TCGR
THE CATALYST GROUP RESOURCES™

Catalysts, Catalytic Processes, and Materials for Renewable Energy Use and Storage

A technical investigation commissioned by the members of the
Catalytic Advances Program (CAP)

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RESEARCH & SCOPE

The subject is timely, since companies and governments across the globe are developing advanced energy storage technologies.

- ✓ **The ability to harness** increasing amounts of solar and wind energy on the grid is being expanded by numerous new energy storage technologies.
- ✓ **The two relevant questions** for this fast-growing form of energy, namely renewable energy, are: i) how to store it, and ii) how to use it, to substitute the use of fossil fuels.
- ✓ **The report clearly lays** out an array of options for energy storage from biomass to H_2 and upgrading of CO_2. This is a dynamic space, as costs for renewable energy generation and storage are decreasing rapidly
- ✓ **One of the great challenges** in the transition to a non-fossil energy system with a high share of fluctuating renewable energy sources, such as solar and wind, is to align consumption and production in an economically satisfactory manner.

This TCGR report analyses the role, gaps and prospects for using catalysis and related technologies and materials in relation to renewable energy storage and use.

REGULATORY DRIVERS

Regulatory drivers for the continued research on materials for renewable energy and storage are:

- ✓ New requirements like **The Low Carbon Fuel Standard** in California has incentivized investment into decarbonization of transportation fuels, often outside of California
- ✓ The **EU's Green Deal** has driven implementation through social pressure towards sustainability and climate change mitigation
- ✓ **The U.S. Department of Energ**y has done extensive work on electrolyzers and H_2 fueling station techno-economic analysis.
- ✓ Advanced biofuels are being identified as part of the **multi-National Lab consortium Co-Optima**, which focuses on the co-evolution of advanced fuels and engines.
- ✓ **Fraunhofer Institute for Solar Energy Systems** (Fraunhofer ISE, 2018) have indicated that renewable energy sources (RES) are already or will soon be the cheaper energy form (besides less impacting from an environmental perspective) with respect to the use of fossil resources
- ✓ **Energy Insights Report** (McKinsey, 2019) evidences how renewable will become cheaper than existing coal and gas in most regions before 2030.

The accelerated RES scenario requires that governments address three main challenges: 1) policy and regulatory uncertainty; 2) high investment risks in developing countries; and 3) system integration of wind and solar in some countries.

TYPE AND POTENTIAL OF RENEWABLE ENERGY SOURCES

- ✓ **Solar Photovoltaic (PV) and onshore wind**, and in a minor extent **hydropower**, are the RES type with higher capacity growth in the next five years and in total account for over 85% of the RES capacity.
- ✓ **The current total energy demand** from China or Europe could be supplied 2.5 times over, while Africa could supply 200 times its current energy demand with renewable energy (RES21, 2017).
- ✓ **Solar potential** is very large with respect to all other RES and also larger than finite resources related to fossil fuels. By considering an efficiency in solar to electricity conversion of 20%, currently at a commercial availability, the use of only about 4% of world land area can provide the world energy need.

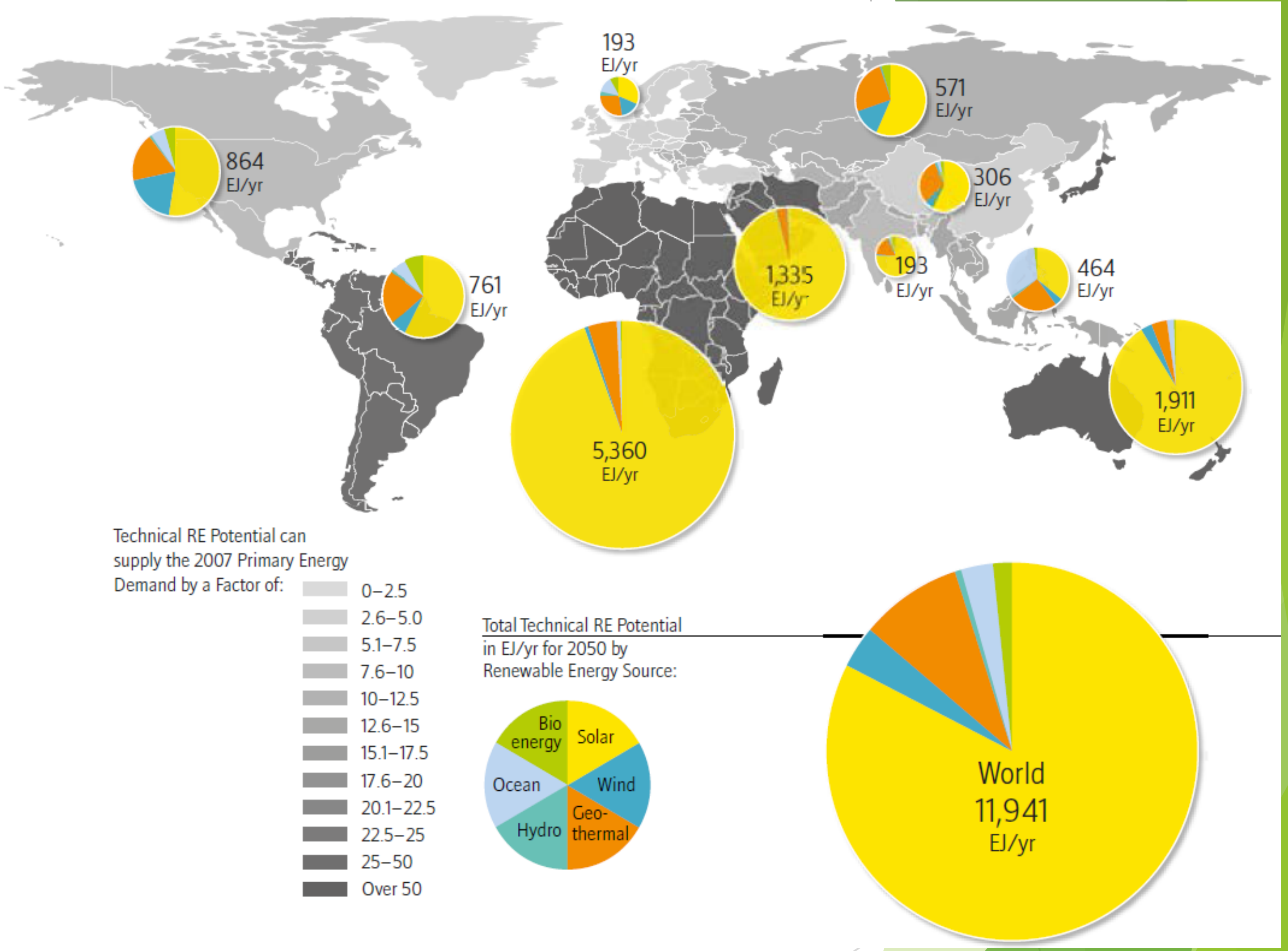


Figure 1: Total technical renewable energy potential in EJ/yr for 2050 Source: RES21, 2017

The total technical renewable energy potential in EJ/y for 2050 is presented in Figure 1 showing also how many times the regional potential (by using the current available technologies) can supply the current primary energy demand.

CHEMICAL ENERGY STORAGE: OVERCOME ISSUES IN USING RENEWABLE ENERGY

Energy storage technologies and systems are diverse and provide storage services at timescales from seconds to years.

Energy Storage is the crucial and necessary element for balancing power and stabilize the grid, i.e. provide reliability to the whole system. The missing element in this scenario is the availability of reliable technologies for seasonal-yearly storage and to transport renewable energy to long distance (above about 1000 km), which is not currently effective through the grid.

Industrial chemistry's use of petroleum accounts for 14% of all greenhouse gas emissions. The use of **fossil fuels** as carbon source accounts for only roughly 20% of total carbon footprint, i.e. most of the fossil use is to provide the energy required in the various processes, including separation.

Renewable Energy can supply two-thirds of the total global energy demand, or even more and contribute to the bulk of the greenhouse gas emissions reduction that is needed between now and 2050 for limiting the average global surface temperature increase below 2°C:

- ✓ Renewable electricity would split abundant molecules such as CO_2, water, oxygen (O_2), and nitrogen into reactive fragments.
- ✓ More renewable electricity would help stitch those chemical pieces together to create the products that modern society relies on and is unlikely to give up.

In integration to **biomass** use and **circular economy**, it is possible to consider and realize a chemical production not based on fossil fuels, or probably more realistic that over 50% of fossil use is avoided in chemical industry between 2030 and 2050.

Changing the lifeblood of industrial chemistry from fossil fuels to renewable electricity will require time, but proper design is essential to enable the transition.

GHG EMISSIONS AND CLOSING THE CARBON CYCLE

Chemical industries contribute to many solutions that increase the energy efficiency in multiple sectors and increase renewable energy supply, thereby reducing and avoiding emissions in many value chains.

There are **six important solutions** to which the chemical industry contributes: wind and solar power, efficient building envelopes, efficient lighting, electric cars, fuel efficient tires and lightweight materials. Another important application is food packaging.

Dechema (Bazzanella and Ausfelder, 2017) more recently analysed the technology options and pathway scenarios to a **2050 carbon neutral chemical sector**. The study focused on the main chemical building blocks used in upstream large volume production processes (i.e., ammonia, methanol, ethylene, propylene, chlorine and the aromatics benzene, toluene and xylene) that collectively represent two-thirds of the sector's current GHG emissions.(Figure 2)

- ✓ The implementation of the technologies indicated above would allow for a very **significant reduction of CO_2 emissions in 2050** (up to 210 MT annually under the Maximum scenario). Including the production and use of fuels related to the pathways considered, the additional CO_2 abatement potential in 2050 exceeds the chemical sector's current emissions even under the intermediate scenario.

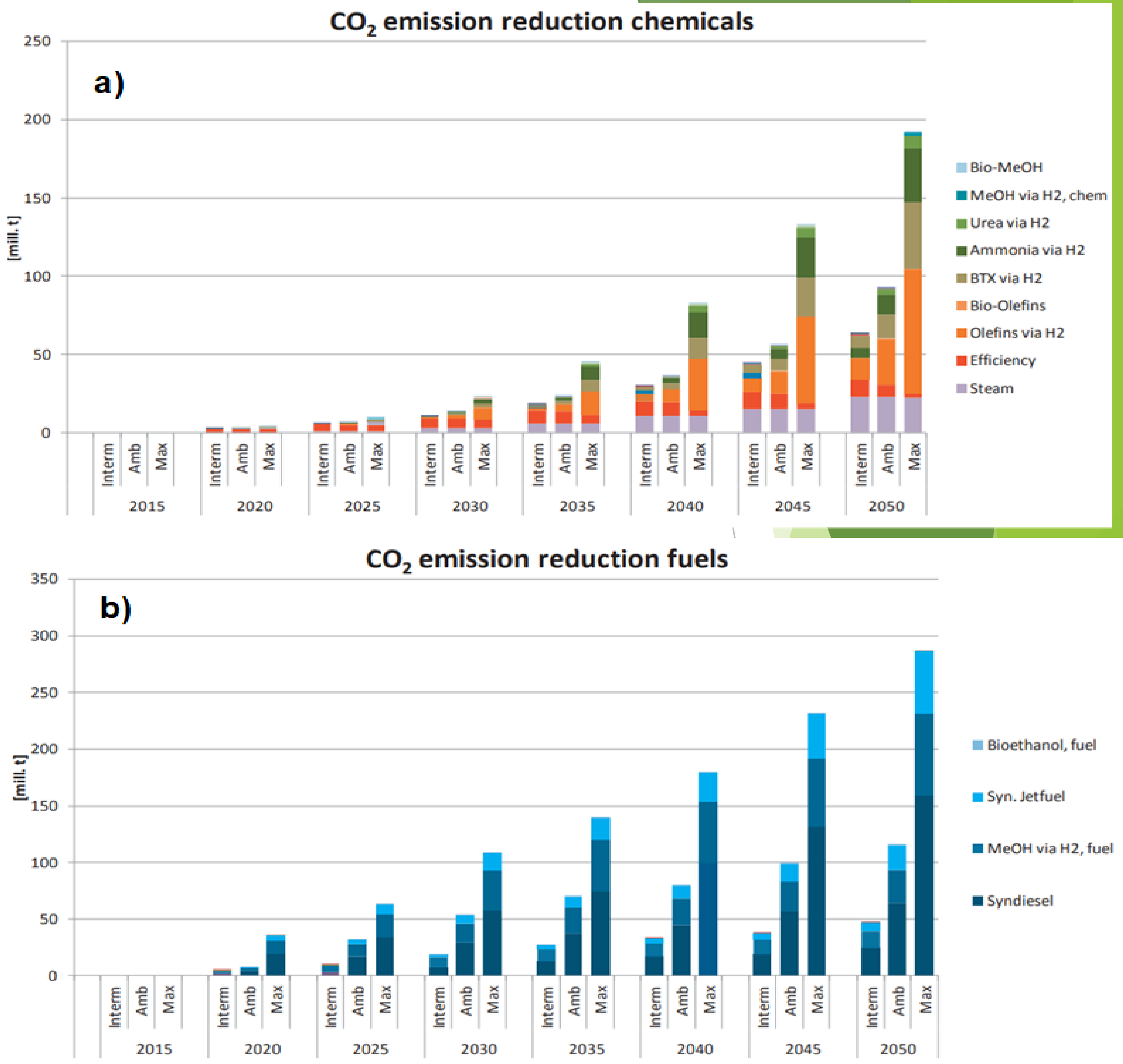


Figure 2: CO_2 emission reductions for all scenarios; a) chemicals; b) fuels. Source: Bazzanella and Ausfelder, 2017

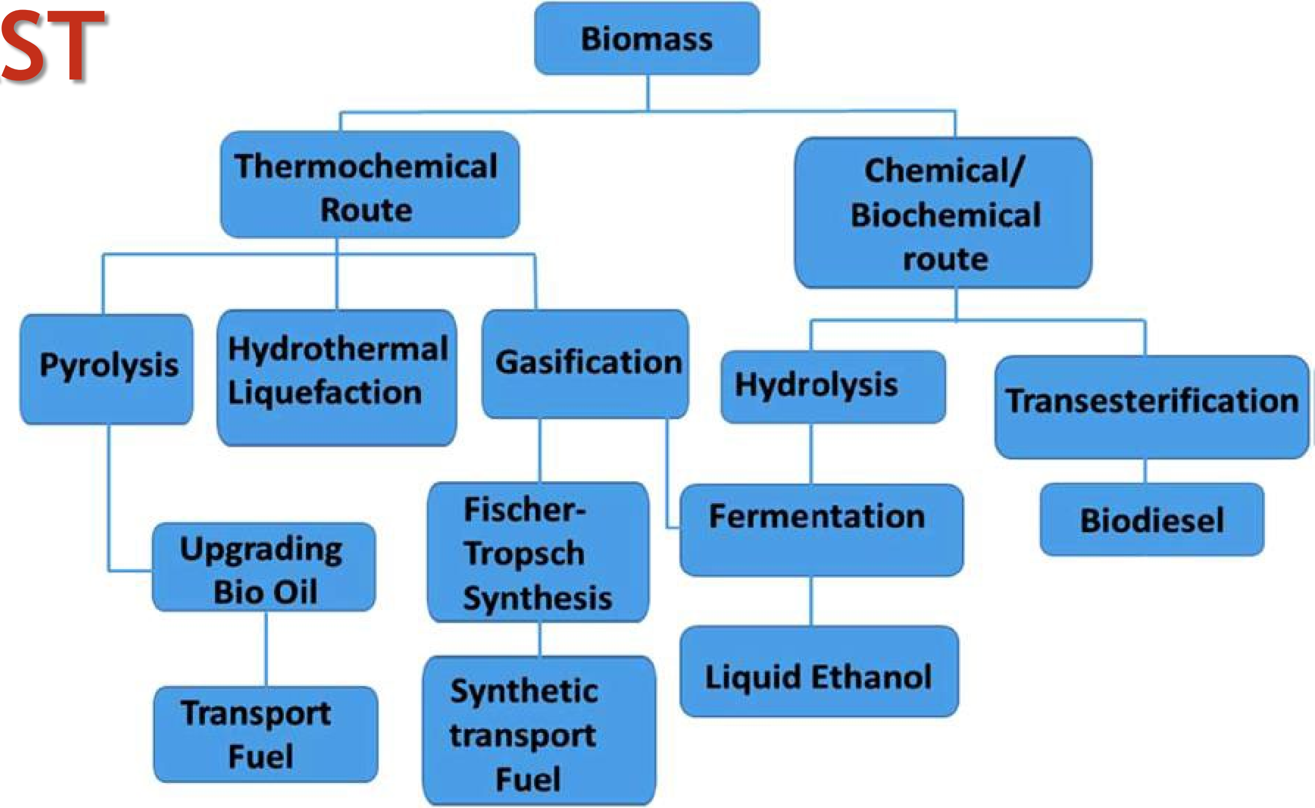
BIOMASS AS A RENEWABLE ENERGY SOURCE

Biomass is derived from organic matter such as wood, crop waste, or garbage, which contributes to overall RES production (~ 5% of total U.S. energy consumption)

- ✓ The thermochemical conversion of biomass to produce useful end products from the initial feedstock can occur through one of 6 different conversion pathways: (1) pyrolysis, (2) gasification, (3) combustion, (4) co-firing, (5) liquefaction, and (6) carbonization. Biomass plays an important role in all scenarios, both in combination with and without CCS.
- ✓ The most recognized technologies available to convert biomass into upgraded solid biofuels are pelletization, pyrolysis and torrefaction (Mousa et al., 2016). The first two are mature and commercially available, while torrefaction entered the commercial demonstration phase and is on the verge of commercialization (Wild et al., 2016).
- ✓ Pyrolysis involves the production of three different phases of products with various chemical reactions of feedstock in the absence of air (Uddin et al., 2018). Depending on the process condition, pyrolysis is further divided into subcategories
  - ✓ Gasification is another kind of thermochemical conversion process that generates gaseous precursors in the presence of a gasifying agent such as steam, air, oxygen, etc. Gasification, with respect to pyrolysis, optimizes the gaseous yield compared to liquid and solid phases, and allows also a bit simpler downstream purification.
  - ✓ Fast pyrolysis is widely used to enhance the liquid yield with moderate temperature and very low residence time. Charcoal is the main product of slow pyrolysis. The use of solar energy is one of the possibilities to lower the carbon footprint of the process (Sobek and Werle, 2018).
  - ✓ Hydrothermal liquefaction uses water at high temperatures/pressure (supercritical conditions). The main advantage of liquefaction over pyrolysis and gasification is that liquefaction does not require dried biomass as the initial feedstock (drying is an energy-consuming process) and it reduces the number of unit operations required in the conversion of biomass to liquid fuels

Biomass use for bioenergy suffers from environmental and GHG emissions related to growing, harvesting and transporting biomass, and converting a quite complex organic matrix.

FOCUS ON: CATALYTIC FAST PYROLYSIS FOR BIOMASS TO LIQUID (BTL)



Catalytic Fast Pyrolysis (CFP) combines the fast pyrolysis of biomass with the catalytic transformation of the primary pyrolysis vapors to more desirable and less oxygenated liquid fuels. These liquid fuels can readily be upgraded to transportable liquids. Any type of biomass can be used as feedstock for pyrolysis and consequently markedly different products can be obtained. Fast and flash pyrolysis at high temperatures with very short residence times convert biomass to a maximum quantity of bio-oil.

- ✓ Pyrolysis is the destructive distillation of dried biomass carried out in the absence of air at temperatures around 500°C.
- ✓ Decomposition of lignocellulosic material began at 200°C, achieving a maximum rate of mass loss at 350°C which continued to 500°C.
- ✓ Last step of the pyrolysis involves a decrease in the temperature, causing the condensation of different products.

The function of the catalyst during the catalytic fast pyrolysis is both to partially transform the products of pyrolysis in the liquid phase and catalytically convert the primary pyrolysis vapors to more desirable and less oxygenated liquid fuels. **Understanding of Main Factors** allowing a better control of i) the product distribution, ii) the various functionalities needed for an optimal control of the wide variety of reactions present, such as dehydration, hydrogenation, decarbonylation, decarboxylation, C–C coupling, and cracking and iii) the stability under fast pyrolysis conditions

FOCUS ON: CATALYTIC PROCESS FOR BIOGAS CONVERSION

Biogas is a key player in bio-based economy and energy transition

Wet (steam) and Dry Catalytic Reforming of methane and CO_2 are quite established technologies, in terms of both catalysts needed, technology and related reaction mechanism, flow batteries and supercaps, with focus on the role of catalysis in these technologies. For the reason of small-scale applications and heat recovery/utilization, dry reforming of methane (DRM) is often considered preferable to steam reforming (SR), which is typically preferable for example for H_2 production.

Commercial and Academic Catalysts

- ✓ **Clariant** has introduced methane steam reforming catalysts **ReforMax 330 LDP** Plus (standard) and **ReforMax 210 LDP** Plus having enhanced performances. The catalysts have an eight-hole flower-like shape designed to optimize catalyst geometry and mechanical strength.
- ✓ **Johnson Matthey** introduced the **Catacel SSR** steam reforming catalyst alloy strip, which are coated with a nickel-based steam-reforming catalyst. The fans are stacked inside of the reformer tubes, but this technology could be suitable for microreactors, another area of development of interest for small-case productions as in biogas case.
- ✓ **BASF AG** with the technology partner **Linde** AG have launched a new DRM catalyst based on nickel and cobalt spinel-type oxides. In addition to reduce the steam demand by up to 60%, DRM produces a CO-rich syngas ($CO:H_2 = 1:1$), which is optimal for directly making DME.
- ✓ A catalyst developed by the Japanese researchers, led by **Hideki Abe at the National Institute for Materials Science** is a metal/oxide nanocomposite with tailored 3-D topology.
- ✓ Malaysian researchers **Aziz et al.** (2020a) reviewed very recently the development of supported bimetallic catalysts for low-temperature DRM, reporting that NiPt and NiCo bimetallic catalysts supported on ZrO_2 are the preferable particularly in terms of coke resistance

FOCUS ON: BIOHYDROGEN FROM PHOTOCATALYTIC PRODUCTION

Biohydrogen: produced by photocatalytic conversion of wastewater streams from bio-based processes.

- ✓ The concept is to demonstrate photoreforming, i.e. combine water splitting with photo-oxidation of the organic species in solution (to CO_2), with the double advantage of accelerating the rate of the reaction (oxygen evolution is the slower and more difficult step in water splitting) and eliminate the organic species from the wastewater, or at least convert them to more easy biodegradable species

Photocatalytic processes appear to be very attractive and promising feasible technologies, although there are many drawbacks often not considered

- ✓ The limited overall rate of reaction of hydrogen formation, and the fact that reactions are essentially confined to a limited depth of the wastewater solution, by using dispersed photocatalysts, large area reactors are necessary
- ✓ The formation of an H_2 stream together with CO_2 (and some CO, O_2, volatile organic species, water vapor and other components which may be present in the wastewater, which may make costly downstream purification and production of a clear pure H_2 stream
- ✓ The need of downstream compressing H_2 (which is an energetically costly operation)
- ✓ The possible formation of harmful chemicals by incomplete photoconversion of the organic material

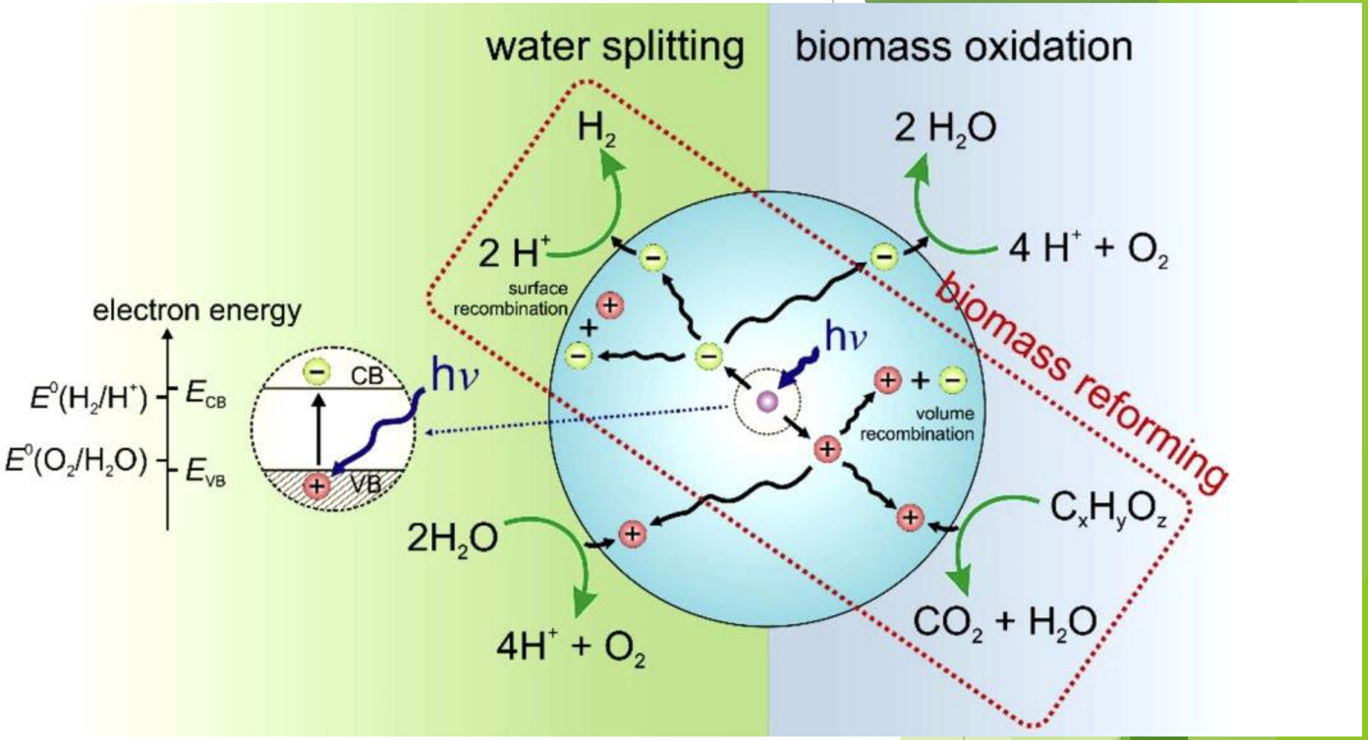


Figure 3: The schematic representation of possible reaction pathways by excitation of the semiconductor with light energy under anaerobic/aerobic conditions: water splitting (left-hand reaction), biomass oxidation (right-hand reaction), and photo-reforming (rectangular reaction) Source: Huang et al., 2019

FOCUS ON: CATALYSIS FOR ELECTRICAL ENERGY STORAGE IN BATTERIES

Li ion batteries are a leading technology in the market but there are two major current limitations: 1) limited energy density (≈ 400 W h kg^{-1}), that restricts their further applications in long-distance transport and large-scale storage systems; 2) unsatisfying safety, that has created public international concern.

The Li-ion battery: Li-O_2 batteries are emerging as a plausible solution to the energy storage limitations of the Li-ion counterparts. These architectures are composed of a Li metal anode, a porous cathode and a Li conducting electrolyte, typically non-aqueous.

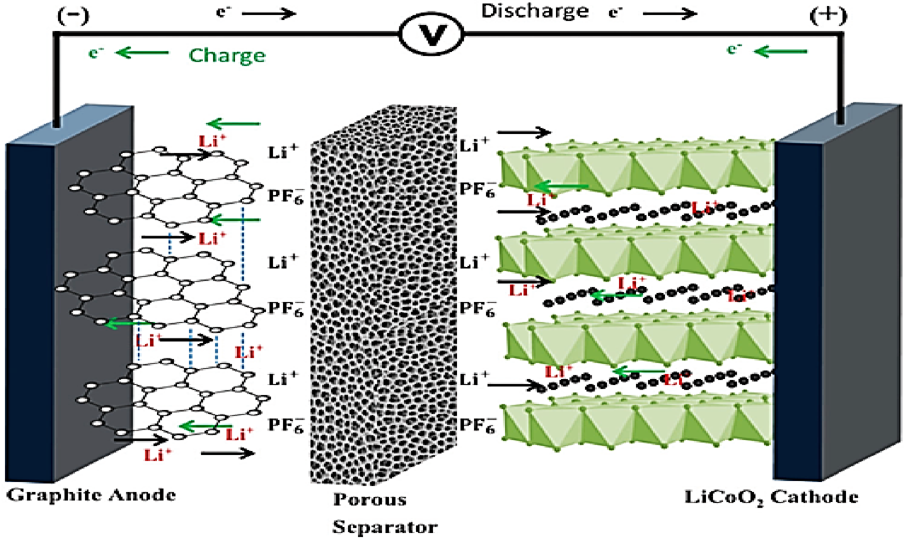


Figure 4: Illustration of first commercial Li-ion battery
Reproduced from Abraham, 2015

- ✓ The slow kinetics of these reactions limit their implementation. Carbon materials, such as carbon powders, nanofibers, and even graphene are good ORR electrocatalysts, but present serious mass transport issues. Their poor OER activity is restricting further applications.
- ✓ The insolubility and immobility of the Li_2O_2 product makes difficult to catalytically address its decomposition (and formation) by solid catalysts incorporated to the surface of the electrode. For this reason, soluble catalysts are being explored as redox mediators to facilitate the complete oxidation of all Li_2O_2 formed during discharge.
- ✓ Metal salts (Mg, Mn, Zn, ...) along strong organic acids have been patented as additives for ionic liquid electrolytes to improve oxygen reduction kinetics and thermodynamics of metal-O_2 batteries
- ✓ Bio-inspired molecules, such as vitamin K2, have also been proposed (Ko et al., 2019). Soluble polyoxometalates exhibited very high stability being all inorganic species, with promising bifunctionality
- ✓ CO_2 should be avoided to enter Li-O_2 batteries since it may react with peroxide to form insoluble carbonates, and electrode passivation (Zhang et al., 2017a). A problem for implementation comes from difficult translation of half-cell studies into prototype cell. Since cathodes with good half-cell cyclability fail in complete cell systems.
- ✓ Beyond cathode reversibility, anode considerations are also problematic, since the Li anode also suffers from cycling problems, including evolution from bulk to porous Li layers, and undesired parasitic reactions
- ✓ Looking forward, wide implementation in multiple markets, only alkaline–S and Li-O_2 batteries show favorable economics, while Li-ion (even as flow batteries) will need cost reductions

CONCLUSIONS & RECOMMENDATIONS

- ✓ The scenario for renewable energy is fast changing with social and regulatory pressures as drivers.
- ✓ Industry reports several Renewable Energy Production Scenarios such as McKinsey Energy Insights where it predicts a peak for fossil fuels around 2030, when the growth in energy demand will be decoupled from the energy growth due to a fast uptake of renewables
- ✓ The role of chemical energy storage is a key factor to enable a large use of renewable energy, but also as the key element for enabling a transformation of energy and chemical production
  - ✓ H_2 is a well-promoted energy vector and a push exists to implement on a large scale, although the limits respect to transport and storage are evident.
  - ✓ Ammonia could represent a valuable alternative, promoted recently in H_2 trading between Australia and Japan, and having the great advantage over alternative H_2-carriers, of better H_2 capacity storage per unit of weight and especially not need to transport back the carrier, because N_2 could be directly released in the atmosphere.
  - ✓ CO_2-based vectors have also this issue of requiring, in principle, to recapture the CO_2, but the great advantages of being drop-in products and thus not requiring large changes in the infrastructure, as necessary for the others energy vectors
  - ✓ In a long-term perspective, photo/electro-catalytic routes for direct conversion of small molecules (N_2, CO_2, H_2O) are indicated as the preferable technology, but still requiring a large investment in R&D before the possible exploitation
- ✓ The catalytic processes for biomass to liquid (BtL) have different possible routes and related prospects and challenges.
  - ✓ From a commercial perspective, the most advanced BtL solutions are to produce aviation fuel range hydrocarbons, and waste-to-chemicals or fuels (methanol, H_2, ethanol) solutions.
- ✓ Beyond costs, the scaling of solar fuels production brings another challenge since the incorporation of electrolyzers to mass production systems has not been properly addressed. Industrial scale predictions show that much higher current densities would be needed to achieve viable operational dimensions in the future
- ✓ The low temperature photoelectrochemical or photochemical processes will need most critical improvements to become competitive.

The report clearly lays out an array of options for energy storage from biomass to H_2 and upgrading of CO_2. This is a dynamic space, as costs for renewable energy generation and storage are decreasing rapidly

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