

SCALE-UP OF A SYSTEM FOR HYDROCARBON PRODUCTION BY ELECTROCHEMICAL REDUCTION OF CO₂

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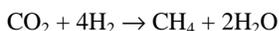
ABSTRACT

This work addresses the scaling up of a system for electrochemical reduction of CO₂ to produce hydrocarbons that can be used as fuel for a regenerative energy storage cycle. Challenges involved in such a task are mentioned. Scaling-up results of a system based on electrodes of high surface area with modified copper deposits are described. Current densities around 100 mA/cm² were obtained. This corresponds to the current density threshold that enables technological applications. At potentials as negative as -1.6 V it was observed that CO₂ reduction still dominated over hydrogen evolution reaction.

1. INTRODUCTION

The provision of electrical power in space missions has always been an important issue and continues to be a major consideration with gallium-arsenide technologies and lithium ion batteries being in the forefront.

The conversion of carbon dioxide into hydrocarbons is a process that has been around since the early 1900s. The Sabatier process involves the conversion of CO₂ and hydrogen into methane and water in the presence of a nickel catalyst at high temperatures and high pressures:



Other approaches for using CO₂ to synthesize a fuel have been considered previously [1], but better CO₂ reduction processes are still lacking and further research in this field is needed. Such a process should use available inexpensive raw materials, have few process stages, be easily scalable and operate at room temperature. One-step electrochemical CO₂ reduction at a metallic electrode yielding a mixture of one- or two-carbon atom hydrocarbons and hydrogen potentially fulfills these requirements. The basic

raw materials for this process are CO₂ and water. Electrochemical reduction of CO₂ to yield fuel requires that hydrogen be present at some step of this reaction. Water can be used simultaneously as electrolyte and as an *in situ* source of hydrogen.

The aim of this ongoing research project is thus to develop a regenerative energy storage cycle.

In this cycle the recharge system, which is composed of an electrochemical cell, converts CO₂ into compounds (hydrocarbons) using an external source of power (e.g. solar power), Fig. 1. The discharge system produces electric energy when hydrocarbons and oxygen from the recharge system are directly supplied to a Solid Oxide Fuel Cell (SOFC).

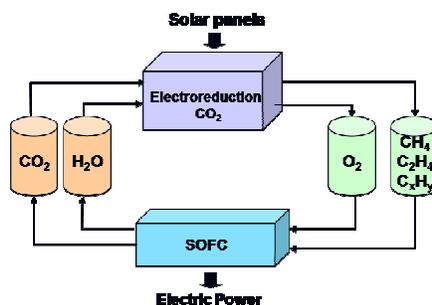


Figure 1. Regenerative energy storage cycle

Several space applications can be envisaged. This system, when placed in satellites, recycles water and CO₂ in a closed cycle into fuel and oxidizer using solar energy panels. When the satellite is experiencing an eclipse and no energy is available from the solar panels, the fuel is used to provide energy for the satellite using an SOFC whilst at the same time regenerating CO₂ and water.

The more ambitious missions of the European Space Agency in the near future are to Mars.

The Martian atmosphere has a composition of 95,3% CO₂, this is enough carbon dioxide to make sustainable human life possible if breathable air, water, and fuel can be generated *in situ*. Water is available on Mars as subterranean ice. So, *in situ* fuel production on Mars requires both atmospheric CO₂ and subterranean ice extraction, since the atmosphere of Mars contains only a trace of water.

This technology can also be used for terrestrial applications to mitigate green-house gas emissions and for example to create fuel self sufficiency in remote communities that have a local excess of renewable energy.

2. CHALLENGES INVOLVED IN SCALING -UP

Although research in CO₂ electrochemical reduction has been undertaken for more than twenty five years, the electrochemical reduction of CO₂ at copper electrodes has not yet been developed and implemented at a scale for demonstration and actual system applications. This is mainly due to the low current densities and or low Faradaic efficiencies exhibited by the state of the art systems.

Indirect reduction of CO₂ was reported for the first time by Petrova G. N. *et al.* [1]. A mercury electrode in an aqueous electrolyte at pH 7, containing TiCl₃, Na₂MoO₄ and pyrocatechol yielded a total Faradaic efficiency for cathodic hydrocarbon generation of about 0.2% at 7 mA/cm², with methane being the major hydrocarbon component. CO₂ has been shown to be reducible to CH₄, CO, and methanol at ruthenium cathodes in CO₂ saturated aqueous Na₂SO₄ electrolyte with Faradaic efficiencies for CH₄ production of up to 42% at current densities up to 0.11 mA/cm² [3]. Copper, 99.99% pure, was used as a cathode with 0.5 M KHCO₃ electrolyte for the electrochemical reduction of CO₂ at ambient temperature and current density of 5.0 mA/cm² for 30 to 60 minutes with Faradaic efficiencies for CH₄ of 37 to 40% [4]. Electrochemical reduction of CO₂ at a 99.999% pure copper cathode in aqueous electrolytes of KCl, KClO₄ and K₂SO₄ at 19°C and current density of 5 mA/cm² showed high Faradaic yields of C₂H₄ of the order of 48%, CH₄ 12% and EtOH 21% [5]. Current literature indicates the use of small current densities and relatively low Faradaic efficiencies. Thus one requirement for a system suitable for a technological application is the production of hydrocarbons both at high current densities and high Faradaic efficiencies. Current densities useful for technological applications should be

around or above 100 mA/cm². The values of the current densities and Faradaic efficiencies mentioned previously are illustrative of two phase systems. A more exhaustive description of the studied systems can be found for instance in [6-7].

The aim of this R&D work is to scale-up a process to produce a stream of hydrocarbon gas to feed a SOFC for the generation of electricity.

Thus another requirement must be met by the system. As CO₂ cannot be processed by the SOFC, its presence in the product mixture is undesirable and should be minimized as much as possible. A two phase system was selected for the scale-up work. In these systems the electrochemical reaction occurs at the electrode – electrolyte solid interface. Three phase systems in which the electrochemical reduction occurs at gas (CO₂)/liquid (electrolyte)/solid (electrode) were not investigated as they lead to high concentrations of CO₂ in the hydrocarbon mixture.

Other obvious system requirements are related to electrode performance. This performance should be stable and long lasting and electrodes should not be easily deactivated. This is one of the most serious problems in a practical use of this process. It has been pointed out that the Faradaic efficiencies for hydrocarbons rapidly decrease about 30 minutes after the start of the electrolysis and the electrode becomes almost completely inactive at longer times [8-9]. Electrode deactivation was attributed to the deposition of poisoning species such as graphitic carbon [10-12], adsorbed organic intermediates [8, 13], or copper oxide [9,14].

The efficiency for the electrochemical conversion of electrical energy to chemical energy was estimated to be around 38% for a biogas upgrading process using state of the art technology [1]. In this application the normally vented CO₂ is converted to additional fuel. To improve the state of the art efficiency one approach could be to develop electrodes that produce higher density fuel mixtures e.g. with higher ethylene content or even higher hydrocarbons such as ethane, propane and butane. The electrochemical system should also be carefully designed to minimize ohmic losses in order to improve energy conversion efficiency. The development of an electrochemical reduction system in which CO₂ reduction would not need a significantly more negative voltage than the thermodynamic requirements would appreciably contribute to the improvement of the energy conversion efficiency. The developmental work was undertaken following these scale-up approaches.

3. SCALE-UP RESULTS

Omnidea in collaboration with research institutes developed new electrodes based upon the modification of copper electrodes for the electrochemical reduction of CO₂ to hydrocarbon fuels (CH₄, C₂H₄ and C₂H₆) [15]. The catalytic behaviour of the copper electrode is enhanced by the presence of electrodeposits, leading to hydrocarbon mixtures with a higher energetic density per unit volume compared to fuel resulting from CO₂ reduction with unmodified copper electrodes. The laboratory studies successfully proved the concept that CO₂ could be reduced to a mixture of C₂ and C₁ hydrocarbons using KHCO₃ as the electrolyte with a Pt mesh as anode, an Ag/AgCl reference electrode and modified copper as the working electrode. The nominal electrodes dimensions were ca. 2 cm².

The laboratory scale reactor had a capacity of 150 ml of electrolyte in each of the cathodic and anodic compartments. The cell design is shown in Fig. 2 and the actual manufactured cell is shown in Fig 3.

This system showed typical maximum ethylene Faradaic yields of ca 33% and current densities in the range of 5-23 mA/cm² at -1.9V vs. Ag/AgCl. It was confirmed that the presence of electrodeposits leads to a steady process of reduction of CO₂ to hydrocarbons over a period of four hours.

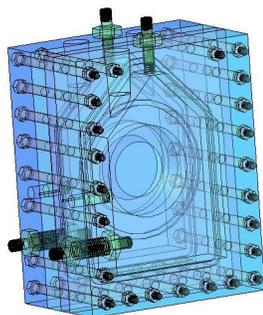


Figure 2. Cell design

Further electrode optimization work was carried out. Fig. 4 shows the cathodic polarization curve for Omnidea electrodes of ca. 5 cm² nominal area in CO₂ saturated electrolyte and N₂ saturated electrolyte.

These results were obtained using a 500 ml glass cell with 250 ml electrolyte in a three electrodes configuration system. Two platinum



Figure 3. Manufactured Cell

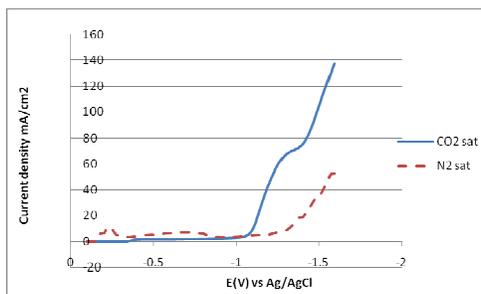


Figure 4. Polarization curve of Omnidea electrodes

electrodes were used as counter electrodes and the reference electrode was an Ag/AgCl. The working electrodes were Omnidea copper deposit modified electrodes. In table 1 the contribution of CO₂ reduction current density to the total current are reported in percentage for several potential values.

Table 1- Contribution of CO₂ reduction current density to the total cell current

Potential (V)	% Current Density
-1.2	88%
-1.4	76%
-1.6	62%

The onset of carbon dioxide reduction starts at ca. -1.0V vs. Ag/AgCl. As the potential becomes more negative the contribution of the hydrogen evolution reaction increases. It should be stressed that as potentials as negative as -1.6V vs. Ag/AgCl CO₂ reduction is still dominant over hydrogen evolution. Current densities near the threshold suitable for technological applications were obtained.

A further scale-up of the system was carried out aiming at determining its energy conversion efficiency. For this task a cylindrical-shaped reactor with two compartments for electrolyte (1.5 l each) and one for a membrane was designed and constructed.

The supports for the working electrode and the counter (or secondary) electrode were designed so as to allow the electrodes to be mounted and un-mounted easily between each experiment, see Fig. 5. All the parts of the reactor are made from acrylic to guarantee electrical isolation. Only the fittings that were used to connect the cell to the gas distribution system are made of stainless steel and the o-rings are made of Viton. In order to add reference and pH electrodes to the system, conical ground acrylic joints similar to those used in the small reactor were made in the top of the cell.

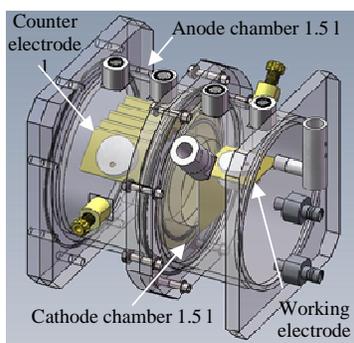


Figure 5. Three litre electrochemical cell



Figure 6. Actual electrochemical cell

4. CONCLUSIONS AND FUTURE PROSPECTS

Encouraging results were obtained with modest nominal size electrodes. Based upon preliminary work Faradaic efficiencies for ethylene production are expected to be higher than 60%. Experimental work is currently being

performed to confirm these projections.

Ongoing work is also addressed to obtaining sustained prolonged electrode performance, enabling the system to operate for extended periods of time so as to produce the 12 litres of gas required for each test in a SOFC.

5. REFERENCES

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