Electrochemical Reduction of Carbon Dioxide to Chemicals and Fuels

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Introduction
The electrochemical conversion of carbon dioxide (CO2) to chemicals and fuels is aimed at minimizing the greenhouse gas reduction and reducing the dependence on petroleum for the synthesis of chemicals. Considering the large emissions from industrial activities, CO2 can easily serve as a chemical feedstock for the synthesis of industrially important chemical intermediates such as HCOOH, HCHO, CO, methanol etc. At present there are no industrial platforms efficiently converting CO2 to chemicals and fuels. Research and development studies performed at Liquid Light in association with Princeton University have shown that CO2 can be converted to various C1-C2 organic chemicals and fuels through the use of heterocyclic amine catalysts [1-3]. In addition, our experiments reveal that through the use of proper catalyst and cathode combination one can produce carbon monoxide (CO) and hydrogen in a ratio similar to syngas [4] which opens the door for the industrial synthesis of diesel-type fuels via a Fischer-Tropsch process.

Materials and Methods
The aqueous phase electrochemical studies have been conducted both in batch as well as flow reactor equipped with either Saturated Calomel Electrode or Ag/AgCl reference using multichannel Arbin potentiostat. The CO2 gas was continuously bubbled to maintain the constant feed of the reactant in the reactor. All the samples have been analyzed by Ion Chromatography and Gas Chromatography equipped with Mass Spectrometry. NMR studies have been performed to understand the stability of catalysts and catalytic processes. SEM and TEM were employed to understand the surface morphology of the cathode before and after the cathodic reactions. The other half of the reaction, which is the anodic oxidation of water to oxygen was performed in collaboration with University of Wisconsin using cobalt based oxides in a nearly quantitative manner [5].

Results and Discussion
CO2 reduction studies were conducted by electrochemical method in aqueous conditions using heterocyclic amine catalysts and the products were confirmed by controlled studies involving 13CO2 gas. The CO2 reduction was efficiently achieved at overpotentials below 500 mV for C1-C2 products and the catalysts appear to be very stable with no degradation as seen in the NMR studies. The stability of the cathodes have been explored using SEM and TEM techniques and showed that the surface morphology of the transition metals were very stable in the time dependent studies conducted over a period of 5 days. The use of appropriate substituted heterocycles in combination with specific cathode materials and cell conditions (pH and electrolyte) provided means of controlling the CO2 reduction product ranging from C1 to C4 chemicals. Stable high surface area cathode structures and coatings have been developed which could allow long-term operation with current densities exceeding 100 mA/cm2. Faradaic efficiencies of up to 80% have been sustained at ambient temperature and pressure. Electrocatalytic pathways for conversion of CO2 and water to synthesis gas have also been discovered. Through materials selection and control of cell conditions, syngas with desirable ratios of carbon monoxide to hydrogen could be produced in a single reactor with overpotentials as low as 200 mV.

Significance
The United States and the rest of the world face the threat climate change brought about by CO2 emissions from the combustion of fossil fuels. Also the dependence on oil for the production of small chemical intermediates is increasing which causes instability due to socio-economic policies on Oil around the world. These two important problems can be addressed using CO2 as feedstock for the production of green chemicals intermediates and eventually decreasing the pollution.

Figure 1. The schematic diagram of the flow reactor used for the electrocatalytic conversion of CO2 to formic acid

References