

Storage of Renewable Energy by Reduction of CO₂ with Hydrogen

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Abstract: The main difference between the past energy economy during the industrialization period which was mainly based on mining of fossil fuels, e.g. coal, oil and methane and the future energy economy based on renewable energy is the requirement for storage of the energy fluxes. Renewable energy, except biomass, appears in time- and location-dependent energy fluxes as heat or electricity upon conversion. Storage and transport of energy requires a high energy density and has to be realized in a closed materials cycle. 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. However, the hydrogen density in a storage system is limited to 20 mass% and 150 kg/m³ which limits the energy density to about half of the energy density in fossil fuels. Introducing CO₂ into the cycle and storing hydrogen by the reduction of CO₂ to hydrocarbons allows renewable energy to be converted into synthetic fuels with the same energy density as fossil fuels. The resulting cycle is a closed cycle (CO₂ neutral) if CO₂ is extracted from the atmosphere. Today's technology allows CO₂ to be reduced either by the Sabatier reaction to methane, by the reversed water gas shift reaction to CO and further reduction of CO by the Fischer–Tropsch synthesis (FTS) to hydrocarbons or over methanol to gasoline. The overall process can only be realized on a very large scale, because the large number of by-products of FTS requires the use of a refinery. Therefore, a well-controlled reaction to a specific product is required for the efficient conversion of renewable energy (electricity) into an easy to store liquid hydrocarbon (fuel). In order to realize a closed hydrocarbon cycle the two major challenges are to extract CO₂ from the atmosphere close to the thermodynamic limit and to reduce CO₂ with hydrogen in a controlled reaction to a specific hydrocarbon. Nanomaterials with nanopores and the unique surface structures of metallic clusters offer new opportunities for the production of synthetic fuels.

Keywords: CO₂ reduction · Energy storage · Hydrides · Hydrogen · Synthetic fuels

Introduction

The steam engine was the basis of the industrialization age that started around 1750 in Manchester, GB.^[1,2] Since then the energy demand has increased by more than an order of magnitude per capita^[3] in the industrialized world and created a very comfortable life for us today. There is a correlation between energy demand and economic wealth of society.^[4] For a gross domestic product (GDP) of less than 15'000 US\$/capita and year, energy demand increases linearly up to 4 kW/capita and then saturates at around 5kW/capita for

higher GDP. The slope of the linear part of the global figure corresponds to 0.4 US\$/kWh. The saturation of the energy demand for a GDP above 15'000 US\$/capita and year at 5 kW can be explained by a change in industrial structure. With an increasing GDP in a country, energy-intensive goods are increasingly imported from countries with a lower GDP. Therefore, the net demand for energy of a wealth society is not only the energy carriers but also the energy included in imported materials and products. This was analyzed in an excellent way by McKay^[5] and is shown in Fig. 1.

The dependence of the GDP on the energy demand leads to the conclusion that wealth is equal to the availability of energy and materials. Therefore, increasing wealth worldwide will increase energy consumption and, according to Hans Rosling's analysis, the population worldwide will grow to 9 billion and saturate in 2050, because of the decreasing birth rate with increasing global wealth.^[6] However, as a consequence energy demand worldwide in 2050 will be three times the current energy demand, assuming that 3 billion humans will achieve the standard of living of the industrialized world. Currently in Europe a paradox is propagated, which is the idea of increasing efficiency in order to reduce

energy demand. This zero order approach is misleading, because an efficiency increase leads to a productivity increase and, therefore, to an overall increase of energy demand. This was already concluded by William Stanley Jevons in his book 'The Coal Question' in 1865.^[7] The energy demand today is mainly covered by fossil fuels, which has two important consequences; reserves of fossil fuels are limited and combustion leads to an increase of the

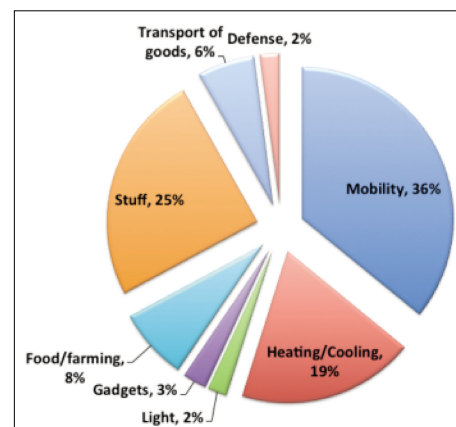


Fig. 1. Energy demand in GB (2008) for the most important sectors, adapted from McKay.^[5] The total energy demand corresponds to 8.1 kW/capita.

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CO₂ concentration in the atmosphere and, therefore, a change of the global climate.^[8] A future sustainable energy economy has to be based on renewable energy and carbon has to be either avoided in the energy cycle or recycled. While fossil energy supply is based on mining energy carriers, *e.g.* coal, oil and natural gas; renewable energy occurs in time- and location-dependent energy fluxes and is converted to heat and electricity.

Hydrogen, Hydrides

Energy fluxes require storage in order to balance short term (day/night) fluctuations and seasonal variations. Therefore, an energy carrier has to be produced from heat or electricity. The energy density is crucial for transport, mobile applications, but also for the protection of the materials resources. Hydrogen offers the highest gravimetric energy density of all combustibles with 39 kWh/kg. Hydrogen can be produced from electricity and heat by means of electrolysis of water (Fig. 2). Electrolysis at ambient temperature and ambient pressure requires a minimum voltage of 1.481 V ($\Delta H^0 = 286 \text{ kJ}\cdot\text{mol}^{-1}$) and, therefore, a minimum energy of 39.7 kWh·kg⁻¹ hydrogen. The equilibrium potential is 1.23 V ($\Delta G^0 = 237 \text{ kJ}\cdot\text{mol}^{-1}$).^[9] Today electrolyser systems consume >45 kWh·kg⁻¹ hydrogen, *i.e.* the efficiency is <82%.^[10] Hydrogen as a gas takes up a large volume in storage. The main challenge in hydrogen storage is to reduce the volume of the gas in equilibrium with the environment.

Hydrogen storage^[11] basically implies the reduction of the enormous volume of the hydrogen gas. 1 kg of hydrogen at ambient temperature and atmospheric pressure takes up a volume of 11 m³. Three parameters allow the density of hydrogen to be decreased: i) increased pressure, ii) lower temperatures and iii) reduction of the volume by the interaction with other materials.^[12] The volumetric hydrogen density of molecular hydrogen is limited by the volume taken up by the hydrogen molecules and, therefore, is less than the density of liquid para-hydrogen at b.p. 70.78 kg·m⁻³. While liquid hydrogen in large-scale storage systems may come close to this value, physisorbed hydrogen and compressed gas reach at maximum half of the density of liquid hydrogen at room temperature. Atomic 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 was found to be 150 kg·m⁻³. The gravimetric hydrogen density of metallic hydrides is less than 3 mass% (Fig. 3).

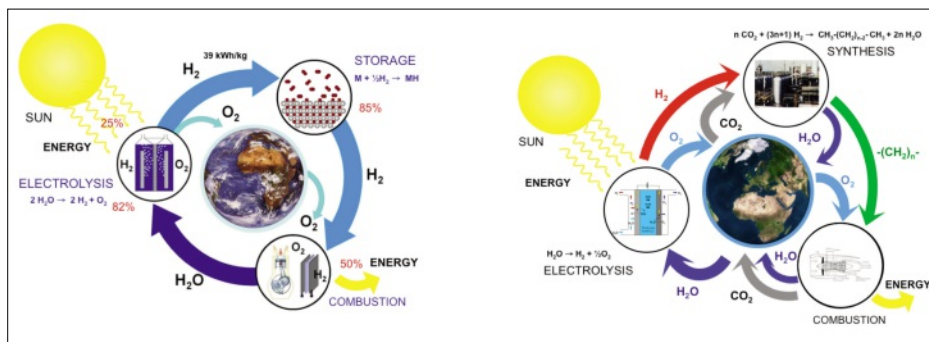


Fig. 2. Schematic representation of the closed hydrogen cycle (left) and synthetic fuel cycle (right). Renewable energy is used to split water into hydrogen and oxygen. CO₂ captured from air is reduced by hydrogen to hydrocarbons (synthetic fuels)

Complex Hydrides

In 1996 Bogdanovic presented^[13,14] first results of hydrogen sorption experiments on Ti-catalyzed NaAlH₄. Pressure-concentration isotherms were measured in a temperature range 150 °C to 244 °C and two distinct and flat plateaux were found. The corresponding reactions are: 1) $3\text{NaAlH}_4 \rightleftharpoons \text{Na}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2$ and 2) $\text{Na}_3\text{AlH}_6 \rightleftharpoons 3\text{NaH} + \text{Al} + 3/2\text{H}_2$; the corresponding enthalpies for the reactions, determined by the Van't Hoff plot are, $\Delta H_1 = 111 \text{ kJ}$ and $\Delta H_2 = 70.5 \text{ kJ}$, respectively. This finding initiated a new research field and hydrogen storage in complex hydrides became feasible. The Ti catalyst shows a reduction of the activation energy for the two reactions from 118 kJ/mol H₂ to 80 kJ/mol H₂ and from 124 kJ/mol H₂ to 96 kJ/mol H₂, respectively. Some years later first results on hydrogen desorption from borohydrides were presented.^[15,16]

Borohydrides are similar compounds to alanates, however, no hexahydride phase is observed and until now no catalyst was found for the hydrogen sorption reaction in borohydrides. Borohydrides contain up to 20 mass% of hydrogen and, therefore, store an order of magnitude more hydrogen compared to metal hydrides. Despite the large number of publications^[17] on the function of the catalyst in alanates only recently a new and consistent model for the mechanism of the Ti catalyst in alkali alanates was described, based on the local structure and thermodynamic considerations.^[18] The mechanism is based on the fact that in both reaction steps of the hydrogen desorption from NaAlH₄ the ions Na⁺ and H⁻ have to be moved from the complex (Na⁺ [AlH₄]⁻) to the neighboring NaAlH₄ and from the hexahydride (3Na⁺ [AlH₆]³⁻) to the elemental hydride NaH. The activation energy is determined by the charge separation, *i.e.* the role of the cata-

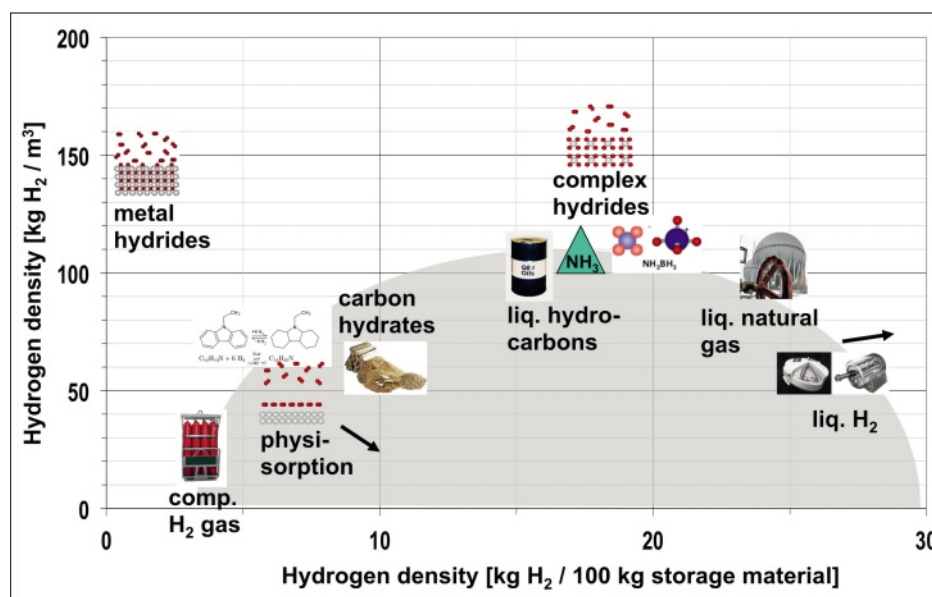


Fig. 3. The volumetric versus the gravimetric hydrogen storage density of the basic storage methods. Compressed gas (molecular H₂); liquid hydrogen (molecular H₂); physisorption (molecular H₂) on materials, *e.g.* carbon with a very large specific surface area; hydrogen (atomic H) intercalation in host metals, metallic hydrides working at RT are fully reversible; complex compounds ([AlH₄]⁻ or [BH₄]⁻), and hydrogen chemically bound in hydrocarbons.

lyst is to bridge between $\text{Na}^+ \dots \text{Ti} \dots \text{H}^-$ and, therefore, allow the two ions to be moved simultaneously without forming NaH . The abundant AlH_3 spontaneously decomposes and releases hydrogen (Fig. 4).

The hydrogen desorption mechanism of borohydrides is still unknown. Due to the absence of a hexahydride phase, the elemental hydride is directly formed during the hydrogen desorption reaction, e.g. $\text{LiBH}_4 \rightarrow \text{LiH} + \text{BH}_3$. The BH_3 molecules, in analogy to AlH_3 , spontaneously decompose (at $T > 200^\circ\text{C}$)^[19] or two BH_3 can form the volatile B_2H_6 .^[20] The latter reaction should be avoided, because it leads to a loss of boron from the material and diborane is a poisonous gas for humans and fuel cells.

The stability of complex hydrides, i.e. alanates and borohydrides, is given by the enthalpy and entropy difference between the hydride and the first stable desorption product, which is in most cases different from the constituent elements. Therefore, we have to distinguish between the stability and the enthalpy of formation of a specific complex hydride. While the enthalpy of formation of a metallic hydride is determined by the local electron density on the interstitial site where hydrogen is hosted^[21,22] and the metal structure undergoes only minor changes upon hydrogen absorption, a complex hydride is not an intercalation compound and forms multiple phases upon hydrogen desorption. The stability of an $[\text{AlH}_4]^-$ or a $[\text{BH}_4]^-$ is determined by the localization of the electron on the Al and B.^[23,24] 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^[25] to be $\Delta H [\text{kJ/mol BH}_4] = 247.4 \cdot \text{EN} - 421.2$ where EN is the Pauling electronegativity of M in $\text{M}(\text{BH}_4)_x$.

Upon hydrogen desorption the alanates and borohydrides either form an elemental hydride from the cation and hydrogen or the element if the elemental hydride is not stable under desorbing conditions. The main difference between the alanates and borohydrides is the formation of the hexahydride in case of the alanates. This introduces an additional level (intermediate) in the desorption and, therefore, divides the desorption enthalpy into two parts. The general relationship between the enthalpy of formation (ΔH_f^0) and the enthalpy of desorption (ΔH_{des}) is $\Delta H_f^0 = \Delta H_{\text{m}} + \Delta H_{\text{des}} + \Delta H_{\text{HM}}$, where ΔH_{des} has two parts ($\Delta H_{\text{des}} = \Delta H_{\text{des}}^1 + \Delta H_{\text{des}}^2$) in case of the formation of the hexahydride. Of course if the desorption occurs from the solid, the melting enthalpy (ΔH_{m}) is zero in the equation. ΔH_{HM} is the enthalpy of formation of the elemental hydride and is given by the Pauling equation $\Delta H_{\text{HM}} [\text{kJ/mol}] = \Delta H_{\text{MM}} [\text{kJ/mol}] + 194 (\text{EN}_{\text{M}} - \text{EN}_{\text{H}})^2$. If no elemental hydride is formed ΔH_{HM} is zero in the equation. The melting enthalpy is in the order of $\Delta H_{\text{m}} = 7 \text{ kJ/mol}$.^[26]

The borohydrides have the potential to store up to 20 mass% of hydrogen, however, the control of the reaction and the development of an easy to handle storage material is still a challenge. The hydrogen storage density of 20 mass% corresponds to an energy density of 7.8 kWh/kg. Therefore, the gravimetric and volumetric energy density

of a hydrogen storage system is limited to less than half of the energy density of hydrocarbon fuels, e.g. diesel (12.8 kWh/kg).

Hydrocarbons

In order to overcome the limitation of the energy density of hydrides hydrogen can be used to reduce CO_2 to hydrocarbons, i.e. a synthetic fuel like diesel as shown on the right-hand side of Fig. 2. Two reactions are well established for the synthesis of hydrocarbons from CO_2 :

i) Sabatier reaction: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$

ii) Reversed water gas shift reaction: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$, combined with the Fischer–Tropsch reaction: $n\text{CO} + (2n+1)\text{H}_2 \rightarrow \text{CH}_3(-\text{CH}_2)_{n-2}-\text{CH}_3 + n\text{H}_2\text{O}$

The Sabatier reaction produces the most stable compound in Fig. 5. Methane activation, i.e. the linking of C atoms starting from methane is today only realized by the partial oxidation of methane ($\text{CH}_4 + 1.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$, $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$) followed by the Fischer–Tropsch synthesis.

On the other hand, the Fischer–Tropsch synthesis leads to a large variety of products, from methane to waxes and even leads to the deposition of carbon and tar on the catalysts.

The catalytic reduction of CO_2 depends on the local availability of hydrogen atoms, the orientation of the CO_2 molecules on the surface of the catalyst and the bonding character between the C and O atoms and the surface atoms. Furthermore, the formation of C–C bonds cannot be controlled and are randomly formed dependent on the reaction conditions. The understanding of the Fischer–Tropsch process is that the conversion of CO to alkanes involves hydrogenation of CO, the dissociation of C–O bonds, and the formation of C–C bonds. The reactions are assumed to proceed on the surface of the catalyst via the initial formation of surface-bound metal carbonyls. The CO ligand may undergo dissociation, possibly into oxide and carbide ligands.^[27] Other intermediates may be various C_1 fragments including formyl (CHO), hydroxycarbene (HCOH), hydroxymethyl (CH_2OH), methyl (CH_3), methylene (CH_2), methyldiene (CH), and hydroxymethyldiene (COH) as schematically shown in Fig. 6.

The distribution of the hydrocarbon products synthesized during the Fischer–Tropsch process is described as an Anderson–Schulz–Flory distribution,^[28] which is expressed as:

$$W_n/n = (1 - \alpha)^2 \alpha^{n-1}$$

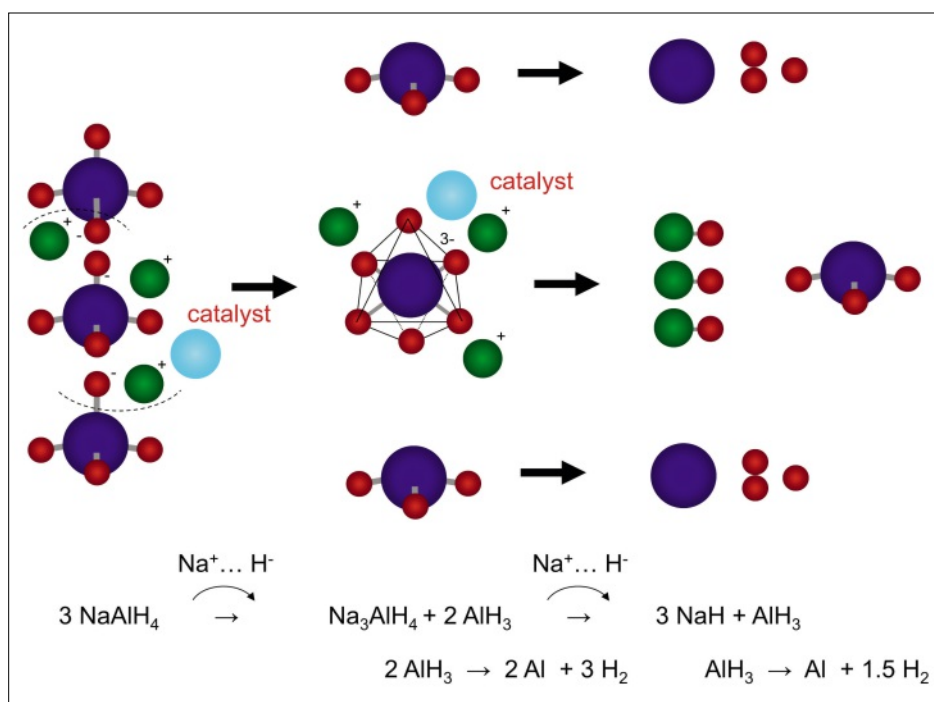


Fig. 4. Schematic representation of the hydrogen desorption reaction from NaAlH_4 .

where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms, α is the probability for chain growth, *i.e.* the probability that a molecule will add an additional C to the chain. In general, the catalyst surface properties and the specific reaction conditions determine α to a large extent.

Methane represents the largest single product according to the Anderson–Schulz–Flory Eqn. for α less than 0.5. For α increasing close to one, the total amount of methane formed minimizes compared to the sum of all longer-chained products ($n \geq 2$). The long-chained hydrocarbons ($n > 12$) are waxes, which are solid at room temperature. Therefore, for the production of liquid fuels for mobility it is necessary to crack long-chained hydrocarbons of the Fischer-Tropsch products. The growth of the hydrocarbon chain can be sterically limited by using surface structuring, zeolites or other catalyst substrates with constrained size pores that restrict the formation of hydrocarbons longer than some characteristic size (usually $n < 10$). The reaction can be controlled so as to maximize the center of the distribution, *e.g.* around $n = 6$, *i.e.* to minimize methane formation without allowing the production of long-chained hydrocarbons. Such efforts have met with only limited success except for the methanol to gasoline process on ZSM-5 catalyst.^[29] Furthermore, and critical to the production of liquid fuels, are reactions that form C–C bonds, such as migratory insertion, the key process in the synthesis of carbon nanostructures like carbon nanotubes. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous Fischer–Tropsch catalysts are poorly developed and not yet of commercial importance.^[30]

Two new approaches are planned in order to control the reaction. Steric hindrance by surface structuring as well as the use of nano cavities and the change of the thermodynamic potential of the intermediates by the binding energy of the carbon atom to the substrate,^[31] *i.e.* tailoring the electronic structure of the surface.

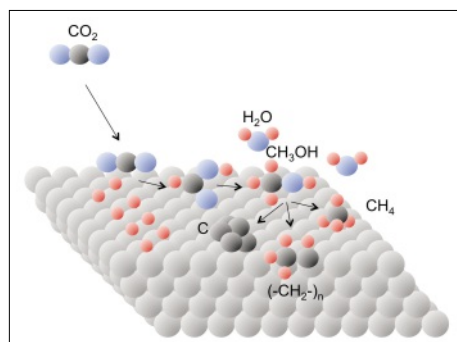


Fig. 6. Schematic model of the CO₂ reduction reaction pathways on the surface of a catalyst, *e.g.* metal hydride.

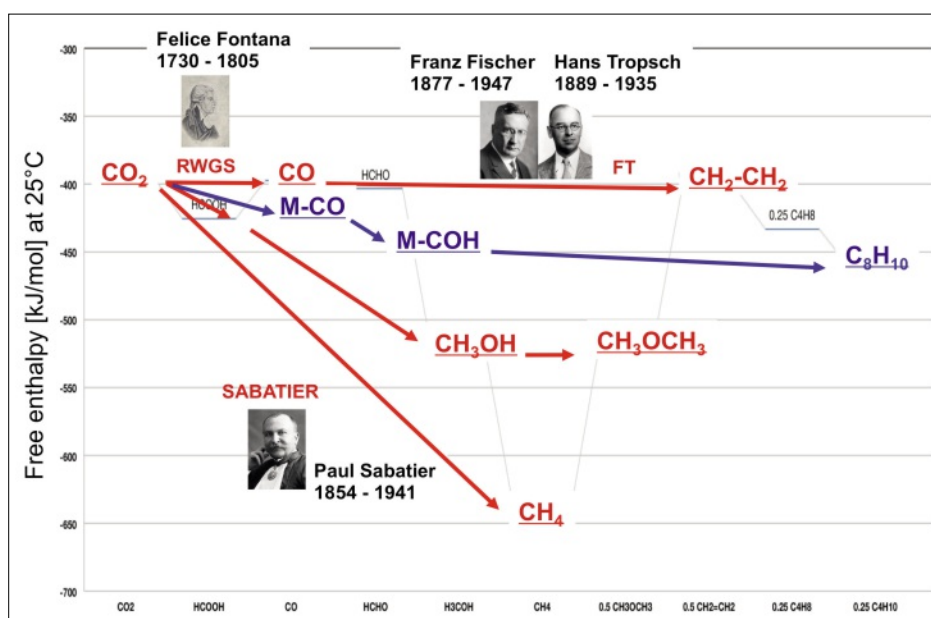


Fig. 5. The Gibbs energy diagram for the reduction of CO₂ to hydrocarbons. The well-established reactions are indicated in red.

The main challenges in order to store renewable energy in synthetic hydrocarbons is the extraction of CO₂ from the atmosphere (400 ppm, partial pressure of 0.4 mbar) and the reduction of CO₂ with hydrogen in a specific well-controlled reaction avoiding the formation of a large number of by-products as in the Fischer–Tropsch synthesis. The thermodynamic free energy for the concentration of 400 ppm CO₂ to 1 bar is $\Delta G = R \cdot T \cdot \ln(p/p_0)$ and equals to 20 kJ/mol, which corresponds to 0.44 kWh/kg C. This is about 5% of the energy stored per

kg of carbon.^[32] In Switzerland roughly 17 MT CO₂ is emitted by cars each year^[33] and the total emissions are 44 MT CO₂/year.^[34] In order to capture this amount of CO₂, according to the American Physical Society, a surface area of 66 km² is needed,^[35] therefore, a surface area of approximately 1.6‰ of Switzerland would be needed to capture the CO₂ emitted in Switzerland. The corresponding surface area required for the conversion of solar energy by photovoltaic is approximately 3% of Switzerland.

The successful development of the

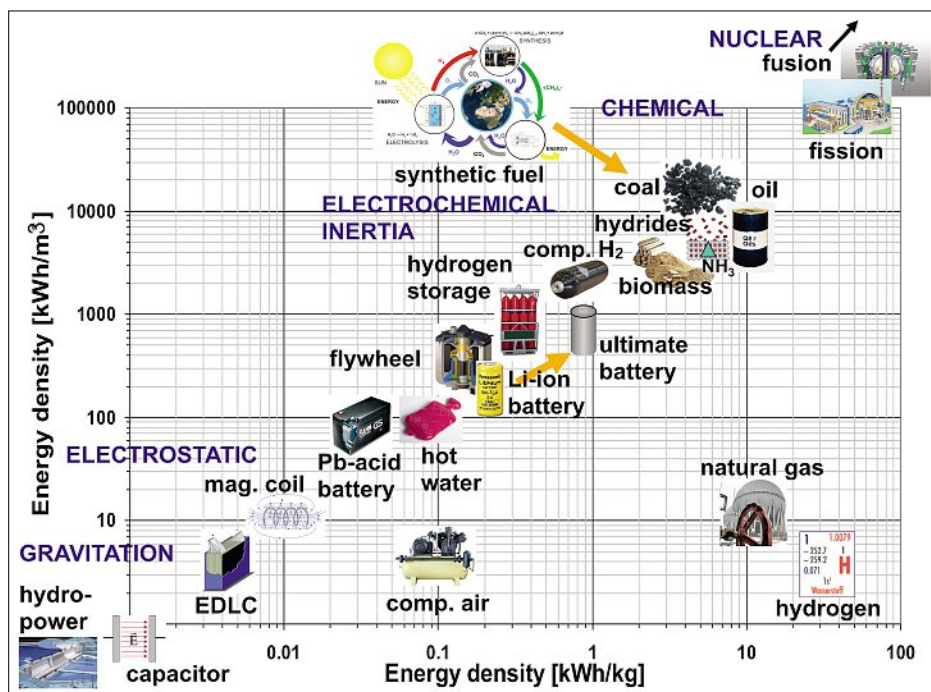


Fig. 7. Volumetric versus gravimetric energy storage systems and materials. Future developments will allow the energy density in batteries to be improved up to 1 kWh/kg and replace fossil fuels with a closed cycle based on the reduction of atmospheric CO₂ with hydrogen from renewable energy and the production of synthetic hydrocarbons.

new materials for the efficient absorption of CO₂ from the atmosphere, the production of hydrogen from renewable energy and the controlled reduction of CO₂ to the desired product, e.g. liquid hydrocarbon like diesel will allow fossil fuels to be completely replaced and introduce a closed cycle for energy materials (Fig. 7). Such an energy economy would be able to fulfill the global energy demand in 2050, which is expected to be approx. three times the energy demand of today.

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