
The symposium consists of invited keynote lectures reviewing the key elements of the hydrogen cycle, i.e. the hydrogen production, hydrogen storage and hydrogen combustion and fuel cells. Furthermore, contributions on the conversion of renewable energy in general and energy carriers beside and beyond hydrogen are very welcome. The world leading experts present the current research challenges and most important results in invited and contributing talks. Early stage and experienced researchers present their newest results and the open questions on posters as well as in a one slide presentation.

The conference will take place in the OYC hotel in Zhaoqing close to Guangzhou in China. The OYC Hotel is set against a group of lakes surrounding the limestone peaks in Zhaoqing, Guangdong Province, China. It enjoys a view blue lakes and mountains which comprise a splendid panoramic landscape to the south of the Five Ridges.

The number of participants is limited to 120.


OYC Hotel******
Xinghu Dadao, Zhaoqing
526060 Guangdong, P. R. China
Tel.: +86 758 218 9887
URL: http://www.oychotel.com
8th INT. SYMPOSIUM
HYDROGEN & ENERGY

16.-21. FEBRUARY 2014
OYC Hotel, Zhaoqing
CHINA

STEERING COMMITTEE
Barnard DAM, Netherlands
Shin-Ichi ORIMO, Japan
Jan ROSSMEISEL, Denmark
Min ZHU, China
Andreas ZÜTTEL, Switzerland

INVITED SPEAKERS
Ping CHEN, China
Young Whan CHO, Korea
Jun CHEN, China
Michael HIRSCHER, Germany
Hannes JONSSON, Iceland
Xing Guo Li, China
Shin-Ichi ORIMO, Japan
Liu Zhang OUYANG, China
Tejs VEGGE, Denmark
Vladimir YARTIS, Norway
Andreas ZÜTTEL, Switzerland
Puru JENA, America

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and
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LOCATION

REGISTRATION
Conference fee USD 600 incl. proceedings and social event, coffee breaks, lunch, dinner, conference dinner, beverages.

- Single room 700 $ p. Person (5 nights)
- Double room 350 $ p. Person (5 nights)
- Special rates incl. hotel room and breakfast

Registration online:
http://hesymposium.ch/

Registration and abstract submission:
before 1. December, 2013
Welcome Address

It is our great pleasure to host such a distinguished group at the picturesque Zhaoqing in China! On behalf of the steering committee of the symposium, we would like to express the warmest welcome to each and every one of you!

In 2012, when Prof. Min Zhu attended the 6th Hydrogen and Energy Symposium in Switzerland, it was in a beautiful snow mountain in Alps. He proposed the idea of host this symposium in Southern China where the winter is very warm, and more importantly, this will provide more chance for Chinese scientists to communicate with European Scientists. This suggestion was strongly been supported by the other colleagues. Prof. Züttel pay a special visit to Guangzhou to arrange the issue of the symposium in Oct. 2013. Thanks to the effort of organizing committee and our colleagues and in particular the symposium is now ready to open.

This time we have about 70 participates to attend the symposium with oral and poster presentation, about 20 from abroad and 50 from China. The symposium will offer a great opportunity to discuss the latest scientific development in the areas of hydrogen production, storage, combustion, and fuel cells, just to name a few. In addition, you will also have plenty of opportunities for networking and interaction during the many breaks and social events in our dense agenda.

Besides, as we are here embraced by all the beautiful lakes, woods and mountains, we also hope you will find time to enjoy the many beautiful attractions in Zhaoqing and Guangzhou.

Finally, we would like to welcome all of you again, and wish you a pleasant stay, and a productive conference. Thank you.

Professor Min Zhu
South China University of Technology
Guangzhou, P. R. China

Professor Andreas Zuttel
EMPA Materials Science and Technology
CH-8600 Dübendorf, Switzerland
# CONTENTS

## Timetable

<table>
<thead>
<tr>
<th>MONDAY morning</th>
<th>Chair: Min ZHU</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:40</td>
<td>Andreas ZÜTTEL, 'CLOSING THE CYCLE WITH HYDROGEN'</td>
</tr>
<tr>
<td>09:40 - 10:05</td>
<td>Xuebin YU, 'The Application of Nanotechnology in Hydrogen Storage'</td>
</tr>
<tr>
<td>10:05 - 10:30</td>
<td>Yongjin ZOU, 'Catalytic Behaviour of Co-Zn-B/Graphene Composite in Hydrogen Generation by Hydrolysis of Alkaline Sodium Borohydride'</td>
</tr>
<tr>
<td>10:30 - 10:55</td>
<td>Sheng GUO, 'Alkali and Alkaline-Earth Borohydrides for Hydrogen Storage'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MONDAY afternoon</th>
<th>Chair: Andreas ZÜTTEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:20 - 11:45</td>
<td>Yongfeng LIU, 'Hydrogen Storage Properties and Mechanisms of alkali-meal-added Li-Mg-N-H system'</td>
</tr>
<tr>
<td>11:45 - 12:10</td>
<td>Huaiyu SHAO, 'Geometrical effect study in Mg-based BCC structure materials for hydrogen storage'</td>
</tr>
<tr>
<td>12:10 - 12:50</td>
<td>Young Whan CHO, 'Control of Thermodynamic and Kinetic Properties of Metal Hydride Composite Confined in Mesopore Cages'</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MONDAY afternoon</th>
<th>Chair: Young Whan CHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 - 14:40</td>
<td>Micheal Hirscher, 'Nanoporous Framework for Hydrogen Storage and H2/D2 Isotope Separation'</td>
</tr>
<tr>
<td>14:40 - 15:05</td>
<td>Yigang YAN, 'New Methods to Apply Nanostructures on Mg(BH4)2'</td>
</tr>
<tr>
<td>15:05 - 15:30</td>
<td>Jianmei Huang, 'Increased air stability and decreased dehydrogenation temperature of LiBH4 via modification within poly(methylmethacrylate)'</td>
</tr>
<tr>
<td>15:30 - 15:55</td>
<td>Ulrich VOGT, 'Development and characterization of gas separation membranes for alkaline water electrolysis'</td>
</tr>
<tr>
<td>Time</td>
<td>Speaker</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------</td>
</tr>
<tr>
<td>16:20 - 16:45</td>
<td>Nicholas STADIE</td>
</tr>
<tr>
<td>16:45 - 17:10</td>
<td>Weitong CAI</td>
</tr>
<tr>
<td>17:10 -17:35</td>
<td>Fangming XIAO</td>
</tr>
<tr>
<td>17:35 - 18:15</td>
<td>Tejs VEGGE</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>TUESDAY</td>
<td></td>
</tr>
<tr>
<td>morning</td>
<td>Chair: Tejs VEGGE</td>
</tr>
<tr>
<td>09:00 - 09:40</td>
<td>Ping CHEN</td>
</tr>
<tr>
<td>09:40 - 10:05</td>
<td>Arndt REMHOF</td>
</tr>
<tr>
<td>10:05 - 10:30</td>
<td>Teng HE</td>
</tr>
<tr>
<td>10:30 - 10:55</td>
<td>Cunke HUANG</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>11:20 - 11:45</td>
<td>Haiyan LENG</td>
</tr>
<tr>
<td>11:45 - 12:10</td>
<td>Haiiliang CHU</td>
</tr>
<tr>
<td>12:10 - 12:50</td>
<td>Hannes JÓNSSON</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>TUESDAY</td>
<td></td>
</tr>
<tr>
<td>afternoon</td>
<td>Chair: Hannes JÓNSSON</td>
</tr>
<tr>
<td>14:00 - 14:40</td>
<td>Xingguo LI</td>
</tr>
<tr>
<td>14:40 - 15:05</td>
<td>Elsa CALLINI</td>
</tr>
<tr>
<td>15:05 - 15:30</td>
<td>Chaoling WU</td>
</tr>
</tbody>
</table>

PROCEEDINGS
<table>
<thead>
<tr>
<th>Time</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>15:30 - 15:55</td>
<td>Moreno DE RESPINIS</td>
<td>'Oxynitrogenography: The Search for Oxynitrides for Solar Water Splitting'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chair: Xingguo LI</td>
</tr>
<tr>
<td>16:20 - 16:45</td>
<td>Yunfeng ZHU</td>
<td>'Recent Study on Hydrogen Storage Properties of Mg-Based Materials Prepared by HCS+MM'</td>
</tr>
<tr>
<td>16:45 - 17:10</td>
<td>Yuan LI</td>
<td>'Preparation and electrochemical characteristics of single-phase'</td>
</tr>
<tr>
<td>17:10 - 17:35</td>
<td>Mariana SPODARYK</td>
<td>'Gas atomized alloy electrodes'</td>
</tr>
<tr>
<td>17:35 - 18:15</td>
<td>Puru JENA</td>
<td>'NANOMATERIALS FOR HYDROGEN STORAGE'</td>
</tr>
</tbody>
</table>

**Wednesday morning** Chair: Puru JENA

<table>
<thead>
<tr>
<th>Time</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>09:00 - 09:40</td>
<td>V.A. YARTYS</td>
<td>'Nanostructured Mg-Based Hydrogen and Energy Storage Materials Probed by In situ Synchrotron and Neutron Powder Diffraction'</td>
</tr>
<tr>
<td>09:40 - 10:05</td>
<td>Xiangdong KANG</td>
<td>'PROMOTED FORMATION OF METAL BORIDES IN THE 2LiBH4-MgH2 COMPOSITES WITH TRANSITION METAL ADDITIVES BY USING A NEW THREE-STEP METHOD'</td>
</tr>
<tr>
<td>10:05 - 10:30</td>
<td>Jiangwen LIU</td>
<td>'Enhancing effect of LPSO on the de/hydrogenation kinetics and structural transformation in Mg96Cu4Y2 Alloy'</td>
</tr>
<tr>
<td>10:30 - 10:55</td>
<td>Baozhong LIU</td>
<td>'Microstructures and Hydrogen storage properties of Mg-RE-Ni alloys'</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chair: V.A. YARTYS</td>
</tr>
<tr>
<td>11:20 - 11:45</td>
<td>Yongtao LI</td>
<td>'Superlattice Structures and Hydrogen Absorption/Desorption Characteristics of R-Mg-Ni Compounds'</td>
</tr>
<tr>
<td>11:45 - 12:10</td>
<td>Renaud DELMELLE</td>
<td>'Rethinking High-Pressure X-Ray Photoelectron Spectroscopy for The Study of Hydride-Forming Materials'</td>
</tr>
<tr>
<td>12:10 - 12:50</td>
<td>Liuzhang OUYANG</td>
<td>'A NEW METHOD TO PREPARE MG BASED HYDROGEN STORAGE MATERIALS WITH IMPROVED DEHYDRIDING THERMODYNAMICS AND KINETICS PROPERTIES'</td>
</tr>
<tr>
<td>Time</td>
<td>Speaker</td>
<td>Title</td>
</tr>
<tr>
<td>------------</td>
<td>------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>09:00 - 09:40</td>
<td>Shin-ichi ORIMO</td>
<td>'Transition and Conduction in Hydrides'</td>
</tr>
<tr>
<td>09:40 - 10:05</td>
<td>Fadime HOSOGLU</td>
<td>'Catalytic Hydrogenation of CO\textsubscript{2} to CH\textsubscript{4} and CO over Pt-K-Ta/Ni/Al\textsubscript{2}O\textsubscript{3}'</td>
</tr>
<tr>
<td>10:05 - 10:30</td>
<td>Hui WANG</td>
<td>'FURTHER STUDY ON HYDROGEN-DEUTERIUM EXCHANGE MECHANISM DURING DESORPTION OF LiBH\textsubscript{4}•MGD\textsubscript{2} SYSTEM'</td>
</tr>
<tr>
<td>10:30 - 10:55</td>
<td>Fang FANG</td>
<td>'Fast hydrogen-induced optical and electrical transitions of Mg-based alloy thin films with amorphous structure'</td>
</tr>
<tr>
<td>11:20 - 11:45</td>
<td>Yijing WANG</td>
<td>'Synthesis and catalytic effects of tiB\textsubscript{2}/TiN@Graphaene nano sheets on hydrogen storage of Magnesium hydride'</td>
</tr>
<tr>
<td>11:45 - 12:10</td>
<td>Guanqiao LI</td>
<td>'Dehydriding Properties of LiBH\textsubscript{4} Combined with Mg\textsubscript{2}FeH\textsubscript{6}'</td>
</tr>
<tr>
<td>12:10 - 12:50</td>
<td>Jun CHEN</td>
<td>'Combination of Lightweight Hydrogen Storage Materials and Nanostructures'</td>
</tr>
<tr>
<td>TUESDAY evening</td>
<td>Chairs: Min ZHU, Andreas ZÜTTEL</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>P01</strong></td>
<td>Ping LI, 'Remarkable dehydrogenation improvement of LiAlH$_4$ catalyzed by CoFe$_2$O$_4$ nanoparticles '</td>
<td></td>
</tr>
<tr>
<td><strong>P02</strong></td>
<td>Yanzhan LU, 'NOVEL MG-IN-NI TERNARY ALLOYS FOR REVERSIBLE HYDROGEN STORAGE '</td>
<td></td>
</tr>
<tr>
<td><strong>P03</strong></td>
<td>Xiaoling SHAN, 'CARBON-SUPPORTED Ni$_3$B NANOPARTICLES AS CATALYSTS FOR HYDROGEN GENERATION FROM HYDROLYSIS OF AMMONIA BORANE'</td>
<td></td>
</tr>
<tr>
<td><strong>P04</strong></td>
<td>Jie SHAO, 'A SYNERGETIC EFFECT OF NANO-CONFINEMENT AND NANOCATALYSIS FOR THE ENHANCED REVERSIBLE HYDROGEN STORAGE OF LIBH$_4$ '</td>
<td></td>
</tr>
<tr>
<td><strong>P05</strong></td>
<td>Shumin HAN, 'Effect of the LaFeO$_3$ on the hydrogenation/dehydrogenation properties of MgH$_2$ '</td>
<td></td>
</tr>
<tr>
<td><strong>P06</strong></td>
<td>Zhijie CAO, 'Structural Characteristics and Hydrogen Storage Properties of Sm$_2$Co$_7$'</td>
<td></td>
</tr>
<tr>
<td><strong>P07</strong></td>
<td>Huizhong YAN, 'Investigation of the Thermodynamic and Kinetic Properties of La-Fe-B System Hydrogen-Storage Alloys'</td>
<td></td>
</tr>
<tr>
<td><strong>P08</strong></td>
<td>Xiaobao YANG, 'Theoretical investigations on the structural stabilities of Magnesium nanostructures and the applications for hydrogen storage'</td>
<td></td>
</tr>
<tr>
<td><strong>P09</strong></td>
<td>Jianmei HUANG, 'Increased air stability and decreased dehydrogenation temperature of LiBH$_4$ via modification within poly (methylmethacrylate)'</td>
<td></td>
</tr>
<tr>
<td><strong>P10</strong></td>
<td>Weitong CAI, 'Remarkable irreversible and reversible dehydrogenation of LiBH$_4$ by doping nanosized Cobalt metalloid compounds'</td>
<td></td>
</tr>
<tr>
<td><strong>P11</strong></td>
<td>Yixiao FU, 'Study on the hydrogen exchange behavior in the metal hydride-LiBH$_4$ composite'</td>
<td></td>
</tr>
<tr>
<td><strong>P12</strong></td>
<td>Huaijun LIN, 'Mg-based amorphous/nano-materials with superior hydrogen storage properties'</td>
<td></td>
</tr>
<tr>
<td><strong>P13</strong></td>
<td>Jie CUI, 'Remarkable enhancement of dehydrogenation of MgH$_2$ by a nano-coating of multi-valence TM-based (TM=Ti, Nb, V, Co, Mo, Ni) catalysts'</td>
<td></td>
</tr>
<tr>
<td><strong>P14</strong></td>
<td>Hao ZHONG, 'Energy efficiency of the cycle of NaBH$_4$ hydrolysis and an inexpensive regeneration method'</td>
<td></td>
</tr>
</tbody>
</table>
P15  Yunfeng ZHU, 'Hydrogen Storage Properties of Mg-Pd/MWCNTs Composite Prepared by Hydriding Combustion Synthesis and Mechanical Milling'

P16  E.CALLINI, 'Vibrational properties of Vanadium and Zirconium based metal hydrides'

P17  Lixian SUN, 'Microporous carbon derived from metal organic framework with high CO₂ and H₂ adsorption heat'

P18  Zhibao LI, 'Improved dehydrogenation performance of LiBH₄ destabilized by (NH₄)₂TiF₆'

P19  Shumao WANG, 'Optimized design of hydrogen storage tanks based on 2LiNH₂-MgH₂ using simulation'

SCIENCE OF HYDROGEN & ENERGY AWARD 109

List of Participants 127

Information 138

Notes
<table>
<thead>
<tr>
<th>Time/Day</th>
<th>Sunday/16.02</th>
<th>Monday/17.02</th>
<th>Tuesday/18.02</th>
<th>Wednesday/19.02</th>
<th>Thursday/20.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>08:00 – 09:40</td>
<td>Registration</td>
<td>I: Michael HIRSCHER</td>
<td>I: Ping CHEN</td>
<td>I: Andries ZÜTTEL</td>
<td>I: Shin-ichi OHMO</td>
</tr>
<tr>
<td>09:40 – 10:05</td>
<td></td>
<td>O: Jinbin YU</td>
<td>O: Amrit REHDER</td>
<td>O: Xiaolin CHU</td>
<td>O: YANTYS</td>
</tr>
<tr>
<td>10:05 – 10:30</td>
<td></td>
<td>O: Yonglin ZHOU</td>
<td>O: Trevor EAST</td>
<td>O: Xiaolin CHU</td>
<td>O: Ying LI</td>
</tr>
<tr>
<td>10:30 – 10:55</td>
<td></td>
<td>O: Jinwen LÜ</td>
<td>O: Chike HUANG</td>
<td>O: Xuesong LÜ</td>
<td>O: Kazuo OHNO</td>
</tr>
<tr>
<td>11:45 – 12:10</td>
<td></td>
<td>O: Junyi ZHANG</td>
<td>O: Shitong YANG</td>
<td>O: Hailiang CHU</td>
<td>O: Renato DE MELLE</td>
</tr>
<tr>
<td>12:10 – 13:30</td>
<td></td>
<td>Lunch</td>
<td>Lunch</td>
<td>Lunch</td>
<td>Lunch</td>
</tr>
<tr>
<td>12:30 – 13:30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13:45 – 14:00</td>
<td></td>
<td>I: Young Whan CHO</td>
<td>I: Hanes JÖRßSEN</td>
<td>I: Jun CHEN</td>
<td></td>
</tr>
<tr>
<td>14:00 – 15:00</td>
<td></td>
<td>O: Chul-hee KIM</td>
<td>O: Tulip WASS</td>
<td>O: Jun CHEN</td>
<td></td>
</tr>
<tr>
<td>15:00 – 16:00</td>
<td></td>
<td>O: Minghai YANG</td>
<td>O: Eran SELARIO</td>
<td>O: Hiroshi YAMADA</td>
<td></td>
</tr>
<tr>
<td>16:00 – 16:30</td>
<td></td>
<td>O: Junhui ZHANG</td>
<td>O: Xiaoyi ZHENG</td>
<td>O: Xiaoyi ZHENG</td>
<td></td>
</tr>
<tr>
<td>16:30 – 17:00</td>
<td></td>
<td>O: Yansong ZHENG</td>
<td>O: Feng ZHAO</td>
<td>O: Yansong ZHENG</td>
<td></td>
</tr>
<tr>
<td>17:00 – 17:30</td>
<td></td>
<td>O: Weibang CHEN</td>
<td>O: Fangming YAO</td>
<td>O: Yansong ZHENG</td>
<td></td>
</tr>
<tr>
<td>17:30 – 18:15</td>
<td></td>
<td>O: Mariana SPODIAR</td>
<td>O: Tei VEIGG</td>
<td>O: Yansong ZHENG</td>
<td></td>
</tr>
<tr>
<td>18:15 – 20:00</td>
<td></td>
<td>O: Yu LI</td>
<td>O: Pu Yu</td>
<td>O: Yansong ZHENG</td>
<td></td>
</tr>
<tr>
<td>20:00 – 21:30</td>
<td></td>
<td>Dinner</td>
<td>Dinner</td>
<td>Dinner</td>
<td>Dinner</td>
</tr>
</tbody>
</table>

**Social event**

**Conference banquet**

**POSTER**
Abstracts
CLOSING THE CYCLE WITH HYDROGEN

Andreas ZÜTTEL

EMPA Materials Sciences & Technology, Dübendorf, Switzerland

The world energy demand continues to increase, the reserves of fossil fuels are limited, the combustion of the fossil fuels leads to an increase of the CO₂ in the atmosphere and therefore to a climate change and finally the economy of the industrialized world is dependent on the fossil fuels. Currently the world operates with an open cycle mining fuels and materials and finally releasing the CO₂ into the atmosphere, polluting the water, creating nuclear waste deposits and depositing garbage. The world economy can become a sustainable economy by closing the materials cycles especially the energy materials cycle. Therefore, hydrogen from renewable energy used the reduce CO₂ from the atmosphere leads to synthetic hydrocarbons in a CO₂ neutral cycle.

Resources

Industrialization was based on an open cycle, i.e. mining of materials and fossil fuels, manufacturing the products and disposal of the used materials as well as release of the CO₂ in the atmosphere.

The sustainability of the post industrialization era is determined by the ability to close the materials cycles i.e. to change from fossil fuels as energy carriers to renewable energy. Since renewable energy (solar, geothermal and planet movement) occurs in energy fluxes, an appropriate energy carrier has to be synthesized.

Closing the cycle

According to statistical considerations the world population will stabilize at approx. 10 billion humans in 2050 thanks to growing wealth in the developing countries. That is an increase in the number of people by 25% and a large increase in demand for resources if all would reach the living standard of western Europe. Only products, which are naturally recycled with the same rate as they are released and neutral products, e.g. water, can be released or deposited without affecting the sustainability. There are just two ways to close the cycle [1]: remove the carbon from the energy cycle and introduce hydrogen as an energy carrier for the solar energy or to extract CO₂ from the atmosphere and to reduce it with hydrogen to synthetic fuels.

Fig. 1 Current economic system based on mining and depositing.

The established routes for the reduction of CO₂ are the Sabatier reaction for methane, the reversed water gas shift reaction for CO combined with the Fischer-Tropsch synthesis for hydrocarbons and the reduction of CO₂ to methanol for dimethylether and hydrocarbons.

Thermodynamicaly the hydrocarbons conserve approx. 76% (5470kJ/7145kJ) of the energy in the hydrogen used to reduce the CO₂.

Fig. 2 Future sustainable economy based on the closed cycle

The established routes for the reduction of CO₂ are the Sabatier reaction for methane, the reversed water gas shift reaction for CO combined with the Fischer-Tropsch synthesis for hydrocarbons and the reduction of CO₂ to methanol for dimethylether and hydrocarbons. Thermodynamically the hydrocarbons conserve approx. 76% (5470kJ/7145kJ) of the energy in the hydrogen used to reduce the CO₂.

References


A. Züttel

Born 22. 8. 1963 in Bern, Switzerland. 1985 Engineering Degree in Chemistry, Burgdorf, Switzerland. 1990 Diploma in Physics from the University of Fribourg (UniFR), Switzerland. 1993 Dr. rer. nat. from the science faculty UniFR. 1994 Post doc "Amorphous hydrides and optical films" with AT&T Bell Labs in Murray Hill, New Jersey, USA. 1997 Lecturer at the Physics Department UniFR. 2003 External professor at the Vrije Universiteit Amsterdam, Netherlands. 2004 Habilitation in experimental physics at the science faculty UniFR. President of the Swiss Hydrogen Association „HYDROPOLE“. 2006 Head of the section “Hydrogen & Energy” at EMPA. Prof. tit. in the Physics department UniFR. 2009 Guest Professor at IMR, Tohoku University in Sendai, Japan. 2012 Visiting Professor at Delft Technical University, The Netherlands. >200 publications, >300 talks, h-index: 44

Corresponding author: Andreas ZÜTTEL, email: andreas.zuettel@empa.ch, Tel. +41 79 484 2553
The Application of Nanotechnology in Hydrogen Storage

Ziwei Tang, Guanglin Xia, Xuebin Yu
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Abstract: To implement the hydrogen-based propulsion systems, a viable, high efficient, safe and inexpensive hydrogen storage method is stringently required. The main challenge for hydrogen storage materials to be practical is to release hydrogen at moderate temperature with high contents. Nanotechnology plays an important role in advancing the properties of hydrogen storage materials. In this presentation, we report our latest results on the synthesis, and dehydrogenation properties of a series of hydrogen storage materials that were modified with various nano-templates. These nanoconfined compounds showed favorable dehydrogenation and rehydrogenation performances at ambient temperature, significantly advanced over their corresponding bulk substances. The achieved favorable properties of these materials make them promising candidates for advanced hydrogen storage.

Figure 1. SEM and TEM images for the electrospun LiNH$_2$/LiH@carbon nanofibers.

Figure 2. Hydrogen storage properties of the electrospun LiNH$_2$/LiH@carbon nanofibers.

References:

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Catalytic Behaviour of Co-Zn-B/Graphene Composite in Hydrogen Generation by Hydrolysis of Alkaline Sodium Borohydride

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Abstract: Hydrogen was generated by hydrolysis of sodium borohydride (NaBH₄) using Co-Zn-B/Graphene composite in this work. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The Co-Zn-B/Graphene nanocomposite catalyst was found to consist of amorphous Co-Zn-B nanoparticles attached to the surface of graphene. The kinetics of hydrolysis of NaBH₄ was investigated. The effect of temperature, NaBH₄ concentration, catalyst concentration and stability of the composite on hydrogen generation was also explored.

Introduction

NaBH₄ has received great attention owing to its combined advantages of high hydrogen capacity, good storability in alkaline solution, moderate operation temperature, et al. Catalyst is necessary to control hydrogen generation from NaBH₄ solution. Numbers of materials have been examined to be effective to accelerate the hydrolysis of NaBH₄. However, most of them are noble metal catalysts, which restrained their use in practical applications. In this work, a highly active Co-Zn-B/graphene composite was prepared and its performance for catalyzing the hydrolysis of NaBH₄ was investigated in detail.

Experimental

In a typical experiment, Co-Zn-B/graphene composite was prepared by chemical reduction method. Graphene was dispersed in CoSO₄ and ZnSO₄ solution and sonicated for 3 h. Subsequently, the alkaline NaBH₄ solution was added in the above solution dropwisely with magnetic stirring. The produced black suspension was filtered and washed repeatedly using distilled water. The catalyst was then dried in vacuum at 60 °C for 24 h. For comparison, Co-B and Co-B/graphene were also prepared.

Results and Conclusion

Graphene supported Co-Zn-B catalyst demonstrated higher catalytic activities than the unsupported Co-Zn-B catalyst. The reaction rates of the alloys were Co-Zn-B/graphene>Co-Zn-B>Co-B. The volumes of hydrogen generation on all catalysts increased linearly with reacting time, suggesting a zeroth order reaction with respect to NaBH₄ concentration. The activation energy for different catalysts was also investigated. The low activation energy of Co-Zn-B/graphene causes its high activity.

References

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ALKALI AND ALKALINE-EARTH BOROHYDRIDES FOR HYDROGEN STORAGE

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The development of a volumetrically and gravimetrically efficient on-board hydrogen store, would greatly accelerate the introduction of hydrogen fuel cell vehicles. There is a range of complex hydrides that have intrinsically high hydrogen storage capacities, but the challenge is to develop a rapidly reversible material with a low hydrogen sorption temperature. We have investigated two types of borohydride materials: disordered Mg(BH₄)₂ and eutectic mixture LiBH₄-Ca(BH₄)₂.

Mg(BH₄)₂ has received attention as (or a component of) a possible storage medium for mobile hydrogen stores, due to its high gravimetric H₂ density (up to 14.9 wt%) with partial reversibility [1]. There are several polymorphs of Mg(BH₄)₂ stable at room temperature, obtained through different synthetic approaches [2]. However, the detailed decomposition mechanism(s), as a function of conditions and of the starting phase, is not clear.

An investigation of the structural and compositional change of the crystalline and disordered γ-Mg(BH₄)₂ as a function of temperature has been carried out [3]. An amorphous Mg(BH₄)₂ phase is produced after ball-milling (in 100 bar H₂) γ-Mg(BH₄)₂ for 2 h. This disordered γ-Mg(BH₄)₂ dehydrogenates via a pathway with release of diborane, which is different from crystalline γ-Mg(BH₄)₂. Various unknown compounds are observed by in situ XRD and Raman measurements, which might be related to the formation of polyboranes during decomposition. Mg, B and finally MgB₂ are observed during heating to 600 °C.

Eutectic Mixture LiBH₄-Ca(BH₄)₂

Mixed borohydride compounds, offer the prospect of more favourable thermodynamic properties and lower decomposition temperatures, and so have been considered as hydrogen storage media. In the binary LiBH₄-Ca(BH₄)₂ system, samples prepared by ball milling were found to exist as physical mixtures, which exhibited eutectic melting at around 200 °C [4]. An in situ NMR study demonstrated that the LiBH₄-Ca(BH₄)₂ mixture can form a solid solution below the eutectic melting point [5]. However, both the mechanism of the exchange of the cations between the borohydrides, and the reaction pathways during decomposition at higher temperatures, need further exploration.

In this work, the decomposition mechanism of a 0.68LiBH₄+0.32Ca(BH₄)₂ mixture has been investigated, utilising various techniques including in-situ XRD and Raman spectroscopy. A new phase is observed when heating and cooling the sample between phase changes and eutectic points for three cycles. The identification of this phase is ongoing, however, it does not appear to correspond to known borohydrides or borohydride-borates. In which case, this phase may be tentatively ascribed to a metastable dual-cation borohydride. A series of phase and melting reactions and the formation of CaB₆, Li₂B₁₂H₁₂, CaB₁₂H₁₂ and amorphous boron are observed in the Raman spectra.

References

HYDROGEN STORAGE PROPERTIES AND MECHANISMS OF ALKALI-MEAL-ADDED LI-MG-N-H SYSTEM

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Abstract

Hydrogen is the most ideal fuel in the comprehensive clean-energy concept. However, hydrogen storage is still a major technical barrier for its on-board application as a transportation fuel. Recently, metal-N-H systems have been attracting significant attention owing to their high gravimetric hydrogen density. Among them, the Li-Mg-N-H material is regarded as one of the very promising systems due to its good reversibility, comparatively high hydrogen content and favorable thermodynamic properties. Unfortunately, a relatively high kinetic barrier retards its practical applications for hydrogen storage. In this work, we present our recent work on improving the hydrogen storage thermodynamics and kinetics of the Li-Mg-N-H system by adding the alkali metal compounds. The K-based halides were first introduced into the Mg(NH$_2$)$_2$-2LiNH$_2$ system. It is found that the KF-added sample exhibits superior hydrogen storage properties as ~ 5.0 wt% of hydrogen can be reversibly stored in the 0.08KF-added sample via a two-stage reaction with an onset dehydrogenation temperature of 80 ºC. However, hydrogen storage behaviours of the samples with KCl, KBr and KI remain almost unchanged. The fact that KF can readily react with LiH to convert to KH and LiF due to the favorable thermodynamics during ball milling should be the primary reason for its significant effects as the presence of KH provides a synergetic thermodynamic and kinetic destabilization in the hydrogen storage reaction of the Mg(NH$_2$)$_2$-2LiH system by declining the activation energy of the first-step dehydrogenation as a catalyst and reducing the desorption enthalpy change of the second step as a reactant. In addition, the introduction of RbF also decreased the de-/hydrogenation temperatures and enhanced the hydrogen storage kinetics of the Mg(NH$_2$)$_2$-2LiH system. At 130 ºC, ~ 70% of hydrogen was rapidly released from the 0.08RbF-doped sample within 180 min, and the fully dehydrogenated sample could absorb ~ 4.8 wt% of hydrogen at 120 ºC. Structural analyses revealed that RbF reacted readily with LiH to convert to RbH and LiF due to the favorable thermodynamics during ball milling. The newly generated RbH participated in the following dehydrogenation reaction, consequently resulting in a decrease in the reaction enthalpy change and activation energy. The understanding on the role played by KF and RbF sheds light on how to further decrease the operating temperature and enhance the hydrogen storage kinetics of the Metal-N-H system.

References


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Yongfeng Liu received his PhD in Materials Science and Engineering from Zhejiang University in 2005. He then moved to National University of Singapore as a postdoctoral research fellow. He joined Zhejiang University as an associate professor and was promoted to Professor in 2012. His research is focused on solid-state hydrogen storage materials and electrode materials of rechargeable batteries.

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GEOMETRICAL EFFECT STUDY IN MG-BASED BCC STRUCTURE MATERIALS FOR HYDROGEN STORAGE

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Abstract Mg-Co body-centred cubic (BCC) structure alloys synthesized by ball milling method show good hydrogen absorption kinetics at even below room temperatures. Large surface area, short diffusion distance, numerous defects introduced from the milling process and the BCC lattice structure are important factors for the kinetics enhancement. Here we will report our unpublished data of experimental and computational work on how the geometric size effect could affect hydrogen occupancy in Mg-based BCC structure materials.

Introduction

Mg-based body-centred cubic (BCC) alloys have been investigated for hydrogen storage research by the authors intensively1-3. Mg₅₅Co₄₅ BCC alloys synthesized by ball milling method can absorb hydrogen at 258 K with a hydrogen capacity around 3.2 wt% without any activation process². The absorption temperature of 258 K is the lowest one reported so far for Mg-based materials to absorb hydrogen. In this paper, we will present our results on how the geometrical size effect could affect hydrogen storage properties in Mg-Co BCC structure nano-materials.

Results and Discussion

The Mg₅₀Co₅₀ alloy milled for 100 h shows BCC structure with a lattice parameter of 0.300(1) nm. The BCC structure can be confirmed from electron diffraction pattern. The SEM image shows a particle size around 1-3 micrometers and the dark-field TEM image indicates a grain size around a few nanometers¹. The micrometer scale particle size and nanometer scale grain size means much larger surface area and shorter diffusion distance for hydrogen absorption.

Up to date, the highest two H/M ratios found for BCC metal lattice hydrides are 1.28 for Mg₅₅Co₄₅H₁₂₈² and 1.33 for Mg₂Ca₃V₄H₆⁴. This can be explained from geometrical size effect in BCC metal lattice interstitial hydrides with a lattice parameter about 0.30 nm (Figure 1). It will be discussed from both experimental and computational aspects in this presentation.

Figure 1. Proposed hydrogen occupancy positions and calculated electron charge mapping in BCC structure hydrides with lattice parameter around 0.30 nm.

References

CONTROL OF THERMODYNAMIC AND KINETIC PROPERTIES OF METAL HYDRIDE COMPOSITE CONFINED IN MESOPORE CAGES

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Light metal complex hydrides such as LiBH$_4$, Mg(BH$_4$)$_2$, and Ca(BH$_4$)$_2$, have high reversible hydrogen storage capacities but dehydrogenation temperature and rehydrogenation reaction kinetics as well as sorption cycle performance are rather poor. There are some possible ways to improve thermodynamic and/or reaction kinetic properties of these metal hydride. They include cation or anion exchange, size reduction and interface control by nano-confinement, mutual destabilization by mixing different hydrides, and combination of these for further improvement. Here our recent work on size reduction and interface control with LiBH$_4$-Ca(BH$_4$)$_2$ eutectic composites infiltrated into different mesopore cages will be presented together with some preliminary explanations.

We have recently observed enhanced hydrogen desorption and absorption properties for a eutectic 0.68LiBH$_4$ + 0.32Ca(BH$_4$)$_2$ composite (LC) co-infiltrated into CMK-3, an ordered mesoporous carbon[1-3]. The dehydrogenation process was accelerated, and the desorption temperature was significantly reduced to about 300 °C, compared with ~ 400 °C for pure LC. In addition, the XRD peak intensity of the borohydrides decreased and the eutectic melting was hardly seen in the DSC curve even after the composite was ball-milled with CMK-3. The DSC peaks were completely disappeared after melt infiltration. Nuclear magnetic resonance (NMR) spectroscopy is indispensable in understanding these phenomena and in probing the local environment of the [BH$_4$]$^-$ anions. The system was found to be suitable for the application of in situ variable temperature (VT) NMR because of the lowered melting temperatures of the two borohydrides (~ 200 °C) and the wide separation of the $^{11}$B NMR shifts for the [BH$_4$]$^-$ anions (~10 ppm) in LiBH$_4$ and Ca(BH$_4$)$_2$. Because nanoconfinement is often achieved through the introduction of hydride particles into host scaffold pores using a melt infiltration method, such in situ spectroscopic observation is believed to be highly valuable. In the present work, we used solid-state magic angle spinning (MAS) NMR to elucidate the local environment of the ionic species in the LC composite and the way in which they interact with various mesopore support materials. The composite borohydrides, combined with the mesopore scaffold materials with a wide range of porosities, were carefully examined in different stages during heating by in situ and ex situ NMR. We also demonstrate the nanoconfinement effect on the hydrogen storage properties of the composite material investigated.

References

Dr. Young Whan Cho is presently a principal research scientist at Korea Institute of Science and Technology and the head of Nanomaterials Science and Engineering at University of Science and Technology. He received a MEng degree from Seoul National University and completed his PhD at Department of Materials Science and Metallurgy of Cambridge University in 1990. His research interests lie at metal hydrides for reversible hydrogen storage and the design and preparation of heterogeneous catalysts for synthetic fuels. Dr. Cho’s research group has published over 90 papers on hydrogen storage materials and alloys for hydrogen separation membrane for the last 10 years.

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NANOPOROUS FRAMEWORKS FOR HYDROGEN STORAGE AND H$_2$/D$_2$ ISOTOPE SEPARATION

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Highly porous coordination polymers or framework materials show high gravimetric hydrogen uptake by physisorption at low temperatures which can be utilized in cryo-adsorption tank systems. Furthermore, the uniform pore size distribution and small apertures can be applied for separation of light isotopes by quantum sieving. Mainly experimental results will be shown on the characterization of hydrogen storage properties and on newest achievements in isotope separation by quantum sieving.

Nanoporous Frameworks

The field of coordination polymers or framework materials has tremendously grown, since the stability of these structures could be shown after removal of the solvent molecules, exhibiting a nanoporous framework with ultra-high porosity and large specific surface area [1]. Different classes of these novel highly porous structures, e.g., metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) or covalent organic frameworks (COFs), have been extensively studied for applications in gas storage. Beside their large surface area, these crystalline frameworks possess well defined pore sizes having a uniform distribution. Frameworks with small pores and/or even smaller apertures can be designed enabling sieving effects for gas separation. Recently, quantum sieving in nanopores with a diameter near the kinetic extension of the hydrogen molecule was proposed as one promising possibility for separating D$_2$/H$_2$ isotope efficiently and effectively [2].

Hydrogen Storage

For the maximum hydrogen uptake at high pressure and 77 K an almost linear correlation with the specific surface area is found for many different nanoporous framework materials [3]. Furthermore, frameworks possessing smaller pores show typically a higher heat of adsorption. Both, maximum hydrogen storage capacity and heat of adsorption have to be considered to optimize the materials for their potential application [4]. The presentation will give a short overview and focus on a new method to determine experimentally the maximum gravimetric and volumetric hydrogen storage capacity for monoliths of porous materials in one isothermal measurement [5].

H$_2$/D$_2$ Isotope Separation

Separating gaseous mixtures of light gas isotopes, especially H$_2$/D$_2$, is a difficult task since size, shape and thermodynamic properties share each other. Quantum sieving [1] in these new crystalline frameworks with uniform pore size which can be tailored may be one solution. Experimental results obtained by low-pressure high-resolution isotherms and cryogenic thermal desorption spectroscopy (TDS) directly on isotope mixtures will show the potential of these frameworks and the importance of pore size and aperture for effective quantum sieving. The experimental findings are rationalized by first-principles calculations in the group of Thomas Heine, Jacobs University, Bremen, Germany, to reach a detailed microscopic picture of the underlying elementary processes [6].

References


Michael Hirscher is group leader at the Max Planck Institute for Intelligent Systems, Stuttgart, Germany. He studied physics at the University of Stuttgart, Germany and at the Oregon State University, Corvallis, USA, receiving a Master’s degree, a Diploma, and Ph.D. degree in 1982, 1984, and 1987, respectively. For his achievements he was awarded the Otto Hahn Medal of the Max Planck Society in 1988. Prior to taking his position in Stuttgart, he spent a post-doctoral fellowship at the University of Pennsylvania, Philadelphia, USA. He published over 100 papers and edited recently the "Handbook of Hydrogen Storage". His current research interests focus on nanoporous and nanoscale materials for gas storage and separation.

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NEW METHOD TO FORM Mg(BH$_4$)$_2$ NANOSTRUCTURES

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Nanoparticles of complex hydrides are usually synthesized via solution impregnation or melt infiltration in nanoporous scaffold. The former suffers from solvent residue and the latter is hindered when a compound (e.g. Mg(BH$_4$)$_2$) decomposes before melting. We developed a new method to synthesize Mg(BH$_4$)$_2$ nanoparticles via the gas-solid reaction between B$_2$H$_6$ and MgH$_2$ nanoparticles. This method has also been successfully applied to synthesize other compounds such as MgB$_{12}$H$_{12}$.

Introduction

Metal borohydrides, with high gravimetric and volumetric densities of hydrogen, have been extensively investigated for solid state hydrogen storage. Among them, Mg(BH$_4$)$_2$ shows a hydrogen capacity of 14.9 wt% and an attractive enthalpy change of -39 kJ/mol H$_2$ in dehydrogenation reaction.[1]

Solution impregnation of Mg(BH$_4$)$_2$ in nanoporous scaffolds, such as activated carbon and CMK3, has been investigated.[2, 3] The drawbacks of solvent residue and unconfined Mg(BH$_4$)$_2$ were reported in this method and the reversible hydrogen sorption was not achieved. Here, we reported a new method to synthesize Mg(BH$_4$)$_2$ nanoparticles via the reaction between MgH$_2$ nanoparticles and B$_2$H$_6$ according to the following reaction:[4]

$$\text{MgH}_2 + \text{B}_2\text{H}_6 \rightarrow \text{Mg(BH}_4\text{)}_2$$

Experimental

MgH$_2$ nanoparticles supported on carbon aerogel, with a MgH$_2$ loading ratio of 10 wt%, were prepared via melt infiltration. The reaction between MgH$_2$ nanoparticles and B$_2$H$_6$ was carried out at room temperature and promoted by ball milling. MgH$_2$ supported on nonporous graphite was investigated to compare the role of carbon matrix.

$^{11}$B MAS NMR, TEM/EELS/EDX, X-ray diffraction, N$_2$-physisorption and TPD-MS were used to characterize the samples.

Results

Figure 1 shows $^{11}$B MAS NMR spectrum of the as-synthesized Mg(BH$_4$)$_2$/carbon nanocomposite. The resonance at -41 ppm was assigned to the [BH$_4$] species. MgB$_{12}$H$_{12}$ was observed as a side product which was located at -16 ppm. The nanocomposite showed a reduced desorption temperature to 100 ºC and reversible hydrogen absorption under mild conditions.

Figure 1. $^{11}$B MAS NMR spectrum of the as-synthesized Mg(BH$_4$)$_2$/carbon nanocomposite, compared with references Mg(BH$_4$)$_2$ and K$_2$B$_{12}$H$_{12}$.

References

Increased air stability and decreased dehydrogenation temperature of LiBH₄ via modification within poly(methyImethacrylate)

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Abstract: An air-stable LiBH₄ polymeric composite was successfully prepared by modifying LiBH₄ with a gas-barrier polymer matrix--Poly (methylmethacrylate) (PMMA). The nanoconfinement of LiBH₄ in the PMMA network pore structure led to fast H₂ release from LiBH₄ molecules at low temperature. Meanwhile, PMMA can not only protect LiBH₄ from water and oxygen but also let hydrogen get in and out freely. LiBH₄@PMMA composite show the good hydrogen desorption property, which started to dehydrogenate at 53 °C and released 5.2 wt.% of hydrogen at 162 °C within 1 h. It could be concluded that PMMA can increase the stability of LiBH₄ in the atmosphere and reduce the dehydrogenation temperature of LiBH₄.

Introduction

Nanoengineering had been demonstrated to be a useful method to reduce the dehydriding/rehydriding temperature of LiBH₄. Nanoscale LiBH₄ is too reactive, so it is necessary to stabilize it for commercial utilization. PMMA had the better gas selectivity than other commonly polymer, with a high permeability ratio of H₂/O₂ [1]. Hence, it was used in hydrogen storage to keep away the water and oxygen but let the hydrogen get in or out freely. In this work, LiBH₄ was nanoconfined by PMMA with fine network pore structure for the first time, which protected from the water and oxygen and decreased the dehydrogenation temperature significantly (scheme1).

Result

The LiBH₄ particles had a diameter distribution of 19-73 nm in the crosslinked network pore structure of PMMA, and showed an amorphous structure. The results indicated that the particle size of LiBH₄ was significantly refined by modifying with PMMA. The LiBH₄@PMMA composite presents a lower onset temperature of 53 °C, and with two main dehydrogenation peaks (figure 1). As the exposure time extending, the intensity of peak at 360 °C became weaker and completely disappeared in the end. The first peak could be contributed to decomposing behavior of the LiBH₄ nanoconfined by the PMMA network pore structure, and the second peak was corresponding to the unconfined LiBH₄ outside the PMMA network pore structure. The above results confirmed that PMMA can protect LiBH₄ from the water and air but let the hydrogen get out freely, and significantly lower the stability of LiBH₄. Moreover, comparing with that the pure LiBH₄ only released 0.6 wt.% of H₂ within 4 h at 260 °C, LiBH₄@PMMA composites could release 5.2 wt.% of hydrogen in 1 h and 5.6 wt.% of hydrogen in 4 h at 162 °C, respectively.

References

Development and characterization of gas separation membranes for alkaline water electrolysis

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For introducing Hydrogen as emission-free energy carrier, hydrogen production via water electrolysis is regaining attention in the global search for alternative energy carriers nowadays. Efficiency enhancement for the Alkaline Electrolysis by means of reducing the electric power consumption is a pre-condition for a successful application of this promising technology. A crucial part of the electrolyser cell is the membrane, which is responsible for separating hydrogen and oxygen gases during the electrolysis process. It has to ensure a high ion conductivity and likewise an excellent chemical stability in 30 wt% KOH at 100°C for long term operation at 30 bar.

Introduction

Although the process of water electrolysis has been known for over two hundred years \[1\], it is now gaining increased attention as a means of energy storage for strongly fluctuating renewable sources in periods of excess energy production on a MW scale. For the well-engineered Lurgi-Zdansky type high-pressure alkaline electrolyser, increase of efficiency as well as cost reduction is a big issue for future commercialization.

Membrane Development & Characteristics

The separation membrane serves as ionic conductor, but electronic insulators and simultaneously prevents the intermixing of hydrogen and oxygen gases produced at cathode and anode side.

\[
\begin{align*}
2 \text{H}_2\text{O} (l) + 2 \text{e}^- & \rightarrow \text{H}_2 (g) + 2\text{OH}^- (aq) \quad \text{(cathode)} \\
2 \text{OH}^- (aq) & \rightarrow \frac{1}{2} \text{O}_2 (g) + \text{H}_2\text{O} (l) + 2 \text{e}^- \quad \text{(anode)} \\
\text{H}_2\text{O} (l) & \rightarrow \text{H}_2 (g) + \frac{1}{2} \text{O}_2 (g) \quad \text{(overall reaction)}
\end{align*}
\]

The OH\textsuperscript{-} conductivity of gas separation membranes strongly influences the efficiency of the electrolysis process. This is influenced by the formation of gas bubbles at the electrodes, which act as physical/electrical resistors in the electrolyte, thus redistributing and reducing current fields and decreasing the electrolyte conductivity \[2\]. The influence of gas bubbles can be reduced by increasing pressure \[3\] and by introducing separator materials featuring good wettability and a low sticking coefficient for gas bubbles.

Approaches to improve the efficiency of alkaline electrolyser are the reduction of the surface-specific cell resistance despite increased current densities (zero-gap cells, low-resistance diaphragms), higher operating temperatures (increased electrolyte conductivity, decreased electrode overpotentials), new electrocatalysts to reduce anodic and cathodic overpotentials \[4\]. Novel membrane developments and their characteristics for low resistance diaphragms will be demonstrated.


Lurgi-Zdansky type alkaline electrolyser at Giovanola, Monthey

Working conditions: 32bar, 85°C, 25wt-% KOH
Production rate: 760 m³/h H\textsubscript{2}, equ. to 3.3 Mw\textsubscript{el}
Energy Consumption: 4.3 – 4.6 kWh/m³ H\textsubscript{2}
Partial load: 25 - 100 % of nominal capacity
H\textsubscript{2} purity: 99.5 - 99.8 vol% 
O\textsubscript{2} purity: 99.3 - 99.6 vol%

PD Dr. Ulrich Vogt is Senior Scientist at the EMPA laboratory “Hydrogen & Energy” and leader of the group electrolysis & membranes. He received his PhD and his PD at the Albert-Ludwig-University Freiburg, Germany. Topics of his research work are hydrogen production via “high temperature steam electrolysis”, “new membrane materials for low temperature alkaline water electrolysis” and catalytic hydrogen combustion for cooking and heating applications by a newly developed catalytic hydrogen burner system. He authored over 50 SCI publications and 10 patents. He is lecturer at the University of Freiburg, with the topic Modern Ceramics, Cements, and Glasses.

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THE MYSTERY OF DIBORANE EVOLUTION DURING THE DECOMPOSITION OF Γ-PHASE MAGNESIUM BOROHYDRIDE

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Abstract: Upon heating, light metal borohydrides decompose to release a large amount (up to 18 wt%) of hydrogen which can be used as a fuel for mobility. While their reversibility and the specific reaction path of dehydrogenation remains under investigation in numerous systems, it is known that the hydrogen evolution is accompanied by diborane release inversely related to the stability of the borohydride. This makes quantification of the hydrogen amount an important task; we solve this using a combination of infrared spectroscopy and gravimetry under gas flow. Magnesium borohydride (Mg(BH₄)₂), which exists in numerous meta-stable phases at ambient conditions, is thought to be a member of the stable borohydride family (materials which do not emit diborane). However, we do in fact measure a significant, specific fraction of diborane released during the heating of the porous γ-phase between 300-500 K. To address the origin of this diborane emission, we use numerous techniques in an attempt to separate the borane impurities from the sample before heating (e.g. if simply a byproduct of synthesis), such as ball-milling and supercritical carbon dioxide drying.

Infrared (IR) Spectroscopy: Quantification
IR absorption spectra of the gaseous products of reaction can be effectively used to quantify and determine their specific contribution to mass loss in the sample.

Results
All materials investigated were weighed during heating in H₂ flow, and the mass loss deconstructed as in Figure 2. The H₂ and B₂H₆ (specific) mass loss are shown below.

<table>
<thead>
<tr>
<th></th>
<th>Total</th>
<th>Diborane</th>
<th>n-Butane</th>
<th>Other</th>
<th>Remainder (H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-MBH (AU)</td>
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<td>--</td>
<td>17-20</td>
<td>5.6-8.6</td>
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Table 1. Comparison of the (calculated) hydrogen mass loss and the measured impurity mass losses between 30-300 °C during the first heating cycle.

Conclusions
Supercritical CO₂ drying pre-treatment techniques were successful at suppressing the emission of diborane in γ-phase Mg(BH₄)₂ during heating, within detection limits of a downstream IR spectrometer. This may be an indication that diborane exists in an adsorbed state within the pores of the material after synthesis. A solvent/diborane-free route to the porous, γ-phase Mg(BH₄)₂ has been presented, yielding a material that decomposes to release very high quantities of H₂.

References

Nick was born in 1985 in Calgary, Alberta, Canada. He received a BS in chemistry from Arizona State University in Tempe, Arizona, USA in 2007. He received a MS and PhD in materials science at Caltech in Pasadena, California, USA with Prof. Brent Fultz and Dr. Channing Ahn, focusing on synthesis and thermodynamic characterization of physisorptive materials for hydrogen storage. In 2013, he joined Empa as a postdoc, and is supported by the EU program Bor4Store, studying new techniques for characterizing the decomposition pathways of light metal complex hydrides.

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TOWARDS EASY AND FULLY REVERSIBLE DEHYDROGENATION OF 
LBH₄ BY CATALYZING OF HIERARCHIC NANOSTRUCTURED COB

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Abstract: LiBH₄ is one of the most promising hydrogen storage materials due to its high gravimetric hydrogen density (18.5wt.%) and volumetric density (121kg/m³)[1,2]. However, LiBH₄ suffers from high thermodynamic stability, kinetics barriers and the resultant poor irreversibility which hinder its practical utilization. In this work, hierarchic nanostructured rod-like, flake-like, chain-like, waxberry-like and mulberry-like CoB catalyst was synthesised and doped into LiBH₄ by ball milling. It was revealed that CoB possessed extraordinary catalytic effect, dependent on its morphology, to improve the hydrogen storage properties of LiBH₄. Its dehydrogenation was dramatically facilitated under lower temperature, and the rehydrogenation was easily realized under mild conditions. Almost full reversibility was achieved with the assistance of mulberry-like CoB.

Hydrogen storage properties of LiBH₄-CoB system

Nanostructured CoB with different morphology of rod-like, flake-like, chain-like, waxberry-like and mulberry-like, was synthesized by controlling chemical reduction method[3], and then was mechanically milled with LiBH₄ in a weight ratio of 1:1. Figure 1 shows the dehydrogenation kinetics of LiBH₄-CoB system. It was found that CoB played as a pure catalyst facilitating the dehydrogenation of LiBH₄, and its morphology influenced greatly catalytic activity. The catalytic effect of those CoB is approximately in the order of mulberry-like > waxberry-like > chain-like > flake-like > rod-like, which is in accordance with their specific surface area from high to low. This led to the different dehydrogenation performance of those CoB doped LiBH₄ at 350°C. Among those nanostructured CoB, mulberry-like CoB showed the best catalytic effect. With its catalyzing, 10.4wt.% hydrogen was liberated from LiBH₄ with 1 h, which was faster than that of pristine LiBH₄ (Figure 1 left). By tuning the rehydrogenation conditions of hydrogen pressure and temperature, a almost full reversibility was achieved under 400°C and 10MPa, remaining stable 9.6wt.% hydrogen capacity at the fourth cycle (Figure 1 right). Conclusively, almost fully reversible dehydrogenation of LiBH₄ has been realized under rather mild condition by using nanostructured CoB catalyst.

Figure 1 Dehydrogenation kinetics of LiBH₄-CoB system with different morphology (left), cyclic dehydrogenation of mulberry-like CoB doped LiBH₄ (right). Hydrogen capacity was calculated with respect to LiBH₄.

References

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Abstract:
Fuel Cell system is a truly zero-emission source of electricity. The Energy conversion process is quiet, pollution-free and two to three times more efficient than combustion. As long as the fuel, the ideal choice of which is hydrogen, is supplied, fuel cells can continuously generate electricity. According to the “2012 Fuel Cell Technologies Market Report” published by U.S. Department of Energy (DOE), the cost of per kilowatt (kW) for high volume production of transportation fuel cells moved closer to DOE’s target of $30 per kW. As a result, the development of fuel cells calls for suitable hydrogen storage system for commercialize application.

Our study focus on the research of rare-earth based metal hydrides, which has both high capacity and low production cost, prepared by rapid quenching method in medium frequency induction furnace. The hydrogen storage capacity of the alloy reach 1.6wt% with flat and broad plateau pressure after heat-treatment as show in figure 1. The discharge capacity of the hydrogen storage canister ST2800L filled with the alloy is 2578.04NL with an efficiency of c.a. 92.07% at 30°C. As shown in figure 2, the discharge properties of 14Nm³ integrated hydrogen storage system composed by 5 ST2800L canisters is tested at 20°C in water bath. The whole system discharges 12196.42NL of hydrogen with an efficiency of 87.12%.

Short CV: Prof. Xiao’s Research Expertise is mainly focus on developing Energy storage materials and nanotechnology, including metal hydrides, Ni-MH batteries, Li-ions batteries and magnetic materials. In the past five years, his research team was granted by several key projects funded by the China National Natural Science foundation and Guangdong government on the research of areas mentioned above, and published over 40 academic articles in professional journals.

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COMPUTATIONAL DESIGN OF NANOPARTICLE CATALYSTS FOR SUSTAINABLE PRODUCTION OF SYNTHETIC FUELS

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Emerging technologies for conversion and storage of energy from renewable and intermittent sources like wind and solar energy remain non-competitive on commercial terms, due to poor activity, selectivity, efficiency, stability or cost. The ability to improve and ultimately design superior materials is therefore paramount in the development of more efficient sustainable energy technologies. Computational methods like density functional theory (DFT) have reached a level, where predictive accuracy can be reached by linking complex morphologies and structures to the functionality.

Materials Predictors for Catalyst Design

We present results using model structures and materials predictors that link the complex functionality of the materials to simple atomic parameters such as the binding energy of critical reaction intermediates, e.g. the nitrogen binding energy on nanoparticle catalysts for electrochemical fixation of N₂ into NH₃ (Figure 1) [1].

Genetic Algorithms for Stability Design

We combine the approaches with database methods and evolutionary algorithms to predict and design superior and stable catalysts, e.g., for the Oxygen Reduction Reaction (ORR) or nanoparticle electrocatalysts for fixation of CO₂ into methane or methanol with improved stability under operational conditions (Figure 2) [2].

Figure 1 Genetic algorithm based prediction of the core-shell configuration of 309 atoms Cu-Ni nanoparticle [2].

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References


Tejs Vegge is a Professor at Department of Energy Conversion and Storage at the Technical University of Denmark, where he is also Head of Section for Atomic Scale Modeling and Materials. His research activities are centered round integrated computational and experimental design and in situ characterization of novel materials for energy conversion and storage, e.g. DFT-based material design from model structures, predictors and genetic algorithms, nanoparticle (electro)catalysts for sustainable production of synthetic fuels and ammonia, batteries and materials for hydrogen storage. Among other things, Prof. Vegge is project manager for “Electrochemical fixation of N₂ and CO₂ into fuels”, under the UNIK project Catalysis for Sustainable Energy (CASE).

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AMIDOBOARANES – FORMATION AND APPLICATIONS

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Abstract: Alkali or alkaline earth amidoboranes can be prepared via the reactions between ammonia borane and metal hydrides or amides. A variety of mono- and bi-metallic amidoboranes have been synthesized and exhibit interesting dehydrogenation properties and tuneable thermodynamics. On top of that, those high hydrogen content chemicals also have unique applications in selective hydrogenation and exfoliation of layered materials.

Amidobranes for H₂ storage

The interaction between ammonia borane (AB) and metal hydride or amides has been widely explored in the synthesis of amidoboranes. LiH or NaH reacts with AB giving rise to LiNH₂BH₃ or NaNH₂BH₃, which releases large amount of hydrogen exothermically. By forming bi-metallic amidoboranes, such as Na₂Mg(NH₂BH₃)₄ and K₂Mg(NH₂BH₃)₄, the dehydrogenation becomes endothermic. The reason for that is due to the formation of more stable reactant (see Fig. 1).

Selective hydrogenation

Lithium amidoborane (LiAB) shows superior reduction capability in reducing ketones or imines directly to corresponding secondary alcohols or amines at room temperature. More importantly, it can chemoselectively reduce α,β-unsaturated carbonyl compounds to allylic alcohols. Mechanistic study indicates that the reduction is through double hydrogen transfer process. Theoretical investigations show that the first and rate-determining step of reduction is the elimination of LiH from LiAB followed by the transfer of H(Li) to C site of unsaturated bond.

Ammonia Borane as efficient exfoliation agent

Nearly quantitative yield in which ca. 25% is single-layer graphene can be obtained by ball milling of graphite with AB (see Fig. 2). Due to the interaction between NH₃BH₃ and the sp² carbon lattice network of graphite, NH₃BH₃ molecules can be readily adsorbed/spread on the surface of graphite under ball milling condition resulting in the weakened interlayer van der Waals interactions and allowing graphene sheets easily to be exfoliated.

References


Ping Chen, is a professor at the Dalian Institute of Chemical Physics (DICP), CAS. Chen received a PhD degree in Chemistry 1997 from Xiamen University, China. Before joining DICP she was the Associate Professor at Department of Chemistry and Department of Physics, National University of Singapore. Her primary research interests include the development of chemical and complex hydrides for hydrogen storage, catalysis, and materials chemistry. She and her team pioneered the research in hydrogen storage over amide-hydride composite and amidoborane system.

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**BOROHYDRIDES: NEW INSIGHTS FROM NMR**

Arndt Remhof1, Yigang Yan1, Daniel Rentsch2, Andreas Züttel1, Zbigniew Łodziana3


Nuclear Magnetic Resonance (NMR) has been intensively used to unveil sorption pathways of borohydrides and other hydrogen storage materials. Based on solid state and solution state NMR, we identified the \([B_3H_8]^-\) species as major intermediate in the hydrogen release reaction of \(Y(BH_4)_3\). In a broader context, we show that NMR data, combined with electronic and structural data provide deeper understanding to the properties of bulk and to nano-sized structures.

**Reaction Pathways**

Understanding and controlling the sorption pathways is crucial for the applicability of a hydrogen storage material. In the hydrogen uptake and release reactions of borohydrides stable intermediates such as dodecaborates or volatile boranes such as \(B_2H_6\) act as boron sinks and reduce reversibility.

We investigated intermediate products and the solid residue of the hydrogen release reaction of \(Y(BH_4)_3\) by solid state and solution state NMR, Raman spectroscopy and by X-ray diffraction [1]. \(Y(BH_4)_3\) decomposed via the \([B_3H_8]^-\) species, while the \([B_{12}H_{12}]^2^-\) and \([B_{10}H_{10}]^2^-\) species were not detected. We therefore conclude the following hydrogen release pathway for \(Y(BH_4)_3\):

\[
Y(BH_4)_3 \rightarrow \frac{1}{3}Y[B_3H_8]_3 + \frac{2}{3}YH_3 + H_2 \quad (1)
\]

Hydrogen release pathways via \([B_3H_8]^-\) are favourable for reversible hydrogen storage [2], making \(Y(BH_4)_3\) an attractive hydrogen storage material.

**Chemical shifts**

NMR is more than a powerful fingerprint technique for the phase identification and quantification in chemical analysis. The key parameter in NMR spectroscopy, the chemical shift, is related to the shielding of the core electrons. In Figure 1 we present the relation between the \(^{11}B\) chemical shift and the total charge of an individual \([BH_4]^-\) ion based on the Bader method [3]. The larger charge on \([BH_4]^-\), the larger \(^{11}B\) chemical shift can be observed for most compounds. Compounds that show deviation from the linear correlation between Bader charge and \(^{11}B\) chemical shift, such as Al\((BH_4)_3\) and Zr\((BH_4)_4\), possess more directional bonds between metal cation and \([BH_4]^-\), indicative of a more covalent nature of the bond.

**Figure 1.** The \(^{11}B\) chemical shift \(\delta\) with respect to the Bader charge of the \((BH_4)\) unit for selected metal borohydrides.

**References**


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TRANSITION METAL CATALYZED DEHYDROGENATION OF B-N-H BASED MATERIALS IN SOLID STATE

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Abstract: Nano-sized transition metal (Fe, Co or Ni) catalyst was successfully synthesized by introducing precursors into B-N-H based hydrogen storage materials (ammonia borane, borohydride ammoniates and borohydride hydrazinates et al.). The experiment results show that the dehydrogenation temperatures of B-N-H based materials decreased dramatically compared with the pristine materials. Characteristic results, i.e. Mössbauer and PDF techniques, reveal that metal-boron amorphous alloy is the activity species during the dehydrogenation of B-N-H based materials.

Introduction

Compounds or complexes with high hydrogen content are viewed as potential hydrogen storage materials. Among them, the B-N-H based materials are promising candidates, for example, Ammonia borane (NH$_3$BH$_3$, AB in short), borohydride ammoniates (MBH$_4$-NH$_3$) and borohydride hydrazinate (MBH$_4$-nN$_2$H$_4$) et al. However the dehydrogenation of these compounds occurs at relatively high temperature with releasing volatile byproducts (NH$_3$, N$_2$, N$_2$H$_4$ and borazine et al.). Thus, in this paper, in situ synthesized metal-boron alloy catalyst was introduced into these B-N-H based materials to decrease the dehydrogenation temperature.

Results

We developed a “co-precipitation” method to introduce nanosized transition metal (Fe, Co and Ni) catalysts into AB in solid state without sacrifying hydrogen content. The experimental results show that about one equivalent hydrogen can be released from doped-AB at a temperature as low as 60 °C with the depression of byproducts (NH$_3$ and borazine) and sample foaming. In contrast to dehydrogenation of neat AB that yields non-crystalline products, the solid-state catalyzed dehydrogenation of AB yields the crystalline polyaminoborane (PAB) as a major product. Mössbauer spectroscopy and X-ray atomic Pair Distribution Functions (PDFs) characterizations show that the metal-boron (M-B) alloy is the active center to the catalytic dehydrogenation.

A new class of hydrogen storage materials, borohydride hydrazinates (for example, LiBH$_4$·nN$_2$H$_4$), was successfully synthesized. In particular, the bidentate NH$_2$NH$_2$ coordinates with LiBH$_4$ in molar ratios of 1:1 and 1:2 giving rise to a monoclinic LiBH$_4$·NH$_2$NH$_2$ and orthorhombic LiBH$_4$·2NH$_2$NH$_2$, respectively. Around 13.0 wt % H$_2$ can be released from LiBH$_4$·NH$_2$NH$_2$ at 140 °C in the presence of Fe-based catalysts. From XRD, FTIR, GC and Raman analysis, we can conclude that the overall decomposition of LiBH$_4$·NH$_2$NH$_2$ in the presence of Fe-based catalyst may follow the reaction R1:

$$3(\text{LiBH}_4\cdot\text{N}_2\text{H}_4)\rightarrow\text{Li}_2\text{BN}_2+2\text{BN}+\text{N}_2+12\text{H}_2 \quad \text{R1}$$

XAFS and Mössbauer results show that Fe-B alloy is the functional species catalyzing the dehydrogenation of LiBH$_4$·N$_2$H$_4$.

Conclusions

In situ synthesized transition metal (Fe, Co and Ni)-boron alloy was successfully introduced into B-N-H based materials. The as-prepared metal-boron alloy is an efficient catalyst for the dehydrogenation of B-N-H based hydrogen storage materials.

References


Dr. Teng HE received his PhD degree from Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP, CAS) under the supervision of Prof. Ping CHEN and Prof. Tao Zhang in 2012 and then was exceptionally promoted to be an associate professor in DICP. His research interests include: 1) synthesis and characterization of B, N based materials for hydrogen storage; 2) catalytic dehydrogenation of B-N-H based hydrogen storage materials; 3) catalytic de/hydrogenation of organic compounds.

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CETi2Al20: A CATALYST-REACTANT INTEGRAL AGENT TO NAALH4 SYNTHESIS

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The cooperative catalytic effect of Ti(3d)–Ce(4f) on the hydrogen storage properties of NaAlH4 was studied. Target and reference samples were prepared by in situ high-energy-vibration ball-milling. In the preparation stage, the degree of reaction and reaction rate with the target system (CeTi2Al20–Al-NaH) were much higher than those observed with the other reference samples. The target sample is also the best in the dehydriding/rehydriding performances. In particular, use of this sample 1) markedly decreased the onset temperature of the reaction, and 2) markedly increased the reaction rate and hydrogen storage capacity. Loose Ti–Ce coupling resulted in a cooperative catalytic effect on dehydriding/rehydriding of NaAlH4 that was weaker than that due to strong Ti–Ce coupling. CeTi2Al20 is a catalyst-reactant integral agent to NaAlH4 synthesis; related highly cooperative catalytic effects are closely associated with strong Ce–Ti–Al coupling.

Fig. 1 XRD profiles of as-BM samples with high-energy-vibration ball-milling under 8MPa hydrogen pressure. No.1: NaH+Al, BM 48h; No.2: Ti+Al+NaH, BM 12h; No.3: Ce+Al+NaH, BM 12h; No.4: Ce+Ti+Al+NaH, BM 12h; No.5: CeTi2Al20+Al+NaH, BM 12h. All the mole ratio of catalytic element to Al was 1:20 and Al to Na was 1:1. For samples No. 4 and No. 5, the mole ratio of Ce to Ti was 1:2. Only NaAlH4 can be distinguished in No.5 situation.

Fig. 2 Dehydriding/rehydriding kinetic profiles of samples. (a) non-isothermal (heating-up speed 1K/min) dehydriding kinetic profiles of samples; (b) isothermal rehydriding kinetic profiles of samples in 383K under 8MPa initial hydrogen pressure. No.1: NaH+Al, BM 48h; No.2: Ti+Al+NaH, BM 12h; No.3: Ce+Al+NaH, BM 12h; No.4: Ce+Ti+Al+NaH, BM 12h; No.5: CeTi2Al20+Al+NaH, BM 12h. Hydriding/dehydriding kinetics properties of No.5 is remarkable better than that of other four samples.

References

Cun-Ke Huang was born in Nanning, China, in 1975. He made his Ph.D degree in the South China University of Technology, major in Material processing engineer with Prof. Min Zhu. He received his Ph.D. degree in 2009, for his study on equilibrium phase relation and defect thermodynamics of Ti doped NaAlH4 with first-principles method. He Now he works in College of Physics Science and Technology, Guangxi University, and he make researcher focus on some new energy functional materials by theoretical and experimental methods.

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EFFECT OF MICROWAVE IRRADIATION ON THE HYDROGEN DESORPTION PROPERTIES OF MGH2/LiBH4 COMPOSITE

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Abstract: The effect of microwave irradiation on the hydrogen desorption properties of MgH2/LiBH4 composite was investigated. It is shown that the composite can be heated rapidly with the addition of LiBH4 by microwave heating which brings about a fast dehydrogenation of MgH2. The hydrogen released from MgH2+10 wt% LiBH4 under microwave is 5 times more than that under conventional heating at 300 °C in 30 min. The sample can be heated even more rapidly by microwave heating after cycling. These results demonstrate that the microwave heating is an effective technology for improving the hydrogen desorption kinetics of MgH2/LiBH4 composite with high energy efficiency.

Introduction

Mg and Mg-based solid hydrogen storage materials are considered to be the most promising solid hydrogen storage media, contributed to their light weight, low cost, and large hydrogen storage capacity [1]. However, high dehydrogenation temperature and relatively slow absorption and desorption dynamics make it unsuitable for practical application. Considering the rapid heating property of LiBH4 under microwave [2], we added LiBH4 into MgH2 and studied the effect of microwave radiation on MgH2/LiBH4 composite system, in order to improve the hydrogen storage performance of the composite.

Experimental

The composites of MgH2·xLiBH4 (x=5-30wt%) were prepared by ball milling method. The dehydrogenation of the samples under microwave irradiation was carried out as follows: about 0.5 g of sample was placed in a crucible of BN which was placed in a hermetic Teflon container. The container equipped with a K-type thermocouple, air inlet and outlet, was inserted into the cavity of multi-mode microwave instrument (SYNO- THERM WG3/2.45). In order to investigate the effect of microwave irradiation on the hydrogen desorption properties of MgH2/LiBH4 composites, the isothermal desorption kinetics of the samples both under microwave heating and conventional electrical resistant heating were measured by volumetric method. The samples before and after microwave irradiation were examined by XRD, FTIR measurements. To prevent sample oxidation, all handleings were performed in a glove box (MBraun Labstar) under high purity Ar.

Results

The temperature curves of the samples under microwave against heating time were measured. For the samples with LiBH4 addition, the heating rates at initial stage are slow, but when the temperature is higher than the lattice transformation temperature (around 107 °C) of LiBH4, the composites are rapidly heated since LiBH4 acts as a strong microwave absorbent. The isothermal desorption kinetics of MgH2·10wt% LiBH4 sample at 300 °C heated by microwave irradiation and conventional heating were measured. The results showed that the sample desorbed only 0.5 wt% H2 under conventional heating within 30 min, while desorbed 3 wt% H2 under microwave heating, which is about 5 times more than that under the conventional heating. Furthermore, the samples after cycling were heated by microwave heating. The results showed that after 2 and 5 cycles, the rehydrogenated samples can be heated even more rapidly up to 500 °C under microwave irradiation, and the slow heating rate stage below 107 °C disappeared. The improved microwave heating performance of the samples after cycling was proposed to be contributed to Li2B12H12, which was formed by LiBH4 during the cycling.

References


Haiyan Leng obtained her PhD from Institute of Metal Research in 2003, and worked in Hiroshima University (Japan) as a JSPS postdoctoral fellow from 2004 to 2006, in AIST (Japan) as a research fellow in 2007, in Institute of Nanotechnology (Germany) as a guest scientist in 2008, and in Shanghai Institute of Microsystem and Information Technology from 2009 to 2011. Now she is an associate professor in Shanghai University. She has published more than 20 SCI cited papers in journals like J. Power Sources, J. Phys. Chem. B, and Int. J. Hydrogen Energy, and several Chinese and international patents. Her interesting research focuses on hydrogen storage materials of light elements, such as Mg-based materials, Amide and Borohydride.

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Calcium Borohydride Modified by N-H Group for Hydrogen Storage

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Abstract: In order to decrease the dehydrogenation temperature, the interaction between calcium borohydride and metal amides (LiNH, Mg(NH)2 and Ca(NH)2, etc.) and ammonia was systematically investigated and some addictives were doped to further decrease dehydrogenation temperature. More than 4.5 and 7 wt% of hydrogen can be released at temperatures as low as ca. 165 and 178 °C from the cobalt-catalyzed Ca(BH)2•2NH3 system, respectively. In addition, isothermal volumetric release measurement at 250 °C of Ca(BH)2•2NH3 shows that it can also desorb 6 equiv. H2 (11.5 wt%). The presence of additive NH3 in Ca(BH)2•2NH3 leads to a shortened N-H•••H-B dihydrogen bond in the structure and may facilitate low-temperature dehydrogenation.

More recently, Ca(BH)2, which has more favorable thermodynamics (32 kJ/mol H2, estimated by density functional theory) than LiBH4, while maintaining attractive hydrogen capacity (11.4 wt %), has been acknowledged as one of the potential candidates for hydrogen storage. However, the decomposition for hydrogen release of Ca(BH)2 is at a temperature as high as 350 °C.

In order to decrease the dehydrogenation temperature, the interaction between calcium borohydride and metal amides (LiNH, Mg(NH)2 and Ca(NH)2, etc.) was systematically investigated and some addictives were doped to further decrease dehydrogenation temperature. More than 4.5 and 7 wt% of hydrogen can be released at temperatures as low as ca. 165 and 178 °C from the cobalt-catalyzed Ca(BH)2•4LiNH2 system, respectively.

The Ca(BH)2•2Mg(NH)2 and Ca(BH)2•2Ca(NH)2 composites are thereby synthesized. It is found that the binary combined systems exhibit an onset dehydrogenation temperature of about 220 °C, which is about 100 °C lower than that of pristine Ca(BH)2. The hydrogen release measurements for Ca(BH)2•2Mg(NH)2 and Ca(BH)2•2Ca(NH)2 samples below 480 °C show desorption amounts of 8.3 and 6.8 wt % hydrogen, respectively, in the pathways of Ca(BH)2•2Mg(NH)2 → 1/3 [CaMg4(2BNH)6] + 8 H2 and Ca(BH)2•2Ca(NH)2 → 1/3 Ca2(2BNH)6 + 8 H2, respectively.

In addition, a new compound Ca(BH)2•2NH3 was synthesized through gas-solid reaction. Thermal decomposition analyses show that, under a dynamic flow mode where gaseous product(s) can be removed immediately from the solid reactant, Ca(BH)2•2NH3 undergoes deammoniation though two steps and forms Ca(BH)2•NH3 and Ca(BH)2, respectively. However, the thermal decomposition is conducted in a close system where the gaseous product is kept in the vicinity of the solid reactant, Ca(BH)2•2NH3 can release 6 equiv. H2 (11.5 wt%) in the temperature range of 100-500 °C according to reaction: Ca(BH)2•2NH3 → 1/4 Ca(BH)2 + 1/4 Ca3(BN)2 + BN + 6 H2, showing the participation of NH3 in the H2 production. Isothermal volumetric release measurement at 250 °C of Ca(BH)2•2NH3 shows that it can also desorb 6 equiv. H2 for 100 h. The presence of additive NH3 in Ca(BH)2•2NH3 leads to a shortened N-H•••H-B dihydrogen bond in the structure and may facilitate low-temperature dehydrogenation.

References
Hailiang Chu was born in Shandong province, China in 1980. He received his B.S. in chemistry from Qufu Normal University in 2002 and Ph.D. in physical chemistry under supervision of Professor Lixian Sun in 2008 from Dalian Institute of Chemical Physics, Chinese Academy of Sciences (DICP, CAS). After graduation, he joined DICP as an Assistant Researcher in Professor Ping Chen’s group. In 2012, He joined Guilin University of Electronic Technology and was awarded associate professorship. His research interest focuses on the synthesis and application of high capacity hydrogen storage materials, including alloys, metal borohydrides, metal-N-H materials, ammonia boranes and their derivatives.

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NANOPARTICLE CATALYSIS OF HYDROGEN EVOLUTION

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Abstract: DFT calculations have been carried out for hydrogen evolution reaction and hydrogen oxidation reaction at edges on Pt nano-particles and the results compared with the Pt(110)-2x1 surfaces and stepped surfaces.

Introduction
The interaction of hydrogen with the surface of platinum metal is of fundamental importance to a wide range of energy technologies including electrolysis of water and hydrogen fuel cells. The metal is typically dispersed as small particles embedded in a matrix. The active sites of such particles can be under-coordinated atoms at edges where crystal facets meet, or at corners where edges meet. A 2 nm particle, which is at the lower end of the size range used in fuel cells today, contains on the order of 1000 atoms. Density functional theory (DFT) calculations of the catalytic activity of a whole nanoparticle of this size generally require a prohibitively large computational effort. An alternative approach is to construct a periodic array of the sites of interest, such as edges between micro-facets.

HER/HOR at Pt nanoparticle edges
The missing-row reconstructed Pt(110)-(1x2) surface can be considered a very small model of edges between (111) facets and has been studied both experimentally and theoretically [1,2]. In the current work [3], the associative desorption of hydrogen at edges and facets on Pt nanoparticles was studied using DFT. The goal was to identify catalytically active sites on Pt nanoparticles for the hydrogen evolution reaction as well as the hydrogen oxidation reaction. The adsorption sites were modeled by periodic, face centered cubic slabs representing an array of edges between two (111) micro-facets or edges between (111) and (100) micro-facets. The width of the facets in the periodic representations was systematically increased to reach converged results for binding and activation energy. Under typical electrochemical conditions (for small applied voltage vs. SHE), edges between (111) micro-facets were found to be several orders of magnitude more active than edges between (100) and (111) micro-facets or at terraces. The desorption mechanism on the former edge involves the formation of a Kubas complex which apparently lowers the desorption barrier. Unlike the missing row Pt(110)-(2 x 1) surface, which has sometimes been used as a simple model for edges between (111) micro-facets, the converged edge model does not show the recently reported reentrant behavior in desorption mechanism [1].

References

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TITLE SYNTHESIS AND PROPERTIES OF NANOSTRUCTURED HYDROGEN STORAGE MATERIALS

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Abstract:

We developed a method to prepare ultrafine Mg nanoparticles around 40 nm by acetylene plasma, which is a revised approach for the traditional hydrogen metal plasma reaction. Due to the short diffusion distance and large specific surface area, the kinetics of hydrogenation and dehydrogenation of the small Mg nanoparticles were improved.

Li$_2$NH and Mg(NH$_2$)$_2$ hollow nanospheres with diameter of 100 nm and thickness of 10 nm were prepared by plasma metal reaction based on the Kirkendall effect in order to improve their hydrogen storage properties. In the synthesis, the bulk lithium and magnesium were vaporized and reacted with ammonia to obtain the hollow nanostructure directly. The results show that the structure dramatically enhanced the hydrogen desorption kinetics because of their short diffusion distance and large specific surface area.

The combination of the use of MOFs as the catalyst precursors and the in situ generation of catalytically active sites leads to dramatically improved H$_2$ releasing rates from AB systems at the operation temperature of proton exchange membrane fuel cells. In the hydrolysis of AB, the MOF based catalyst (MOF1cat) exhibits high catalytic activity and good recycling properties at room temperature in the air.

![Figure 1. TEM images of Mg nanoparticles prepared with acetylene fraction of (a) 28 %, (b) 21.7 %, (c) 14.3 %, (d) 5.3 %, (e) 0 %, and the particle size distribution of Mg nanoparticles prepared with 21.7 % acetylene (f).](image)

Short CV: Xingguo Li is Professor and Director of New Energy and Nano materials Laboratory, deputy chair of the Inorganic Chemistry Institute at Peking University. His research interests focus on hydrogen storage materials, hydrogen generation and purification, battery electrode materials and nano materials. He has carried out more than 30 projects supported by NSFC, MOE, MOST and other organizations and companies as well as Japanese NEDO. Prof. Li has already published more than 200 papers in important journals such as Adv. Mater., Nano Letter, Nano Energy, ACS Nano, Small, Biomaterials, Chem. Mater., Chem. Eur. J., Chem Commun., Applied Catalysis B, APL, JPCB, JPCC, Crystal Growth & Design, Inter. J. Hydrogen Energy, Acta Materialia, Langmuir, Nanotechnology, contributed chapters to two books published by Nova Science Publishers, Inc. and American Scientific Publishers, and applied 18 patents. He has presented over 140 talks around the world with over twenty plenary and keynote lectures. He has received the National Distinguished Young Investigator Fund (2000), Lectureship Award of Japan Research Institute of Material Technology (2002) and GM foundation Science & Technology Achievement Award (2005).

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SPONTANEOUS DEHYDROGENATION REACTIONS INVESTIGATED BY IN-SITU SPECTROSCOPY

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Abstract

Several new transition metal borohydrides e.g. Ti(BH₄)₃ have been synthesized and the dehydrogenation reaction was investigated in view of the thermodynamics and intermediate products formed by means of thermo gravimetry, mass spectroscopy and IR-spectroscopy. The hydrogen desorption kinetics was analyzed and the intermediate products were identified.

Synthesis of Ti(BH₄)₃

The new compound Ti(BH₄)₃ was synthesized by the metathesis reaction and reactive milling. The intermediates and/or products formed during the hydrogen desorption reactions are thermodynamically unstable. Their characterization and measurement as a function of time and temperature is a key challenge to understand the reaction mechanisms and the upscaling. [1].

We analysed the formation of intermediate species, studying LiBH₄, one of the materials with the highest gravimetric hydrogen density considered for hydrogen storage. The following reaction was investigated:

\[ \text{TiCl}_3 + 3 \text{LiBH}_4 \rightarrow \text{Ti(BH}_4)_3 + 3 \text{LiCl} \rightarrow \frac{3}{2} \text{B}_2\text{H}_6 + \frac{1}{2} \text{H}_2 + \text{TiH}_2 + 3 \text{LiCl} \]

The identification and characterization of Ti(BH₄)₃ is a technical issue because it is extremely reactive in air, spontaneously decomposes within few hours at room temperature and it is volatile. Therefore, different in situ techniques i.e. thermogravimetric balance, mass and IR-spectroscopy were combined in order to determine the thermodynamics of the reaction, the emitted and the intermediate products. [2]

Stability and the Intermediate Species

We found that the metathesis product, Ti(BH₄)₃, decomposes into diborane, hydrogen and TiH₂. Therefore it is an intermediate phase in the dehydrogenation reaction of TiCl₃ added LiBH₄. Ti(BH₄)₃ is stable at room temperature for few hours and therefore its detection is possible. This species, under these experimental conditions, does not catalyze the decomposition reaction of LiBH₄. These findings open a new perspective in the research of additives to destabilize complex hydrides.

Related compounds

Several intermediate species have been theoretically predicted but never experimentally shown: V(BH₄)₃ or Zn(BH₄)₂. The spontaneous release of gas species from the products of the reaction of LiBH₄ with AlCl₃ [3], ZnCl₂, and VCl₃, will be analyzed. A comprehensive bulk, surface and gas phase analysis of the reactions products and eventually formed intermediate species will be presented, pointing out the route towards the control of spontaneous dehydrogenation reactions and the stabilization of the intermediate species.

References


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Born 13.1.1982 in Varese, Italy. In 2011 she graduated in Physics in Bologna, Italy, with Prof. E. Bonetti. During her studies she collaborates with the Danish Technical University in Copenhagen, Denmark, with Prof. T. Bohr; the Department of Chemistry of the Aarhus University in Denmark, with Prof. T. R. Jensen and with the California Institute of Technology in Pasadena (CA), with Prof. B. Fultz and Dr. C. Ahn. Since 2011 she is PostDoc in the Complex Hydrides Group in the Laboratory Hydrogen & Energy at Empa, Dübendorf, Switzerland.

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RAPID SOLIDIFICATION TO AFFECT ON PROPERTIES OF V-BASED HYDROGEN STORAGE ALLOYS

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Abstract The V-based BCC alloys have high reversible hydrogen capacities around 2~3mass% at room temperature and are therefore expected to be applied as on-board hydrogen storage materials. During the first 10 hydrogenation/dehydrogenation cycles, the capacities decrease markedly by about 10~15%, which hinders the large-scale application of the alloys. One of the reasons is accumulating of microstrain in the lattice during cycles. In order to reduce the microstrain, rapid solidification method to manufacture the alloy was investigated. Both the grain size and the initial dehydrogenation capacity are reduced comparing with those of the arc-melted ingot. However, after homogenizing heat treatment at high temperature, the needle-like alloy shows higher initial dehydrogenation capacity with an increase of the annealing temperature. Stress relief annealing at 673K was also discussed. The initial dehydrogenation capacity does not change much. However, after 10 hydrogenation/dehydrogenation cycles, the microstrain in the lattice is reduced to a degree, indicating that the cycle stability is improved.

References

Fig. 1 Rapid solidified V-Ti-Cr-Fe alloys: a) without annealing; b) 1373K for 0.5h; c) 1473K for 0.5h; d) 1573K for 0.5h.


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OXYNITROGENOGRAPHY: THE SEARCH FOR OXYNITRIDES FOR SOLAR WATER SPLITTING

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Abstract The solar hydrogen production via photoelectrochemical (PEC) water splitting requires an ideal semiconductor material with a high stability and a good absorption of the solar spectrum. Oxides are generally stable in aqueous solutions, but their bandgap is usually too large to efficiently absorb sunlight. Nitrides, on the other hand, have ideal bandgaps but they are prone to corrosion. Oxynitrides are therefore potential candidates to obtain the best of both worlds: the oxide's stability and the nitride's strong light absorption. One of the most promising oxynitrides for solar water splitting is tantalum oxynitride (β-TaON). Due to its favorable band positions, it is thermodynamically able to split water without any external bias. However, its synthesis is very challenging. In this study, we propose 'oxynitrogenography' as an approach towards the controlled and reproducible synthesis of any Ta-O-N phase, including the desired β-TaON phase. Tantalum oxide thin films were nitridated in a tube furnace under controlled flows of ammonia, water and hydrogen, while following the optical transmission of the film in-situ. The optical absorption changes in the film can be directly correlated to the presence of different phases (Ta₂O₅, TaOₓNᵧ, Ta₃N₅), due to their different absorption edges. As a result, the thermodynamic equilibrium conditions to obtain these various phases were determined, and a phase diagram was constructed. The physical characteristics, electronic properties, and PEC performance of these phases were investigated. It was found out that the stability of the TaOₓNᵧ samples was a major challenge, which was tackled by the addition of convenient graphite-based protective layers and the deposition of a surface catalysts such as NiOOH.

Reference
Moreno de Respinis received his bachelor degree in physics at the University of Milan in 2008, and earned his master degree in sustainable energy with study line hydrogen and fuel cells at the Technical University of Denmark (DTU) in 2011. He concluded his master with a fellowship at the Lawrence Berkeley National Laboratory (LBNL) in Dr. Heinz M. Frei’s group, where he performed mechanistic studies of water photo-oxidation by visible-light driven $\text{Co}_3\text{O}_4$ catalyst. He is currently a Ph.D. student at the Delft University of Technology (TUDelft) where he is researching on hydrogen production and storage via photo-electrochemical solar water splitting.

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RECENT STUDY ON HYDROGEN STORAGE PROPERTIES OF MG-BASED MATERIALS PREPARED BY HCS+MM

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Abstract: Mg-based material is still an attractive material for hydrogen storage due to its high hydrogen storage capacity, abundant resources, low cost and low environmental impact [1]. However, the sluggish hydrogen absorption/desorption kinetics at moderate temperatures and the high thermodynamic stability of MgH₂ hinder its application. We have developed a method, namely hydriding combustion synthesis plus mechanical milling (HCS+MM), to prepare advanced Mg-based hydrogen storage materials for hydrogen storage and hydrogen production [2-4]. The process of HCS+MM has the advantages of low energy consumption, short processing time and high activity of the product. Here we present some recent studies on hydrogen storage properties of Mg-based materials prepared by HCS+MM in our group.

Mg₉₅Ni₅-Zr₀.₇Ti₀.₃Mn₂-MWCNT system

In order to improve the hydrogen storage properties of Mg-based material, the Laves phase compound Zr₀.₇Ti₀.₃Mn₂ and MWCNT were co-added to form an Mg₉₅Ni₅-Zr₀.₇Ti₀.₃Mn₂-MWCNT composite by the process of HCS+MM. For comparison, the composites of Mg₉₅Ni₅, Mg₉₅Ni₅-Zr₀.₇Ti₀.₃Mn₂ and Mg₉₅Ni₅-MWCNT were also prepared by HCS+MM. It is found that the Mg₉₅Ni₅-10 wt.% Zr₀.₇Ti₀.₃Mn₂-3 wt.% MWCNT composite shows the best hydriding/dehydriding properties, which absorbs 6.07 wt.% hydrogen within 100 s at 373 K and desorbs 95.1% hydrogen within 1800 s at 523 K. Moreover, the composite also has a good stability of hydriding kinetics at 423 K under 3 MPa hydrogen pressure. As shown in Fig. 1, after 10 hydrogen absorption/desorption cycles, the composite can still absorb 5.58 wt.% hydrogen within 100 s. The dehydrogenation activation energy of the composite is 83.7 kJ/mol, which is much lower than that of as-received MgH₂ (153 kJ/mol). The improved hydrogen storage properties are related to the structural features derived from the HCS+MM process and the synergistic catalytic effect of nanosized Zr₀.₇Ti₀.₃Mn₂ and MWCNT.

Mg-M/MWCNT (M=Ni, Pd) system

Two systems of Mg-Ni/MWCNT and Mg-Pd/MWCNT have been investigated. Ni or Pd nano-particles were first loaded uniformly on the surface of MWCNT, then the as-prepared Ni/MWCNT or Pd/MWCNT was added to Mg to form Mg-M/MWCNT (M=Ni, Pd) composites by the process of HCS+MM. The structural and hydrogen storage properties of the composites have been investigated by XRD, SEM, TEM and hydriding/dehydriding measurements. Preliminary studies show both of the Ni/MWCNT and Pd/MWCNT can improve greatly the hydrogen storage properties of Mg. The mechanism of the improvement has been discussed.

Fig. 1 Cyclic hydriding kinetics of the Mg₉₅Ni₅-Zr₀.₇Ti₀.₃Mn₂-MWCNT composite prepared by HCS+MM measured at 423 K under 3 MPa hydrogen pressure.

References


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Preparation and electrochemical characteristics of single-phase La–Mg–Ni-based alloys with super-stacking structures

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Abstract: La–Mg–Ni-based hydrogen storage alloys are considered as a promising negative electrode candidate to replace traditional AB5-type alloys due to their large discharge capacity [1]. The preparation of single-phase La–Mg–Ni-based alloys is necessary for systematic investigation but this is of full of difficulty and the reports on the single-phase alloys are rare. Our group explored the formation mechanism of the super-stacking phases and succeeded in preparing single-phase AB3-, A2B7- and A5B19-type La–Mg–Ni-based alloys by step-wise sintering and long-time annealing method [2-4]. The phase conversions during hydrogen absorption/desorption and the relationship between the super-stacking structures and the electrochemical properties are investigated. The single-phase PuNi3-type LaMgNi9 alloy can be activated within just two cycles, but the discharge retention after 100 cycles (S100) decreases to 66.1%. The maximum discharge capacity (Cmax) of the single-phase Ce2Ni7-type La0.6Mg0.4Ni3.5 alloy is as high as 398 mAh g−1 and the S100 is 82.8%, which is much higher than that of the single PuNi3-type alloy. The Ce2Ni7-type crystal structure remains unchanged after initial hydrogen absorption/desorption cycles. But it decomposes into amorphous La and Mg and nanocrystalline LaNi5 and Ni phases after 20 cycles. The LaMgNi19 alloy with a single Pr5Co19-type phase gains a Cmax of 364 mAh g−1 and a good high rate dischargeability (HRD) of 67.2% at 900 mA g−1. The appearance of minor phases cases obvious effects on the electrochemical properties of the alloys. It is found that when the abundance ratio of PuNi3- to Ce2Ni7-type phases is close to 1:1, the alloy possesses good electrochemical performances. Small amount of LaNi5 phase appearing in the A2B7-type phase improves HRD. The alloy with 80 wt.% of Pr5Co19-type phase and 20 wt.% of Ce2Ni7-type phase presents better electrochemical properties than the single Pr5Co19-type alloy.

References

Fig. 1 Rieveld analysis of the single Ce2Ni7-type La0.6Mg0.4Ni3.5 alloy
Fig. 2 TEM results of the single Ce2Ni7-type La0.6Mg0.4Ni3.5 alloy after 20 charge/discharge cycles

Shumin Han, Doctor, Professor, research field: hydrogen storage materials, electrode materials, and rare earth chemistry.

In recent years, Professor Han and his group’s work focuses mainly on Mg–based hydrogen storage alloys, light weight hydrogen storage materials and rare earth–Mg–Ni-based electrode materials.

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GAS ATOMIZED ALLOY ELECTRODES

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AB₅ type gas atomized alloy powders are non-equilibrium materials for nickel metal hydride batteries. The investigated gas atomized alloy electrodes activate within a few cycles, show high rate discharge kinetics up to 1C and a cycle stability comparable with cast alloy. The effect of the production technology and the composition of the alloys on the electrode properties are discussed in detail.

Introduction

High pressure gas atomization (HPGA) is a synthesis method, allowing to produce spherical AB₅ type alloy particles in the micrometer size range with a high cooling rate of approx. 10⁶ K/s. The particle surface possesses enhanced corrosion resistance, e.g. leading to an increased cycle stability [1]. The HPGA technology can produce a large quantity of alloy particles (1g – 10 kg /h) with a wide range in particle-size and a well-defined surface and morphology. Therefore, applying this technology results directly in small particles and reduces the standard long route for manufacturing the AB₅ type materials for battery electrodes. [1, 2]

The effect of the HPGA method on the properties of the electrode materials is discussed controversially. Bowmann et al. found no significant difference in hydrogen storage capacity and stability, i.e. equilibrium pressure, between gas atomized alloys and as cast alloys [3]. Lim et al. reported a reduced specific hydrogen storage capacity and slower activation with cycling for gas-atomized compared to cast alloy material [4]. Therefore, the relationship between the production method, the resulting surface and bulk materials characteristics and the electrochemical properties is investigated and analyzed in great detail.

Results

The phase composition, morphology, structure, and the surface state of gas atomized and as cast LaNi₄.₅Al₀.₅ and LaNi₂.₅Co₂.₄Al₀.₁ alloy powders have been investigated. All investigated samples exhibit the hexagonal CaCu₅-type structure. The powder particles of gas atomized alloy have mostly a spherical shape with a loose, grainy structure and a typical diameter of approx. 200 μm.

However, the shape of particles is also dependent on the alloy composition.

The reaction resistance was investigated by means of Tafel plot and impedance spectroscopy. The reaction resistance is not dependent on the charge state of the electrode and is around 0.43 Ω and 0.69 Ω for LaNi₄.₅Al₀.₅ and LaNi₂.₅Co₂.₄Al₀.₁, respectively. The resistance of the alloy electrode has a strong effect on the high current discharge capacity, 50% of the maximum discharge capacity, i.e. 300 mAh/g and 275 mAh/g, was found at 12C and 2C discharge rate for LaNi₄.₅Al₀.₅ and LaNi₂.₅Co₂.₄Al₀.₁, respectively. The cycle stability of electrodes made from LaNi₂.₅Co₂.₄Al₀.₁ alloy powders is higher than that of LaNi₄.₅Al₀.₅ electrodes.

References


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The limited supply of fossil fuels, its adverse effect on the environment, and growing worldwide demand for energy has necessitated the search for new and clean sources of energy. Hydrogen, the third most abundant element on Earth, is considered as an alternative to fossil fuels. However, hydrogen, like electricity, is not an energy source but an energy carrier. It needs to be produced. While considerable challenges need to be overcome for its production, distribution, and use in fuel cells, it’s safe, efficient, and economical storage is considered to be critical for a successful hydrogen economy. For the mobile industry which is responsible for nearly 80% of our oil needs, hydrogen storage materials need to have high gravimetric and volumetric density and operate at ambient thermodynamic conditions, as the current methods for storing hydrogen as a compressed gas or liquid are not suitable for wide commercial applications. In order for the host materials to have gravimetric density of about 10 wt%, they have to consist of elements lighter than Aluminum. Unfortunately, the bonding of hydrogen in these materials is either too strong or too weak. Ways must, therefore, be found to tune the hydrogen bond strength so that host materials composed of light elements can be used as effective hydrogen storage materials.

This talk will discuss how the novel properties of materials at the nanoscale can improve the thermodynamics and kinetics of hydrogen. In particular, I will discuss how carbon based nanostructures such as nanotubes and fullerenes can not only be used as catalysts to improve hydrogen uptake and release in complex light metal hydrides such as sodium alanate, but also how they can be functionalized with metal and B atoms to adsorb hydrogen in a novel quasi-molecular form. Such a bonding can improve the kinetics and thermodynamics of hydrogen sorption. I will also discuss the role of electric field in hydrogen storage. These results, based upon density functional theory and quantum molecular dynamics, provide a fundamental understanding of the interaction of molecular hydrogen with hosts consisting of light elements. It is hoped that the understanding gained here can be useful in designing better materials for hydrogen storage. Results will be compared with available experimental data.

References

Dr. Jena received his B.Sc. (Hons) and M. Sc. in Physics from Utkal University in India in 1964 and 1966, respectively, and Ph. D. in Physics from the University of California, Riverside in 1970. He is currently Distinguished Professor of Physics in Virginia Commonwealth University. He has also served as a Program Director at the National Science Foundation as well as Jefferson Science Fellow and Senior Science Advisor at the US Department of State. He works in wide range of fields in physics, chemistry, and materials science dealing with structure-property relationships of materials in 0, 1, 2, and 3- dimensions. He is the author of about 500 papers including 12 edited books. Among many honors he has received are: Virginia Commonwealth University’s Outstanding Scholar Award in 1987, the University Award of Excellence, its highest academic honor, in 1993, Virginia’s Outstanding Faculty Award from the Governor of Virginia in 2001, Jefferson Science Fellow in 2007, Member of the Presidential Commission to Russia in 2010, and Virginia Commonwealth’s Presidential Medallion in 2011.

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NANOSTRUCTURED Mg-BASED HYDROGEN AND ENERGY STORAGE MATERIALS PROBED BY IN SITU SYNCHROTRON AND NEUTRON POWDER DIFFRACTION

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Abstract. Complementarity of high flux SR XRD and NPD in situ experiments performed in real conditions, i.e. in operando, allows time resolved measurements probing phase-structural transformations proceeding at fast rates, in just seconds, and gives a basic understanding of the systems in question. This work was focused on studies of Mg-based materials for hydrogen and energy storage including (a) Catalyzed nanostructured Mg-hydride based materials; (b) Ternary AB 3 compounds (La,Pr,Nd)-Mg-Ni intermetallics were magnesium improves performance of the electrodes of the rechargeable Ni-MH batteries; (c) High pressure hydrides for “hybrid” H storage.

Nanostructured Mg-based hydrides

Studies of MgH 2-based systems are aimed on achieving faster H exchange and tailoring the thermodynamics of the Mg-H interactions. Nanostructuring of the Mg-Rare Earth-Ni systems, by using Reactive Ball Milling in H 2, Rapid Solidification, Equal Channel Angular Pressing and Powder Metallurgy processing proved to be effective in reaching these objectives. Time resolved in situ SR XRD, NPD studies and TEM investigations were used to characterise the mechanism and kinetics of the phase-structural transformations in the materials. Nanostructuring increases the hydrogenation rates and decreases the stabilities of the hydrides, in some cases dramatically, by several hundred K [1,2].

RE-Mg-Ni alloys for Ni/MH batteries

For the ternary AB x/AB y/n Early-Earth-Ni systems, by utilizing Reactive Ball Milling in H 2, Rapid Solidification, Equal Channel Angular Pressing and Powder Metallurgy processing proved to be effective in reaching these objectives. Time resolved in situ SR XRD, NPD studies and TEM investigations were used to characterise the mechanism and kinetics of the phase-structural transformations in the materials. Nanostructuring increases the hydrogenation rates and decreases the stabilities of the hydrides, in some cases dramatically, by several hundred K [1,2].

High pressure hydrides

While LaNi 5 is prone to the hydrogen-induced disproportionation, Mg-containing LaMg 2Ni 5 intermetallic reversibly forms a stable during cycling hydride with ΔH reversible=24.0 kJ/mol and equilibrium pressure of H 2 desorption of 18 bar at 20 °C. The overall chemical composition LaMg 2Ni 5H 2.5 can be presented as LaNi 5H 7.5 + 2*MgNi 2H 1.9 and indicates that the hydrogenation of the MgNi 2 slab proceeds at rather mild H 2/D 2 pressure conditions as compared to individual MgNi 2 (2 kBar H 2). A partial filling by D atoms of the four types of the tetrahedral interstices takes place in the MgNi 2 slab; these include two types of the available [MgNi 2] and two types of the [Mg 3 Ni 3 ] tetrahedra [5].

References

PROMOTED FORMATION OF METAL BORIDES IN THE 2LiBH4-MgH2 COMPOSITES WITH TRANSITION METAL ADDITIVES BY USING A NEW THREE-STEP METHOD

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Abstract

The tailored formation of MgB2 in the dehydrogenation process of 2LiBH4-MgH2 composite is a prerequisite for the improved reversible dehydrogenation property. But the formation of MgB2 is retarded by a long incubation period. Recent studies have demonstrated that addition of transition metal (TM) compounds can properly address this problem. Mechanistic studies suggest that TM additives act as precursors for the formation TM borides, which provide heterogeneous nucleation sites for the MgB2 product and consequently, enhances the dehydrogenation kinetics of the composite. Therefore, novel methods for efficiently and homogeneously incorporating the TM boride nanoparticles, preferably between the LiBH4-Mg phase boundaries, are highly desirable. Herein, we report a new three-step method for incorporating TM boride nanoparticles into the 2LiBH4-MgH2 composite. Specifically, two representative TM additives (TiF3 and Nb2O5) are selected to demonstrate the new three-step method effective in improving the dehydrogenation property of the 2LiBH4-MgH2 composite. Overall, in comparison with the conventional one-step milling method, the three-step method can effectively promote the formation of TM boride and meanwhile, ensure its homogeneous dispersion in the composite matrix. As a result, the composite sample prepared by the new method exhibits a favourable combination of high hydrogen capacity, fast reaction kinetics and satisfactory cyclic stability.

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Enhancing effect of LPSO on the de/hydrogenation kinetics and structural transformation in Mg$_{94}$Cu$_4$Y$_2$ Alloy

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Abstract: We report the hydrogen storage properties and structural transformations of an Mg$_{94}$Cu$_4$Y$_2$ alloy during the hydrogen absorption/desorption cycles. The alloy shows good reversible hydrogen capacities and fast dehydrogenation kinetics, and rather complex microstructural transformation. The nanocomposite produced by decomposition of LPSO promoted de/hydrogenation reactions.

Introduction

Mg-Ni-Y alloys containing long period ordered structure (LPSO) present rather good hydrogen storage properties [1-3]. The structural mechanism of LPSO alloy during de/hydrogenation reactions was studied using careful TEM study [3]. In this work, we designed an Mg$_{94}$Cu$_4$Y$_2$ LPSO alloy. The purpose of the research is to evaluate the hydrogen storage properties of the alloy, and to explore the mechanism of microstructural effecting on de/hydrogenation kinetics of Mg$_{94}$Cu$_4$Y$_2$ LPSO alloy.

Experimental

The alloy Mg$_{94}$Cu$_4$Y$_2$ was prepared by vacuum induction melting, then mechanically cut and pulverized to about 400 um followed by 2 hours of ball milling under argon atmosphere. The de/hydrogenation kinetics, and cycle stability were measured using Advanced Materials Corporation gas reaction controller at 250-350 °C. The microstructures of the samples were characterized using XRD (Philips X'pert Pro), SEM (Zeiss Supra 40), and TEM (JEM2100).

Results and Discussion

The microstructure of the cast alloy consists of about 50% LPSO(18R- and 14H-type), 35% Mg and 15% Mg$_2$Cu (Fig.1a,b). XRD and TEM studies (Fig.1b, c) indicate that the de/hydrogenation reactions and structural transformations in the alloy can be describes as follows:

First Hydrogenation:

LPSO (Mg,Cu,Y) + H$ightarrow$ MgH$_2$+MgCu$_2$+YH$_3$

Mg$_2$H$_2$→MgH$_2$+Mg

De/hydrogenation cycles:

MgH$_2$ ↔ Mg + H$_2$

MgH$_2$+MgCu$_2$ ↔ Mg$_2$Cu+H$_2$

YH$_3$ ↔ YH$_2$+H$_2$

The reversible hydrogen absorption/desorption capacities of the alloy is about 5wt% at 300°C. Approximate 4.5wt% hydrogen can be released at 300°C in 180 min as shown in Fig. 1d. The good hydrogen storage performance is related to the special LPSO structure. The decomposition of LPSO during the first hydrogenation provides highly even distributed nanocomposite (MgH$_2$+MgCu$_2$+YH$_3$). This type of microstructure acts as inner catalytic effects and promotes the dehydrogenation property. Also the MgH$_2$+MgCu$_2$ ↔ Mg$_2$Cu+H$_2$ reaction affect the overall de/hydrogenation kinetics of alloy.

Acknowledgements

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Fig.1 (a)SEM morphology of the as cast alloy;(b)XRD Patterns with the states of as cast, hydrogenated and dehydrogenated;(c)HRTEM micrograph of the dehydrogenated sample;(d)Isothermal dehydrogenation kinetics.

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MICROSTRUCTURES AND HYDROGEN STORAGE PROPERTIES OF MG-RE-NI ALLOYS

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Abstract Mg-RE-Ni alloys have attracted lots attention due to the excellent hydrogen storage properties. Recently, we have prepared various La-Mg-Ni multiphase Mg-bases alloy in terms of La-Mg-Ni ternary phase diagram by different methods (as-casting, copper-mould-casting, ultrahigh pressure (UHP), etc.), and investigated the phase compositions, phase morphologies and hydrogen storage properties of the alloys.

Both pure magnesium (Mg) and Mg-based alloys are attractive candidate materials for reversible hydrogen storage due to their high hydrogen storage capacity, outstanding reversibility and low cost. Unfortunately, the hydrogen desorption temperature of Mg-based alloys is usually very high due to the strong affinity between magnesium and hydrogen. Another reason is that the dehydrogenation kinetics of MgH₂ is poor at moderate temperatures. Both of them slow down the application rhythm of Mg-based alloys as hydrogen storage materials. Alloying Mg with rare-earth (RE) elements and nickel is one of the effective approaches to enhance the reaction thermodynamics and kinetics [1]. The multiphase La-Mg-Ni alloys exhibit excellent hydrogen sorption kinetics, which is regarded as a potential hydrogen storage material.

The phase transformation and phase interaction of La-Mg-Ni alloys has been investigated. The results showed that the simultaneous interaction between in situ forming Mg and Mg₂Ni phase and the catalytic effect of in situ forming RE hydride can obviously reduce the hydrogen sorption temperature and enhance the hydrogen sorption kinetics [2,3]. Moreover, TEM results show that he LaH₂₃ phase was distributed homogeneously throughout the Mg phase and that the Mg crystals were coated with LaH₂₃ crystals in the matrix. This microstructure exhibited an obvious volume contraction and resulted in a distinct strain of MgH₂ when the LaH₂₃ phase released H₂, which effectively promotes the hydrogen desorption of MgH₂ [4]. In addition, refining the microstructure by UHP [5] and copper-mould-casting can obviously improve the hydrogen storage properties of the alloy due to the better catalytic effect among RE hydride, Mg₂Ni phase and Mg phase and more phase boundary as hydrogen diffusion channel, which should be ascribed to the more homogeneous distribution of La hydride, Mg₂NiH₄ and MgH₂ phases. The dehydrizing onset temperature of the UHP sample (5 GPa and 973 K) is about 490 K and obviously lower than that of the as-cast alloy (560 K). The amount of hydrogen desorption in the UHP alloy (5 GPa at 973 K) is 2.69 wt.% at 573 K, which corresponds to 89.6% of the saturated capacity. However, the corresponding values change to 1.75 wt.% and 58.3% in the as-cast alloy, respectively. It is confirmed the refining the microstructure is one of effective approaches to tune the hydrogen storage performances of those rare earth-magnesium-nickel alloys.

References

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SUPERLATTICE STRUCTURES AND HYDROGEN ABSORPTION/DESORPTION CHARACTERISTICS OF R-Mg-Ni COMPOUNDS

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Abstract The realization of supper-lattice rearrangement in X-Mg-Ni (X = Ca, Y, and rare earth metals) alloys is a challenge for obtaining better hydrogen storage properties. In this report, we reveal the correlation between composition, structural features, lattice strains and hydrogen absorption/desorption behaviors of ternary X-Mg-Ni compounds, which would help us to understand the nature of hydrogen storage in other metal hydrides.

Background
As compared to highly H-containing chemical hydrides such as NaAlH₄, LiBH₄, BH₃NH₃, and their related derivatives,[1] the advantages of using the hydride-forming intermetallics as hydrogen storage materials lie in simpler chemical process, better reversibility, higher hydrogen purity and lower working temperature. However, to meet the demands for practical onboard application, the development of new intermetallics with higher capacity is quite necessary, which could be achieved by the substitution of light metals for heavy ones. For instance, ternary X-Mg-Ni (X = Ca, Y and rare earth metals) compounds have been developed from corresponding binary X-Ni compounds.[2] The X-Mg-Ni have layered structures where [XMgNi₄] and [XNi₅] units stack along the c-axis alternatively according to certain combination. Hence, fundamental understanding of this supper-lattice nature is necessary for improving hydrogen storage properties of ternary X-Mg-Ni compounds.

Present work
In the present work, a systematic study of the ternary X-Mg-Ni (X = Ca, Y, and rare earth metals) compounds was carried out to determine the structural features and hydrogen absorption-desorption characteristics. First, the crystal structure of the ternary X-Mg-Ni (X = Ca, Y, and rare earth metals) compounds derived from XNi₃ and X₂Ni₇ are presented for comparison. In the meantime, the existence of the 2H and 3R variants was confirmed by crystallographic analyses. The polymorphic transition between the 2H and 3R phases was subsequently revealed by quenching the X-Mg-Ni samples at various temperatures, and a crystallographic model for this transition was proposed. The enthalpy changes for the hydrogen absorption and desorption of ternary X-Mg-Ni compounds were then determined from the P-C isotherms measured at different temperatures. The possibility of improving the hydrogen storage properties by adjusting the X(Ca)/Mg ratio is also reported. Finally, both gaseous and electrochemical hydrogen absorption and desorption behaviors were analyzed to reveal the change in the hydriding/dehydriding process.

Summary
(1) Ternary R-Mg-Ni compounds with supper-lattice structures are more interesting than other hydrogen storage alloys.
(2) Their fundamental investigations can help us to understand the complex nature of hydrogen storage in other metal hydrides.
(3) Ternary R-Mg-Ni compounds have larger hydrogen capacities than LaNi₅-based alloys, thus exhibiting great potential applications for MH/Ni batteries.

References

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RETHINKING HIGH-PRESSURE X-RAY PHOTOELECTRON SPECTROSCOPY FOR THE STUDY OF HYDRIDE-FORMING MATERIALS

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Abstract

We report on the development of a new in-situ experimental approach for the surface analysis of hydride-forming materials by means of X-ray photoelectron spectroscopy (XPS). This new set-up allows to expose specimens to high hydrogen pressures while keeping the analysis chamber in high vacuum conditions, and is thereby a simple, effective and cheap alternative to existing environmental XPS techniques.

XPS is a powerful tool for the surface analysis of various materials, providing insightful information about the elements present on a given surface, including their respective chemical state and concentrations across a few up to a few tens of atomic layers. Therefore, XPS is a key experimental technique regarding the understanding of surface phenomena occurring during the formation and decomposition of hydrides, provided that the latter critically influence the efficiency of applications such as solid-state hydrogen storage, hydrogen permeation and hydrogen sensors. However, the short mean free path of electrons with energies below 1500 eV in a gas at ambient pressure does not allow XPS analyses to be performed in realistic experimental conditions from the applications point of view. So does the required vacuum levels for X-ray anodes and channeltrons. These problems can be overcome by performing so-called "environmental", "ambient-pressure" or "high-pressure" XPS [1]. These techniques rely on the use of differential pumping stages, the minimization of the sample-aperture distance in the high pressure regions and, for the most recent systems, on the addition of electrostatic lenses to focus the electrons through the differential pumping scheme [2]. Nonetheless, these techniques suffer from drawbacks, i.e. reduction of the energy resolution and sample freedom of movement, high cost and accessibility of the facilities due to the fact that most of them have been developed for operation at synchrotron light sources.

A new experimental approach is proposed here in order to study materials exposed to high hydrogen pressures while keeping the analysis chamber in high vacuum. A new type of sample holder has been designed in this respect, consisting of a Pd-Ag membrane fed on one side with a high hydrogen pressure, and exposed on the other side to the X-ray beam at UHV compatible pressures. Since this alloy exhibits low dissociation barrier, the proper hydrogen absorption enthalpy and fast hydrogen diffusion kinetics, monoatomic hydrogen is rapidly generated and transferred through the bulk of the membrane to the surface exposed to vacuum. Moreover, this also results in a high hydrogen concentration on that surface, because the hydrogen permeation is limited by desorption from the low pressure side of the membrane. By capping the membrane with any hydride-forming material, one is then able to study hydrides by means of XPS with realistic hydrogen concentrations. This new experimental approach will be presented, with particular focus on the effect of the surface properties on the hydrogen permeation through Pd-Ag membranes.

References


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A NEW METHOD TO PREPARE MG BASED HYDROGEN STORAGE MATERIALS
WITH IMPROVED DEHYDRIDING THERMODYNAMICS AND KINETICS PROPERTIES


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Abstract:
The reversible formation of Mg(In) solid solution provides a new way to tune the dehydriding thermodynamics of MgH₂. However, the preparation of this solid solution is quite difficult and its dehydriding kinetics is rather sluggish. This work offers a novel technique, plasma milling (P-milling), to solve the two problems simultaneously. The efficiency of the synthesis of Mg(In) solid solution, with a hydrogen capacity of up to 5.16 wt.%, is improved significantly. Meanwhile, the kinetics is also modified by the catalyzing effect of in situ synthesized MgF₂. Mg₂In₀.₁Ni solid solution with an Mg₂Ni-type structure has also been synthesized and its hydrogen storage properties have been investigated. The results showed that the introduction of In into Mg₂Ni not only significantly improved the dehydrogenation kinetics but also greatly lowered the thermodynamic stability.

Enhanced thermodynamic and kinetic properties of Mg-In- MgF₂ system prepared by dielectric barrier discharge plasma assisted milling
Mg based alloys suffers from a large reaction enthalpy and a large activation energy. The sluggish kinetic property has been solved in recent years but the tuning of the enthalpy unavoidably leads to sluggish kinetic properties. Therefore, the dual tuning of both the thermodynamic and kinetic properties is the key issue to be solved. This work shows that both the desorption thermodynamic properties and the kinetic properties of MgH₂ could be tuned via the introduction of In using dielectric barrier discharge plasma-assisted ball milling (denoted here as DBDP milling). Mg-In system catalyzed with in situ formed MgF₂ was prepared by DBDP milling. MgH₂ is thermodynamically destabilized via the introduction of In by DBDP milling (∆H=69.2 kJ/mol H₂). Mg-In system produced using DBDP milling shows improved desorption kinetics (Eₐ=127.7 kJ/mol). Dual tuning of the thermodynamic and kinetic properties of MgH₂ is realized.

Dual-tuning effect of In on the dehydriding kinetics and thermodynamics properties of Mg₂Ni
Mg₂In₀.₁Ni solid solution with an Mg₂Ni-type structure is prepared. The results show that the incorporation of In into the lattice of Mg₂Ni could realize this goal and this study suggests a means of improving both the kinetics and thermodynamics of hydrogen storage materials. The dehydrogenation activation energy (Eₐ) and enthalpy change (∆H) decreased from 80 kJ/mol and 64.5 kJ/mol H₂ to 28.9 kJ/mol and 38.4 kJ/mol H₂, respectively. The obtained results point to a method for improving not only the thermodynamic but also the kinetic properties of hydrogen storage materials. This work may also have a great impact on the advancement of hydrogen towards on-board applications.

References

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Recent progresses on hydrides, relating to high-density hydrogen storage as well as Li/Na fast-ionic conduction and high-performance battery devices using complex hydrides, will be presented in the lecture.

**Transition of Bonding States in Hydrides for Hydrogen Storage**

We have been focusing on transition between bonding states of hydrogen, to increase hydrogen density in hydrides [1-4].

An example of the transition was found in YMn$_2$ hydrides, that is, the hydrides showed the continuous transition from the metal hydride YMn$_2$H$_x$ to the complex hydride YMn$_2$H$_6$ with [MnH$_6$]$_{5^-}$ complex anion, even under rather mild conditions. Some computational and experimental studies including EXAFS have been carried out to extend the novel property; "increasing hydrogen densities of metal hydrides by using continuous transition into complex hydrides".

Adjustment of imbalanced charge is of great importance to promote the transition of bonding states. It was experimentally demonstrated that the addition of Li (or LiH) enabled the formation of new complex hydride YLiFeH$_6$ with the [FeH$_6$]$^{4-}$ complex anion from the intermetallic compound YFe$_2$ which has not been considered to transform into a complex hydride on its own. The method can be applied to many other intermetallic compounds even if they are composed of only elements that do not form intermetallic compounds or solid solution alloys with Li, which will greatly contribute to the increase in the variety of complex hydrides.

**Conduction in Complex Hydrides for Electrochemical-Energy Storage**

We have reported that, the LiBH$_4$ based complex hydrides show Li and Na fast-ionic conductivities, and that, the function can be applied to various battery devices [5]. Actually, bulk-type all-solid-state lithium rechargeable battery using LiBH$_4$-based solid electrolytes allows noticeable charge–discharge cycles [6].

**References**


Shin-ichi ORIMO received his Ph. D. in materials science/physics from Hiroshima University in 1995. He was a JSPS research fellow (1993-1995), a research associate in Hiroshima University (1995-2002), and a guest researcher of Max-Planck Institute for Metal Research awarded by Alexander von Humboldt Fellowship and MEXT Fellowship (1998-1999); and is a professor of WPI-AIMR / IMR, and a Special Advisor to the University President, Tohoku University. His research interests are fundamentals and energy-related applications of hydrides. He was awarded "The Prize for Science and Technology (Research Category), The Commendation for Science and Technology by the Minister, MEXT (2012)".

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Catalytic Hydrogenation of CO\textsubscript{2} to CH\textsubscript{4} and CO over Pt-K-Ta/Ni/Al\textsubscript{2}O\textsubscript{3}

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Abstract: The catalytic hydrogenations of CO\textsubscript{2} over bimetallic catalyst were investigated. Bimetallic catalysts X-Ni/Al\textsubscript{2}O\textsubscript{3} (X= Pt, K and Ta) were synthesized as precursors of mixed oxides by co precipitation method. The samples were extensively characterized by XRD, SEM, N\textsubscript{2}-physisorption, porosity and tested for the catalytic conversion of CO\textsubscript{2} through the hydrogenation reaction. CO\textsubscript{2} hydrogenation over bimetallic catalysts was analyzed by catalytic activity measurement with a flow reactor completed by Infrared spectroscopy. We validate that for the hydrogenation of CO\textsubscript{2} reaction, the effect of the different promoter catalyst.

Introduction

Recently, CO\textsubscript{2} accumulation in the atmosphere which comes from combustion of fossil fuels is feared as the major cause of greenhouse effect. Therefore, there are several possible strategies to control amount of the CO\textsubscript{2} such as: CO\textsubscript{2} separation and collection technology, CO\textsubscript{2} capture technology, utilization of CO\textsubscript{2} and reducing of CO\textsubscript{2}. In this context, catalytic conversion of CO\textsubscript{2} over suitable catalyst has been widely explored [1,2].

Hydrogen has greatest properties for the storage and transportation of energy provided it can be efficiently produced from renewable energy sources. Hydrogen can be also found in many organic compounds, such as hydrocarbons, gasoline, natural gas and methanol. Recently, catalytic conversion of carbon dioxide by hydrogenation is one of the most efficient ways in order to produce energy and store hydrogen. Hydrogen can also be stored on to the materials by adsorption such as metal hydrides.

Reducing CO\textsubscript{2} accumulation would be the chemical transformation of CO\textsubscript{2} into valuable compounds using suitable catalysts. Catalyst system for the hydrogenation of CO\textsubscript{2} has been developed to obtain more valuable chemical feedstock such as light olefins, liquid hydrocarbons, CH\textsubscript{4} and CO.

Experimental set up

The catalytic reaction is occurred in a stainless steel tubular reactor which has a diameter of 18 mm and a length of 450 mm. Quantity of the catalyst was 1g. The gas flows were controlled by thermal mass flow meters from MKS Instruments connected to a Lab view interface. Flow rates CO\textsubscript{2} were 40 ml/min and for 200 ml/min H\textsubscript{2}.

Results

Conversion of the CO\textsubscript{2} as a function of temperature is presented on Figure 1. For all catalysts the catalytic activity in term of the percentage of CO\textsubscript{2} conversion showed progressive increment with the increasing reaction temperature. At low temperature Pt-Ni/Al\textsubscript{2}O\textsubscript{3} is higher than other catalysts. At high temperature conversion of CO\textsubscript{2} over Pt is maximum (90 \%) and Ta-Ni/Al\textsubscript{2}O\textsubscript{3} has similar catalytic conversion of CO\textsubscript{2}.

Conclusions

It was observed that catalytic conversion of CO\textsubscript{2} by hydrogenation is more active at low temperature over Pt-Ni/Al\textsubscript{2}O\textsubscript{3}. On the other hand for CO\textsubscript{2} hydrogenation Ta can be an alternative promoter catalyst due to its high catalytic activity according to Pt catalyst.

References

FURTHER STUDY ON HYDROGEN-DEUTERIUM EXCHANGE MECHANISM DURING DESORPTION OF LIBH₄-MGD₂ SYSTEM

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Abstract: This work aims to further understand the dynamic process of hydrogen exchange mechanism in LiBH₄-MGD₂ system. By investigating the different decomposition behaviour in LiBH₄-MGD₂, NaBH₄-MGD₂, and LiBH₄-VD₂ systems, it is found that the hydrogen exchange is strongly dependent on the gap between the melting point of complex hydride and the decomposition temperature of metal hydride. As a result, the dynamic hydrogen exchange process is proposed.

Introduction

The previous study [1] has proposed the concept of “hydrogen-exchange” in the LiBH₄-MGD₂ system, which was proven in LiBH₄ by the detection of B-D vibration. The so-called hydrogen-exchange mechanism is believed to increase the decomposition temperature of MgH₂, but lower the decomposition temperature of LiBH₄. To further investigate the dynamic process of hydrogen exchange, the decomposition of LiBH₄-MGD₂, NaBH₄-MGD₂ and LiBH₄-VD₂ systems, which are prepared by hand milling for 5 minutes under identical conditions, are investigated by TPD-MS and FTIR.

Results

TPD-MS results (Figure 1) show different D release behaviour for three samples. In the LiBH₄-MGD₂ system, the majority of D releases in the form of HD, whereas major D₂ could be detected in the NaBH₄-MGD₂ system, indicating weak hydrogen exchange between NaBH₄ and MgD₂. We believe the difference should be due to higher melting point for the NaBH₄ than that of LiBH₄. For the LiBH₄-VD₂ system, the decomposition temperature of VD₂ is lower than the melting point of LiBH₄. As shown in Figure 1, the on-set decomposition of pure VD₂ is indicated by the D₂ peak at 275°C, however, the intensity of D₂ signal significantly decreases and HD signal appears in intensive strength, which should be due to the melting of LiBH₄ and the resultant intensive H-D exchange. Above results clearly indicate the influence of LiBH₄ melting in H-D exchange.

As a result, a hydrogen exchange mechanism in LiBH₄-MGD₂ system is proposed as follows: The released D atoms from MgD₂ diffuse to its surface but trapped by the molten layer of LiBH₄, thus the D atoms recombination is considerably inhibited. Afterwards, the H-D exchange happens, and H atoms in the LiBH₄ become free and escape from the molten LiBH₄ to form H₂ gas. In addition, partial H atoms also combine with D atoms to form HD gas.

References


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His research interest is focused on reversible hydrogen storage of MgH₂ modified with nanostructure, core-shell structure, compositing structure, alloying and catalyst doping.

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**SYNTHESIS AND CATALYTIC EFFECTS OF TiB$_2$/TiN @GRAPHAENE NANO SHEETS ON HYDROGEN STORAGE OF MAGNESIUM HYDRIDE**

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Abstract: Magnesium hydride has attracted much attention for hydrogen storage applications because of its high gravimetric (7.6 wt%) and volumetric (110 kg/m$^3$) capacity as well as low cost[1]. However, the high hydrogen desorption temperature >300°C and sluggish sorption kinetics of MgH$_2$ have limited its practical applications [2]. In the presented work, a series of transition metal compound decorated highly crumpled graphene nanosheets (GNSs) have been successfully synthesised and their catalytic effect on the sorption performance of MgH$_2$ has been systematically discussed. Experimental measurements confirm that the peak desorption temperature of MgH$_2$,5wt%TiB$_2$/GNSs composites can be lowered more than 44 °C than the pure as-milled MgH$_2$ (DSC measurement). And the dehydrogenation kinetics of TiB$_2$/GNSs-doped MgH$_2$ is severalfold acceleration compared to the pure as-milled MgH$_2$. After adding TiN@GNSs, the as-prepared MgH$_2$-TiN@GNSs sample can release hydrogen at remarkable lower temperature (about 167 °C). X-Ray diffraction and XPS results reveal that as-prepared TiN@GNSs nanopowders possess excellent catalytic stability. HP–DSC analysis clearly shows that excellent performances for H$_2$ desorption and absorption can be obtained upon the addition of TiN@GNSs catalyst.

**Introduction**

Developing a safe and efficient hydrogen storage medium has become an urgent issue for realizing the hydrogen economy and various hydrogen storage materials have been investigated in the last decades. Among these options, one of the most promising materials is MgH$_2$. However, the practical application of MgH$_2$ is limited by high thermal stability and sluggish sorption kinetics. To overcome these drawbacks, numerous efforts have been paid including alloying [3], nano-confinement [4], doping[5] and so on. Another notable method to modify the hydrogen storage properties of MgH$_2$ is to combine MgH$_2$ with different catalysts. Here, we report the synthesis of amorphous TiB$_2$ nanoparticles on GNSs and TiN@GNSs nanohybrids. Their catalytic effect on the kinetics and thermodynamics of MgH$_2$ have been investigated.

**Results and conclusion**

The prepared TiB$_2$/GNSs exhibits an excellent catalytic effect on dehydrogenation of MgH$_2$ compared with the pure milled MgH$_2$, and much better than the individual component of TiB$_2$ or GNSs. It is demonstrated that the peak desorption temperature of MgH$_2$-TiB$_2$/GNSs nanocomposites decreases ~44 °C by means of differential scanning calorimetry (DSC) measurement, and the dehydrogenation kinetics of MgH$_2$-TiB$_2$/GNSs nanocomposites is further improved. Microstructure measurements and modeling study indicate that TiB$_2$/GNSs is highly efficient for dehydrogenation kinetics of MgH$_2$, and the synergistic effect of nano-GNSs and TiB$_2$ nanoparticles contributes to the excellent dehydrogenation performance.

TEM and SEM experiment demonstrate that TiN nanocrystals uniformly anchored onto the surface of GNSs. Thermodynamics and isothermal decomposition experiment show that adding TiN@rGO to the MgH$_2$ can significantly facilitate the dehydrogenation of MgH$_2$.

**Acknowledgment**

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**References**


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Dehydriding Properties of LiBH\textsubscript{4} Combined with Mg\textsubscript{2}FeH\textsubscript{6}

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By mechanically milling LiBH\textsubscript{4} with Mg\textsubscript{2}FeH\textsubscript{6}, an unreported solid solution having both non-metal based complex anion [BH\textsubscript{4}]\textsuperscript{-} and transition metal based complex anion [FeH\textsubscript{6}]\textsuperscript{4-} may have formed. The dehydriding properties and crystal structures of the LiBH\textsubscript{4} and Mg\textsubscript{2}FeH\textsubscript{6} combined samples are investigated and discussed.

Introduction

Combining hydrides with different characteristics is an effective method to develop new materials having better hydrogen storage properties or disclose novel functionalities. New compounds having both [BH\textsubscript{4}]\textsuperscript{-} and [NH\textsubscript{3}]\textsuperscript{-} complex anions have been synthesized by combining LiBH\textsubscript{4} with LiNH\textsubscript{2}. The new compounds have ion conductivity 4 orders of magnitude higher than LiBH\textsubscript{4} and release pure hydrogen without undesired ammonia or borane [1].

Mg\textsubscript{2}FeH\textsubscript{6} is one of the most prospective hydrogen storage materials in transition metal based complex hydrides [2]. Although the formation of new hydride has been revealed by combining Mg\textsubscript{2}FeH\textsubscript{6} with the other transition metal based complex hydride Mg\textsubscript{2}CoH\textsubscript{6} [3], hydrides having both non-metal based complex anion and transition metal complex anion have not been reported.

Therefore, we have made an attempt at synthesizing new complex hydrides by combining the non-metal based complex hydride LiBH\textsubscript{4} with Mg\textsubscript{2}FeH\textsubscript{6} as well as investigating the hydrogen storage properties of the combined system.

Synthesis and characterization of xLiBH\textsubscript{4} + (1-x)Mg\textsubscript{2}FeH\textsubscript{6}

Home synthesized Mg\textsubscript{2}FeH\textsubscript{6} (> 95 %) is mixed with LiBH\textsubscript{4} (95 %, Aldrich) at molar ratios range from 9:1 (x = 0.1) to 1.5 (x = 0.83) by mechanical milling for 5 h under argon. The dehydriding properties are examined by Thermogravimetric analysis-mass spectrometry (Rigaku TG8120, He flow of 150 ml/min, heating rate of 5 K/min). Crystal structure analysis is achieved by both \textit{ex-situ} X-ray diffraction (PANalytical X'Pert-Pro, CuK\textalpha) and \textit{in-situ} high-resolution synchrotron X-ray diffraction (the Swiss-Norwegian Beam Line, BM01B).

Results and discussion

The dehydriding reaction of pure LiBH\textsubscript{4} and Mg\textsubscript{2}FeH\textsubscript{6} each starts approximately at 650 and 450 K, 12.5 and 4.3 mass\% hydrogen are released respectively. The dehydriding behavior changes drastically in the LiBH\textsubscript{4} and Mg\textsubscript{2}FeH\textsubscript{6} combined samples. Within the composition range 0.1 ≤ x ≤ 0.5, LiBH\textsubscript{4} and Mg\textsubscript{2}FeH\textsubscript{6} release hydrogen simultaneously. The dehydriding temperatures and quantities of released hydrogen shift along with x. The lattice parameter of Mg\textsubscript{2}FeH\textsubscript{6} phase in the combined samples measured by \textit{in-situ} high-resolution synchrotron X-ray diffraction suggests the possibility of forming solid solution Li\textsubscript{1-x}Mg\textsubscript{2}x(BH\textsubscript{4})\textsubscript{4}(FeH\textsubscript{6})\textsubscript{1-x}, having both [BH\textsubscript{4}]\textsuperscript{-} and [FeH\textsubscript{6}]\textsuperscript{4-} complex anions [4].

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COMBINATION OF LIGHTWEIGHT HYDROGEN STORAGE MATERIALS AND NANOSTRUCTURES

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Abstract: Efficient hydrogen storage plays an important role in ideal hydrogen economy. However, it still remains a challenge to develop hydrogen storage materials with high capacity and fast kinetics. To achieve this target, the combination of lightweight materials and nanostructures should offer great opportunities. Our studies focus on enhancing the hydrogen storage properties of lightweight Mg/MgH₂ system and ammonia borane (NH₃BH₃, AB) with nanostructures.

Introduction

Hydrogen as a clean fuel has received worldwide attention. Unfortunately, the practical application of the hydrogen storage system is plagued by several factors. A major challenge is the development of on-board hydrogen storage materials with high hydrogen density [1]. In this regard, many hydrogen storage materials have been exploited and investigated. Among them, special attention is paid to Mg/MgH₂ system and AB because both of them belong to lightweight materials and have the potential to store a significant percent of hydrogen. Our attempts are aiming at increasing their hydrogen generation rates and lowering the desorption temperature with the combination of lightweight hydrogen storage materials and nanostructures.

Efficient hydrogen storage with Mg/MgH₂ and AB

MgH₂ contains 7.6wt% hydrogen, making it an attractive lightweight hydrogen storage material. However, the sluggish kinetics and high operation temperature limit its practical application [2]. To overcome the drawbacks, special attention has been paid to Mg-based nanomaterials. We synthesized Mg nanowires with different diameters and studied their size-dependent hydrogen storage properties. The results show that the thinner Mg/MgH₂ nanowires have a much lower desorption energy than that of thicker nanowires or bulk Mg/MgH₂, indicating that combination of lightweight system and nanostructures offers the potential to achieve efficient hydrogen storage [3].

AB, as an on-board hydrogen storage material, contains 19.6wt% hydrogen. H₂ can be released through pyrolysis or hydrolysis route [4]. In the aspect of pyrolysis, we used the materials such as silica hollow nanospheres [5], porous MnO₂ hollow cubes [6] and poly (methyl acrylate) [7] to confine AB. Those approaches efficiently lower the hydrogen release temperature. For hydrolysis of AB, we have prepared Pt-Ni alloy (such as Ni₁₋ₓPtₓ, Co₁₋ₓ@Ptₓ, and Niₓ@Ptₓ nanoparticles [8,9,10]), nanoporous Ni and Ni-Fe catalysts [11] to improve the hydrolytic performance of AB. The results show that AB nanoconfinement and catalyst additives are essential for the enhancement of hydrogen releasing.

Conclusion

Efforts have been dedicated to investigate the hydrogen storage performance of lightweight materials. The results shed light onto the application of Mg/MgH₂ and AB as efficient hydrogen storage materials.

References


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Remarkable dehydrogenation improvement of LiAlH$_4$ catalyzed by CoFe$_2$O$_4$ nanoparticles

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Abstract: The catalytic effects of CoFe$_2$O$_4$ nanoparticles on the dehydrogenation properties of LiAlH$_4$, prepared by ball-milling, are investigated for the first time. The onset desorption temperature of 2 mol% CoFe$_2$O$_4$ doped LiAlH$_4$ for the first two stages is 65 °C, 90 °C lower than those of the as-received LiAlH$_4$, with approximately 7.2 wt% hydrogen released by 250 °C. Isothermal desorption results at 120 °C reveal that 2 mol% CoFe$_2$O$_4$ doped sample can release 6.8 wt% of hydrogen within 160 min, which is 6.1 wt% higher than that of the pristine LiAlH$_4$ under the same conditions, indicating significantly improved dehydrogenation properties. Through the differential scanning calorimetry (DSC) and the Kissinger desorption kinetics analyses, the apparent activation energies $E_a$ of the 2 mol% CoFe$_2$O$_4$ doped sample are calculated to be 73.1 kJ/mol and 86.1 kJ/mol, for the first two decomposition reactions, which are 41.2 kJ/mol and 86.5 kJ/mol lower than those of pristine LiAlH$_4$, respectively, indicating a considerably decreased desorption barrier compared with other reported catalysts. Through Fourier transform infrared (FTIR), and X-ray diffraction (XRD) analyses, a series of finely dispersed Fe and Co species with a range of valence states couple with the reactions between LiAlH$_4$ and CoFe$_2$O$_4$ together play a synergistic role in remarkably improving dehydrogenation properties of LiAlH$_4$.

Keywords: Lithium aluminum hydride; Cobalt ferrite; Dehydrogenation performance; Kinetics desorption; Dehydrogenation mechanism.
NOVEL Mg-IN-NI TERNARY ALLOYS FOR REVERSIBLE HYDROGEN STORAGE

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Abstract: Mg_90In_5Ni_5 alloy was synthesized by ball-milling Mg(In) solid solution with Ni powders. Two new Mg-In-Ni ternary phases X1 and X2 are respectively formed at the hydrogenation and dehydrogenation states of Mg_90In_5Ni_5 alloy, which have never been reported in the literature. The results indicate two dehydrogenation reaction characteristics of Mg_90In_5Ni_5 alloy, namely MgH_2 + X1 ↔ X2 + H_2 and MgH_2 ↔ Mg + H_2. The X2 phase has a stoichiometric composition of Mg_70In_15Ni_15 with tetragonal structure, a reversible hydrogen storage capacity of ca. 1.8 wt.% and desorption enthalpy of 71.29 kJ/mol-H are determined.

Introduction

Mg is considered to be a promising metallic hydrogen storage material with high capacity, abundant resource and inexpensive price. However, the over-high operating temperature due to unfavourable thermodynamics of magnesium hydride (MgH_2) hinders its practical applications. Composition and structure modification have been proven to be effective in improving the hydrogen storage properties of MgH_2. For example, we found that Mg(In) and Mg(In,Al) solid solutions could be reversibly formed by dehydriding from their hydrogenated products with lowered desorption enthalpy [1]. Herein we investigate the reversible phase transformation of Mg-In-Ni ternary alloys during de-/hydrogenation cycles, and their de-/hydridding thermodynamic and kinetic properties.

Results

The Mg_90In_5Ni_5 alloy was milled from the Mg(In) solid solution and Ni powders for a rather long time (170h), the elemental Ni is still present. Upon hydrogenation, the Mg_90In_5Ni_5 alloy transforms to MgH_2 and a new Mg-In-Ni ternary phase X1. After dehydrogenation, Mg and another new Mg-In-Ni ternary phase X2 are formed. This X1 ↔ X2 phase transition could be reproduced after more than five de-/re-hydrogenation cycles. The milled Mg_90In_5Ni_5 alloy shows excellent hydrogen desorption kinetics, and the PCI testing could be carried out at a low temperature of 230 °C (see Fig.1 (a)).

The X2 phase is deduced to have a stoichiometry of Mg_70In_15Ni_15 with tetragonal structure, a reversible hydrogen storage capacity of ca. 1.8 wt.% and desorption enthalpy of 71.29 kJ/mol-H are determined according to the PCI results in Fig.1 (b).

Fig.1 The PCI curves for the hydrogen desorption of Mg_90In_5Ni_5 (a) and Mg_70In_15Ni_15 (b).

References


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CARBON-SUPPORTED Ni₃B NANOPARTICLES AS CATALYSTS FOR HYDROGEN GENERATION FROM HYDROLYSIS OF AMMONIA BORANE

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Abstract: We report the preparation of Ni₃B and carbon-supported Ni₃B (denoted as Ni₃B/C) nanoparticles and their catalytic performance from hydrolytic dehydrogenation of ammonia borane (NH₃BH₃, AB). The as-obtained Ni₃B catalysts are in well-defined crystalline state and the carbon-supported Ni₃B catalysts have a high dispersion in the carbon. The hydrogen generation measurement shows that Ni₃B/C presents enhanced catalyst activity during hydrolytic dehydrogenation of AB. Among the nanoparticles, Ni₃B/C with 34.25 wt% Ni₃B loading displays the highest catalytic activity, with a high hydrogen release rate of 1168 mL min⁻¹ g⁻¹ and low activation energy of 46.27 kJ mol⁻¹.

Introduction

Hydrogen has been considered as an attractive alternative energy carrier because of its abundance, high-energy density, and environmental friendliness [1]. For the known hydrogen storage materials, ammonia borane (NH₃BH₃, AB) complex has been identified as one of the most compelling candidates for chemical hydrogen storage owing to its high hydrogen content (19.6 wt%) and high stability at room temperature [2]. So far, many metal catalysts have been reported for hydrogen generation from hydroysis of AB [3,4]. Herein, we prepared non-precious Ni₃B nanoparticles and carbon-supported Ni₃B (Ni₃B/C) catalysts with different loading contents as catalysts for hydroysis of AB. The as-prepared carbon-supported Ni₃B catalysts exhibit higher catalytic activities for the hydroysis of AB. This result sheds light on the development of cheap catalysts for the hydroysis of AB.

Preparation, characterization and hydrogen generation measurement of the catalysts

The catalysts were prepared by a direct solution synthesis route. The chemical reagents include nickel chloride, potassium borohydride, tetraethylene glycol and carbon black. Small sized and well dispersed Ni₃B nanoparticles were obtained by adding the supporting carbon. The structure, morphology, and chemical composition of the obtained samples are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscopy (TEM). A series of experiments were carried out in order to investigate the catalytic activities of the as-synthesized catalysts for hydrogen generation of AB aqueous solution. The effects of carbon content, reaction temperature, amount of catalyst and concentration of AB on the hydroysis reaction were studied in detail.

Conclusion

In summary, Ni₃B and Ni₃B/C catalysts have been synthesized in solution with a modified polyol process. As the catalyst for hydrogen generation of AB hydroysis, the as-prepared Ni₃B/C composites show significantly enhanced catalytic activity in comparison with pure Ni₃B catalyst due to the reduced particle size and the well-dispersed structure. In the Ni₃B/C series, Ni₃B/C with 34.25 wt% Ni₃B loading shows the highest catalytic activity, affording hydrogen release rate exceeding 1100 mL min⁻¹ g⁻¹ at 25°C and low activation energy of 46.27 kJ mol⁻¹. The results indicate that carbon-supported Ni₃B has the potential to be used as a low-cost catalyst for the hydroysis of AB.

References

A SYNERGETIC EFFECT OF NANO-CONFINEMENT AND NANO-CATALYSIS FOR THE ENHANCED REVERSIBLE HYDROGEN STORAGE OF LiBH₄

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LiBH₄ has been infiltrated into highly ordered mesoporous carbon scaffold containing dispersed NbF₅ nanoparticles to investigate the possible synergetic effect of nano-confinement and nano-catalysis on the reversible hydrogen storage performance of LiBH₄. A systematic study shows that the onset desorption temperature for nano-confined LiBH₄@MC-NbF₅ system is reduced to 150 °C, 225 °C lower than that of the bulk LiBH₄. The activation energy of hydrogen desorption is reduced from 189.4 kJ mol⁻¹ for bulk LiBH₄ to 97.8 kJ mol⁻¹ for LiBH₄@MC-NbF₅ sample. Furthermore, rehydrogenation of LiBH₄ is achieved under mild conditions (200 °C and 60 bar H₂). These results are attributed to the active Nb-containing species (NbHₓ and NbB₂) and the function of F anions, as well as the nanosized pores and high specific surface area of the MC scaffold, which facilitates the dissociation, diffusion and recombination of hydrogen molecules on the surface and grain boundaries. The combination of nano-confinement and nano-catalysis may develop to become an important strategy within the nanotechnology for improving reversible hydrogen storage properties of various complex hydrides.

Introduction

Intensive interest has arisen on complex hydrides, especially for LiBH₄, owing to its high gravimetric and volumetric hydrogen capacities. Unfortunately, high thermostability, sluggish kinetics and undesirable rehydrogenation conditions limit its practical application as a hydrogen storage medium. Herein, we report an effective strategy to modify both kinetics and thermodynamics of LiBH₄ by combining nano-confinement and NbF₅ nano-catalysis, which shows a favorable synergetic effect on the reversible hydrogen storage of LiBH₄.

Results

The results show that the onset desorption temperature for nano-confined LiBH₄@MC-NbF₅ system reduces to 150 °C, 225 °C lower than that of the bulk LiBH₄. More importantly, rehydrogenation of LiBH₄ is achieved at 200 °C and 60 bar H₂, which are the lowest conditions reported to date. The activation energy of hydrogen desorption is reduced from 189.4 kJ mol⁻¹ for bulk LiBH₄ to 97.8 kJ mol⁻¹ for LiBH₄@MC-NbF₅ sample, indicating a reduced kinetic barrier. All these have been demonstrated that there is a favorable synergetic effect between nano-confinement and NbF₅ addition. The combination of nano-confinement and functionalized nanoporous scaffolds may develop to become an important strategy within the nanotechnology for improving properties of variety complex hydrides.

References


Jie Shao is currently pursuing his Ph.D. in Department of Materials Science and Engineering at the Zhejiang University under the supervision of Prof. Lixin Chen. His current research interests are the basic researches and applications on renewable energy storage materials.

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Effect of the LaFeO₃ on the hydrogenation/dehydrogenation properties of MgH₂

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Abstract: In order to improve hydrogen properties of magnesium hydride, the novel additive LaFeO₃ was used to forming MgH₂+20 wt.% LaFeO₃ composite by mechanically milling method. P-C-T tests indicated the MgH₂+20 wt.% LaFeO₃ composite could absorb 3.417 wt.% of hydrogen at 423 K within 21 min while the MgH₂ is only 0.977 wt.% under the same condition. The MgH₂+20 wt.% LaFeO₃ also presented excellent dehydrogenation properties with 3.894 wt.% of hydrogen released at 623 K, which was almost twice than the MgH₂. The TPD measurement showed that the onset dissociation temperature of the MgH₂+20 wt.% LaFeO₃ composite was 570 K, which was decreased 80 K with respect to the MgH₂. From the Kissinger plot analysis of the MgH₂+20 wt.% LaFeO₃ composite, the activation energy $E_{\text{des}}$ for hydrogen desorption process was estimated to be 86.69 kJ/mol, which was 36 kJ/mol lower than that of MgH₂. The new additive LaFeO₃ was not only beneficial to the reduction of the particle size but also acted as an inhibitor to keep the particles from clustering during the ball-milled process, which was responsible for the improved hydrogenation-dehydrogenation properties of MgH₂+20 wt.% LaFeO₃ system [1-2].

References

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Structural Characteristics and Hydrogen Storage Properties of Sm$_2$Co$_7$

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Abstract: The Structural characteristics and hydrogen storage properties of Sm$_2$Co$_7$ alloy were investigated by X-ray diffraction and PCI measurement. Two plateaus were clearly observed in the PCI curves where the first and second plateaus corresponded to Sm$_2$Co$_7$H$_{2.9}$ and Sm$_2$Co$_7$H$_{6.4}$, respectively, and their desorption enthalpy changes were 42.0 and 48.5 kJ/mol H$_2$, respectively. Sm$_2$Co$_7$ showed an excellent cycle stability without obvious capacity loss after 50$^{th}$ hydrogenation and dehydrogenation cycles. This alloy also displayed very quick hydrogenation kinetics at ambient temperature, and the hydrogenation process followed a three-dimensional interface controlled reaction.

Introduction

Among the family of intermetallics, R$_2$Co$_7$ (R= rare earth element) have attracted interest due to their applications as permanent magnets. Apostolov et al. \cite{1} ever reported the magnetic properties of the compounds R$_2$Co$_7$ (R = Pr, Sm, Ho and Tb), but they only paid attention to the magnetic properties of the hydrides with hydrogen concentration corresponding to β and γ phases. Sm$_2$Co$_7$ was also found to be able to act as hydrogen acceptors in the dehydrogenation of methanol \cite{2}. In this study, we attempted to synthesize Sm$_2$Co$_7$ and study its structural characteristics and hydrogen storage properties.

Experimental details

The Sm$_2$Co$_7$ alloy was prepared by arc-melting Sm (99.9%) with Co (99.9%) under a high atmosphere of high-purity argon (99.999%). The crystal structures of these samples were determined by X-ray diffraction (XRD) analysis using a Philips X’pert-MPD instrument equipped with Cu-Kα radiation. The thermodynamics of Sm$_2$Co$_7$ determined by the P-C isotherms and its kinetic curves were evaluated on an Advanced Materials Corporation (AMC) gas reaction.

Conclusions

The as-melted alloy was composed of Sm$_2$Co$_7$ phase, and a small amount of SmCo$_5$ phase. The Sm$_2$Co$_7$ alloy consisted of double layers of hexagonal structural blocks for CaCu$_5$-type SmCo$_5$ alternating with double layers of MgCu$_2$-type cubic blocks SmCo$_2$ along the common hexagonal axis. Two plateaus were clearly observed in the PCI curves where the first and second plateaus corresponded to Sm$_2$Co$_7$H$_{2.9}$ and Sm$_2$Co$_7$H$_{6.4}$, respectively, and their desorption enthalpy changes were 42.0 and 48.5 kJ/mol H$_2$, respectively. Sm$_2$Co$_7$ showed an excellent cycle stability without obvious capacity loss after 50$^{th}$ hydrogenation and dehydrogenation cycles. This alloy also displayed very quick hydrogenation kinetics at ambient temperature, and the hydrogenation process followed a three-dimensional interface controlled reaction.

Fig. 1. (a) Rietveld refinement of the observed XRD pattern for the as-prepared Sm$_2$Co$_7$ alloy, (b) Pressure-composition isotherm curves for the Sm$_2$Co$_7$H system at the temperatures between 348 K and 453 K.

References


Investigation of the Thermodynamic and Kinetic Properties of La-Fe-B System Hydrogen-storage Alloys

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Abstract: Alloys of three different chemical compositions obtained by the partial replacement of iron and boron in La$_8$Fe$_{27}$B$_{24}$, La$_{15}$Fe$_{77}$B$_8$ and La$_{17}$Fe$_{78}$B$_7$ by nickel, manganese and aluminium were investigated in this work: La$_8$Fe$_{1.5}$Ni$_{42}$B$_{1.5}$Mn$_5$Al, La$_{15}$Fe$_2$Ni$_{72}$Mn$_7$B$_2$Al$_2$ and La$_{17}$Fe$_3$Ni$_{73}$B$_2$Mn$_3$Al$_2$. Based on their La content, the three alloys were denoted L8, L15 and L17, respectively. La-Fe-B hydrogen-storage alloys were prepared using a vacuum induction-quenching furnace with a rotating copper wheel. The thermodynamic and kinetic properties of the La-Fe-B hydrogen-storage alloys were investigated in this work. The $P$–$C$–$I$ curves of the La-Fe-B alloys were measured over a $H_2$ pressure range of $10^{-3}$ MPa to 2.0 MPa at temperatures of 313, 328, 343 and 353 K. The $P$–$C$–$I$ curves revealed that the maximum hydrogen-storage capacity of the alloys exceeded 1.23 wt% at a pressure of approximately 1.0 MPa and temperature of 313 K. The standard enthalpy of formation $\Delta H$ and standard entropy of formation $\Delta S$ for the alloys’ hydrides, obtained according to the van’t Hoff equation, were consistent with their application as anode materials in alkaline media. The alloys also exhibited good absorption/desorption kinetics at room temperature.

Table

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<th>$\Delta S$/J·K$^{-1}$·mol$^{-1}$H$_2$</th>
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THEORETICAL INVESTIGATIONS ON THE STRUCTURAL STABILITIES OF MAGNESIUM NANOSTRUCTURES AND THE APPLICATIONS FOR HYDROGEN STORAGE

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Abstract Magnesium (Mg), which is fairly accessible at low cost, is a promising hydrogen carrying medium for the onboard applications due to the high gravimetric hydrogen content, high volumetric density, and the highest energy density. However, there are two main hurdles for MgH$_2$ for practical usage: (i) slow kinetics in the reaction of hydrogenation, which may account for surface oxidation of magnesium, low dissociation rate of H$_2$ on magnesium surface, and hydrogen penetration blocking induced by a surface magnesium hydride layer; (ii) a high temperature of 350−400 °C and a high hydrogen pressure of more than 3 MPa are required for the hydrogenation and dehydrogenation reactions, which is ascribed to its high thermodynamic stability. Both theoretical [1] and experimental [2] investigations showed that nanostructuring of magnesium materials provides rapid storage kinetics, especially in the hydrogen desorption process, since it lowered the activation energies of hydrogenation and dehydrogenation.

In our recent study [3], we have studied hydrogen adsorption on the Mg(0001) surface under biaxial strain, using density-functional theory calculations. A phase diagram is obtained for an intuitive sense of how the strain and hydrogen chemical potential affect the structural stabilities of Mg−H system. It is found that the compressive (negative) strains facilitate the formation of the H−Mg−H tri-layers, a precursor of the transition to magnesium hydride, due to the fact that the lattice constant of H−Mg−H tri-layer is shorter than that of pure Mg.

Besides the thin film and surface of Mg, we use the bond energy model to estimate the structural stabilities of Mg nano-clusters. According to the Generalized Wulff Construction [4], the stabilities of clusters depend on the contributions of inner atoms, surface atoms and the edges. We describe the cluster with the number of various kinds of bonds and search the possible structures through the Wang-Landau method. We will finally determine the stable Mg clusters with various size and investigate the hydrogen storage in these stable clusters.

References

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Increased air stability and decreased dehydrogenation temperature of LiBH₄ via modification within poly(methylmethacrylate)

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Abstract: An air-stable LiBH₄ polymeric composite was successfully prepared by modifying LiBH₄ with a gas-barrier polymer matrix—Poly (methylmethacrylate) (PMMA). The nanoconfinement of LiBH₄ in the PMMA network pore structure leaded to fast H₂ release from LiBH₄ molecules at low temperature. Meanwhile, PMMA can not only protect LiBH₄ from water and oxygen but also let hydrogen get in and out freely. LiBH₄@PMMA composite show the good hydrogen desorption property, which started to dehydrogenate at 53 °C and released 5.2 wt.% of hydrogen at 162 °C within 1 h. It could be concluded that PMMA can increase the stability of LiBH₄ in the atmosphere and reduce the dehydrogenation temperature of LiBH₄.

Introduction

Nanoengineering had been demonstrated to be a useful method to reduce the dehydriding/rehydriding temperature of LiBH₄. Nanoscale LiBH₄ is too reactive, so it is necessary to stabilize it for commercial utilization. PMMA had the better gas selectivity than other commonly polymer, with a high permeability ratio of H₂/O₂.[1] Hence, it was used in hydrogen storage to keep away the water and oxygen but let the hydrogen get in or out freely. In this work, LiBH₄ was nanoconfined by PMMA with fine network pore structure for the first time, which protected from the water and oxygen and decreased the dehydrogenation temperature significantly (scheme1).

Result

The LiBH₄ particles had a diameter distribution of 19-73 nm in the crosslinked network pore structure of PMMA, and showed an amorphous structure. The results indicated that the particle size of LiBH₄ was significantly refined by modifying with PMMA. The LiBH₄@PMMA composite presents a lower onset temperature of 53 °C, and with two mian dehydrogenation peaks (figure 1). As the exposure time extending, the intensity of peak at 360 °C became weaker and completely disappeared in the end. The first peak could be contributed to decomposing behavior of the LiBH₄ nanoconfined by the PMMA network pore structure, and the second peak was corresponding to the unconfined LiBH₄ outside the PMMA network pore structure. The above results confirmed that PMMA can protect LiBH₄ from the water and air but let the hydrogen get out freely, and significantly lower the stability of LiBH₄. Moreover, comparing with that the pure LiBH₄ only released 0.6 wt.% of H₂ within 4 h at 260 °C, LiBH₄@PMMA composites could release 5.2 wt.% of hydrogen in 1 h and 5.6 wt.% of hydrogen in 4 h at 162 °C, respectively.

Figure 1. MS hydrogen signals of the LiBH₄@PMMA composite(c) and after exposure the LiBH₄@PMMA composite to air for 1h (d), 4h (e), 8h (f). compared with the pure PMMA (a) and LiBH₄(b).

References


Jianmei Huang is a PhD candidate in Materials Processing from the South China University of Technology. Her current research interests are focused on the metal borohydrides for hydrogen storage.

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TOWARDS EASY AND FULLY REVERSIBLE DEHYDROGENATION OF LiBH₄ BY CATALYZING OF HIERARCHIC NANOSTRUCTURED COB

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Abstract: LiBH₄ is one of the most promising hydrogen storage materials due to its high gravimetric hydrogen density (18.5wt.%) and volumetric density (121kg/m³)⁠[1,2]. However, LiBH₄ suffers from high thermodynamic stability, kinetics barriers and the resultant poor irreversibility which hinder its practical utilization. In this work, hierarchic nanostructured rod-like, flake-like, chain-like, waxberry-like and mulberry-like CoB catalyst was synthesised and doped into LiBH₄ by ball milling. It was revealed that CoB possessed extraordinary catalytic effect, dependent on its morphology, to improve the hydrogen storage properties of LiBH₄. Its dehydrogenation was dramatically facilitated under lower temperature, and the rehydrogenation was easily realized under mild conditions. Almost full reversibility was achieved with the assistance of mulberry-like CoB.

Hydrogen storage properties of LiBH₄-CoB system

Nanostructured CoB with different morphology of rod-like, flake-like, chain-like, waxberry-like and mulberry-like, was synthesized by controlling chemical reduction method[3], and then was mechanically milled with LiBH₄ in a weight ratio of 1:1. Figure 1 shows the dehydrogenation kinetics of LiBH₄-CoB system. It was found that CoB played as a pure catalyst facilitating the dehydrogenation of LiBH₄, and its morphology influenced greatly catalytic activity. The catalytic effect of those CoB is approximately in the order of mulberry-like > waxberry-like > chain-like > flake-like > rod-like, which is in accordance with their specific surface area from high to low. This led to the different dehydrogenation performance of those CoB doped LiBH₄ at 350°C. Among those nanostructured CoB, mulberry-like CoB showed the best catalytic effect. With its catalyzing, 10.4wt.% hydrogen was liberated from LiBH₄ with 1 h, which was faster than that of pristine LiBH₄ (Figure 1 left). By tuning the rehydrogenation conditions of hydrogen pressure and temperature, a almost full reversibility was achieved under 400°C and 10MPa, remaining stable 9.6wt.% hydrogen capacity at the fourth cycle (Figure 1 right). Conclusively, almost fully reversible dehydrogenation of LiBH₄ has been realized under rather mild condition by using nanostructured CoB catalyst.

Figure 1 Dehydrogenation kinetics of LiBH₄-CoB system with different morphology (left), cyclic dehydrogenation of mulberry-like CoB doped LiBH₄ (right). Hydrogen capacity was calculated with respect to LiBH₄.

References

Weitong Cai was born on 20 Nov. 1986 in Guangdong, P. R. China. 2005 Bachelor in School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P.R.China.

At present, he is a Ph.D. candidate at the Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, Guangzhou 510640, P. R. China.

His research field is complex hydrides (LiBH₄).

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The “Science of Hydrogen & Energy” award is a prize, just similar to the Nobel price, for an extraordinary contribution to the sciences of hydrogen. The aim is to award a prize to a distinct scientist for his scientific work of a life time.
SCIENCE OF HYDROGEN & ENERGY AWARD 2007

Ronald Pierre Griessen, was born March 7, 1945 in Switzerland. He received 1964 his Baccalauréat, from Gymnase français in Bienne, Switzerland. From 1964 – 1969 he studied Physics and Mathematics at the Swiss Federal Institute of Technology (ETH) in Zürich and finished with a Diploma-thesis on: "Magnetostriction of type-II superconductors". From 1969 – 1973 he was PhD student in the Low Temperature Physics Group of Prof.dr J.L. Olsen at the ETH. PhD-thesis on: "Oscillatory Magnetostriction and the stress dependence of the Fermi Surface of Al, In, Zn and Mg". From 1974 – 1976 he was Research Associate at the McLennan Physical Laboratory of the University of Toronto, Canada where he worked on the electronic structure of spin-density-wave systems and quantum oscillations. In 1976 he was visiting scientist at the ETH, Zürich and from 1976 – 1980 senior lecturer at the Vrije Universiteit in Amsterdam. Since 1980 he is Full Professor in charge of the Department of Condensed Matter Physics.

Ronald Griessen has investigated the thermodynamics of palladium films and the isotope effect on the electronic structure of hydrides. Furthermore, the effect of anharmonicity and Debye-Waller factor on superconductivity of PdHx and PdDx have been studied by Ronald before he developed a semi-empirical model for the heat of solution of hydrogen in transition metals. He also studied the trapping energy for hydrogen on lattice defects as well as the heat of solution of disordered transition metals. The volume expansion upon hydrogen absorption, the Gorsky-effect, the diffusion, electromigration and the hydrogen diffusion in magnetig fields are just a few other subjects treated and described by Ronald Griessen. Then Ronald decided to test the world of high pressure hydrogen and described the properties of hydrides formed at very high pressure as well as the properties of hydrogen gas in a wide temperature and pressure range. During the intense investigation of superconductors and metal hydrides under high hydrogen pressure in a diamond anvil cell, Ronald has discovered the switchable optical properties of yttrium and lanthanum hydride films. This has then stimulated Ronald to investigate thin films with optical methods and to develop new methods for the combinatorial search of new hydride phases as well as for the determination of the thermodynamic parameters e.g. stability and kinetics of the hydrides. Furthermore, new applications for hydrides as hydrogen detectors and optical filters have been developed in his group.
Louis Schlapbach started his scientific work in 1970, 38 years ago, with the investigation of the Hall effect, electrical transport and magnetic susceptibility of liquid rare earth elements like Cerium. 30 years ago in 1970 he was coauthor with Busch and Waldirich on a paper about the hydrides of La-Ni compounds. LaNi5 was subsequently investigated in view of the structure, surface segregations, hydrogen occupation of interstitial sites and as electrode material. LaNi5 is still the base material for most of the electrochemical applications of metal hydrides today. The work on LaNi5 was complemented by the research on FeTi. Louis Schlapbach realized the importance of the surface composition for the hydrogen sorption process and he was able to describe the role of the surface-active species. Furthermore, he investigated the changes of the surface composition of LaNi5 and FeTi in oxidizing atmospheres and he found the formation of metallic clusters as superparamagnetic particles acting as the active sites in hydrogen dissociation and recombination. The investigation of the surface of metal hydrides was further intensified by means of X-ray photoelectron spectroscopy. Louis Schlapbach was the first scientist correctly describing the activation process of a metal hydride and, furthermore, to model the chemical composition and states of the elements in a surface profile. He also succeeded to analyze the electronic structure of rare earth elements and their hydrides by means of photoemission spectroscopy. In 1990 Louis Schlapbach edited the two books "Hydrogen in Intermetallic Compounds I & II" of the Springer Series. The books became a very important reference for all the researchers active in the field of hydrides.
SCIENCE OF HYDROGEN & ENERGY AWARD 2009

Gary Sandrock received his master from the Institute of Technology, Cleveland in 1965 and his Ph.D. from the Western Reserve University, Cleveland in 1971. He worked from 1962-1969 as a research metallurgist in the NASA Lewis Research Center, Cleveland, Ohio. From 1971-1983 he was Section Manager of Energy Systems at Inco Research and Development Center, Suffern, NY. From 1983-1991 he was Vice President and Director of Technology at Ergenics, Inc., Ringwood, NJ. From 1992-1993 Gary Sandrock was visiting professor at the Kogakuin University, Hachioji, Tokyo, Japan where he developed a new chemical surface treatment and investigated the activation characteristics of chemical treated AB5 alloys. Gary then became the president of SunaTech, Inc., Ringwood, NJ, where he developed reversible hydrogen storage systems. At the same time Gary Operating Agent, International Energy Agency Hydrogen Implementing agreement Tasks 12 & 17 (Hydrogen Storage Materials) and worked as a consultant for the US DOE via Sandia National Laboratories, Livermore, CA.

In 1995 Gary Sandrock started to creat and maintain Hydride Databases of IEA(HIA)/DOE/SNL (http://hydpark.ca.sandia.gov) and he is author of several book chapters and review papers e.g. “A panoramic overview of hydrogen storage alloys from a gas reaction point of view”. His recent research concentrates on the catalysis of the hydrogen desorption from alanates and most recently Gary investigated the hydrogen desorption behavior of AlH3 and explained the mechanism of the kinetic stabilisation of aluminumhydrid. Furthermore, he published a paper entitled “Accelerated thermal decomposition of AlH3 for hydrogen-fueled vehicles” where he shows the possible ways to change the activation barrier for the hydrogen desorption in a controlled way.

Gary Sandrock not only made significant achievements in understanding metal hydrides he also built the bridge from sciences to application. Furthermore, his scientific review papers and the hydride database are inestimably value for the hydride society.
Jens Norskov was born on September 21 in 1952. He received his Master degree in physics and chemistry from the University of Aarhus, Denmark in 1976 and his PhD in theoretical physics in 1979. During his PhD he published papers about the electronic structure of H and He in metal vacancies and the contraction of diatomic molecules upon chemisorption. Jens Norskov was a Post Doc at IBM in Yorktown Heights, New York in 1979 and was affiliated with Nordita, (Nordic Institute for Theoretical Physics) in Copenhagen before he became a member of the scientific staff of Haldor Topsøe A/S, Lyngby in 1981. He continued the investigation of gas molecules at the surface of metals and developed a picture of adsorption and desorption of hydrogen emerging from self-consistent model calculations. In 1992 he was appointed as a professor of theoretical physics in the department of physics at the Technical University of Denmark, Lyngby and became the director of the Center for Atomic-scale Materials Physics (CAMP), Department of Physics, Technical University of Denmark, Lyngby.

Recent research of the group of Jens Norskov covers several of the most relevant topics: 1) The development of theoretical methods e.g. “Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces”; 2) Theoretical surface science e.g. “Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces”; 3) Nanostructures and materials properties e.g. Atomic-scale imaging of carbon nanofiber growth”; 4) Heterogeneous catalysis e.g. “Ammonia synthesis from first principles calculations”; 5) Biomolecules e.g. “Biomimetic hydrogen evolution”; 6) Electrochemistry and fuel cells e.g. “The origin of the overpotential for oxygen reduction at a fuel cell cathode”; 7) Hydrogen storage e.g. “Metal ammine complexes for hydrogen storage”

Jens Norskov is not only a creative and brilliant scientist, he also belongs to the few scientist able to successfully combine theoretical approaches with experimental observations for the understanding of the basic phenomena. It is always a great pleasure to listen to Jens Norskovs talks, which are exciting eye opening stories combined with some great new stimulating ideas.
Rüdiger Bormann was born September, 14 1952 in Germany. He received 1977 his diploma in physics (Metalphysics), from the University Göttingen and 1979 his Dr. rer. nat. from the University Göttingen. From 1981 to 1982 he was visiting scientist in the Dept. of Applied Physics at Stanford University, U.S.A. From 1982 to 1988 he was Assistant Professor (Hochschulassistent) at the University Göttingen where he received the Habilitation University Göttingen, venia legendi in 1988. From 1989 to 1997 he was Professor of Metalphysics (GKSS Research Centre, Geesthacht and Hamburg University of Technology) and from 1996 to 2009 he was director of the Institute for Materials Research, GKSS Research Centre, Geesthacht and since 2009 he is Professor of Applied Materials Physics and President of the University of Bayreuth. Rüdiger Bormann died on 13. January 2013 in an accident in Cologne, Germany.

Prof. Rüdiger Bormann investigated 20 years ago the free energy of metallic glasses, metastable crystalline and amorphous alloys as well as the thermodynamics and kinetics of the amorphous phase formation by mechanical alloying. This was the basis for the investigation of Mg and Mg-Ni hydrides and the thermodynamics of nanoscale magnesim hydride. The discovery catalytic effect of metal oxides on the hydrogen sorption kinetics of magnesium was a great step forward in the development of hydrogen storage materials. Furthermore, very important was also the interpretation of the role of the grain boundaries for the diffusion of hydrogen in the passivating hydride phase formation. Recently the discovery of the so called reactive hydride composites by the combination of two hydrides has opened a new field of materials design for hydrogen storage. Therefore, we award Prof. Rüdiger Bormann with the Science of Hydrogen & Energy prize 2010.
SCIENCE OF HYDROGEN & ENERGY AWARD 2010

Ivor Rex Harris was born August 31, 1939 in United Kingdom. In 1960 he received his B.Sc. in Physical Metallurgy from the University of Birmingham, 1964 his Ph.D and became a ICI Research Fellow. From 1966 he was lecturer in the Department of Physical Metallurgy and 1988 he became a full Professor of Materials Science. From 1989 to 2002 he was Head of School, Metallurgy and Materials and from 2004 to 2005 acting director of the Institute for Energy Research and Policy. Since 2008 he is Honorary Professor of Materials Science of the School of Metallurgy and Materials at the University of Birmingham.

Prof. Dr. Ivor Rex Harris

For around 40 years, Rex Harris was leader of the Applied Alloy Chemistry Group (AACG) in Metallurgy and Materials. During this time he maintained a long-standing research interest in the fields of rare earth alloys, permanent magnets and hydrogen purification and storage materials. He developed a close synergy between these fields with the development and application of the Hydrogen Decrepitation (HD) process to the manufacture of NdFeB magnets. The HD process resulted in up to a 25% saving in production cost and is now used world-wide in the fabrication of NdFeB sintered magnets. These materials are playing a vital role in the production of energy efficient electric drives, actuators and generators. The latest development within the group is the use of the HD process in the recycling of 2/17 and NdFeB magnets. His research also made a very significant contribution to the development and understanding of the Hydrogenation, Disproportionation, Desorption and Recombination (HDDR) process which enabled coercive powder and hence bonded magnets to be formed from bulk NdFeB alloys. He has published over 500 scientific papers and edited and co-edited a number of books. During these years he has successfully supervised around 120 postgraduate students, many of whom are still working in applied materials science and occupy senior positions in industry, government and academia throughout the world. Since stepping down as group leader and head of school he has focused his activities on the application of NdFeB magnets and hydrogen storage materials to practical demonstrators such as the Ross Barlow hybrid canal boat. This zero-carbon emission craft is serving to highlight the huge potential of magnets and hydrogen in the drive towards a sustainable transport system and he has given a large number of public lectures on this subject with the aim of raising public awareness of the dual threats of climate change and resource depletion. He continues to be very active in this campaign which he considers to be of paramount importance. Therefore, we award Prof. Rex Harris with the Science of Hydrogen & Energy prize 2010.
SCIENCE OF HYDROGEN & ENERGY AWARD 2010

Rainer Kirchheim was born May 24, 1943 in Halle/Saale, Germany. He studied Physics at the University of Stuttgart from 1966-1971 and received the diploma for the work “Electrochemical studies of oxygen solid solutions in high melting metals” at the Max-Planck-Institut für Metallforschung/University of Stuttgart. He received his Ph.D. for the thesis entitled “Thermo- and electrotransport of oxygen and nitrogen in Va metals “ from the University of Stuttgart, Max-Planck-Institut für Metallforschung in 1973. In 1988 he received the Habilitation “Measurements and modelling of hydrogen solubility and diffusivity in disordered metal lattices” from the University of Stuttgart, Faculty of Chemistry Metallurgy. Since 1993 he is Full Professor (Gustav Tamman Chair) University of Göttingen Göttingen Germany and Director Georg-August-Universitaet Goettingen, Institut für Materialphysik Göttingen Germany.

Prof. Rainer Kirchheim has investigated 30 years ago oxygen in metals, especially diffusion, thermo-transport and thermo-power of oxygen in transition metals and alloys. In 1980 he started to study diffusion of hydrogen in dilute alloys of copper and niobium in palladium. He developed an electrochemical method for the measurement of the hydrogen diffusion in palladium and palladium alloys and performed fundamental studies on the diffusion mechanism of interstitial species. The interaction of hydrogen with dislocations in palladium and the interpretation with a model based on the Fermi-Dirac distribution are of great importance for the understanding of the interstitial site occupation of hydrogen in alloys and amorphous metals. For the enormous contributions on the hydrogen dynamics and thermodynamics in metals as well as the hydrogen interaction with dislocations, grain bounderies and interfaces we award Prof. Rainer Kirchheim with the Science of Hydrogen & Energy prize 2010.
Prof. Dr. Koji Hashimoto

Prof. emeritus Koji Hashimoto has published over 520 papers in scientific journals in addition to review articles and book chapters. He has worked on corrosion-resistant alloys, electrolysis, especially he pioneered the electrolysis of seawater. He tailored the catalysts for carbon dioxide methanation, in particular, he has built a prototype plant for global CO₂ recycling in 1995 on the roof top of the Institute for Materials Research, Tohoku University. The plant consists of power generation by photovoltaic cells, hydrogen production by seawater electrolysis and methane formation by the reaction of carbon dioxide with hydrogen, carbon dioxide recovery at an energy consuming district, and transportation of carbon dioxide. The plant uses tailored key materials with high performance and durability, that is, cathodes for hydrogen production, anodes for only oxygen evolution without chlorine evolution in seawater electrolysis, and catalysts for rapid and selective production of methane by the reaction of carbon dioxide with hydrogen. The performance of the plant has substantiated that global CO₂ recycling can supply abundant energy generated from solar energy on deserts in the form of methane and can really prevent global warming induced by carbon dioxide emissions. In 2003, he has built a pilot plant of global CO₂ recycling at Tohoku Institute of Technology which is the minimum unit of industrial scale for seawater electrolysis and carbon dioxide methanation.

He is in the Editorial Board of "Corrosion Science", a Member of NACE International, the Electrochemical Society and the International Society of Electrochemistry. Member of Japan Society of Corrosion Engineering, the Japan Institute of Metals, the Surface Finishing Society of Japan, the Iron and Steel Institute of Japan, the Electrochemical Society of Japan, the Society of Chemical Engineers, Japan, the Chemical Society of Japan, and other scientific societies in Japan.

He received many awards among those also The Electrochemical Society Fellow Award in 1997 in recognition of contribution to the advancement of science and technology, for leadership in electrochemical and solid state science and technology and for active participation in the affairs of the Electrochemical Society, Inc.

We award Prof. Koji Hashimoto for his outstanding work on the production of hydrogen and the use of hydrogen for the reduction of CO₂ with the Science of Hydrogen & Energy prize 2011.
Mogens Mogenson is research professor in the fuel cells and solid state chemistry division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark (DTU). He has spent 37 years in electrochemistry. He received his MSc in 1973 and PhD in 1976 from the Department of Metallurgy, DTU. After a postdoctoral period at the Department of Chemistry A, DTU, and a short period in the battery industry (Hellesens A/S), he was employed at Risø National Laboratory in 1980. He was manager for numerous projects and programs (mainly within R&D of practical electrochemical cells such as solid oxide fuel cells) and now the Strategic Electrochemistry Research Center (SERC). He has coauthored more than 250 scientific papers and reports, and has 16 patents/patent applications.

Prof. Dr. Mogens MOGENSON

Prof. Mogens Mogensen from the Risø National Laboratory for sustainable Energy made an enormous contribution in the development for electrochemical systems like SOFCs (High Temperature Solid Oxide Fuel cells), SOEC (Solid Oxide Electrolyser Cells) as well as oxygen separation membranes over the last 20 years. His topics in this field include the material development for electrodes, electrolytes as well as interconnects, coatings and sealing’s. Mogens is known for his broad knowledge and understanding of the total systems and especially the deep knowledge of the thermodynamics and electrochemical behavior of the cells. The driving force behind his research activities are the principle understanding of the aging mechanisms in SOEC and SOFC systems, the electrochemical behavior, but also the development of new materials for better performance and competitive prices. In the field of advanced materials he was very active and successful in the development of catalytic metal oxides with fluoride and perovskite related structures. These compounds are extremely flexible with respect to substitution of host cations and non-stoichiometry. By this purpose he has done “material engineering” by tailoring the basic materials properties for aspects like high electronic and ionic conductivity, matching thermal expansion coefficient, stability in hydrogen and/or oxygen atmosphere, etc. The development of novel materials was leading to the “world record” in power density for electrochemical cells, accompanied by a low aging- and degradation rate (>1%/1000h) and an outstanding mechanical strength and flexibility. Mogensen was also very active in cells and stack development with high electrical efficiency and fuel flexibility including natural gas, biogas, diesel, LPG, methanol, DME and ethanol. Recently his topic and interest are the synthetic fuels derived from water and CO₂. This is interesting as the produced syngas (H₂ + CO) can react to form methane, which is a more suitable energy carrier. In this process, the catalytic process is taking place inside the cell, so the reaction heat can be utilized.

We award Prof. Mogens Mogenson for his outstanding work on the electrochemistry of electrolyser and fuel cells with the Science of Hydrogen & Energy prize 2012.
Mr. Katsuhiko HIROSE

Katsuhiko HIROSE has a very important role in the development of hydrogen for mobility by building the bridge between industry (Toyota) and academia as well as the bridge between Asia and Europe.

He initiate the hydrogen's economical value assessments. Hydrogen fuel is valuable for the economy as well as for the environment. The value-chain analysis of Fuel Cell vehicles and Hydrogen Energy analysis identifies the big economical value of the use of hydrogen as a fuel. This analysis has re-ignited many activities on hydrogen all over the world.

He also initiated the H2Mobility activities and brought many OEM and stakeholder into these activities. Resulting in the German H2mobility report. A portfolio of power-trains for Europe: a fact-based analysis, which stimulated the hydrogen activities world wide again.

The large number of key-note speeches in both engineering conference and academic conference stand for his continuous efforts as an interpreter between the industries and academic scientists.

He is responsible for the world leading research in hydrogen storage by means of hybrid tank systems, i.e. the combination of pressurized hydrogen gas and metal hydrides, which leads to a hydrogen storage with greater gravimetric and volumetric hydrogen density as compared to the individual system. Furthermore, he also developed a Cryo-adsorption tank system.

We award Mr. Katsuhiko HIROSE for his outstanding work on the implementation of hydrogen for mobility and for linking the key people worldwide together with the Science of Hydrogen & Energy prize 2013.
Hans Geerlings studied experimental physics in Amsterdam, where he received his PhD degree in 1987. In that year he moved to Shell, where he worked in research on a number of topics including synthesis gas conversion, hydrogen storage and CO$_2$ capture and storage. In 2007 he was appointed as a part time professor at the Delft University of Technology. His current research interests are in the area of ‘Solar Fuel synthesis’ and ‘Mineralization of CO$_2$.‘

**Prof. Dr. Hans GEERLINGS**

Hans Geerlings has worked on complex hydrides, i.e. alanates, especially on the synthesis and the characterization of MgAlH$_4$ and CaAlH$_4$, before he focused on the CO$_2$ capture and mineralization. Recently, he published a paper in Environmental Science entitled “Efficient Production of Solar Fuel Using Existing Large Scale Production Technologies” in which the efficient production of solar fuels today using existing technologies is described. The feasibility of liquid hydrocarbon fuels production from CO$_2$ and water with efficiencies approaching 10% from solar energy is demonstrated, this is about an order of magnitude higher than alternative technologies currently under development. The reduction of CO$_2$ with hydrogen for the production of synthetic fuels is a new challenging research branch with an enormous potential for the future energy economy.

We award Prof. Hans Geerlings for his outstanding work on the hydrogen production and storage as well as his effort to open new fields in a world leading oil producing company with the Science of Hydrogen & Energy prize 2013.
SCIENCE OF HYDROGEN & ENERGY AWARD 2014

Prof. Dr. Andreas ZÜTTEL

Andreas Züttel has worked on metal hydride electrodes and developed new overstoichiometric AB$_2$ Laves-phase alloys where the B atoms partially occupy A-sites. He developed a mathematical model for the capacity of a metal hydride electrode. With the discovery of carbon nanotubes and first reports about the great hydrogen storage capacity of single wall carbon nanotubes he started to investigate the interaction of hydrogen with nanostructures by means of electrochemical sorption measurements and described the relationship between the hydrogen density and the materials surface area of nanostructures. Furthermore, the size dependent hydrogen sorption properties of monodisperse Palladium clusters as small as 55 atoms were investigated electrochemically and modeled by A. Züttel. He initiated research on borohydrides for hydrogen storage 10 years ago and published together with S.I. Orimo important papers on the properties of borohydrides e.g. a model for the stability and the hydrogen sorption mechanism. Recently his activities have expanded to the reduction of CO$_2$ with hydrogen for the production of synthetic hydrocarbons as fuels. This is the basis to close the materials cycle for hydrocarbons as energy carriers.

We award Prof. Andreas Züttel for his outstanding work in the science on the interaction of hydrogen with solids e.g. intermetallic compounds, nanostructures and complex hydrides with the Science of Hydrogen & Energy prize 2014.
Qidong Wang is a professor of Department of Materials Science and Engineering, Zhejiang University. He was born in 1921, and obtained his BSc degree in 1943 from Zhejiang University of China, MSc degree in 1948 from Stanford University and PhD in 1951 in the University of Iowa of USA, majoring in the heat power of mechanical engineering. He returned China in January of 1951 to teach and do research in Zhejiang University until he retired in 2011. His main research work focuses on hydrogen storage materials and their actual applications. Besides the researching tasks and teaching, he has also done many administrative and social services.

Prof. Qidong Wang

Prof. Qidong Wang from the Department of Materials Science and Engineering of Zhejiang University was involved in the fields of mechanical engineering, metallurgical engineering and functional materials in his 60 years’ research career. He has made many outstanding contributions in the topics such as process intensification of melting procedure in cupola, precision casting of high speed steel cutting tools and developments of new hydrogen storage materials and systems. In particular, he is well known as a pioneer in the development and applications of hydrogen storage alloys in China. He has done a lot of excellent work in the research fields of rare earth based hydrogen storage materials and new metal-hydride systems. His research interests also focus on the purification and transportation of hydrogen as well as Ni-MH batteries.

Since 1978 he devoted himself into the research on hydrogen storage alloys and compounds and their applications for storing and transporting hydrogen and the use of hydrogen as supplementary fuel for internal combustion engines. He firstly used lanthanum-rich mischmetal, which has almost the same hydrogen storage capability but the cost of the alloy lowers by one third, to replace the pure lanthanum. Moreover he firstly employed mechanical milling method to prepare mischmetal cathode materials for hydrogen storage batteries, which hereafter were widely accepted by peers. He has contributed with his coworkers more than 500 scientific papers and reports and he has 18 patents and more than 20 awards on his contributions in scientific researches, teaching and social contributions. So far, his scientific papers have been cited more than 5000 times and his H-index reached as high as 33.

Even though at an advanced age, he is still concerning on the development of hydrogen economy. His endurance and diligence are the merits we scientific workers should learn from.

We award Prof. Qidong Wang for his outstanding work on hydrogen storage materials and their applications with the Science of Hydrogen & Energy prize 2014.
Ms. Alondra TORRES TRUEBA

“Hydrogen Storage in Structure II Clathrate Hydrates with Various Promoters”

Department of Process & Energy, Delft University of Technology, Delft, Netherlands

M.Sc. Alondra Torres earned her bachelor degree from Universidad Autonoma del Estado de Mexico and her master degree (cum laude) from Universidad Iberoamericana in Mexico City. Currently Alondra Torres is appointed as a Ph.D. student at Delft University of Technology in the Netherlands. During her studies Alondra Torres has been involved in several projects including; heavy metals removal from waste water with organic material and the formation of polymeric membranes with supercritical CO₂ for gas separation. Her current Ph.D. project involves the study of the potential of clathrate hydrates for hydrogen storage.

Hydrogen Storage in Structure II Clathrate Hydrates with Various Promoters

Hydrogen (H₂) is a promising alternative to fossil fuels, because it offers a solution for three main global challenges: (i) reduction of greenhouse gas emissions, (ii) fulfillment of energy requirements and (iii) reduction of local air pollution. However, due to the difficulty in finding an effective storage medium, the application of H₂, for instance in the automotive sector, is currently limited. Clathrate hydrates, have been regarded as a favorable alternative for H₂ storage. Their profitability, safety, fast and high reversibility and efficient production make them more suitable for this application than other H₂ storage materials.
“HOW TO WATCH HYDROGEN DIFFUSE IN ANY ABSORBING MATERIAL”

The kinetics of interstitial hydrogen are of great interest and importance for many technologies. In particular nano-sized materials motivate fascinating applications and scientific questions. Even though diffusion is one of the most studied phenomena the complex combination of quantum effects and dynamic interplay with the displacement of host atoms [1,4] is still only partially understood. We present a method to quantify chemical diffusion of hydrogen in nano-sized materials. The changes in the absorptance of a vanadium single crystal thin-film, induced by hydrogen, are observed visually and in real-time as a function of position. Concentration profiles and their evolution in time, during chemical diffusion, can be measured down to a hydrogen content corresponding to just a few effective monolayers, randomly distributed within VH_x.
BEST POSTER AWARD 2013

Mr. Moreno DE RESPINIS

“Optimization of Anneal Procedure in Metal Oxides: Case Study of Nanostructured Tungsten Processed via Low-Energy Helium-Ions”

Delft University of Technology, Faculty of Applied Sciences, Department of Chemical Engineering, Materials for Energy Conversion and Storage; Julianalaan 136, 2628 BL Delft, The Netherlands

Moreno de Respinis received his bachelor degree in physics at the University of Milan in 2008, and earned his master degree in sustainable energy with study line hydrogen and fuel cells at the Technical University of Denmark (DTU) in 2011. He concluded his master with a fellowship at the Lawrence Berkeley National Laboratory with Dr. Heinz M. Frei’s group, in which he performed mechanistic studies of water photooxidation by visible-light driven Co3O4 catalyst. He is currently a Ph.D. student at Delft University of Technology where he is researching on photoanodes for solar water splitting.

“Optimization of Anneal Procedure in Metal Oxides: Case Study of Nanostructured Tungsten Processed via Low-Energy Helium-Ions”

One challenge in developing highly efficient nanostructured photoelectrodes is to control their morphology, crystal phase and stoichiometry. We present a novel physical processing route that uses high-flux of low-energy helium- ion to generate porous structures on tungsten targets. Optimal anneal condition to form WO3 photoanode is determined via in-situ XRD. SEM images show mesoporous crystalline structure, and feature sizes depend on substrate temperature and can be tuned between 30 nm and 1 μm. Our research shows that a two-step anneal procedure is optimal to oxidize surface nanostructures into crystalline WO3, preserving the bulk as metallic W for good electrical contact. As a result, IPCE of 20% is obtained, resulting in an AM1.5 photocurrent of 0.75 mA/cm^2 at 1.23 V_RHE (compared to 0.15 mA/cm^2 after standard thermal oxidative anneal). The excellent control over feature size offers an exciting new processing route to nanostructure materials for e.g. solar water splitting.
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</table>
Information
Map from Guangzhou Baiyun International Airport to Zhaoqing

Map of OYC Hotel and DingHu Mountain (Social event) in Zhaoqing
EMERGENCY TELEPHONE NUMBERS

country code for China +86

POLICE 110

FIRE FIGHTERS 119

AMBULANCE 120

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Website: http://www.oychotel.com