} 2 \text{H}_2 + \text{CH}_3\text{COOH} & (2)
\end{align*}
\]

References

Ken-ichi Fujita received Ph.D. degree in 1997 from Kyoto University under the direction of Professor Take-aki Mitsudo. In 1997, he was appointed as an assistant professor at Faculty of Integrated Human Studies, Kyoto University. In 2006, he worked as a postdoctoral fellow with Professor John F. Hartwig at Yale University. He was promoted to an associate professor in 2006 and a full professor in 2015 at Graduate School of Human and Environmental Studies, Kyoto University. He received the Incentive Award in Synthetic Organic Chemistry, Japan in 2006, Nagase Foundation Award in 2017, and The Chemical Society of Japan Award for Creative Work in 2018. His current field of research is organometallic chemistry, synthetic organic chemistry, and homogeneous catalytic chemistry.

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FIRST PRINCIPLES STUDY OF HYDRIDE ION CONDUCTOR

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Hydride (H) ions have attracted attention because of their potential to enable high-performance electrochemical storage device based on hydrogen. In this study, we focus on semiconductor- and metal-type H ion conductors, i.e. LaLiHO and BaTiO$_3$H$_x$. The first-principles calculations were conducted to reveal the H$^+$ ion conduction mechanism. For example, the Bader-charge analysis indicated that the H placed at oxygen sites in LaLiHO and BaTiO$_3$H$_x$ has negative charge c.a. -0.6. We also calculated that the activation energy of H$^+$ ion conduction path in LaLiHO is 0.48 eV, and the negative charge H$^-$ state was retained. We will further investigate charge state of several type of H defect in the near future.

Introduction

Hydride H$^+$ conduction has been recently confirmed in the La$_{2-x}$Sr$_x$LiH$_{1+x}$O$_{3-y}$ type oxyhydride material. [1] However, little is known about the H$^+$ diffusion mechanism in this oxyhydride material. The H$^+$ ion conductors of La$_2$LiHO$_x$ [1] and BaTiO$_3$H$_x$ [2,3] are expected to show different H$^+$ conduction mechanism because their electronic conductivity is different from each other: LaLiHO$_x$ and BaTiO$_3$H$_x$ have the semiconductor- and metal-type band structure, respectively.

Computational

Density functional theory (DFT) calculations were performed within pseudopotential framework implemented in the Quantum Espresso package. [4] Defect-formation energies are defined as the change in total energy due to the intercalation of a defect into a supercell. [5]

Results and Discussion

We performed the Bader-charge analysis firstly. The results indicated that the H placed at oxygen sites in both LaLiHO$_x$ and BaTiO$_3$H$_x$ crystal has negative charge c.a. -0.6. We also conducted the nudged elastic band (NEB) calculation to estimate the activation energy of H$^+$ ion conduction path. Consequently, the activation energy of H$^+$ diffusion in LaLiHO$_x$ was obtained as 0.48 eV, which value is consistent with previous studies. [6, 7] In the ion conduction path, the negative charge H$^-$ state was always retained. We will further investigate charge state of several type of H defect in the near future.

References


Fig. 1 Energy profile for H$^+$ conduction path in La$_2$LiHO$_x$.

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NEW ASSAY METHOD FOR THE ENZYMES REACTING WITH GASEOUS SUBSTRATES BY RAMAN SPECTROSCOPY

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We have developed a new assay system for measuring the enzymatic reactions involving gaseous substrates by Raman spectroscopy. This system permits continuous monitoring of the gas composition in the reaction cuvette in a non-invasive manner over a prolonged time period. We have applied this system to the H/D exchange reaction of the [NiFe] hydrogenase. Based on a kinetic model, the ratio of the rate constants of the H/D exchange reaction at the active site and product release rate were successfully estimated.

Introduction

Dihydrogen is spot-lighted as one of the clean energy carriers. At present, dihydrogen is mainly produced by steam reforming of natural gas. It has been well known that the enzyme, hydrogenases, catalyze the production and decomposition of dihydrogen from biomass. We have studied the structures of [NiFe]-hydrogenases by x-ray crystallography in conjunction with various spectroscopic methods to elucidate the essential structural unit for the catalytic reaction. Since rapid and precise screening of the potential enzymes are prerequisite for developing the next-generation hydrogen bio-fuel cells, simple and reliable assay method for hydrogenases will provide a valuable tool for the discovery of new excellent hydrogenases, which are more active, resistant against O₂ or thermostable.

Hydrogenases also catalyze non-physiological two reactions, H/D exchange reaction between H₂O(D₂O) and D₂H₂, and the nuclear spin isomer conversion reaction between para-H₂ and ortho-H₂. The H/D exchange reaction is conventionally measured by gas chromatography, mass spectrometry, or a combination thereof (GC/MS). Although these methods are well established, they require the sampling of the gas from the cuvette at regular intervals, resulting in the changes the pressure of the gas phase after each operation. Alternatively, the gas composition can be measured in situ using Raman spectroscopy without sampling. This means that Raman method enables us to trace the time course of the reaction without any data corrections. Raman spectroscopy has the additional advantage of permitting the continuous and simultaneous measurement.

Results and Discussion

The time course of the Raman peak intensities of H/D exchange reaction by [NiFe]-hydrogenase in the D₂/H₂O system was successfully monitored. The Raman peak intensities of D₂ and H₂ exhibited a simple decay and rise, respectively. The calculated initial production rate of HD (0.0018±0.0002 min⁻¹) was almost equal to that of H₂ (0.0022±0.0003 min⁻¹). These results indicate that not only the single exchange reactions (D₂ + H⁺ → HD + D⁺) but also the double exchange reaction (D₂ + 2H⁺ → H₂ + 2D⁺) occurred macroscopically in the reaction cuvette.

To analyze the time course of the H/D exchange reaction in the D₂/H₂O system quantitatively, we adopted the reaction model proposed by Leroux et al.[1] In this model, k is the rate constant of the H/D exchange reaction at the active site and kₕ and kₛₑᵣₑ are the rate constants for the trapping and release of the substrates, respectively. To obtain the ratios of k to kₛₑᵣₑ, the time courses of D₂, HD and H₂ at several enzyme concentrations were fitted against the analytical solutions derived from the model equations. The calculated values of k/kₛₑᵣₑ (1.8–2.1) were approximately constant for enzyme concentrations in the range of 2–20 µM. Recent new results will be also presented in the poster.

References


Yoshiki Higuchi is a full professor in the Graduate School of Life Science, University of Hyogo. He obtained his Ph.D. from Osaka University (1984). After a postdoctoral position at Osaka University, he was appointed as an assistant professor at the Himeji Institute of Technology (1985). He moved to Kyoto University in 1995 as an associate professor of the Graduate School of Science. In 2002, he moved to the Himeji Institute of Technology (presently University of Hyogo) to become a full professor in the Graduate School of Science (presently Graduate School of Life Science). He received the award of The Crystallographic Society of Japan in 1999, 38th Iue Culture Award for Science and Technology in 2014, and Hyogo Science Award in 2017.

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Epitaxial growth of Ca$_2$NH thin films using reactive magnetron sputtering

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Abstract

We here present the epitaxial growth of Ca$_2$NH films on MgO(110) substrates. The study opens up the way to quantitatively investigate the catalytic activities on the surfaces of Ca$_2$NH.

Introduction

CaN$_x$H$_y$ is a promising catalyst for the production of ammonia, which is an important industrial chemical such as fertilizers [1,2]. Among the compounds, CaN$_x$H$_y$ attracts much attention due to its high catalytic activity [2]. To precisely understand the mechanism of such catalytic reaction, preparation of well-defined surfaces with a smooth and highly-oriented structure is required. For this purpose, epitaxial thin films can provide an ideal platform. However, due to its chemical instability, neither thin film nor single crystal has not been reported to date. In this study, we introduce our approach to fabricate Ca$_2$NH epitaxial thin films using reactive magnetron sputtering.

Experimental / Computational

Ca$_2$NH thin films were deposited on MgO(110) substrates using reactive magnetron sputtering. A Ca metal plate (1 inch.) was used as a target material. The substrate temperature was set to 500°C, and RF power of 30 W was supplied. During the deposition, Ar, N$_2$, and H$_2$ gases were introduced to the growth chamber with flow rates of 10 sccm, 5 sccm, and 0.5 sccm, respectively. The total pressure was set to 1.0 Pa. The deposition time and typical film thickness was 1 hour, and 160 nm, respectively. Note that the thicknesses were measured in the air using a stylus profiler. The structural properties of thin films were characterized by X-ray diffraction (XRD) using a custom-built vacuum cell to avoid atmospheric air.

Results and Discussion

Figure 1 shows an out-of-plane XRD pattern of an obtained CaN$_x$H$_y$ film. A single peak has appeared at $2\theta = 51.4^\circ$. However, it is difficult to distinguish its chemical composition with the data due to the structural similarity between CaN$_x$H$_y$ phases such as Ca$_2$NH 440 ($2\theta = 51.0^\circ$), CaNH 220 ($2\theta = 50.3^\circ$) and Ca(NH$_2$)$_2$ 204 ($2\theta = 50.1^\circ$). Therefore, reciprocal space mapping was performed. The results indicate the fabrication of a single-phase Ca$_2$NH. Additionally, the epitaxial relationship between the substrate and thin film was verified through pole figure measurements.

References


H-ION CONDUCTION AND ANHARMONIC VIBRATION IN OXYGEN-DOPED LANTHANUM HYDRIDE

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Fast ionic conductors have considerable potential to enable novel technological development for energy storage and conversion. Hydride (H+) ions are a unique species because of their natural abundance, light mass, and large polarizability. Herein, we investigate characteristic H+ conduction, i.e., fast ionic conduction controlled by a pre-exponential factor. Oxygen-doped LaH3 (LaH3−xOx) has an optimum ionic conductivity of 2.6 × 10−2 S cm−1—the highest conductivity reported to date among H+ conductors at intermediate temperatures. With increasing oxygen content, the relatively high activation energy remains unchanged, whereas the pre-exponential factor decreases dramatically. In this presentation, we discuss the origin of the large pre-exponential factor in terms of anharmonic vibrations of hydride ion.

Introduction

Hydride ion (H+) which has a high standard redox potential (−2.3 V) has recently attracted much interest as not only an energy storage with high energy density, but also an active species for chemical processes. H+ conduction in solids has recently been reported1, 2, however, a high H+ conduction is only achieved at relatively high temperature. In order to utilize the advantage of H+ for the applications, H+ electrolyte with a high conductivity at lower temperature is highly required.

Experimental / Computational

Here we study the electric properties of lanthanum oxyhydride (LaH3−xOx). By utilizing a high pressure synthesis technique, we successfully synthesized the new phase of LaH3−xOx with a fcc structure over a wide composition range (0 ≤ x ≤ 1). For structure analyses we used XRD and NPD. The electronic and ionic conductivity were measured by DC polarization and AC impedance techniques, respectively.

Results and Discussion

Fig.1 is Arrhenius plots of the ionic conductivity (σi) measured by impedance spectroscopy. At 340°C a high σi over 10−3 S cm−1 was obtained at x = 0.25. The transport number of the ionic conductivity was estimated to be more than 99%, indicating that the conduction is purely ionic. Upon increasing x, the activation energy of ~1.2 eV remains almost unchanged, whereas the pre-exponential factor decreases dramatically from the extraordinarily large value of 1012 S cm−1 K at x = 0.24 to 108 at x = 0.99. This indicates that the pre-factor determines the high σi and its dependence on oxygen content. In this presentation, we discuss the origin of the large pre-exponential factor in terms of anharmonic vibrations of hydride ion.

Fig. 1 Arrhenius plots for ionic conductivity of LaH3−xOx[3]

References


I received the Ph.D. degree in materials science from Tokyo Institute of Technology, Tokyo, Japan, in 2017. I'm currently working as an Assistant Professor in Materials Research Center for Element Strategy at Tokyo Tech. My research interests are to discover new materials such as superconductors, semiconductors, and ionic conductors based on new design principles. It was around early 2011 that I first recognized the usefulness of hydrogen in materials science. At that time I used hydride ion as electron dopant for iron-based superconductors in order to suppress the magnetism and induce superconductivity. Nowadays, I'm interested in exploring materials functionality derived from intrinsic properties of hydrogen, such as high ionic conductivity, low thermal conductivity.

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SOSHI IIMURA
GLASS-PHASE COORDINATION POLYMER DISPLAYING PROTON CONDUCTIVITY AND GUEST-ACCESSIBLE POROSITY

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Abstract
We describe the preparation of the crystalline and glassy state of a coordination polymer displaying proton conduction and guest-accessible porosity. EXAFS and solid-state NMR analyses indicated that pyrophosphate and phosphate ions are the main proton transporters in the glass and that homogeneously distributed 5-chloro-1H-benzimidazole in the glass provide the porosity.

Introduction
Metal-organic frameworks (MOFs) and coordination polymers (CPs) have recently emerged as interesting classes of proton-conductive solids because of their diverse crystal structures, and reasonably high thermal and chemical stability. Although some MOFs and CPs with high proton conductivity (above c.a. 10^{-2} S cm^{-1}) have been reported, their use as, for example, electrolytes in fuel cells has been limited. In fact, improvements with respect to their conductivity, thermal durability, and forming ability are still required for these species to be used in the devices. Herein, we report the preparation of a porous CP in crystalline and glassy states.[1]

Results and Discussion
Crystalline powder sample of CP (hereafter referred to as 1) was synthesized from ZnO, 5-chloro-1H-benzimidazole (Clbim), and an H_{3}PO_{4} solution (85%) via the liquid-assisted mechanochemical method using methanol (Fig. 1). To obtain the activated 1 (1a), 1 was heated at 120 °C under vacuum. The glass-phase derivative of 1 (1g) was prepared, in turn, by melt-quenching 1a. The powder X-ray diffraction (PXRD) pattern of 1a displays slight differences with respect to that of 1, suggesting that only small changes occur in the crystalline structure. The PXRD pattern of 1g was broadened with respect to that of 1, suggesting that the structure of the former is amorphous. The DSC profile of 1g shows a baseline shift at 72 °C, supporting that 1g is in glassy state.

The maximum uptake values of water and methanol were 118.0 and 61.5 mL g^{-1} (4.3 and 2.3 molecules per unit formula) in the case of 1g. In AC impedance experiments, 1g displayed proton conductivity at 130 °C was 1.2 \times 10^{-6} S cm^{-1}, and the activation energy was 1.5 eV. We also measured the proton conductivity of 1g at 298 K under humid conditions. The conductivity under 98% relative humidity condition was 1.2 \times 10^{-4} S cm^{-1}. The high proton conductivity would be originated from effective proton transport in the adsorbed water molecules in the porosity. The guest-accessible porosity is useful to enhance the conductivity of the glass CP. To investigate the mechanism of proton conduction and the structures of 1a and 1g, we conducted EXAFS and solid-state NMR. The results will be shown in poster presentation.

Fig. 1 Crystal structure of 1 viewed along the a axis at 223 K and (c) DSC curve of glass-form 1 (1g).

References

M. Inukai studied solid-state NMR and received his Ph.D. (science) from Osaka University in 2009. After a postdoctoral fellow in the solid-state NMR group of K. Takegoshi (2009-2011) and material science group of S. Kitagawa (2011-2014) in Kyoto University, he has been associate professor of chemical physics in Tokushima University. His research interests focus on solid-state NMR, coordination polymers/metal-organic frameworks, and ion conductors.

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THEORETICAL STUDY OF H/D ISOTOPE EFFECT WITH METAL BY USING COMBINED PLANE WAVE AND LOCALIZED BASIS SET APPROACH

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Abstract

H/D isotope effect has attracted attention in various fields, such as adsorption of atoms/molecules on metal surface and hydrogen absorption in metal. Electronic structure calculation is an effective tool to analyse the details of H/D isotope effect. However, it is difficult to take into account the quantum effect of proton/deuteron with metal electronic structure of surface or bulk in the conventional method. To tackle this problem, we developed combined approach of plane wave and localized orbital treatment, named "combined plane wave and localized basis sets (CPLB)" method. By using this method, we analysed the H/D isotope effect with metal surface and bulk metal.

Introduction

The behavior of hydrogen (H) in the material has extensively attracted attention in the proton conduction, hydrogen absorption, and so on. In particular, the interaction between hydrogen and transition metals is dominant factors to control the absorption and diffusion properties of H in the metal. In these analyses, the deuterium (D) substitution from H are used to obtain the detailed information of the difference of H/D behavior. The H/D isotope effects are extensively studied by both experimental and theoretical approaches to understand the quantum mechanical principles. Generally, H/D isotope effects are induced by the difference of quantum nature of proton and deuteron. The quantum effects are clarified, such as zero-point energy, nuclear tunneling, vibrational excitation, and so on. The H/D isotope effects are observed in the various fields in chemistry, biochemistry, physics, and other related fields.

To consider the geometrical difference by H/D isotope effect in the theoretical calculation, the both treatments of nuclear quantum effect and surface or bulk structure of metal are necessary. Recently, we proposed the combined plane wave and localized basis set (CPLB) method [1]. This method is possible to perform high accurate calculation including nuclear quantum effect by localized (LO) basis sets with the large scale electronic structure calculation for metal part by plane wave (PW). In this study, we analyzed the H/D isotope effect in metal surface and bulk by using the our developed CPLB method.

Computational Details

For the PW based electronic structure calculation, we used the Vienna ab initio simulation package (VASP) with the projector-augmented wave method. The PBE approximation with a generalized gradient approximation was used for the exchange and correlation functional. The cutoff energy was set to be 400 eV. For the LO based electronic structure calculation, we used multi-component density functional theory (MC_DFT) approach to treat nuclear quantum effect directly as well as electrons [3]. Implemented Gaussian 16 program package was used for MC_DFT. The B3LYP with LanL2DZ electronic basis sets was used for all calculation. The single s-type Gaussian-type function was set for proton and deuteron. The optimized geometry and absorption energy were obtained in the framework of CPLB approach.

Results and Discussion

Figure 1 shows an example of H/D absorption in Pd metal. As a Pd bulk, we prepared the 108 atomic system. H or D atom was placed in the both O and T sites. We clearly demonstrated that the difference of quantum effect of proton and deuteron affected to the geometrical structure of surrounding Pd atoms. Detailed analysis for H/D isotope effect will be discussed in the presentation.

References


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DEVELOPMENT OF POWDER NEUTRON HOLOGRAPHY FOR INVESTIGATION OF HYDRIDES

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Abstract

Hydrogeneration of materials provide various and exotic properties. To understand these properties, we propose a novel method that can visualize the local structures of around hydrogen, powder neutron holography. In this study, we simulated the signal of powder neutron holography in Cu and YH₂. We discuss the difference of the two materials.

Introduction

Hydrogeneration of materials provides many exotic properties such as hydrogen induced ferromagnetism or change of transparency. In the view of structural physics, hydrogen position or atomic structure around hydrogen (local structure) is important for understanding these properties. Though information on local structures are obtained by X-ray absorption fine structure (XAFS) or Pair Distribution Function (PDF) methods, these methods have no sensitivity of hydrogen or element selectivity. To overcome this, Neutron Holography (NH) was firstly proposed by Cser in 2001 [1]. We succeeded in enhancing the accuracy drastically by using white neutrons [2]. However, preparation of single crystals of hydrides, which includes information of Radial Distribution Function (RDF), is indispensable for NH, is difficult because of hydrogen embrittlement. Therefore, we propose world-first powder neutron holography (PNH). Holography of powder samples using X-ray already demonstrated by Nishino in 2001 [3].

Computational

In PNH, neutron wavenumber \( k = \frac{2\pi}{\lambda} \) dependence of γ-ray intensity, \( \chi(k) \), is measured, which includes information of Radial Distribution Function (RDF). \( \chi(k) \) is calculated by the following formula (1).

\[
\chi(k) = 2\ln \sum_i \frac{b_i}{k r_i^2} e^{2kr_i} \tag{1}
\]

where \( b_i \) and \( r_i \) are neutron scattering length of i-th atom and distance between selected atom and the i-th atoms, respectively. In this study, we simulated \( \chi(k) \) of Cu and YH₂ powder in the range of \( k = 1\sim11 \text{Å}^{-1} \). The cluster size are 100 Å.

Results and Discussion

Fig. 1 (a) and (b) are simulated \( \chi(k) \) of Cu and YH₂, respectively. The amplitude of the oscillation is about \( 10^{-3} \), \( 10^{-4} \). Sharp peaks are contained in Fig. 1. Note that the peak positions can be explained by Bragg condition with \( 2\theta = \pi \), indicating that these peaks are caused by interference of incident neutron and the Bragg scattering. Moreover, in Fig. 1(a), sharp peaks are positive, while, for YH₂, some of sharp peaks are negative. This is due to the difference of sign of \( b_i \) of Cu and H. These calculations suggest that PNH is feasible in principle though high neutron flux measurement and development of accurate data-correction are required. If PNH will be realized, it will be an important prove of materials science, in particular, Hydrogenomics.

References


Yuki Kanazawa was born in Iwate, Japan in 1996. He obtained his B. Eng. in Ibaraki univ. (2017). He belong to institute of Quantum Beam Science, Ibaraki University graduate school of Sc. and Eng.. His main research field is investigation of materials science by novel methods, neutron holography.

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ATTEMPT TO CONTROL H⁺ TRANSFER IN MOLECULAR BILAYERS FOR A FUTURE HYDROGENOMIC DEVICE

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Introduction
The H⁺-electron correlated properties of pure organic molecular crystals have recently been materialized by Mori and coworkers synthesizing Cat-TTF derivatives [1, 2], and provide great interests in material science. In this study, it has been tried to construct the H⁺-electron correlated system in the two-dimensional molecular layer on solid substrates. We have challenged to form Cat-TTF adlayer bonding to the Im-SAM-covered Au substrate (Fig. 1) in the manner of self-assembly, and characterized the bilayer using several spectroscopic and microscopic methods with theoretical calculations [3, 4].

Results and Discussion
The bilayer is designed with the connection via hydrogen bonds between the hydroxyl group (H⁺ donor) of Cat-TTF derivative and the imino N site (H⁺ acceptor) of imidazole group in Im-SAM (Fig. 1). The H⁺ transfer between the two layers should be assisted by well-arranged bilayer configuration and strong hydrogen bonds. Actually, we confirmed the nearly ideal bilayer structure, molecular amounts, and especially strong hydrogen bonds in the prepared bilayers. Then, we theoretically evaluated the potential for H⁺ transfer between the H⁺ donor and acceptor sites. As a result, we found that, in the prepared bilayer, H⁺ can transfer between the two sites under a sufficient electric field.

Experimental / Computational
Heterogeneous bilayers on the Au(111) surfaces were created by sequential two-step immersions of the substrates into individual solutions at room temperature: first, the cleaned Au substrate was immersed in the deoxygenated ethanol solution containing 1 mM 1-(11-mercaptoundecyl)-imidazole (Im-(CH₂)₁₁-SH) for more than 20 h, and second, the Im-SAM-covered substrates were immersed in deoxygenated chloroform solution containing 1 mM synthesized Cat-TTF derivatives for more than 20 h [3]. The bilayer morphology, amount of the molecules, and their adsorption states were examined using AFM, XPS, and IRAS, respectively. The DFT calculations were also performed for estimation of H⁺ transfer potential curves depending on applied electric field.

References

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ALL SOLID-STATE BATTERIES USING LiBH₄-BASED SOLID ELECTROLYTE AND LITHIUM METAL ELECTRODE

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The LiBH₄-based complex hydrides have been collecting attention as a new class of solid electrolytes for all-solid-state lithium batteries. The notable features of LiBH₄-based complex hydrides are their strong reducing ability. The ability is expected to ensure high compatibility with lithium metal, a material that itself has a reducing ability. In the presentation, a comprehensive understanding of the phenomena at the interface between a lithium metal anode and two types of LiBH₄-based solid electrolytes (LiBH₄ and Li(CH₄)₃) are to be explained. Also, the performances of all-solid-state battery fabricated using a Li metal anode and Li(CH₄)₃ electrolyte will be presented.

Introduction

Lithium metal is one of the most promising anode materials for next-generation energy storage systems owing to its high energy density derived from its low redox potential (-3.045 V vs. SHE) and high theoretical capacity (3,860 mAh g⁻¹) [1]. Although LiBH₄-based solid electrolytes are known as a promising candidate with high compatibility with lithium metal due to its high reducing ability and deformability [2], the capability of LiBH₄-based complex hydrides for the formation of a stable interface against lithium metal has not been verified yet. In this study, we aim to achieve a comprehensive understanding of the phenomena at the interface between a lithium metal anode and two types of LiBH₄-based solid electrolytes (LiBH₄ and Li(CH₄)₃) to verify the high compatibility of LiBH₄-based solid electrolytes with a lithium metal anode.

Experimental

Li(CH₄)₃ solid electrolyte was prepared via the mechanical milling method [3]. The stability against lithium electrode of the electrolyte was investigated by monitoring the voltage evolution in a symmetric cell at a constant current density of 0.2 mA cm⁻² for 30 min. Sulfur-carbon (S-C) composites were also prepared using the mechanical milling method. A battery cell consisting of S-C composite and Li(CH₄)₃ were assembled using a stainless electrochemical cell holder.

Results and Discussion

To investigate the electrochemical stability of the interface during lithium plating/stripping, charge and discharge measurements over 100 cycles were implemented for a lithium metal/solid electrolyte/lithium metal symmetric cell. For Li(CH₄)₃, there was no change in the voltage transient during the test (Fig. 1 left). The electrochemical stability was also confirmed using Nyquist plots obtained before and after the lithium plating/stripping test (Fig. 1 right). The intersection of the portions of semi-circles in the plots corresponding to the bulk resistance did not change after the test. Moreover, no additional semicircles attributed to interface and/or grain boundary resistance were observed [4]. In our presentation, the performances of all-solid-state battery fabricated using a Li(CH₄)₃ electrolyte, Li metal anode, and S-C composite cathode will also be presented.

Fig. 1 Voltage transients during Li plating/stripping with Nyquist plots before and after Li plating and stripping process for Li(CH₄)₃ at 90°C.

References


Kazuaki Kisu received his Ph.D. in engineering in 2015 from Tokyo University of Agriculture and Technology. He worked as a project assistant professor (2015–2018) in Tokyo University of Agriculture and Technology, and is currently an assistant professor in the Orimo group at the Advanced Institute for Materials Research (AIMR), Tohoku University. His research interests are the electrochemistry and solid-state ionics for electrochemical energy storage devices.

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LANTHANUM OXYHYDRIDES SUPPORTED RUTHENIUM CATALYST FOR AMMONIA SYNTHESIS

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Lanthanum oxyhydrides (LaHx-yOy, x = 0.125−1.0) with high hydride ion conductivity have been synthesized by hydrogenation treatment of the mixture of LaH3 and La2O3. All lanthanum oxyhydrides were demonstrated to function as efficient and stable promoters for ruthenium catalysts in low-temperature ammonia synthesis, and their catalytic activities are much higher than those of Ru/La2O3 and Ru/LaH3. Ru/LaH2.5O0.25 exhibited the highest activity (818 μmol g⁻¹ h⁻¹) at 0.1 MPa and 260°C with much lower activation energy than conventional Ru catalysts.

Introduction
Catalytic ammonia synthesis is essential for the production of synthetic fertilizers and chemical products. However, high temperature (400-500°C) and high pressure (10-30 MPa) are required for industrial ammonia synthesis (Haber-Bosch process) because the bond energy of N≡N bonds is extremely large. We have recently reported that hydride materials such as Ca2NH, CaH2 and LaH2-x as support materials of Ru catalyst in ammonia synthesis.

Results and Discussion
LaH3-2xOx with various hydrogen content were prepared by controlling the mixing ratio of LaH3 and La2O3. XRD analysis revealed that LaH3-2xOx has tetragonal fluorite-like structure. Figure 1 shows the ammonia synthesis activities of Ru/LaH2.5O0.25 and reference catalysts at atmospheric pressure. Although the catalytic activity is independent of the hydrogen content in Ru/LaH2.5O0.25, these activities are lower than Ru/La2O3 and Ru/LaH3. The maximum ammonia synthesis rate (818 μmol g⁻¹ h⁻¹) was recorded for Ru/LaH2.5O0.25. Furthermore, the Ru/LaH2.5O0.25 exhibits ammonia synthesis activity down to 160°C, which is lower by 100°C than the case of Ru/La2O3. As a consequence, the apparent activation energy of Ru/LaH2.5O0.25 for ammonia synthesis is determined to be 64 kJ mol⁻¹, which is close to those for Ru-loaded electrides and hydride materials (50-60 kJ mol⁻¹). As we reported previously, the formation of anionic electrons at hydride vacancy sites accounts for the strong electron donation ability that facilitates efficient N2 cleavage on Ru. It is thus considered that the hydride vacancies are formed at Ru/LaH2.5O0.25 interface during ammonia synthesis, which imparts high catalytic performance of Ru nanoparticles. In addition, reversible exchange between H ions and anionic electrons effectively takes place over Ru/LaH3 because the LaH3-2xOx has high hydride ion conductivity.

Fig. 1 Catalytic activity for ammonia synthesis over 2 wt% Ru/LaH2.5O0.25, Ru/LaH3, and Ru/La2O3 at 0.1 MPa as a function of reaction temperature.

References

Masaaki Kitano studied chemical engineering and received his Ph.D. degree from Osaka Prefecture University in 2006 under the supervision of Prof. Masakazu Anpo who is an expert in photocatalysis. After a stint with Prof. Michikazu Hara as a postdoctoral research fellow at Kanagawa Academy of Science and Technology, he joined the Tokyo Institute of Technology in 2009 as an assistant professor and was promoted to associate professor in 2013. His research interests in ammonia synthesis and various hydrogenation reactions using electrode- and hydride-based catalysts, synthesis of alloy nanoparticles, and solid acid catalysts.

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EFFETS OF Ni-CONTAING POROUS CARBON SHEETS (Ni-PCS) ON THE DEHYDROGENATION PROPERTIES OF Mg(AlH₄)₂

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Complex hydrides have high theoretical hydrogen capacity as fuel for PEMFC automobiles. Among the complex hydrides, magnesium alanate has high hydrogen storage capacity and releases hydrogen at low temperature (150 °C), but still not matched to PEMFC operation temperature. Therefore, we prepared Ni-PCS catalyst with Mg(AlH₄)₂ to investigate the effect of catalyst and enhance hydrogen release.

Introduction

Hydrogen storage under moderate temperature and pressure is needed to commercialize and spread the use of the fuel cell system. The alkaline earth metal alanates are considered as candidate materials due to high hydrogen capacity and relatively low decomposition temperature.¹ Among the alkali and alkali earth metal alanates, magnesium alanate, Mg(AlH₄)₂, has a high theoretical hydrogen capacity of 9.3 wt.% and decomposes below 150 °C at the first decomposition step.² To meet the PEMFC operating temperature, research is being conducted to lower the decomposition temperature of LiAlH₄ or NaAlH₄ using catalysts.³,⁴ In this study, the Mg(AlH₄)₂ was synthesized with Ni-PCS to investigate the catalytic effect of decomposition temperature.

Experimental

The synthesis of magnesium alanate proceeds via the metathesis method. The commercial LiAlH₄, MgCl₂, NiCl₂ were used as received. The Diethyl ether was purified with sorbent to remove remaining water. LiAlH₄ and MgCl₂ were mixed by a high energy ball mill (SPEX sample prep 8000). The porous carbon sheets (PCS) were synthesized using sucrose and phosphorus pentoxide. At first, sucrose and phosphorous pentoxide were ground well. The mixture was put into the autoclave and heat to 200 °C for pre-carbonation. Then, the pre-carbonated black powder was calcined to 900 °C with Ar flow. For the deposition of Ni nanoparticle onto PCS, Ni nanoparticle was synthesized by the polyol method.

Results and Discussion

In-situ XRD was conducted for confirming the crystal phase during heating from RT to 300 °C. Hydrogen release amount and decomposition temperature were measured by Pressure-composition-temperature (PCT). The hydrogen release temperature of magnesium alanate decreased with Ni-PCS catalytic effect.

References


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Born in 1992, Republic of Korea. Youngdon Ko graduated B.Sc. and M.Sc. degree from Konkuk University in 2019, Republic of Korea. During this time, he worked in the field of proton exchange membrane fuel cell (PEMFC) with self-humidifying system, catalyst for oxygen reduction reaction (ORR). After finished his master degree, he joined Prof. Andreas Züttel’s group in EPFL as a doctoral assistant. His current research focused on hydrogen storage with complex metal hydride.
CARBON DOPING OF HYDROGEN BORIDE SHEET REDUCES H\textsubscript{2} RELEASE TEMPERATURE

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We have prepared carbon-doped (C-doped) hydrogen boride sheets by using C-doped MgB\textsubscript{2} as a starting material for ion-exchange reaction and analyze its hydrogen release temperature by thermal desorption spectroscopy.

**Introduction**

Recently, we revealed that the hydrogen boride (HB) sheet, with an empirical formula of H-B\textsubscript{1}, can be experimentally prepared by exfoliation and complete ion-exchange between protons and magnesium cations in magnesium diboride (MgB\textsubscript{2}) at room temperature [1]. Our extensive analysis revealed that the prepared HB sheets did not show any long range order, but have a local structure of a hexagonal boron network with bridge hydrogens. HB sheets release their hydrogen as H\textsubscript{2} molecules by UV irradiation even at room temperature [2], while hydrogen can also be released by heating in a wide temperature range from 423 to 1473 K [1]. Theoretically, the release temperature of hydrogen by heating is expected to be lower by electron doping to HB, because of the electron occupation of anti-bonding orbital of H-B bonds by electron doping [3]. In this work, we have prepared C-doped HB sheets by using C-doped MgB\textsubscript{2} as a starting material for ion-exchange reaction and analyze its hydrogen release temperature by thermal desorption spectroscopy (TDS).

**Results and Discussion**

Figure 1 shows TDS results of H\textsubscript{2} from HB and that from C-doped (10 at\%) HB. As reported previously, there are three H\textsubscript{2} desorption peaks at \~500 K, \~900 K, and \~1200 K [1]. In the case of C-doped HB, similar desorption profile is observed except for the second peak temperature position. The second peak temperature is located at \~800 K which is approximately 100 K lower compared to that for HB.

To understand the origin of the decrease of hydrogen release temperature by C-doping in HB, we have calculated the electronic structure of C-doped HB by density functional theory (DFT), where we have introduced carbon atoms (\~1.6 at\%) by replacing boron as substitute doping. The stabilized C-doped HB structure was then obtained. The work function derived from DFT calculations are 3.40 eV and 3.36 eV for HB and C-doped (1.6 at\%) HB, respectively. The lower work function for C-doped HB is originated from electron doping in HB and can explain the decrease of H\textsubscript{2} release temperature in Fig. 1.

**Fig. 1 TDS of HB and C-doped HB**

**References**


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LOCAL STRUCTURE STUDY OF METAL–HYDROGEN SYSTEMS BY X-RAY TOTAL SCATTERING

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Structural information of a metal hydride provides important knowledge to understand its properties. Average structural information is not sufficient to elucidate the mechanism of hydrogen absorption, and therefore local structural information is also necessary. Atomic pair distribution function, which can be obtained from the total scattering measurement, is one of potential tools to investigate the local structures of materials. We have constructed a rapid acquisition pair distribution function experimental system at BL22XU in SPring-8. BL22XU and have applied the pair distribution function method to investigate metal-hydrogen systems.

Introduction
Many functional materials are inherently inhomogeneous in their compositions or structures. X-ray diffraction (XRD) analysis is the most popular method to determine a crystal structure. In metal-hydrogen systems, the absorbed hydrogen atoms largely expand the metal lattice and induce a structural phase transition on the hydrogenation reaction. From a nanoscale structural point of view, a large number of crystallographic defects, such as dislocations, and lattice distortion are formed during hydrogenation reaction, and are considered to influence the properties of the metal hydrides. However, the conventional XRD method is insufficient for the analysis of these inhomogeneous or heavily disordered structures. An atomic pair distribution function (PDF) is suitable to analyse the local- to middle-range structure. We developed the rapid-acquisition (RA)-PDF measurement [1] system in BL22XU at SPring-8 and applied the PDF analysis to investigate metal hydrides [2-4].

Experimental / Computational
PDFs are obtained by a Fourier transformation of the total scattering data of specimens. BL22XU enables us to perform RA-PDF experiments using a large-area two-dimensional detector and high-energy X-rays up to 70 keV (wavelength of approximately 0.177 Å). Powdered sample was sealed in the polyimide capillary with an inner diameter of 1 mm.

Results and Discussion
Under the standard PDF measurement setup in BL22XU, the maximum Q range of the obtained total scattering pattern reaches 20 Å⁻¹. Obtained PDFs show peaks even above ~100 Å allowing us to investigate even middle-range structural features. Developed in-situ measurement setup with hydrogen gas pressure up to 1 MPa enables us to study change in both average and local structures in either equilibrium or non-equilibrium states. We succeeded in measuring the total scattering patterns during hydrogenation process of some hydrogen absorbing alloys, such as LaNi₄.₅Al₀.₅, V-Ti-Cr, and etc. The XRDs and PDFs of LaNi₅-based alloys suggest formation of the intermediate state with locally distorted structure during hydrogenation.

References

[Image: Akihiko Machida]

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LOW TEMPERATURE HYDROGEN ION BEAM IRRADIATION FOR EXPLORING EXOTIC PHYSICAL PROPERTIES

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Abstract
We have developed a compact low temperature hydrogen ion irradiation apparatus with in situ physical property measurements. This apparatus allowed us to perform heavy hydrogen doping into materials of interest and explore exotic physical properties. We succeeded in heavy interstitial hydrogen doping into SrTiO₃ and ZnO. These insulators turned into degenerated semiconductors by heavy hydrogen doping, and showed unprecedented irreversible thermal hysteresis in electrical resistivity.

Introduction
Hydrogen doping can drastically change physical properties of materials, although the doping amount is limited in the case of conventional doping methods such as hydrogen gas pressure and electrochemical sorption. The low temperature hydrogen ion beam irradiation is a powerful method for heavy hydrogen doping. To evaluate the doping effects, in situ physical property measurements are necessary. We have developed a low temperature hydrogen ion beam irradiation apparatus with in situ transport measurement and explored exotic physical properties of oxides induced by heavy hydrogen doping.

Experimental
Epitaxial thin films (~100 nm thick) of SrTiO₃ and ZnO (wurtzite) were fabricated on LSAT (001) and α-Al₂O₃ (001) substrates, respectively, by pulse laser deposition and RF magnetron sputtering, respectively. The hydrogen ion beam was irradiated on the thin films with the low acceleration voltage (≤5kV) at room temperature or low temperatures down to 7 K by using the home-made apparatus (Fig.1) [1]. The resistivity of thin films was measured in situ by van der Pauw method.

Results and Discussion
Both insulating oxides showed metallic temperature dependence of resistivity after the heavy hydrogen doping. The hydrogen ion irradiation on SrTiO₃ at 150 K induced larger decrease in resistivity than that of 300 K irradiation, but the resistivity irreversibly increased upon heating at 300 K, indicating partial desorption of doped hydrogen by thermal annealing [2]. In the case of ZnO, we observed a giant isotope effect. The hydrogen irradiation at 7 K instantly induced very large decrease in resistivity, while the deuterium irradiation at 7 K resulted in only slight decrease in resistivity of ZnO. The subsequent heating caused huge irreversible thermal hysteresis in the resistivity of deuterium doped ZnO.

Fig. 1 Hydrogen ion beam irradiation apparatus

References

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ANALYSIS OF AMMONIA ABSORPTION STATE OF METAL BOROHYDRIDE

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Abstract
In this work, the NH₃ absorption state of alkali(-earth) metal borohydride M(BH₄)ₓ is analysed by pressure-composition-isothermal measurements and various spectroscopies such as nuclear magnetic resonance (NMR), infra-red, and Raman spectroscopy. Although NaBH₄ forms liquid NH₃ absorption state in all region, Mg(BH₄)₂ and Ca(BH₄)₂ shows solid ones. On the other hand, LiBH₄ shows complicated NH₃ absorption process. 1, 2, and 3 mol NH₃ absorption state is solid, liquid, and solid phase, respectively. From the NMR analyses, H⁺ in (BH₄)⁻ and H⁺ in NH₃ are clearly distinguished. With increase in the amount of absorbed NH₃, the chemical states of both H are simultaneously changed, suggesting that the interaction between H⁺ and H⁺ would be related to the NH₃ absorption state of NaBH₄.

Introduction
Alkali(-earth) metal borohydrides M(BH₄)ₓ are studied as hydrogen storage materials with high capacity so far. Recently, various functional properties of M(BH₄)ₓ as ammonia (NH₃) absorption materials and ion conductors are reported[1-3]. Some M(BH₄)ₓ absorb NH₃ as molecular state to form ammine complexes phases by following chemical reactions,

\[ M(BH_4)_x + nNH_3 \leftrightarrow M(NH_3)_n(BH_4)_x \]

It is expected that the interesting behaviors are revealed for ammine complexes of borohydrides due to interaction between coexistent H⁺ in (BH₄)⁻ anion and H⁺ in NH₃. However, detailed states of the hydrogens, reaction mechanism, and the fundamental properties of the ammine complexes are not understood yet. In this work, the variation of chemical state of H in M(BH₄)ₓ with NH₃ absorption are investigated by various spectroscopy and discussed.

Experimental
The NH₃ absorption reactions of various M(BH₄)ₓ (M=Li, Na, Mg, Ca) are investigated by pressure-composition-isotherm (PCI) measurements, in-situ nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR), and Raman spectroscopy under NH₃ pressure.

Results and Discussion
In the case of NaBH₄, the plateau corresponding to formation of liquid Na(NH₃)ₓBH₄ appeared at 0.09 MPa. After the plateau region, the liquid solution of NH₃ and NaBH₄ Na(NH₃)ₓBH₄ (x>2) is formed. When NH₃ in the solution independently exists, the H NMR signal of NH₃ should be split into three peaks by N-H coupling due to nuclear spins of ¹⁴N (1, 0, −1). However, the peak splitting was not observed for the Na(NH₃)ₓBH₄ solution phase although the peak split was observed in pure liquid NH₃. Furthermore, the positions of signals corresponding to both of H in NH₃ and in (BH₄)⁻ are synchronously shifted with increase in NH₃ composition. The above results suggest that H⁺ in NH₃ interacts with H⁺ in (BH₄)⁻ each other, and the chemical states are changed with the NH₃ concentration.

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References

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LOCAL DIFFUSION COEFFICIENT OF DEUTERIUM PERMEATING THROUGH STAINLESS STEEL MEMBRANE

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We have developed an operando hydrogen microscope to visualize hydrogen permeation. Deuterium was supplied from the back of the stainless steel sample for a long period of time during the experiment to visualize the deuterium permeation. After 65-hour experiment, we found that the deuterium showed different permeation volume and diffusion speed depending on the grains. We calculated the diffusion coefficient of each grain from the time-dependent deuterium permeation.

Introduction

It is important to clarify the behaviour of hydrogen in metals to understand the mechanisms of hydrogen embrittlement and storage. There are various models of hydrogen diffusion in metal, none of which are definitive. We have studied the behaviour of hydrogen in metals by visualizing sequentially spatial distributions of hydrogen permeated through a stainless-steel membrane.

It is crucial to understand a permeation phenomenon of hydrogen in a metal that is formed from many crystal grains and grain boundaries, to develop fine structural materials for hydrogen production, storage and transport.

Experimental

The experiment was performed in the operando hydrogen microscope¹², which visualized hydrogen permeated through metal in ultrahigh vacuum condition (UHV). We exposed hydrogen or deuterium to the back side of the metal sample. After being absorbed into the sample, the hydrogen or deuterium diffused to the opposite side, then it was visualized in two dimensions by desorption induced by electronic transition (DIET) method.

The experimental setup is shown in Fig.1. Two-dimensional pulse counting system is synchronized with the scanning electron beam. The sample is SUS304 stainless steel which has austenite structure with martensite dislocations made by cold working. The diameters of austenite grains are 50-150 μm and the thickness of the sample is 100 μm.

The sample temperature was 473 K. The pressure of deuterium introduced to the back side of the sample was 1×10⁻¹³ Pa. We waited for the permeated deuterium on the opposite side of the sample in UHV room, and observed deuterium by DIET method.

Results and Discussion

Permeated deuterium was visualised in 520 hydrogen maps during the 65-hour experiment. We couldn't define any patterns that reflected local difference of deuterium until 20 hours after exposure. The difference in the amount of permeation, which depends on the grain shape, appeared in maps around 40 hours later.

We found a significant difference in the diffusion coefficient of deuterium at local position by focusing on the permeation speed and volume of deuterium at each region.

Fig. 1 Experimental set up

References

ANHYDROUS PROTON CONDUCTIVITY OF IMIDAZOLIUM HYDROGEN DICARBOXYLATES

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In order to obtain the strategy towards high-performance anhydrous organic proton conductors, the proton-conductivity measurements, the X-ray structure analyses, and the solid-state ²H-NMR experiments were performed by using single/powdered crystals of the three imidazolium hydrogen dicarboxylates, (1) succinate, (2) glutarate, and (3) fumarate salts. The results revealed that (i) the hydrogen (H)-bond network structures, (ii) small ΔpKa between constituent acid and base molecules, and (iii) the libration motion of imidazolium molecules are the key factors for the anhydrous proton conductivity. This study suggests that not only the “static” H-bond network structures but also the “dynamics” of the constituent molecules synergistically play important roles in the anhydrous proton conduction.

Introduction
Anhydrous proton conductors are important materials owing to not only their potential applications for solid electrolyte above 100 °C but also scientific interests for the proton conduction mechanism mediated not by water molecules. The rich designability of organic materials enable us to design and synthesize proton conductors, and to systematically investigate structure-property relationship and proton conduction mechanism for development of anhydrous purely organic proton conductors with high performance. In this study, anisotropic proton conductivity reflecting molecular arrangements [1], effects of proton donating abilities (pKa) of constituent molecules, and molecular dynamics effects on high-quality single/powdered crystals of a series of the imidazolium hydrogen dicarboxylates.

Experimental / Computational
Single crystals of imidazolium hydrogen dicarboxylates, (1) succinate, (2) glutarate, and (3) fumarate salts were obtained by slow evaporation. The crystal structure analyses at T = 23–103 °C, the measurements of thermal stability by DSC, proton conductivity by an ac impedance analyser, and solid-state ²H-NMR were performed.

Results and Discussion
In this research, the effects of (i) the arrangements, (ii) proton donating abilities, and (iii) dynamics of constituent molecules on the proton conductivity were investigated using high-quality single crystals of a series of the imidazolium hydrogen dicarboxylates. As for (i), the large anisotropy of the conductivity between the intra and inter directions of (1)-(3) indicates that the proton conduction occurs more readily in the H-bond networks than in its perpendicular direction. About (ii), in comparison with (1)-(3), the proton donating ability of dicarboxylic acids is turned to be a key factor for tuning the proton conductivity of these salts, that is, small ΔpKa between constituent acid and base molecules is one of the important factors to achieve the anhydrous proton conductivity. For (iii), the clear positive correlation between proton conductivity and libration angle of imidazole by solid-state ²H-NMR measurement indicates that the libration motion of imidazolium cations promotes anhydrous proton conduction in imidazolium hydrogen dicarboxylates. These results demonstrate that both of the H-bond network structures and the dynamics of organic molecules synergistically play important roles in the anhydrous proton conduction.

Fig. 1 Molecular arrangement in the high-T structure of imidazolium hydrogen succinate. The orange belt, red dashed lines, brown dashed lines, gray dashed lines, and blue arrows represent the possible proton conducting path, H-bonds, disordered atom···O contacts, C···H···O contacts, and direction of the libration motion.

References

Hatsumi MORI is the Director and professor at the Institute for Solid State Physics (ISSP), the University of Tokyo. She obtained her D. Sc. degree from the University of Tokyo in 1992. She was a technical associate at ISSP (1986-1989), a researcher at International Superconductivity Technology Center (1989-2001), and an associate professor at ISSP (2001-2010). Since 2010, she has been a professor at ISSP. She has worked on the development and the characterization of molecular functional materials by utilizing molecular degrees of freedom, e.g. novel molecular electron-proton coupled conductors, purely organic proton conductors for fuel cell, etc.

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ADVANCED MOLECULAR MATERIALS BASED ON PHOTOCHROMIC DIARYLETHENES BEARING HYDROGEN-FUNCTIONAL UNITS

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Toward the development of molecular devices with advanced hydrogen functions we synthesized photochromic diarylethene molecules having hydrogen-bonding or proton-accepting units and examined their photochemical and photophysical properties. Diarylethene derivatives having imidazole rings formed intermolecular hydrogen-bonding chain structures in single crystals. A fluorescent diarylethene derivative having a dimethylamino group changed the fluorescent properties in response to pH change.

Introduction
Photochromic molecules, which reversibly change their colors as well as other physical and chemical properties upon photoisomerization, have a potential for applications to optoelectronic devices, such as optical memory media, optical switches, and displays. Among various types of photochromic molecules, diarylethene [1] is one of the most promising candidates for practical application because of its outstanding properties, such as thermal stability of two isomers, fatigue resistance, and rapid response (Fig. 1). Here we examined the integration of photochromic reactions with hydrogen functions, such as photochromic crystals having intermolecular hydrogen-bonding networks and photo/proton-responsive fluorescent molecules, toward the development of advanced molecular functional devices.

Experimental
Single crystals of diarylethene derivatives were prepared by recrystallization from appropriate organic solvents and were subjected to X-ray crystallographic analysis and polarized absorption spectral measurement. Fluorescence spectra and fluorescence quantum yields in solutions were measured with a fluorescence spectrophotometer or an absolute PL quantum yield measurement system.

Results and Discussion
Diarylethene derivatives possessing imidazole rings as hydrogen-bonding units were synthesized. X-Ray crystallographic analysis revealed that most of the derivatives form one-dimensional chain structures of the imidazole rings via intermolecular hydrogen-bonding interactions in the crystal. Upon alternate irradiation with ultraviolet (UV) and visible light the diarylethene molecules underwent reversible photoisomerization even in the hydrogen-bonding networks.

A fluorescent diarylethene derivative [2] having a dimethylamino group underwent turn-on mode switching of fluorescence upon UV induced ring-closing isomerization and also changed the fluorescent properties in response to pH change. Upon addition of strong acid, the fluorescence spectrum of the closed-ring isomer showed a significant hypsochromic shift and the fluorescence intensity dramatically increased. Such pH-responsive property is ascribed to the suppression of intramolecular charge transfer character upon the protonation of the electron-donating dimethylamino group.

References

Masakazu Morimoto received his B.S. (2001), M.S. (2003), and Ph.D. (2006) degrees from Kyushu University. From 2006–2007, he engaged as a postdoctoral researcher at the Graduate School of Science, Tohoku University. In 2007, he moved to the Department of Chemistry, Rikkyo University, as an assistant professor. He was appointed as an associate professor at the same university in 2010 and was promoted to a full professor in 2017. His research interests include the development of advanced photofunctional molecules and materials based on photochromic diarylethenes.

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HIGH-PRESSURE AND HIGH-TEMPERATURE SYNTHESIS OF NOVEL AL-TM (TM=Zr, Hf) HYDRIDES

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For the purpose of synthesizing novel Al-TM (TM = Ti, Zr, and Hf) hydrides with high Al composition, starting materials (sintered compacts with molar ratios with Al/Zr = 2:1, 3:2, 1:1, 2:3 and 1:3, Al/Hf, and Al/Hf alloys) were hydrogenated at 9 GPa and 750°C. Novel hydride Al2HfH4.7 with high Al composition was synthesized. For Al-Zr system, novel hydrides with high Al composition have not been achieved yet, though novel Al2ZrH5.6 was obtained.

Introduction
We have searched for novel hydrides with high Al composition and have synthesized several kinds of them at high-pressures and high-temperatures, where reactivity of hydrogen is increased. For Al-TM (TM = Ti, Zr, and Hf) hydrides, hydrides with low Al compositions have been reported [1-3], but those with high Al compositions have not been reported. The purpose of the present study is to synthesize novel Al-TM hydrides with high Al composition.

Experimental
For Al-Zr system, the starting materials were sintered compacts with molar ratios of Al/Zr = 2:1, 3:2, 1:1, 2:3, and 1:3. They were prepared by sintering powdered mixture at 1200°C for 1 h using an IR furnace. For Al-Hf system, Al/Hf and Al/Hf alloys that were prepared by an arc melting furnace were used. A cubic-type multi-anvil press was used to generate high-pressure and high-temperature conditions. Starting materials were compressed to 9 GPa, then heated to 750°C, and kept in hydrogen fluid. The hydrogenated samples were cooled to the room temperature and depressurized to the ambient pressure. The recovered samples were analysed by a powder X-ray diffractometer and a SEM-EDS.

Results and Discussion
For Al-Zr system, a novel hydride Al2ZrH5.6 was obtained when the sintered compact with the molar ratio of Al/Zr = 2:3 was hydrogenated (Fig. 1 top). This hydride was a modification of known Al2ZrH3.0 [2] with higher hydrogen concentration. Partial formation of Al2ZrH5.8 was observed when other starting materials were used. A formation of novel hydride with high Al composition was not achieved.

Fig. 1 X-ray diffraction profiles of Al2Zr3H5.6 and Al2HfH4.7.

References

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HYDROGEN ON AND IN CERIA AND HYDROGENATION OF UNSATURATED HYDROCARBONS

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Inspired by the report that oxides, and in particular ceria may be used as hydrogenation catalysts[1], depending on the degree of reduction, we have started surface science studies on well-defined CeO$_2$(111) films grown on a Ru(0001) single crystal metal surface and studied the interaction of a fully oxidized ceria surface in comparison with a partially reduced surface with respect to its interaction with hydrogen from the gas phase. We will show that a hydride is formed in the subsurface region in the case of reduced ceria leading to a re-oxidation of the ceria sublattice.[2-4] Also, the interaction with propylene, both, regular and isotopically labelled with the ceria surface has been studied.[5]

Introduction

Two mechanisms for H$_2$ dissociation on metal oxide surfaces have been identified:[6; 7] One is the homolytic dissociation, which produces two hydrogen atoms at two oxygen sites according to the formation of two OH groups and the concomitant reduction of two surface metal ions; the other one is the heterolytic (polar) dissociation, which entails the formation of a hydride, H-, and a proton, H+, at metal and oxygen sites, yielding M-H and OH species, respectively. The H-ad-atoms on metal oxide surfaces can migrate into the subsurface region and further into the bulk to form hydroxyl and hydride species therein.

Experimental / Computational

CeO$_2$(111) thin film preparation, H$_2$ treatment, and corresponding XPS and Electron Energy Loss Spectroscopy (EELS) measurements and Low Electron Energy Diffraction (LEED) were performed in two ultrahigh vacuum (UHV) systems with a base pressure of ~1x10$^{-10}$ mbar, which are described in detail elsewhere.[2]

Results and Discussion

Figure 1 shows Ce 3d and O 1s X-ray Photoelectron Spectroscopy (XPS) results on the freshly prepared CeO$_2$(111) thin film. Spectra where recorded in both normal (0°) and grazing (surface-sensitive) emission geometry (θ=60°), which differ in the angle θ between surface normal and XPS analyzer.

![CeO$_2$(111) Thin Films](image)

Fig. 1 Ce 3d and O 1s XP spectra of CeO$_2$(111) thin film in normal (0°) and grazing (60°) emission geometry: (a) Freshly prepared CeO$_2$(111), (b) CeO$_2$(111) exposed to 10 mbar D$_2$ at 300 K.

Figures 1 shows XP-spectra of reduced CeO$_2$(111) films upon interaction with molecular hydrogen. The clean CeO$_2$(111) thin film was exposed to 10 mbar D$_2$ at 300 K for 15 min. Figure 1 shows Ce 3d and O 1s XP spectra obtained after D$_2$ exposure. In the Ce 3d spectra, the Ce$^{3+}$ concentration significantly decreases after 10 mbar D$_2$ exposure in both normal and grazing emission modes. This phenomenon occurs both in surface-near and deeper layers. First experiments on acetylene and propane adsorption and reaction have been performed on the various oxidized and reduced Ceria films.

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References


Hans-Joachim Freund is a scientific member at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin where he was the head of the Department of Chemical Physics from 1995 until March 2019. The department was dedicated to the study of model catalysts, applying a large number of techniques and instruments, some of which were newly developed within the department to investigate oxide surfaces and oxide metal interfaces. He received the Gaede-Langmuir Award of the American Vacuum Society and is the recipient of the 2015 Michel Boudart for the Advancement of Catalysis by the North American Catalysis Society and the European Federation of Catalysis Societies. In 2019 he received the prestigious ACS Award in Surface Chemistry. He has held a number of named lectureships around the world. He has educated more than 130 PhD students and collaborated with more than 80 postdoctoral associates.

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CATALYST DESIGN FOR PRODUCTION AND DECOMPOSITION OF AMMONIA AS A HYDROGEN CARRIER

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Development of a H2 storage and transportation system using NH3 has been motivated by the desire to achieve a carbon-free society. To establish such a system, we found that composite rare-earth oxide supported Ru catalysts like Ru/La0.5Ce0.5O1.75 and Ru/Ba0.1La0.45Ce0.45O1.68 exhibit high ammonia synthesis rates under mild reaction conditions. On the other hand, we demonstrated H2 production process by supplying ammonia and oxygen at room temperature to a pre-treated Ru/Y-Al2O3 catalyst without external heating.

Introduction

Ammonia is an important chemical feedstock, and more than 80% of the synthesized ammonia is used to produce fertilizer. Ammonia is also being considered as a H2 carrier for utilizing renewable energy (1) because it has a high energy density (12.8 GJ m-3) and a high hydrogen content (17.6 wt%). (2) because infrastructure for ammonia storage and transportation is already established, and (3) because CO2 is not emitted when ammonia is decomposed to produce H2. To establish such a system, development of advanced catalytic process for ammonia synthesis and decomposition is strongly demanded.

Results and Discussion

At first, we investigated influence of reduction temperature on the ammonia-synthesis activity of Ru/La0.5Ce0.5O1.75, a catalyst consisting of Ru supported on a La0.5Ce0.5O1.75 solid solution1. After pre-reduction at the unusually high temperature of 650 °C, the catalyst exhibited high ammonia synthesis activity from 300 to 400 °C at 1.0 MPa. This catalyst consisted of fine Ru particles anchored on a heat-tolerant complex-oxide support. During pre-reduction, the particle size of the Ru particles remained unchanged, but the particles became partially covered with partially reduced La0.5Ce0.5O1.75. A strong interaction between the Ru active sites and the reduced support accelerated the rate-determining step, N2 dissociation, of ammonia synthesis. By using this strategy, we found that Ru/Pr0.5La0.5O1.5 reduced at 650 °C shows comparable activity with Ru/La0.5Ce0.5O1.75. Furthermore, we discovered that Ru/Ba0.1La0.45Ce0.45O1.68 pre-reduced at 700 °C catalyses ammonia synthesis at the highest rate among oxide-supported Ru catalysts reported so far (350 °C, 1.0 MPa).

On the other hand, we discovered that H2 is produced by supplying ammonia and oxygen at room temperature to a pre-treated RuO2/γ-Al2O3 catalyst without external heating. The heat evolved by ammonia adsorption onto the catalyst increases its temperature to the catalytic auto-ignition temperature of ammonia, and subsequently H2 production by ammonia oxidative decomposition begins.

![Fig. 1. Renewable H2 storage and transportation system using NH3 as a hydrogen carrier.](image)

**References**


Katsutoshi Nagaoka received his Ph. D. at Tokyo Institute of Technology in 2001. After Post Doctor in the university and Humboldt fellow in Technical University in Muenchon, he moved to Oita University as a Lecturer in 2004. Next year he was promoted to an Associate Professor. Since April in 2019, he has been appointed as a Full Professor in Nagoya University. His research interests involve heterogeneous catalysis for solving global energy and environmental issues. He was awarded The Japan Petroleum Institute Prize for Encouragement (2009) and Catalysis Society of Japan Prize for Encouragement (2010).

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THE ROLE OF HYDRIDES IN N₂ REDUCTION AND NH₃ FORMATION

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Abstract: Catalytic ammonia synthesis from dinitrogen and dihydrogen is usually carried out over Ru or Fe metal surface where active centers composed of multiple metals mediate electron and mass transfers. The adsorption energies and reaction barriers of reacting species on the active centers are correlated resulting in effective ammonia synthesis under mild conditions unattainable. In this talk I will show that alkali or alkaline earth metal hydride can be actively involved in the activation and conversion of dinitrogen and change the scenario of catalytic ammonia synthesis.

Introduction

Ammonia is a promising carbon-free energy carrier, but it is synthesized industrially under harsh conditions. Synthesizing ammonia under lower temperature and pressure could therefore improve its prospects as a chemical means to store and transport energy. Tremendous research efforts have been devoted to this topic over decades, which significantly enrich the fundamental understanding of heterogeneous catalysis. Conventional catalysts are based on Fe and Ru metals, additives such as oxides of alkali or alkaline earth metals play important roles in modifying the electronic/structural properties of Fe or Ru.

Results and Discussion

With the understanding of the interactions of hydrides/imides of alkali and alkaline earth metals (AM 1) with 3d metals and their nitrides, we recently developed a catalyst system, i.e., AMH-3d transition metals, for NH₃ synthesis. Both early and late 3d metals are highly active upon combining with hydrides. The unique chemistry among transition metals, alkali/alkaline earth metals, N and H creates an energy-favourable pathway allowing NH₃ synthesis under mild conditions, i.e., catalytic NH₃ formation is detectable at 150 °C over the Mn-, Fe- and Co-LiH (or BaH₂) composite catalysts, respectively (Figure 1).[1, 2]

We further identified alkali and alkaline earth metal imides as nitrogen carriers that mediate ammonia production via a two-step chemical looping process. Nitrogen is first fixed through the reduction of N₂ by alkali or alkaline earth metal hydrides to form imides and subsequently, the imides are hydrogenated to produce NH₃ and regenerate the hydrides. The oxidation state of hydrogen therefore switches among -1 (hydride), 0 (H₂), and +1 (imide and NH₃). Late 3d metals especially Ni and Co can accelerate the reaction rates of both steps. The chemical loop mediated by BaNH and catalyzed by Ni produces NH₃ with unprecedented rates in the temperature range of 100-300 °C and atmospheric pressure (Figure 1).[3]

Fig. 1 Ammonia production via thermal catalytic process catalyzed by 3d TM-LiH (Upper panel) and chemical looping process mediated by alkali or alkaline earth imides (Bottom panel)

References


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Her primary research interests include the materials development for hydrogen storage and heterogeneous catalysis. She pioneered the research in the amide-hydride system for hydrogen storage and the alkali/alkaline earth hydride-transition metal composite catalyst system for NH₃ synthesis. She has more than 170 peer-reviewed journal articles, delivered ca. 70 invited/keynote speeches.

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HYDROGENATION OF FORMATE ON THE Pd-Cu SINGLE ATOM ALLOY MODEL CATALYSTS

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Abstract

We investigated the adsorption of formic acid, the decomposition into bidentate formate and the subsequent hydrogenation of bidentate formate on the Pd-Cu(997) single atom alloy model catalyst using SR-X-ray photoelectron spectroscopy (XPS). The present XPS results indicate that hydrogenation of bidentate formate occurs below 300 K.

Introduction

Methanol synthesis from carbon dioxide has been of great interest from the viewpoint of a renewable carbon source and global environmental problems. Cu/ZnO-based catalysts have been used to synthesize methanol from H₂ and CO₂ [1]. In the reaction process, formate is formed as a stable intermediate on the catalyst surface. The hydrogenation of formate on the Cu substrate is important for methanol synthesis, but Cu is not very active for H₂ dissociation due to the high activation energy (0.4 eV). Here, we have used Pd as a cocatalyst on the Cu surface for H₂ dissociation because the activation energy of the dissociation on Pd(111) surface is almost no barrier [2]. We have prepared a Pd single atom alloy model catalyst on the Cu substrate, where a small amount of Pd atoms were deposited and embedded in the first layer of Cu surface. This Pd atom provides the active site for hydrogen dissociation without losing the catalytic nature of Cu. In this study, we investigated the formation of formate from formic acid and the hydrogenation of formate on the single atom alloy Pd-Cu model catalyst using high-resolution X-ray photoelectron spectroscopy (XPS).

Experimental

After the preparation of the Cu(997) clean surface, we deposited Pd atoms on the Cu(997) clean surface at 380K. Next, the Pd-Cu(997) surface was exposed to gaseous formic acid at 80 K, and the sample was heated to 300 K to form bidentate formate species. The bidentate formate on Pd-Cu(997) was exposed to gaseous hydrogen at 80 K. Finally, the H/formate/Pd-Cu(997) surface was heated to higher temperature. We have measured XPS spectra for each process. All XPS measurements were carried out using the Phoibos100 system at BL-13B in KEK-PF.

Results and Discussion

We measured C1s, O1s, Pd3d XPS spectra for the adsorption and decomposition processes of formic acid into bidentate formate on Pd-Cu(997). The peak assignments were referred to our previous study about the adsorption and decomposition of formic acid on Cu(111) and Cu(997) [3]. At 80 K, a dominant peak was observed at 290.0 eV, which is assigned to molecular formic acid. A small component was also observed at 288.4eV, which is assigned to monodentate formate. By heating to 150 K, a part of formic acid was desorbed and the amount of monodentate species was increased. By heating to 300 K, all adsorbed species become bidentate formate (287.5 eV).

Thus prepared bidentate formate on Pd-Cu(997) was exposed to 800 L H₂ at 80 K and subsequently heated to 300 K. By this process, the bidentate formate O1s peak at 531.0 eV was decreased in intensity by ~20% and atomic oxygen was newly observed at 529.4 eV (~10% of the original bidentate formate). The C1s peak of bidentate species was also decreased by ~20%. We propose that a part of bidentate species are reacted with adsorbed hydrogen atoms on Pd-Cu(997) and the desorption of hydrogenated species (probably, formaldehyde and methanol) occurs below 300 K.

References


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DINITROGEN ACTIVATION BY MOLECULAR MULTIMETALLIC TITANIUM POLYHYDRIDES

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Abstract
Dinitrogen activation and hydrogenation by transition metal complexes have attracted much current attention. Here we report the N₂ activation by multinuclear titanium polyhydride complexes. We found that N₂ activation and hydrogenation are achieved by the cooperation of the multiple metal sites, and the hydride ligands serve as the source of both electron and proton, thus enabling the cleavage and hydrogenation of dinitrogen without extra reducing agents and proton sources.

Introduction
Dinitrogen activation and functionalization by molecular transition metal complexes have attracted extensive attention. This work presents multimetallic titanium polyhydride complexes that react with N₂ through N≡N bond cleavage and N−H bond formation under mild conditions. The activated nitrogen species can react with a wide range of organic acyl chlorides, leading to formation of the corresponding organic nitriles.

Results
Hydrogenolysis of the titanium trialkyl complex [CpTi(CH₃SiMe₃)₃] (Cp' = C₅Me₅) with H₂ afforded the trinuclear titanium heptahydride complex [(Cp'Ti)(μ-H)(μ-H)₂][H₂] (1) (Fig. 1). Complex 1 readily reacted with N₂ (1 atm) at room temperature, giving an imido/nitrido complex 2 via N−N bond cleavage and N−H bond formation. Monitoring the reaction by ¹H and ¹⁵N NMR revealed the initial formation of a dinitrogen complex 3 with release of two molecules of H₂, followed by N−N bond cleavage to give a dinitrido complex 4, and hydride migration from titanium to the μ-nitrido unit to give 2. Obviously, the hydride ligands in 1 served as the source of both electron and proton for the dinitrogen cleavage and hydrogenation.

When the hydrogenolysis of [CpTi(CH₃SiMe₃)₃] with H₂ was carried out in the presence of N₂, a tetranuclear diimido/tetrahydrido complex 5 was obtained. Complex 5 reacted with N₂ (1 atm) to afford a mixed diimido/dinitrido complex 6 with release of two molecules of H₂ (Fig. 1).

Remarkably, the imido and nitride species in 6 could be easily converted to nitriles through reaction with acid chlorides (Fig. 1). This transformation did not require any extra reagents and was compatible with functional groups such as aromatic C−X (X = Cl, Br, I) bonds, nitro group, aldehyde and chloromethyl moieties.

Fig. 1. Dinitrogen cleavage and hydrogenation by titanium polyhydride complexes.

References

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DETERMINATION OF BCx HYDROGEN BINDING ENERGIES BY HIGH PRESSURE, VARIABLE TEMPERATURE ¹H NMR SPECTROSCOPY

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Abstract. Boron doped graphene (BCx) has received considerable attention as a potential hydrogen storage material. Notably, researchers at the National Renewable Energy Laboratory (NREL) have reported detection of strong (> 10 kJ/mol) hydrogen binding sites in BCx.[1] However, there have been conflicting reports regarding the hydrogen storage properties of BCx materials. This follows a general trend that has persisted in efforts to quantify hydrogen capacities and binding energies associated with physi-sorbed hydrogen. Typically, PCT and TGA analysis have been used to study the physical properties of physi-sorbed hydrogen. These methods have been shown to require very exacting procedures to obtain reproducible results. Additionally, BCx materials contain multiple types of hydrogen sorption sites which are difficult to differentiate by PCT or TGA analysis. Alternatively, we have studied hydrogen binding by BCx materials using variable temperature ¹H nuclear magnetic resonance (NMR) spectroscopy. Our studies, conducted at ambient conditions and above, allow us to focus on solely the strong hydrogen bindings sites. Monitoring the equilibrium populations of bound and free hydrogen over the temperature range of 25 to 125 °C has allow the determination of a 11.4 kJ/mol binding energy for hydrogen in the sites of interest in NREL produced BCx. We will present the details of our studies as well as the implications out results bring to bear on the nature of the strong hydrogen binding in BCx. The possible application of our novel technique to other classes of hydrogen storage materials will also be discussed.

Fig. 1 ¹H NMR spectrum of BCx under 2000 psi of hydrogen at 125 °C showing the line fitting analysis used for deconvolution and quantification of the overlapping signals of free and bound hydrogen.

Fig 2. Van’t Hoff plot of relative populations of free and bound hydrogen above the 25-125 °C temperature range indicating a hydrogen binding energy of 11.4 kJ/mol.

References

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NOVEL SPECTROSCOPY USING FAR UV LIGHT APPLIED FOR ELECTRONIC STATES ANALYSES OF INTERFACIAL ELECTROLYTE AND HYDROGEN STORING MATERIALS

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Abstract : A novel spectroscopic method which can measure absorbance spectra close to the electrode under electrochemical conditions in the far UV region (EC-ATR-FUV) was developed and successfully applied to the analyses of potential dependent behaviour of electrolyte close to the electrode and to the identification of electrolytic hydrogen storing materials.

Introduction

Identification of the electronic states of chemical species at the electrode interfaces is important for understanding the electron transfer (ET) process and the chemical transformation occurring in accordance with the ET process for the electrochemical devices. Recently, we have developed a novel spectroscopic method which can measure absorbance in the far UV region close to the electrode under electrochemical conditions (EC-ATR-FUV) and reported its application to such interfacial analyses [1,2]. In the far UV region with the attenuated total reflection (ATR) configuration (Fig. 1), the penetration depth, which corresponds to the evanescent wave length, is short (<50 nm), thus enabling one to choose the interfacial electronic transition. In the present study, we report some examples of this novel analysis including the behavior of electrolytic hydrogen storing polymers [3].

Experimental / Computational

The developed EC-ATR-FUV (Fig. 1) was used for measuring the interfacial absorbance in far UV and UV region. Experimentally obtained spectra were analyzed by time-dependent density functional theory (TD-DFT) calculation.

Results and Discussion

As an example of electrode potential dependent behavior, inter-ion electron transition for the ionic liquid which is particularly enhanced at positive electrode potential, will be explained [1]. Then, the hydrogen storing behaviour in accordance with the electrolytic transformation of ketone/alcohol polymer (fluorenone/fluorenol) (Fig.1).

![Fig. 1 Schematic of EC-ATR-FUV and its application to a hydrogen storing material.](image)

References


Ken-ichi Fukui received his Doctor of Science from the University of Tokyo in 1994. He has been a Professor in Chemistry at Osaka University since 2008 after his research career at the University of Tokyo and Tokyo Institute of Technology. His present research interests cover the microscopic mechanism of catalyses at solid surfaces/interfaces and the molecular view of electric double layer at liquid/solid interfaces for efficient energy conversion. He has also been working as an Editor of Surface Science (Elsevier) since 2015.

Representative awards he received are Young Researcher Award in Surface Science from the Kao Foundation for Arts and Sciences (2006), Fellow of the Surface Science Society of Japan (2012), NanoProbe Technology Award from the JSPS (2015), and the CSJ Award for Creative Work from Chemical Society of Japan (2017).

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ELECTRODEPOSITED COPPER CATALYST FOR CO₂ REDUCTION REACTION

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Abstract Using electrochemical methods to reduce CO₂ has the advantages of mild reaction conditions and clean energy sources. Metallic copper as the catalyst for the reduction of CO₂ to hydrocarbons is attractive to researchers. Nanoporous copper films were prepared by electrodeposition and electrochemical etching. The catalytic properties of electroreduction of CO₂ to ethylene and ethane were investigated.

Introduction

The concentration of atmospheric CO₂ has risen continuously due to accelerated burning of fossil fuel year by year. Electrochemical reduction of CO₂ has some advantages such as reacting in mild conditions and using clean energy sources. Cu-based catalysts, including Cu nanoparticles, nanoporous Cu and Cu alloys, were studied by many researchers for improving the catalytic conversion efficiency of CO₂ to chemical fuels. In this work, Nanoporous copper films were electrodeposited and the catalytic performances were measured.

Experimental

Cu-Zn alloy was electrodeposited on a carbon paper or a stainless steel plate from the electrolyte containing CuSO₄ and ZnSO₄. And then the sample was put into a dilute sulfuric acid for dissolving Zn in the Cu-Zn alloy and remaining nanopores in the Cu film. The catalytic performance of nanoporous copper was tested in an electrolyte of 0.1 mol/L KHCO₃ at a constant potential by using graphite electrode and Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively.

Results and Discussion

Cu-Zn alloys with different Zn contents and different film thickness could be obtained by adjusting electrodeposition process. After dissolving Zn, the porous structure of the metal layer was observed as Fig.1 (b) shown. The content of Cu and Zn in the porous metal layer after de-alloying was 92.51 at% and 1.07 at%. CO₂ was electroreductively reduced at a constant potential of -1.4 V, and the Faraday efficiency of the C₂ product (ethylene and ethane) was more than 10%.

Fig. 1 (a) and (b) SEM images of porous copper on carbon paper; (c) contents of porous copper; (d) products of CO₂ reduction reaction at -1.4V vs. RHE.

References


Associate Prof. Dr. Jinqiu ZHANG was born in 1979 in Heilongjiang, China. Jinqiu Zhang graduated with a Ph.D in Chemical Engineering and Technology from Harbin Institute of Technology (HIT) in 2009. She works at Department of Electrochemical Engineering of HIT and her research filed is electrodeposition of functional materials.

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NUCLEAR QUANTUM EFFECTS OF HYDROGEN IN MATERIALS

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Ab initio path integral molecular dynamics (PIMD) is a first-principles technique, which is able to compute the thermal equilibrium of a system where the whole entity of many electrons and nuclei are assumed to be quantum mechanical particles. Here I will introduce two recent applications of the method; the structure of liquid water in the ambient condition, and the hydrogen diffusion in face-centered-cubic palladium, focusing on their isotope effects. The results of PIMD were in better agreement with experimental data available compared with those of the standard ab initio molecular dynamics, showing the importance of nuclear quantum effects.

The isotopologs of liquid water, H$_2$O, D$_2$O, and T$_2$O, were studied systematically by ab initio PIMD simulations (Fig.1). The simulation results are in reasonable agreement with available experimental data on isotope effects, in particular, on the peak shift in the radial distributions of H$_2$O and D$_2$O and the shift in the evaporation energies. It is found that, due to differences in nuclear quantum effects, the H atoms in the OH bonds more easily access the dissociative region up to the hydrogen bond center than the D (T) atoms in the OD (OT) bonds.

Hydrogen diffusion in metals is a recurrent theme in materials physics. The results from the PIMD simulations revealed that, for preferential H location at octahedral sites, as in unstrained Pd, the activation barrier for H migration was drastically increased with decreasing temperature owing to nuclear quantum effects [2]. This implies that the nature of the diffusion mechanism gradually changes from quantum- to classical-like as the strain is increased.

It was also found that the temperature dependence of H isotope diffusivities in face-centered-cubic (fcc) Pd has an unconventional “reversed S” shape on Arrhenius plots [3] which leads to a peculiar situation, where the heavier T diffuses faster than the lighter H in the limited temperature range of 80-400 K. This mechanism explains the anomalous crossovers between the normal and reversed isotope effects observed in the experiments at high and low temperatures.

![Fig. 1: A snapshot from PIMD of liquid water: Black: oxygen atoms, white: hydrogen atoms.](image)

References


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Dr. Motoyuki Shiga has received Ph.D from Tokyo Institute of Technology in 1999. He became a staff member in Japan Atomic Energy Agency in the same year. He won Humboldt Research Fellowship in 2007. He received Distinguished Young Scientist of Japan Society for Molecular Science (2010) and Academic Award of The Molecular Simulation Society of Japan (2010). He is now Principal Researcher in Japan Atomic Energy Agency.
MISCIBILITY IN LiBH₄

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An overview of miscibility of LiBH₄ with other compounds will be presented to tailor H₂ storage properties and Li-ion conductivity. Solubility in both cationic and anionic sublattices, as well as in the liquid phase, will be outlined, highlighted the role of chemical bonds and coordination in the crystal structure. A limited miscibility with oxides will be reported.

Introduction

LiBH₄ is a promising material for future energy-storage applications, both for attractive H₂ storage capacity and for Li-ion superionic conductivity in the hexagonal phase. Mixtures with other compounds in the solid state may show the formation of solutions or can form compounds. In some cases, only a limited miscibility is observed. The tailoring of properties of LiBH₄ by mixing with other compounds, both in solid and liquid phases, will be presented.

Experimental / Computational

Parent materials have been mixed by ball milling, sometimes followed by a thermal treatment. Phase transformations and properties have been characterized by a combination of experimental techniques (e.g. PXD, ATR, TPD, TGA, EIS).

Results and Discussion

Binary, ternary, quaternary and quinary mixtures of LiBH₄ with other borohydrides in the solid state shows full or partial miscibility, as well as the formation of compounds, whereas a full miscibility in the liquid phase is always observed (Fig. 1) [1-3]. For selected systems, thermodynamic properties and phase diagrams have been assessed, allowing the determination of the enthalpy of mixing in solid and liquid phases [4-5]. The eutectic mixtures of LiBH₄ show interesting hydrogen desorption properties [6-7]. Anion substitutions in LiBH₄ brings to the formation of an extended hexagonal solid solutions (I', Br', Cl') [8], as well as the formation of compounds (NH₂, NH³) [9-10]. The mixture of LiBH₄ with various oxides develops the formation of high conductive layers at the interface, to be explored as solid state electrolytes [11].

Fig. 1. Summary on the cation interactions of LiBH₄ with NaBH₄, KBH₄, Mg(BH₄)₂ and Ca(BH₄)₂, both in the solid (A) and liquid (B) phases. From ref. [3].

References


Marcello BARICCO obtained the PhD in Chemistry in 1987 and he is full professor in Materials Science and Technology at the University of Turin. He has been responsible for the University of Torino in several European projects on hydrogen storage materials (COSY, FLYHY, BOR4STORE, SSH2S, ECOSTORE). He is an expert in the Task 40 of the IEA HIA, coordinator of JU-FCH project HyCARE and responsible of the sub program on “Hydrogen Storage” at the European Energy Research Alliance (EERA). The scientific contributions have been presented in about 300 papers, published in international and national journals, and in several invited talk in international meetings.

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HYDROGEN FUNCTIONS IN 2D NANOSHEETS AND RELATED COMPOUNDS

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Abstract

We present soft-chemical approaches for designing functional layered metal oxides and exfoliated 2D nanosheets with hydrogen properties. Soft-chemical reactions such as ion-exchange and acid-base reactions have been utilized to synthesize novel metastable layered inorganic solids, to exfoliate them into individual 2D nanosheets, and to reassemble them as thin films and nanocomposite materials. Such soft-chemical approaches enable the design of hydrogen materials for diverse applications.

Introduction

Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness, have been emerging as important new materials due to their unique properties. In particular, the recent development of graphene has opened up the possibility of isolating and exploring the fascinating properties of 2D nanosheets of other layered materials, which upon reduction to single/few atomic layers, will offer functional flexibility, new properties and novel applications. In this talk, we review the progress made in the synthesis, characterization and properties of 2D oxide nanosheets and related layered compounds, highlighting emerging functionalities in hydrogen materials.

Results and Discussion

Soft-chemical reactions such as ion-exchange and acid-base reactions have been extensively investigated to synthesize novel metastable layered inorganic solids, to exfoliate them into individual nanosheets, and to reassemble them as thin films and nanocomposite materials [1]. These reactions proceed at room temperature and enable the synthesis of a rich variety of structures by stepwise reactions. A variety of 2D oxide nanosheets (such as TiO₂, MnO₂, TiNbO₃ and perovskites) were synthesized by delaminating layered precursors into their single sheets via soft-chemical process. Protonic oxides (such as HTiO₂, HMnO₂, HTiNbO₃, HCa₃Nb₂O₇) were used as the starting point for soft-chemical synthesis of 2D nanosheets by acid leaching and exfoliation. These H⁺-exchanged layered oxides are promising materials for use as a solid acid catalyst due to the generation of strong acidity within the interlayer space. In these materials, H⁺ ions are highly accumulated into the interlayer space, which will allow us to induce the high-order functions of hydrogen by controlling proton conduction and multi-electron transfer processes inside materials and at their interfaces. Soft-chemical reactions have also been utilized to rationally design and tailor the properties of functional layered metal oxides [2]. Layer-by-layer assembly has provided insight into covalent interactions that stabilize oxide-supported nanoparticle catalysts. In addition, topochemical reactions have been utilized to tune the compositions of layered perovskite oxides in order to break inversion symmetry, resulting in ferroelectric properties. Such soft-chemical approaches enable the design of functional materials for diverse applications that include catalysis, energy storage, fuel cells, optical sensors and ferroic materials.

References


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LIGHT-DRIVEN C–H CARBOXYLATION BY CARBON DIOXIDE

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Here we report direct photochemical C–H carboxylation of aromatic compounds with various combinations of substituents. They showed distinct photoreactivity (e.g., carboxylation by CO₂, dimerization and oligomerization) depending on not only kinds and numbers of the substituent but also their combination and position.

Introduction

CO₂ fixation utilizing light energy have been extensively developed owing to global energy and environmental issues such as shortage of energy/chemical resources and increasing atmospheric CO₂ concentration. Many of the researches have represented photocatalytic CO₂ reduction to produce C1 compounds.¹ Meanwhile, carboxylation of organic compounds using CO₂ as the substrate is also an important process.² The research interests have been expanded to develop mild and atom/step economical systems without the use of additives such as reductant and base.

We have reported photochemical H₂ production using [Fe(opda)]₂(ClO₄)₂ (opda: ortho-phenylenediamine) at room temperature.³ Photoexcitation of opda activates the amine N–H bond producing hydrogen atom as the key intermediate for H₂ formation (Fig. 1a). Furthermore, another intermediate, i.e., anilino radical of opda, was found to proceed carboxylation of its aromatic C–H bond in the presence of CO₂ (Fig. 1b).⁴ These findings allow us to expand variation synthesis of carboxylic acids driven by light energy.

Results and Discussion

Aromatic compounds substituted by heteroatomic functional groups showed distinct photoreactivity depending on not only kinds and numbers of the substituent but also their combination and position (Fig. 2). Their photochemical and photophysical properties will also be discussed in detail.

Fig. 1 Photochemical reaction of [Fe(opda)₂](ClO₄)₂ under (a) N₂ and (b) CO₂ atmospheres.

Fig. 2 Photochemical reactivities of various substituted aromatic compounds under CO₂ atmosphere.

References


Akinobu Nakada is Assistant Professor at Department of Applied Chemistry, Faculty of Science and Engineering of Chuo University. He received his PhD in 2017 from Tokyo Institute of Technology under the supervision of Profs. Osamu Ishitani and Kazuhiro Maeda. In 2014, he visited The University of North Carolina at Chapel Hill (Prof. Thomas J. Meyer) as a research scholar for three months. In 2017, he joined the group of Prof. Ryu Abe at Kyoto University as a Postdoctoral Fellow and was promoted to an Assistant Professor (special appointment with CREST/JST) in the same year. In 2019, he joined the group of Prof. Ho-Chol Chang at Chuo University as an Assistant Professor. He received the Seiich Tejima Doctoral Dissertation Award at Tokyo Institute of Technology in 2018. His research interests include metal complex and semiconductor photocatalysts for energy and chemical conversion.

Corresponding author: Ho-Chol Chang, chang@kc.chuo-u.ac.jp, +81-3-3817-1897.
ENHANCEMENT OF LITHIUM ION CONDUCTIVITY OF COMPLEX HYDRIDES BY BORON NITRIDE ADDITIVES

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Abstract

Lithium ion conductivity and H₂ desorption properties of LiAlH₄/BN composites were analyzed in this study. Effects of boron nitrides with different structures (hexagonal BN(h-BN), turbostratic BN(t-BN), cubic BN(c-BN)) on the properties were investigated. Among all the composites, LiAlH₄/t-BN composite showed the highest conductivity. The conductivity of 40wt% t-BN composite at 90 °C reached as high as 1.4 × 10⁻² S cm⁻¹. Also, B-H bond formation was observed during H₂ desorption process of t-BN composite, suggesting the boron edge site of BN would have a catalytic effect on H₂ desorption kinetics. In the c-BN composite, a large amount of stainless impurity was introduced by ball-milling, which caused the H₂ release without melting.

Introduction

Hexagonal boron nitride (h-BN) is known as an effective additive to improve H₂ ab/desorption properties of complex hydrides. The remarkable ab/desorption properties were achieved in ball-milled LiBH₄/BN composites, probably due to the enhancement of H₂ dissociation, H⁻ diffusion and Li⁺ diffusion by nanoscale BN [1]. In our previous study, we added h-BN to LiAlH₄ system. The addition of h-BN caused the decrease of melting point, the delay of desorption kinetics in the 1st step, and the enhancement of kinetics in the 2nd step [2]. The decrease of melting point suggests that h-BN would have an interaction with Li+ cation rather than [AlH₄]⁻ anion. In this study, three kinds of boron nitrides(h-BN, t-BN(turbostratic BN) and c-BN(cubic BN)) were added to LiAlH₄. The effect of each BN addition on Li ion conductivity and H₂ desorption properties were evaluated.

Experimental

h-BN (Sigma Aldrich, 98%) and c-BN (Tomei Diamond, 99.9%) was used as received. Turbostratic BN(t-BN) was synthesized by ball-milling of h-BN for 2hr. LiAlH₄/BN composites were prepared by ball-milling with 400 rpm for 2 hr. The ion conductivity was evaluated by AC impedance measurements and H₂ desorption properties were analyzed by Thermogravimetry - Differential Thermal Analysis - Mass Spectrometry (TG-DTA-MS). Microstructures of the composites were observed by Scanning Transmission Electron Microscope (STEM).

Results and Discussion

First, we investigated Li ion conductivity of ball-milled LiAlH₄ without BN additives. Ball-milling of LiAlH₄ for 2 hr enhanced the conductivity by 2-3 orders of magnitude compared to that of pristine material. The conductivity of LiAlH₄/h-BN composite was 10 times higher than that of milled LiAlH₄. The increment of carrier concentration would be the origin of conductivity enhancement. Among all the composites, LiAlH₄/t-BN composite showed the highest ion conductivity. The conductivity of 40wt% t-BN composite at 90 °C reached as high as 1.4 × 10⁻² S cm⁻¹. In the case of c-BN composite, a large amount of stainless impurity (Fe, Cr, Ni) was introduced by ball-milling due to the hardness of c-BN, thus it is difficult to distinguish the effect of c-BN on the conductivity. From the investigation of H₂ desorption process, the melting peak at 127 °C was observed in the LiAlH₄/tBN composite. Also, the B-H bond formation after the melting peak suggests the boron edge of BN would have a catalytic effect on H₂ desorption kinetics of LiAlH₄.

References


Acknowledgement

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Born in 1988, Sapporo, Japan. Yuki Nakagawa graduated with Ph.D degree in the Division of Materials Science and Engineering from Hokkaido University in 2016. During this time, he worked in the field of B-N based reactive hydride composites for hydrogen storage. His current research is focused on complex hydrides for ion conduction, transmission electron microscope (TEM) analysis of light-element hydrides, and ion implantation effects on energy conversion materials at Hokkaido University in the group of Prof. Tamaki Shibayama.

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EFFECT OF HYDROPHOBIC CATIONS ON THE HYDROGEN OXIDATION/EVOLUTION REACTIONS ON SINGLE-CRYSTAL PT ELECTRODES

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Abstract

We evaluated the activity for the hydrogen oxidation/evolution reactions (HOR/HER) on Pt single-crystal electrodes modified with hydrophobic cations. The HOR/HER activities on Pt(100) and Pt(110) were enhanced by the hydrophobic organic cations. The hydrophobic polymer electrolytes also activate the HOR/HER on Pt(110). The hydrogen-bonding structure in the electrical double layer affects the HOR/HER activity, and hydration water of hydrophobic cation may facilitate the proton transfer to the Pt(110) surface.

Introduction

Efficient hydrogen production from water is necessary to develop the new energy source such as fuel cell. Water electrolysis is one of the important methods for hydrogen evolution. Platinum (Pt) is used as electrocatalysts for fuel cells and water electrolysis. Recently, we found a significant enhancement of oxygen reduction reaction (ORR) by the addition of small amount of tetrahexylammonium cations that have a strong hydrophobicity because of long alkyl chains [1]. In this study, activities for the ORR on Pt single-crystal electrodes were investigated in acid/alkaline solutions containing hydrophobic cations (tetraalkylammonium cation (TMA⁺), tetraalkyl phosphonium cation (TMP⁺) and hydrophobic polymer electrolytes.

Experimental / Computational

A single crystal bead of Pt was prepared with the Clavilier’s method. The crystal was oriented using the reflection beam of He–Ne laser from (1 1 1) and (1 0 0) facets on the crystal [2], and then mechanically polished with diamond slurries. The polished surface was annealed in H2/O2 flame at about 1300 °C. Electrolytic solutions were prepared from ultrapure water and suprapur grade chemicals. The activity for the HOR/HER was estimated by the exchange current density using Butler–Volmer approximation in the low overpotential region.

Results and Discussion

Fig. 1 shows the HOR/HER activity on Pt(hkl) electrodes modified by hydrophobic cations in acidic solution. Tetrahexylammonium cation (THA⁺) and tetrabutyl phosphonium cation (TBP⁺) activates the HOR/HER on Pt(100) and Pt(110). The hydrophobic polymer electrolytes also activate the HOR/HER on Pt(110). We found that the ORR on Pt(111) was activated by THA⁺ because the ORR inhibitor (OH⁻) was destabilized by the hydrophobic cation [1]. However, no OH⁻ is adsorbed on the surface in the HOR/HER potential region. Therefore, hydrogen-bonding structure of hydration water with hydrophobic cation may facilitate the proton transfer to the Pt(100) and Pt(110) surface.

Fig. 1 HOR/HER activity on Pt(hkl) modified with hydrophobic organic cations

References


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SOFT X-RAY ABSORPTION SPECTROSCOPIC STUDIES ON HYDROGENATED TITANIUM DIOXIDE

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Black hydrogenated TiO₂ prepared by the hydrogenation treatment is a promising narrow band-gap material showing high photocatalytic activity. To understand the nature of hydrogenous species in the black hydrogenated TiO₂, in this study, electronic and local structure of the hydrogenated TiO₂ specimens were investigated by soft X-ray absorption spectroscopy. The absorption spectra of Ti L-edge shifted to the lower energy position. These spectral changes indicate that TiO₂ was reduced by the hydrogenation treatment, indicating that the major part of incorporated hydrogen is considered to become proton and provides electron to the host structure.

Introduction

Hydrogen production using renewable energy sources like solar light and wind is a key for the realization of sustainable development and green society. For the efficient solar-driven hydrogen production from water molecules, TiO₂ is a promising photo catalyst. To improve insufficient photo absorption in visible and infrared ranges due to wide band gap, metal- and nonmetal-doping was examined widely [1-3]. Among these attempts, excellent photo absorption properties and photo-catalytic activity of the black hydrogenated TiO₂ was reported by Chen et al. [3]. Although black hydrogenated TiO₂ showed excellent optical and photo-catalytic properties, true roles of incorporated hydrogenous species in the host structure is not understood well so far. In this study, we synthesized black hydrogenated TiO₂ and investigated the electronic and local structures by soft X-ray absorption spectroscopy. The function of incorporated hydrogenous species is discussed.

Experimental

Hydrogenated TiO₂ specimens were prepared by exposing the pristine TiO₂ to atomic hydrogen using a heated W filament in 1.3 x 10⁻¹ Pa H₂ atmosphere at 573 K for 15 h. For powder samples, intermediate homogenizations were performed every 1h. X-ray absorption spectroscopy was carried out at BL27SU, SPring-8, Japan. Ti L-edge (453-473 eV) and O K-edge (525-555 eV) spectra were recorded by both total electron yielding and partial fluorescence yielding modes.

Results and Discussion

Figure 1 shows the X-ray absorption spectra at the Ti L-edge of the commercial anatase TiO₂ powder, blue hydrogenated TiO₂ and black hydrogenated TiO₂ single crystal (Rutile) recorded by the total electron yielding mode. In Ti L-edge spectra, lower energy peaks indicated by c-e are Ti-LII edge and those indicated by f and g are Ti-LIII edge. In hydrogenated specimens, lower energy peak of the L₂ and L₃ edge shifted to the lower energy position compared with the pristine TiO₂. These spectral changes strongly indicate that TiO₂ are reduced by the hydrogenation treatment. Since the nonstoichiometric variation of the oxygen/metal ratio in TiO₂ is negligibly small, the major part of the incorporated hydrogenous species is considered to be proton and provide electron to the host structure [4].

References


Acknowledgement

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EFFECTIVE COULOMB INTERACTION IN STRONTIUM VANADIUM OXYHYDRIDES EVALUATED BY THE CONSTRAINED RANDOM-PHASE APPROXIMATION

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Abstract Transition metal oxides have been one of the central objects in the studies of electron correlation effects because of their rich variety of physical properties. Recently, it was pointed out that oxyhydrides can offer a unique playground of strongly correlated low-dimensional electronic structure, where the s orbitals of hydrogen break a chemical bond between the cation \(t_{2g}\) orbitals. In this study, we evaluate the effective Coulomb interaction in low-energy effective models for strontium vanadium oxyhydrides \(\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n\) \((n = 1 \text{ and } \infty)\) using the constrained random-phase approximation. We find unique screening effects take place in strontium vanadium oxyhydrides.

Introduction

Transition metal oxides have been one of the central objects in the studies of condensed matter physics because of their rich variety of physical properties. Recently, oxyhydrides, where oxygen atoms in oxides are partially replaced with hydrogen atoms, have attracted much attention as a new platform of materials science [1]. In this study, we evaluate the effective Coulomb interaction strength in strontium vanadium oxyhydrides \(\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n\) \((n = 1 \text{ and } \infty)\) using the constrained random-phase approximation. We find unique screening effects take place in strontium vanadium oxyhydrides.

Experimental / Computational

In this study [2], we evaluate the effective Coulomb interaction strength in strontium vanadium oxyhydrides \(\text{Sr}_{n+1}\text{V}_n\text{O}_{2n+1}\text{H}_n\) \((n = 1 \text{ and } \infty)\) [3-4], which are prototypical transition metal oxyhydrides, where the antiferromagnetic order [3] and a pressure-induced metal-insulator transition [5] were experimentally observed. First, we perform first-principles band calculation, and then extract the Wannier functions. After that, we evaluate the effective Coulomb interaction parameters among the Wannier orbitals using the constrained-random-phase approximation with the RESPACK software [6]. We also investigate the transfer integrals among the Wannier orbitals.

Results and Discussion

We find that the effective interaction in the \(t_{2g}\) model, where only the \(t_{2g}\) orbitals are explicitly considered, is strongly screened by the \(e_g\) bands compared with that for oxides, because the \(e_g\) bands are strongly entangled with the \(t_{2g}\) bands in the oxyhydrides. On the other hand, the effective interaction is rather strong in the \(d\) model, where all the vanadium \(d\) orbitals are explicitly considered, owing to a large energy separation between the V-\(d\) bands and the anion bands (O-p and H-s). These findings suggest that nontrivial and unique correlation effects can take place in strontium vanadium oxyhydrides.

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CHALLENGE OF DETERMINATION OF HYDROGEN POSITIONS IN HYDRIDES BY WHITE NEUTRON HOLOGRAPHY

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Abstract

We will show advantages and recent results of newly developed white neutron holography, which is an powerful probe to determine H positions in hydrides, even though H has no translation symmetry. We succeeded in visualising H around B in 0.26% B doped Si.

Introduction

We have developed a novel technique to visualise atomic images around a selected atom in materials with atomic resolution, called white neutron holography in J-PARC. This method is a powerful probe to determine the positions of dopants in materials [1,2]. We have already established the technique to determine B positions in functional materials, such as semiconductor B doped Si, thermoelectric materials B doped Mg₂Si, LED material B doped SiC, and so on. Based on this progress, we are developing a technique to apply this method to hydrides under the support of Hydrogenomics. If it will be practical, one can observe the atomic structure around H in principle; thus, H positions in hydrides can be determined even for the case that H has no translation symmetry. Since this method is quite unique as a probe of H, it can provide strong impacts to science of hydrides. On the other hand, since the present neutron holography requires single crystalline samples with a size of ~1 cc, we are trying to develop a technique for powder samples to apply this method to hydrides.

Experimental

Experiments are performed at BL10 in Japan Proton Accelerator Research Complex (J-PARC) at Tokai, Japan under strong support of the instrumental team.

Results and Discussion

Fig.1 shows a recent result, which is the atomic image around B in 0.26 at% B doped Si, indicating that B is located at Si positions in the diamond structure, as well known. This indicates that neutron holography is an effective probe to determine positions of light element dopants. Since the signals from H is weak in comparison with B, we are trying to observe H around B in B doped Si as the first step in this project in Hydrogenomics. We will also show results of hydrogenated B doped Si, and present status of powder neutron holography in Poster 33 and 34.

Fig. 1 Local atomic structure around B (Green) in 0.26 at% B doped Si. (Reproduced from Ref.2 with permission[2].)

References


Kenji Ohoyama was born in Tokyo, Japan in 1961. He obtained his B.Sc.(1986) and M.Sc. (1988) degrees from Tohoku University and Ph.D. from Tohoku University in 1992. He worked in Tohoku University as a research associate (1992–2003) and associate professor (2003–2015). He moved to Ibaraki University as a full professor in 2015. His main research fields are investigations of materials science and magnetism in strongly correlated electron systems using neutron scattering. In particular, he has been developing the novel technique, white neutron holography.

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Poly(dihydroxybenzoquinone): Its High-density and Robust Charge Storage Capability in Rechargeable Acidic Polymer-air Batteries

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Abstract
2,5-Dihydroxy-1,4-benzoquinone (DHBQ) undergoes a two-electron, two-proton redox process in a single step at a potential of +0.2 V (vs. Ag/AgCl) in acidic aqueous electrolyte at pH 1, which suggests that DHBQ is a potential candidate for use as an anode-active material with high energy density. Furthermore, simple addition condensation of DHBQ yields poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM). For the first time, a rechargeable acidic polymer-air battery was fabricated with PDBM as the anode, the conventional Pt/C cathode catalyst, and an acidic aqueous electrolyte (pH 1). This battery yielded a discharge voltage of 0.70 V and a high discharging capacity of 352 mAh/g with a long-lifetime of 500 cycles and high rate capabilities (up to 10 C), maintaining the moderate energy density of 172 mWh/g.

Introduction
Recently, electrochemical energy storage devices have been intensively pursued for the future energy network, to buffer the unpredictable energy generation, to facilitate the efficient use of renewable energy sources, and to reduce environmental impact. Aqueous air batteries have gained revived interest to achieve much larger energy density for the increasing demand and lower environmental burden [1]. Aqueous air batteries combine the design features of both conventional batteries and fuel cells and are fabricated with a metal anode and an air-breathing cathode in a proper aqueous electrolyte. The rechargeable air batteries are still under development due to the low cycle performance as a result of the formation of dendrites on the metal anodes. In addition, the use of a basic aqueous solution often causes the carbonate clogging problem, which arises from the CO₂ reaction in the air [2].

On the other hand, organic materials, with their inexpensive, abundant and readily available building blocks (H C O N S) and tunable properties, have been proposed as replacements for inorganic electrode-active materials. Especially, organic redox polymers have progressed significantly, which are composed of redox-active groups as a repeating unit and are characterized by high charge transport and storage capability based on their densely populated redox sites [3].

In the current work, organic redox polymer and acidic aqueous solution were used as an anode-active material and electrolyte, respectively, for the rechargeable air battery. They released the rechargeable air battery from its particular problems.

Results and Discussion
Simple addition condensation of DHBQ yielded PDBM. A rechargeable acidic polymer-air battery was fabricated with the PDBM electrode as the anode, the conventional Pt/C cathode catalyst, and an acidic aqueous electrolyte (pH 1). The charging-discharging curves of the battery at 5 C exhibited a plateau voltage at 0.7 V and their coulombic efficiencies were >99%, demonstrating the reversible charge storage property of the cell. The capacity for the anode used in the battery was 349 mAh/g, suggesting that almost all of the DHBQ moieties contributed to the charge storage. The battery kept the almost full discharging capacity of 348 mAh/g even at a rapid discharging of 10 C which corresponded to the full discharging within 360 s. The high capacities of 88% after 500 cycles were still maintained, which demonstrated the long-life ability.

References

PhD student, Supervisor: Prof. Kenichi Oyaizu, Waseda University
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2017 Poster Presentation Award; 17th IUPAC International Symposium on MacroMolecular Complexes, Japan.

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CRYSTAL STRUCTURE PREDICTION OF Li(CB$_9$H$_{10}$) BY XRD-ASSISTED MOLECULAR DYNAMIC SIMULATION

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Abstract

Crystal structure of complex hydrides, Li(CB$_9$H$_{10}$), has been studied by XRD-assisted molecular dynamic (MD) simulation. Hcp-like trigonal structure of (CB$_9$H$_{10}$)$^-$ anions is obtained from these MD simulations as an candidate, whose calculated XRD pattern almost agrees with that of experimental one.

Introduction

All-solid-state battery is one of the most promising candidates to resolve the intrinsic drawbacks of current lithium-ion batteries, such as electrolyte leakage, flammability, and limited energy density. Recently, a class of complex hydrides, represented as Li(CB$_9$H$_{10}$) and Na(CB$_9$H$_{10}$), is paid considerable attention, because of its high ionic conductivity and stability against metal anode [1]. Conductivity measurement and structure analysis suggest that the disorder of (CB$_9$H$_{10}$)$^-$ anions plays a critical role of this high ionic conductivity, whereas the exact orientation of these anions has not been clarified yet. Under such circumstance, recently, our group develop an efficient approach to predict the crystal structure by combining molecular dynamic (MD) simulation and data-assimilation utilizing XRD pattern [2]. Here, we report the result of crystal structure prediction of Li(CB$_9$H$_{10}$) based on the XRD-assisted MD simulation.

Simulation Methodology

LAMMPS and VASP codes are employed for molecular dynamic (MD) simulation and ab initio calculation, respectively. Reax-FF potential are employed for classical MD simulation. PBE-GGA is employed for exchange correlation function in ab initio calculation. The data-assimilation approach to combine XRD pattern with MD simulation follows that in ref. [2].

Results and Discussion

As a test calculation, the configurations of (B$_{10}$H$_{10}$)$^{2-}$ anions in the reported crystal structure of Li$_2$(B$_{10}$H$_{10}$) [3] has been predicted from the random configuration of (B$_{10}$H$_{10}$)$^{2-}$ anions by MD simulation with XRD pattern of Li$_2$(B$_{10}$H$_{10}$). these MD simulations could predict the configurations of B$_{10}$H$_{10}$ in Li$_2$(B$_{10}$H$_{10}$) crystal 8 times out of 50 simulations, suggesting that this XRD-assisted MD simulation potentially could predict the crystal structure of Li(CB$_9$H$_{10}$). 4 out of 50 MD simulations for (CB$_9$H$_{10}$)$^-$ anions with XRD pattern of Li(CB$_9$H$_{10}$) show the hcp-like trigonal structure, as shown in Figure 1. (Note that the positions of Li$^+$ ions are determined by subsequent XRD-assisted ab initio MD simulations.) Although more than 60% of simulations show the almost same center of gravity positions of CB$_9$H$_{10}$ anions as that of figure 1, the orientation of anions is different and the obtained XRD patterns less agree with the experiment. In addition, it is confirmed that the potential energies of those simulations are almost comparable suggesting the effectiveness of data-assimilation to find the crystal structure where the orientation of cluster is important.

References


Ryuhei Sato received his Ph. D. in 2018, at the department of Materials Engineering, The University of Tokyo. After half-year Postdoctoral research fellow in Japan Society for the Promotion of Science, he joined Prof. Tsuneyuki’s group as Postdoctoral researcher. His research topics have centered around the protons. In previous position, he mainly studies the proton conduction phenomenon on oxide surface and, in current position, the crystal structure prediction including the position of hydrogen, proton, hydrides.

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Fig. 1 Li(CB$_9$H$_{10}$) structure predicted from XRD-assisted MD simulation
THEORETICAL ANALYSIS ON STRUCTURES OF RESTING OXIDIZED STATES OF [NIFE] HYDROGENASE

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Abstract We performed QM/MM analysis of structures of resting oxidized states and compared with the X-ray crystallography experimental data. We assigned the bridge ligand and charge/spin state for known Ni-A and Ni-B states as –O– bridge with Ni(III) spin state and OH bridge and Ni(II) low spin state, respectively. We also found that the novel resting structures for two different charge states were theoretically reproduced.

Introduction

[NiFe] hydrogenase plays an important role in anaerobic metabolism and catalyzes the reversible redox reaction of H₂. For resting oxidized states, Ni-A and Ni-B states were obtained by X-ray crystallographic analysis (Fig. 1) [1]. Recently, novel Ni-A like structure (Ni-A’), where sulphenyl ligand bridges Ni and Fe, is obtained by Higuchi’s group. However, the electronic state of Ni and Fe atoms and oxygen species contained in the active site are unknown for this structure. In this study, we access these structures by changing the valence state and oxygen species using QM/MM calculation.

Computational details

QM/MM calculations were performed for –O–, -OH, and -H₂O coordination between Ni and Fe atoms and 3 different charge states. For QM part, amino acids and ligands within 9 Å around the active site and a few additional amino acids were included. NWChem (ver. 6.3) was used for the calculations [2]. A stable state was obtained by measuring root mean square deviation (RMSD) measured from new crystal structure.

Results and Discussion

For the Ni-A state, we evaluated all possible combinations of the ligands, charge states, and spin states and concluded that the Ni-A state is presumably characterized by –O– bridge between Fe and Ni and Ni(III) low spin state considering the EPR experimental result. However, further analysis is needed to determine it by considering methodology dependency of calculation. For the Ni-B state, we assigned the state as OH bridge and Ni(III) low spin state by comparing local structure around metal site with X-ray structure. For the Ni-A’ structure, we optimized the structure using QM/MM model and obtained stable structures for different charge states. For Ni(II) and Ni(III), high and low spin states are ground states.

References


Yasuteru Shigeta, a Theoretical Chemist and Biophysicist, graduated from Department of Chemistry, Osaka University and obtained a Doctor of Science degree at there in 2000. He pursued his postdoctoral researches at Osaka University, Kansas State University, and the University of Tokyo from 2000 to 2004. He worked at the University of Tokyo during 2004-2007 as an assistant professor, University of Tsukuba during 2007-2008 as a lecturer, University of Hyogo during 2008-2010 as a research associate professor, Osaka University during 2010-2014 as an associate professor, and now joined University of Tsukuba as a full professor since 2014. He has published more than 200 scientific papers and received international awards such as PCCP award of Royal Society of Chemistry (UK) in 2007 and QSCP Promising Scientist Prize of CMOA (France) in 2017.

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HYDROGENATION PROPERTIES OF TITANIUM WITH SURFACE MODIFICATION BY CARBON

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Abstract
Titanium (Ti) requires effective surface modification to improve the hydrogenation kinetics. From previous works about Ti milled with acetone, it is suggested that carbon is important element for surface modification of Ti. In this work, we investigated the effect of graphite for surface modification of Ti. The Ti milled with graphite is able to be hydrogenated at around room temperature. It is noteworthy that the high reactivity is preserved even after 7 days although the reactivity of Ti milled with acetone is lost during only few days. Raman scattering spectra revealed a similarity between Ti milled with graphite and acetone, indicating that the surface modification mechanism of both cases is similar.

Introduction
Ti and Ti-based alloys are promising materials as a functional materials such as hydrogen storage, hydrogen chemical compressor, and thermochemical heat storage. However, Ti is easily oxidized, and its oxide layer inhibits the reaction with H₂. Recently, we reported that the Ti milled with acetone shows high reactivity and selectivity for hydrogen although the surface modification effects are lost after few days [1]. It was suggested from previous results that carbon is important element for surface modification of Ti. Thus, in this work, we investigated the effect of carbon for hydrogenation and reaction selectivity of Ti.

Experimental
Graphite (99.995%, 2-15 micron, Alfa Aesar) was used as the carbon additive. 1:0.5 molar ratio of Ti (99.7%, 100 mesh, Sigma Aldrich) and graphite were mixed, and then the mixture and 20 of balls made of ZrO₂ were put into milling pot. The samples were ball-milled for 3 hours. To avoid temperature increases, the milling was stopped every 10 min for 1 min. The hydrogenation properties of the sample were investigated by thermogravimetry analysis after keeping in glovebox. The degradation with time of sample was evaluated day-by-day.

Results and Discussion
The hydrogenation curves of Ti + graphite were shown in Figure 1. The hydrogenation temperature of Ti milled with acetone was increased to 125 °C after keeping for 7 days [1]. On the other hand, the Ti milled with graphite shows high reactivity even after 7 days. This result indicates that graphite is effective for the improvement of the hydrogenation properties on Ti. In other words, the graphite suppressed surface oxidation of Ti. The chemical state of carbon of Ti milled with graphite and acetone were analysed by Raman scattering. As a result, characteristic peaks corresponding to graphite structure (G- and D-bands) were observed for both of samples, suggesting that hexatomic structure affects the surface modification. In fact, in the case of Ti milled with acetone, the above peaks disappeared with lost of the surface modification effects.

References

Fig. 1 Hydrogenation curves of Ti + graphite at 50 °C under 1 atm H₂ flow.

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DEVELOPMENT OF MULTICOMPONENT QUANTUM CHEMISTRY METHODS FOR ACCURATE PREDICTION AND ELUCIDATION OF HYDROGEN-FUNCTIONAL MECHANISM

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Abstract: Nuclear Quantum Effect (NQE), such as zero-point vibrational energy, tunneling, and its H/D isotope effect, is quite important in various systems from small molecules to material or biochemical complex species. Especially, in the case of "Low Barier Hydrogen Bonding (LBHB) systems", NQE of proton (or deuteron) is indispensable. To elucidate such hydrogen-functional mechanism, we will develop some ab initio approaches for multi-component systems including both electrons and nuclei quantum-mechanically: (I) Multi-component density functional theory (MC_DFT) and (II) ab initio path integral molecular dynamics (PIMD) methods.

Introduction

Recently, Mori et al. [1, 2] developed the \(\kappa-H_2(Cat-EDT-TTF)_2\) (H-TTF, Figure 1) with a hydrogen-bonded \(\kappa\)-electron system, which was found to reveal C2\(\kappa\)-c symmetry in 50-293 K, while its isotopeologue, \(\kappa-D_2(Cat-EDT-TTF)_2\) (D-TTF), showed the phase transition at 185 K from C2\(\kappa\)-c to P\(\kappa\)-1. To elucidate the origin of such difference, we have theoretically analyzed the difference between H-TTF and D-TTF using quantum chemistry approaches.

Computational

First, we calculated the potential energy curves (PECs) with respect to hydrogen-transfer coordinate for model systems by conventional DFT method, to analyze which inter-molecular interaction would be dominant for the contribution to the shape of PEC. The shape of PEC for 3-unit model including \(b_1\) interaction between nearest neighboring units was drastically changed from that for 1-unit model. On the other hand, the shapes of the PECs of other models including \(b_2\), \(p\), and \(q\) interactions did not drastically change from those of 3-unit model. Thus, we have found that the interaction by \(b_1\) (\(\pi-\pi\) stacking) shows the dominant contribution to shape of PEC, which explicitly demonstrated the coupling of H-bonded hydrogen/deuteron dynamics and the \(\pi\)-electron.

Results and Discussion

Then, we performed multicomponent density functional theory (MC_DFT) calculations, taking account of the nuclear quantum effect with the 3-unit model that considering interaction by \(b_1\) (\(\pi-\pi\) stacking). In the H-TTF, the shape of the eff-PEC becomes single-well potential, since the energy barrier obtained with conventional DFT is removed by protonic quantum effect. This is in reasonable agreement with the corresponding experimental observation that the hydrogen is located at the center of H-bond in X-ray structures of H-TTF both at 50 and 293 K. On the other hand, in the D-TTF, the eff-PEC still holds double-well. This means that deuterium is localized at one side of oxygen rather than the center of H-bond in low temperature phase, due to the small thermal effect. Therefore, it is expected that the phase transition in D-TTF occurs due to the localization of the deuterium. We would like to mention that the phase transition temperature of D-TTF is determined by the \(\pi-\pi\) interaction and the nuclear quantum effect [3].

References


Short CV: Dr. Masanori Tachikawa got Ph.D. in Waseda University in 1995, became a JSPS(PD) in Emory University, and a Special Postdoctoral Researcher (SPDR) in RIKEN in 2000. In 2003 he moved to Yokohama City University as an associate professor, became a professor in 2006, and now director of Department of Materials Science, Graduate School of NanobioScience. His research area is “Computational Chemistry” and “Quantum Chemistry”. He is developing new quantum simulation methods, in which both electrons and hydrogen nuclei are treated quantum mechanically. He has applied these methods to the various systems from material science to biochemistry. He has earned the awards for “Young Scholar Lectures of the Chemical Society of Japan, 2006”, “The Young Scientists’ Prize, The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology 2007”, and, recently, “Award of Society of Computational Chemistry, Japan, 2017”.

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CONTROL OF ELECTRICAL PROPERTIES ON TRANSITION METAL OXIDES VIA PROTONIC-ELECTRONIC COUPLING

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Abstract: We report hydrogen doping into NdNiO₃, SmNiO₃, EuNiO₃ thin films. All films exhibited large enhancement of electrical resistance by hydrogen doping. Furthermore, a SmNiO₃ microwire with symmetric Pt and Au microgap electrode and microwire EuNiO₃ with symmetric Pt electrodes showed electric field induced resistance change of about 10% in the in-plane two terminal device geometry.

Introduction
The electrical properties of materials such as transition metal oxides, are quite sensitive to the valence state of the transition metals, which can be easily changed by chemical doping. A range of ionic species can be used to modify the properties of materials or design metastable phases. Use of protons is particularly suited, and as a strong reducer can be used to realize powerful control over the valence states in materials. For example, it was reported that hydrogenation into SmNiO₃ film causes huge increase on resistivity by eight orders of magnitude, owing to electron doped Mott transition. Furthermore, a SmNiO₃ microwire showed electric field induced resistance change of about 10% in the in-plane two terminal device geometry as shown in Fig. 1. The application of a positive bias at the Pt electrode leads to reduction of the hydrogenated area. With this property, proton-based resistive memory devices can be fabricated. Also in NdNiO₃ it was reported similar proton-based resistive switching memory devices.

Experimental / Computational
The NdNiO₃, SmNiO₃, EuNiO₃ thin films were deposited on SrTiO₃ (001) substrate, and hydrogen was doped by using the Pt catalytic spill over method in the 5%H₂/Ar gas atmosphere. A SmNiO₃ microwire with asymmetric Pt and Au microgap electrode (gap distance 8μm) and microwire EuNiO₃ (gap distance 10μm, wire width 1μm) fabricated using photolithography with symmetric Pt electrodes.

Results and Discussion
Hydrogen doping into NdNiO₃, SmNiO₃, EuNiO₃ thin films bring large enhancement of electrical resistance. Furthermore, a SmNiO₃ microwire with asymmetric Pt and Au microgap electrode and microwire EuNiO₃ with symmetric Pt electrodes showed electric field induced resistance change of about 10% in the in-plane two terminal device geometry as shown in Fig. 1. The application of a positive bias at the Pt electrode leads to the enlargement of the hydrogenated area (which is the high resistive state) due to the migration of protons into the entire film, while the negative bias application results in the reduction of the hydrogenated area. With this property, proton-based resistive memory devices can be fabricated. Also in NdNiO₃ it was reported similar proton-based resistive switching memory devices.

References

Fig. 1 Optical microscope image of a SmNiO₃ microwire with asymmetric Pt and Au microgap electrode fabricated using photolithography (Left). Resistance modulation applying by alternating positive/negative bias voltage in the SmNiO₃ microwire device (Right)

Short CV
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CALCULATING THE pKw OF SUBCRITICAL AND SUPERCRITICAL H2O AND D2O

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In this study we seek to calculate the pKw of Sub- and Critical water using Path Integral Molecular Dynamics (PIMD). Using this method, we are able to capture both the dynamical effects of solvent relaxation and the isotope substitution effect. This makes this method ideal for studying the large change in pKw water undergoes at the temperature and pressure is increased towards supercritical levels, and the isotope effect on these changes.

Introduction

The auto ionization product of water changes drastically as the pressure and temperature is increased [1]. The increased acidity of supercritical water is hypothesized to have a role in driving reactions under these conditions. It is therefore important to understand both the classical and quantum effects driving this change, and we therefore wish to study both the classical Ab-initio molecular dynamics and the quantum PIMD behaviour by elucidating the effect of isotope exchange on the pKw of subcritical and supercritical water.

Experimental / Computational

A water box containing 32 water molecules were used for all simulations, the size of the box was modified to fit the experimentally reported density of water at different temperatures and pressures. We used the PIMD program [2] to propagate the Ab-initio and PIMD trajectories. The electronic structure energies and gradients were provided by DFTB+ using the ob-3 set of parameters for DFTB.

Results and Discussion

We present here our preliminary findings for H2O, D2O and T2O at 300 K, the free energy differences for the breaking of the O-H/D/T bond can be found in Fig. 1. We also carried out a calculating using only one bead, which resulted in almost identical free energy profiles across isotopes. The calculated pKw values for the 12 bead PIMD calculation were 14.02, 14.85 and 14.87 for H2O, D2O and T2O respectively. This matches well with the reported experimental difference between light and heavy water of 0.87 pKw units. We hope to report further results on the temperature dependence and structural differences in water and heavy water at the meeting.

![Fig. 1](image)

**Fig. 1** The calculated difference in free energy with respect to bond length of the O-H/D/T bond in a solution of H2O, D2O and T2O at 300K/1bar.

References


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2014 – PhD in Chemistry, Aarhus University, “Developments and Generalizations in Molecular Vibrational Structure Theory”.

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HYDROSILYLATION OF BENZOPHENONE DERIVATIVES CATALYZED BY RARE-EARTH METAL COMPLEXES: IMPORTANCE OF AGOSTIC INTERACTION BETWEEN RARE-EARTH METALS AND HYDROSILANE

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Rare-earth metal complexes, Ln[N(SiHMe$_2$)$_2$]$_2$(THF) (Ln = La (1), Ce (2), Y (3); L = N,N’-bis(pentafluorophenyl)-diethylenetramine dianion), were synthesized by treating LH$_2$ with Ln[N(SiHMe$_2$)$_2$]$_2$(THF)$_2$. X-ray analysis of 1-3 reveals that there is agostic interaction between the metal center and Si-H moiety of the siylamido ligand: complexes 1 and 2 possess stronger agostic interaction than yttrium complex 3. Complexes 1 and 2 showed high catalytic activity for hydrosilylation of benzophenone derivatives with HN(SiHMe$_2$)$_2$.

**Introduction**

Hydrosilylation of carbonyl compounds is important organic transformation to convert the carbonyl functionality to the reduced form. The key step for the hydrosilylation is activation of a Si-H bond of hydrosilanes: oxidative addition of hydrosilanes to late transition metals affords silymetal hydrides, and subsequent insertion of the carbonyl group into the M-H bond gives the hydrosilylation products after reductive elimination, while Lewis acid activation of a Si-H bond in the presence of carbonyl compounds produces the hydrosilylation product via generation of the cationic silyl intermediate. Herein, we report hydrosilylation of benzophenone derivatives with HN(SiHMe$_2$)$_2$ catalyzed by rare-earth metal complexes, in which agostic interaction of the rare-earth metal centers and Si-M moiety is a key for improving the catalytic activity.

**Experimental**

Reaction of Ln[N(SiHMe$_2$)$_2$]$_2$(thf)$_2$ with N,N’-bis(pentafluorophenyl)diethylenetramine ligand (LH$_2$) yielded mononuclear rare-earth metal complexes, Ln[N(SiHMe$_2$)$_2$](THF) (Ln = La (1), Ce (2), Y (3); L = N,N’-bis(pentafluorophenyl)diethylenetramine dianion) along with two equivalents of HN(SiHMe$_2$)$_2$. The complexes 1-3 were characterized by $^1$H and $^{19}$F NMR spectra and IR measurement as well as X-ray diffraction study of the single crystals. Upon combined with HN(SiHMe$_2$)$_2$, complexes 1-3 (5 mol%) were used as catalysts for hydrosilylation of benzophenone derivatives, and their catalytic activities were evaluated by comparing the yield of the corresponding diphenylethylenol derivatives obtained after hydrolysis of the reaction mixture.

**Results and Discussion**

Solid-state structures of 1-3 (Figure 1 for 2) clarify the presence of agostic Si-H interaction between the N(SiHMe$_2$)$_2$ ligand and the rare-earth metal center: the larger value of Si1—N4—Si2 indicates agostic interaction of two Si—H moieties of the N(SiHMe$_2$)$_2$ ligand to the metal center in 1 and 2, while the smaller value of Si1—N4—Si2 and Y—N4—Si1 suggests one Si—H moiety interacting with yttrium in 3. In the IR measurement, two separated absorptions were observed at 2051 cm$^{-1}$ and 2107 cm$^{-1}$ for yttrium complex 3, the latter of which was typical for a Si-H bond without any significant agostic interaction, whereas one broad absorption was observed at 2002 cm$^{-1}$ for 1 and 2017 cm$^{-1}$ for 2, respectively. It is interesting to note that the complexes 1 and 2, having two agostic Si-H interaction, exhibited high catalytic activity for hydrosilylation of benzophenone derivatives with HN(SiHMe$_2$)$_2$. According to the generally accepted hydrosilylation mechanism, we propose that strong Si-H agostic interaction facilitates insertion of the C=O moiety of benzophenone derivatives due to the formation of cationic silicon center. Further mechanistic study of the catalytic reaction is presented.

![Fig. 1 Molecular structure of cerium complex 2.](image)

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ROLE OF HYDROGENS AROUND HETEROINTERFACES IN IMPROVING PASSIVATION PERFORMANCE OF SOLAR CELLS

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We report on the role of hydrogens around heterointerfaces in improving passivation performance of silicon-based heterojunction solar cells. Thermal desorption spectroscopy of atomic layer deposited TiOₓ with hydrogen clarified that silicon dihydride bonding energy increases when passivation performance is improved. In addition, nuclear reaction analysis of hydrogenated amorphous Si deposited on crystalline Si suggested that local rearrangement of hydrogens at the molecular level is responsible for the improved passivation performance. The both examples indicate the importance of controlling hydrogens around heterointerfaces to increase conversion efficiency of heterojunction solar cells.

Introduction

High passivation performance of the surface of crystalline silicon (c-Si) is one of prerequisites to realize high efficiency silicon-based heterojunction solar cells. Hydrogenated amorphous Si (a-Si:H) is known to provide excellent passivation performance. Recently, atomic layer deposited metal oxide such as TiOₓ (ALD-TiOₓ) attracts attention as carrier selective passivating contacts. Passivation performance could be modified by surface treatment of the c-Si substrate prior to deposition, conditions of deposition, and post-deposition process. Therefore, it is important to understand underlying physics during the process to establish the guideline how to improve passivation performance.

Experimental

All experiments were carried out on double-side mirror-polished float-zone grown c-Si(100) substrates. After various chemical treatments to form SiOₓ interlayer with different densities, TiOₓ layers including hydrogens were deposited at 150 °C by a thermal ALD (GEMStar-6, Arradiance). In addition, the intrinsic a-Si:H was deposited by plasma enhanced chemical vapor deposition (PECVD) at various temperatures followed by post-annealing. Effective carrier lifetimes were measured by WCT-120 lifetime tester (Sinton Instruments) to investigate passivation performance. For a part of samples, the desorption of hydrogens was characterized by thermal desorption spectroscopy (TDS), and nuclear reaction analysis (NRA) was performed to investigate hydrogen depth profiles.

Results and Discussion

The effective carrier lifetime was largely improved when ultra-thin SiOₓ interlayer was formed by so-called SC-2 solution (HCl:H₂O:H₂O=1:1:5) prior to deposit ALD-TiOₓ. We speculate that low-density SiOₓ enhanced diffusion of Ti and O atoms during post deposition annealing [1], leading to formation of mixed-oxides with hydrogens. In fact, higher silicon dihydride bonding energy was confirmed by TDS, suggesting that hydrogens play a role in improving passivation performance [2].

Effective carrier lifetime in a-Si:H/Si increased with increasing deposition temperature or increasing post deposition annealing up to 200 °C. NRA clarified that the hydrogen concentration decreases with increasing deposition temperature, while no significant change was observed after post deposition annealing at 200 °C. These suggest that local rearrangement of hydrogens at the molecular level that results in enhanced hydrogenation of dangling bonds would be responsible for the improved passivation performance [3].

References


Noritaka Usami received the B.E. M.E., and D.E. degrees from the University of Tokyo in 1991, 1993, and 1998, respectively. From 1994 to 2000, he worked as a research associate at the University of Tokyo. From 2000 to 2013, he worked as an associate professor at Tohoku University. Since April 2013, he has been with Nagoya University as a professor. His research interest covers a new methodology for materials development by utilizing data science, materials and process for silicon-based solar cells, and so on. He has received various awards, including the best paper award at PVSEC (2009), JSPS Innovative PV Award (2017), and so on. He has authored over 420 publications in international journals.

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APPLICATION OF PROTON-COUPLED ELECTRON TRANSFER REACTION TOWARD THERMOCELL WITH HIGH SEEBECK COEFFICIENT

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Abstract

Seebeck coefficient of thermocell, a kind of thermoelectric conversion devices, is improved by the utilization of proton-coupled electron transfer reaction of ruthenium complexes. \([\text{Ru}(\text{biim})_3]\) (biim = 2,2'-biimidazole, \(x = 0-2\)) shows 1e/0H, 1e/1H, 1e/2H and 1e/3H redox reactions by changing pH and solvent ratio, and the Se is improved up to −3.7 mV K\(^{-1}\). The increment of the Seebeck coefficient is proportional to the dissociated proton, which is in good agreement with the theory.

Thermocells are a class of thermoelectric conversion devices capable of recovering waste heat and converting it to electrical energy using the offset of the redox potential. The low cost and the high Seebeck coefficient (voltage difference per unit temperature, \(S_e\)) have recently aroused great interest; however, the efficiency of the thermoelectric conversion, or figure-of-merit, of the thermocell remains lower by an order of magnitude than that of conventional thermoelectric devices, and the thermocells require a new process to improve the performance of it.

We reported improved Se from ca. 2.0 mV K\(^{-1}\) by introducing host-guest chemistry and found that the concentration of redox-active species varied with the change in temperature.\(^{[1][6]}\) Ring-opening reaction of polysulfide was also utilized.\(^{[6]}\)

In addition to them, we utilized proton-coupled electron transfer reaction of ruthenium complexes (Figure 1) that have large redox entropy according to the association or dissociation of proton accompanying to the redox reaction. \([\text{Ru}(\text{biim})_3]\) (biim = 2,2'-biimidazole, \(x = 0-2\)) shows 1e/0H, 1e/1H, 1e/2H and 1e/3H redox reactions by changing pH and solvent ratio, and was used as a redox species of thermocells.

Thermocell measurement revealed the high Se of −3.7 mV K\(^{-1}\), which was in good agreement with the shift of peak voltage in various-temperature square-wave voltammetry. The \(S_e\) of thermocell increases with the increase of dissociating proton along with the redox reaction. One proton dissociation corresponds to roughly 1.0 to 1.5 mV/K, which is in good agreement with the protonation entropy of buffer chemicals.

Fig. 1 The chemical structure of Ru(biim)\(_3\) and a schematic figure of thermocell consisting of Ru(biim)\(_3\).

References


He received his BS (2001) and MS (2003) degrees in Science from the University of Tokyo under the supervision of Professor Hiroshi Nishihara. After he worked at Mitsubishi Chemical Corporation (2003–2004), he moved to Kyushu University as a researcher and an assistant professor (2005–2010). He received his Ph.D. in Science from Kyushu University under the guidance of Professor Hiroshi Kitagawa in 2010. He then moved to Kyoto University as an assistant professor (2010–2012). Then he moved back to Kyushu University as an associate professor in Faculty of Engineering. His current research focuses on the combination of electrochemistry and nanoporous materials. Supramolecular thermocells, Ionics in metal-organic frameworks, MOF battery, asymmetric plastic crystals are studied.

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STUDY OF HYDROGEN POSITION IN HYDRIDES USING WHITE NEUTRON HOLOGRAPHY


Abstract We are aiming at determining H positions in hydrogen strange materials. We visualized the H structure around B in B-doped Si by newly developed white neutron holography.

Introduction

For hydrogen storage materials, determination of the position of H is important. However, when H does not form a crystal lattice, hydrogen cannot be observed by diffraction. A challenging method to observe H without translation symmetry is newly developed white neutron holography which can observe the local atomic structures around H in principle. We have already established the technique to observe local atomic structure around doped B in materials. The final goal of this project is visualization of atomic images around H to determine H positions. As the first step, we tried to observe local structures of H around B in hydrogenated B-doped Si.

Experimental

We prepared two samples of 0.26% B-doped Si with the same cylindrical shape. One sample was hydrogenated under 9 MPa H2 gas in three weeks and another was not hydrogenated. We measured the two samples using white neutrons under the same condition at J-PARC.

Results and Discussion

Fig. 1 shows atomic images around B in 0.26% B-doped Si. The green circles indicate Si positions, indicating that Si around B was observed in both samples. On the other hand, for the hydrogenated sample (Fig.1 (b)), there are some images, such as the white image with the arrow, whose positions cannot be explained by that of Si (green circles). This implies that we successfully visualized H around doped B. The blue circles indicate interstitial positions between Si, which are consistent with the white atomic images, indicating that H around B is probably located at the interstitial position.

Fig. 1 Atomic image of 0.26% B-doped Si without H (a). An atomic image of 0.26% B-doped Si containing H (b).

Takayoshi Yamamoto was born in Chiba, Japan in 1995. He obtained his B Eng. in Ibaraki Univ. He belongs to Ibaraki University graduate school of Sci. and Eng. His main research is the local atomic structures around H in hydrogen storage materials using white neutron holography.

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FIRST-PRINCIPLES CALCULATIONS OF HYDROGEN DIFFUSION VIA NONADIABATIC CARRIER CAPTURE

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An impurity in material can diffuse through hopping via charge state change by carrier capture. This process is possibly important for hydrogen (H) diffusion because H atom can have large non-adiabatic coupling due to its light mass. We have investigated such possibility for H atom in silicon from first principles calculations. The rate for nonadiabatic carrier capture is obtained with the Fermi’s golden rule based on DFT/HSE06 calculations. Based on the calculated rate, we will discuss the diffusion of H impurity in silicon via nonadiabatic carrier capture.

Introduction
An impurity in material can diffuse through hopping via charge state change by carrier capture, known as, e.g., Bourgoin-Corbett process [1]. This process is likely to be important for hydrogen (H) impurity because H atom can have large non-adiabatic coupling due to its light mass. Regardless of its possible importance, this process has not been discussed thoroughly due to experimental difficulty to detect this kind of diffusion and computational difficulty to treat nonadiabatic process. In this study, we discuss hydrogen diffusion via charge state change from first principles.

Computational
The rate for charge state change was calculated with the Fermi’s golden rule by considering nonradiative carrier capture via multiphonon process [2]. Within this formalism, anharmonic effect of phonon can be taken into account by imposing 1D approximation for ionic degrees of freedom and solving the Schrödinger equation for the 1D potential energy surface [3]. Treating anharmonic effect is crucial to study H diffusion because there exists long distance between stable sites for each charge state. We used DFT/HSE06 method for electronic structure calculations.

Results and Discussion
Figure 1 shows the calculated potential energy surface (PES) and the calculated rate for $\text{H} \rightarrow \text{H}^0 + e^-$ transition. The PES shows large anharmonicity due to large difference in H atom position between the two stable sites. Compared to the experimental rate [4], the calculated rate is underestimated by 1/100 and also shows 0.2 eV difference in its activation energy. The origin of the discrepancy is likely to be 1D approximation of the PES and inaccuracy of electronic structure methods. With the calculated rate, we discuss the H atom diffusion in Si including process via charge state change.

Fig. 1 Left: calculated potential energy surface for the transition between $\text{H}$ and $\text{H}^0$. Right: calculated rate for the transition $\text{H} \rightarrow \text{H}^0 + e^-$. 

References

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FAST AND SLOW DYNAMICS OF HYDROGEN CLUSTER MATERIAL Li₆NbH₁₁

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We have performed the quasielastic neutron scattering (QENS) measurement of Li₆NbH₁₁, which contains unusual ninefold hydrogen-coordinated clusters. Two different QENS signals, corresponding to the relaxational motions of H atoms, appeared between 150 K and 300 K. The slower motion should be due to the classical rotation of the NbH₉ clusters, while the origin of the faster one is still under discussion.

Introduction

Recently, Orimo group (Tohoku Univ.) has synthesized a series of novel materials LiₓMHₓ₁₁, which contain unusual ninefold hydrogen-coordinated clusters MₓHₓ (x = 5 or 6, M = Nb, Mo, W, Ta) [1]. These are of interest since they have high hydrogen density and possible high Li ionic conductivity. The dynamics of MₓHₓ cluster may play important roles in determining the physical properties of the materials. We have performed the quasielastic neutron scattering (QENS) measurements of Li₆NbH₁₁.

Experimental

The QENS measurements of Li₆NbH₁₁ was conducted with a backscattering spectrometer DNA, which is installed at MLF, J-PARC. The sample of 20 mg was checked by a neutron powder diffraction with NOVA at MLF, J-PARC. QENS is a powerful method to study the dynamics of H atoms since the incoherent scattering cross-section of a H-atom is much larger than those of other atoms including Li and Nb.

Results and Discussion

Two different QENS signals, corresponding to the relaxational motions of H atoms, appeared between 150 K and 300 K. Figure 1 shows the Arrhenius plot of the relaxation times which were derived by fitting the QENS spectra to Lorentz functions. For both relaxations, it is remarkable that the temperature dependence of the relaxation time is very small, implying that the activation energy is very small. From the Q-dependence of the width and area of the QENS peak, the slower motion is considered to be due to the classical rotation of the NbH₉ clusters, while the origin of the faster one is still under discussion.

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References


Fig. 1 Arrhenius plot for the relaxation times derived from the QENS data of Li₆NbH₁₁.

Osamu Yamamuro

Osamu Yamamuro received his Ph.D. at Graduate School of Science, Osaka University in 1987. After working as a research associate and assistant professor at Osaka University, he moved to Institute for Solid State Physics, The University of Tokyo as an associate professor in 2004. He got promoted to a full professor in 2013. He is studying chemical physics of complex condensed matters; e.g., glasses and supercooled liquids, water and related materials, ionic liquids, hydrogen storage/conducting solids and their nano-particles. They are investigated by neutron scattering, x-ray diffraction, heat capacity, dielectric and rheometric measurements. The ultimate aim of his study is to find simple rules involved in complex systems from the three different points of view, i.e., structure, dynamics, and thermodynamic.

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CATALYTIC ENHANCEMENT ON RUTHENIUM-IRON NANOALLOY CATALYSTS FOR AMMONIA SYNTHESIS

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Despite many advancements, an inexpensive ammonia synthesis catalyst free from hydro-gen and nitrogen poisoning, and capable of synthesizing ammonia under mild conditions is still unknown and is long sought-after. Here we present an active nanoalloy catalyst, RuFe, formed by alloying highly active Ru and inexpensive Fe, capable of activating both N2 and H2 without blocking the surface active sites thereby overcoming the major hurdle faced by the current best performing pure metal catalysts. This novel RuFe nanoalloy catalyst operates under milder conditions than the conventional Fe catalyst and is less expensive than the so far best performing Ru-based catalysts providing additional advantages. Most importantly, by integrating theory and experiments, we identified the underlying mechanisms responsible for lower surface poisoning of this catalyst, which will provide directions for fabricating poison-free efficient NH3 synthesis catalysts in future.

Introduction
Ammonia (NH3) is a strategic chemical produced in large quantities. NH3 is synthesized through Haber-Bosh process which contributes around one-third to the overall greenhouse gas emissions and many researchers challenge to work towards finding an alternative NH3 synthesis catalyst. For the enhancement of durability of ammonia synthesis catalysts, we choose a simple strategy where we alloyed high performance Ru and Fe catalysts.

Experimental
We prepared the Ru-Fe/MgO catalysts by hydrogen reduction of precipitates produced on MgO supports via thermal decomposition of impregnated carbonyl complexes of Ru and Fe ions. In this method, metal compositions were controllable by changing a mixing ratio of metal complexes. Both MgO supported Ru and Fe nanoparticles catalysts (Ru/MgO and Fe/MgO, respectively) were prepared in a similar way.

The NH3 synthesis rate on the catalyst was measured using a conventional flow system (BEL-REA, BEL Japan). An H2/N2 gas mixture with an H2/N2 molar ratio of 3 (gas hourly space velocity = 18,000 mL h⁻¹ g⁻¹) was then fed to the catalyst.

Results and Discussion
Scanning electron microscope (STEM) images for Ru/MgO, RuFe/MgO, and Fe/MgO suggested that nanoparticles are well dispersed on MgO supports (Fig. 1). Catalytic performances at 400 °C for Ru-Fe/MgO with various compositions of Ru and Fe are shown in Fig. 1.

Surprisingly, RuFe/MgO exhibited the highest catalytic performance under 0.5 and 1 MPa whereas we could not observe any products on Fe/MgO, suggesting that Fe/MgO cannot promote NH3 synthesis reaction under the conditions applied here. Under 0.1 MPa, turn over frequencies (TOFs) on Ru/MgO and RuFe/MgO below 400 °C seemed almost the same. Meanwhile, at 500 °C, RuFe/MgO showed twice the performance on Ru/MgO. Furthermore, under 1 MPa at 600 °C, RuFe/MgO showed three times higher performance compared to that on Ru/MgO.

References

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Miho Yamauchi is a professor in International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University. Her research interests involve hydrogen related properties of metal and alloy nanoparticles, selective catalysis by using the structure controlled nanoalloy catalysts and materials development for efficient energy conversion.

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MAGNESIUM HYDRIDE ON NITROGEN DOPED GRAPHENE FOR HYDROGEN STORAGE

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The nitrogen doped graphene oxide was synthesized and used as a support for MgH\textsubscript{2}. The nitrogen in graphene oxide increases the hydrogen storage capacity and reversibility, it also decrease the hydrogen release temperature due to bond with Mg in MgH\textsubscript{2}. This material has a potential to apply in hydrogen storage at low temperature.

Introduction

Hydrogen energy is one of the alternative energy sources that can replace fossil fuels that can actively replace climate change due to global warming and become depleted. The hydrogen storage method developed so far includes a method of storing liquid hydrogen, a method of storing gaseous hydrogen, and a method of storing in the form of hydrogen alloy. Gas hydrogen storage or liquid hydrogen storage method is explosion risk at room temperature, storage cost is high [1]. Complex hydrides are attractive hydrogen storage materials due to their high hydrogen capacity, but generally have the disadvantage of high hydrogen desorption temperatures and poor re-hydriding reactions.

In this study, MgH\textsubscript{2} were prepared to improve the stability and the reversibility of hydrogen adsorption/desorption by controlling the size of hydrides and using supports. Other parts are that doped carbon materials are introduced to decrease hydrogen release temperature and exhibit a complete reversibility of the hydrogen adsorption.

Experimental

First, graphene oxide were pretreated with HNO\textsubscript{3} solution. After that, HNO\textsubscript{3}-pretreated graphene oxide were filtered and washed until pH became neutral. Then, HNO\textsubscript{3}-pretreated CB was added to the mixture of dicyandiamide with deionized water while stirring. The mixture was then placed in a tubular furnace and heated under an Ar atmosphere. After finalizing the heating process, the sample was allowed to naturally cool to room temperature under an Ar purge [2]. This nitrogen doped graphene oxide was mixed with MgH\textsubscript{2} by ball-milling with different time.

Results and Discussion

The MgH\textsubscript{2} with nitrogen doped graphene oxide were then synthesized by ball-milling and confirmed by XRD. The FT-IR analysis was conducted to confirm the functional groups of the nitrogen doped graphene oxide and the XPS analysis is conducted and the relative intensities. The effect of nitrogen for bonding with MgH\textsubscript{2} was investigated by in-situ XRD. This MgH\textsubscript{2} on nitrogen doped graphene oxide decrease the hydrogen release temperature compared with MgH\textsubscript{2}.

![Graphene, Nitrogen, Magnesium](image)

Fig. 1 MgH\textsubscript{2} on nitrogen doped graphene oxide.

References


Born in 1986 in Seoul, Republic of Korea, Heena Yang graduated with a Ph.D. degree in Materials Chemistry and Engineering from Konkuk university in 2016. During this time, she worked as an undergraduate research assistant in the field of nanostructured materials and proton exchange fuel cells at Konkuk university. Her current research is focused on complex hydride for hydrogen storage at Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland.

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QUANTUM TRANSITION OF HYDROGEN/ELECTRONS IN SOLID AND SURFACES

-Some theoretical aspects-

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Abstract: A systematic theoretical method for quantum transition is provided by energy loss spectral function (ELSF) for hydrogen and electron embedded in an interacting medium. Based on this approach hydrogen hopping rate in solids is obtained in a wide temperature range.

Introduction

In hopping processes of hydrogen in solid or liquid, quantum nature prevails with lowering temperature. Quantum transitions of hydrogen are similar in certain aspects to those of electrons coupled with phonons and electromagnetic environment and both can be understood by a unified theory. This talk provides a systematic view of quantum behavior of hydrogen or electron in solids and surfaces focusing on interacting effects of disturbing environment medium.

Computational/Theoretical

Quantum transition of a particle (hydrogen, proton, electron) causes disturbance of various degrees of freedom of external medium (phonons, solvents, electromagnetic environment,...) which governs the transition rate and its dependence on energy balance and temperature. The disturbances are generally described by an energy loss spectral function (ELSF), which is a correlation function of external medium before and after the transition. With introducing harmonic and linear coupling models for external medium, a general form of ELSF can be derived. Based on analyses of ELSF for phonons, hydrogen quantum hopping rate as well as its temperature and energy balance dependence can be obtained. For case of metals, the effect of conduction electrons on the hydrogen hopping rate can be described in a similar framework. We will show a general trend of temperature dependence of hydrogen diffusion rate in a metal in a wide range.

For the case of electron, quantum transitions in nano junctions can be formulated by ELSF. We clarified how features of I-V curve such as zero bias anomaly, and $d^2I/dV^2$ for small voltages are closely related with the energy dependence of ELSF. Contribution of electromagnetic environment to ELSF is also obtained in a similar way as the case of phonons, with introducing a model formed of a number of tiny LC circuits. The dissipation mechanism is related with the observation problem in single-electron processes.

If the initial and the final state of quantum transition are of considerably different character, a semi-classical model of particle motion is appropriate and gives us a comprehensive understanding of involved phenomena as well as ELSF. We studied a Landau-Zener process embedded in disturbing random medium, and clarified effect of medium on an adiabatic or non-adiabatic transition probability at a point of state crossing. The results of stochastic trajectory calculations indicated suppression of adiabatic pathway. The results are consistent with a general picture obtained by ELSF.

Results and Discussion

Effects of interaction of external medium on quantum transition of hydrogen and electron are systematically formulated by energy loss spectral function (ELSF). Using the analyses of ELSF, quantum hopping rates of hydrogen in metals are obtained in a wide temperature range, which reproduces well many experimental results. This theoretical method can be applied to many quantum tunneling processes of hydrogen including, e.g., in organic molecules, hydrogen reaction at surfaces, and so on.

References


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SYSTHESIS OF SUPERHYDRIDES UNDER HIGH PRESSURE

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High-temperature superconductors with the critical temperature exceeding 200 K were recently found in highly compressed hydrides, so-called “super-hydrides”. The superconducting hydrides consist of a lot of hydrogen atoms which were synthesized from a mother element and hydrogen under pressure above 100 GPa and laser-heat treatment. We have investigated the synthesis method and the superconducting properties of the superconductive superhydrides by using high-pressure techniques.

Introduction

The “room-temperature superconductivity” was predicted in a metallic state of hydrogen [1]. Hydrogen is not yet become metallic since hydrogen is a very compressive molecular solid, and it requires very high pressure exceeding the current experimental limit. A pre-compression of hydrogen is proposed which could realize the metallic state of hydrogen in a hydrogen-rich hydride with reducing the critical pressure of the metallization. [2] Actually the result of the superconductivity of the compressed sulfur hydride (H₂S) [3] is one of the hydrogen-rich systems. We conducted the structural studies of the H₂S and revealed that H₂S was generated from H₂S through molecular dissociation as shown by the following equation: [4-7] 3H₂S → 2H₂S + S. To prevent the shortage of hydrogen, the synthesis of H₂S through the direct conversion from pure H₂ and S was performed under hydrogen excessive condition.

Experimental

A diamond anvil cell (DAC) is a compact pressure device and easy to be assembled to a refrigerator. We have developed the electrical resistance measurement in the pressure range exceeding 100 GPa and the technical achievements are widely shared with the researcher over the world. The sample pure sulfur crystal was cut into a rectangular shape and placed in the gasket chamber. The chamber was filled with pure liquid hydrogen at low temperature < 20 K in a cryostat and the pressure cell was compressed up to 150 GPa at room temperature. The sulfur sample became metallic and absorbed the infrared laser light and heated. The electrical resistance as well as the X-ray diffraction (XRD) image was monitored during the heating.

Results and Discussion

The high purity and high crystallinity in synthesized H₂S was successfully synthesized. It was expected that the higher onset temperature than the previous low-temperature compression method, however, observed Tc was almost comparable. We expect that the direct synthesis method can be applied to the further synthesis of hydrogen-rich systems. [8]

Summary

Recently, superconductivity > 250 K at around 180 GPa in lanthanum hydride was reported. [9,10]. The metallic-hydrogen-like electronic structure seemed to be stabilized in the superhydrides in the frame of a mother element under pressure. Comparing to the speed of progress in theoretical work, the experimental is slow. We may need to find the synthesis pathway, “a cooking recipe” of hydrogen. The improvement of the high-pressure technology and the accuracy of theoretical calculation may lead to the discovery of the room-temperature superconductivity in the near future.

References


Our group: KYOKUGEN (Center for Science and Technology under Extreme Conditions) have developed a multi-extreme condition (<50 mK, >3000 K, >300 GPa, >18 T) using their original designed diamond-anvil cells (DAC) to investigate pressure-induced phenomena in several systems such as elemental materials, organic and inorganic molecular crystals and so on. Frontier studies and developments for the pressure-induced novel properties such as superconductivity, magnetism and metallization of simple systems. The unique experimental technique is now essential and widely spreading to the community of materials science for future applications.

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QUANTUM CRYSTAL STRUCTURE IN THE 250 K SUPERCONDUCTING LANTHANUM HYDRIDE

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Motivated by the recent discovery of high Tc superconductivity in LaH$_{10}$ under high pressure, we performed first-principles calculation, taking account of the effects of the zero-point motion and phonon anharmonicity. We found that LaH$_{10}$ is a "quantum crystal" in that the quantum effects stabilize the symmetric crystalline form (Fm-3m) which favors superconductivity, otherwise the colossal electron-phonon coupling would destroy the system. We also succeeded in reproducing the experimental Tc accurately.

Introduction

Over the years, searching for a room temperature superconductor has been the Holy Grail in condensed matter physics. In 2017, Peng et al. [1] and Liu et al. [2] proposed that LaH$_{10}$, a hydride of lanthanum having a clathrate-like host-guest structure, can have an extremely high superconducting transition temperature Tc.

Recently, Somayazulu et al. [3] and Drozdov et al. [4], have reported striking evidences indicating that LaH$_{10}$ subject to a pressure of 120–185 GPa indeed has Tc as high as 250-260 K.

Computational

With the stochastic self-consistent harmonic approximation, we studied the effect of quantum atomic fluctuations (i.e., zero-point energy) on the stability of the high-symmetric Fm-3m structure.

We also calculated Tc within the framework of anisotropic Migdal-Éliashberg theory and superconducting theory, taking account of strong anharmonicity of low-energy phonons.

Results and Discussion

We found that quantum effects are extremely large in LaH$_{10}$. They induce not just a simple hydrogen bond symmetrization, but a full reshaping of the potential energy landscape [5]. LaH$_{10}$ is a "quantum crystal" in that quantum fluctuations stabilize a special crystalline form which favors superconductivity. Otherwise the colossal electron-phonon coupling would destroy it. We also succeeded in reproducing the experimental Tc [3,4] accurately (Fig.1).

![Calculated superconducting transition temperatures, compared with the experimental measurements (Refs. [2] and [3]).](image)

\textbf{Fig. 1} Calculated superconducting transition temperatures, compared with the experimental measurements (Refs. [2] and [3]).

References


Ryotaro Arita is a Professor in the Department of Applied Physics at the University of Tokyo and a Team Leader at RIKEN Center for Emergent Matter Science. He obtained Ph.D. from the University of Tokyo in 2000, and his postdoctoral work was carried out at the Max Planck Institute for Solid State Research in Stuttgart. He is a recipient of the Ryogo Kubo Memorial Prize and Highly Cited Researchers (Clarivate Analytics). His main interests are in first-principles studies on high Tc superconductors, functional magnets, strongly correlated electron systems, and topological materials.

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VIOLATION OF THE SWITENDICK CRITERION IN METAL HYDRIDES EVIDENCED BY INELASTIC NEUTRON SCATTERING

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Abstract: Only 37.5% of the interstitial sites in the intermetallic hydride ZrV$_2$H$_x$ can be occupied by hydrogen as a result of the short-range correlations avoiding direct next H-H interaction. We present inelastic neutron scattering experiments showing non-expected scattering at low-energy transfer. The analysis of the inelastic neutron scattering spectra reveals that these structures originate from hydrogen vibrations confined by neighbouring hydrogens, partially at distances as short as 1.6 Å. This is an experimental demonstration of the violation of Switendick’s criterion, which predicts the minimal possible hydrogen-hydrogen distance at around 2.1 Å. We use DFT modelling and high performance computing (HPC) to determine the nature of these sites and compare with experimental data.

Introduction
The Switendick limit is a consequence of the interaction between two protons and associated electrons. In molecular hydrogen with its H-H distance of 0.74 Å, the strongly repulsive Coulomb force of the protons is outweighed by the strong covalent bond. In metal hydrides, a locally increased electron density between H-atoms is not possible as the hydrogen electrons share bonds with the metal electrons, and thus do not disturb the Coulomb repulsion of the proton. As a result, the minimal hydrogen-hydrogen distance in conventional metal hydrides is around 2.1 Å under ambient conditions.

Experimental / Computational

Fig. 1 Configurational energy per 8 formula units of ZrV2H4 of with hydrogens occupying different sites.

To better understand and interpret the experimental results, we performed atomistic first-principle calculations, using the TITAN supercomputer at ORNL, the properties of ZrV$_2$ with various hydrogen stoichiometries and coordination. Extensive combinatorial calculations of the energetics of 3200 different minimized structures of hydrogen-loaded ZrV$_2$ that support the finding of anomalous short H-H distances in the material, Fig 1.

Results and Discussion

Finite spectral intensity at around 50 meV occurs only when H-H distances that are less than 2 Å. The number of hydrogen atoms violating the Switendick criterion is small, but strong enough to generate the unexpected peak at 50 meV. The results give insights into the creation of new materials with novel properties such as very high Tc superconductivity at ambient pressure. Searching the literature, there evidence of this behaviour in other similar compounds and materials.

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METAL-ORGANIC FRAMEWORKS FOR THE HYDROGEN ECONOMY

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Metal-organic frameworks are interesting materials for the hydrogen economy as they offer multiple ways of interacting with hydrogen (physisorption, catalytic activation), and with other materials that enable their integration in devices, such as fuel-cell membranes. I will present my group’s latest results focusing on how to modulate the interaction strength between the metal-organic framework hosts and guest molecules/ions with potential in facilitating the hydrogen economy.

Introduction

Metal-organic frameworks are hybrid inorganic-organic frameworks (MOFs) are porous crystalline inorganic-organic hybrid materials with tuneable chemistry and textural properties. [1] We have previously demonstrated that the interaction of small molecules [2], metal atoms [3] and metal nanoclusters [4] may result in altering the properties of the guests. This change consequently can be exploited to tune the properties of the guest for particular functions, such as applications for the hydrogen economy, of which a few examples will be given.

Experimental / Computational

Metal-organic frameworks with pore sizes near and below 1 nm (UiO-66, ZIF-8) have been synthesised and functionalised directly or post-synthetically by grafting various functional groups on the organic linker and/or embedding metal nanoclusters in their pores. The samples were screened for their interaction with hydrogen, and hydroxide ions to uncover the relevant host-guest interactions and their impact on the materials’ function.

Results and Discussion

I will be reviewing our latest results on three different possible applications in the hydrogen economy: i) hydrogen storage, ii) catalysis, and iii) alkaline fuel cells. We have found that i) the functionalisation and grafting of MOFs significantly change their hydrogen-storage properties including the nature and strength of the store-hydrogen bonds; ii) superior hydrogenation catalysts may be obtained using systems in which nanocluster catalysts are embedded in the pores of MOFs; and iii) self-supporting flexible MOF membranes can be synthesised and functionalised resulting in the possibility to engineer their hydroxide-ion conductivity to increase by several orders of magnitude. The last may be applied in alkaline fuel cells.

Fig. 1 Scanning electron micrograph of a self-supporting MOF-based membrane for alkaline fuel cells

References


Short CV I obtained PhD degrees in 2008 in Chemistry (University Eötvös Loránd, Budapest Hungary) and in Physics (University Paul Sabatier, Toulouse France). I previously held postdoctoral positions at the Laboratory of Coordination Chemistry of the CNRS (France), Edinburgh University (UK), Delft University of Technology (Netherlands), and academic positions at Curtin University (Australia), University of Greenwich (UK). I am currently a Lecturer in Functional Materials and I am heading the Advanced Functional Hybrid Materials research group.

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Phase transitions and ultra-high mechanical stress in Nb-H thin films

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Hydrogen absorption in metals commonly leads to lattice expansion. This expansion is restricted when the metal adheres to a rigid substrate since this does not allow for expansion at the interface. Consequently, high mechanical stresses arise upon hydrogen uptake. Theoretically, these stresses can reach about -10 GPa for 1 H/M. Usually metals cannot yield such high stresses and deform plastically by dislocation formation. Therefore, maximum compressive mechanical stress of -2 to -3 GPa is measured for 100 nm Nb thin films adhered to Sapphire substrates. We demonstrate here that upon size reduction plastic deformation can be hindered and even suppressed. In this case the system behaves linearly elastic and the theoretically determined ultra-high stress of about -10 GPa can be experimentally achieved.\textsuperscript{[1]} This will be demonstrated for epitaxial Nb-H thin films, as an example for vertical size reduction. We suggest further strategies to maintain the coherent phase transformation even for larger film thicknesses.\textsuperscript{[2]} Such high mechanical stresses result in changes of the materials thermodynamics.\textsuperscript{[3]} In the case of Nb-H thin films of less than 8 nm thickness, the common phase transformation from the α-phase solid solution to the hydride phase is completely suppressed, at 300 K.\textsuperscript{[4,5]} This affects the storage applications of nano-sized systems.


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A NEW TECHNIQUE FOR VISUALIZATION OF HYDROGEN PERMEATED THROUGH PURE IRON USING AN IRIDUUM COMPLEX

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Abstract
An in-situ technique for hydrogen visualization in a pure iron using an iridium complex was developed in this study. One side of the iron surface was plated with palladium, and then coated with a thin film of the iridium complex. Hydrogen was electrochemically introduced to the opposite side of the bare iron surface. The color of the iridium complex corresponding to the hydrogen-charged area changed soon after hydrogen was introduced into the iron. This result indicates that the iridium complex can be applied for visualization of hydrogen in metals.

Introduction
In recent years, hydrogen embrittlement (HE) of steels has been a great concern because the HE susceptibility of steels is highly relevant with the strength of the steels. Since the hydrogen atoms, which induce HE, will not be distributed homogeneously in most cases, this distribution is of great importance for HE. Hence, there is a high demand for visualizing hydrogen distribution.

It is known that the color of aqua (2,2'-bipyridine-6,6'-dionato)(pentamethylcyclopentadienyl) iridium (III)¹ (hereafter, Ir complex) changes from yellow to orange when it reacts with hydrogen. We hypothesized that the Ir complex on a metal substrates could visualize the hydrogen distribution. Aiming at a novel hydrogen visualization technique using the Ir complex, we tried to see the distribution of hydrogen permeated through an iron membrane in this study.

Experimental procedure
In this study, we used a 30 mm x 30 mm pure iron sheet, with a thickness of 0.25 mm. One side of the iron surface, which was used for the hydrogen-detection side, was electroplated with palladium (Pd) to a thickness of about 400 nm. Subsequently, a thin film of the Ir complex was formed on the Pd coated surface by putting 1 mL of a methanol solution containing 5 mg of the Ir complex and by drying. From the opposite side of the iron surface, hydrogen was electrochemically introduced. During the hydrogen charging, the Ir complex film on the iron substrate was monitored by a digital camera.

Results and Discussion
Figures 1 (a) and (b) show the surface images of the Ir complex film on the iron sheet before and after the hydrogen charging for 1 hour, respectively. The backside of the left-hand side of the iron sheet was masked to avoid hydrogen entry. The color of the Ir complex on the right-hand side where hydrogen permeated was obviously changed by hydrogen permeation.

This result indicates that the Ir complex can be applied for the hydrogen visualization in metals. In the presentation, quantitative analysis of the time-dependent change in color according to hydrogen permeation will also be introduced.

Fig. 1 Surface images of the Ir complex on the iron sheet (a) before and (b) after the hydrogen charging for 1 hour.

References

Saya Ajito received her Ph. D. from Tokyo Institute of Technology, Japan in 2019. She is now working in Institute for Materials Research at Tohoku University, Japan, as a postdoc. Her main interest is hydrogen absorption into steel during corrosion, which relates to hydrogen embrittlement.

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COMPLEX HYDRIDES FOR CO\textsubscript{2} CAPTURE AND TRANSFORMATION

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Abstract Ionic liquids with borohydride as anion can capture and reduce CO\textsubscript{2} from the atmosphere to formate, which represents a new application to complex hydrides.

Introduction
Carbon dioxide is the main contributor for global warming, but it also represents a cheap, abundant and safe carbon source. During the last years, CO\textsubscript{2} capture and utilization has been a global intensive research area. Conversion of CO\textsubscript{2} to chemicals or synthetic fuels represents a promising way to valorise this greenhouse gas\textsuperscript{[1]}, thus limiting the climate change. However, mild conditions reactions is challenging due to CO\textsubscript{2} stability. Here we demonstrates the CO\textsubscript{2} reduction from air under mild conditions by combining ionic liquids (IL) with borohydride. IL cation has strong interaction with CO\textsubscript{2}, allowing its reduction with BH\textsubscript{4}–.

Experimental
1-ethyl-1-methylpyrrolidinium borohydride ([EMPY][BH\textsubscript{4}]) was synthesized following our previous method.\textsuperscript{[2]} CO\textsubscript{2} reduction with [EMPY][BH\textsubscript{4}] was studied by NMR, FT-IR, microbalance, and DSC.

Results and Discussion
As shown in our previous studies, the large electronegativity of nitrogen based IL cations destabilized BH\textsubscript{4}– anion by charge transfer, increasing the reactivity of borohydride. When the white powder is exposed to CO\textsubscript{2} at atmospheric pressure and room temperature, we can observe an increase in volume followed by a phase transition to liquid. Based on NMR and microbalance measurements, the number of CO\textsubscript{2} fixed to the borohydride was determined to be between 2 and 3 (see Fig. 1). Based on analysis and literature, the obtained product appears to be triformatoborohydride. The reaction can proceed at room temperature even at low CO\textsubscript{2} concentration (6 vol% CO\textsubscript{2}, 94 vol% N\textsubscript{2}). Remarkably, [EMPY][BH\textsubscript{4}] was able to fix and reduce CO\textsubscript{2} from air (360 ppm) at 70 °C. The product can then be treated with NaOH or HCl solution to collect formate/formic acid and the IL.

This approach represents an interesting way to capture and reduce CO\textsubscript{2} from the atmosphere into fuel.

Fig. 1 CO\textsubscript{2} reduction with [EMPY][BH\textsubscript{4}] followed by the mass change.

References

Born in 1992, Sion, Switzerland. Loris Lombardo graduated M.S degree in Molecular and Biological Chemistry from Ecole Polytechnique Fédérale de Lausanne (EPFL), in 2017. During this time, he worked in the fields of catalysis for CO\textsubscript{2} reduction, water splitting, and biomass conversion. His current research is focusing on complex hydride for hydrogen storage and CO\textsubscript{2} reduction at EPFL, Switzerland in the group of Prof. Andreas Züttel.
MULTIFUNCTIONAL METAL HYDRIDES

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This work addresses the use of neutron diffraction and synchrotron radiation X-ray scattering methods as important tools to study the properties of functional metal hydrides. The presentation will cover determination of crystal structure, understanding of absorption and desorption processes and understanding of the effect of additives. Furthermore, recent results using metal hydrides as a solid-state electrolyte will be presented.

Introduction

Metal hydrides form large varieties of different types of materials. The traditional applications are related to hydrogen storage, but during the last decade it has found that these compounds are also important for battery applications, smart windows, sensors, heat storage, magnetism and compressors [1].

During the last 10-15 years complex hydrides based on aluminum, boron and nitrogen, respectively, have been extensively investigated. Such materials have a much higher gravimetric hydrogen capacity than the traditional transition metal based hydrides, and thus potential candidates for hydrogen storage application [2, 3]. Recently it has been found that boron-based complex hydrides, for example hexagonal LiBH4, has a high Li conduction, and thus such materials are also possible candidates as solid-state electrolytes in Li-ion batteries [4].

Recently, high entropy alloys have been considered as interesting compounds for hydrogen storage [5].

Results and Discussion

Hydrogen uptake and release are complicated in many of these compounds, with presence of several intermediate steps and phases that can be both crystalline and amorphous. Thus, synchrotron radiation X-ray diffraction in combination with neutron diffraction are the key methods for detailed structural characterization. Diffraction experiments during hydrogen desorption and absorption are important for clarifications of the intermediate phases and the processes for hydrogen uptake and release. Furthermore, catalysts and additives are important to promote the reactions, and therefore the combination of XANES/EXAFS and diffraction methods are needed to understand the effect of additives.

Selected examples of novel compounds, efforts to understand hydrogenation/dehydrogenation properties including effect of selected additives will be presented. The combination of neutron and synchrotron radiation X-ray scattering will in particular be emphasized. Total scattering methods will also be presented as an important method to study disordered compounds.

Acknowledgements

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References


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STRUCTURAL STUDY OF HYDRIDES BY A HIGH INTENSITY TOTAL SCATTERING INSTRUMENT, NOVA

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A neutron total diffractometer, NOVA, which was installed at the high-intensity neutron source at J-PARC to analyse structure of crystalline and non-crystalline materials. Hydrides are important target of NOVA and instrument developments for obtaining accurate hydrogen observation are on-going.

Introduction

Neutron has large scattering cross section of light elements, especially hydrogen, and its energy (meV) and wavelength (Å) is given by $E = 81.8/\lambda^2$. Therefore, neutron is unique tool to observe position and dynamics of hydrogen in materials. A neutron total diffractometer, NOVA, was designed to perform total scattering of crystalline and non-crystalline materials with high intensity and wide momentum transfer, Q, range from 0.03 Å$^{-1}$ to 100 Å$^{-1}$ in J-PARC (Japan Proton Accelerator Research Complex). It is feasible to measure the static structure factor S(Q) of the order of several ten mg samples with reasonable resolution ($\Delta Q/Q \sim 0.5 \%$) and the atomic pair distribution function which derived by the Fourier transformation of S(Q) is reliable up to 200 Å$^{-1}$ [1].

Experimental

Utilizing specifications of NOVA, variety of materials such as hydrogen storage materials, secondary battery materials, magnetic materials, super conducting materials, liquid and glassy materials have been investigated. In order to obtain accurate pair distribution function, data reduction to absolute coherent neutron scattering cross section is essential.

To improve the ability to observe positions of hydrogen in materials by NOVA following developments are on-going: 1) inelasticity correction for determination of positions of $^1$H atom, 2) polarized neutron apparatus for reduction of incoherent scattering cross section of $^1$H atom, 3) scattered neutron collimation for capillary size sample.

Results and Discussion

Inelasticity correction of hydrogen is a long-standing problem. Adopting one of the new approaches, the intermolecular partial pair correlation functions (H-H, H-O and O-O) of liquid water at ambient temperature were obtained with statistically accurate diffraction data of liquid H$_2$O, HDO, and D$_2$O measured by NOVA and discussed differences the results of molecular dynamics (MD) simulation studies employing classical water-water potentials [2]. Further approaches for inelasticity correction and recent results of the structure analyses of hydrides on NOVA will be presented. This work was partially supported by the Neutron Scattering Program Advisory Committee of IMSS, KEK (Proposal No. 2019S06) and JSPS KAKENHI Grant Numbers JP18H05518, 18H01994, 16K05508.

References

STRUCTURE AND DYNAMICS OF HYDROGEN CLUSTER MATERIAL Li₆NbH₁₁

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Neutron powder diffraction (NPD) and quasielastic neutron scattering (QENS) measurements were performed for Li₆NbH₁₁, which contains unusual ninefold hydrogen-coordinated clusters. The NPD pattern shows a hexagonal structure in which the NbH₃ cluster is orientationally disordered. The QENS spectra of Li₆NbH₁₁ exhibit clear peak broadening suggesting the rotational relaxation of the NbH₃ clusters above 240 K.

Introduction

Recently, Orimo group (Tohoku Univ.) has synthesized a series of materials Li₆NbH₁₁, Li₆MoH₁₁, Li₆WH₁₁, Li₆TaH₁₁, which contain unusual ninefold hydrogen-coordinated clusters MH₃ (M= Nb, Mo, W, Ta) [1]. These are of interest since they have high hydrogen density and possible high Li ionic conductivity. The dynamics of MH₃ cluster may play important roles in determining the physical properties of the materials. We have performed the neutron powder diffraction (NPD) and quasielastic neutron scattering (QENS) measurements of Li₆NbH₁₁.

Experimental

The NPD and QENS measurements of Li₆NbH₁₁ was conducted with a high-intensity total scattering instrument NOVA and a backscattering spectrometer DNA, respectively. Both instruments are installed at MLF, J-PARC. Neutron scattering is a powerful method to study materials with H atoms since the scattering cross-section of a H-atom, especially incoherent one, is large.

Results and Discussion

The NPD pattern of Li₆NbH₁₁ was consistent with the hexagonal structure predicted by the DFT calculation [1], in which the NbH₃ cluster is orientationally disordered. Figure 1 shows the QENS spectra of Li₆NbH₁₁. When the temperature is raised, the width of the spectrum increases, indicating that the motion of the NbH₃ cluster is thermally activated. In the symposium, we will show how the QENS intensity and the relaxation time depend on the scattering vector and temperature, and discuss the dynamics of NbH₃ cluster more deeply.

Fig. 1 Quasielastic neutron scattering spectra of Li₆NbH₁₁.

References


Yoshinori Ohmasa

Yoshinori Ohmasa received his diploma and PhD in physics from Kyoto University. His doctoral thesis is about the structure and the phase transitions of chalcogen mixed crystals under high pressure. He worked for Kyoto University from 1996 to 2008, and moved to Hiroshima Institute of Technology, and then to Kansai University. Since 2019 he has belonged to the Institute for Solid State Physics (ISSP), the University of Tokyo as a project researcher. His research interest covers the field of structurally disordered materials, such as liquid, glass, alloys and disordered crystals. He is currently studying the dynamics of hydrogen cluster materials using neutron scattering techniques.

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RECENT DEVELOPMENTS IN HIGH TEMPERATURE METAL HYDRIES FOR THERMAL BATTERY APPLICATIONS

Terry D. Hymphries¹, M. Veronica Sofianos¹, Mariana Tortoza¹, Arnaud Griffond¹, Mark Paskevicius¹, Craig E. Buckley¹

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Thermal energy storage (TES) has been developed to solve power intermittency problems in Concentrating Solar Thermal power (CSP) plants [1, 2]. By collecting heat during the daytime and storing excess for use at night time or dull periods, CSP shows considerable advantages over other renewable sources such as wind power. Although the first generation of CSP with integrated TES has been highly successful, the next generation of plants will require TES materials that can operate at higher temperatures (>600 °C) that are currently unattainable by molten nitrate salts. Metal hydrides have the potential to become the 2nd generation TES material due to their high heat storage capacity that is in the order of 20 times larger than molten salts, which leads to an inherent reduction in volume of materials, cost of raw materials and engineering costs.

The Hydrogen Storage Research Group at Curtin University have been developing metal hydride materials that reversibly absorb hydrogen at elevated temperatures. A range of compounds have been developed using thermodynamic stability calculations and further tuned to enable technological applications. Fluorine substitution of hydrogen in metal hydrides has provided an approach that allows thermodynamic stabilization of metal hydrides to form NaH₃Fₓ, Mg(H₁₋xFₓ)₂ and NaMgH₃xFₓ systems, all of which show significantly increased operating temperatures compared to their hydride counterparts [3-5]. This has not only allowed the operating temperature of these materials to increase at moderate pressures, but has also diminished the problems associated with metal segregation. Upon desorption of hydrogen the metals formed, including Mg and Na, have low vapour pressures but the formation of metal fluorides prohibits evaporation at elevated temperatures. Thermodynamically stable metal hydrides, including CaH₂, that are only reversible at temperatures above 850 °C, have been destabilised to allow reversibility at temperatures of ~700 °C [6, 7]. Addition of metal halides and Si have been shown to be effective.

The development of high temperature metal hydrides will be discussed including thermodynamic calculations, synthesis and characterisation. Each of the systems have been studied by in situ X-ray diffraction and thermodynamic assessment by PCI analysis and DSC-TGA. These materials have now been shown to be appropriate for upscaling towards application as thermal batteries.

References

Dr. Terry Humphries is a Research Fellow at Curtin University. He is an Inorganic Chemist with a particular interest in metal-hydrides for hydrogen storage applications. Terry excels in the synthesis of novel air/moisture sensitive compounds and the subsequent characterisation using a variety of analytical methods including X-ray and neutron diffraction, multi-nuclear NMR and vibrational spectroscopy. Dr. Terry Humphries was awarded his Ph.D. in 2011 at the University of New Brunswick (UNB), Canada. He completed his first Post-doctoral role at the Institutt for energiteknikk (IFe), Norway, and has subsequently been provided with the opportunity to be a guest researcher at the University of Hawaii, USA, and University of Aarhus, Denmark. Dr Humphries also completed a Research Fellowship at the Advanced Institute for Materials Research (WPI-AIMR), Tohoku University, Sendai, Japan.

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NOVEL METAL HYDRIDES DISCOVERY AND APPLICATION

Martin Dornheim
Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Abstract
In this presentation results on selected hydrides and hydride composites as well as measures for scale-up of materials synthesis and testing are reported. A newly built infrastructure for testing of scaled-up hydrogen storage systems is presented. The potential of metal hydrides for hydrogen storage applications is discussed.

Introduction
While significant work on metal hydrides for hydrogen storage started already in the 1980s, so far only few materials are utilized for hydrogen storage or hydrogen compression applications.

In recent years a huge number of novel light weight hydrides as well as so-called Reactive Hydride Composites has been discovered with many of them showing rather good cycling stability and enhanced gravimetric storage capacity.

Experimental / Computational
Reactive Hydride Composites were characterized by different techniques as in-situ XRD, small angle X-ray scattering, EXAFS and XANES, volumetric Sieverts' type measurements, TEM, in-situ neutron radiography etc..

A novel tank testing apparatus for large scale hydrogen storage testing has been developed. Its properties and capability will be reported.

Results and Discussion
Insights about reaction mechanisms, sorption behaviour, cycling stability of light weight hydrides and Reactive Hydride Composites, the influence and optimisation of compaction on such materials to pellets and the behaviour of such pellets under in-situ conditions are given.

The possibility for scale-up of the synthesis as well as the kinetic and cycle behavior of larger sample batches considering for example the effect of temperature inhomogeneities on the performance and cycle life time of the storage materials has been studied. An overview about methods and achieved results on the scale-up of synthesis and testing of different hydrides is shown.

Advantages and limitations of their possible usage for hydrogen storage applications will be discussed.

Fig. 1 Reaction Scheme of Reactive Hydride Composites

References

Employment records:
Scientific and Strategic Deputy Director of the Materials Technology division at HZG since 2014.
Lecturer at Helmut-Schmidt University, Hamburg, Germany since 2012
Lecturer at Hamburg University of Technology since 2005.
Head of the Nanotechnology Department, at HZG since 2005.

Education:
Dr. rer. nat. (PhD) in experimental Material Physics, Universität Göttingen, Germany, 2002.
Vordiplom (~bachelor) in Physics: Universität Hamburg, Hamburg, Germany 1994

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HYDRIDE-BASED SOLID STATE LI-ION BATTERIES FOR ENERGY STORAGE

Michel Latroche¹, Anh Ha Dao¹,², Pedro López-Aranguren², Junxian Zhang¹, Fermín Cuevas¹ and Christian Jordy²

Affiliation ¹ICMPE (UMR7182), CNRS, UPEC, F-94320 Thiais, France, ²Saft, 111 Bd. A. Daney, 33074 Bordeaux, France.

Abstract: Looking for safe and efficient energy storage systems is a very high challenge for the energy transition. It is therefore necessary to develop new, affordable and safe systems able to fulfil the requirements for efficient storage operating near ambient conditions. Metal and complex hydrides are widely studied for their astonishing properties. They are foreseen for H₂ gas storage or batteries to harvest renewable energies. In the present work, we propose the combination of various materials, including metal and complex hydrides to develop practical solid-state Li-ion batteries.

Introduction

Solid-State Lithium-ion Batteries (SS-LiBs) are widely studied as they offer solutions to some drawbacks of conventional batteries such as safety issues, energy density and power limitations. For LiBs, metallic and complex hydrides may act either as negative active materials or solid electrolytes (SE) in next generation of SS-LiBs. LiBH₄-based SEs have shown recently good properties as solid ionic conductors; however, their operating range remains above room temperature limiting their application domains [1-5].

Experimental

Solid-state cells were assembled by pelletizing materials with a 10-mm diameter die into a sealed Teflon Swagelok cell. The cathode consisted of 25:5:70 wt% of active material (NMC-LiNi₀.₅Mn₁.₅Co₀.₃ or TiS₂): carbon C65: SE. Substituted argyrodites LiₓPSₓ₁ₓₓₓₓₓₓ(BH₄)₁₋ₓ (X=Cl, Br, I) were used as SEs [6]. Three mg of cathode material and 80 mg of SE were pressed at 2 tons to make 2-layer pellets. A 9-mm-diameter indium-lithium double-layer disk was placed on top of the SE side, where indium is sandwiched between Li and SE, and pressed with the pellet. The cell was heat-treated overnight at 75°C and then cycled with a battery tester (MPG-2, Biologic) near RT.

Results and Discussion

In the present work, we combined cathode materials of different potentials (NMC or TiS₂) with Li-In anode using substituted argyrodites as SE. These SEs provide high ionic conductivity near RT [6]. As an example, Fig. 1 shows the potential profiles of an NMC/C65/SE | SE | Li-In solid-state cell operated either at 25 or 40°C using LiₓPSₓ₁ₓₓₓₓₓₓ(BH₄)₁₋ₓ argyrodite as SE.

![Fig. 1 First charge/discharge cycles at 25 and 40°C for an NMC/C65/SE | SE | Li-In solid-state battery.](image)

References


Dr. Michel LATROCHE is currently Director of Research at ICMPE CNRS in France. He studied at Nantes University (F) and obtained his PhD at the Institut Jean Rouxel in the field of Solid state Chemistry. After a post-doctoral position with Prof. J. Ibers at the Chemistry Department of Northwestern University in Chicago (USA), he joined the group of Dr. A. Percheron-Guégan in Meudon (F) to work in the field of metal hydrides. His research works deal with structural, physical, thermodynamic and electrochemical properties of metals or intermetallics and their hydrides. His research activities are devoted to fundamental aspects of these materials in relation with their applications such as negative electrode for NiMH and Li-ion batteries or hydrogen gas storage for fuel cells. He has published more than two hundred fifty publications in this field and filed twelve patents.

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HIGH-PRESSURE SYNTHESIS OF NOVEL ALUMINUM-BASED HYDRIDES USING SYNCHROTRON RADIATION X-RAYS

H. Saitoh¹,², M. Tanikami¹,², A. Machida¹, T. Watanuki¹,², T. Sato³, S. Takagi³, S. Orimo³, K. Ikeda⁴ and T. Otomo⁴

¹ National Institutes for Quantum and Radiological Science and Technology, 2 Hyogo university, 3 Tohoku University, 4 High Energy Accelerator Research Organization

Novel aluminum-based hydrides have been synthesized using high-pressure and high-temperature techniques, where in situ synchrotron radiation x-ray diffraction measurement are effectively used to find synthetic conditions, to optimized them, and to investigate the reaction mechanisms. The obtained hydrides were recovered at ambient conditions and characterized by synchrotron radiation and neutron diffraction techniques to investigate their crystal structures.

Introduction
Chemical potential of hydrogen becomes extremely high at high pressure above 1 GPa and reacts with metals and alloys to form hydrides which cannot be obtained around ambient pressure. We are trying to synthesize novel aluminium-based hydrides with the aid of synchrotron radiation X-ray diffraction measurement. Synchrotron radiation X-ray diffraction measurement enables us to find synthetic conditions of target materials, to optimize these conditions, and to clarify these reaction mechanisms. The obtained hydrides are recovered at ambient conditions and characterized.

Experimental
Starting materials were pressurized to target pressures at room temperature and then were heated to target temperatures in hydrogen fluid. High-pressure and high-temperature conditions were generated using a cubic-type multi-anvil high-pressure apparatus. Structural changes of samples were monitored by in situ synchrotron radiation X-ray diffraction measurement system installed at BL14B1 at SPring-8 [1]. The recovered samples were characterized by synchrotron radiation x-ray (SPring-8 BL22XU) and neutron (J-PARC NOVA) diffraction techniques.

Results and Discussion
We have synthesized some novel aluminium-based hydrides, such as Al-TM (TM: Cr, Mn, Fe, Co, Zr, and Hf) in addition to the previously reported Al₂CuH₈ [2]. Crystal structures of some of them have been analysed and clarified. The detailed results will be presented.

This work was supported by JSPS KAKENHI, Grant Numbers, JP18H05513 and JP18H05518, and the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University (Proposal Nos. 18K0032 and 19K0049). The neutron scattering experiment was approved by the Neutron Scattering Program Advisory Committee of IMSS, KEK (Proposal No. 2014S06).

References

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MATERIAL DEVELOPMENT OF H⁻ CONDUCTIVE OXYHYDRIDES

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¹ Institute for Molecular Science, National Institutes of Natural Sciences, 2 The Graduate University for Advanced Studies (SOKENDAI)

Hydrogen transport in solids is a key technology for electrochemical devices such as fuel cells, batteries, and chemical reactors. Recently, hydride (H⁻) has come to be recognized as a new charge carrier for hydrogen transport, which opened up a new frontier in solid state ionicics and electrochemistry. Here, we report on the current states and prospects for the material exploration for H⁻ conductors, targeting H⁻ conductive oxyhydriones we have developed so far.

Introduction

A hydride ion (H⁻) is an attractive charge carrier because it exhibits promising features for fast ionic conduction; namely, monovalence, suitable ionic size similar to that of F⁻ and O²⁻, and high polarizability. Furthermore, hydride ions exhibit strong reducing properties through the standard H⁺/H₂ redox potential (−2.3 V vs. SHE), which can be expected to be applied to novel electrochemical devices. In 2016, H⁻ conduction in oxide-based framework structure has been realized in 2016 by finding a series of H⁻ conductive oxyhydriones La₂₋ₓSrₓLiH₁₋ₓO₃₋ₓ (LSLHO)¹ with the KZNIFS-type structure, possessing capability of H⁻ solid electrolytes. The discovery of LSLHO has triggered materials exploration for H⁻ conductors, and several H⁻ conductive oxyhydriones with the KZNIFS-type and fluoride-type structures have been reported so far²⁴. In the presented study, I would like to introduce our material development of H⁻ conductors, focusing on KZNF₈-type oxyhydriones.

Experimental

Hydride conductive oxyhydriones were synthesized by solid state reaction using oxides and hydrides of each element as the starting materials. As needed, high pressure was applied to the synthesis system to suppress loss of hydrogen source. The crystal structures for the obtained compounds were determined by Rietveld analysis to X-ray and neutron diffraction data. Ion conductivities for the samples were measured by electrochemical impedance spectroscopy (EIS). The transport number for each sample was confirmed by the Hebb-Wagner polarization method and electromotive force measurements using hydrogen concentration cells.

Results and Discussion

In the KZNIFS-type oxyhydriones represented as AₓBₓO₄ (X = H, O), anion configuration depends on the valance of cations at the A- and B-sites. Hydride ions in the Sc-based oxyhydrate occupy the apical site rather than the equatorial site in the ScₓO₆ octahedra, which is clearly contrasted to that of Li-series¹. This tendency can be understood by electrostatic argument; the less charged H⁻ (compared to O²⁻) ions prefer the site showing the smaller bond strength sums. The relationship between conductivity and structure will be discussed in the presentation.

Fig. 1 Comparison of the crystal structure of LnₓLiHₒ₃ (Ln = La, Pr, Nd) and Ba²ScHₒ₃

References


Genki Kobayashi currently an Associate Professor based at the Department of Materials Molecular Science at the Institute for Molecular Science, Japan, where I have held this position since 2018. Based on fundamental studies into solid-state chemistry, I have been investigating materials for use in electrochemical energy storage/conversion devices since 2006. His current research focuses on hydride ion (H⁻) conduction in solids. He recently developed H⁻ conductive oxyhydriones, and demonstrated the first battery reaction based on H⁻ diffusion. In addition, he received the several research awards, such as the Spriggs Phase Equilibria Award in 2010 from the American Ceramic Society, the 39th Honda Memorial Young Researcher Award in 2018 from the Honda Memorial Foundation, 7th Ishida Award in 2018, from Nagoya Univ., and Tagawa Memorial Young Researcher Award in 2019 from Electrochemical Society of Japan.

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HETEROGENEOUS CATALYTIC REACTIONS FROM VAN DER WAALS DENSITY FUNCTIONAL

Ikutaro Hamada
Department of Precision Science and Technology, Graduate School of Engineering, Osaka University

Accurate description of molecular surface interaction is prerequisite for microscopic understanding of molecular adsorption and chemical reaction that take place on the surface and interface. Herein I present recent results of theoretical study on molecular adsorptions and chemical reactions on metal surfaces by using the van der Waals density functional that is able to describe both covalent and noncovalent interactions accurately, including carbon dioxide hydrogenation and formic acid dehydrogenation on a metal surface. The mechanisms of these reaction are discussed in detail.

Introduction
Understanding of the microscopic mechanisms of the heterogeneous catalytic reactions that take place at surfaces and interfaces is crucial to develop efficient energy and material conversion devices, such as fuel cells and three way catalysts for automotive exhaust. Density functional theory within the semilocal approximation, i.e., generalized gradient approximation (GGA), has been used for this purpose. However, it is well known that the semilocal approximation fails to accurately describe dispersion, or van der Waals (vdW) forces, which is essential in inter-molecular and molecule-surface interactions. The development of the van der Waals density functional [1] and its offsprings [2,3], and their efficient implementation [4,5] enables one to describe the vdW forces accurately and efficiently, which leads to more precise description of molecular adsorption and heterogeneous catalytic reactions on solid surfaces.

Hydrogenation of CO₂ on Cu(111)
Adsorption and reaction of CO₂ on solid surfaces are of technological importance concerning the energy and environmental management. Elucidating the reaction mechanism is crucial to develop more efficient catalysts for CO₂ utilization. We study the CO₂ adsorption and reaction on Cu(111) by means of vdW-DF. We propose that the CO₂ hydrogenation to formate takes place via the Eley-Rideal mechanism[6]. Furthermore, we predict that vibrational O-C-O bending mode of CO₂ enhances the hydrogenation of CO₂ [6], which has been verified experimentally [7].

Formic acid adsorption and decomposition on Cu(111)
Formic acid (HCOOH) has been considered as a potential material for hydrogen storage for proton exchange membrane fuel cells, and elucidating its decomposition mechanism is important for utilization of HCOOH. We use vdW-DF to study adsorption and decomposition of HCOOH on Cu(111). We found that vdW-DF improves the adsorption energy of HCOOH on Cu(111) over GGA and the calculated adsorption energy agrees well with the experiment. We then investigated the decomposition of HCOOH and found that the activation barrier is lower than the desorption (adsorption) energy, implying that decomposition is preferred over desorption, in contradiction with the experiment at room temperature. To resolve the contradiction, we performed the reaction rate analysis base on the vdW-DF calculations. We found that at room temperature, the calculated desorption rate is higher because of larger preexponential factor, suggesting that no HCOOH decomposition takes place [8].

Acknowledgment
This work was partially supported by Grant-In-Aid for Scientific Research on Innovative Area "Hydrogenomics" (contract No. JP19H05519). This work has been done in collaboration with Yoshitada Morikawa, Kouji Inagaki, Yuji Hamamoto, Fahdzi Muttaquin, and Septia Eka Marsha Putra.

References
SCIENCE OF HYDROGEN & ENERGY AWARD

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2009
Dr. Gary Sandrock

2009
Prof. Dr. Jens Norskov

2010
Prof. Dr. Rüdiger Bormann

2010
Prof. Dr. Ivor Rex Harris

2010
Prof. Dr. Rainer Kirchheim

2011
Prof. Dr. Koji Hashimoto

2012
Prof. Dr. Mogens Mogenson
2014-now Deputy Research Director of the Institute of Materials Technology and Centre for Hydrogen Technology at the Helmholtz-Zentrum Geesthacht, Germany

2005-now Head of the Department of Nanotechnology and the Hydrogen Storage Activities at the Helmholtz-Zentrum Geesthacht

2003-2005 Deputy Head of the Department of Nanotechnology, Helmholtz-Zentrum Geesthacht

2002-2003 Deputy Group Leader “Hydrogen in Metals”, Georg-August-Universität, Göttingen

2002 PhD., Material Physics, „Impact of stress and strain on thermodynamics of metal hydride systems“, Georg-August-Universität, Göttingen

1998 Dipl.-Phys, Theoretical Solid State Physics, “atomistic simulations of misfit dislocations in semiconductor heterostructures“, Georg-August-Universität, Göttingen

1994 Phys.-Vordipl., Universität Hamburg

After his early work on the effect of stress and strains on the phase boundaries of hydride phases in yttrium and niobium thin films he moved to the Helmholtz-Zentrum Geesthacht where he continued to work on hydrides and the effect of additives on nucleation and growth as well as on the grain sizes and grain size stability in magnesium hydride. He was involved in the discovery of the formation of different borohydrides (LiBH4, NaBH4 and Ca(BH4)2) starting from MgB2 and the respective alkali(ne earth) metal hydrides and led the comprehensive investigations on the reaction mechanisms in Reactive Hydride Composites (RHCs). He started, developed and led new comprehensive in-situ measurements on the reaction mechanism and the effect of additives in RHCs, which led to an enormous increase of cycling stability of RHCs and composites of RHCs and polymers. Under his leadership, HZG started in 2005 the development and characterisation of hydrogen stores based on interstitial hydrides, complex hydrides and hydride composites for a wide range of applications from the gram scale of hydrogen up to the tens of kg of hydrogen scale.

We award Dr. Martin Dornheim for outstanding work in the science of hydrides, the discovery and characterization of reaction mechanisms of new hydride systems as well as the development and characterization of hydrogen storage tank systems based thereon with the Science of Hydrogen & Energy prize 2020.
Dr. Michel Latroche main scientific interests are focussed on metallic compounds obtained by combining various metals such as rare earths, transition elements, or p-elements. These intermetallics have original physical and chemical properties with the ability to reversibly absorb hydrogen over a wide range of temperature and pressure to form metal hydrides. Dr. Michel Latroche had developed in the nineties new experimental set-up to follow in-situ the hydrogenation reaction of these materials using neutron diffraction. These experiments have been later extended to the electrochemical reactivity of these materials allowing to elucidate the complex mechanisms involved in the reversible hydrogenation reaction and leading to improved materials for energy storage applications. Dr. Michel Latroche has also investigated the properties of metallic hydrides dispersed at the nanoscale in various porous materials (Carbon, MOFs) to form composites with peculiar properties combining ad- and absorption of hydrogen. More recently, Dr. Michel Latroche has developed the use of metallic hydrides as anode materials for Li-ion batteries showing the high capacity of these materials by using a conversion reaction with lithium. He has set up a prototype for an electrochemical cell combining hydrides used both as anode and electrolyte.

We award Dr. Michel LATROCHE for outstanding work in the science of hydrides, the discovery of new hydride systems, reaction mechanisms and tunable properties of hydrides with the Science of Hydrogen & Energy prize 2020.
BEST POSTER AWARDS

2007
Ms. Alondra Torres Trueba

2012
Mr. Andreas Bliersbach

2013
Mr. Moreno De Respinis

2014
Mr. Yixiao Fu

2015
Dr. Shunsuke Kato

2015
Mr. Nikolai Biliskov

2016
Ms. Efi Hadjixenophonotos

2016
Ms. Guanqiao Li

2017
Ms. Marina Chong
Dr. Young-Su Lee

"INTERFACE ENHANCED LITHIUM ION CONDUCTION IN LIBHA-OXIDE MIXTURES"

High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea

Young-Su Lee majored in materials science and engineering and her specialty is first-principles simulation. She received PhD degree in 2006 from Massachusetts Institute of Technology, and started her career as a senior research scientist at Korea Institute of Science and Technology in 2007. Ever since she joined KIST, her research activities have centered around the materials for hydrogen energy, such as structural/thermodynamical properties of metal borohydrides, nanostructuring of hydrides for hydrogen storage, metallic hydrogen separation membranes, etc. Current research focuses are room temperature hydrogen storage materials and ionic conduction in hydrides.

"INTERFACE ENHANCED LITHIUM ION CONDUCTION IN LIBHA-OXIDE MIXTURES"

A solid-state Li ion conductor composed of LiBH₄ and SiO₂/Al₂O₃ was synthesized by a simple ball-milling process. The ionic conductivity of the mixture reached as high as 2x10⁻⁴ S cm⁻¹ at room temperature when the volume fraction and the particle size of the oxide material were optimized. The interface between LiBH₄ and oxides is likely to support such high ionic conductivity. By applying a continuum percolation model, the interface conductivity was estimated to be 10⁴~10⁵ times higher than that of pure LiBH₄. The increase in conductivity is accompanied by the lowered activation energy for the Li ion conduction. First-principles calculation demonstrated that the Li ion migration barrier in LiBH₄ is as small as ~0.2 eV and suggested that Li ion defect accumulation at interface may deliver the remarkable rise in conductivity.
BEST POSTER AWARD 2019

Dr. Marco Calizzi

"FeCO NANOPARTICLES FOR CO\textsubscript{2} HYDROGENATION"

Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering (ISIC), Basic Science Faculty (SB), École polytechnique fédérale de Lausanne (EPFL) Valais/Wallis, Energypolis, Sion, Switzerland

Born in October 1989 in Bologna.

2013 - Master degree in Physics at University of Bologna, Italy, thesis "The nanostructured Mg-Ti system for solid state hydrogen storage", supervisor Prof. Luca Pasquini in collaboration with ICMPECNRS in Paris, France with Dr. F. Cuevas.

2017 - PhD in Physics at University of Bologna, Italy, with thesis "Advances in nanoparticle condensation from the gas phase: Mg-based and TiO\textsubscript{2}-based materials for energy applications", supervisor Prof. Luca Pasquini.

Since July 2017 - Post-doc in Prof. Andreas Züttel's Laboratory of Materials for Renewable Energy (LMER), École Polytechnique Fédérale de Lausanne (EPFL) Valais / Wallis, Sion, Switzerland, working on thermal CO\textsubscript{2} reduction.

"FeCO NANOPARTICLES FOR CO\textsubscript{2} HYDROGENATION"

The idea of producing synthetic fuels is a very attractive option: retaining all the benefits of fossil fuels and, at the same time, having a closed and sustainable energy cycle, where the CO\textsubscript{2} produced from combustion is captured and converted into fuel again. In this framework, the need of a material that efficiently catalyzes the synthesis of hydrocarbons is of key importance. For such world scale application, heterogeneous catalysis is the preferred one because of its high throughput capability. In this work we synthesized FeCo alloy nanoparticles (NPs) at different Fe/Co ratio via Inert Gas Condensation. Structural and morphological properties like NPs size distribution, Fe/Co ratio are determined by SEM, STEM, EDX, and XRD. The reaction conditions, stability, catalytic activity, and selectivity towards products of CO\textsubscript{2} hydrogenation are studied, with special focus on C2+ hydrocarbons, with a lab-scale reactor coupled with a mass spectrometer and gas chromatograph for products analysis. The alloy NPs have new catalytic properties compared to pure Fe and pure Co NPs, showing activity towards the catalysis of C2+ hydrocarbons.
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ACCESS

Map from New Chitose Airport to Sapporo

Map of Sapporo region
Travel to Hotel Monterey Edelhof Sapporo from New Chitose Airport:

1. **New Chitose Airport => Sapporo**
   Please take the "Rapid Airport Express" train on the JR Chitose Line to JR Sapporo Station (about 40 minutes / JPY1,070 per adult).

   **Rapid Airport Express**
   The Rapid Airport Express is always standing by at the New Chitose Airport. Departing every 15 minutes during the day.

   **Stops**
   *Stops may differ depending on the train.

   1. Get on the Elevator in the Domestic Terminal and go to B1F.
   2. The JR Information Desk is located to the right of the elevator on B1F.
   3. JR Information Desk
   Exchange rail passes and purchase JR tickets here.
   4. JR New Chitose Airport Station Ticket Gate
   Platforms are on B2F.
2. Sapporo Station => Hotel Monterey Edelhof Sapporo

Please disembark at JR Sapporo station. After getting off at JR Sapporo Station, pass through the East ticket Gate and go out the South Exit. It takes about 7 minutes by walk from the South Exit to Hotel Monterey Edelhof Sapporo.
EMERGENCY TELEPHONE NUMBERS

Country code for Japan: +81

POLICE 110

FIRE FIGHTERS / ANBURANCE 119

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https://www.hotelmonterey.co.jp/en/edelhof/
CLIMATE

The maximum snow depth between December and February can reach up to approximately 1 m, and the annual cumulative snowfall is about 5 m. The average temperature in January is -3 degrees.

Clothing and footwear:

We recommend a down jacket or thick coat that is waterproof and retains heat, while also capable of keeping the snow and cold wind out. If you plan to play in the snow or be out in the cold for long hours, we suggest that you wear heavy winter outerwear over your trousers.

It is dangerous to walk the frozen winter streets of Sapporo with sneakers, high heels or leather soled shoes. For your safety, we recommend a pair of waterproof thermal boots with non-skid soles.
SOCIAL EVENTS

Otaru Canal Cruise:
Otaru Canal Cruise is the new must do activity for visitors to Otaru! Otaru once prospered as the gateway to Hokkaido and retains a rich history from that time. Our captains will each introduce that history in their own way during a leisurely, 40-minute cruise down the Otaru Canal.

Otaru Canal Boat LLC
5-4, Minatomachi, Otaru, Hokkaido, 047-0007, Japan
Tel: 0134-31-1733
URL: https://otaru.cc/en/
LOCAL GUIDE / SAPPORO

Hokkaido’s capital city of Sapporo retains a unique mixture of modern Japanese efficiency and technology with a more relaxed approach to daily life influenced by the environment and climate, making any visit a pleasant change from the frenetic pace of other major centers in the country.

Drawing its name from the indigenous Ainu terminology meaning “river-lined-with-large-reed-bed”, Sapporo was officially founded in 1869 - very early in Japan’s Meiji Era. Designed on a grid pattern and boasting several train and subway lines and even a tram line, Sapporo is one of Japan’s easiest cities to navigate.

Adding to this distinctiveness, Sapporo is spared a rainy season, unlike the rest of Japan. A mild spring, pleasant summer, cool autumn and snowy winter characterize a year in Sapporo. Average temperatures during most months make Sapporo an ideal destination and base for an outdoor or nature enthusiast, while winter brings perfect temperatures for snow and winter sports. Ski Season generally starts in mid-December and can last as long as late April!

FOOD:

Mention Hokkaido, and especially Sapporo, and most Japanese will inevitably mention food. Famed throughout the country for its produce, dairy products and seafood a visitor will find a massive variety of ingredients and dishes to sample during their stay.

Some of the more famous dishes include:

- **Genghis Khan.** The dish is named after the notorious Mongol Warlord and consists of premium mutton grilled with vegetables at the table. Delicious Genghis khan restaurants abound throughout Sapporo.

- **Fresh seafood, especially salmon, crab, and sea urchin are renowned all over Japan. Early winter and late summer are the best time for Sapporo’s famous crab while early Autumn is salmon and sea urchin season.**

- **Miso Ramen Noodles.** Sapporo is the birthplace of this nationwide favorite and aficionados still flock to establishments in the city to sample the authentic dish.

Attractions and Local Specialties:

Sapporo city abounds in tourist attractions. Some of the highlights to consider include:

- **Odori-koen.** Running about 1.5 kilometers and apparently the starting point for Sapporo’s layout when it was being planned, this park is the city’s focus in every season. Whether acting as a host site for the famous Snow Festival in February, transformed into a massive flower garden in May or acting as city-wide beer garden in the summer this is first stop on every visitor’s trip to the city.
- Sapporo Beer Museum, established in 1890, now offers historical and brewery tours as well as tastings and a family friendly beer hall.
- Tanuki Koji Shopping Arcade. At nearly 1 km long and offering 200 shops you can find a huge variety of restaurants and local shops as well as souvenir shops offering some of Sapporo's famous souvenirs such as Marusei Butter Raisin cookies, Shiroi Koibito or, of course, ramen sets.
- Hitsujigaoka Observation Hill. Located just outside of Sapporo main centre, this mountain top offers fantastic views of the city, set in a beautiful park.
- Confectionery factory tour. For something a little different but fun for all ages, take a tour of one of Sapporo's celebrated chocolate or cookie producers then try your hand at making your own!

Events & Activities:
Sapporo has no shortage of events and festivals.
- Sapporo Snow Festival - perhaps the most internationally notable event in Hokkaido. Held every February and attracting participants and visitors from around Japan and the world, Sapporo is utterly transformed into a world of fantastic ice and snow sculptures that astound and enthral.
- Sapporo White Illumination - preceding the Snow Festival from November to early February, Sapporo becomes a celebration of lights as nearly 400 thousand orbs are employed to brighten Sapporo during the Sapporo White Illumination.
- Sapporo Summer Festival - Odori-koen again takes centre stage during this festival which highlights Sapporo's food, people and even unique take on Japanese traditional Bon Dancing.

Ref.:
http://www.sapporo.travel/?lang=en
https://www.hotelmonterey.co.jp/en/edelhof/localguide/
SOUVENIR

Hydrogenomics Original Tumbler & Portable Straw

[Tumbler]
- Capacity: 400ml
- Material / Heat resistance:
  - Lid: Polypropylene / 90 degrees
  - Body: Polypropylene / 90 degrees
  - Packing: Silicone rubber / 130 degrees
- Please note the following when using.
  - The lid is not completely sealed with the main body.
  - Please note that the contents may spill if it falls over.
  - Do not drop or give a strong impact.
  - Do not put the drinks above the heat-resistant temperature, dry ice or alcohol.
  - Do not use a dishwasher, microwave ovens or open flames.
  - Do not place near fire or high temperatures.
  - There is a risk of damage if put in the freezer.
  - Please keep out of small children’s reach.

[Portable Straw]
- A straw that can be easily carried in a special case, washed and used repeatedly. With cleaning brush.
- Straw length: 21cm
- Material:
  - Straw: Stainless steel
  - Brush: Hair: Nylon / Handle: Stainless steel
  - Case: ABS resin / POM
- Please note the following when using.
  - Cold drink only. Do not use for hot drinks. Do not use for anything other than its intended purpose.
  - Do not use anything other than neutral detergents.
  - Do not drop or give a strong impact. Do not use if damaged or deformed.
  - Do not use a dishwasher.
  - Do not place near fire or high temperatures.
  - Please keep out of small children’s reach.
NOTES