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Mogensen, Mogens Bjerg

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Electrochemical Routes towards Sustainable Hydrocarbon Fuels

Mogens Mogensen

Risø National Laboratory for Sustainable Energy,
Technical University of Denmark, DTU
P.O. Box 49, DK-4000 Roskilde, Denmark

Internationally there is an increasing wish to increase the amount of sustainable CO₂ neutral energy production because of the "green house" effect due to the increasing CO₂ concentration in the atmosphere, and because that a threatening increase of fuel prices because there may not be enough inexpensive oils and natural gas in the relative near future. Further, there will not be enough biomass available to substitute the fossil fuels. Therefore, Denmark has decided to become independent of fossil fuel. The Danish Government's aim is that Denmark in 2050 is independent of coal, oil and gas.

Fortunately, enough renewable energy is potentially available. The influx of energy from the sun to the whole earth is ca. 10,000 times more than we need, i.e. if we use 0.1 % of the area and have a collection efficiency of 10 %, we have ca. the energy that we need. Thus, from the overall energy supply point of view the problems should be possible to solve.

The sustainable energy from wind and sun are fluctuating, and therefore affordable conversion and storage technologies are necessary. Also CO₂ free nuclear power could be more efficiently utilized if a good storage technology is available as nuclear power plants run most efficient at constant high load.

This paper argues that electrolysis will almost unavoidable be at least a part of a sustainable energy system as sustainable power are in most cases harvested using technologies that provide electricity. The argument will be supported by comparison with other known methods.

Hydrogen may be an option for stationary storage, but will be difficult for the transportation sector. Hydrocarbons are from an energy density point of view the most suitable energy storage possibilities as shown in Table 1. Further, if we can use synthetic hydro-carbon fuels then we can use our existing infrastructure.

Table 1. Comparison of various storage possibilities.

Type	MJ/L	MJ/kg	Boiling point °C
Gasoline	33	47	40 - 200
Dimethyl ether - DME	22	30	- 25
Liquid hydrogen	(10)	(141)	-253
Water at 100 m elevation	10-3	10-3	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

The power density in handling various types of energy is an even stronger argument in favor of synthetic hydrocarbon fuels. A gasoline filling rate of 20 L/min equivalents 11 MW of power and means 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. 3.5 kW, i.e. it takes 8 h to get 150 MJ on board.

Several types of electrolyser cells based on various electrolytes have been investigated and reported. Only few have been commercialized until now, and from

an energy conversion and storage point of view it is most fair to say that none of them are commercial in today's energy markets. The cell types are:

1. Simple aqueous electrolytes (e.g. KOH or K₂CO₃), room temperature to ca. 100 °C.
2. Low temperature "solid" proton conductor membrane (PEM), 70 – 90 °C, and high temperature PEM 120 - 190 °C.
3. Immobilized aqueous K₂CO₃, Na₂CO₃ etc. in mesoporous structures – pressurized, 200 – 300 °C
4. Solid acids, 200 – 250 °C.
5. Molten carbonate electrolytes
6. High temperature solid oxide ion conductor (stabilized zirconia), 650 – 950 °C

The classical alkaline electrolyser was commercialized during the first half of the 20th century. If we were to produce significant amounts of synfuel using electrolysis in the very near future (the next few years) then the only option would be the alkaline electrolyser, because production facilities of a reasonable scale is 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 is that the hydrogen gets to expensive due low production rate per cell area or a low efficiency. Further, the hydrogen has to be reacted with CO₂ (and not CO) in order to make synfuel.

Low temperature PEM electrolysers are commercialized in the sense that it is possible to buy them, but due to precious metals and metal oxides in the electrodes and expensive stack materials they will not be commercial viable cells unless much less expensive materials are developed. Similar problems exist for high temperature PEM electrolysers.

Electrochemical reduction of CO₂ and H₂O at room temperature has been demonstrated [Y. Hori et al., *J. Chem. Soc. Faraday Trans. 1*, **85** (1989) 2309], but only 5 mA cm⁻² at -1.5 V vs. NHE and a yield of CH₄ of ca. 45 % was obtained. In order to have a chance to make commercial CO₂ electrolysis, a current density of ca. 1 A cm⁻² at -0.8 to -1.0 V vs. NHE and with more than 80 % yield is necessary. Thus, the results of Hori et al. are very far from the goal.

New improved electrocatalysts and/or higher temperatures are necessary. A 23 MUSD and 5 year Danish (DTU) initiative called CASE (Catalysis for Sustainable Energy) is working on this. Risø DTU has begun activities on CO₂ reduction in the temperature range 200 – 300 °C, pressure 50 -100 bar using ACEC = aqueous carbonate electrolyser cell and PCEC = proton conductor electrolyser cell.

Only the high temperature (600 - 1000 °C) solid oxide electrolyser cell (SOEC) has been reported practical for co-electrolysis of H₂O and CO₂ even though it is not yet commercialized. Electrolysis of H₂O and CO₂ into H₂ and CO using SOEC is advantageous because electrolysis is a heat consuming process. The Joule heat contributes to the splitting of the water and CO₂ molecules. Thus, the higher the temperature, the less electrical energy is needed for the splitting. The SOEC may be operated self cooling if the operation voltage is the thermoneutral voltage. Further, the rate of the electrochemical processes is much faster at high temperature. More m³ H₂ and CO per m² cell per minute gives lower capital costs per cubic meter fuel gas. Finally, the SOEC consists of relatively inexpensive materials and may be produced using low cost processes.