

# Electrolysis for Integration of Renewable Electricity and Routes towards Sustainable Fuels

M. Mogensen<sup>1</sup>, F. Allebrod, J.R. Bowen, C. Chatzichristodoulou, M. Chen, S.D. Ebbesen, C. Graves, J. Hallinder, A. Hauch, P.V. Hendriksen, P. Holtappels, J. V. T. Høgh, S.H. Jensen, A. Lapina, P.L. Mollerup, X. Sun

**Abstract:** The possibility of transforming our energy supply into 100 % sustainable energy is briefly discussed. It is - based on recent literature - argued that electrolysis has a great potential helping realize this. In particular high temperature solid oxide cells (SOC) seem to have the potential of entering the market within a foreseeable future. Long term R&D in electrolysis at lower temperature is taking place but need a breakthrough in electrocatalysis before it can be commercialized.

**Index Terms:** Electrolysis, Sustainable Fuels

## I. INTRODUCTION

There is a wish to increase the amount of sustainable CO<sub>2</sub> neutral energy production because of the "green house" effect, and because there may not be enough inexpensive oil and natural gas in the relative near future. It is Denmark's aim is to become independent of coal, oil and gas by 2050 [1]. It is then natural to look for photosynthesis products (biomass) to replace fossil fuel, but there will not be enough biomass available to substitute the fossil fuels [2].

Fortunately, enough renewable energy is potentially available. The annual global influx of energy from the sun to the earth is about  $3 - 4 \cdot 10^{24}$  J [3, 4] while the marketed energy consumption is ca.  $5 \cdot 10^{20}$  J [5], *i.e.* the earth receives ca. 6 - 8,000 times more energy from the sun than we need. Thus, if we use 0.2 % of the earth's area (ca. 1 mill. km<sup>2</sup> or 15 % of Australia) and have a collection efficiency of 10 %, we get the energy that we need. Besides solar we also have geothermal and nuclear (fusion and fission) potential energy sources. The crude numbers above are just to illustrate that the problem appears solvable from the energy availability point.

## II. INTEGRATION OF SUSTAINABLE POWER TECHNOLOGIES

Solar, geothermal and nuclear energy may be collected in the form of heat (hot water), but as heat only is exploitable relatively locally, the heat is usually turned into electricity immediately. Solar power is mainly harvested by

photovoltaics that provide electricity directly. Wind, hydro and wave energy sources, which are indirect solar sources, are all harvested in the form of electricity. All will preferably deliver the electricity to the grid.

The sustainable energy from sun, wind and waves are strongly fluctuating, and therefore affordable conversion and storage technologies are necessary. Also nuclear power will benefit from inexpensive energy storage, because the nuclear power plant runs most economically when it is on full power.

Evidently, it is by far the most advantageous to use this electricity directly from the grid to the largest possible extent, because most kinds of energy conversion of electricity are associated with significant energy (exergy) losses, and consequently, large efforts are done to average the fluctuation by long distance transportation and to absorb the fluctuations by varying the electricity consumption by make the grid "intelligent". This will most certainly ease the problems of fluctuation, but it is difficult to imagine that a 100 % sustainable electricity production of a larger area, *e.g.* like Europe, can cope with the fluctuations without extensive conversion of electric energy into storable energy. Furthermore, long distance transmission of electricity is costly, both in terms of infrastructure and energy losses.

Apart from the fluctuating nature of sustainable energy sources there is another reason for conversion and storage. There is a need for energy for transportation, and this energy cannot be supplied directly from the grid. Airplanes, ships, trucks and cars need transportable energy and, therefore, also call for efficient energy storage.

## III. STORAGE OF SUSTAINABLE ELECTRICITY

There are several ways of storing sustainable energy. They can be roughly divided into physical and chemical methods. The physical storage types are *e.g.* pumping water to high altitude reservoirs, compression of air, flywheel, magnetic storage and super capacitors. They are generally characterized with relatively low energy density. Chemical storage types are *e.g.* biomass, synthetic fuels and batteries. Even though batteries are often referred to as "electric storage" in contrast to synthetic fuel, batteries are certainly chemical storage.

Table 1 gives some examples of energy density of various storage media. It is clearly seen that hydrogen is having by far the highest gravimetric energy density followed by methane, CH<sub>4</sub>, also called substitute or synthetic natural gas (SNG). However, both are gasses and need rather heavy

<sup>1</sup>All authors are from Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DTU, Roskilde, Denmark. Corresponding author: [momo@risoe.dtu.dk](mailto:momo@risoe.dtu.dk).

This work was supported in part by The Danish Agency for Science, Technology and Innovation through The Strategic Electrochemistry Research Center ([www.serc.dk](http://www.serc.dk) - contract 2104-06-0011) and Catalysis for Sustainable Energy ([www.case.dtu.dk](http://www.case.dtu.dk)).

containments. In case suitable geological structures for high altitude water storage are locally available this is a very cheap option, which is already utilized extensively in countries like Norway and Switzerland. Batteries do not look like real options in the near future in spite of the recent hype around battery powered passenger cars. New types of lithium batteries such as the Li-air type have to be developed in order for batteries to become an option in large scale energy storage. Hydrogen may be an option for stationary storage, but will be difficult for the transportation sector due to its low volumetric energy density and the difficulties in handling it (high pressure of 700 bar or liquid at extreme low temperature). Hydrocarbons are from an energy density point of view the most suitable energy storage possibilities as shown in Table 1. The greatest advantage of using synthetic hydrocarbon fuels is that our existing infrastructure can be used without major modifications.

Table 1. Comparison of various storage possibilities.

| Type of storage         | Energy density |           | Boiling point, °C |
|-------------------------|----------------|-----------|-------------------|
|                         | MJ/L           | MJ/kg     |                   |
| Liquid methane (SNG)    | 24             | 56*       | -162              |
| Gasoline                | 33             | 47        | 40 - 200          |
| Dimethyl ether – DME    | 22             | 30*       | - 25              |
| Liquid hydrogen         | 10             | 141       | -253              |
| Lead acid batteries     | 0.4            | 0.15      |                   |
| Li-ion batteries        | 1              | 0.5       |                   |
| Water at 1 km elevation | $10^{-2}$      | $10^{-2}$ |                   |

\*Container material not included

The power density in handling various types of energy is an even stronger argument in favor of biological or synthetic hydrocarbon fuels than the energy density, especially when compared to batteries. This is illustrated by the passenger car as an example. A gasoline filling rate of 20 L/min is equivalent to 11 MW of power and it takes 2½ min to get 50 l = 1650 MJ on board a vehicle. If Li-batteries are used instead it will require 8 h to get a 300 kg battery package (0.5 MJ/kg) recharged using a power of ca. 5 kW, *i.e.* it takes 8 h to get 150 MJ on board.

#### IV. CONVERSION OF ENERGY INTO HYDROCARBONS

There are several methods of converting sustainable energy into hydrogen or hydrocarbons. Conversion of solar energy into biomass, which is easily storable, is the most advantageous, but there will not be enough biomass available [2] unless novel methods for harvesting biomass for the oceans are made available. Therefore, there will be a need for production of synthetic hydrocarbons and hydrogen from sustainable energy in the future.

Several methods for converting energy, H<sub>2</sub>O and CO<sub>2</sub> into synthetic fuel have been investigated during the recent decades. The research in CO<sub>2</sub> recycling technology, which includes CO<sub>2</sub> capture, H<sub>2</sub>O and CO<sub>2</sub> dissociation into syngas (H<sub>2</sub> + CO) that is further reacted into hydrocarbon using already commercialized catalytic methods, have recently been critically reviewed [6]. The type of system is sketched

in Fig. 1. Dissociation methods included thermolysis, thermochemical cycles, electrolysis, and photoelectrolysis of CO<sub>2</sub> and/or H<sub>2</sub>O. It was found that high temperature co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> makes very efficient use of electricity. Further, capturing CO<sub>2</sub> from the atmosphere using a solid sorbent, electrolyzing H<sub>2</sub>O and CO<sub>2</sub> in solid oxide electrolysis cells to yield syngas, and converting the syngas to gasoline or diesel by Fischer-Tropsch synthesis was identified as one of the most promising routes.

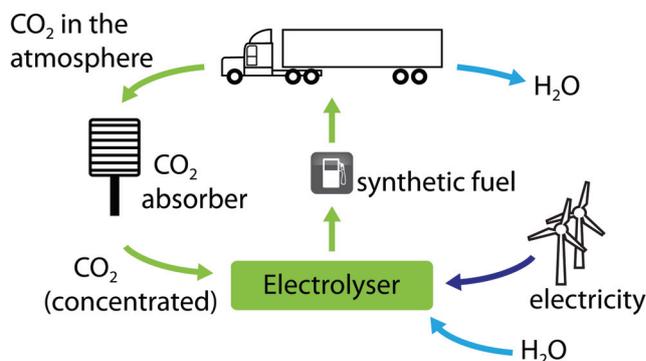


Fig.1. Capture and recycling of CO<sub>2</sub> using CO<sub>2</sub> absorption and electrolysis cells for synthetic fuel production via electrolysis of CO<sub>2</sub> and H<sub>2</sub>O.

Other promising synthesis products are methane (SNG) and dimethyl ether (DME). The latter two products have the advantage of not being poisonous in contrast to most other hydrocarbon fuels, and their production processes are relatively simple and thus less expensive. However, other synthetic fuels including hydrogen also have potential as energy storage compounds and energy carriers. The electrolysis cells are usually reversible. This means that the cell can also work as fuel cells that produce electricity from hydrogen or synthetic fuel when needed. This makes reversible power conversion systems of the type shown in Fig. 2 possible.

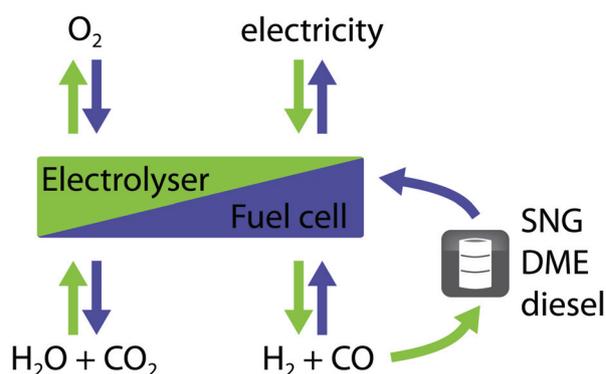


Fig. 2. Reversible electrochemical cell that can be used as an electrolyser for production of synthetic fuels, such as methane (synthetic natural gas, SNG), dimethyl ether (DME) or diesel, and used as a fuel cell for electric power generation.

## V. ELECTROLYSIS TECHNOLOGIES

As electrolysis seems to be a most efficient way of converting electricity into chemical fuel the various kinds of electrolyser types will be described briefly, but before doing this it is important to state the following about conversion efficiencies. The loss associated with electrochemical conversion of electricity into energy rich chemical compounds, whether it is by electrolysis or by charging a battery (conversion of the compounds inside the battery) will increase by increasing the current density (the reaction rate). It is great misunderstanding when many workers claim that the efficiency of batteries is about 80 % whereas electrolysis is much lower. The efficiency of batteries is often higher in today's practical use, because they are loaded very differently. The uses of the two types of storage are totally different, and current densities in batteries are typically in the order of 10 - 50 mA cm<sup>-2</sup>, whereas electrolyser current densities are in the range from 200 mA cm<sup>-2</sup> up to 1 A cm<sup>-2</sup>. In the case of energy storage only the costs are important, and the cost per kWh will depend on both conversion efficiency and investment cost. The latter will be much dependent on the current density that can be obtained at a given cell overvoltage. In this light electrolysis will be preferable and seems to be the obvious way to transform the sustainable energy into hydrogen, hydrocarbons or other chemical energy carriers.

Several types of electrolyser cells have been investigated, and some are commercially available. However, from an energy conversion and storage point of view, it seems most fair to say that none of them are commercial in today's energy markets. Recent detailed reviews of electrolysis technology have been carried out for electrolysis in general [7] and for high temperature electrolysis [8].

The cell types may be categorized according to the electrolytes with several subtypes:

1. Simple aqueous electrolytes (e.g. KOH or K<sub>2</sub>CO<sub>3</sub>), operation temperature from room temperature to ca. 100 °C. The classical alkaline electrolyser cell (AEC) belongs here.
2. Low temperature "solid" proton conductor membrane electrolyser cell (LT-PEMEC), ca. 60 - 80 °C, and high temperature, HT-PEMEC ca. 150 °C.
3. Immobilized aqueous K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> etc. in mesoporous structures – pressurized, 200 – 300 °C
4. Solid acids, 200 – 300 °C.
5. Proton conducting ceramic cells, 400 - 700 °C.
6. Molten carbonate electrolytes, 650 – 900 °C.
7. Solid oxide ion conductor cells, 600 – 1000 °C

The classical alkaline electrolyser cell (AEC) was commercialized early in the 20th century. It works at around 100 °C. If we were to produce significant amounts of syngas using electrolysis in the next few years then the only option would be the alkaline electrolyser, because production facilities of a reasonable scale are only available for this kind of electrolysers. The market for the alkaline electrolyser is the production of very clean hydrogen for special purposes. The problem with the alkaline electrolyser in the context of energy storage is that the hydrogen gets too expensive due to relative low production rate per cell area or

a low efficiency. A further possibility is that the hydrogen is reacted with CO<sub>2</sub> into syngas.

The most inexpensive balance of plant materials and the most flexible systems could be fabricated if it was possible to make electrolyser cells with high performance at room temperature. Therefore, a considerable international effort has taken place on room temperature electrolysis. Electrochemical reduction of CO<sub>2</sub> and H<sub>2</sub>O at room temperature has been demonstrated 20 years ago [9], but only 5 mA cm<sup>-2</sup> at -1.5 V vs. NHE and a yield of CH<sub>4</sub> of ca. 45 % was obtained. Later experiments [10] at 25 °C have shown somewhat higher levels of current density (80 mA cm<sup>-2</sup>) for syngas (CO + H<sub>2</sub>), but this is still far too low. In order to have a chance to make commercial CO<sub>2</sub> electrolysis, a current density of ca. 1 A cm<sup>-2</sup> at -0.8 to -1.0 V vs. NHE (normal hydrogen electrode) and with more than 80 % yield is necessary [11]. New greatly improved electrocatalysts and/or higher temperatures are necessary. A Danish (DTU) initiative called CASE (Catalysis for Sustainable Energy, [www.case.dtu.dk](http://www.case.dtu.dk), 23 MUSD over 5 year) is working on this. DTU Physics are pursuing greatly improved catalysts, and Risø DTU has begun activities on CO<sub>2</sub> reduction in the temperature range of 200 – 300 °C, pressure range of 20 - 50 bar using ACEC = aqueous carbonate electrolyser cell and PCEC = proton conductor electrolyser cell including solid acids.

LT-PEMECs are commercialized in the sense that it is possible to buy them, but due to precious metals and metal oxides in the electrodes and very expensive stack materials it will not be commercially viable cells unless much less expensive materials are developed. Similar problems exist for HT-PEMEC, but the potential for decreasing the costs sufficiently is significantly higher than for LT-PEMEC, in particular if the operation temperature can be raised to 200 °C or above. The basis for this statement is the general knowledge about catalysis (and electrocatalysis) that for these types of reactions the catalytic rates become much faster and reach acceptable levels for inexpensive catalysts when the temperature exceeds 200 – 250 °C. Below this temperature only very expensive nano-sized noble metals with limited stability work satisfactory.

Recently, a break-through in electrolysis of CO<sub>2</sub> into CO has occurred [12]. More work is needed, however, before the potential of this technology can be further assessed.

The high temperature (600 - 1000 °C) solid oxide electrolyser cell (SOEC) has been reported practical for co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> even though it is not yet commercialized. The technology has been demonstrated with cell stacks of kW size [6,11,13,14]. Topsoe Fuel Cell A/S is producing such stacks in Denmark. This cell is fully reversible [11], and actually the very same cell as used for the solid oxide fuel cell (SOFC) may be used. Therefore, the cell is often referred to as SOC. Electrolysis of H<sub>2</sub>O and CO<sub>2</sub> into H<sub>2</sub> and CO using SOEC at high temperature is advantageous because electrolysis is a heat consuming process. The Joule heat contributes to the splitting of the water and CO<sub>2</sub> molecules. Thus, the higher the temperature, the less electrical energy is need for the splitting. The SOEC may be operated self-cooling if the operation voltage is the thermo-neutral voltage. Further, the rate of the

electrochemical processes is much faster at high temperature. More  $\text{m}^3 \text{H}_2$  and  $\text{CO}$  per  $\text{m}^2$  cell per minute gives lower capital costs per  $\text{m}^3$  fuel gas. Finally, the SOEC consists of relatively inexpensive materials and may be produced using low cost processes. An application, where hydrogen production using SOEC seems particularly advantageous, is in the context of upgrading biogas in order to be able to supply this to the natural gas network [15].

The Fuel Cells and Solid State Chemistry Division of Risø DTU has over 20 years of experience with SOEC. Since 2002 both electrolyser and fuel cell applications have been comprehensively researched in cooperation with Danish and European Industry. An effort of about 20 man-year per year is taking place in the Division. A high pressure laboratory for electrolysis is being established as part of the Strategic Electrochemistry Research Center ([www.serc.dk](http://www.serc.dk) – 10 MUSD over 6 years) [16] and the first experiments have been carried out [17]. The results show that pressurized hydrogen can be produced using the same or less electric energy as non-pressurized because pressurization increases the electrode kinetics significantly.

## VI. VISIONS AND CONCLUSIONS

One vision is that synthetic fuel in the future will be produced from sustainable energy using electrolysis and catalysis. In areas where a natural gas pipeline exists like the North Sea, the pressurized electrolyser systems will be powered by off-shore windmill parks and the synthetic fuel will be SNG that can be transported in the existing pipelines without any modification of the infrastructure.

Another vision is that electrolyser systems producing liquid synthetic fuel like gasoline, diesel or DME are powered by e.g. huge photovoltaic cell arrays in the Australian deserts or geothermal power in Iceland, because renewable energy is often most abundant in remote areas.

Based on the referenced literature it is concluded that electrolysis in general, and SOEC in particular, has a very high potential as an instrument that may help in the integration of renewable energy into the existing infrastructure. The investment costs of transformation of our energy supply may be much lower using electrolysis based synthetic fuel options compared to a new hydrogen infrastructure or very long distance electricity transmission.

## VII. REFERENCES

- [1] Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, [http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy\\_Strategy\\_2050.pdf](http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf)
- [2] H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, <http://www.concito.info/en/udgivelser.php>
- [3] A. Evans, V. Strezov, T.J. Evans, in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., pp. 109-129, ISBN: 978-1-60876-022-0.
- [4] Earth's energy budget, Wikipedia, [http://en.wikipedia.org/wiki/Earth's\\_energy\\_budget](http://en.wikipedia.org/wiki/Earth's_energy_budget)
- [5] International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, <http://www.eia.gov/oiaf/ieo/index.html>
- [6] C. Graves, S.D. Ebbesen, M. Mogensen, K. S. Lackner, "Sustainable hydrocarbon fuels by recycling  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with renewable or nuclear energy," *Renewable and Sustainable Energy Reviews*, vol. 15, pp. 1–23, 2011.
- [7] J.O. Jensen, V. Bandur, N.J. Bjerrum, S.H. Jensen, S. Ebbesen, M. Mogensen, N. Tophøj, L. Yde, Pre-investigation of Water Electrolysis, PSO-F&U 2006-1-6287, April 2008, <http://130.226.56.153/rispubl/NEI/NEI-DK-5057.pdf>
- [8] A. Hauch, S.D. Ebbesen, S.H. Jensen, M. Mogensen, "Highly efficient high temperature electrolysis", *J. Mater. Chem.*, vol. 18, pp. 2331–2340, 2008.
- [9] Y. Hori, A. Murata, R. Takahashi, "Formation of Hydrocarbons in the Electrochemical Reduction of Carbon Dioxide at a Copper Electrode in Aqueous Solution," *J. Chem. Soc. Faraday Trans. I*, vol. 85(8), pp. 2309-2326, 1989.
- [10] C. Delacourt, P.L. Ridgway, J.B. Kerr, John Newman, "Design of an Electrochemical Cell Making Syngas ( $\text{CO} + \text{H}_2$ ) from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  Reduction at Room Temperature," *Journal of The Electrochemical Society*, vol. 155(1), pp. B42-B49, 2008.
- [11] S.H. Jensen, P.H. Larsen, M. Mogensen, "Hydrogen and synthetic fuel production from renewable energy sources," *International Journal of Hydrogen Energy*, vol. 32, pp. 3253–3257, 2007.
- [12] V. Kaplan, E. Wachtel, K. Gartsman, Y. Feldman, I. Lubomirsky, "Conversion of  $\text{CO}_2$  to  $\text{CO}$  by Electrolysis of Molten Lithium Carbonate," *Journal of the Electrochemical Society*, vol. 157(4), pp. B552-B556, 2010.
- [13] C.M. Stoots, J.E. O'Brien, K. Condie, L. Moore-McAteer, G. Housley, J.J. Hartvigsen, J.S. Herring, "The high-temperature electrolysis integrated laboratory-scale experiment." *Nuclear Technology*, vol. 166(1), pp. 32-42, 2009.
- [14] S.D. Ebbesen, J. Høgh, K.A. Nielsen, J.U. Nielsen, M. Mogensen, "Durable SOEC stacks for production of hydrogen and synthesis gas by high temperature electrolysis," *International Journal of Hydrogen Energy*, vol. 36, pp. 7363-7373.
- [15] GreenSynFuels, EUDP report, project 64010-0011, March 2011, <http://www.dti.dk/30339.1,1>.
- [16] M. Mogensen, K.V. Hansen, "The Strategic Electrochemical Research Center in Denmark," *ECS Transactions*, vol. 35 (1), pp. 43-52, 2011.
- [17] S.H. Jensen, X. Sun, S.D. Ebbesen, R. Knibbe, M. Mogensen, "Hydrogen and synthetic fuel production using pressurized solid oxide electrolysis cells," *International Journal of Hydrogen Energy*, vol. 35(18), pp. 9544-9549, 2010.