

An "Atmospherically Healthy" Recipe for Carbon-Neutral Fuels: A synthetic fuel made from sunlight, CO₂, and water

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ABSTRACT

The concept of carbon neutral hydrocarbon fuels formed from "carbon free" energy, atmospheric CO₂, and water is discussed. The three required technologies – cost competitive "carbon free" energy, efficient atmospheric capture of CO₂, and conversion of CO₂ to hydrocarbons are highlighted. Of these three, Atmospheric CO₂ extraction is shown to be one of the key technology enablers. Methods for atmospheric CO₂ capture are discussed. Experimental data of novel electrochemical carbon capture using ion exchange membranes and room temperature ionic liquid membranes is shown. Current efficiencies approaching 30% for atmospheric CO₂ concentrations are demonstrated. The ionic liquid membranes with their inherently low solvent loss are observed to be very robust to degradation.

Keywords: CO₂, carbon capture, synthetic fuels, ionic liquids

1 INTRODUCTION

With the recent rise in oil prices, the decline in oil reserves and in order to improve air quality, to reduce our dependence on imported oil, and reduce the emissions of greenhouse gasses, some have discussed alternative transportation fuels including ethanol, methanol, hydrogen, and electrochemical storage (batteries). As opposed to some clean fuels such as hydrogen, alternate sources of hydrocarbon fuels have a high potential of becoming a common source of energy for transportation. They can be easily handled, have high energy densities and as liquids allow relatively simple energy storage. Most of the hydrocarbon fuels in the U.S. are currently produced from fossil fuels. As an alternative to fossil based production, bio-mass converted to syn-gas, fermented to ethanol, or otherwise converted to fuel can be used, but with several drawbacks such as the large arable land required. As outlined in his book, "Beyond Oil and Gas; the Methanol Economy", George Olah proposes a direct reaction of CO₂ into fuel. Olah suggests supplying the required electricity for electrolysis and hydrogenation via wind, solar or nuclear sources thus creating carbon neutral methanol [1]. Such a fuel is frequently referred to as "synthetic fuel" to distinguish it from bio-fuel technology.

A potential CO₂ source for synthetic fuel production could be from air. A new DOE report on greenhouse gas emission scenarios predicts that by 2100 global CO₂ emissions could be tripled leading to worldwide disastrous

consequences [2]. One of the proposed mitigation options will require capturing the excess CO₂ which can then be sequestered underground with a limited capacity, or alternatively be used as a source for industrial processes such as synthetic fuel production. To extract CO₂ from air, current technologies focus on are capturing CO₂ from flue gasses of existing fixed CO₂ sources such as coal fired power plants. However, approximately 30% of all CO₂ emissions in the US are from mobile sources such as vehicle emissions for which there exist no viable technologies to capture and sequester CO₂.

There is no available system today that could potentially extract post combustion CO₂ from the atmosphere efficiently and inexpensively. As CO₂ is free and available everywhere, such a technology would eliminate transportation costs and reduce storage requirements thus reducing subsequent sequestration or synthetic fuel costs. Energy efficient CO₂ extraction solutions have been designed for aerospace and naval applications [3] but these would be extremely expensive and enormous if intended for extracting CO₂ from much lower concentrations and much larger air volumes.

2 SYNTHETIC FUEL

The concept for non-biological conversion of CO₂ to fuel has been in existence for several decades [4,5]. It has been especially attractive in applications where access to fossil based fuels is difficult or expensive such as for ships at sea or remote locations. The concept is outlined below in figure 1.

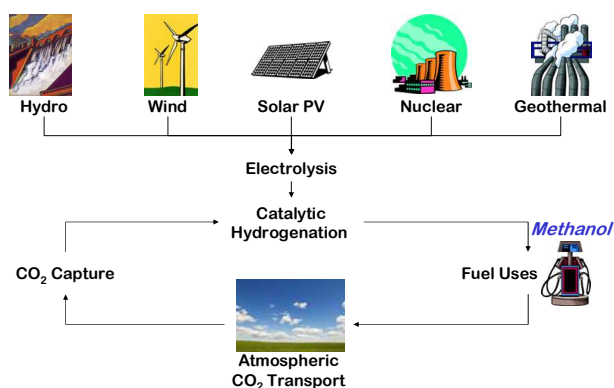


Figure 1. Synthetic Fuel Flowchart

In one possible embodiment non-carbon emitting power sources such as solar, wind, geothermal, nuclear, and

hydroelectric are used to power both CO₂ capture and to hydrolyze water to form hydrogen. The captured CO₂ and hydrogen are reacted over specific catalysts in a process similar to that of methanol synthesis from syn-gas. The methanol can be used directly for fuel or optionally the methanol can be converted to higher order hydrocarbons through processes such as the methanol to gas (MTG) conversion process.

The energy efficiencies of such a process and alternate embodiments have been analyzed previously [6]. Efficiencies of 50% have been estimated for conversion of electrical energy to fuel. Recent work at Los Alamos National Laboratory has predicted that a synthetic fuel process tied to a nuclear power plant could be cost competitive when the retail price of gasoline is in the neighborhood of \$4.60 per US gallon [7]. This is excluding any government incentives such as a “carbon tax” or cap and trade system for CO₂ emission regulation. Such policies could help to make carbon free synthetic fuels more competitive and speed their development and adoption. The cost of solar electricity is too high presently to make this process viable in the short term; however, as the cost of solar PV (or other solar energy) drops over time and becomes competitive with fossil fuel based electricity, solar to synthetic fuel conversion will begin to be competitive as a transportation fuel option.

Processes for CO₂ to hydrocarbons are well known. Bench scale plants have been constructed and evaluated [8]. The process conditions required are similar to those for the syn-gas based methanol synthesis done at many large scale production facilities around the world. Scale up of CO₂ to methanol production would certainly entail a significant number of engineering and scientific challenges; however, with the fundamental process well documented and the construction of similar facilities accomplished, the risks are significantly reduced over other possible routes to synthetic fuel production.

The capture of CO₂, while accomplished on industrial scales for a variety of applications, has not been developed for efficient operation at atmospheric concentrations. Sweetening of natural gas, capture and sequestration of flue gas, and processing of cabin breathing air in spacecraft and submersibles are examples of present uses of CO₂ capture. In each of these applications, the value of the product (natural gas, breathable air) or the starting concentration of the CO₂ (3-15% in flue gas) is high enough that the process is economical. Processes for atmospheric capture have been reported, but with energy expenditures of 300 – 1000 kJ/mol or higher. These are excessive when compared with the free energy of mixing which defines the minimum energy required to separate CO₂ from 380 ppm in air at atmospheric pressure - ~20 kJ/mol.

One of the most efficient continuous carbon capture technologies for CO₂ concentrations <1000 ppm employs electrochemical or “polarization” membranes [3]. The energy cost of this process is as low as ~300 kJ/mol at atmospheric conditions. However, the current efficiency is

approximately 20% (i.e. 5 electrons are required to pass through the external load for each CO₂ molecule captured). Improvements in the Faradaic efficiency of the electrochemical carbon capture cells could significantly reduce the energy consumption and enable efficient, continuous CO₂ extraction under atmospheric conditions.

3 ELECTROCHEMICAL CARBON CAPTURE

The basic principle and the relevant chemical reactions of electrochemical carbon capture are outlined in figure 2.

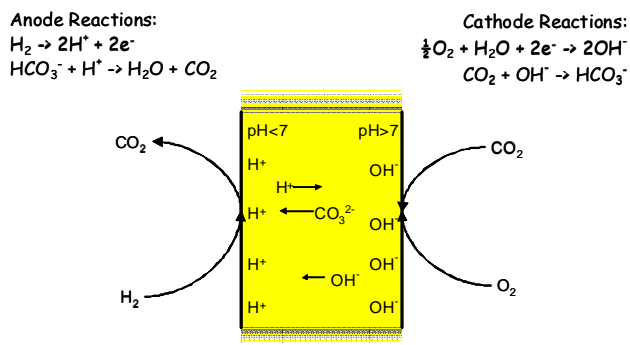


Figure 2. Schematic and relevant reactions of electrochemical CO₂ capture

The membrane is typically a porous support wetted with an electrolyte solution (i.e. aqueous carbonates). The porous support can be any inert porous material. Porous cellulose was used in these tests. Gas diffusion electrodes and flow fields are placed on either side of the membrane and the external circuit is completed with the connection of a variable load. The anodic output of such a capture system will be a mixture of H₂ and CO₂; however, as long as the concentration of CO₂ is in excess of that required for hydrogenation and fuel formation (approximately 20%), no further concentrating will be required.

Previous reports of electrochemical carbon capture used exclusively aqueous electrolyte membranes. This has a least two disadvantages. First, the aqueous membranes are non-selective with respect to ionic current. In addition to the desired carbonate and bicarbonate diffusion, protons and hydroxyl ions will be transported across the cell membrane reducing the utilization of the cell current. Second, the membrane will be susceptible to solvent (water) loss. The input gasses require near complete humidification to avoid drying and subsequent failure of the aqueous membrane.

To test improvements to the previous electrochemical separators cells using commercial ion exchange membranes were constructed and tested. A picture of a partially disassembled cell is shown in figure 3.

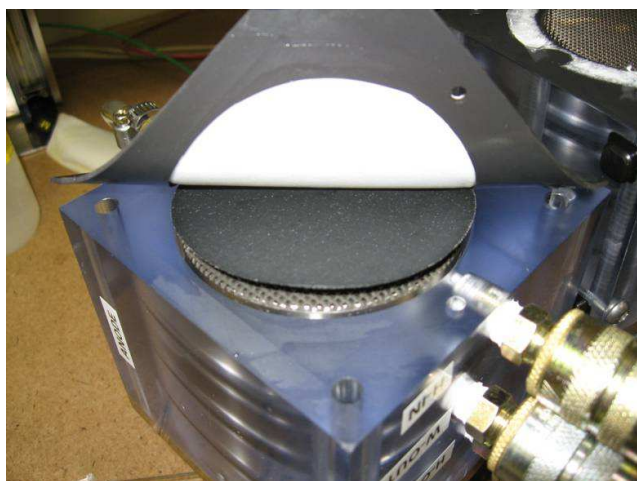


Figure 3. Picture of anode half of partially disassembled electrochemical CO₂ capture cell with gas diffusion layer, membrane, and gasket seal (cathode side not shown)

A manually cut disk of anion exchange membrane FTAM from Fumatech AG, a trimethyl benzyl ammonium based AEM, was used. Prior to cell assembly, the membrane was soaked in a saturated aqueous solution of Cs₂CO₃ for 24 hours to precondition the membrane. Input air was blended for bottled N₂, O₂, and CO₂ at appropriate flow rates. All gasses were brought to approximately 100% relative humidity prior to introduction to the cell. The results are shown in figure 4. Current utilization efficiencies as high as 25% for near atmospheric conditions were observed - approximately a factor of 2 improvement over prior aqueous membranes. The cell was sensitive to moisture content and would fail rapidly (<10 min) if the RH was lowered to less than 80%.

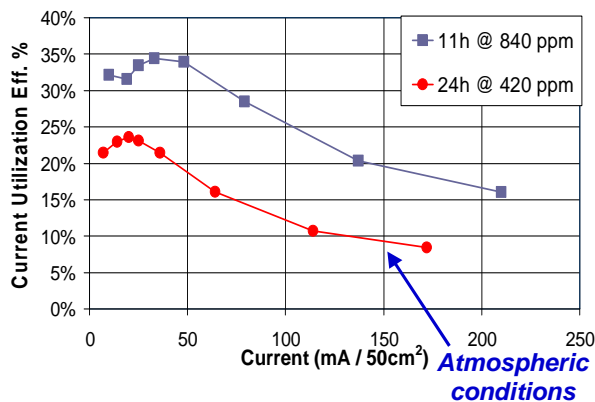


Figure 4. Current utilization v. current density using Anion Exchange Membrane at 25°C and 3slm Air & 70sccm H₂

Recently much research has been conducted on room temperature ionic liquids (RTIL) motivated by their unique properties and the possibility to use them as solvents in

synthesis and electrochemical applications. RTIL have negligible vapor pressure and good stability under electrochemical conditions. Appropriate RTIL might be more robust to solvent loss in electrochemical CO₂ capture cells.

To test the basic function of a cell using a RTIL, a 1 M solution of Cs₂CO₃ in 1-Butyl-1-methylpyrrolidinium dicyanamide with various amounts of water added (0 – 20%). Porous cellulose paper was soaked in these solutions, placed between the gas diffusion electrodes and loaded into the electrochemical CO₂ capture cell. Other than the membrane electrolyte solution used, the construction of the cell was identical to that used with the aqueous electrolytes and the AEM. Figure 5 shows the performance of the cell with different electrolytes over 12 hour periods.

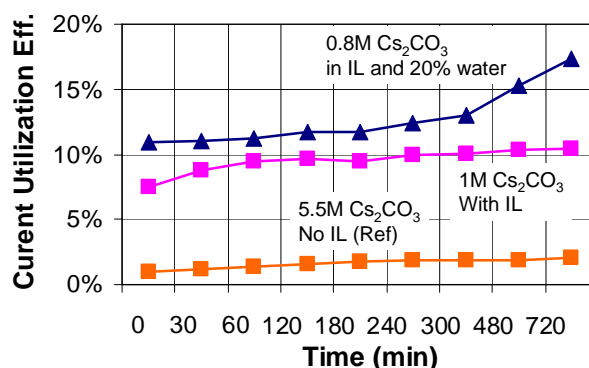


Figure 5. Current Utilization efficiency over 12 hours at 400 ppm cathode inlet CO₂ concentration and 400 mV cell operating potential using various Cs₂CO₃ membrane electrolyte solutions.

The performance of the RTIL based membrane was very good and demonstrated current utilization efficiencies of up to 30%. In addition, the RTIL based capture cell showed no failure with RH as low as 75% over a 12 hour period – a condition under which an aqueous membrane would have failed within minutes.

4 CONCLUSIONS

Synthetic fuel production using “carbon free” energy, efficient atmospheric CO₂ capture and catalytic hydrogenation of CO₂ to hydrocarbon fuel could enable carbon neutral fuels compatible with our existing transportation infrastructure. Of the three technologies required, efficient CO₂ capture has had the least attention. Electrochemical methods of capture may be some of the most efficient possible solutions; however, they show certain drawbacks such as low current utilization and susceptibility to drying. Anion exchange membranes and room temperature ionic liquid based membranes show promise as solutions which could enable this efficient

carbon capture from the atmosphere and, eventually, carbon free hydrocarbon fuels.

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