

Electrochemical Systems for Production of Syngas and Co-Products

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Syngas is a very useful mixture of H_2 and CO that can be utilized to synthesize a great variety of commodity chemicals and transportation fuels using established methods. Conventional methods create syngas using fossil resources which releases carbon into the atmosphere. Electrochemistry offers a clean method of producing this gas mixture. Two major technical issues exist for efficient electrochemical reduction of CO_2 : 1) mass transport limitations due to the limited aqueous solubility of CO_2 and 2) kinetic limitations leading to loss of energy efficiency. The first limitation can be dealt with by using gas diffusion electrodes (GDE) and pressurized cells. The second limitation results in reduced efficiency and will require additional catalyst development to improve. However, there may be situations where low value electricity or grid isolated energy sources (wind and solar) could overcome efficiency losses. Thus this process could be configured to act as a load leveling device for intermittent electrical supplies and converting this energy to a useful product. This abstract describes a project which has used technical data from previous work in both CO_2 and H_2O electrochemical reduction to build electrochemical systems to produce syngas mixtures. This project's goal is to collect data to enable pilot scale design and production.

To increase the current density for CO_2 reduction, mass transport must be increased beyond that possible on conventional flat electrodes. Using previous work^{1,2,3} on CO_2 reduction as a guide, an alternative pressurized electrolysis system has been constructed which operates at elevated CO_2 pressure and performs CO_2 reduction on Ag-catalyzed GDE (Silflon). Both the ambient pressure and elevated pressure systems utilize filter-press cell designs to minimize resistive losses and provide data for scale-up. Dimensionally stable anodes were used to evolve O_2 from a caustic solution. The cathode solution chemistry is largely determined by carbonate acid-base equilibria. While protons are consumed by the cathodic reactions, CO_2 reacts with hydroxide to produce carbonate salts. A variety of solution chemistries and both anion exchange membranes (AEM) and cation exchange membranes (CEM) have been studied.

Using the ambient pressure system a number of process variables were investigated.⁴ Electrolysis cells such as those used in alkaline water electrolysis operate at elevated temperature where resistive and kinetic losses heat the system. The increased temperature reduced the overall cell voltage and cathode voltage, particularly at higher current densities. The Faradaic efficiency (FE) for CO decreases slightly with temperature. Increasing the current density has a more pronounced effect on the FE for CO, where the H_2 :CO ratio increases. Another factor controlling the H_2 :CO ratio is the CO_2 flow rate into the GDE: by varying the flow rate it was possible to achieve specific H_2 :CO ratios between 3:1 and 1:9. This effect provides significant product selectivity control needed to

provide specific syngas ratios for downstream conversion to hydrocarbon products.

Reproducibility data show that the system was reproducible both in terms of the potentials necessary for CO_2 reduction, but also in its ability to produce a specified syngas composition. System stability was demonstrated by operating the cell for many hours at various operating conditions. After an initial stabilization period of 40 min, long-term cell performance was stable. The present design has shown bench scale reduction of CO_2 can be performed at current densities which are near those currently employed in industrial alkaline electrolysis cells.

The influence of S poisoning on Ag electrodes⁵ and the impact of membrane type and electrolyte composition⁶ on syngas production have also investigated and will be discussed. In addition to the ambient pressure measurements described above, work using pressurized CO_2 has been performed.⁷ The pressurized system displays reproducible behavior at both room and elevated temperatures and the quantity of CO which can be generated is 5 times that observed using similar electrodes at ambient pressure. Above 15 atm it is possible to generate CO at 80% FE at 225 mA/cm². The FE for CO was 92% at 24.7 atm and 350 mA/cm². It was found the pressurized cell operates at lower cell voltage than obtained using the same electrode materials at ambient pressure. Work is continuing to develop this system to couple the electrolysis products to catalytic systems for conversion to hydrocarbon products.

Recently, work has been performed on a novel process called chlor-syngas. This process links two electrochemical technologies that dovetails into chemical process streams already in practice: 1) The co-electrolysis of H_2O/CO_2 to generate syngas and 2) oxidative production of Cl_2 gas is an industrial practice. The proposed process would utilize recycled HCl from industrial chlorination reactions and CO_2 from combustion sources. By performing two useful synthetic processes (Cl_2 + syngas) using the same power input and consuming two waste streams (CO_2 and HCl), the economics can be swayed in the favor of clean technologies. Initial bench-scale work has shown great promise despite low pH values observed within the catholyte⁸. The maintenance of high CO production at low pH was thought to be due to the pore structure of the GDE, where pH is defined by the chemistry due to electrolysis versus the bulk electrolyte.

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