Edited by Michael Hirscher

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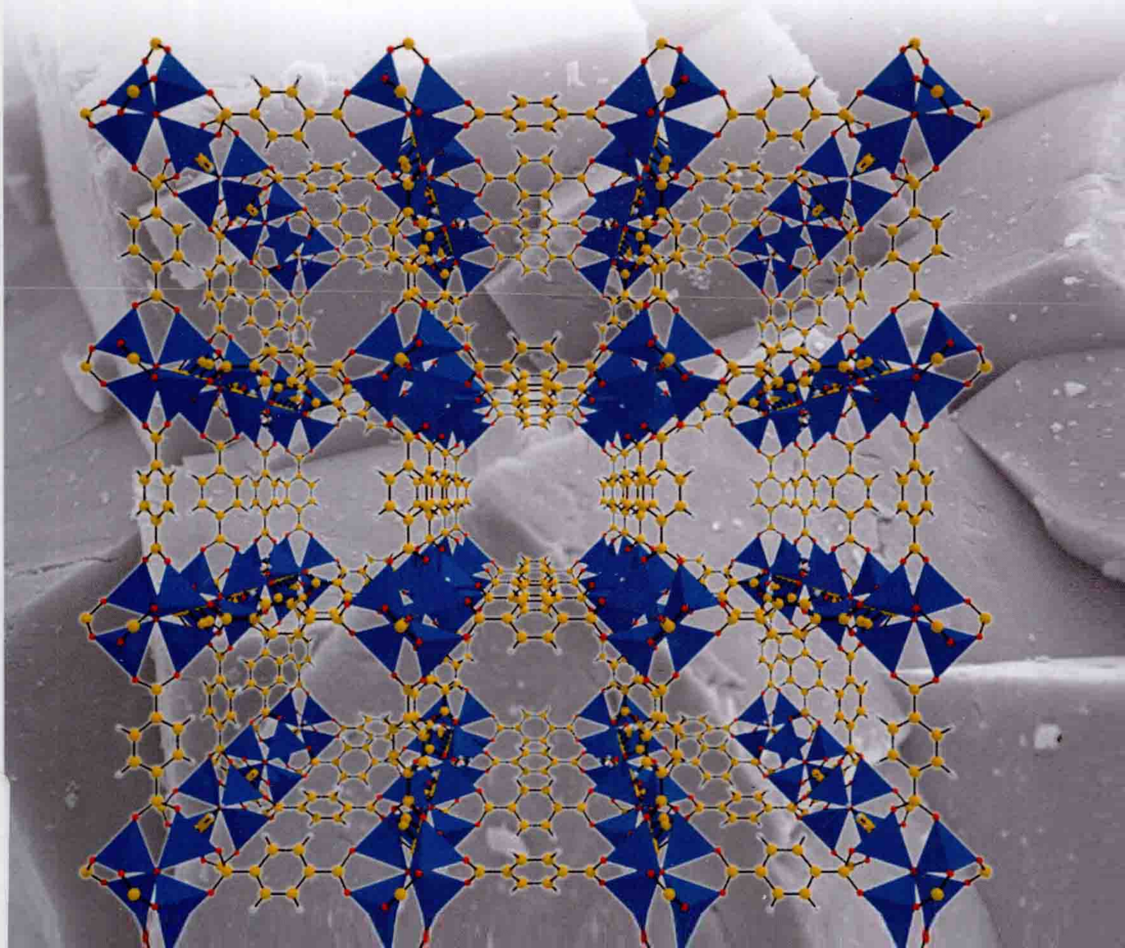
Handbook of Hydrogen Storage

New Materials for Future Energy Storage

With a Foreword by Katsuhiko Hirose



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The Editor

Dr. Michael Hirscher
Max-Planck-Institut für
Metallforschung
Heisenbergstr. 3
70569 Stuttgart

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Crystal structure of metal-organic framework MOF-5 constructed of ZnO_4 tetrahedra and carboxylate ligands. Background showing a scanning electron microscope picture of cubic MOF-5 crystals.

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Foreword

Our children need your great ideas and effort for hydrogen storage technologies innovations.
Sustainable/Hydrogen society construction rely on your brain and hand of research.
Katsuhiko Hirose, Project General Manager, Strategic Planning Department, Fuel Cell System Engineering Division, Toyota Motor Corporation

The human race has a long history of desiring mobility. I believe that is why even in the Stone Age and Bronze Age people traveled long distances to exchange information and goods.

In the last century this mobility expanded dramatically through the invention of the automobile and the use of oil as its fuel. This combination of oil and automobile seemed perfect until it became an environmental problem. Local environmental issues were partly solved by the introduction of catalysts and precise emission control through the tremendous efforts of catalyst material scientists and engineers. However, automobiles are again facing very high hurdles such as global warming and energy security issues.

In 2008 the world experienced the great shock of high oil prices. Not only the automobile industry but also everyday lives are massively affected by high oil prices. The cause was not the previously predicted scenario (peak oil), the problem was brought about without the collapse of any oil fields, just high oil prices created in the market. We have recognized that we now need to accelerate efforts to move away from oil as an automobile fuel and, at the same time, meet future requirements for reduced carbon dioxide emissions. There are only a few technologies able to achieve these targets while meeting user requirements such as low cost, long range travel and quick, easy refueling capabilities.

Hydrogen is the most promising technology and the automobile industry has spent billions of dollars to bring it onto the roads. As a result, vehicle technologies have reached very high levels, out-performing the current internal combustion engines two- or three-fold in terms of thermal efficiency, and at the same time reaching current vehicle levels of cold start capability down to $-30\ ^{\circ}C$ and other performance targets. However, the biggest and most difficult issue remaining is cost reduction of the technologies to current vehicle levels, which is essential for hydro-

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gen to be popular enough to solve both the energy security and carbon dioxide issues. There had seemed to be a similar pattern of cost reduction for fuel cell stacks and components to that for current technologies, since they both include steps such as reducing the number of parts and improving performance to reduce size and materials usage. However, hydrogen storage is a little bit different. Currently, the only available technology is a carbon fiber reinforced plastic composite high-pressure tank system, but this technology leaves several problems for future cost reduction. The quantities of expensive materials used constrain potential cost reduction and the large cylindrical shape limits installation of the tank in conventional vehicles.

The world's major automotive companies have announced fuel cell vehicle commercialization from 2015. The automotive industry recognizes that hydrogen storage still needs innovative ideas and materials in order to transform it into a popular technology for the future. The important requirements for hydrogen storage technologies are energy efficiency, size and weight, as well as easy adaptation to supply infrastructures and cost.

This problem cannot be solved by either academia or industry alone, so scientists and engineers must work together to achieve this difficult but indispensable task. I believe the current good collaboration will bring this about and we will be able to leave a clean, green globe for our children.

December 2009 *Katsuhiko Hirose*

Preface

The limited fossil fuel resources and the environmental impact of their use require a change to renewable energy sources in the near future. For mobile application an efficient energy carrier is needed that can be produced and used in a closed cycle. Presently, hydrogen is the only energy carrier that can be produced easily in large amounts and in an appropriate time scale. Electric energy, either from renewable energies, for example, solar and wind, or future fusion reactors, can be used to produce hydrogen from water by electrolysis. The combustion of hydrogen leads again only to water and the cycle is closed. A comprehensive overview of the hydrogen cycle was given recently in the book "Hydrogen as a Future Energy Carrier" edited by Züttel *et al.* [1].

For individual motor car traffic, currently, three concepts are discussed by major auto manufacturers, fuel-cell vehicles, extended-range electric vehicles and battery-electric vehicles, for example, see the GM road map [2, 3] in Figure 1. The use of these three technologies depends on the application field and is related to the different energy densities of these energy carriers (see Figure 2). To achieve a driving range of 500 km for a conventional vehicle with today's Diesel technology requires a tank system weighing approximately 43 kg with a volume of 46 L. A zero-emission vehicle driven by a fuel cell with hydrogen will need a 700 bar high-pressure tank system of about 125 kg and 260 L to achieve the same driving range. A battery-electric vehicle will require an energy storage system (comprising battery cells, heat management and power electronics) which, using the most advanced Li-ion-battery technology (energy density $120\,\mathrm{Wh\,kg^{-1}}$), would weigh almost 1000 kg with a volume of 670 L. This value assumes that the total electric energy of the battery is used, which would significantly reduce the cycle life of the device. More realistic is a maximum usage of 80% of the stored energy. The loading of a battery will take between several hours at a high-voltage high-current station and about one day at a conventional 230 V power socket with 16 A. Fast charging stations (about 50 kW, 30 to 90 min reloading), on the other hand, would require a very considerable infrastructure investment of several billion euros for a European nation such as France or Germany, comparable to a hydrogen infrastructure. The refueling of the high-pressure hydrogen vessel will take about 3 min, which is comparable to the Diesel tank. Furthermore, a hydrogen storage system for a driving range of 500 km will cost about 3000 US$ if produced in

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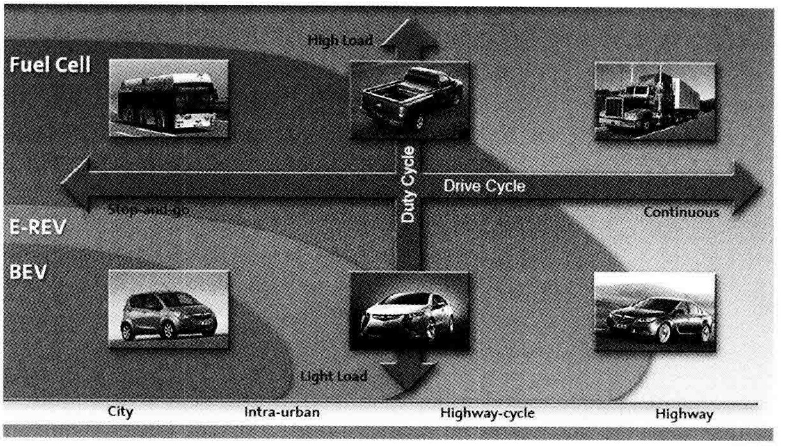

Figure 1 Application map for various electric vehicle technologies, from battery-electric vehicles (BEV), extended-range electric vehicles (E-REV) to fuel-cell vehicles, considering driving distance and load [2, 3].

high volumes. A comparable battery system would be in the price range of 50 000 US$.

According to these constraints, a battery-electric vehicle (BEV) would be the choice for light-weight vehicles and driving ranges up to 150 km. Extended-range electric vehicles (E-REV) could be the solution for users who only occasionally need longer driving ranges, up to 500 km. However, for long driving ranges or high load the fuel-cell vehicle possesses clear advantages due to zero emission in all operating

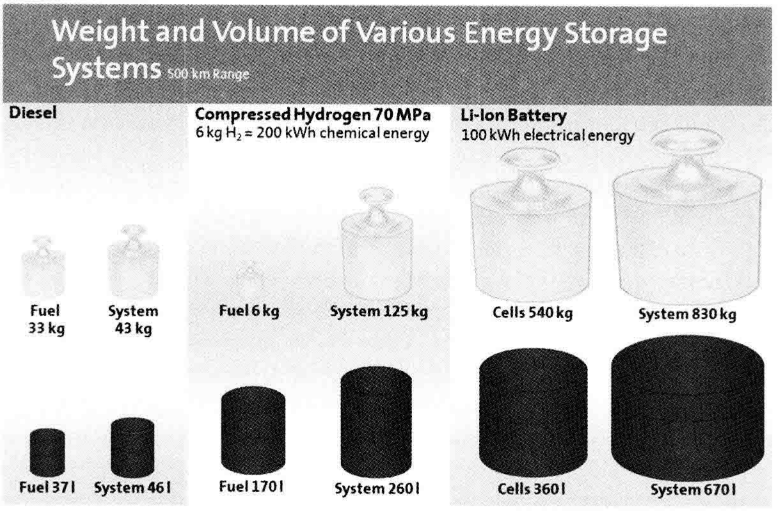

Figure 2 Weights and volumes of different energy carriers and systems used in vehicles to achieve a total driving range of 500 km [2, 3].

conditions and fast refueling times. Figure 1 shows an application map for the various technologies.

Nevertheless, current technologies, such as compressed gas or liquefied hydrogen, have severe disadvantages (especially in volumetric terms) compared to fossil fuels and the storage of hydrogen in light-weight solids could be the solution to further enhance the energy density of hydrogen tanks. The benchmark for all these solid-state systems needs to be an improvement over a 70 MPa tank system. In particular, fundamental knowledge of the atomistic processes is required to design optimized novel materials with new physical properties.

For automotive application of solid state absorbers, there are, more or less, two operating regimes envisaged to achieve such a technology breakthrough:

1) Room temperature storage at pressures up to 35 MPa
2) Cryogenic storage at pressures up to 5 MPa.

This handbook gives a comprehensive overview of novel solid hydrogen storage materials, highlighting their main advantages and drawbacks. The first chapter is devoted to the storage of hydrogen in a pure form giving the state-of-the-art for compressed and liquid hydrogen. In Chapter 2 adsorption materials for hydrogen storage by physisorption of hydrogen molecules are analyzed for possible cryo-adsorption systems. Chapter 3 describes the potential of clathrate hydrates as storage materials. Chapter 4 gives a review of conventional hydrides, including techniques to improve them by nanostructuring. Chapters 5–9 are devoted to novel light-weight materials, ranging from complex hydrides; amides, imides and mixtures; tailoring of reaction enthalpies; ammonia, borane and related compounds; and aluminum hydride. Finally, Chapter 10 concentrates on nanoparticles, mainly in systems confined by scaffold materials.

December 2009 *Michael Hirscher*

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List of Contributors

Philipp Adelhelm
Utrecht University
Inorganic Chemistry and Catalysis
Debye Institute for Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Felix Baitalow
TU Bergakademie Freiberg
Department of Energy Process Engineering and Chemical Engineering
Fuchsmuehlenweg 9
Building 1
09596 Freiberg
Germany

Martin Dornheim
GKSS Research Centre Geesthacht
Institute of Materials Research
Max-Planck-Straße 1
21502 Geesthacht
Germany

Michael Felderhoff
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim/Ruhr
Germany

Michael Hirscher
Max-Planck-Institut für Metallforschung
Heisenbergstr. 3
70569 Stuttgart
Germany

Jacques Huot
Université du Québec à Trois-Rivières
Institut de Recherche sur l'Hydrogène
3351 des Forges
PO Box 500, Trois-Rivières (Qc) G9A 5H7
Canada

Takayuki Ichikawa
Hiroshima University
Institute for Advanced Materials Research
1-3-1 Kagamiyama
Higashi-Hiroshima, 739-8530
Japan

Petra E. de Jongh
Utrecht University
Inorganic Chemistry and Catalysis,
Debye Institute for Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

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Manfred Klell
Hydrogen Center Austria
Inffeldgasse 15
A-8010 Graz
Austria

Florian Mertens
TU Bergakademie Freiberg
Department of Physical Chemistry
Leipziger Str. 29
09596 Freiberg
Germany

Barbara Panella
ETH Zurich
Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences,
Hönggerberg
8093 Zürich
Switzerland

and

Max-Planck-Institut für Metallforschung
Heisenbergstr. 3
70569 Stuttgart
Germany

Cor J. Peters
Delft University of Technology
Faculty of Mechanical, Maritime and Materials Engineering
Department of Process and Energy
Laboratory of Process Equipment
Leeghwaterstraat 44
2628 CA Delft
The Netherlands

and

The Petroleum Institute
Department of Chemical Engineering
P.O. Box 2533
Abu Dhabi
United Arab Emirates

Sona Raeissi
Shiraz University
Chemical and Petroleum Engineering Department
Shiraz 71345
Iran

Alireza Shariati
Shiraz University
Chemical and Petroleum Engineering Department
Shiraz 71345
Iran

Claudia Weidenthaler
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
45470 Mülheim/Ruhr
Germany

Gert Wolf
TU Bergakademie Freiberg
Department of Physical Chemistry
Leipziger Str. 29
09596 Freiberg
Germany

Ragaiy Zidan
Savannah River National Laboratory
Energy Security Directorate
Aiken
SC 29803
USA

Contents

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