Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O101] Oral 101

Chair: Shin-ichi Orimo (Tohoku Univ.) Mon. Dec 11, 2023 1:30 PM - 3:20 PM Session 1 (Room C-1)

[B3-O101-01 (Symposium Keynote)]	Hydrogen the Key Element for the Storage and Distribution of Renewable Energy
	*Andreas ZÜTTEL ¹ (1. École Polytechnique Fédérale de
	Lausanne (EPFL) (Switzerland))
	1:30 PM - 2:10 PM
[B3-O101-02 (Symposium Keynote)]	Catalyst Materials for Efficient Production of
	Hydrogen in a Sustainable Economy Driven by
	Renewable Energies.
	*Juan Ramón Morante ^{1,2} (1. IREC (Spain), 2. The University
	of Barcelona (Spain))
	2:10 PM - 2:50 PM
[B3-O101-03 (Symposium Invited)]	New Zealand Green-hydrogen technology
	platform
	*John V KENNEDY ^{1,2} (1. GNS Science (New Zealand), 2.
	Victoria University of Wellington (New Zealand))
	2:50 PM - 3:20 PM

[Abstract Guideline (Leave two lines for presentation number)]

Hydrogen the key element for the storage and distribution of renewable energy

<u>Andreas ZÜTTEL</u> École Polytechnique Fédérale de Lausanne (EPFL), Switzerland <u>andreas.zuettel@gmx.ch</u> Keywords: Hydrogen, Renewable energy, Storage

Countries like Australia have large area with high solar intensity and are, therefore, ideal for harvesting renewable energy with photovoltaics. The renewable energy can be used to produce hydrogen and products from hydrogen with nitrogen and carbon. The chemical energy carriers are shipped to the whole world and replace the fossil fuels. Three parameters are of great importance, the energy density, the conversion efficiency and the final cost of energy for the future renewable energy economy. On the example of Switzerland and Japan the various storage and transport options for renewable energy will be elaborated and the cost of the energy estimated.

[Abstract Guideline (Leave two lines for presentation number)]

Catalyst materials for efficient production of hydrogen in a sustainable economy driven by renewable energies.

J. R. Morante

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A sustainable economy based on renewable energy requires the industrial feasibility of electrochemical production of hydrogen from renewable energy. This is conditioned by the cost of production, which, on the one hand, is directly related to the cost of renewable energy and, on the other hand, is related to the productivity and efficiency of the electrolyzer system. In this context, reaching high working current densities in the electrolyzer is a real challenge and exceeding high amperages per cm² requires the use of catalyst materials with a very high density of active sites and with a very high intrinsic activity that must be accompanied by effective configurations to prevent the blockage of the active sites by the gases produced in the cell.

In this talk, the rational design and use of different catalyst materials for both the anode and the cathode, as well as their implementation in cells, will be reviewed under the objective of achieving productions based on current densities greater than several amperes per square centimeter without losing significantly energy efficiency in production. Likewise, the implications imposed on the design of the electrodes and the cell will also be considered.

Thus, attention will be paid to the emerging robust and stable electrocatalysts that are more efficient and stable at large current densities in HER and OER, with an outstanding electrocatalytic activity and large stability from commercial criteria. Typically, international electrolyzer programs claims for higher current densities than 2A/cm².



Catalyst materials for efficient production of hydrogen in a sustainable economy driven by renewable energies

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New Zealand Green-hydrogen technology platform

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Keywords: Hydrogen generation, Electrocatalysis, Hydr

New Zealand's ambitious goal of presenting a net-zero carbon emissions budget by 2050 depends on progressively phasing out fossil fuels as an energy source. Recently we started the Green Hydrogen Technology Platform aimed to deliver transformative technologies that will drive New Zealand's future as a globally connected 'green-hydrogen' economy. The Platform's focus is on technologies that sustainably produce hydrogen to replace fossil fuels for electricity generation and transportation, as well as creating smaller-scale green-hydrogen applications suitable for distributed generation.

Our research themes (Electrocatalysis, Direct photocatalysis and Plasma Catalysis) are focussed on developing technologies for green hydrogen production that will transform both New Zealand and global hydrogen production. An overview of our recent research activities will be presented as well as our latest findings on one-step Fabrication of Earth-Abundant Electrocatalysts for Hydrogen Evolution and Ammonia Production.

Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O201] Oral 201

Chair: Hiroyuki Saitoh (National Institutes for Quantum Science and Technology (QST)) Tue. Dec 12, 2023 10:00 AM - 12:00 PM Session 14 (Room J)

[B3-O201-01 (Symposium Invited)]	Hydrogen embrittlement of metastable
	austenitic steels
	*Motomichi Koyama ¹ , Eiji Akiyama ¹ (1. Tohoku University
	(Japan))
	10:00 AM - 10:30 AM
[B3-O201-02]	Effect of Oxygen on Plasma Driven Permeation
	of Hydrogen Through Metal Membranes
	*Arseniy Kuzmin ¹ , Keisuke Miura ¹ , Shora Kurokawa ¹ , Taiichi
	Shikama ¹ , Masahiro Hasuo ¹ (1. Kyoto University (Japan))
	10:30 AM - 10:50 AM
[B3-O201-04]	Fabrication of Zirconium Nitride Hydride
	Epitaxial Films by Alternating-Target Pulsed-
	Laser Deposition
	*Daichi Miyazaki ¹ , Ziyang Cao ¹ , Takuto Soma ¹ , Akira Ohtomo ¹
	(1. Tokyo Tech. (Japan))
	11:10 AM - 11:30 AM

Hydrogen embrittlement of metastable austenitic steels

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¹ Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aobaku, Sendai, Miyagi, Japan 980-8577 *<u>motomichi.koyama.c5@tohoku.ac.jp</u> (Corresponding author) Keywords: Hydrogen embrittlement, Austenitic steel, Metastable phase, Martensitic transformation

Hydrogen plays various roles in structural and functional materials. In the case of steels, hydrogen acts as an element causing embrittlement, i.e., hydrogen embrittlement. The hydrogen embrittlement issue has been regarded as a bottleneck for developing hydrogen-energy-related infrastructures. In this regard, austenitic steels, which are composed of a face-centered cubic (FCC) phase, show significant resistance to hydrogen embrittlement. However, the austenitic steels can also be susceptible to hydrogen embrittlement when the FCC phase is metastable against other phases such as hexagonal close-packed (HCP) and body-centered cubic (BCC) phases. More specifically, when deformation-induced martensitic transformation (diffusionless transformation) occurs during plastic deformation is the origin of the high ductility of the austenitic steels, the metastability plays ambivalent roles in mechanical performance in the hydrogen atmosphere. In this talk, we present examples of hydrogen-assisted cracking and subsequent failure behaviors in metastable austenitic steels toward understanding and controlling the hydrogen-related cracking behavior associated with martensitic transformation.

The first case is the hydrogen embrittlement of a Fe-Mn-based steel that shows deformation-induced FCC-HCP martensitic transformation [1]. When the stacking fault energy is low, the austenitic steel shows deformation-induced FCC-HCP martensitic transformation. Hydrogen promotes the FCC-HCP martensitic transformation, which accelerates HCP-martensite-related crack/void initiation. All of the small cracks/voids were fully arrested in the remaining austenite regions until the critical strain for restarting damage growth via coalescence of the micro-damages. Furthermore, lowering the strain rate accelerated the HCP-martensite-related damage growth, which is related to martensite fraction and hydrogen localization [2]. The HCP-martensite-related damage with hydrogen finally results in intergranular and quasi-cleavage fractures.

Another example is a case of FCC-HCP-BCC martensitic transformation in austenitic stainless steels such as SUS304. Because the BCC martensitic phase is the most susceptible to hydrogen embrittlement, it is generally known that hydrogen-related cracking occurs at a region where BCC martensite formation preferentially occurs. In this context, to control the hydrogen-related cracking, the hydrogen-transformation-cracking relationship must be understood. The BCC martensite-related cracking behavior was clarified by in situ deformation experiments with scanning electron microscopy. According to our analyses, hydrogen promotes FCC-HCP martensitic transformation as in the Fe-Mn steel, but the effect of hydrogen on HCP-BCC transformation depends on deformation temperature. Specifically, hydrogen promotes the formation of BCC martensite at ambient temperature, however, suppresses at cryogenic temperature. This implies that the hydrogen effect suppressing BCC martensite formation requires hydrogen diffusion from HCP/BCC phase interface to the BCC martensite region. To support this interpretation, we will present some experimental results in this talk, in terms of microstructure distribution and hydrogen desorption during deformation.

References

1) C. Hao, M. Koyama and E. Akiyama. Metallurgical and Materials Transactions A 51, 6184-6192 (2020).

2) C. Hao, M. Koyama, S. Ajito and E. Akiyama. Int. J. Hydrogen Energy 46 (2021) 27221-27233.

Effect of Oxygen on Plasma Driven Permeation of Hydrogen Through Metal Membranes

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Keywords: superpermeability, PdCu, hydrogen, plasma-driven permeation, Ni

Methods for reduction or enhancement of hydrogen penetration in structural materials, specifically metals, are sought after in various technical applications, such as hydrogen energy, fission and fusion projects, and hydrogen generation. In this work we investigate the effect of oxygen addition in hydrogen plasma on hydrogen transport through 20 μm PdCu and 500 μm Ni membranes.

Normally, oxides ponder the hydrogen transport through metals¹). On the other hand, hydrogen permeation increases if atomic hydrogen is present on the upstream side of a membrane, known as superpermeability, which strongly depends on the surface conditions²).

According to Livshits²⁾, the presence of a contamination film on the surface of a metal reduces the rate of atomic hydrogen recombination into molecules, which in turn increases the permeation. Under plasma exposure the contamination is removed, and the permeation flux reduces. Such behavior is especially noticeable for Ni, where the permeation flux *J* initially raises fast, reaches a maximum, and then reduces to a steady-state value, as one can see in Fig. 1 b (black line).

In our experiments, we tested this idea by investigating the evolution of the surface oxygen concentration n_0 at different times after the beginning of plasma exposure. The experimental setup consists of two vacuum chambers separated by a membrane, one side of which is exposed to plasma³⁾. A laser breakdown spectroscopy (LIBS) is used to evaluate n_0 from the intensity of OI line (777.1944nm). A constant oxygen concentration in the fuel mixture $c_{0_2} =$ 15 at. % is maintained. As one can see from Fig. 1 a, n_0 increases with exposure time. Thus, the previous explanation of such behavior is not satisfactory for the presented result. Our hypothesis is that instead of being removed, the surface contamination grows and at some the pondering of hydrogen permeation by the slow diffusion in the oxide becomes stronger than the increase in permeation from the decrease recombination of hydrogen atoms on the surface.

In Fig. 2 the dependence of J on c_{O_2} is presented for both metals. Strikingly, one can see the significant increase in J for both cases up to a maximum at $c_{O_2} = 10 - 20 \text{ at. }\%$. After the maximum J starts to decrease for both metals. For Ni, this decrease is quite severe and $c_{O_2} = 30 \text{ at. }\% J$ goes below the J(0) for pure hydrogen experiments. For PdCu, however, the rate of decrease is quite minimal and J remains more than on order of magnitude above J(0). This result is especially fimportant, because it suggests that the supermeability through PdCu could be maintained by creating a thick oxide layer, which seems to lead only to a minimal degradation of permeation.

References:

- 1) H. Amundusson, et al., J. Membr. Sci. 153, 259-267 (2000).
- 2) A. Livshits, et al., J. Nucl. Mater. 170, 79-94 (1990).
- 3) A. Kuzmin, et al., Fusion Eng. Des. 189, 113462 (2023).



Fig. 1. Dynamics of hydrogen plasma driven permeation through Ni at $c_{o_2} = 15 at. \%$. a – surface concentration of oxygen, estimated with LIBS, b – time traces of the permeation flux.





[Abstract Guideline (Leave two lines for presentation number)]

Fabrication of Zirconium Nitride Hydride Epitaxial Films by Alternating-Target Pulsed-Laser Deposition

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Keywords: Mixed-anion compounds, Metal hydrides, Nitride hydrides, Pulsed-laser deposition, Epitaxy

Metal nitride hydrides are mixed anion compounds with nitride and hydride ions. This class of mixed anion compounds exhibits intriguing properties, such as fast hydride conduction in Ba₂NH [1] and catalytic activity of Ca₂NH for ammonia synthesis [2]. However, the synthesis of *ionic* nitride hydrides has been limited to group I and II metals, and as for transition metals, oxyhydrides have been widely explored. Furthermore, the fabrication of single crystalline films of nitride hydrides remains exceptionally unexplored, perhaps due to hydrogen desorption at high temperatures, which are favorably applied for epitaxial growth. In this study, we have attained to fabricate *metallic* zirconium (Zr) nitride hydride at *high temperatures* by using pulsed-laser deposition (PLD).

We previously succeeded in PLD of ZrH_y ($0.7 \le y \le 3.3$) epitaxial films at temperature as high as 600 °C by laser ablation of a Zr tablet in hydrogen atmospheres. When switched to a ZrN tablet, however, incorporation of hydrogens into ZrN_x films was found to be inactive: y < 0.05 in ZrN_xH_y . In an alternate approach, we employed alternating-target PLD with taking advantage of strong hydrogen affinity of pure Zr. The Zr nitride hydride films were fabricated on Al₂O₃ (0001) substrates at 600 °C in 1×10^{-3} Torr of H₂. The ZrN and Zr tablets were ablated alternately and the single loop [ZrN/Zr with number of laser pulses in total, N (360 or 180 pulses)] was repeated a few hundred times to deposit multilayer films with thickness ranging from 200 to 800 nm. X-ray diffraction (XRD) analysis of the films revealed interesting trends: the peak corresponding to ZrN (111) gradually shifted toward δ -ZrH₂ (111) with increasing N_{Zr} , and a secondary peak at lower angles was observed for H-rich multilayers [Fig. 1 (a)]. The latter indicates the formation of ZrH_y (y > 3). The lattice spacings of each reflection are plotted in Fig. 1 (b). These findings suggest a mechanism of Zr nitride hydride formation in our method in which interlayer hydrogen (nitrogen) transfer occurs leading to not only homogenous anion distribution [Fig. 1 (c)] but also phase separation between N-poor ZrN_xH_y and ZrH_y (y > 3) phases.



Fig. 1. (a) XRD profiles for single and multilayer Zr-based films grown on Al_2O_3 substrates. (b) Lattice spacing d_{111} as a function of N_{ZrN} . Filled and open circles indicate ZrN_xH_y phase and H-rich ZrH_y phase, respectively. Broken lines show literature values of bulks. Error bars indicate full width at half maximum for each peak. (c) Schematic illustration for the formation of ZrN_xH_y phase.

References

1) F. Altorfer, W. Biihrer, B. Winlder, G. Coddens, R. Essmann, H. Jacobs, Solid State Ionics 70, 272-277 (1994).

2) M. Kitano, Y. Inoue, H. Ishikawa, K. Yamagata, T. Nakao, T. Tada, S. Matsuishi, T. Yokoyama, M. Hara, H. Hosono, Chem. Sci. 7, 4036-4043 (2016).

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Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O202] Oral 202

Chair: Shigeyuki Takagi (Tohoku University) Tue. Dec 12, 2023 2:00 PM - 4:00 PM Session 14 (Room J)

[B3-O202-01 (Symposium Keynote)]	Improving Hydrogen Storage in Metal-Organic Frameworks
	Linda Zhang ^{1,2} , Rafael Balderas-Xicohténcatl ¹ , *Michael Hirscher ^{1,2} (1. Max Planck Institite for Intelligent Systems (Germany), 2. AIMR, Tohoku Univ. (Japan)) 2:00 PM - 2:40 PM
[B3-O202-O2]	From Kinetic and Chemical Affinity Sieving and Beyond: A Metal– Organic Framework for Hydrogen Isotope Separation *Linda Zhang ^{1,2} , Richard Röß-Ohlenroth ³ , Dirk Volkmer ³ , Vanessa K Peterson ⁴ , Robert Dinnebier ⁵ , Michael Hirscher ² (1. Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University (Japan), 2. Max Planck Institute for Intelligent Systems (Germany), 3. Universität Augsburg (Germany), 4. Australian Nuclear Science and Technology Organisation (Australia), 5. Max Planck Institute for Solid State Research (Germany))
[B3-O202-03]	Tubular MIL-68@ZnIn ₂ S ₄ for Enhanced Photocatalytic Hydrogen Production Yu-Hsuan Fan ¹ , *Tai-Chou Lee ¹ (1. National Central Univ. (Taiwan)) 3:00 PM - 3:20 PM
[B3-O202-04]	Ambipolarity of Dilute Hydrogen in Power Semiconductor β -Ga ₂ O ₃ Revealed by μ SR *Masatoshi Hiraishi ^{1,2} , Hirotaka Okabe ^{1,3} , Akihiro Koda ¹ , Ryosuke Kadono ¹ , Takeo Ohsawa ⁴ , Naoki Ohashi ⁴ , Keisuke Ide ⁵ , Toshio Kamiya ^{5,6} , Hideo Hosono ⁶ (1. KEK-IMSS (Japan), 2. Ibaraki Univ. (Japan), 3. Tohoku Univ. IMR (Japan), 4. NIMS (Japan), 5. Tokyo Inst. Tech. (Japan), 6. MCES Tokyo Inst. Tech. (Japan))
[B3-O202-05]	3:20 PM - 3:40 PM Local electronic structure of interstitial hydrogen in MgH ₂ inferred from muon study *Ryosuke Kadono ¹ , Masatoshi Hiraishi ² , Hirotaka Okabe ³ , Akihiro Koda ^{1,4} , Takashi U. Ito ⁵ (1. Inst. Mater. Struct. Sci., KEK (Japan), 2. Ibaraki Univ. (Japan), 3. Inst. Mater. Res., Tohoku Univ. (Japan), 4. Sokendai (Japan), 5. ASRC, JAEA (Japan)) 3:40 PM - 4:00 PM

Improving Hydrogen Storage in Metal-Organic Frameworks

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Keywords: Hydrogen storage, porous materials, adsorption, metal-organic frameworks (MOFs)

Hydrogen storage in nanoporous materials has been attracting a great deal of attention in recent years, as high gravimetric H_2 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 has fast kinetics.

Experimental gravimetric and volumetric hydrogen uptake data have been analysed for many MOFs showing a linear correlation of the gravimetric absolute uptake with the specific surface area (Chahine's rule) [1]. Using the packing density of the powder as well as the single-crystal density, a linear relation is found between the volumetric absolute hydrogen uptake and the volumetric surface area [2]. 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. Based on these results, a phenomenological model is developed for the volumetric absolute uptake as a function of the gravimetric absolute uptake, see Fig. 1 [2]. The key to improving the volumetric storage capacity is closing the gap between the low-density powder towards the theoretical upper limit of the single crystal by either compaction, pelletizing, or monoliths. Furthermore, interpenetrated frameworks show generally higher volumetric hydrogen uptakes [3]. Finally, for technical applications, the key parameter is the usable or working 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 [4].

The presentation will give an overview of the current status and discuss future concepts [5,6].



Fig. 1. Volumetric vs gravimetric absolute hydrogen uptake of porous materials measured at 77 K and 2.0-2.5 MPa. The volumetric uptake was calculated using packing density (red) and single-crystal density (blue). (Taken from [2])

References:

- 1) M. Schlichtenmayer, M. Hirscher, J. Mater. Chem. 22, 10134 (2012).
- 2) R. Balderas-Xicohténcatl et al., Energy Technol. 6, 578 (2018).
- 3) R. Balderas-Xicohténcatl et al., *Energy Technol.* 6, 510 (2018).
- 4) M. Schlichtenmayer, M. Hirscher, Appl Phys A 122, 379 (2016).
- 5) D.P. Broom et al., Int. J. Hydrogen Energy 44, 7768 (2019).
- 6) L. Zhang et al., Progress in Energy 4, 042013 (2022).

From Kinetic and Chemical Affinity Sieving and Beyond: A Metal–Organic Framework for Hydrogen Isotope Separation

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Keywords: Hydrogen energy, Isotope separation, Thermal desorption spectroscopy, Neutron diffraction

Separating H_2/D_2 mixtures is one of the most challenging issues in modern separation science and technology since the isotopes have identical size, shape and thermodynamic properties. A promising alternative is the use of porous materials to separate directly gaseous mixture of isotopes based on two different mechanisms, kinetic quantum sieving (KQS) [1], here D_2 can diffuse faster through small pores than H_2 , and chemical affinity quantum sieving (CAQS) [2], where the difference in zero-point energy leads to a stronger adsorption of the heavier isotope. We investigated various porous materials, e.g., metal-organic frameworks (MOFs) [3-5], covalent organic frameworks (COFs) [6], and organic porous molecules (POCs) [7] and the best separation factors are around 11 to 13 for KQS below 50 K and for CAQS at 60 to 100 K [8]. At material combining both effects, CAQS and KQS, showed the highest selectivity of 26 at 77 K so far [9].

Herein, we report a comprehensive mechanistic study of hydrogen isotope separation in a milestone MOF compound, metal-azolate framework $M(ta)_2$, the deuterium selectivity of which is among the highest reported as far among all porous materials. Thermal desorption spectroscopy (TDS) measurements indicate this dia type coordination framework can separate D_2 from anisotope mixture efficiently, with a selectivity of 32.5 at 60 K.



Fig. 1. $D_2\!/H_2$ separation performance of the $M(ta)_2$ at different temperatures

Furthermore, deuterium is enriched to 75% from one cycle from an initial concentration of 5%., leading a selectivity over 75. From neutron powder diffraction experiments and accurate data analysis, we revealed the exact locations of the hydrogen/deuterium molecules in $M(ta)_2$.

Two adsorption sites of gas molecules have been determined: I) the entrance of the pore-surface pockets, which are defined by six ta-ligands arranged alternatively, and II) the channels connecting adjacent cavities, which are constructed from vertex sharing tetrahedra. We found that separation of hydrogen isotopes takes place at the channel sites, in which the D₂ interactions are enhanced due to the simultaneously adsorption. Interestingly, this simultaneously adsorption at site II are exclusive to H₂ molecules. Our results also indicate a larger expansion of lattice parameter after H₂ loading other than its D₂ counterpart, leading a favored adsorption of D₂ in this framework. Our findings shed light on a new mechanism for optimal selectivity for D₂ capture from its isotopic mixture, that rational development of new MOF compounds should focus or ange an orange at the selective of t



References:

[1] J. J. M. Beenakker, et al., Chem. Phys. Lett. 1995, 232, 379. [2] A. FitzGerald, et al., J. Am. Chem. Soc. 2013, 135, 9458. [3] J. Teufel, et al., Adv. Mater. 2013, 25, 635. [4] J. Y. Kim, et al., J. Am. Chem. Soc. 2017, 139, 17743. [5] L. Zhang, et al., J. Am. Chem. Soc. 2019, 141, 19850. [6] H. Oh, et al., Angew. Chem. 2013, 125, 13461. [7] M. Liu, et al., Science, 2019, 366, 613. [8] J. Y. Kim, et al., Adv. Mater. 2019, 31, e1970147. [9] J. Y. Kim, et al., J. Am. Chem. Soc. 2017, 139, 15135.

Tubular MIL-68@ZnIn₂S₄ for Enhanced Photocatalytic Hydrogen **Production**

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Keywords: Solar Hydrogen, Photocatalyst, Metal-organic-framework

In recent years, there has been an increasing emphasis on energy-related concerns, specifically regarding environmental conservation and the limited availability of energy resources. Finding solutions to these challenges is of utmost importance for the future. Among the various energy carriers, hydrogen has emerged as a widely recognized clean and versatile source. The production of hydrogen through solar-driven water splitting, known as renewable hydrogen, has gained significant attention. Hence, the development of efficient photocatalysts for hydrogen energy applications is crucial.

ZnIn2S4 (ZIS) is a transition metal sulfide photocatalyst known for its low cost and visible-light activity, making it suitable for photocatalytic hydrogen evolution. However, ZIS faces challenges such as low photocatalytic activity and rapid recombination of photo-generated carriers, resulting in poor efficiency. To

address these issues, this study aimed to modify ZIS using a combination of metal-organic framework (MOF).

By employing a simple oil bath method, a tubular heterostructure composite was obtained by incorporating indium-based MOF (MIL-68) particles in the ZIS precursor. MIL-68 possesses a tubular structure and higher specific surface areas, thereby increasing the surface area available for light absorption and exposing more active sites for the reaction. Additionally, the heterostructure composite (see Fig. 1) effectively facilitate the charge separation. Excess

To maintain cost-effectiveness, this study did not employ precious metals such as Pt and Au as co-catalysts. Various MIL-68/ZIS samples were prepared, and the hydrogen production was carried out under 300W Xe lamp with the intensity of 100 mW/cm^2 at room temperature.



Fig. 1: SEM image of the MIL@ZIS composite photocatalyst.

Ambipolarity of Dilute Hydrogen in Power Semiconductor β -Ga₂O₃ Revealed by μ SR

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Keywords: β-Ga₂O₃, Hydrogen, Muon spin rotation

Gallium oxide β -Ga₂O₃ has been attracting attention as a semiconductor for high-voltage power devices because of its large band gap $E_g \sim 4.9$ eV. Recent theoretical calculation suggest that interstitial hydrogen can be the origin of *n*-type doping [1]. In order to investigate the electronic structure of hydrogen in the dilute limit, we have performed muon spin rotation/relaxation (μ SR) experiments on β -Ga₂O₃ at the S1 beamline of MLF, J-PARC to study the electronic structure of muons as pseudo-hydrogen. The local electronic structure of muons is almost identical to that of hydrogen after a small correction due to the difference in the reduced electron mass (~0.43%), and can be inferred from the hyperfine interaction with the nuclear magnetic moments and/or the electrons.

We demonstrate by μ SR study combined with the first principles calculations that muons in β -Ga₂O₃ have two electronic structures: a state corresponding to hydrogen that acts as an electron donor (Mu₁), bounded to three-coordinated oxygen, and a hydride-like state in rapid motion (Mu₂) [2]. Furthermore, we imply from the Hall effect measurements that the fractional yield of Mu₂ exhibits a close link with the mobility and density of the carriers (electrons).

The recently established ambipolar model assumes ambipolarity in the sense that muons can take on donor and

acceptor states simultaneously as such metastable states (relaxed-excited states) [3]. The present experimental results are in good agreement with this model, since $E^{+/0}$ is present in the conduction band, as shown in Fig. 1(a), which means that the corresponding H (or Mu) is always ionized $[H \rightarrow H^+ + e^-,$ see Fig. 1(b)] to provide electrons, causing unintended *n*-type conduction. In addition, while $E^{0/-}$ is located close to the conduction band, it is on the lower energy side (left side of the figure) than the charge neutral level Eint, suggesting that the state corresponding to $E^{0/-}$ can actually function as an acceptor and exchange electrons with the conduction band $[Mu_2 = Mu^- \rightleftharpoons Mu^0 + e^-$, see Fig. 1(b)] to exhibit fast diffusion motion through the neutral state.



(a) The relationship between the forma- tion energy of $Mu^q (q = 0,\pm 1)$ and the Fermi energy in β -Ga₂O₃ [1], where the symbols $E^{+/0}$, $E^{0/-}$, and $E^{+/-}$ correspond to mutual intersection points among each formation energy of the charged states. (b) Schematic diagram of the band structure corresponding to the donor (Mu⁺ = Mu¹) and acceptor (Mu⁻ = Mu²) levels.

References:

- 1) H. Li and J. Rovertson, J. Appl. Phys., 115, 203708 (2014).
- 2) M. Hiraishi, et al., Phys. Rev. B, 132, 105701 (2023).
- 3) M. Hiraishi, et al., J. Appl. Phys., 132, 105701 (2022).

Local electronic structure of interstitial hydrogen in MgH₂ inferred from muon study

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Keywords: hydrogen storage, interstitial hydrogen, electronic structure, muon spin rotation

Metal hydrides have attracted attention as one of the candidate materials that can serve as safe and efficient hydrogen (H) storages. In particular, MgH₂ has great potential as a solid H-storage material because of its high storage capacity of 7.6wt%. However, its slow hydrogenation and dehydrogenation rates and the high decomposition temperature (~300°C) are major obstacles to the practical applications. To understand the microscopic mechanisms of the H-related processes, the information on the electronic state of interstitial H (which exists as an intermediate state in the H kinetics) is crucial in gaining insight into the rate-limiting processes. The preceding studies on the microscopic state of H in MgH₂ have been mainly via computational approaches based on density functional theory (DFT), but there have been few experimental investigations to validate the prediction of DFT calculations. To overcome this situation, we have introduced muon (Mu) as pseudo-H into MgH₂, and studied their electronic and dynamical properties in detail to elucidate the corresponding interstitial H states.

As a result, we found four species of Mu states which are interpreted as two pairs of acceptor-like and donor-like states predicted by the recently developed "ambipolarity model" combined with DFT calculation [1]: in contrast to H whose electronic state is determined by the charge conversion level ($E^{+/-}$), that of the paired Mu states can be predicted from the positions of acceptor ($E^{0/-}$) and donor ($E^{+/0}$) levels in the band structure [2]. A majority pair is



Fig. 1: The formation energy (Ξ^q) of H-related defects vs the Fermi level (E_F) in MgH₂ obtained by DFT calculations, where (a) is for the case of interstitial H atoms (H_i^q, $q = 0, \pm$), and (b) is for the interstitial molecules ([H₂]_i^q, $q = 0, \pm, 2\pm$), respectively corresponding to Mu_i and [HMu]_i. The paramagnetic states are expressed as 'para' and the diamagnetic states as 'dia'. The levels for acceptor $(E^{0/-})$ and donor (E^{+r0}) are determined as cross points between $\Xi^{++}(E_F)$ and $\Xi^{0}(E_F)$. The dashed line shows the intrinsic charge neutral level obtained from the DFT calculation. (Adapted from Ref.[3]) Schematic band diagrams for the single electron energy associated with the donor/acceptor levels (single-charge conversion levels only) in (a) and (b) are shown in (c) and (d), respectively. The level indicated by a dashed line near the CBM in (d) is a shallow state suggested from DFT calculations.

identified as Mu_i^{-} and $Mu_i^{+/0}$ corresponding to the interstitial H (H_i), and another pair is $[HMu]_i^{0}$ and $[HMu]_i^{+}$ for the interstitial molecules ($[H_2]_i$), respectively (see Fig. 1). These findings provide an indirect support for the DFT calculations on which the model is based via the donor/acceptor levels [3].

An important implication of the muon results is that the improvement in hydrogen kinetics, such as by ball milling with oxidants, is due to dehydrogenation acting as a 'reduction' for hydrides and stabilizing the interstitial H⁻ state [1]. As can be seen in Fig. 1(a), when E_F is pushed up above E_F^{int} by dehydrogenation, the interstitial H becomes stable in the H_i⁻ state, and H can exhibit interstitial diffusion without binding to the ligand H⁻.

References:

1) R. Kadono, M. Hiraishi, H. Okabe, A. Koda, and T. U. Ito, J. Phys.: Condens. Matt. 35, 285503 (2023).

- 2) M. Hiraishi, H. Okabe, A. Koda, R. Kadono, and H. Hosono, J. Appl. Phys. 132, 105701 (2022).
- 3) A. Roy, A. Janotti, and C. G. Van de Walle, Appl. Phys. Lett. 102, 033902 (2013).

Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O203] Oral 203

Chair: Hiroyuki Saitoh (National Institutes for Quantum Science and Technology (QST)) Tue. Dec 12, 2023 4:30 PM - 6:30 PM Session 14 (Room J)

[B3-O203-01] Hydrogen Storage Properties and Crystal Structures of an $\rm AB_3$ based alloy

*Toyoto Sato¹, Kazuki Obana¹, Denis Sheptyakov², Takashi Honda^{3,4}, Hajime Sagayama⁴, Kouji Sakaki⁵, Shigeyuki Takagi⁶, Tatsuoki Kono⁶, Heena Yang^{7,8}, Wen Luo^{7,8}, Loris Lombardo^{7,8}, Andreas Züttel^{7,8}, Shin-ichi Orimo^{6,9} (1. Shibaura Institute of Technology (Japan), 2. Paul Scherrer Institut (Switzerland), 3. J-PARC Center, High Energy Accelerator Research Organization (KEK) (Japan), 4. Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK) (Japan), 6. Institute for Materials Research, Tohoku University (Japan), 7. Institute of Chemical Sciences and Engineering, Basic Science Faculty, École Polytechnique Fédérale de Lausanne (EPFL) Valais/Wallis (Switzerland), 8. Empa Materials Science and Technology (Switzerland), 9. Advanced Institute for Materials Research (WPI-AIMR), Tohoku University (Japan)) 4:30 PM - 4:50 PM

[B3-O203-02] Formation Gap in Transition Metal Hydrides

*Hiroshi MIZOGUCHI¹, S.-W. PARK^{1,2}, Hideo HOSONO^{1,2} (1. National Institute for Materials Science (Japan), 2. Tokyo Institute of Technology (Japan)) 4:50 PM - 5:10 PM

[B3-O203-O3] How to evaluate hydrogen storage properties by van't Hoff plots and Sieverts' method in the pressure range up to 100 MPa *Véronique Charbonnier¹, Kohta Asano¹, Hyunjeong Kim¹, Kouji Sakaki¹ (1. National Inst. of Advanced Indus. Sci. and Tech. (AIST) (Japan)) 5:10 PM - 5:30 PM

[B3-O203-04] Nitrogen Dissociation and Ammonia Synthesis Properties of Lithium based Compounds

*Hiroki Miyaoka¹, Hitoshi Saima¹, Takayuki Ichikawa¹ (1. Hiroshima Univ. (Japan)) 5:30 PM - 5:50 PM

[B3-O203-05] Complex hydrides for carbon capture and conversion

*Loris Lombardo¹, Andreas Züttel², Satoshi Horike¹ (1. Kyoto Univ. (Japan), 2. EPFL (Switzerland)) 5:50 PM - 6:10 PM

Hydrogen Storage Properties and Crystal Structures of an AB₃ based alloy

^{*}<u>T. Sato¹</u>, K. Obana¹, D. Sheptyakov,² T. Honda,^{3, 4} H. Sagayama,⁴ K. Sakaki,⁵ S. Takagi,⁶ T. Kono,⁶ H. Yang,^{7, 8} W. Luo,^{7, 8} L. Lombardo,^{7, 8} A. Züttel,^{7, 8} S. Orimo,^{6, 9}

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Keywords: Hydrogen Storage, Crystal structure, Neutron and X-ray diffraction

Hydrogen storage materials have higher volumetric hydrogen densities, which indicate compact hydrogen storage methods, than gaseous and liquid hydrogen. For the reason, many hydrogen storage materials have been reported. Typical hydrogen storage materials, which refer to AB_x alloys (typically x = 1-5) composed of A and B metal elements (A: elements in Group 1-5; B: elements in Group 6-12), store hydrogen atoms in interstitial sites in their lattices. Although LaNi₅ based alloys (so-called AB₅ alloys) have been presently used as practical hydrogen storage materials, new materials with higher hydrogen storage capacity have been demanded.

Recently, we reported reversible hydrogen absorption and desorption reactions on AB₂ based alloys, which were (Y, Mg)(Co, Ni)₂ synthesized from YCo₂ and MgNi₂. In the results, their equilibrium hydrogen pressures and hydrogen storage capacities were depended on amounts of Mg and Co.^{1,2} On the other hand, using YCo₂ and MgCo₂ as starting materials, AB₃ based alloys (Y, Mg)Co₃ were formed instead of AB₂ based alloys. Interestingly, (Y, Mg)Co₃ exhibited reversible hydrogen absorption and desorption reactions at 303 K with less equilibrium hydrogen pressure differences between the hydrogen absorption and desorption reactions (so-called less hysteresis) as shown in Figure 1. In addition, the equilibrium hydrogen pressures and hydrogen storage capacities were maintained up to 100 cycles. To understand the reactions viewed from atomic arrangements, we observed crystal structures by neutron diffraction under D₂ pressure. Based on the Rietveld refinements on the neutron diffraction patterns before and after deuterium absorption reactions were reasonably reproduced by rhombohedral crystal structure models (a = 4.99719(67) Å and c = 24.16062(533) Å before D₂ absorption reaction, and a = 5.27370(64) Å and c = 25.68827(553) Å after D₂ absorption reaction).

In our presentation at MRM2023/IUMRS-ICA2023 Grand Meeting, we will present details of syntheses, hydrogen storage properties and crystal structures of (Y, Mg)Co₃.

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Neutron diffraction experiments were performed on the HRPT at the SINQ, PSI, Switzerland (Proposal No.: 20202035). Synchrotron powder X-ray diffraction were performed on the BL-8A at the PF, KEK, Japan (Proposal No. 2019G572).





Black and red indicate on the 3rd and 100th cycles, respectively. Open and closed circles indicate absorption and desorption, respectively

References:

1) T. Sato, K. Ikeda, T. Honda, L. L. Daemen, Y. Cheng, T. Otomo, H. Sagayama, A. J. Ramirez-Cuesta, S. Takagi, T. Kono, H. Yang, W. Luo, L. Lombardo, A. Züttel, S. Orimo, J. Phys. Chem. C 126, 16943-16951 (2022).

2) T. Sato, T. Mochizuki, K. Ikeda, T. Honda, T. Otomo, H. Sagayama, H. Yang, W. Luo, L. Lombardo, A. Züttel, S. Takagi, T. Kono, S. Orimo, ACS Omega 5, 31192-31198 (2020).

[Abstract Guideline (Leave two lines for presentation number)]

Formation Gap in Transition Metal Hydrides

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Keywords: Hydrogen, intermetallics, chemical bond, electronic structure

In hydrogen society, metal hydrides which are carriers of hydrogen will play crucial role in the application such as hydrogen storage, fuel cell, catalytic reactions, and hydrogen penetration.¹⁾ **Fig. 1(a)** shows the classification of binary hydrides in the view point of chemical bonding character. We can see four regions in the periodic table. Interestingly, there is a no formation region around late transition metals (LTMs), which is called as "hydride gap". Besides, we notice unsolved problems related to the gap. For example, (a)Pd locates in the region exceptionally, although it has strong affinity with hydrogen. (b) The incorporation of a small amount (10–20 mol %) of electropositive metal into an LTM collapses the gap region, and the hydrogen (H) storage ability improves markedly, as seen in H storage intermetallics (IMs) such as LaNi₅. We analyzed the chemical bonding between LTMs and H over various IMs.

We first clarified the characteristic chemical bonding in Pd hydride (PdH), using DFT calculations, and subsequently, found strong covalent interaction of Pd 4d-H 1s. This is due to close energy levels of these orbitals. And it is consistent with large workfunction of Pd $(\sim 5.1 \text{ eV})^{20}$. We found the unique property of Pd originates from its lattice softness.³⁾ **Fig. 1(b)** shows the bulk modulus values of elements. We easily found the threshold value (~ 180 GPa) of hydride formation. Although Cu, Ag, and Au have B values smaller than 180 GPa, these metals do not form hydrides owing to the fully occupied d¹⁰ state. Besides, most of the known H storage IMs including LaNi₅ also meets the above criterion (**Fig. 1(b**)). Indeed, negatively charged LTM ions, such as Ni^{δ-} in LaNi₅, play a crucial role in hydrogenation. These ions cause lattice softening, which renders H solution possible. The criterion proposed seems to provide a guide to design new H storage materials. We are currently verifying its effectiveness by applying to various IMs.



Fig. 1(a) Formation map of metal hydrides. Late transition metals (LTMs) cannot form hydrides, while most elements can form stable hydrides. An exception is Pd locating around the center of LTMs in the periodic table. (b) Bulk modulus values of transition metals and several H storage intermetallic compounds. The elements with H storage ability are written as blue text. Transition metals are hard generally, because of the contribution of d electrons into chemical bonding. One can easily found the threshold value (~180 GPa) of hydride formation.

References :

1) R. Mohtadi, S. Orimo, Nat. Rev. Mater. 2, 16091/1-15 (2017)

2) H. B. Michaelson, J. Appl. Phys. 48, 4729-4733 (1977)

3) H. Mizoguchi, S.-W. Park, H. Hosono, J. Am. Chem. Soc. 143, 11345-11348 (2021)

How to evaluate hydrogen storage properties by van't Hoff plots and Sieverts' method in the pressure range up to 100 MPa

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National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan *v.charbonnier@aist.go.jp and kouji.sakaki@aist.go.jp Keywords: high hydrogen pressure, metal hydride, Sieverts' method, van't Hoff plot

Recently, interest in metal hydride forming compounds with high sorption pressures for compressor applications has raised. This enthusiasm can be explained by the possibility to run compression on waste heat rather than electricity, giving the possibility to lower energy consumption. But together with the exploration of the as yet little studied high-pressure regions, new problems to be tackled have emerged.

Calculation of van't Hoff plots at high pressure

In this field, a simplified van't Hoff equation that links the pressure to the inverse temperature is often used to predict sorption pressures (red in Fig. 1). For research in high pressure applications, it becomes especially useful because in most laboratories, a hydrogen pressure higher than 10 MPa is difficult to achieve. In this talk, we will explain that this equation is true at low pressures, but that its use for extrapolation in the high-pressure range leads to overestimation of the sorption pressures.

P-c isotherms of an AB_2 compound have been measured in a wide range of pressure and temperatures. The data points in Fig. 1 show the middle of their sorption plateaus (\blacksquare absorption, \Box desorption). The pink data points are derived from low pressure and temperature measurements. These pink data points were used to calculate Van't Hoff plots shown in Fig. 1 with two methods (red and green lines). The red van't Hoff plots are linear fits, i.e. the van't Hoff plots derived from the simplified equation described above. The green van't Hoff plots, considering the fugacity, f, clearly shows better agreement with the blue



Figure 1: Comparison of van't Hoff plots considering fugacity (green) and not considering fugacity (red). The symbols are the experimental data corresponding to the middle of the plateaus of the P-c isotherms for absorption \blacksquare and desorption \square of an AB_2 Laves phase compound. Only the pink data points were used to draw the van't Hoff plots.

high pressure data points. Showing that the fugacity should be considered instead of pressure in the high-pressure range. Here, we will explain how to use the fugacity to solve this issue [1], and hereby calculate correct and curved van't Hoff plots (green).

High-pressure equipment related issues

The investigation of high pressure is full of surprises and here we will also introduce unexpected issues that we faced and solved when setting up our high-pressure apparatus (up to 100 MPa). These issues are related to the inner volume of the valve that separates the sample holder from the PCT apparatus, the pressure increment that results from the closure of this valve and the change in sample volume induced by sorption of hydrogen by the samples [2].

References:

[1] V. Charbonnier, H. Enoki, K. Asano, H. Kim, K. Sakaki, Int J Hydrogen Energy 46, 36369-80 (2021).

[2] V. Charbonnier, K. Asano, H. Kim, K. Sakaki, J. Alloys Compd. under review.

Nitrogen Dissociation and Ammonia Synthesis Properties of Lithium based Compounds

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Keywords: Ammonia, Lithium, Chemical looping, Hydride, Alloy

Ammonia (NH₃) is recently recognized as an attractive energy or hydrogen carrier to effectively store and transport renewable energy because of the high gravimetric and volumetric energy density. For the NH₃ production from unstable renewable energy, research and development of the effective small-scale NH₃ synthesis processes operated under lower pressure than those of the conventional mass production system are required. The chemical looping process composed of several chemical reaction are potential techniques to establish the above small-scale NH₃ production system.

In this work, the NH₃ synthesis processes by chemical looping using Lithium (Li) based compounds, which are Li-14 group element (M = Si, Ge, Sn. Pb) alloys and LiH, are studied¹⁻⁴⁾. The nitrogen (N₂) dissociation properties of the Li compounds were systematically investigated by the reaction with 0.1 MPa of N₂ gas and compared with the chemical state of Li in the compounds, which is characterized by nuclear magnetic resonance (NMR) analysis. The correlation between the N₂ dissociation temperature and metallic feature of Li was clarified⁴⁾, namely the more metallic Li can interact with N₂ molecules at lower temperature. In the case of LiH, the N₂ dissociation temperature is the highest because Li is ionic state (Li⁺).

The NH_3 synthesis by chemical looping of LiH is composed of following two step exothermic reactions operated under 0.1 MPa of N_2 and $H_2^{3,5)}$.

$4LiH + N_2$	$\rightarrow 2Li_2NH + H_2$
$2Li_2NH + 4H_2$	$\rightarrow 2NH_3 + 4LiH$

The improvement of reaction kinetics is issue for the NH_3 synthesis by LiH since the melting and agglomeration of intermediate phase occurred during the reaction with N_2 . By mixing scaffolds such as Li₂O and BN to prevent the agglomeration, the reaction kinetics is drastically improved, and the reaction yield is reached to be almost 100% within 20 min³). To realize effective NH_3 synthesis, suitable reaction processes including heat management should be designed considering the unstable H_2 supply from renewable energy in future works.

The chemical looping process of the Li-M alloys is composed of following three step reactions, which are N_2 dissociation to form Li₃N, NH₃ synthesis by reaction between Li₃N and H₂, and regeneration of initial alloys from LiH⁴.

$$\begin{array}{rcl} \text{Li}_{4.4}\text{M} + (x/2)\text{N}_2 & \longrightarrow x\text{Li}_3\text{N} + \text{Li}_{4.4\cdot3x}\text{M} \\ \text{xLi}_3\text{N} + 3x\text{H}_2 & \longrightarrow x\text{NH}_3 + 3x\text{LiH} \\ \text{Li}_{4.4\cdot3x}\text{M} + 3x\text{LiH} & \longrightarrow \text{Li}_{4.4}\text{M} + (3x/2)\text{H}_2 \end{array}$$

For all the alloys, NH₃ can be synthesized below 500 °C under 0.1 MPa by a gas-switching process $(N_2 \rightarrow H_2 \rightarrow Ar)$. Although the synthesis processes are complicated compared with that of LiH, high durability can be expected due to the characteristic atom dynamics based on the high diffusivity of Li²).

This work is supported Grant-in-Aid for Scientific Research (B), JP20H02465 subsidized by JSPS and a project, JPNP2004, subsidized by the New Energy and Industrial Technology Development Organization (NEDO). We would like to thank Research Center for Nitrogen Recycling Energy Carrier at Hiroshima University.

References:

1) T. Yamaguchi, K. Shinzato, K. Yamamoto, Y. Wang, Y. Nakagawa, S. Isobe, T. Ichikawa, H. Miyaoka, and T. Ichikawa, Int. J. Hydrogen Energy, 45, 6806–6812 (2020).

2) S. Yamaguchi, T. Ichikawa, Y. Wang, Y. Nakagawa, S. Isobe, Y. Kojima, and H. Miyaoka, ACS Omega, 2, 1081–1088 (2017).

3) K. Tagawa, H. Gi, K. Shinzato, H. Miyaoka, and T. Ichikawa, J. Phys. Chem. C, 126, 2403–2409 (2022).

4) K. Shinzato, K. Tagawa, K. Tsunematsu, H. Gi, P. K. Singh, T. Ichikawa, and H. Miyaoka, ACS Appl. Energy Mater., 5, 4765–4773(2022).

5) W. Gao, J. Guo, P. Wang, Q. Wang, F. Chang, Q. Pei, W. Zhang, L. Liu, P. Chen, Nat. Energy, 3, 1067–1075 (2018).

Complex hydrides for carbon capture and conversion

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Keywords: Borohydride, Ammonia Borane, Carbon Dioxide

Carbon dioxide (CO₂) emission is responsible for global warming but also represents a cheap, abundant, and safe carbon source. During the last few years, CO₂ capture and utilization have been a global-intensive research area. Conversion of CO₂ to chemicals or synthetic fuels is a promising method to valorise this greenhouse gas and tackle climate change. However, due to CO₂ stability, expensive catalysts or harsh conditions are often required.

Here we demonstrate how to use complex hydrides, well-known materials for solid-state hydrogen storage, for CO_2 capture and reduction.^[1] Organic borohydrides reactivity allows the capture and reduction of CO_2 from dilute sources and even from the atmosphere, formate being the main reaction product.^[2,3] The increase in reactivity comes from the charge transfer between the ammonium cation and borohydride anion.

By using ammonia borane (AB) instead of borohydrides, new valuable products can be obtained. We demonstrate the catalyst- and solvent-free reduction of CO₂ with AB by carefully controlling the reaction pressure and temperature (Fig. 1). The kinetics, thermodynamics, and mechanism were studied by microbalance, FT-IR, and NMR. Under optimal conditions, up to 38 mmol of CO2 was reduced per gram of AB (1.68 gCO2 · g-1AB). Formamide was identified as the main product, indicating a transfer of formate from the boron to the nitrogen. Adding a secondary amine to the AB provides the N-formylation product in 48% yield. Finally, N-doped carbon was obtained by calcinating the reaction product between AB and CO₂, which represents a new method for the synthesis of functionalized carbon materials from CO₂.

These findings can promote the use of complex hydrides for the valorisation of CO_2 to chemicals and materials under mild conditions.



Fig. 1: (a) Schematic representation of the reaction between ammonia-borane and CO_2 ; (b) the amount of CO_2 absorbed in function of temperature: (c) sample appearance after reaction with CO_2 .

References

- [1] L. Lombardo, H. Yang, S. Horike, A. Züttel, *MRS Bull.* **2022**, *47*, 424–431.
- [2] L. Lombardo, H. Yang, K. Zhao, P. J. Dyson, A. Züttel, *ChemSusChem* 2020, 13, 2025–2031.
- [3] L. Lombardo, Y. Ko, K. Zhao, H. Yang, A. Züttel, Angew. Chem. Int. Ed. 2021, 60, 9580–9589.

Poster Session | B. Energy | [B-3] Hydrogenomics

[B3-P204] Poster 204

Tue. Dec 12, 2023 6:30 PM - 8:30 PM Poster (Annex)

[B3-P204-01]	The effective treatment of hydrogen boride (HB) sheets for the long-
	term stabilization as the hydrogen storage *Shin-ichi Ito ¹ , Miwa Hikichi ¹ , Natsumi Noguchi ¹ , Mei Yuan ¹ , Zihao Kang ¹ , Kosei Fukuda ¹ , Masahiro Miyauchi ² Jwao Matsuda ³ Takahiro Kondo ^{1,4} (1 Univ. of Tsukuba (Japan), 2
[B3-P204-02]	Tokyo Inst. of Tech. (Japan), 3. The Univ. of Tokyo (Japan), 4. Tohoku Univ. (Japan)) Effects of High-temperature Heating of Hydrogen Boride Sheets
	White Verside ¹ Kerner Cete ² Vidi Nebelee ³ Peire Utermi ⁴ Utermiti Ceitel ⁵ Ceterki
	6 Yukiniro Yasuda , Kazuno Goto , Yuki Nakanara , Keina Utsumi , Hiroyuki Salton , Satoshi Nakana ⁶ Shin johi Ita ⁷ Miwa Hikichi ⁸ Shin johi Orima ⁹ Takahira Kanda ¹⁰ (1 Univ
	Teukuba (Janan) 2 Univ. Teukuba (Janan) 3 OST (Janan) 4 OST (Janan) 5 OST (Janan)
	6 NIMS (Japan), 7 Univ Tsukuba (Japan), 8 Univ Tsukuba (Japan), 9 Tohoku Univ
	(Japan) 10 Univ Tsukuba (Japan))
[B3-P204-03]	Controlling Ultraviolet Photo-Induced H. Release Rate by Tuning B-H
[00 20 00]	Bonds in Free-Standing Borophane
	*Miwa Hikichi ¹ , Junpei Takeshita ² , Natsumi Noguchi ¹ , Shin-ichi Ito ¹ , Luong Thi Ta ^{3,4} , Kurt
	Irvin M. Rojas ³ , Iwao Matsuda ⁵ , Satoshi Tominaka ^{6,7} , Yoshitada Morikawa ³ , Ikutaro Hamada
	³ , Masahiro Miyauchi ² , Takahiro Kondo ^{1,8} (1. Univ. Tsukuba (Japan), 2. Tokyo Tech.
	(Japan), 3. Osaka Univ. (Japan), 4. Vietnam Maritime Univ. (Viet Nam), 5. Univ. Tokyo
	(Japan), 6. CBRM (Japan), 7. NIMS (Japan), 8. Tohoku Univ. (Japan))
[B3-P204-04]	Evaluation of NH ₃ adsorption properties on hydrogen bolide sheets
	*Kosei Fukuda ¹ , Shin-ichi Ito ² , Miwa Hikchi ² , Iwao Matsuda ³ , Takahiro Kondo ^{2,4} (1.
	Graduated school of Pure and Applied Sciences, Tsukuba Univ. (Japan), 2. Department of
	Materials Science and Tsukuba Research Center for Energy Materials Science, Institute of
	Pure and Applied Sciences, Tsukuba Univ. (Japan), 3. Institute for Solid State Physics,
	Tokyo Univ. (Japan), 4. The Advanced Institute for Materials Research, Tohoku Univ.
	(Japan))
[B3-P204-05]	Investigation on the Catalytic Performance of Hydrogen Boride for the Conversion of Ethanol and Ethanol Solution
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	Univ. Tohoku (Japan))
[B3-P204-06]	Electronic and optical properties of the hydrogen boride sheet from the many-body perturbation theory
	*Luong Thi Ta 1 , Yoshitada Morikawa 1 , Ikutaro Hamada 1 (1. Osaka Univ. (Japan))
[B3-P204-07]	Interplay of Hydrogen Boride Sheets with Water: Insights into Surface and Edge Stability
	*Kurt Irvin Medina Rojas ¹ , Yoshitada Morikawa ^{1,2} , Ikutaro Hamada ¹ (1. Department of
	Precision Engineering, Graduate School of Engineering, Osaka University (Japan), 2.
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	University (Japan))
[B3-P204-08]	Investigation of carrier properties of rhombohedral boron
	monosulfide and changes in properties due to impurity doping
	*Norinobu Watanabe ¹ , Keisuke Miyazaki ² , Masayuki Toyoda ² , Koutarou Takeyasu ¹ , Naohito
	Tsujij ³ Haruki Kusaka ¹ Akiyasu Yamamoto ⁴ Susumu Saito ² Masashi Miyakawa ³ Takashi
	Taniguchi ³ Takashi Aizawa ³ Takao Mori ³ Masahiro Miyauchi ² Takahiro Kondo ^{$1,5$} (1
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	AIMP. Toboku Univ. (Japan))
[B3-D304-00]	Edge dominated Hydrogen Evolution Peactions in Illtra narrow MeS
[D3-1204-03]	Naporibbon Arrays
	*Ding Dui Chan ^{1,2,3} Has Ting Chin ^{1,2,3} Maria Hafmann ⁴ Va Ding Haish ^{1,2,3} (1
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[B3-P204-10]	Diffusion-restricted Cation Exchange Synthesis Of Ultrafine Rh
	Electrocatalyst For Hydrazine Assisted Hydrogen Production
	*Hak Hyeon Lee', Ji Hoon Choi' (1. Sungkyunkwan Univ. (Korea))
[B3-P204-11]	Photocatalytic Hydrogen Production from Na ₂ S/Na ₂ SO ₃ Solution with
	Visible Light Responsible $g-C_3N_4/(CuAg)_{0.1}In_{0.2}Zn_{1.6}S_2$
	*Satoshi Asakuma ¹ , Mai Furukawa ¹ , Ikki Tateishi ¹ , Hideyuki Katsumata ¹ , Satoshi Kaneco ¹
	(1. Mie Univ. (Japan))
[B3-P204-12]	Construction of highly active photocatalytic system using edge-
	grafted g-C ₃ N ₄
	*Mayu Yoshimura ¹ , Hideyuki Katsumata ¹ , Ikki Tateishi ¹ , Mai Furukawa ¹ , Satoshi Kaneco ¹
	(1. Mie Univ. (Japan))
[B3-P204-13]	Study on LaFeO ₃ photocathode for long-term stable
	photoelectrochemical water splitting
	*Hyunwoong Seo ¹ , Kyumi Han ¹ , Min-Kyu Son ² (1. Inje Univ. (Korea), 2. Korea Inst. of
	Ceramic (Korea))
[B3-P204-14]	Electrodeposited Cu ₂ O with a reduced interfacial amorphous phase
	using artificially oriented ITO and their enhanced
	photoelectrochemical solar to H ₂ efficiency
	*Ji Hoon Choi ¹ , Hak Hyeon Lee ¹ , Hyung Koun Cho ¹ (1. Sungkyunkwan Univ. (Korea))
[B3-P204-15]	Simulation of Water Electrolysis of Polymer Electrolyte Membranes
	Kentaro Haraguchi ¹ , Ryo Mitsui ² , *Hidekazu Yokomakura ³ (1. Toyota Technical
	Development Corp. (Japan), 2. Toyota Technical Development Corp. (Japan), 3. Toyota
	Technical Development Corp. (Japan))
[B3-P204-16]	Eco-friendly Electrochemical Ammonia Oxidation of NiCuP
[Electrocatalyst for Hydrogen production
	*Chanmin lo^1 Subramani Surendran ¹ Pildo $lung^2$ Dongijin Lee ² II Goo Kim ² Lik Sim ^{1,2} (1
	Korea Inst of Energy Tech (Korea) 2 NEEL Sci INC (Korea))
[R3-P204-17]	Membrane Reactor Combining V-based Hydrogen Permeable Alloy
	Membrane with Ammonia Decomposition Catalyst for Direct High-
	Purity Hydrogen Production from Ammonia

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- [B3-P204-18] The effect of ball milling on hydrogen release property of TiH₂ *Mei Yuan¹, takahiro Kondo^{1,2} (1. Tsukuba Univ. (Japan), 2. Tohoku Univ. (Japan))
- [B3-P204-19] Hydrogen-gasochromic Properties of Y-Mg, Ni-Mg, Mn-Mg and Gd Switchable Mirror Films

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- [B3-P204-20] Fabrication of all-solid-state thin film thermal switches using hydro-/dehydrogenation reactions of Y-Mg or Ni-Mg switching-mirror films *Haruna Ogiwara¹, Ryuto Nishimura¹, Makoto Kashiwagi¹, Yuki Oguchi¹, Yuichiro Yamashita^{2,1}, Takashi Yagi^{2,1}, Naoyuki Taketoshi^{2,1}, Yuzo Shigesato¹ (1. Aoyama Gakuin Univ. (Japan), 2. National Inst. of Advanced Indus. Sci. and Tech. (Japan))
- [B3-P204-21] Thermal conductivity changes of electrochemically hydrogenated and dehydrogenated Pd-catalyzed Ni-Mg alloy thin film *Daiki Murakami¹, Yuichiro Yamashita^{2,1}, Takashi Yagi^{2,1}, Makoto Kashiwagi¹, Yuki Oguchi¹ , Naoyuki Taketoshi^{2,1}, Yuzo Shigesato¹ (1. Aoyama Gakuin Univ. (Japan), 2. National Institute of Advanced Industrial Science and Technology (Japan))
- [B3-P204-22] Reversible electrical and thermal conductivities change of Pdcatalyzed Co-Mg films by gasochromic hydrogenation using N₂-H₂(3 %) gas

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[B3-P204-23] Electrical, thermophysical and structural properties change for Gd hydrides thin films controlled by gasochromic hydro-/dehydrogenation

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- [B3-P204-24] Changes in Electrical and Thermal Conductivities of Sm Film by Gasochromic Hydrogenation and Dehydrogenation
 *Miki Ueno¹, Yuichiro Yamashita^{1,2}, Takashi Yagi^{1,2}, Makoto Kashiwagi¹, Iesari Fabio³, Toshihiro Okajima^{1,3}, Yuki Oguchi¹, Naoyuki Taketoshi^{1,2}, Yuzo Shigesato¹ (1. Aoyama Gakuin Univ. (Japan), 2. National Institute of Advanced Industrial Science and Technology (Japan), 3. Aichi Synchrotron Radiation Center (Japan))
- [B3-P204-25] Development of Power Flow Simulation of Distributed Hydrogen System with Transient Characteristics Enabling Cost Analysis And Control Study

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[B3-P204-26] Zinc Aqueous Battery Anode Coated with Zinc Ion Conductive Polymer for Suppression of Dendrite Growth and Inhibition of Irreversible Hydrogen Evolution Reaction *Dae Yeop Jeong¹ (1. Hanyang Univ. (Korea))

The effective treatment of hydrogen boride (HB) sheets for the long-term stabilization as the hydrogen storage

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Keywords: Hydrogen boride, hydrogen emission, hydrogen storage, long-term preservation

Two-dimensional hydrogen boride (HB), or borophane sheets, prepared by ion-exchange reactions from magnesium diboride have been reported to have some interesting properties¹⁾⁻³⁾. HB sheets prepared by the ion exchange method have a small amount of water-reactive parts⁴⁾. In order to preserve the HB sheet for a long time and use it for various purposes, it is important that it does not contain such a small amount of reactive parts. In this study, we report on effective processing of HB sheets for long-term stabilization.⁵⁾ As shown in Fig. 1, the HB sheets were intentionally reacted with water, the highly reactive portion was removed, and the results were compared and examined under different conditions over 9 months. The HB sheet obtained by mixing the HB sheet and water and then redispersing the dried sample in acetonitrile and filtering showed excellent long-term stability. Subsequent temperature-programmed desorption (TPD) experiments also showed that hydrogen was stably released by raising the temperature (Fig. 2).



Fig. 1 Treatment of HB sheets for long-term stability. 5)



Fig. 2 H₂-TPD of the original HB and treated HB kept in a refrigerator for 9 months after the treatment. ⁵⁾

References

- 1) S. Ito et al., Chem. Lett. 49, 789-793 (2020).
- 2) N. Noguchi et al., Molecules 27, 8261 (2022).
- 3) T. Goto et al., Commun. Chem. 5, 118 (2022).
- 4) K. I. M. Rojas et al., Commun. Mater. 2, 81 (2021).
- 5) S. Ito et al., Phys. Chem. Chem. Phys. (2023) in press (DOI: 10.1039/D3CP01256E).

Effects of High-temperature Heating of Hydrogen Boride Sheets Under High-Hydrogen Partial Pressure

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Keywords: hydrogen boride sheets, hydrogen storage materials, two-dimensional materials

Two-dimensional (2D) materials are used in various fields such as electrode catalysts, photocatalysts, electronics, optoelectronics, inserts and lubricants because of its superior properties. In 2017, experimental realization of the hydrogen boride sheets (HB sheets) have been reported as a new 2D materials¹⁾. HB sheets are composed of boron and hydrogen with stoichiometric 1:1. HB sheets theoretically take the structure of a six-membered ring of boron bridged by hydrogen, but it is only a local structure. In fact, it is reported that HB sheets have two types of bonds: one is three-center, two-electron (3c-2e) bond (B-H-B bond) and the other is two-center, two-electron (2c-2e) bond (B-H bond)²⁾. HB sheets are expected to be used as a hydrogen storage material. It is estimated to exhibit a hydrogen storage of 8.5 wt% and releases hydrogen by heating. Not only itself but also complexes with HB sheets are expected to exhibit a high level of hydrogen storage. For example, Li doped HB sheets theoretically indicate up to hydrogen storage of 11.57 wt%³⁾. However, hydrogen dissociation temperature

of HB sheets is very wide because of its structural inhomogeneity, so it is important to control its structure and evaluate hydrogen dissociation characteristics. In this study, HB sheets were heated under extreme conditions such as high-hydrogen partial pressure or ultrahigh pressure to induce structural changes while preventing the decomposition and desorption of hydrogen from the HB sheets.

The purpose of this study is to examine the effects of heating the HB sheets and to clarify how the pressure and temperature conditions affects the physical properties, especially hydrogen dissociation characteristics of the HB sheets.

We have conducted heating of HB sheets under $573\sim1073$ K temperature condition and $5\sim11$ MPa hydrogen partial pressure. We have also conducted heating under ultrahigh pressure (3500 and 5000 MPa) without hydrogen.

Figure 1 shows M/z=2 thermal desorption spectroscopy (TDS) of normal HB sheets and heated HB sheets. Intensity values are normalized with the maximum value as 1. An interesting point is that the peak of hydrogen dissociation shifts toward higher temperatures as the heating temperature increases. Fouriertransformed infrared absorption (FTIR) spectroscopy measurements were also conducted to examine changes in structure, and there were not significant spectral differences between the samples under different heating conditions in terms of peak positions of BHB and BH vibrational modes. In addition, Xray diffraction patterns of B2O3 I and B2O3 II were detected in sample heated at ultrahigh pressure.

References:

- 1) H. Nishino, et al., J. Am. Chem. Soc. 139 (2017) 13761-13769.
- 2) S. Tominaka, et al., Chem. 6 (2020) 406-418.
- 3) L. Chen, et al., Phys. Chem. Chem. Phys. 20 (2018) 30304-30311.



Figure 1. M/z=2 TDS of normal HB sheets and some annealed HB sheets (Intensity values are normalized with the maximum value as 1)

[Abstract Guideline (Leave two lines for presentation number)]

Controlling ultraviolet photo-induced H₂ release rate by tuning B-H bonds in free-standing borophane

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Keywords (Hydrogen boride, Hydrogen release, Boron, Two-dimensional materials):

Hydrogen boride (HB), a freestanding two-dimensional hydrogenated-borophene (borophane) polymorph, is synthesized via ion exchange.¹⁾ HB sheets with a B/H atomic ratio of 1.0 have been confirmed to contain three-center–two-electron B–H–B bonds and two-center–two-electron terminal B–H bonds.²⁾ It has been reported that H₂ is released from HB sheets by UV irradiation.³⁾ The optical properties of HB sheets; however, this has not yet been achieved. Herein, we demonstrate that controlling the BHB/BH bond ratio in the HB sheets is possible without altering the hydrogen content by adjusting the volume of ion-exchange resin during synthesis, thus enabling the tuning of the photoinduced H₂ release under UV irradiation.⁴⁾ Furthermore, the fluorescence intensity correlates with the absorbance ratio of the BHB and BH vibrational modes in FT-IR spectra. Increasing the BHB/BH bond ratio enhances the luminescence intensity, whereas reducing it enhances the photoinduced H₂ release rate under UV irradiation (Figure 1). The ability to control the BHB/BH bond ratio of HB sheets provides new avenues for optimizing their properties for various applications, including hydrogen storage and photocatalysis.



Figure 1 Increasing the BHB/BH bond ratio of borophane (hydrogen boride) sheets enhances the luminescence intensity, whereas reducing it enhances the photoinduced H_2 release rate under UV irradiation.⁴⁾

References

- 1) Nishino, H. et al. J. Am. Chem. Soc. 139, 13761-13769 (2017).
- 2) Tominaka, S. et al., Chem 6, 406-418 (2020).
- 3) Kawamura, R. et al., Nature Commun. 10, 4880 (2019).
- 4) Hikichi, M. et al., submitted.

Evaluation of NH₃ adsorption properties on hydrogen bolide sheets

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Keywords: Ammonia adsorption, boron, borophane, hydrogen borides.

Hydrogen boride (HB) sheets are two-dimensional materials firstly synthesized in 2017¹, which consist of negatively charged boron and positively charged hydrogen at a molar ratio of 1:1. In this study, we focused on the positively charged hydrogen in HB sheets and aimed to clarify whether the adsorption of NH₃ molecules occurs or not, and its mechanism. HB sheets were synthesized as reported previously¹. We then exposed the HB sheets to ammonia vapor. Specifically, the small bottle with HB (20 mg) was put in the large bottle with 10 mL ammonia water and the large bottle was closed. After specific time had passed, we picked out the small bottle and heated it under vacuum for 30 min under 343 K to dry and got the dried sample. The obtained sample was examined by weight measurement, Fourier transform infrared absorption spectroscopy (FT-IR), temperature programmed desorption mass spectrometry (TPD-MS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

The mass of the dried sample was found to increase with increasing exposure time of ammonia water as shown in Figure 1. The maximum mass change of the sample was about 180%. This is larger amount compared to the case of pure water exposure (137%), indicating that NH₃ is adsorbed on HB sheets even after 343 K heating. In FT-IR spectra, the distinct peak was observed near 2500 cm⁻¹ for original HB sheets as shown in Fig. 2, which can be attributing to the terminal B-H stretching vibrational mode.² The absorption peak position was found to shift about 40 cm⁻¹ to lower wavenumber for the sample after the exposure of ammonia water vapor followed by drying, indicating that B-H bond gets weakened when NH₃ is absorbed on the HB sheets. In TPD-MS, NH₃ (m/z=17) desorption peaks were observed at 450 K and 640 K. Based on the analysis of other samples, the former peak (450 K) could be ascribed to the decomposition of ammonium borate while the latter peak (640 K) could be ascribed to the NH₃ adsorbed on the HB sheets. Detail of NH3 adsorption will be presented.

References

- 1. Nishino, H. et al. J. Am. Chem. Soc. 139, 13761 (2017).
- 2. Tominaka, S. et al. Chem 6, 406 (2020).



Fig. 1 Mass change of the HB sheets after exposure of ammonia water vapor and pure water.



Wavenumber (cm⁻¹) Fig. 2 FT-IR spectrum of HB sheets before and after the exposure to ammonia vapor with 2-144 h, followed by drying.

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Investigation on the Catalytic Performance of Hydrogen Boride for the Conversion of Ethanol and Ethanol Solution

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Keywords: Two-dimensional catalyst, Hydrogen Boride, Ethanol conversion

The two-dimensional nano sheet materials obtained by the stripping of layered materials, due to their large surface area and special electronic state, are expected to be used in various fields such as catalysts and electronic devices. In previous studies in our laboratory, it has been proved that hydrogen boride (HB) sheets play a role as a solid acid catalyst^{1, 2} and the sheets are chemically stable against water.³ Specifically, in the presence of HB sheets, ethanol was found to be converted to ethylene with high selectivity.¹ Moreover, there was an indication that mixture of water in ethanol may change the reaction product, i.e., the selectivity of ethanol conversion may control by controlling water content. In this study, therefore, effects of water mixture for the ethanol conversion by hydrogen boride sheets will be examined.

The prepared HB sheets⁴ were loaded into a fixed bed reactor. As pre-treatment, the sample was heated at 300 °C in argon gas environment for 1 hour and cooled to room temperature, then reheated to 300 °C with introducing ethanol. The conversion of ethanol was found to increase at 180 °C with heating. Its selectivity to ethylene is more than 80% when ethanol was flow without adding water at 300 °C as shown in Figs. 1 and 2. The W/F (weight of catalyst/ethanol flow rate) was changed by adjusting the ethanol flow rate. It was found that under different W/F conditions, the product selectivity did not change (Fig. 1), but the conversion rate of ethanol changed (Fig. 2). Next we tested HB with 15 wt% ethanol solution. We found that the conversion and selectivity significantly changed with the addition of water to ethanol (Figs. 3 and 4). The detail results will be discussed in presentation.



References:

- 1) A. Fujino, et al., ACS Omega. 4 (2019) 14100-14104.
- 2) A. Fujino, et al., Phys. Chem. Chem. Phys. 23 (2021) 7724-7734.
- 3) K. Rojas, et al., *Commun. Mater.* 2 (2021) 81
- 4) H. Nishino, et al., J. Am. Chem. Soc. 139 (2017) 13761.

Electronic and optical properties of the hydrogen boride sheet from the many-body perturbation theory

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Keywords: Hydrogen boride, GW, electronic structure, optical spectra, 2D.

The hydrogen boride (HB) sheet is a new member of two-dimensional (2D) boron-based materials and possesses great potential in electronic and catalytic applications due to its facile synthesis, chemical stability, and interesting optoelectronic properties.¹⁾ However, the predicted different electronic structures (i.e., semimetallic versus semiconductor) depend on the level of theory and are controversial, which calls for a more rigorous calculation of the electronic structure.^{2,3)}

In this work, we used many-body perturbation theory to calculate a more accurate band structure of the HB sheet than those of the conventional density functional theory. We used the perturbative GW (G_0W_0) calculation without the plasmon-pole approximation (i.e., full frequency G_0W_0). We carefully study the convergence parameters, such as the cutoff energy and the number of unoccupied states to calculate the dielectric constant and obtained well-converged quasiparticle energies. We found that the HB sheet possesses a semimetallic electronic structure, which supports the finding based on the semilocal DFT calculations. Furthermore, we calculated the optical spectra based on the G_0W_0 quasiparticle energy and the random-phase approximation, which agrees well with the photoabsorption measurement and explains the experimental findings.⁴



Fig. 1. Band structure and density of states (DOS) of the HB sheet obtained at the G_0W_0 level of theory (dot), along with that obtained at the PBE level of theory (solid line), and the geometry of HB.

References

- 1) H. Nishino et al., J. Am. Chem. Soc. 139, 13761–13769 (2017)
- 2) R. Kawamura et al., Nat. Commun. 10, 1–8 (2019)
- 3) Li Shao, Physical Chemistry Chemical Physics 14, 7630-7634 (2019).
- 4) L. T. Ta, Y. Morikawa, and I. Hamada (submitted).

Interplay of Hydrogen Boride Sheets with Water: Insights into Surface and **Edge Stability**

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Keywords: Hydrogen boride, Density functional theory, Surface, Edge, Stability

Two-dimensional hydrogen boride (HB) sheets with a 1:1 stoichiometric ratio of boron and hydrogen have been recently synthesized from magnesium diboride (MgB₂) via ion-exchange process (Fig. 1).^[1] Recent investigations have revealed remarkable properties of HB sheets, including outstanding solid-acid catalytic activity, semimetal electronic character, high sensitivity to gases, and the ability to release hydrogen under ultraviolet light. Consequently, the HB sheet holds great promise as a material for various applications such as batteries, gas and light sensors, and electrodes.^[2] Nonetheless, the potential instability of HB sheets remain a concern due to the well-known reactivity of the parent material, MgB₂, and boron hydrides, which are susceptible to hydrolysis in the presence of water - a common substance in typical operating environments.



In this investigation, our focus was to explore the interaction between hydrogen boride sheets and water using density functional theory calculations.^[3] Specifically, we concentrated on studying the surface and edge interactions. Regarding the surface interactions, we examined both pristine and vacancy-defected models, observing their behavior upon contact with water. Our findings revealed an exceptionally weak interaction between water and HB sheet, displaying no evidence of chemical bonding or substantial structural deformation that typically onsets a hydrolysis reaction. However, we observed that the interaction strength increased proportional to the size of the defect, albeit still considerably weak. We attribute the stability of the HB sheets to

the robust B-B bonding inherent in the sheet's honeycomb structure.

The investigation of the edges becomes particularly intriguing since the stability advantage offered by the B-B network is only partially present in these regions. Upon closer examination, we discovered a notable distinction in not only the adsorption environment for water but also the inherent structure of HB itself depending on the edge orientation - armchair or zigzag. With only a passivation layer for the boron edge atoms, we analyze the structure first. Similar to the HB sheet's



honeycomb structure, the armchair edges remain intact; however, the zigzag edge undergoes significant deformation, forming *fringe*-like edges (Fig. 2A). This observation directly indicates that the edges exhibit weaker B-B support compared to the surface. Subsequently, when water was introduced, we obtained adsorption energies similar to that of surface-adsorbed water. This phenomenon could be attributed to the presence of hydrogen termination that passivates the edge. To explore the reactivity of a non-passivated HB edge, we induced a hydrogen vacancy on the armchair edge. Remarkably, when water adsorbed onto the H-vacant armchair edge, multiple indicators such as adsorption energy, density of states, and charge density difference revealed evidence of chemical bonding (Fig. 2B). Notably, the bonding between the oxygen and boron was observed, signifying the initiation of the hydrolysis reaction in HB sheets.

References:

1) H. Nishino, et al., J. Am. Chem. Soc. 139, 13761 (2017).

2) T. Goto, et al., Commun. Chem. 5, 118 (2022).

3) K. I. M. Rojas, et al., Commun. Mater. 2, 81 (2021).

Investigation of carrier properties of rhombohedral boron monosulfide and changes in properties due to impurity doping

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Keywords: 2D material, Boron, Nonmetal material, High pressure and high temperature synthesis

Due to their unique properties, two-dimensional materials are used in a wide range of applications, such as electronic devices and catalysts. The polymorphic properties of boron-based materials make them suitable for the development of boron-based two-dimensional materials. Among them, rhombohedral boron monosulfide (r-BS) (Fig. 1) has attracted much attention in recent years because of its unique layered structure similar to transition metal dichalcogenides and layer-dependent band gap [1]. However, experimental evidence that identifies the type of charge carriers in r-BS semiconductors is lacking. In this study, we synthesized r-BS and evaluated its performance as a semiconductor by measuring the Seebeck coefficient and photo-electrochemical responses [2].

In both measurements, properties characteristic of p-type semiconductors were observed (Fig. 2), indicating that the synthesized r-BS is a p-type semiconductor. In addition, Fourier transform infrared absorption spectroscopy showed a Fano resonance, which is attributed to the Fano resonance between the E(2) (TO) phonon mode and the electrons in the r-BS band structure, indicating that the synthesized r-BS is intrinsically doped with p-type carriers. These results provide experimental evidence for future applications of r-BS.

To investigate the changes in the properties of r-BS due to impurity doping, we recently synthesized carbon-doped r-BS as an additional experiment. Measurements of the properties of this material and a discussion of the r-BS carrier will be mentioned on the day of the session.

References:

- [1] H. Kusaka, et al., J. Mater. Chem. A. 2021, 9, 24631.
- [2] N. Watanabe, et al., Molecules 2023, 28, 1896.
- [3] K. Momma, F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272.



Fig. 1. The structure of r-BS [1-3].



Fig. 2. Temperature dependence of the Seebeck coefficient of the synthesized r-BS [2]

Edge-dominated Hydrogen Evolution Reactions in Ultra-narrow MoS₂ Nanoribbon Arrays

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Keywords: MoS₂, nanoribbons, Hydrogen evolution reaction, ultranarrow, dry etching

Future energy generation and storage requirements emphasize the importance of high-performance electrocatalysis. MoS_2 edges exhibit ideal energetics for hydrogen evolution reactions (HER) if challenges in their kinetics are addressed. We here investigate the emergence of edge-dominated electrochemical reaction kinetics in ultra-narrow MoS_2 nanoribbons. A templated subtractive patterning process (TSPP) that yielded large arrays of MoS_2 nanoribbons that served as a powerful platform. Nanoribbons with widths below 30nm exhibit significantly increased reaction kinetics, as evidenced by a ~200-fold enhanced turn-over frequency, an 18-fold increased exchange current density, and a 38% decreased Tafel slope. (Fig. 1) These improvements are due to an increased charge transfer efficiency from the basal plane toward the edge sites. Photo-electrocatalytic measurements and carrier transport simulation reveal the impact of suppressed band bending in nanoribbons below the depletion width in achieving edge-dominated HER. Our results demonstrate the potential of confinement in electrocatalysis and provide a universal route toward nanoribbon-enhanced electrochemistry.



Fig. 1. Efficient hydrogen evolution reaction in ultra-narrow MoS₂ nanoribbon arrays

Diffusion-restricted Cation Exchange Synthesis Of Ultrafine Rh Electrocatalyst For Hydrazine Assisted Hydrogen Production

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Keywords: Cation Exchange Synthesis, Rh Electrocatalyst, Hydrazine Oxidation Reaction, Hydrogen Production

Water splitting driven by renewable energy is a promising hydrogen production method without carbon emission. However, oxygen evolution reaction still diminishes the total cell's efficiency due to its large overpotential and sluggish kinetics.¹⁾ Rh is a highly active catalyst for the electrochemical oxidation of hydrazine, which has the potential to replace the oxygen evolution reaction and lower operating voltage.²⁾ Unfortunately, Rh is an expensive noble metal, but only few studies have explored ways to reduce the amount of Rh used. This study proposes using the diffusion-restricted cation exchange (CE) process to decrease the mass of inactive Rh and improve mass activity.³⁾ By immersing the NiOOH substrate in a Rh³⁺ solution, Rh³⁺ atoms are exchanged with Ni³⁺ atoms on the surface, RhOOH forms on the outer layer. The RhOOH layers are reduced again into metallic rhodium by an electrochemical reduction process, resulting in fine Rh nanoparticles less than 2 nm in size. This approach can suppress Rh aggregation, doubling the mass activity for electrocatalytic hydrazine oxidation compared to conventional electrodeposited Rh catalysts. As a result, the proposed CE-derived Rh catalyst shows stability for over 36 hours in the two-electrode hydrazine splitting system and allows the hydrogen production by single CIGS solar cell.



Figure 1. The proposed synthetic process of Rh electrocatalyst based on diffusion-restricted cation exchange and corresponding electrochemical hydrazine oxidation performance with SEM images.

References

1) M. Wang, L. Zhang, Y. He, H. Zhu, J. Mater. Chem. A 9, 5320-63 (2021).

2) D. A. Finkelstein, R. Imbeault, S. Garbarino, L. Roue, D. Guay, J. Phys. Chem. C 120, 4717 (2016).

3) H.H. Lee, D.S. Kim, S. Sarker, J.H. Choi, H.S. Lee, H.K. Cho, Energy Environ. Mater. 0, e12556 (2023).

$Photocatalytic Hydrogen Production from Na_2S/Na_2SO_3 \ Solution \ with Visible Light Responsible g-C_3N_4/(CuAg)_{0.1}In_{0.2}Zn_{1.6}S_2$

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Keywords: Photocatalytic hydrogen production, (CuAg)_{0.1}In_{0.2}Zn_{1.6}S₂, visible light irradiation, g-C₃N₄,

[Introduction] Great progress has been achieved in photocatalytic H₂ production technologies since the photochemical splitting of water over a TiO₂ electrode was first reported by Fujishima et al. So far, most reported photocatalysts have large band gap energy ($E_g > 3.0 \text{ eV}$) and so they are only active under ultraviolet light, which occupies only 5% of the solar spectrum. Designing visible-light-driven photocatalysts with high photocatalytic activity and visible-light absorption to make full use of the solar spectrum has therefore been an important research focus. In this study, (CuAg)_{0.1}In_{0.2}Zn_{1.6}S₂ was used as an inexpensive photocatalyst to improve and enhance the H₂ production efficiency under visible light irradiation.

[Experimental] The photocatalyst $(CuAg)_{0.1}In_{0.2}Zn_{1.6}S_2$ was prepared by hydrothermal synthesis. AgNO₃ (1 mmol) 0.169 g, Zn(NO₃)₂·6H₂O (16 mmol) 4.752 g, and In(NO₃)₂ (2 mmol) 0.709 g were dissolved in 10 mL distilled water (pure water), and nitrogen was purged into the solution for 30 minutes. To the solution were added 0.099 g of CuCl (1 mmol), 1.37 g of CTAB (3.76 mmol), and 6.010 g of TAA (80 mmol). The resulting solution was heated in an autoclave and then was naturally cooled. The product was centrifuged and washed twice with distilled water and ethanol. After the vacuum drying at 60°C for 24 h, $(CuAg)_{0.1}In_{0.2}Zn_{1.6}S_2$ was obtained. The catalytic activity of the photocatalyst was evaluated by hydrogen production. 50 mg of photocatalyst, Ru standard solution (1000 ppm), and a mixture of sodium sulfide (0.5 M) and sodium sulfite (0.4 M) were added as a second co-catalyst. The solution was dispersed for 3 minutes under an ultrasonic irradiation. The resulting solution was then irradiated with light using an Xe lamp for 6 h while stirring, and the amount of hydrogen production was measured by gas chromatography-TCD after 3 and 6 hours.

[Results and Discussion]

The hydrogen production with second cocatalyst became worse except for $g-C_3N_4$. The addition of $g-C_3N_4$ improved the photocatalytic H₂ production in the presence of Ru catalyst. The effect of the amount of $g-C_3N_4$ in the presence of Ru was investigated. The H₂ amount with 0.5 wt% $g-C_3N_4$ was greatest. The addition of $g-C_3N_4$ in the presence of Ru improved the amount of hydrogen production.

The mechanism of H_2 production is shown in Fig. 1. When a photocatalyst is irradiated with visible light, electrons in the valence band are excited in the conductor, forming photoexcited electrons and holes. The generated holes efficiently oxidize S²⁻ and SO₃²⁻ to produce protons, suppressing



Fig. 1. Mechanism of hydrogen production with $g-C_3N_4/(CuAg)_{0.1}In_{0.2}Zn_{1.6}S_2$ in Na_2S/Na_2SO_3 aqueous solution.

the recombination of photoexcited electrons and holes and promoting charge separation. The photoexcited electrons in the conduction band are transferred to $g-C_3N_4$ and then to Ru_2S_3 supported on the photocatalyst. The electrons can reduce H⁺ and efficiently generates hydrogen. Furthermore, some Ru_2S_3 is converted to RuS_2 , and hydrogen is generated by the redox cycle between Ru_2S_3 and RuS_2 . [Conclusion]

The effective second co-catalyst was $g-C_3N_4$ in the production of hydrogen from Na_2S/Na_2SO_3 solution under visible light irradiation with $Ru/(CuAg_{)0.1}In_{0.2}Zn_{1.6}S_2$. The best amount of $g-C_3N_4$ was 0.5 wt%, at which the hydrogen production rate was 1447 μ mol· g^{-1} ·h⁻¹. The present work can facilitate the research for highly efficient and stable water splitting photocatalysts.

Construction of highly active photocatalytic system using edge-grafted g-C₃N₄

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Keywords: g-C₃N₄, photocatalyst, pyridine, O-dope, hydrogen evolution

To achieve a decarbonized society, next-generation clean energy is attracting attention, and hydrogen energy, one of them, is a clean and sustainable energy with high energy density. Currently, hydrogen consumed industrially is mainly produced by reforming fossil fuels (coal and natural gas), which consumes high energy and emits CO_2 . In contrast, photocatalytic water splitting can produce hydrogen using water and solar energy, and the reaction takes place at room temperature and pressure, making it an environmentally friendly and simple method. Graphitic carbon nitride (g-C₃N₄) is a metal-free photocatalyst and has the advantages of visible light responsiveness, low cost, and excellent photochemical stability. However, its performance is severely limited by the immediate recombination of photogenerated electron-hole pairs. In this study, by introducing a pyridine ring and an oxygen atom into the g-C₃N₄ framework, we have improved the photocatalytic activity by extending the absorption wavelength range and increasing the charge separation efficiency.

Photocatalytic g- C_3N_4 (CN) samples were synthesized by direct calcination of urea in air at 550 °C for 4 hours . POCN samples edge-grafted with pyridine rings and oxygen atoms were prepared as follows. urea mixed with 2-aminopyridine and ammonium formate were uniformly ground and the collected mixture was placed in a crucible with a lid and heated as in the CN synthesis process above. PCN sample obtained by mixing only urea and 2-aminopyridine and an OCN sample obtained by mixing only urea and ammonium formate were also prepared and compared for hydrogen evolution.

The experimental procedure for hydrogen production is as follows. 40 mg of catalyst was placed in a reaction vessel with water, triethanolamine, and hexachloroplatinum acid, and nitrogen purged for 30 minutes before light irradiation. A xenon lamp was used as the light source, and the reaction system was exposed to light for 6 hours through a 420 nm cutoff filter and measured by gas chromatography. Characterization was also performed to confirm photocatalytic activity.

Photocatalytic activity results show that CN had no confirmed hydrogen production, while PCN, OCN, and POCN had the high hydrogen production rates of 16 μ mol g⁻¹ h⁻¹, 100 μ mol g⁻¹ h⁻¹, and 202 μ mol g⁻¹ h⁻¹, respectively. PL measurements showed a decrease in fluorescence due to the introduction of oxygen; EIS measurements showed that co-dope of pyridine and oxygen to carbon nitride decreased the charge resistance to the solution interface. These results of enhanced photocatalytic activity of POCN suggest that electron delocalization by substitution of oxygen atoms results in suppression of electron-hole pair recombination. In addition, the pyridine ring introduced at the end of the carbon nitride skeleton functions as an electron donor, improving the charge transfer efficiency.

This indicates that the dual modification of the pyridine ring and oxygen synergistically enhances the photocatalytic activity of $g-C_3N_4$.

Table 1. Experimental conditions		
Photocatalyst	Photocatalysts (40 mg) / Pt (0.8 mg : 2.0 wt%)	
Medium	Water (35.2 mL) , TEOA (4 mL : 10 vol%), H2PtCl6 (0.8 mL : 1000 ppm)	
Reactor	Pyrex glass vessel (Volume:123 mL)	
Temperature	Room temperature (25 °C)	
Light source	Xenon lamp ($\lambda \ge 420 \text{ nm } 10 \text{ mW/cm}^2$)	
Analysis	Gas chromatography (TCD)	



Fig. 3. EIS Nyquist plots of CN, PCN, OCN and POCN.

Reference

1) C. Li, H. Wu, D. Zhu, T Zhou, M. Yan, G. Chen, J. Sun, G. Dai, F. Ge, H. Dong, Appl. Catal. B: Environ. 297, 120433(2021).

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Study on LaFeO₃ photocathode for long-term stable photoelectrochemical water splitting

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Keywords: Photoelectrochemical water splitting, LaFeO₃, Green hydrogen

Most of conventional hydrogen production methods were based on unenvironmental-friendly processes such as natural gas steam reforming, coal gasification, and so on. The more the hydrogen demand increases, the more green hydrogen production techniques are necessary. Photoelectrochemical (PEC) water splitting is one of very attractive solutions for eco-friendly hydrogen production.¹⁻³ The photo-generated electrons and holes participate in the hydrogen evolution reaction at the photocathode and the oxygen evolution reaction at the photoanode, respectively. PEC water splitting needs only solar energy not any environmental-pollutional resources. However, it has some limits in technical aspects. Especially, long-term stability is one of significant issues in PEC water splitting. Most of semiconductor photocathodes reported so far were poor stability against aqueous solutions. Lanthanum iron oxide (LaFeO₃) is a promising p-type semiconductor to overcome this drawback because of its photocatalytic capability, optical characteristics and good stability in an aqueous solution. In addition, it is visible

light-responsive, enabling the utilization of abundant solar energy because its band gap energy is around 2.1-2.6 eV.4-6 Furthermore, it does not contain any copper component so that it is resistant to photocorrosion in aqueous solutions. Here, a crystalline LaFeO₃ thin film was prepared by radio frequency magnetron sputtering deposition. It was used as a PEC photocathode after post-annealing treatment in air. Figure 1 shows XRD patterns of sputtered LaFeO3 film according to the postannealing temperatures and SEM cross-view image of the crystalline sputtered LaFeO3 film. The morphological, compositional, optical and electronic properties of LaFeO3 photocathode were analyzed and optimized. It exhibited stable PEC performance in a strong alkaline solution during PEC operation without any protection layers. As a result, it was concluded that the crystalline LaFeO3 would be feasible to apply as a long-term stable PEC photocathode. Detailed results and analysis will be presented on the conference site.



Fig. 1. XRD patterns of sputtered LaFeO₃ film with/without the postannealing process at different temperatures and SEM image of LaFeO₃ film with the post-annealing process at 550 °C (inset).

References

1) M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori and N. S. Lewis, Chem. Rev., 110, 6446–6473 (2010).

2) C. Jiang, S. J. A. Moniz, A. Wang, T. Zhang and J. Tang, Chem. Soc. Rev., 46, 4645–4660 (2017).

3) J. H. Kim, D. Hansora, P. Sharma, J.-W. Jang and J. S. Lee, Chem. Soc. Rev., 48, 1908–1971 (2019).

4) S. N. Tijare, M. V. Joshi, P. S. Padole, P. A. Mangrulkar, S. S. Rayalu and N. K. Labhsetwar, Int. J. Hydrogen Energy, 37, 10451–10456 (2012).

5) M. D. Scafetta, A. M. Cordi, J. M. Rondinelli and S. J. May, J. Phys.: Condens. Matter, 26, 505502 (2014).
6) K. Peng, L. Fu, H. Yang and J. Ouyang, Sci. Rep., 6, 19723 (2016).

Electrodeposited Cu₂O with a Reduced Interfacial Amorphous Phase Using Artificially Oriented ITO and Their Enhanced Photoelectrochemical Solar to H₂ Efficiency

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The Insufficient light harvesting, quick charge recombination, and sluggish water reduction kinetics severely limit the efficiency of photoelectrochemical (PEC) water splitting. A photoelectrode needs to be purposefully constructed since the existence of amorphous phases in the interfaces makes it difficult to overcome these innate restrictions. Here, we used synthetic techniques to manipulate the crystallographic orientation of indium tin oxide (ITO) in order to identify the orientation that has the least amount of lattice misfit at the Cu₂O interface. This considerably reduced the amount of amorphous phase during the first stages of electrodeposition nucleation. By establishing an ideal interface with preferentially developed (111) oriented Cu₂O and minimizing the amorphous area, the [222]/[400] mixed orientation ITO largely exposed the {400} surface planes and accelerated charge transfer. In order to theoretically confirm which plane is more active for building the photoactivation layer, the ITO surface energy was also estimated using the density functional theory. The ITO/Cu₂O/Al-dope ZnO/TiO₂/Rh-P device, which was rationally built with each layer performing a distinct function, produced an effective solar-to-hydrogen conversion photocathode with a photocurrent density of 8.23 mA cm⁻² at 0 V_{RHE} under AM 1.5 G irradiation.

References (Example: non-mandatory, 10-point) :

1) J. H. Choi, H. Seok, D. Sung, D. S. Kim, H. H. Le, S. Hong, H. Kim, H. K. Cho, J. Eng. Chem. 82, 277-286 (2023)

[Abstract Guideline (Leave two lines for presentation number)]

Simulation of Water Electrolysis of Polymer Electrolyte Membranes

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Keywords: PEM, Electrolysis, Simulation, Hydrogen

For climate change issues, water electrolysis, which is one of a hydrogen gas generation method from carbon free electric power, is researched and developed for increasing in performance and decreasing costs. Polymer electrolyte membranes type as proton exchange membranes (PEM) electrolysis have similar structure to proton exchange membrane type of Fuel Cell.

It is necessary to utilize iridium as high cost catalysis for PEM electrolysis on the market. So it is important to develop efficient device. Then a water electrolysis cell is in experiment and simulation¹.

The efficiency of electric power generation is believed to be hindered by stagnant gas near porous feeder. This gas covers the electrode and prevents water from coming into contact with electrode². Additionally, there is a concern that the generated gas will accumulate downstream as it flows along the water channel¹.

We refer fuel cell model³ and introduce each simulation of fluid, thermal conduction and flow rate, along with an equivalent circuit model. We show the simulation model in fig. 1, and the thickness of each area of water electrolysis cell in table 1. The simulations are combined and we calculate the volume ratio of liquid and

fluid, saturation ratio. Furthermore, the simulation model incorporates the effect of stagnant gas that covers the electrode. Our model in fig. 2 demonstrates an increase in the saturation ratio and a decrease in the fluid flow rate of oxygen and hydrogen compared to a simulation model that does not consider the effect of stagnant gas. This indicate that our model can qualitatively represent the effect of stagnant gas covering the electrode.

References :

 T. Murakami, T. Hikosaka, T. Aranaga, K. Onda, K. Ito, IEEJ Transactions on Power and Energy 120-B(2), 256-263 (2000).
 D. L. Fritz, J. Mergel, D. Stolten, ECS Transactions 58(19), 1-9 (2014).
 H. Masuda, K. Ito, Y. Kakimoto, K. Sasaki, Transactions of the JSME (in Japanese) Vol. 73, No. 727, 855-862 (2007).

Table 1. Water electrolysis size		
No	Item	Thickness[cm]
1	anode channel(oxygen electrode)	0.03
2	anode porous feeder	0.05
3	proton-exchange membrane(PEM)	0.0178
4	cathode porous feeder	0.05
5	cathode channel(hydrogen electrode)	0.03



Fig. 1. Water electrolysis with proton-exchange membrane



Fig. 2. Saturation and material flow rate of bubble effect model(wt) normalized by result of without bubble effect(wo).

Eco-friendly Electrochemical Ammonia Oxidation of NiCuP Electrocatalyst for Hydrogen Production

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Keywords : Ammonia electrolysis, Ammonia Oxidation, Nickel copper phosphide, Hydrogen carrier, Hydrogen production

As a means to realize carbon neutrality, hydrogen, an alternative energy source, is in the limelight. However, since hydrogen is difficult to liquefy for transportation, it is important to use a hydrogen carrier that is relatively convenient to transport and has a high hydrogen storage capacity. Ammonia has a high potential for use as a hydrogen carrier, and it can theoretically convert hydrogen with low reaction energy through electro-oxidation, and COx is not generated as a product. In order to replace precious metals such as Pt, Ru, and Ir, research on non-noble metal catalysts is being actively conducted. In this work, a NiCuP electrocatalyst, a non-precious metal-based catalyst, was synthesized, and electrochemical analysis was performed on ammonia electrolysis, including ammonia oxidation reaction and hydrogen generation based on the electrochemical ammonia oxidation reaction was measured. NiCuP electrocatalyst presents the possibility of using ammonia as a hydrogen carrier for non-precious metal-based electrocatalysts.

Membrane Reactor Combining V-based Hydrogen Permeable Alloy Membrane with Ammonia Decomposition Catalyst for Direct High-Purity Hydrogen Production from Ammonia

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Keywords : Membrane reactor, Hydrogen carrier, Ammonia decomposition, Hydrogen separation, Metal membrane

Ammonia, NH₃, has recently attracted attention as one of the hydrogen carriers. Producing hydrogen fuel from NH₃ generally requires two steps: breaking down NH₃ into H₂ and N₂ and separating and purifying H₂. This study attempts to fabricate a membrane reactor for producing H₂ directly from NH₃ by combining a V-10mol%Fe hydrogen permeable alloy membrane¹⁾ and a Ru/Cs₂O/Pr₆O₁₁ catalyst²⁾ for NH₃ decomposition³⁾.

A schematic illustration of a membrane reactor for H_2 separation and purification from NH₃ is shown in Fig. 1. The membrane sample is sandwiched between SUS316L gaskets and fixed using Swagelok VCR fittings as the sample holder. 200 mg of the catalyst granules are set on the membrane sample and fixed with quartz wool. The sample holder is heated to 623 K using a tubular electric furnace. The NH₃ gas is fed to the catalyst from the outer tube of the inlet side at a flow rate of 10 or 20 mL min⁻¹ and a pressure of 0.15-0.30 MPa and decomposed to N₂ and H₂. The produced H₂ is separated selectively through the membrane to the outlet side evacuated using a turbo-molecular pump.

The results of the NH₃ decomposition using the membrane reactor are shown in Fig. 2. The conversion for Ru/Cs₂O/Pr₆O₁₁ catalyst alone, which is the result of the SUS-316L plate instead of the V-10mol%Fe membrane, is also shown in the figure for comparison. While the NH₃ conversion for the catalyst alone is 60% or less, combining the catalyst and V-10mol%Fe alloy membrane

increases the conversion to 80% or more. The hydrogen poisoning for the catalyst or the reverse reaction is suppressed by removing the H₂ with the membrane during the NH₃ decomposition, resulting in improved NH₃ conversion. The conversion tends to increase with increasing the reaction pressure in contrast to the catalyst alone. The maximum conversion is 88.5% at 0.3 MPa. According to the H₂ flow rate on the outlet side, 89.4% of the H₂ produced by NH₃ decomposition is permeated through the alloy membrane at this condition. Therefore, the ratio of H₂ separated directly to hydrogen contained in NH₃ is calculated as 79% by multiplying 88.5% of the NH₃ conversion and 89.4% of the separated H₂ ratio.

The Ru/Cs₂O/Pr₆O₁₁ catalyst and the V-10mol%Fe alloy membrane are highly durable, and the initial performance of the H₂ production rate lasts for more than 3000 h. In addition, the produced H₂ gas conforms to ISO 14687e2:2019 Grade D for fuel cell vehicles because the NH₃ and N₂ concentrations are less than 0.1 and 100 ppm, respectively.



Fig. 1. Schematic illustration of the membrane reactor.



Fig. 2. Changes in NH_3 conversion depending on total pressure with the membrane reactor.

References

A. Suzuki, H. Yukawa, T. Nambu, Y. Matsumoto, Y. Murata, Int. J. Hydrog. Energy 42,22325-22329 (2017).
 K. Nagaoka, T. Ebosh, N. Abe, S. Miyahara, K. Honda, K. Sato, Int. J. Hydrog. Energy 39, 20731-20735 (2014).

3) K. Omata, K. Sato, K. Nagaoka, H. Yukawa, Y. Matsumoto, T. Nambu, Int. J. Hydrog. Energy 47, 8372-8381 (2022).

The effect of ball milling on hydrogen release property of TiH₂

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Keywords: Titanium hydride, Ball milling, Hydrogen storage

Ti based compounds have been reported as excellent catalysts added into other metal hydrogen storage materials to improve the property of release and uptake hydrogen^{1,2}. TiH₂ is one of the commonly used catalysts that can significantly reduce the onset temperature of the material to release hydrogen³. Therefore, TiH₂ is a fascinating hydrogen storage material that deserves further discussion and research. However, regarding TiH₂ as a catalyst, no definition or explicit elucidation of its mechanism has been achieved thus far. Meanwhile, ball milling stands as the most commonly employed method for mechanically blending materials and enhancing the

performance of hydrogen storage materials. Hence, we conducted a systematic and fundamental study on the effect of ball milling on the performance of TiH_2 , such as shape, size, material composition, and hydrogen release capabilities.

Firstly, as received TiH₂ Powder was subjected to mechanical milling using a planetary ball milling at 400 rpm/min for 10min, 20min,30min, 1h, 2h and 4h. The ball to sample ratio was set to 75:1. Then the ball milled powders were collected and stored in glove box. All the sample handling was executed on glove box filled with high-purity N₂. Then all of samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (TDS) and so on.

The morphology and crystal size of ball-milled TiH₂ with different time of 10, 20, 30 min and 1, 2, 4 h were examined by SEM and XRD peaks using Scherrer equation. As ball milling time increased, crystal size and powder size were found to decrease significantly: crystal size was decreased from 23.7 to 3.2 nm, for commercial TiH₂ to 4 h ball-milled TiH₂.

Figure 1 hydrogen release property of different ball-milled sample and commercial sample. A significant decrease in the onset temperature of the first-step hydrogen release was found for ball-milled TiH₂, reducing from around 430 °C to approximately 150 °C. While the temperature for the principal hydrogen release in this step decreases from 450 °C to around 280 °C. However, with an increase in the ball milling time above 1h, temperature for the principal hydrogen release in the first step, from 280 °C to 320 °C. On the other hand, the temperature for the second-step hydrogen release continuously decreased from 510 °C to 400 °C. The details mechanism of the change in H₂ release temperature will be discussed in the presentation.

In summary, systematic study has been presented for the effect of different ball milling time on the performance of TiH₂. The results suggest that ball milling produces smaller sized TiH₂ enables to reduce the first-step hydrogen release temperature about 150 °C and reduce the onset temperature as much as 280 °C.



Fig. 1 TDS analysis of commercial TiH₂ and TiH₂ ball -milled for 10, 20, 30 min and 1, 2, 4 h.

References:

1) Sandrock, G., Gross, K. & Thomas, G. Journal of Alloys and Compounds. 339, 299-308 (2002).

2) Peng, C., Yang, C. & Zhang, Q. J. Mater. Chem. A 10, 12409–12417 (2022).

3) Snider, J. L. et al. Int. J. Hydrogen Energy 47, 403–419 (2022).

Hydrogen-gasochromic properties of Y-Mg, Ni-Mg, Mn-Mg and Gd switchable mirror films

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Keywords: hydrogen-gasochromism, hydro-/dehydrogenation, Y-Mg, Ni-Mg, Mn-Mg, Gd

Recently, thermal control solid-state devices that mimic electric circuits have been attracting attentions [1-4]. The switchable mirror materials such as Y-Mg, Ni-Mg, Mn-Mg, Gd, etc., can be reversibly switched between semiconductor (transparent) and metallic (reflective) states through hydrogenation and dehydrogenation reactions, respectively [4-8]. However, it is characterized by its lack of memory property since it cannot maintain the hydrogenated state unless hydrogen is continuously supplied. There are two methods of switching. One is the gasochromic method in which hydro-/dehydrogenation are performed directly by switching between hydrogen gas and atmosphere, respectively [6-8], whereas the another is the electrochromic method in which hydro-/dehydrogenation are performed by electrochemically driving hydrogen in the alkaline electrolyte [3].

Since the hydro-/dehydrogenation reactions of the switchable mirrors are reversible reactions, and as shown in previous studies, the thermal conductivity before and after hydrogenation is large, which could be expected to be applied to thermal switches [4,7,8]. As for the basic understanding on these reactions, it should be quite important to analyze on the temperature dependence of the reaction behavior. In this study, the gasochromic method was adopted as the switching method. We deposited the 100 nm-thick Y-Mg and Ni-Mg alloy films

top-caped with a 5 nm-thick Pd film as catalyst by dc sputtering. The in-situ analyses of optical and electrical properties were performed under a mixture of 3% H₂ and 97% N₂ gases. The hydro-/dehydrogenation kinetics of the gasochromic processes were analyzed in the temperature range from 30° C to 110° C (Fig. 1). In the case of Ni-Mg, hydrogenation kinetics over a narrower temperature range was analyzed. It was also found that once hydrogenated at the certain high temperature and then hydrogenated again at room temperature (25° C), the hydrogenation properties could not be restored [9]. The activation energies derived from

the temperature dependence of the hydro-/dehydrogenations reaction rates for the Y-Mg film in the reversible temperature range are shown in Fig. 2 (left) and (right), respectively.

We would also like to analyze the temperature dependence on the reactions of the other materials, such as Mn-Mg or Gd films. The differences in the gasocromic reactions and their activation energies for hydro-/dehydrogenation will be discussed in detail.



Fig. 1. The resistance changing rates of the Ni-Mg and Y-Mg films at the various temperatures.



References:

Fig. 2. Activation energies for hydrogenation (left) and dehydrogenation (right) reactions for the Y-Mg films estimated by Arrhenius plots in the reversible temperature ranges.

[1] K. Kim, et al., Phys. Rev. B 94, (2016) 155203. [2] G. Wehmeyer, et al., Appl. Phys. Rev. 4 (2017) 041304.
[3] H. Kizuka, et al., Jpn. J. Appl. Phys., Vol. 54, No. 5, (2015) 053201. [4] H. Saito, et al., Proc. 40th Jpn. Symp. Thermophys Prop. (2019) B223. [5] J. N. Huiberts, et al., Nature Vol. 380, No.6571, (1996) 231. [6] H. Yoshimura, et al., Jpn. J. Appl. Phys. 45, (2006) 3479. [7] K. Sugimoto, et al., Proc. 42th Jpn. Symp. Thermophys Prop. (2021) B312. [8] H. Yagi, et al., Proc. 42th Jpn. Symp. Thermophys. Prop. (2021) B312. [8] H. Yagi, et al., Proc. 42th Jpn. Symp. Thermophys. Prop. (2021) B313, (2022) B233. [9] K. Yoshimura, et al, Jpn. J. Appl. Phys. Vol. 46, No. 7A, pp. (2007) 4260.

Fabrication of all-solid-state thin film thermal switches using hydro-/dehydrogenation reactions of Y-Mg or Ni-Mg switching-mirror films

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Keywords: Y-Mg, Ni-Mg, all-solid-state thermal switches, hydro-/dehydrogenation, 3w method

All-solid-state thermal devices using laminated thin films are attracting attention as a variety of energy efficiency technologies, such as the ability to use waste heat applications. The advantages of the all-solid-state devices are that they can be switched using only laminated solid thin films. They should be also secureness, convenience and reliable because the electrolyte of "liquid-solution" is not used. The switchable mirror materials (SMMs) can reversibly change between semiconductor (transparent) state and metallic (mirror) state, which are caused by hydro-/dehydrogenation, respectively [1]. We have been reporting on the large changes in thermal conductivities of various SMM films depending on the changes in the electrical conductivity caused by hydro-/dehydrogenation controlled by both gasochromic and electrochromic methods [2-6]. In this study we are focusing on fabrication of the "all-solid-state thermal switches", in which the thermal conductivity can be largely controlled by hydro-/dehydrogenations. All the 7 layers in the devises were deposited by magnetron sputtering, i.e. transparent conducting film (ITO) / the switchable mirror films (Y-Mg or Ni-Mg) / catalyst film (Pd) / leakcurrent barrier film (thin-WO₃) / ion (proton) conducting film (Ta₂O₅) / ion storage film (thick-WO₃) / ITO on the glass substrate. The Pd layer is responsible for introducing and releasing hydrogen ions into the SMM layer and acts as a catalyst for hydro-/dehydrogenation reactions [2-6]. The ion-conducting layer Ta₂O₅ is an ion conductor that does not allow electrons to pass through, whereas allows hydrogen ions to pass through. The ion storage layer, WO₃, acts as a counter electrode of the SMM films and to store the hydrogen ions. The separation layer of the thin-WO₃ is to supress leakage current.

Figure 1 shows the schematic illustrations of the all-solid-state thermal switching devices [5]. The changes in transparency by applying ± 5 V are shown in Fig. 2. Effective thermal conductivities of all the layers for the each states were analyzed quntitatively by the 3ω method. In the case of using the Y-Mg film, the effective thermal conductivity for the dehydrogenated metalic state was 2.9 W m⁻¹ K⁻¹, whereas the one for the hydrogenated state was 1.7 W m⁻¹ K⁻¹. The thermal conductivities for the devices using the Ni-Mg film instead of the Y-Mg film will be also discussed in detail.



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Fig1. Schematic illustrations of the all-solid-state thermal switching devices using the laminated films.

Fig2. The switching device using the Y-Mg film in the metal or semiconductor states. 15 mm x 15 mm in size.

[1] Y. Yamada et al., Sol. Enegy Mater. Sol. Cells 99(2012) 73. [2] H. Yagi, et al., Proc. 42th Jpn. Symp. Thermophys. Proc. Prop. (2021) B313, (2022) B233. [3] K. Sugimoto, et al., Proc. 42th and 43th Jpn. Symp. Thermophys. Prop. (2021) B312 and (2022) B312. [4] H. Saito, et al., Proc. 40th Jpn. Symp. Thermophys. Prop. (2019) B223. [5] R. Nishimura, et al., Proc. 43th Jpn. Symp. Thermophys. Proc. (2022) B313. [6] D. Murakami, et al., Proc. 43th Jpn. Symp. Thermophys. Proc. (2022) B313.

Thermal conductivity changes of electrochemically hydrogenated and dehydrogenated Pd-catalyzed Ni-Mg alloy thin film

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Keywords: thermal switching device, Ni-Mg alloy film, electrochemical hydrogenation/dehydrogenation, thermal conductivity

Ni-Mg alloy films are known as the switchable mirror film not including rare earth elements. The switchable mirror materials can be reversibly changed between semiconductor and metallic states by hydro- and dehydrogenation reactions, respectively.¹) Since the free electron density is quite different between these two states, the Ni-Mg alloy films are expected to be utilized for thermal switching devices in which thermal conductivity can be controlled in the wide range.²) Saito *et al.* have reported that the thermal conductivity of the Y-Mg alloy thin film, the typical switchable mirror, can change between 7.1 W m⁻¹ K⁻¹ and 2.1 W m⁻¹ K⁻¹ by hydro- and dehydrogenation reactions.³) Since the electrical conductivity of Ni-Mg alloy is larger than those of Y-Mg alloy, the better thermal switching characteristics for the Ni-Mg alloy is expected. In this study, the hydrogenated and dehydrogenated states of a Pd-caped Ni-Mg alloy film were electrochemically controlled and thermal conductivities of both states were investigated using the in-situ rear-hearing/rear-detection type thermoreflectance apparatus.

The Cr/Ni-Mg/Pd three-layered thin films were fabricated on unheated synthetic quartz glass substrates by de magnetron sputtering using Cr, Ni-Mg alloy (Mg: 84 at%), and Pd targets. Nominal thicknesses of the Cr, Ni-Mg, and Pd films were 100 nm, 200 nm, and 5 nm, respectively. A pressure of Ar gas (99.999% in purity) during the Ni-Mg sputter depositions was kept at 5.0 Pa. The Ni-Mg alloy and Pd were laminated without exposure to the air. The Cr film plays roles of an electrode for electrochemical hydrogen intercalation and a reflective layer for the insitu thermoreflectance measurements. The thin Pd layer is a catalyst of the hydro-/dehydrogenations reactions. A

cyclic voltammetry (CV) using an electrochemical cell filed with 1M KOH aqueous solution was performed for three cycles with a scan rate of $8 \,\mathrm{mVs^{-1}}$ and a scanning range from -1.2 V to 0 V for the sufficient hydrogenation of the Ni-Mg alloy film after the thermal conductivity measurements in the as-deposited state. Based on these electrochemical analyses, the hydrogenation and dehydrogenation potentials were determined as -1.05 V and +0.3 V vs. Ag/AgCl, respectively. After applying certain potentials, thermal conductivities of the film at the hydro- and dehydrogenated states were measured.

Figure 1 shows the thermoreflectance signals of the Ni-Mg alloy film in the as-deposited, hydro-, and dehydrogenated states. The thermoreflectance signals show the clear difference between the hydro-/dehydrogenated states. Furthermore, it is found that the thermoreflectance signal returns to almost the same as that in the as-deposited state if the hydrogen was removed from the Ni-Mg hydride film. The thermal conductivities and the other physical properties will be reported in detail at the presentation.



Fig. 1. Thermoreflectance signals in the asdeposited state, the hydrogenated state at -1.05 V vs. Ag/AgCl and dehydrogenated state at +0.3 V for the Ni-Mg alloy film through the in-situ measurement using 1M KOH aq.

Acknowledgements

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References

1) K. Yoshimura, J. Vac. Soc. Jpn. 57 (2014) 84 (in Japanese). 2) H. Yagi, et al., Proc. the 42nd Jpn. Symp. Thermophys. Prop. (Online, October 25-27, 2021) B313 (in Japanese). 3) H. Saito, et al., Proc. of the 40th Japan Symposium on Thermophys. Prop. (Nagasaki, October 28-30, 2019) B223 (in Japanese).

Reversible electrical and thermal conductivities change of Pd-catalyzed Co-Mg films by gasochromic hydrogenation using N₂-H₂(3 %) gas

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Keywords: switchable mirror, Co-Mg alloy, thermal conductivity switch, hydro-/dehydrogenation, time domain thermoreflectance method

Co-Mg alloy is classified as one of the third-generation switchable mirror materials that consist of magnesium and transition metals, such as Ni and Mn¹). The Co-Mg alloy is considered to be mixtures of two binary intermetallic compounds (hexagonal MgCo₂ and cubic MgCo)²) and hexagonal close-packed Mg. On the other hand, the Co-Mg alloy hydride, that is semiconductor, consists of a mixture of rutile MgH₂ and tetragonal Mg₂CoH₅²). Since hydrogens leave the Co-Mg alloy hydride in the air, the Co-Mg alloy in the dehydrogenated state has same chemical composition of the as-deposited state. This study aims to clarify the thermal conductivity change of the Co-Mg alloy due to the hydro-/dehydrogenation reactions, i.e., metal-semiconductor transition, as expected as those of the Ni-Mg alloy³).

The Co-Mg alloy films with a nominal thickness of 200 nm were deposited on the unheated quartz glass substrates by dc magnetron sputtering using a Co-Mg alloy target (Mg: 50 at%) and Mg pellets with a total gas pressure of Ar of 3.0 Pa, followed by the deposition of the catalyst Pd films with a nominal thickness of 5 nm without exposure to the air. For the thermal conductivity measurement specimen, a Mo transducer film was deposited before the deposition of the Co-Mg layer. The chemical composition of the Co-Mg alloy film was analyzed to be Co : Mg = 28 : 72 by EPMA. The thermal conductivities were measured using the in-situ rear heating/rear detection type picosecond pulsed light heating thermoreflectance apparatus. The all in-situ measurements were started after 1 hour





exposing the sample to the N_2 -H₂(3 %) gas, whereas the measurements in the dehydrogenated state were carried out after at least half an hour exposure to air again to remove all hydrogen. Figure 1 shows the electrical conductivity of the Co-Mg layer in each state. The electrical conductivity of the dehydrogenated state is about 27 times as large as that of the hydrogenated state. Figure 2 shows the thermoreflectance signals of the Pd/Co-Mg/Mo layered film in each state. The signal in the hydrogenated state clearly differ from those of the others and the signal in the dehydrogenated state corresponds to that in the as-deposited state. The thermal conductivities in the hydrogenated and dehydrogenated states are 0.9 W m⁻¹ K⁻¹ and 7.5 W m⁻¹ K⁻¹, respectively. Consequently, we conclude that the electrical and thermophysical conductivities of Co-Mg alloy film change reversibly through hydro-/dehydrogenation reactions. Structural analysis including XAFS will be shown in the poster presentation. **Acknowledgement**

A part of this work was supported by JSPS Grants-in-Aid for Scientific Research (KAKENHI), Grant Number 23H01362.

References

1) Y. Kazuki et al., Synthesiology (in Japanese), Vol.5, No.4 (2012) 253.

2) van Geest-Lokhorst, A. C., Reflections on Switchable Mirror Devices, VRIJE University, 2006, Ph. D thesis.

3) H. Yagi, et al., Proceedings of the 43rd Japan Symposium on Thermophysical Properties (2022) B233.

Electrical, thermophysical and structural properties change for Gd hydrides thin films controlled by gasochromic hydro-/dehydrogenation

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Keywords: switchable mirror, gadolinium (Gd), gasochromism, hydrogenation, thermal switch

A thermal switch is a component of heat flow control technologies and has a sharp contrast in thermal conductivity between two on-/off-states controlled by external fields [1] or chemical reactions [2, 3]. Sugimoto et al. have focused on the switchable mirror materials which allows reversible switching between metal and semiconductor using hydro-/dehydrogenation reactions and have reported the thermal conductivity contrast of 6.1 times for the Y-Mg hydrides thin film [3]. In this study, we focus on Gd hydrides [4] whose electrical conductivity contrast is expected to be much greater than that of Y-Mg hydride. The purposes of this study are to directly fabricate GdH₂ film to avoid the damage caused by the internal stresses due to a volume expansion of 7.4 % from Gd to GdH₃ and to investigate the structural, electrical, and thermophysical properties of Gd and Gd hydrides in the hydro-/dehydrogenated states.

The Pd/GdH₂ (or Gd) /Mo films were fabricated by dc reactive magnetron sputtering under 1.0 Pa of a mixture of Ar and H₂ gases with the H₂ flow ratios of 0, 5, 30, and 50 %. The nominal thicknesses of Pd, GdH₂ (or Gd), and Mo are 5 nm, 300 nm, and 100 nm, respectively. The thermal conductivities of the films were measured using an in-situ time-domain thermoreflectance apparatus. The Pd/GdH₂ (or Gd) films were also prepared under the same sputtering conditions for the in-situ electrical and structural properties analyses. The measurements in the hydrogenated and dehydrogenated states were carried out after 90 min exposure to a mixture of Ar and H₂ (3 %) gases and after 90 min exposure to air, respectively. The measurement proceeded in the order of the as-deposited, hydrogenated, and dehydrogenated states.

Figure 1 shows the XRD patterns of Pd/GdH₂ (or Gd) films in the as-deposited state. Diffraction peaks of GdH₂ appear in all Pd/GdH₂ samples in the as-deposited state, confirming that GdH₂ films could be fabricated directly. Figure 2 shows the electrical conductivities of the Pd/GdH₂ (or Gd) films in the as-deposited, hydrogenated, and dehydrogenated states. The electrical conductivities of all GdH₂ films are smaller than the bulk value of 2.3×10^6 S[·] m⁻¹ [5]. The contrast between the hydrogenated and dehydrogenated states for the Pd/GdH₂ film, 52 (5 %), 2 (30 %), and 46 (50 %) times, are smaller than that of 334 times for the Pd/Gd film. Further results will be reported in the presentation.



Acknowledgement

A part of this work was supported by JSPS Grants-in-Aid for Scientific Research, Grant Number 23H01362. References

1) G. Wehmeyer et al., Appl. Phys. Rev., Vol. 4, 041304 (2017)., 2) H. Saito et al., Proc. Jpn. Symp. on Thermophys. Prop., B223 (2019)., 3) K. Sugimoto et al., Proc. Jpn. Symp. on Thermophys. Prop., B312 (2022)., 4) K. Yoshimura, J. Vac. Soc. Jpn., Vol. 57, No. 3, pp. 84-90 (2014)., 5) J. P. Burger et al., J. Less-Common Met., Vol. 103, pp. 381-388 (1984).

Changes in electrical and thermal conductivities of Sm film by gasochromic hydrogenation and dehydrogenation

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Keywords: hydrogen gasochromism, switchable mirror, Samarium, hydrogenation/dehydrogenation, thermal switch

Recently, thermal switching devices that can switch between low and high thermal conductivities have attracted attention [1], because of their effective use of waste heat energy for energy conservation. Kumar *et al.* have reported on the changes in optical properties of the Sm films due to the electrochemical hydro-/dehydrogenation reactions [2]. A metallic SmH₂ with a certain catalyst easily reacts on a dilute H₂ gas to SmH₃, which is a semiconductor and transparent. The reverse reaction, from SmH₃ to SmH₂, also occurs under an ambient atmosphere. Such a transformation between metal and semiconductor is expected to cause a change in thermal conductivity due to the different dominant heat carriers each other. In this study, in-situ analyses of the electrical and thermal conductivities of a Sm film in the hydro-/dehydrogenated states were carried out by means of a gasochromic method.

The Sm film with a thickness of 200 nm was deposited on a 100 nm thick Mo film coated quartz glass substrate by dc magnetron sputtering using a Sm metal target (99.5 % in purity) at 1.0 Pa of an Ar gas. The surface of the Sm film was capped with a Pd film with a nominal thickness of 5 nm by sputtering without exposure to the air. For the in-situ electrical conductivity measurement, a Sm single layer was also deposited on a quartz glass substrate under the same sputtering conditions. The Sm films were exposed to a mixture of 3 % H₂ and N₂ gases for 1 hour to hydrogenate the film, whereas the hydrogenated films were exposed to the air for 1 hour to dehydrogenate the film.

Figure 1 shows the electrical conductivities of the Sm film in the as-deposited(Sm), hydrogenated(SmH₃), and dehydrogenated(SmH₂) state. The electrical conductivity for the hydrogenated state is about 200 times lower than that of the dehydrogenated state. Figure 2 shows the thermoreflectance signals of the Pd/Sm/Mo three-layer film for the as-deposited state and 2 cycles of hydro-/dehydrogenated states. The thermoreflectance signals for the hydrogenated state decrease more slowly than those for the dehydrogenated state, which implies that thermal conductivity changes due to the hydrogenated and dehydrogenated states in the 2^{nd} cycle is smaller than that in the 1^{st} cycle. The thermal conductivity of the Sm film in each state will be presented at the conference.



hydro-/dehydrogenated states.

Acknowledgement

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References

[1] G. Wehmeyer et al, Appl. Phys. Rev. 4, 041304 (2017). [2] P. Kumar et al., Electrochem. Acta 49, 3355 (2004).

[Abstract Guideline (Leave two lines for presentation number)]

Development of Power Flow Simulation of Distributed Hydrogen System with Transient Characteristics Enabling Cost Analysis and Control Study

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Keywords: Distributed Hydrogen System, Physical model, Simulation, EMS, Electrolysis

In recent years, the utilization of renewable energy, especially solar power, has been active from the perspective of both global energy issues and the transformation to decarbonized society. However, since renewable energy is greatly influenced by nature, the surplus power generated is a major issue of its penetration.

Thus, Distributed Hydrogen Systems (DHSs) using water electrolysis cell (EC) to keep the power balance, as shown in Fig. 1, are attracting attention [1]. DHSs enable energy time-shift by storing surplus power from renewable energy sources as hydrogen. However, the high cost of EC as well as its auxiliary equipment, and complex system control, such as coordinating a huge amount of modules and stacks while limiting the number of startups and shutdowns due to the enlargement of DHSs, are challenges for their introduction.

In this study, a multi-domain power-flow DHS simulator has been developed in MATLAB/Simulink, which enables cost analysis and control studies (Fig. 2). Meanwhile, for EC, a key technology to decarbonized society, a physical model with overvoltage separation has been developed to represent transient characteristics under different temperature [2, 3].

With the cooperation of RIKEN, this study compared simulation result with real data from RIKEN's DHS, confirming that it is possible to reproduce the qualitative behavior of transient characteristics at multiple temperature levels of the entire system. It is also confirmed that accurate cost analysis is possible by conducting 1-year simulation with solar radiation data within Japan.

By simulating the transient behavior of multiple devices, this model enables system control studies for DHSs. Also, it is expected to be put to practical use for studies such as



Fig. 1. A Distributed Hydrogen System (DHS) proposed by RIKEN.



photovoltaics (PV).

the energy power storage with Business Continuity Plan considered and energy management working to keep the power balance.

References:

1) D. Yamashita, K. Tsuno, K. Koike, K. Fujii, S. Wada, M. Sugiyama, Int. J. Hydrog. Energy, 44, 27542-27552 (2019).

2) Z. Abdin, C.J. Webb, E.MacA. Gray, Int. J. Hydrog. Energy, 40, 13243-13257 (2015).

3) V. Liso, G. Savoia, S.S. Araya, G. Cinti, S.K. Kær, Energies, 11, 3273 (2018).

Zinc Aqueous Battery Anode Coated with Zinc Ion Conductive Polymer for Suppression of Dendrite Growth and Inhibition of Irreversible Hydrogen Evolution Reaction

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Keywords : Zinc ion battery, Zn metal anode, protective layer, PMMA

Zinc aqueous ion batteries offer significant advantages in terms of their low cost, high theoretical capacity, and recyclability. However, the cyclic performance of these batteries is hampered by challenges related to dendrite growth and irreversible hydrogen evolution reactions occurring at the zinc metal anodes and in the aqueous electrolyte. ^[1, 2] In this study, we propose an approach to address these challenges by introducing a protective layer composed of a zinc salt-added polymethylmethacrylate (PMMA:Zn) on the anode surface. The PMMA:Zn layer effectively mitigates direct contact between the electrode and electrolyte, thereby suppressing the undesired hydrogen evolution reaction. Moreover, the incorporation of uniformly dispersed zinc salts within the PMMA layer enhances ion conduction across the protective coating, promoting uniform zinc deposition between the current collector and the PMMA:Zn layer. As a result, this simple PMMA:Zn coating demonstrates remarkable improvements in cyclic performance, achieving a high Coulomb efficiency of nearly 100% for extended periods exceeding 2,000 hours, and enabling stable operation even at high current densities of 10 mA cm⁻².

References

1) T. Wang, C. Li, X. Xie, B. Lu, Z. He, S. Liang, J. Zhou, *ACS Nano* 2020, 14, 12, 16321–16347. 2) L. E. Blanc, D. Kundu, L. F. Nazar, Joule 4, 771–799, April15, 2020 Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O301] Oral 301

Chair:Toyoto Sato (Shibaura Institute of Technology) Wed. Dec 13, 2023 10:00 AM - 12:00 PM Session 14 (Room J)

[B3-O301-01 (Symposium Invited)]	A "Data-Theory-Methodology-Experiment"
	Framework to Design Effective Materials for
	Hydrogen Generation and Utilization
	*Hao Li ¹ (1. Tohoku Univ. (Japan))
	10:00 AM - 10:30 AM
[B3-O301-02]	Boron monosulfide as an electrocatalyst for the
	oxygen evolution reaction
	*Linghui Li', Satoshi Hagiwara ² , Cheng Jiang ³ , Haruki Kusaka', Norinobu Watanabe ¹ , Takeshi Fujita ⁴ , Fumiaki Kuroda ² ,
	Akiyasu Yamamoto ⁵ Masashi Miyakawa ⁶ Takashi Taniguchi ⁶
	Hideo Hosono ^{7,6} , Minoru Otani ² , Takahiro Kondo ^{8,9} (1.
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	Tsukuba, Tsukuba (Japan), 3. Inst. of Technical and
	Macromolecular Chemistry, RWTH Aachen Univ., Aachen
	(Germany), 4. School of Environmental Sci. and Engineering,
	Kochi Univ. of Tech., Kochi (Japan), 5. Tokyo Univ. of
	Agriculture and Tech., Tokyo (Japan), 6. Res. Center for
	Functional Materials, NIMS, Tsukuba (Japan), 7. Materials Res.
	Center for Element Strategy, Tokyo Inst. of Tech., Yokohama
	(Japan), 8. Department of Materials Sci. and Tsukuba Res.
	Center for Energy Materials Science, Inst. of Pure and Applied
	Sci., Univ. of Tsukuba, Tsukuba (Japan), 9. Advanced Inst. for
	Materials Res., Tohoku Univ., Sendai (Japan))
	10:30 AM - 10:50 AM
[B3-O301-03]	Reducing H ₂ Release Temperature From MgH ₂ Using Ni/HB Nanocomposite
	*Natsumi Noguchi ¹ , Kazuho Goto ¹ , Shin-ichi Ito ¹ , Takeshi Fuiita
	² . Hideo Hosono ^{3,4} . Shin-ichi Orimo ^{5,6} . Takahiro Kondo ^{5,7,8} (1.
	Univ. Tsukuba (Japan), 2. Kochi Univ. Tech. (Japan), 3. Tokyo
	Tech. (Japan). 4. NIMS (Japan). 5. WPI-AIMR. Tohoku Univ.
	(Japan) 6 JMR Tohoku Univ. (Japan) 7 TREMS Univ. Tsukuba
	(Japan) 8 ZeroFEM Univ Tsukuba (Japan))
	10.50 AM - 11.10 AM
[B3-0301-05]	Ammonia Electrolysis Using Ni P@N-C
[20 0001 00]	Electrocatalyst for Eco-friendly Hydrogen
	Production
	*Chanmin lo^1 Subramani Surendran ¹ Min-Cheol Kim ²
	Gnanaprakasam Janani ¹ Dae Jun Moon ^{1,3} Joon Young Kim ^{1,3}
	lung Kyu Kim ² Uk Sim ^{1,3} (1 Korea last of Energy Tach
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(Korea), 2. Sungkyunkwan Univ. (Korea), 3. NEEL Sci., INC. (Korea)) 11:30 AM - 11:50 AM

[Abstract Guideline (Leave two lines for presentation number)]

A "Data-Theory-Methodology-Experiment" Framework to Design Effective Materials for Hydrogen Generation and Utilization

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Keywords: Materials Theory, Materials Design, Electrocatalyst, Electrolyte, Hydrogen Storage

The design of solid-state materials for hydrogen generation and utilization is essential for a sustainable future. However, conventional materials search sometimes relies on the trial-and-error process from experiments. Meanwhile, theoretical analysis of materials is sometimes too complicated to develop a clear guideline for experiments. This talk will discuss an avenue to realize a data-driven framework for hydrogen-related materials design combining data-mining, materials theory, computational methodology development, and experiments. In particular, we will discuss i) how to reduce the complexity in catalyst design by materials theory and ii) how to develop new computational methods (i.e., new package, model, and algorithm) to accelerate materials simulation. This talk will show the predictive power of theory in electrochemical and thermal catalysis,¹⁻³ solid-state hydride electrolytes, and solid-state hydrogen storage materials.⁴⁻⁵ We will also discuss the successful design of an "electron-refinery" strategy by transforming high-temperature thermal catalysis into low-temperature electrocatalysis.⁶ Finally, we will discuss the practical design of materials combining data science, materials theory, computational screening, computational methodology development, and experiments.

References:

1) H. Li, S. Kelly, D. Guevarrac, Z. Wang, Y. Wang, J. A. Haber, M. Anand, G. Gunasooriya, C. S. Abraham, S. Vijay, J. M. Gregoire, J. K. Nørskov. Nature Catal. 4, 463-468 (2021)

2) M. Li, X, Wang, K. Liu, H. Sun, K. Huang, D. Sun, Y. Tang, W. Xing, H. Li, G. Fu, Adv. Mater. 2302462 (2023)

3) C. Liu, Z. Yu, F. She, J. Chen, F. Liu, J. Qu, J. M. Cairney, C. Wu, K. Liu, W. Yang, H. Zheng, Y. Chen, H. Li, L. Wei, Energy Environ. Sci. 16, 446-459 (2023)

4) S. Dong, C. Li, J. Wang, H. Liu, Z. Ding, Z. Gao, W. Yang, W. Lv, L. Wei, Y. Wu, H. Li, J. Mater. Chem. A, 10, 22363-22372 (2022).

5) S. Dong, C. Lia, E. Lv, J. Wang, H. Liu, Z. Gao, Z. Ding, W. Xiong, W. Yang, H. Li, J. Mater. Chem. A, 10, 19839-19851 (2022).

6) H. Li, C. S. Abraham, M. Anand, A. Cao, J. K. Nørskov, J. Phys. Chem. Lett., 13, 9, 2057–2063 (2022)

Boron monosulfide as an electrocatalyst for the oxygen evolution reaction

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Keywords : boron monosulfide, electrocatalyst, oxygen evolution reaction, renewable energy device

As a clean and reliable energy technology, hydrogen is regarded as an appropriate alternative to fossil fuel, while water electrolysis using intermittent electric energy represents a promising commercial technology for industrial hydrogen production [1]. Water splitting reaction consists of hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. Compared with the HER, the OER has sluggish kinetics and a large reaction barrier, limiting the efficiency of electrocatalytic water splitting [2]. Thus, the development of highly active oxygen evolution electrocatalysts has become a

research hotspot. Currently, noble metals and metal oxides are the most widely used catalysts for OER electrocatalysis. However, metal-based catalysts often suffer from multiple disadvantages, including high cost, low selectivity, poor durability, impurity poisoning and fuel crossover effects [3]. Therefore, metal-free catalysts have received increasing interest as promising electrocatalysts for advanced energy conversion and storage.

We focused on rhombohedral boron monosulfide (r-BS), which is a new metal-free catalyst. r-BS was synthesized by a previously reported high-pressure solid-state reaction [4], wherein a mixture of amorphous boron and sulfur with an atomic ratio of 1:1. Here, we report that r-BS mixed with graphene (r-BS+G) as a new metal-free electrocatalyst, shows promising electrocatalytic activity with much better performance than most published metal-based catalysts in 1M KOH solution [5].

To prepare the r-BS+G mixture, r-BS powder and GNP were combined in ethanol and then exposed to bath sonication. As shown in Fig. 1a and 1b, the r-BS+G shows significantly enhanced OER activity with the ultralow an overpotential of 259 mV at 10 mA cm⁻², which is 41 mV better than commercial RuO₂. Furthermore, the overpotential (259 mV) of r-BS+G is much lower than those of most reported metal-free OER electrocatalysts [6]. The mixing process was just a simple sonication but probably ameliorated the conductivity to effectively used active sites of r-BS. And the stability of r-BS was explored by cyclic voltammetry (CV), as Fig. 1b exhibited, after CV between 1.20 and 1.53 V (v s. RHE) for 500 cycles, r-BS+G showed negligible degradation, demonstrating its good durability.



Fig. 1 a, Linear sweep voltammetry curves toward OER. **b,** Linear sweep voltammetry curves of r-BS+G after 500 CV cycles (1.20 V-1.53 V) [5].

In summary, we have developed a new effective metal-free electrocatalyst for OER, and it gives a new strategy to study high-efficient electrocatalysts for future potential applications.

References:

- 1) Z. Y.Yu, Y. Duan, et al. Adv. Mater. 33, e2007100 (2021).
- 2) P. Zhai, C.Wang, et al. Nat. Commun. 14, 1873 (2023).
- 3) S. Pan, H. Li, D. Liu, et al. Nat. Commu. 13, 1-10 (2022).
- 4) H. Kusaka, et al., J. Mater. Chem. A, 9, 24631 (2021).
- 5) Li. L, et al., Submitted.
- 6) Z. P. Wu, et al., Adv. Fun. Mater. 30, 1910274 (2020).

Reducing H₂ Release Temperature From MgH₂ Using Ni/HB Nanocomposite

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Keywords : HB sheets, Ni nanocluster, Hydrogen storage material, 2D material, Nano-composites

Hydrogen boride (HB) sheets are two-dimensional materials comprising a negatively charged hexagonal boron network and positively charged hydrogen atoms with a stoichiometric ratio of 1:1.¹ In a previous study, it was reported that HB sheets reduce metals with redox potentials higher than Ni to form metal nanocomposites.² We reported the spontaneous formation of highly dispersed Ni nanoclusters on HB sheets.³ The product is called Ni/HB composite. The spontaneous reduction of Ni ions by the HB sheet was monitored by in situ measurements with a UV-visible spectrometer. Considering the increase in absorbance over time, the results suggest that Ni metal clusters were growing on the HB sheet. Based on the results of transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and selected area electron diffraction, Ni nanoclusters were spontaneously formed on the HB sheet, small (1-3 nm in diameter) and randomly distributed (Fig. 1) ³.

Mg-based alloys, including MgH₂, are attracting attention⁴ as hydrogen storage materials because Mg is abundant on earth, they are lighter in weight than other alloy-based materials, have a high gravimetric hydrogen density (up to 7.6 wt%), and can be safely transported due to their thermodynamic stability ($\Delta H = -74.5 \text{ kJ/mol}$). However, hydrogen release and absorption are slow due to the strong bonding between Mg and hydrogen, and the amount of hydrogen absorbed decreases with repeated absorption and desorption. In addition, MgH₂ is thermodynamically stable and thus safe, but requires high temperatures for hydrogen release. Therefore, a reduction in temperature and an increase in the rate of hydrogen absorption and release are required for practical use. To solve these problems, supporting finely processed MgH₂ on two-dimensional materials with catalysts has been widely used^{4.5}. In particular, the use of Ni as a metal catalyst has been reported to increase hydrogen absorption and lower hydrogen release and absorption temperatures⁶. Herein, we will report that MgH₂ supported on Ni/HB composite (MgH₂-Ni/HB) shows lower H₂ release temperature. We hypothesized that by loading MgH₂ onto Ni/HB, the aggregation of MgH₂ would be prevented and the catalytic effect of Ni would lower the H₂ release

temperature. Practically, the H_2 release temperature of MgH₂-Ni/HB was 567 K, about 130 K lower than that of commercial MgH₂ (700 K) (Fig. 2). It is also interesting to note that the shape of the hydrogen intensity peak remained unchanged as a single peak. If only the MgH₂ in the Ni contact area were affected, there would be MgH₂ with different compositions and the peak would be split into two or more. Thus, this result suggests that 2wt% Ni affects the entire MgH₂, not just the Ni-MgH₂ contact area. Therefore, it is possible that Ni acts as a catalyst, lowering the activation energy, or a new compound is formed from Ni, HB, and MgH₂, raising the energy of the reactants and lowering the apparent activation energy. The details of the results including thermodynamic parameters measurements will be presented.

References :

1) Nishino, H. et al. J. Am. Chem. Soc. 139, 13761 (2017).

- 2) Ito, S. I. et al., Chem. Lett. 49, 789 (2020).
- 3) Noguchi, N. et al., Molecules 27, 8261 (2022).
- 4) L. Ren, et al., Nano-Micro Lett. 14, 144 (2022)
- 5) C. Duan, et al., Renewable Energy. 187, 417 (2022)
- 6) Dan, et al., ACS Appl. Energy Mater. 5, 4976 (2022)



Fig. 1 TEM image of Ni/HB composite, and histogram of diameter of Ni nanoclusters³.



Fig. 2 H₂ release during heating.

Ammonia Electrolysis Using Ni₂P@N-C Electrocatalyst for Eco-friendly Hydrogen Production

<u>Chanmin Jo¹</u>, Subramani Surendran¹, Min-Cheol Kim², Gnanaprakasam Janani¹, Dae Jun Moon^{1,3}, Joon Young Kim^{1,3}, Jung Kyu Kim² and ^{*}Uk Sim^{1,3}

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Keywords : Ammonia electrolysis, Ammonia Oxidation, Nickel phosphide, Hydrogen carrier, Hydrogen production

Hydrogen, an alternative energy source, is emerging to realize carbon neutrality through substitution of fossil fuels. There is a need to improve transportation efficiency by using hydrogen carriers instead of hydrogen, which has limitations in transportation. Ammonia is a promising material for use as a hydrogen carrier. Such ammonia can be converted into hydrogen through ammonia electrolysis, and theoretically, energy consumption is low and COx is not generated. Ammonia electrolysis is carried out through an oxidation reaction (AOR) at the anode and a hydrogen generation reaction (HER) at the cathode. Non-noble metal catalysts, which are catalytic materials to replace noble metals such as Pt, are being studied. Among them, nickel is a material with excellent AOR activity, but it has a corrosion problem. To solve this problem, it was synthesized in the form of a phosphide known to have good corrosion resistance.

In this work, nickel phosphide (Ni₂P@N-C) supported on nitrogen-doped carbon for ammonia electrolysis was synthesized by hydrothermal method. To determine whether AOR or not, a three-electrode system was constructed to measure the ammonia concentration profile. based on the electrical conductivity and charge dynamics of the catalyst improved by the formation of the N-doped carbon matrix, about 78% of the ammonia decomposition was confirmed compared to the initial concentration. In the whole cell system, 11.2 mL of hydrogen generated during 30 minutes was captured. Ammonia electrolysis shows improved hydrogen production over water electrolysis.

References :

1) C Jo, S. Surendran, M.-C. Kim, T.-Y. An, Y. Lim, H. Choi, G. Janani, S. C. Jesudass, D. J. Moon, J. Kim, J. Y. Kim, C. H. Choi, M. Kim, J. K. Kim, and U. Sim, Chem. Eng. J. 463, 142314 (2023).



Fig. 1. H_2 generation of $Ni_2P@N\text{-}C$ with and without NH_4OH

Oral Session | B. Energy | [B-3] Hydrogenomics

[B3-O401] Oral 401

Chair: Takahiro Kondo (University of Tsukuba), Takahiro Ishikawa (The University of Tokyo) Thu. Dec 14, 2023 9:00 AM - 12:00 PM Session 14 (Room J)

[B3-O401-01]	Topological Data Analysis Based on Persistent Homology for the Superionic Conductors *Ryuhei Sato ¹ , Kazuto Akagi ¹ , Shigeyuki Takagi ² , Kartik Sau ^{1,3} , Kazuaki Kisu ² , Hao Li ¹ , Shinichi Orimo ^{1,2} (1. Advanced Insitute for Materials Research, Tohoku University (Japan), 2. Institute for Materials Research, Tohoku University (Japan), 3. Mathematics for Advanced Materials Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology (Japan))
[B3-O401-02]	9:00 AM - 9:20 AM A Comprehensive Study of Correlation Effects on Ion Conduction in Hydrides *Kartik Sau ^{1,2} , Shigeyuki Takagi ³ , Tamio Ikeshoji ² , Kazuaki Kisu ³ , Ryuhei Sato ¹ , Shin-ichi Orimo ^{1,2} (1. Advanced Institute for Materials Research (WPI-AIMR), Tohoku University (Japan), 2. Mathematics for Advanced Materials Open Innovation Laboratory (MathAM-OIL), AIST, c/o WPI-AIMR, Tohoku University, Sendai 980-8577, Japan (Japan), 3. Institute for Materials Research (IMR), Tohoku University, Sendai 980- 8577, Japan (Japan)) 9:20 AM - 9:40 AM
[B3-O401-03]	Evolutionary Search for Superconducting Phases in the Lanthanum-Nitrogen-Hydrogen System with Universal Neural Network Potential PFP *Takahiro Ishikawa ¹ , Shinji Tsuneyuki ¹ (1. The Univ. of Tokyo (Japan)) 9:40 AM - 10:00 AM
[B3-O401-04 (Symposium Invited)]	Development of High-pressure Diffusion Control Method for Synthesizing Metastable Materials *Masaya Fujioka ^{1,2} (1. Advanced Industrial Science and Technology (Japan), 2. Hokkaido Univ. (Japan)) 10:20 AM - 10:50 AM
[B3-O401-05]	Synthesis of Complex Transition Metal Hydrides Containing Polynuclear Hydride Complexes with High Hydrogen Coordination *Shigeyuki Takagi ¹ , Takehiro Hashimoto ¹ , Kenjiro Otsuki ¹ , Reina Utsumi ^{2,3} , Yuki Nakahira ² , Hiroyuki Saitoh ^{2,3} , Shin-ichi Orimo ^{1,4} (1. Institute for Materials Research, Tohoku University (Japan), 2. National Institutes for Quantum Science

	and Technology (Japan), 3. University of Hyogo (Japan), 4. Advanced Institute for Materials Research, Tohoku University (Japan)) 10:50 AM - 11:10 AM
[B3-O401-06]	Mn-rich Al– Mn alloy hydrides synthesized under high pressure and high temperature with the aid of in-situ synchrotron radiation X-ray diffraction measurement
	*Reina Utsumi ^{1,2} , Saya Ajito ³ , Yuki Nakahira ¹ , Hiroyuki Saitoh ^{1,2} , Tetsu Watanuki ^{1,2} , Toyoto Sato ⁴ , Shigeyuki Takagi ³ , Eiji Akiyama ³ , Shin-ichi Orimo ³ (1. National Inst. for Quantum Sci. and Tech. (Japan), 2. Univ. of Hyogo (Japan), 3. Tohoku Univ. (Japan), 4. Shibaura Inst. Tech. (Japan)) 11:10 AM - 11:30 AM
[B3-O401-07]	High-pressure and high-temperature synthesis of novel hydrides with the aid of in-situ synchrotron radiation x-ray diffraction measurement *Hiroyuki Saitoh ¹ (1. National Institutes for Quantum Science and Technology (Japan)) 11:30 AM - 11:50 AM

Topological Data Analysis Based on Persistent Homology for the Superionic Conductors

*<u>Ryuhei Sato 1</u>, Kazuto Akagi¹, Shigeyuki Takagi², Kartik Sau^{1,3}, Kazuaki Kisu², Hao Li¹, Shin-ichi Orimo^{1,2}

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Keywords: Topological data analysis, Persistent homology, Superionic conductor, concerted motion

There is a common phenomenon in hydride-based superionic conductors such as $LiCB_9H_{10}^{1}$ and Ba-Li oxyhydrides² called the concerted motion of ions. In this concerted motion of ions, multiple ions migrate simultaneously. In this phenomenon, the interaction between mobile ions and the interaction between the mobile ion and the lattice (or complex hydrides) must be taken into account. In other words, the concerted motion of ions is a complex many-body problem. Therefore, it is difficult to understand such phenomena from conventional two-body correlation functions or macroscopic properties of the entire system.

Topological data analysis based on persistent homology is a method to analyze a pore or ring structure composed of atoms in a given atomic coordinate. The persistence diagram obtained from this analysis is a distribution of the obtained ring structure and the ring structure composed of multiple atoms can be easily converted into two-dimensional information. Considering the conventional picture in defect chemistry, ion migration occurs around ionic defects. Ionic defects can be analyzed as large ring or pore structures on the persistence diagram. Therefore, it is considered that ion migration can be analyzed from the changes in this ring structure related to the ionic defect during ion migration. Here, we performed topological data analysis on molecular dynamics simulations of superionic conductors to clarify whether such a persistent diagram is applicable to the analysis of complex ion migration like concerted motion of ions³.

The figure shows the time-averaged persistence diagram of α -AgI (a known solid-state superionic conductor) during 3-ns NVT molecular dynamics simulations. AgI shows a phase transition around 440 K and α -phase shows high conductivity. In this calculation, only the α -phase is obtained because the cell size is fixed for that of α -phase, but superionic conduction is observed in the temperature range above 440K. Comparison of the

persistence diagrams shows that a new ring structure (black dotted line) appears with superionic conduction. Therefore, these new ring structures are considered to be related to the ion migration. We obtained statistics on the shape of the ring structure, such as the number of ions and the distance between ions, and determined the averaged structure for each (Birth,Death) mesh. Based on the obtained statistics, the new ring structures along the black dotted line are four-membered rings. The concerted motion of Ag ions via the four-membered ring is reproduced by deforming the four-membered ring along the dotted line, as shown in Fig (b), showing us that topological data analysis is effective for complex ion migration like concerted motion of ions.

References : 1) S. Kim et al. *Nat. Commun.*, 10 (2019) 1081. 2) F. Takeiri et. al., *Nat. Mater.*, 21 (2022) 325. 3) R. Sato et al., *J. Chem. Phys.*, 158 (2023) 144116.



Figure (a) Time-averaged persistence diagram of the ring structure during MD simulations of α -Agl at 360 and 1000K. (b) Ag migration via four-membered ring reproduced from the reverse analysis of persistence diagram³.

MRS-Japan

Investigating Correlation Effects on Cationic Conduction in Hydrides: A Comprehensive Study

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Keywords: Molecular dynamics simulation, Ion conduction, Ion-ion correlation

Complex metal hydrides have received significant attention as potential solid electrolytes in all-solid-state batteries [1, 2]. Their remarkable ionic conductivity in the high-temperature phase makes them suitable candidates for such applications. However, their conductivity at room temperature is considerably low, and achieving a high conducting phase at low temperatures presents a challenge that has attracted substantial research interest. Despite recent efforts to understand the origin and factors influencing high ionic conductivity at high temperatures, many aspects remain elusive. In this study, we aim to shed light on the role of cation-cation, anion-cation, and anion-anion correlations (Figure 1) in cationic conduction by employing molecular dynamics (MD) simulations. Specifically, we will focus on $Li_2B_{12}H_{12}$, $LiCB_{11}H_{12}$, and $C_2B_{10}H_{12}$ and utilize a previously established force-field.



Figure 1. (a) Ball and stick model of Ordered structure of $Li_2B_{12}H_{12}$. Schematic diagram of (b) cation-cation, (c) anion-cation (paddlewheel mechanism), and (d) anion-anion correlation. Where the red, green, and blue balls are Li, B, and H, respectively and the blue arrow indicates the translational or diffusional motion.

The previously developed force-field has successfully demonstrated the ordered-disordered phase transition, as well as the structural and dynamical behavior of this series of complex hydrides [3, 4]. By conducting comparative MD simulations on these materials, we can gain insights into the relationship between cation-cation, anion-cation, and anion-anion correlations.Furthermore, we can analyze the correlation study by altering the anionic ordering, specifically between body-centered or face-centered positions. Understanding how such changes in anionic ordering affects the transition temperature of the ordered-disordered phase transition is crucial for lowering the transition temperature.

In summary, this study aims to elucidate the influence of cation-cation, anion-cation, and anion-anion correlations on cationic conduction in complex hydrides. By utilizing MD simulations and a well-established force-field, we can gain valuable insights into the behavior of these materials and their potential for improving the performance of all-solid-state batteries.

References: [1] Mohtadi and Orimo, Nat. Rev. Mater. (2017). [2] Kim et al., Nat. Commun. (2019). [3] Sau et al., Chem. Mater. (2021). [4] Sau et al., Mater. Adv. (2023).

Evolutionary Search for Superconducting Phases in the Lanthanum-Nitrogen-Hydrogen System with Universal Neural Network Potential PFP

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Keywords: Hydride, Superconductivity, Evolutionary algorithm, First-principles calculations, Universal neural network potential

Lanthanum hydride (La-H) has attracted much attention as a potential candidate for room-temperature superconductivity since the discovery of the superconductivity at 260 K at pressure of 170 GPa^{1,2}. Further experiments for the La-H system revealed that the superconducting critical temperature T_c shows further increase to 556 K by subsequent thermal excursions to high temperatures³. Although the reason for the significant enhancement of T_c remains unknown, it has been considered that the enhancement is caused by some reactions of the La-H compounds with nitrogen (N) and boron (B) originating from ammonia borane, NH₃BH₃, used for a hydrogen-source material. Hence, it is crucial to search for stable phases in the La-N-H, La-B-H, and La-B-N-H systems and verify whether they show high- T_c superconductivity.

In this study, we searched for stable and metastable phases in the La-N-H system at 20 GPa using the evolutionary construction scheme of a formation-energy convex hull⁴. At each generation, first, we quickly optimized a few thousand structures created by our search scheme using universal neural network potentials named Preferred Potential (PFP)⁵ version 3.0.0 on Matlantis⁶, and then extracted only a few ten structures emerging in the region of $\Delta H \leq 4.4$ mRy/atom, where ΔH denotes the enthalpy difference to the convex. Next, for the extracted structures, we performed structural optimization based on the density functional theory with the Quantum ESPRESSO (QE) code⁷ and updated the convex hull. We repeated this process up to the 8th generation. For the stable compounds, we calculated the electron-phonon coupling constant λ and the logarithmic averaged phonon frequency ω_{\log} using the QE code⁷ and evaluated T_c using the Allen-Dynes formula⁸.

We obtained La₃NH₆, LaNH₂, La₂NH₃, La₂N₅H₉, LaN₂H₃, and La₅N₂H₃ as stable ternary compounds, and La₃NH₄, La₆N₂H₉, and La₅NH₄ as moderately metastable ones which can be synthesized by experiments. In these hydrides, La₃NH₄, La₆N₂H₉, and La₅NH₄ show the superconductivity at 20 GPa. The highest T_c value, however, is 8.6 K ($\lambda = 0.7246$ and $\omega_{log} = 217$ K) predicted in La₃NH₄, which is far from high T_c superconductivity.

This work is supported by ENEOS Corporation.

References:

1) M. Somayazulu, M. Ahart, A. K. Mishra, Z. M. Geballe, M. Baldini, Y. Meng, V. V. Struzhkin, R. J. Hemley, Phys. Rev. Lett. 122, 027001 (2019).

2) A. P. Drozdov, P. P. Kong, V. S. Minkov, S. P. Besedin, M. A. Kuzovnikov, S. Mozaffari, L. Balicas, F. F. Balakirev, D. E. Graf, V. B. Prakapenka, E. Greenberg, D. A. Knyazev, M. Tkacz, and M. I. Eremets. Nature 569, 528 (2019).

3) A. D. Grockowiak, M. Ahart, T. Helm, W. A. Coniglio, R. Kumar, K. Glazyrin, G. Garbarino, Y. Meng, M. Oliff, V. Williams, N. W. Ashcroft, R. J. Hemley, M. Somayazulu, and S. W. Tozer, Front. Electron. Mater. 2, 837651 (2022).

4) T. Ishikawa and T. Miyake, Phys. Rev. B 101, 214106 (2020).

5) S. Takamoto, C. Shinagawa, D. Motoki, K. Nakago, W. Li, I. Kurata, T. Watanabe, Y. Yayama, H. Iriguchi, Y. Asano, T. Onodera, T. Ishii, T. Kudo, H. Ono, R. Sawada, R. Ishitani, M. Ong, T. Yamaguchi, T. Kataoka, A. Hayashi, N. Charoenphakdee, and T. Ibuka, Nat Commun 13, 2991 (2022).

6) Matlantis (<u>https://matlantis.com/</u>), software as a service style material discovery tool.

7) P. Giannozzi et al., J. Phys.: Condens. Matter 21, 395502 (2009).

8) P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).

Development of High-pressure Diffusion Control Method for Synthesizing Metastable Materials

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Keywords: High pressure, Ion diffusion, Metastable materials

Our research interest is the synthesis of metastable materials by controlling anisotropic ion diffusion. The controllable ions in a compound should have the weakest chemical bounding state among the constituent elements. Additionally, other elements should be strongly connected to each other and maintain the basic crystal structure against the diffusion of controllable ions. If such controllable ions can be extracted, introduced, or exchanged by utilizing ion diffusion, metastable materials can be synthesized. Also, it is necessary to apply a driving force at an appropriate temperature at which only controllable ions are thermally excited. The most commonly used driving force is an electric field. However, this way is not applicable to electron-conducting materials due to electrostatic shielding. On the other hand, the gradient of chemical potential ($\Delta \mu$) can be available as the driving force regardless of electric properties.

According to this idea, some metastable materials based on ion diffusion control have been synthesized by developing the synthesis methods skilfully inducing $\Delta \mu$. For example, the anisotropic diffusion control (ADC) method homogeneously extracted Na ions from a large single crystalline Na₂₄Si₁₃₆ with metallic conductivity. Then, the cage-like covalent framework of Si₁₃₆ was obtained as a metastable phase ¹). The proton-driven ion introduction (PDII) is the synthesis method that can introduce the various guest ions into host materials by utilizing proton irradiation to solid electrolytes. The PDII successfully synthesized metastable Ag_{2.5}ZrTe₃ by introducing Ag ions into transition metal trichlcogenides: ZrTe₃ with metallic conductivity ²).

Thus, the methods utilizing ion diffusion: ADC, and PDII, are effective in synthesizing metastable compounds. However, such a macroscopic compositional change may cause strain due to a change in the sample volume, forming cracks and irregularities suppressing ion diffusion. This problem is particularly conspicuous at the grain boundaries of polycrystalline samples. In addition, during macroscopic compositional changes under high temperatures, materials absorb atmospheric gases, such as oxygen, and undergo unexpected chemical reactions that compensate for the compositional changes. Thus, these factors often impede ideal material synthesis based on anisotropic ion diffusion.

To address these challenges, we developed the high-pressure diffusion control (HPDC) method; the cubic multi-anvil apparatus and the technique of ADC were combined. Figures 1(a) and 1(b) show the conventional and novel cells for high-pressure (HP) synthesis and HPDC, respectively. In the novel cell, the temperature can be controlled by energizing a heater through Cu or Mo electrodes on the side surface so that the upper and lower Mo electrodes are connected to the inside of the sample space, enabling electrical processing. As shown in Figure 1(c), since the temperature rises to 1000°C with an input power of 600 W, the heater electrodes function well even in the introduction from the side surface. In this way, HPDC can adjust the three synthesis parameters: temperature, pressure, and voltage (Figure 1(d))³⁾, and is also expected to produce hydrides. The details of HPDC and the obtained compounds will be presented at the conference.

References

- 1) S. Iwasaki et.al., Adv. Mater. 34, 2106754 (2022).
- 2) M. Fujioka et. al., Adv. Funct. Mater. 33, 2208702 (2023).
- 3) M. Fujioka et. al., Chem. Mater. 35, 3008-3014 (2023).



Figure 1. (a), (b) Cross section of (a) HP and (b) HPDC cell. (c) Relationship between power and temperature. (d) Journal cover.

Synthesis of Complex Transition Metal Hydrides Containing Polynuclear Hydride Complexes with High Hydrogen Coordination

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Keywords: Complex Transition Metal Hydrides, High Hydrogen Coordination, Polynuclear Hydride Complexes

Hydrogen exhibits an exceptionally rich chemistry, forming various chemical bonds in hydrides. The chemical flexibility is a source of many interesting functionalities of hydrides.¹⁾ Especially, the discovery of the superconductivity at 203 K in the sulfur hydride system²⁾ has spurred tremendous research activities toward the exploration of hydrogen-rich materials.

The complex transition metal hydrides are a class of typical hydrogen-rich materials. In these hydrides, a number of H atoms covalently bind to a single transition metal to form various homoleptic transition-metal hydride complexes with a remarkably rich variety of hydrogen coordination modes. At the same time, transition metals that form such complexes had been limited to the Groups 7–12;^{3,4}) this had precluded further discovery of hydride complexes with higher hydrogen coordination, since the coordination number tends to increase when going from right to left along a period due primarily to the increasing trend in the atomic size, which allows more H atoms to bind. In this regard, we have overcome the limitation using high-pressure and high-temperature (HPHT) technique and successfully synthesized a novel complex transition metal hydride Mg₃CrH₈ containing the first Group 6 hydride complex $CrH_7^{5,.5}$ We also synthesized novel complex transition-metal hydrides Li_6NbH_{11} , Li_5MoH_{11} , and Li_5WH_{11} containing Groups 5 and 6 hydride complexes with ninefold hydrogen coordination, NbH₉⁴⁻, TaH₉⁴⁻, MoH₉³⁻, and WH₉³⁻, respectively⁶.

In this study, we searched for novel complex transition metal hydrides containing the first Hf-based hydride complex with high hydrogen coordination by means of theoretical prediction and in-situ synchrotron X-ray diffraction measurements. We found that Hf forms a binuclear hydride complex, where two gyroelongated square pyramidal HfH₉ units share four H atoms to form Hf₂H₁₄⁶⁻ (Fig. 1). The detailed results will be discussed in the presentation.



Fig. 1. Structure of novel binuclear hydride complex $Hf_2H_{14}^{6-}$.

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References

- 1) S. Takagi and S. Orimo, Scripta Mater. (Viewpoint paper) 109, 1 (2015).
- 2) A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov and S. I. Shylin, Nature 525, 73 (2015).
- 3) W. Bronger, Angew. Chem. 30, 759 (1991).
- 4) K. Yvon, CHIMIA 52, 613 (1998).
- 5) S. Takagi, Y. Iijima, T. Sato, H. Saitoh, K. Ikeda, T. Otomo, K. Miwa, T. Ikeshoji, K. Aoki and S. Orimo, Angew. Chem. Int. Ed. 54, 5650 (2015).
- 6) S. Takagi, Y. Iijima, T. Sato, H. Saitoh, K. Ikeda, T. Otomo, K. Miwa, T. Ikeshoji and S. Orimo, Sci. Rep. 7, 44253 (2017).

[Abstract Guideline (Leave two lines for presentation number)]

Mn-rich Al–Mn alloy hydrides synthesized under high pressure and high temperature with the aid of in-situ synchrotron radiation X-ray diffraction measurement

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Keywords: Hydride, High-pressure synthesis, Synchrotron radiation X-ray diffraction, Al-Mn alloy

In general, hydrides have been synthesized by mixing elements with low and high hydrogen affinities. We have tried to synthesize novel metal hydrides containing only metals with low hydrogen affinity by using a high-pressure and high-temperature method. We have succeeded in synthesizing some Al-transition metal (TM) hydrides (e.g. Al₃FeH₄ [1], Al₂CuH₃ [2]), where Al, Fe and Cu have low hydrogen affinities. It is noteworthy that hydrogenation of Al–TM alloys were considered difficult due to the very low hydrogen affinity of aluminum. To broaden the variety of Al-containing hydrides and realize light-weight inexpensive Al-based hydrogen storage materials, we have searched novel Al-TM hydrides under high pressure. In the present study, we have tried to synthesize Mn-rich Al-Mn alloy hydrides that had not yet been investigated.

Al_xMn_{1-x} (x = 0.1, 0.2, 0.3) alloys with a β -Mn-type structure produced in solid state reactions at high pressures were used as starting materials. The samples were hydrogenated at a hydrogen pressure of 9 GPa and 750°C for 2 h using a cubic-type multi-anvil press. We investigated the crystal structures of the samples during hydrogenation reactions by in-situ synchrotron radiation X-ray diffraction measurement system at BL14B1, SPring-8. Hydrogen evolution from the recovered samples was investigated using a thermal desorption spectroscopy system for hydrogen analysis (HTDS).

Novel Al_xMn_{1-x} (x = 0.1, 0.2, 0.3) alloy hydrides with a hexagonal close-packed (hcp) structure were synthesized at 9 GPa and 750°C. Figure 1 shows in-situ powder X-ray diffraction profiles of the Al_{0.3}Mn_{0.7} alloy in fluid hydrogen. The crystal structure of the sample changed from a β -Mn-type structure to an hcp structure a few minutes after the sample was heated to 750°C at 9 GPa in fluid hydrogen, indicating a formation of a novel Al_{0.3}Mn_{0.7} alloy hydride with an hcp structure. The sample was cooled to room temperature and then depressurized to ambient pressure. The hcp phase was recovered at ambient conditions.

The atomic ratio between hydrogen and metal atoms (H/M) of the recovered Al–Mn alloy hydrides decreased with increasing Al content. H/M of the recovered Al_xMn_{1-x} (x = 0.1, 0.2, 0.3) alloy hydrides were estimated to be 0.85,



Fig. 1. In situ synchrotron radiation X-ray powder diffraction profiles of $Al_{0.3}Mn_{0.7}$ alloy in fluid hydrogen. Triangles and circles represent Bragg peaks from β -Mn-type and hcp structures, respectively.

0.56 and 0.45, respectively. Furthermore, the hydrogen release temperature of the recovered Al_xMn_{1-x} (x = 0.2, 0.3) alloy hydrides increased with increasing Al content.

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References:

- 1) H. Saitoh, T. Sato, M. Tanikami, K. Ikeda, A. Machida, T. Watanuki et al., Mater. Des. 208, 109953 (2021).
- 2) H. Saitoh, S. Takagi, N. Endo, A. Machida, K. Aoki, S. Orimo et al., APL Mater. 1, 032113 (2013).

High-pressure and high-temperature synthesis of novel hydrides with the aid of in-situ synchrotron radiation x-ray diffraction measurement

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 Keywords: Metal hydrides, High pressure and high temperature, Synchrotron radiation x-ray diffraction, Aluminum-based alloys

Exploration of novel hydrides is underway due to their wide range of functionalities such as hydrogen storage, high-temperature superconductivity, fast ionic conduction, and H^- conduction. Hydrogenation reactions of metals are one of the simple methods to obtain hydrides. Since hydrogenation reactions are thermodynamically expected to proceed more easily at high pressure and high temperature, high-pressure and high-temperature synthesis is one of the effective methods for the exploration of novel hydrides.

The advantages of high-pressure hydrogenation generally become more pronounced above 1 GPa. There are mainly two kinds of apparatuses for hydrogenating metals under such high pressure. One is a diamond anvil cell, which pressurizes the sample with diamonds, and the other is a multi-anvil press, which can apply high pressure to a relatively large volume of sample using hydraulic presses. The author's group have synthesized novel hydrides under high pressure up to 10 GPa using a cubic-type multi-anvil press.

In high-pressure and high-temperature synthesis, pressure is added to the synthesis parameters, which complicates the determination of synthesis conditions. In addition, since it is difficult to obtain information on a sample under high pressure, synthesis conditions are gradually changed and the recovered samples are analyzed under ambient pressure to optimize the synthesis conditions.

We have used in-situ synchrotron radiation x-ray diffraction technique to detect the progress of novel hydrogenation reaction, which enables us to optimize the synthesis conditions effectively¹). Figure shows the optical photograph of the high-pressure apparatus. We have synthesized novel hydrides, especially aluminum-based alloy hydrides, by using the apparatus. Recent results of syntheses of aluminum-based hydrides will be presented^{2,3}).

This work was supported by JSPS KAKENHI (Nos. JP18H05513 and JP22H01821), and grants from the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University (202012-RDKGE-0066, 202012-RDKGE-0066, and 202212-RDKGE-0068).



Figure. Optical photograph of the cubic-type multi-anvil apparatus installed on the beamline BL14B1, SPring-8.

References:

- 1) H. Saitoh, A. Machida and K. Aoki, Chin. Sci. Bull. 59, 5290 (2014).
- 2) H. Saitoh, T. Sato, M. Tanikami, K. Ikeda, A. Machida, T. Watanuki et al., Mater. Des. 208, 109953 (2021).
- 3) H. Saitoh, S. Takagi, N. Endo, A. Machida, K. Aoki, S. Orimo et al., APL Mater. 1, 032113 (2013).

Late Breaking News | B. Energy | Late Breaking News

[B-L304] Late Breaking News

Wed. Dec 13, 2023 6:30 PM - 8:30 PM Poster (Annex)

[B-L304-01]	Epitaxial Growth of LaH_x Thin Films and Hydrogen Diffusion at the LaH_x /Zr Interface
[B-L304-02]	*Ziyang Cao ¹ , Daichi Miyazaki ¹ , Takuto Soma ¹ , Akira Ohtomo ¹ (1. Tokyo Tech. (Japan)) Laser-Induced Graphene: A Three-Dimensional Electrocatalyst Support for Efficient Oxygen and Hydrogen Evolution in Alkaline Media *IBRAHIM KHAN ¹ Sanghyuk Wooh ¹ (1. Chung Ang University (Korea))
[B-L304-03]	*Jose Ordonez ¹ , Roman Anufriev ¹ , Masahiro Nomura ¹ , Sebastian Volz ¹ (1. CNRS - The
[B-L304-04]	Tuning the Spin-Valence States of Atomically Dispersed Vanadium on Carbon-based Substrates for Oxygen Reduction Reactions
[B-L304-05]	Design of N-Type Textured Bi ₂ Te ₃ with Robust Mechanical Properties for Thermoelectric Micro-Refrigeration Application
[B-L304-06]	*Yu-Ke Zhu', Zihang Liu', Jiehe Sui' (1. State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China. (China)) Thermal Stability Improvement of Nanostructured MgAgSb Bulk Materials Through Grain Boundary Segregation
	and Joining, Harbin Institute of Technology, Harbin 150001. (China), 2. I. Physikalisches
[B-L304-07]	Ternary Pt– Ni– Au alloy catalyst for Oxygen Reduction Reaction *xianxian xie xie ¹ (1 Charles University (Czech Republic))
[B-L304-08]	Navigating a Visible-driven Photocatalyst for Efficient Green Hydrogen Generation
	*Shin Chwen Yeh ¹ , Wen Yin Ko ¹ , Kuan Jiuh Lin ¹ (1. National Chung Hsing University (Taiwan))
[B-L304-09]	Fast proton conducting acid-base nanocomposite membranes with functional silanes
[B-L304-10]	*Yeji park', SuMin Jeong', Md Shahjahan Kabir Chowdury', SungBum Park ² , Yong-il Park' (1. Kumoh National Institute of Tech. (Korea), 2. Dongguk Univ. WISE Campus (Korea)) Improvement of Proton Transfer Channels through Acid-Base Pairs in Proton Exchange Mombrane Eucl Colls (PEMECs)
	*Md Shahjahan Kabir Chowdury ¹ , Ye Ji Park ¹ , Jeong Su Min Jeong ¹ , Sung Bum Park ² , Yong-il Park ¹ (1. Kumoh National Institute of Technology (Korea), 2. Dongguk University Gyeongju
[B-L304-11]	Record-high thermoelectric performance in Al-doped ZnO via Anderson localization of band edge states *Illia Serhiienko ^{1,2} , Takao Mori ^{1,2} (1. University of Tsukuba (Japan), 2. National Institute for Materials Science (Japan))

[B-L304-12] Polaron Surface State Nanomaterials for Green Energy Conversion Devices

*Yi-Sheng Lai¹, Hung-Yu Shen¹, Min-Chi Chen¹ (1. National of Chung Cheng University (Taiwan))

[B-L304-13] Role of H permeation on surface oxidation of Ni-based alloy in hightemperature water environment

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[B-L304-14] Magnesium-Based Metallic Glass for Brazing Paste Application in Thermoelectric Module Fabrication

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Epitaxial Growth of LaH_x Thin Films and Hydrogen Diffusion at the LaH_x/Zr Interface

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Keywords: Metal hydrides, Pulsed-laser deposition, Interface, Hydrogen diffusion

Lanthnum hydrogen compounds have recently gained attention due to the discovery of high-temperature superconductivity in LaH_{10+x} and fast hydride-ion conduction in LaH_{3-2x}O_x. On the other hand, it is known that LaH_x ($2 \le x \le 3$) transitions from a metal to an insulator with increasing x [1]. To apply these materials for developing solid-state ionic devices, it is important to investigate dynamics of hydrogen diffusion in an ideal sample. We previously synthesized oriented thin films of group IV hydrides using pulsed-laser deposition (PLD) technique, and revealed their unique properties [2]. Building upon this progress, in the present study, we focused on the fabrication of LaH_x epitaxial films. This allows us to investigate the diffusion of hydrogen at metalized interface between LaH_x and Zr.

In our experimental setup, pressed LaH_x pellet was used as a target for PLD, and (111)-oriented LaH_x thin films with a thickness of ~70 nm were grown on Al₂O₃ (0001) substrates at room temperature under vacuum condition. The crystal structure of the films was investigated by x-ray diffraction (XRD). No trace of LaO_x phases suggests that a capping layer of 200-nm-thick amorphous Al₂O₃ (a-Al₂O₃) prevented LaH_x from oxidation. Furthermore, when the bilayer films were annealed under vacuum conditions at 230 °C, the formation of Zr hydride phases was observed after 10^4 -sec-annealing, suggesting the diffusion of hydrogen from the LaH_x to Zr layers [Fig. 1 (a)]. The characteristic lattice spacing are plotted in Fig. 1 (b). The original hcp lattice of as-grown Zr layer tends to expand and disappear due to hydrogen incorporation, while a new phase assignable to δ -ZrH₂ or ZrH_x (x > 2) appears. This phenomenon adds an intriguing aspect to create multilayered structures with metalized interfaces between, for example, LaH_{3-2x}O_x and ZrH_x in terms of applications to solid-state ionic devices.



Fig. 1. (a) XRD profiles for the LaH_x thin films on Zr layer, forming a bilayer structure on the Al₂O₃ substrate. Insets depict schematic sample cross-sections of the as grown film. Note that all the samples are covered with a-Al₂O₃ layers. (b) Lattice spacing d_{111} as a function of annealing time. Filled and open circles indicate Zr phase and H-rich ZrH_y phase, respectively. Broken lines show literature values of bulks. Error bars indicate full width at half maximum for each peak.

References:

K. Fukui, S. Iimura, A. Iskandarov, T. Tada, H. Hosono, J. Am. Chem. Soc. 144, 1523-1527 (2022).
 K. Yoshimatsu, T. Suzuki, N. Tsuchimine, K. Horiba, H. Kumigashira, T. Oshima, A. Ohtomo, Appl. Phys. Express 8, 6–10 (2015).

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