Storing Renewable Energy in the Hydrogen Cycle

Andreas Züttel*ab, Elsa Calliniab, Shunsuke Katoab, and Züleyha Özlem Kocabas Atakib

Abstract: An energy economy based on renewable energy requires massive energy storage, approx. half of the annual energy consumption. Therefore, the production of a synthetic energy carrier, e.g. hydrogen, is necessary. The hydrogen cycle, i.e. production of hydrogen from water by renewable energy, storage and use of hydrogen in fuel cells, combustion engines or turbines is a closed cycle. Electrolysis splits water into hydrogen and oxygen and represents a mature technology in the power range up to 100 kW. However, the major technological challenge is to build electrolyzers in the power range of several MW producing high purity hydrogen with a high efficiency. After the production of hydrogen, large scale and safe hydrogen storage is required. Hydrogen is stored either as a molecule or as an atom in the case of hydrides. The maximum volumetric hydrogen density of a molecular hydrogen storage is limited to the density of liquid hydrogen. In a complex hydride the hydrogen density is limited to 20 mass% and 150 kg/m³ which corresponds to twice the density of liquid hydrogen. Current research focuses on the investigation of new storage materials based on combinations of complex hydrides with amides and the understanding of the hydrogen sorption mechanism in order to better control the reaction for the hydrogen storage applications.

Keywords: Electrolysis · Energy storage · Hydrides · Hydrogen · Synthetic hydrocarbons

Introduction

The energy turnaround requires the storage of large amounts of renewable energy, including seasonal storage. In central Europe for the complete coverage of our energy demands a storage capacity that corresponds to 2000 kg of oil per capita would be required. The transition from an energy economy based on mining resources, i.e. materials and fossil fuels, to a society based on renewable energy and closed materials cycles is essential for the global development towards a sustainable and prosperous economy. The growth of the world population depends on wealth distribution, and according to the analysis of Hans Rosling the world population is going to increase to approx. 11 billion people in 2100. The extrapolation is based on the assumption that global wealth will continue to grow and the birth rate will accordingly decrease worldwide. The global energy demand is expected to increase from today to 2050 by a factor of 3. This will only be possible if the materials cycles are closed, especially the materials used as energy carriers. Despite the plans to reduce energy consumption in the western industrialized countries in the future the political strategies are to grow economically, which is only possible with growing consumption. Physically, wealth is the availability of materials and energy, therefore, increasing wealth requires an increase in energy and material consumption. More than 80% of the energy demand today is covered by fossil fuels, i.e. hydrocarbons that release CO₂ and H₂O upon combustion with air. Unlike water CO₂ does not precipitate out of the atmosphere. Due to the limited resources of fossil fuels and materials, and the effect of the increasing CO₂ concentration in the atmosphere on the climate, a large part of the increasing energy demand must be covered by renewable energy sources. Therefore, the hydrogen cycle, i.e. the production of hydrogen from renewable energy and water, the storage of hydrogen and the combustion of hydrogen in a fuel cell, internal combustion engine or a turbine offers a technical feasible solution to produce an energy carrier directly from renewable energy in a naturally closed cycle. In this article we describe the basis and current level of technological development of water electrolysis and hydrogen storage in hydrides and describe the recent developments and achievements connected to the Swiss Competence Center in Energy Research (SCCER).

Hydrogen Production by Electrolysis

The Swiss company Lonza SA was founded in Gampel (VS) in 1897 and used electricity to produce calcium carbide and acetylene. In the beginning of the 20th century the products expanded to synthetic fertilizers from nitrogen and ammonia and, therefore, the need for hydrogen grew. Around 1940 Lonza decided to produce the hydrogen on site. Ewald A. Zdansky was mandated to develop a gas generator able to deliver the hydrogen requirements for the chemical production. Due to the hydroelectric power available in the region Zdansky worked on the construction of an industrial electrolyzer in collaboration with the Giovanola Frères SA (GFSA), located in Monthey, that had the large manufacturing tools to produce the first prototype electrolyzer.[1] In 1950 the development led to a patent of the high-pressure industrial electrolyzer (Zdansky-system) manufactured at GFSA and commissioned at Lonza.[2] The market demand for electrolyzers was growing and Lonza sold the intellectual property of the high pressure electrolyzer to LURGI (“Metallurgische Gesellschaft”) in Butzbach, Germany. LURGI commercialized the electrolyzers and further improved the design of the electrodes and the mechanical assembly in collaboration with GFSA in Monthey, where Jürgen Borchardt (a LURGI engineer) managed the research and development. More than 100 alkaline high-pressure electrolyzers with a power
of up to 4 MW were installed worldwide. In 1996, the intellectual property as well as the customer database were acquired by GFSA and LURGI discontinued the electrolyzer development and manufacture and closed the electrolyzer section. However, GFSA faced financial shortages in 2001 and the daughter company, GTec SA, created in 2002 based on the electrolysis activities, also went out of business soon after. Finally, the technology of the high-pressure electrolysis was transferred to a new company, IHT Industrie Haute Technologie SA (IHT) in 2003 with the goal to further develop the large-scale electrolyzer units and replace the asbestos membranes with new materials keeping the particular properties of very long lifetime (>30 years) and high energy efficiency (>80%).

Electrolysis is based on the splitting of water by means of an electrical potential. Hydrogen is evolved on the cathode (−) and oxygen on the anode (+). Between the electrodes is an electrolyte, which acts as an electrical insulator and ionic conductor. The ions transferred between the electrodes are H+, OH− or O2− and the corresponding electrolyzers are called acidic (PEM), alkaline or solid oxide. Between the electrodes a membrane separates the evolved gases H2 and O2.

The membrane has to fulfill several requirements, e.g. stability under operating conditions, separation of the gases, mechanical separation of the electrodes, ion conduction and mechanical support for pressure differences between the two sides in the cell. Electrolysis requires catalytic electrode materials for a low over potential of the electron transfer and an electrolyte, which provides high conductivity for ions rates the two gases hydrogen and oxygen.

A technical electrolyzer is a compromise between the ion conductivity of the electrolyte and the mechanical stability and gas separation of the membrane.

The polymer electrolyte membrane (PEM) electrolyzer transports H+ ions in a solid polymer (Nafion®) at around 60 °C (Fig. 1a). The ion conductivity of the PEM is in the order of 6 S/m and water is provided on the oxygen side (anode). Therefore, high purity hydrogen is produced on the cathode. The challenges in the further technical development of PEM electrolyzers are the increase of the conductivity of the polymer membrane, the chemical and mechanical stability of the polymer and the dissipation of the heat produced during the electrolysis process.

The alkaline electrolyzer consists of a microporous membrane (ZrO2 in poly-phenylene sulphide, Ziron PERL®) filled with electrolyte that provides the OH− ion conductivity in the order of 120 S/m at 80 °C (Fig. 1b). The 25wt% KOH in water electrolyte is pumped on the anode and cathode side, while the water is consumed on the cathode (H2) electrode and half of it appears on the anode (O2) electrode. Therefore, the electrolyte concentrates at the cathode and dilutes on the anode, the electrolyte from the two sides has to be mixed in order to compensate for the concentration difference. The evolved gases hydrogen and oxygen are extracted from the circulation electrolyte in gas separation units. A heat exchanger allows to maintain the electrolyte at the operation temperature.

The solid oxide electrolyzer (SOEC) transports O2− ions in a solid oxide (ZrO2 + 8 mol% Y2O3, La0.6Sr0.4Ga0.8Mg0.2O3−δ) with a conductivity of 1 S/m at 500–850 °C (Fig. 1c). Water vapor is provided on the cathode and therefore the evolved hydrogen contains water and is dried subsequently, while the oxygen on the anode is pure.[5] The major advantage of high-temperature water electrolysis is the possibility to split water partially by heat provided by the steam in installations where lots of high-temperature heat is available.

The LURGI high-pressure electrolyzers are still the most efficient and world largest electrolyzers today, followed by the ambient pressure alkaline electrolyzers from NEL[6] (former Norsk Hydro) (Fig. 2). Currently mainly alkaline systems are found at a production rate above 30 Nm3/h hydrogen. These large scale electrolyzers exhibit a significantly higher efficiency compared to PEM electrolyzers of comparable power. There are only a few suppliers of electrolyzers on the western market. Very little is known about the developments in Asia, where certainly companies in China and Japan are working on the development of large-scale electrolyzers. Hydrogenics[7] delivers alkaline electrolyzers (250 kW) and Proton OnSite (Diamond Lite SA) delivers PEM electrolyzers with a power up to 200 kW. Recent development for large-scale PEM electrolyzers by Proton OnSite[8] and SIEMENS[9] will soon make systems >1 MW available.

**Hydrogen Storage**

The critical point of hydrogen is at a temperature of 32 K,[11] therefore, hydrogen does not exist as a liquid at ambient temperature.[12] The volume of the hydrogen is reduced by compression, liquefaction at 20 K, or interaction of hydrogen with materials by physisorption, chemisorption, intercalation and chemical reaction. 1 kg of hydrogen at ambient temperature and atmospheric pressure takes a volume of 11.2 m3, while the volume of 1 kg liquid hydrogen is 0.01413 m3 (density of liquid para-hydrogen at 20.217 K is 70.78 kg⋅m−3).

Compression of hydrogen allows increasing the density of the gas up to approximately half of the density of liquid hydrogen at ambient conditions (35 kg/m3) and requires an isothermal compression work corresponding to 1 kWh/kg per pressure decade or less than 3% of the heating value. Modern high-pressure composite cylinders[13] allow to store up to 4 mass% of compressed hydrogen at pressures up to 800 bar. The mechanical stability[14] of the composite over many hundred pressure cycles and the hydrogen diffusion across the material are beside the safety concerns the major challenges of the development of high pressure hydrogen storage systems.

Liquid hydrogen[15] storage at 20 K is a non-equilibrium storage method and suf-
furs from continuous loss of hydrogen due to evaporation at ambient temperature. The storage systems are open or semi-open in order to limit the pressure increase in the storage tank. The energy demand for the liquefaction process is theoretically 3.92 kWh/kg, technically around 10 kWh/kg. The hydrogen density in the storage system depends on the size of the storage. Liquid hydrogen storage is the method of choice to be modified and therefore influences the stability of the hydride formed. The thermodynamics of the hydride formation is described by the lattice gas model[23] and leads to the Van’t Hoff equation[24] R·ln(p/p₀) = ΔH/T - ΔS. At low concentration (up to 0.1 H/M) hydrogen forms a solid solution followed by a phase transition from solid solution into the hydride phase (1 H/M). The entropy change upon hydrogen adsorption ΔS corresponds for many systems to the standard entropy of hydrogen ΔS = 130 J/(mol·K) and an equilibrium pressure of 1 bar at 20 °C is found for a hydride with ΔH = T·ΔS = -38 kJ/mol H₂. Hydrogen occupies sites with a radius greater than 0.037 nm[25] and a distance between intercalated hydrogen atoms greater than 0.21 nm.[26] Intercalated hydrogen can reach more than twice the density of liquid hydrogen, e.g. in metal hydrides and complex hydrides. The highest volumetric density was found in metal hydrides[27] to be 150 kg·m⁻³. Metal hydrides have many applications, e.g. battery electrode materials, catalysts, sensors, stationary and marine hydrogen storage and hydrogen purifiers, selective separators and compressors. The gravimetric hydrogen density of metallic hydrides is less than 3 mass%.

The elements Al and B form complex hydrides with hydrogen, e.g. alanates NaAlH₄ and borohydrides LiBH₄. With the discovery of the Ti-catalyzed hydrogen desorption from NaAlH₄ in 1996[28] a wide research field on a new class of solid storage materials was opened. Few years later the alanates were complemented by the borohydrides.[29,30] The stability of the complex hydrides is determined by the localization of the charge[31] on the central atom (Al, B) and, therefore, is proportional to the electronegativity of the cation-forming element. The enthalpy of formation of a series of borohydrides was computed by DFT calculation and a linear correlation between the enthalpy of formation and the electronegativity of the cation-forming element was found.[32] ΔH [kJ/mol BH₄⁻] = 247.4·EN – 421.2 where EN is the Pauling electronegativity[33] of M in M(BH₄⁻). A similar equation can be derived for alanates ΔH [kJ/mol AlH₄⁻] = 308·EN – 411. Therefore, by applying the Pauling electronegativity of B (2.04) and Al (1.61), a general equation for the enthalpy of formation is derived ΔH [kJ/mol ZHₓ⁻] = 143·EN(B, Al) – 224·EN(B, Al).[34] The formation of the complex hydrides requires wet chemical synthesis; only a few products have been successfully synthesized from the elements. The formation reaction is often different from the hydrogen desorption reaction. Furthermore, the enthalpy of formation of the complex hydride is much larger than the enthalpy of the hydrogen desorption reaction.[35] Alanates tend to desorb via an intermediate hexahydride

---

**Fig. 2.** Specific energy vs. the power of the stack for polymer electrolyte membrane electrolyzer (PEM) and for alkaline electrolyzer (AEL), adapted from NOW-Studie[10]

**Fig. 3.** Lenard-Jones potential[10] of a hydrogen molecule approaching the surface of a solid metal. Compressed gas (molar H₂): liquid hydrogen (molar H₂): physiosorption (molar H₂) on materials, e.g. carbon with a very large specific surface area; hydrogen (atomic H) intercalation in host metals, metallic hydrides working at RT are fully reversible; complex compounds ([AlH₃]⁺ or [BH₄]⁻); and hydrogen chemically bound in hydrocarbons.

---

**Table 1:** Specific energy vs. the power of the stack for polymer electrolyte membrane electrolyzer (PEM) and for alkaline electrolyzer (AEL).
and finally form the elemental hydride, while borohydrides do not exhibit a hexahydride. The hydrogen desorption reaction from borohydrides is accompanied by the desorption of diborane, a product of a side reaction of the hydrogen desorption. This side reaction depends on the stability and mobility of B₃H₆ and BH₃, respectively, therefore, above a temperatures of 200 °C no diborane is observed. The alanates and borohydrides have the potential to store up to 7 mass% and 20 mass% of hydrogen, respectively. The volumetric hydrogen density reaches, similar to metal hydrides, above a temperatures of 200 °C.

**Outlook**

The potential of complex hydrides for large-scale hydrogen storage is huge, but requires a better understanding and improved control of the hydrogen sorption reaction. The reaction pathway in complex hydrides exhibits various intermediates and transition states depending on the type of the central atom, Al, B, or N, and on the reaction conditions. The knowledge of the reaction pathway and the identification of the transient states is of fundamental importance in order to control the hydrogen absorption and desorption processes. Furthermore, development of new materials requires methods to synthesize the complex hydrides as well as overcome the activation barriers by an appropriate catalyst. In other cases it may be important to develop methods to stabilize a certain hydride or to avoid the formation of undesired intermediates, e.g. diborane or ammonia. Finally, the knowledge of the reaction mechanism represents an added value concerning all safety issues of complex hydrides. Beside the pure hydrides, composites, e.g. borohydrides and amides, represent a wide field of new storage materials with interesting properties. While the complex hydrides are in a very early stage of development to the hydrogen storage application, metal hydrides are on a technology readiness level requires methods to synthesize the complex hydrides and as well as overcome the activation barriers by an appropriate catalyst. In other cases it may be important to develop methods to stabilize a certain hydride or to avoid the formation of undesired intermediates, e.g. diborane or ammonia. Finally, the knowledge of the reaction mechanism represents an added value concerning all safety issues of complex hydrides. Beside the pure hydrides, composites, e.g. borohydrides and amides, represent a wide field of new storage materials with interesting properties. While the complex hydrides are in a very early stage of development to the hydrogen storage application, metal hydrides are on a technology readiness level that allows the construction of large-scale hydrogen storage systems.

Metal hydrides represent surfaces, which offer atomic hydrogen and absorb CO and, therefore, provide sites for the catalytic reduction of CO₂ to hydrocarbons. The reaction mechanism of the CO₂ reduction will be investigated in detail with the goal to identify the parameters determining the C–H and C–C bonds. The understanding and control of the CO₂ reduction reaction bridges between the pure hydrogen storage and the storage of hydrogen in synthetic hydrocarbons.

**Acknowledgements**

The financial support of KTI/CTI for the Swiss Competence Center Energy Research (SCCER) ‘Heat & Electricity Storage’ is acknowledged.

Received: August 23, 2015

---

[1] E. Burkhalter, Hydrogen Report Switzerland HRS 13/14, 2013, www.hydroprole.ch.
[2] E. A. Zalansky, ‘Pressure electrolyzers’, Patent US 2717872 A, Priority date Aug 12, 1950, DE879543C.
[3] http://www.agfa.com/sp/global/en/binariteit/Zinfin%20Per%20TP%20%50_08_tcm617-1337.pdf.
[4] M. N. M. K. H. Leung, D. Y. C. Leung, Int. J. Hydrogen Ener. 2008, 33, 2337.
[5] M. S. Sohal, J. E. O’Brien, C. M. Stoots, M. G. McKellar, E. A. Harvey, J. S. Herring, ‘Challenges in Generating Hydrogen by High Temperature Electrolysis Using Solid Oxide Cells’, NHA 08 Idaho National Laboratory, March 2008.
[6] http://wwwstatistic.dium.no/www.net-hydrogen.com/2015/01/Efficient_Electrolyzers_for_Hydrogen_Production.pdf.
[7] http://www.hydrogenics.com/hydrogen-products-solutions/industrial-hydrogen-generators-by-electrolysis.
[8] http://protononsite.com/products/mot.
[9] http://www.industry.siemens.com/topic/global/energy-electrolyser/talysizer/pages/talysizer.aspx.
[10] T. Smolinka, M. Günther, J. Garcke, NOW-Studie ‘Stand und Entwicklungs potenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien’, Kurzfassung des Abschlussberichts, Redaktionsstand: 22.12.2010, Revision 1 vom 05.07.2011.
[11] ‘Ullmann’s Encyclopedia of Industrial Chemistry’, ‘Hydrogen’, Eds. P. Häussinger, R. Lohmüller, A. M. Watson, published online: 15 June 2000, DOI: 10.1002/14356001.a13_297.
[12] W. B. Leung, H. J. March, H. Motz, Phys. Lett. 1976, 56A, 425.
[13] Dynetek Europe GmbH, Breitscheider Weg 117a, D-40885 Ratingen, URL: http://www.dynetek.de.
[14] W. Matek, D. Muhs, H. Wittel, M. Becker, ‘Rollof/Matek Maschinenelemente’, Viewegs Fachbücher der Technik, 1994, 690 pp, ISBN: 3-528-74028-0.
[15] J. E. Lennard-Jones, Trans. Faraday Soc. 1932, 28, 333.
[16] J. Stanga, P. Neksä, E. Brendenge, ‘On the design of an efficient hydrogen liquefaction process’, WHEC 16 / 13-16 June 2006 – Lyon, France, http://www.cderz/A2H2/Medias/Download/Proc%20PDF/posterG/GV%20Hydrides%20480.pdf.
[17] B. Schünert, U. Möller, N. Trukhan, M. Schubert, G. Férey, M. Hirscher, ChemPhysChem 2008, 9, 2181.
[18] A. Züttel, P. Sudan, P. Mauron, T. Kiyobayashi, C. Emmenegger, L. Schlappbach, Int. J. Hydrogen Ener. 2002, 27, 203.
[19] M. G. Nijkamp, J. Raaymakers, A. J. Van Dillen, K. P. De Jong, 
Appl. Phys. A 2001, 72, 619.

[20] S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc. 1938, 60, 309.

[21] L. Schlappbach, in “Intermetallic Compounds I”, Chap. 1, Ed. L. Schlappbach. Springer Series 
Topics in Applied Physics, Vol. 63, Springer–Verlag, 1988, p. 10.

[22] J. K. Norskov, F. Besenbacher, J. Less-Common Metals 1987, 130, 475.

[23] H. Hemmes, E. Salomons, R. Griessen, P. Sänger, A. Driessen, Phys. Rev. B Condens. 
Matter. 1989, 39, 10606.

[24] P. Atkins, J. De Paula, “Physical Chemistry”, 8th ed., 2006. W.H. Freeman and Company, p. 212. 
ISBN 0-7167-8759-8.

[25] D. G. Westlake, J. Less Common Metals 1983, 91, 275.

[26] A. C. Switendick, Z. Phys. Chem. N.F. 1979, 117, 89.

[27] A. Züttel, Naturwissenschaften 2004, 91, 157.

[28] B. Bogdanovic, M. Schwierkarat, J. Alloys Comp. 1997, 253, 1.

[29] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, P. Mauron, C. Emmenegger, J. Power Sources 
2003, 118, 1.

[30] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Obha, S. Towata, A. Züttel, J. Alloys Comp. 
2005, 404, 427.

[31] P. Jena, Virginia Commonwealth University, Richmond, VA, to be published.

[32] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Obha, S.-I. Towata, A. Züttel, S. Orimo, Phys. 
Rev. B 2006, 74, 1.

[33] L. Pauling, J. Am. Chem. Soc. 1929, 51, 1010.

[34] A. Züttel, P. Mauron, S. Kato, E. Callini, M. Holzer, J. Huang, CHIMIA 2015, 69, 264.

[35] Z. O. Kocabas Alakt, E. Callini, S. Kato, P. Mauron, S. Orimo, A. Züttel, PhysChemChemPhys 2015, 17, 20932.

[36] S. Kato, A. Borgschulte, D. Ferri, M. Bielmann, J-C. Crivello, D. Wiedenmann, M. Parlinska- 
Wojtan, P. Rossbach, Y. Lu, A. Remhof, A. Züttel, PhysChemChemPhys 2012, 14, 5518.