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Short communication

Electrochemical reduction of CO_2 with clathrate hydrate electrolytes and copper foam electrodes

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ABSTRACT

We report on the first use of clathrate hydrates as electrolyte additive in the electrochemical reduction of carbon dioxide. Clathrate hydrates allow the enrichment of significantly larger volumes of gas than liquids can usually dissolve. Electrolyte solutions containing $10\%_{mass}$ THF with and without CO_2 containing clathrate hydrates were investigated with a copper-foam working electrode. Our results show that at −1.0 V vs Ag/AgCl the Faradaic efficiency for the production of CO and further reduced carbonaceous products was 80% with clathrates vs 20% with non-clathrate electrolytes of identical chemical composition at nearly equal temperature.

1. Introduction

Interest in the electrochemical reduction of CO_2 at metal electrodes has increased significantly in recent years in response to the rising cost of petroleum, increasing demand for sustainable products, and a growing renewable energy industry with its corresponding need for large-scale energy storage [1–4]. In 1985, Y. Hori et al. published a comprehensive study of this reaction at different metal electrodes [5]. They found that copper was the best electrocatalyst for reducing CO_2 to an assortment of high-value products including methane, formic acid, and ethylene. Although these products were produced at reasonably high Faradaic efficiencies (FEs) [6], this reaction proceeds at high overpotentials, is non-selective, and is accompanied by the competing hydrogen evolution reaction (HER). Nevertheless, copper remains the electrocatalyst of choice for converting CO_2 into hydrocarbons.

Typically, electroreduction of CO_2 at a metal electrode is performed in an electrolyte solution saturated with CO_2. Previous studies suggest that this reaction may be limited by the relatively low CO_2 solubility of 0.1 mol% in water [7] at 0 °C and ambient pressure [8]. Increasing the pressure of the system is one option for increasing the concentration of CO_2 in the electrolyte, but mechanical pressurization increases the complexity of the reactor design and overall costs. Reducing the temperature of the system is another option for increasing the concentration of CO_2 in solution, but with limited effect; the CO_2 concentration in water increases from 0.04 mol% at 20 °C to only 0.1 mol% at 0 °C [7]. Ice-like substances, called clathrate hydrates, can be used to capture large quantities of CO_2. Compositions of water, clathrate hydrates, and electrolytes form an electrolytic fluid with a high overall CO_2 concentration that has the appearance of snow slush. Here we report the use of such electrolytic fluids as a novel approach for increasing the Faradaic efficiency of the electrochemical CO_2 reduction. We do not yet know whether the enrichment of CO_2 in the clathrates causes a local supersaturation at the working electrode. Nevertheless, we do observe the shift of the relative rates of electrochemical reduction of CO_2 and H^+ to favor the production of carbonaceous products compared to electrolyte fluids with identical chemical composition but without clathrates and therefore reduced overall CO_2 concentration.

Water containing solvated gasses with molecular diameters between 0.275 nm and 0.75 nm can form inclusion compounds called clathrate hydrates under suitable thermodynamic conditions. The gas-solute molecules occupy and stabilize, but do not bond to clathrate hydrates [9]. Gasses known to form clathrate hydrates include CO_2 [10–13], CH_4 [14,15], N_2 [16], CO [17,18], H_2 [19] and hydrocarbons [20,21]. As much as 170 L of CO_2 gas [9] can be trapped in 1 L of clathrate hydrates, two orders of magnitude greater than the solubility of CO_2 in water. Linga et al. [22–24] demonstrated the addition of tetrahydrofuran (THF) drastically reduces the pressure required for clathrate formation and allows for formation in the absence of solute gasses. The density of the clathrate/aqueous slush is related to the amount of THF added. For a solution containing 1.5 mol% THF, clathrate hydrates form under ambient pressure when the solution temperature is approximately 0 °C [23,25]. The THF will occupy some of the larger clathrate structures leaving fewer vacancies for gasses to occupy [13]. Enrichment of THF clathrate hydrate cages with CO_2 proceeds spontaneously at

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ambient pressure. Consequently, highly concentrated CO_2 is available in the electrolyte and can be delivered to the working electrode without the need of mechanical pressurization, an attractive feature for industry-scale utilization of CO_2.

The gas stream of CO_2 does not have to be pure. Both CO_2 and N_2 mostly occupy the small clathrate cages when THF is present. The CO_2 mole fraction in clathrates can be enriched relative to that of a mixed gas stream. For instance, using a 1 mol% THF water solution at 277 K and a gas mixture with a 30 mol% CO_2 and 70 mol% N_2 at 7 bar total pressure yields clathrates with 50 mol% CO_2 [26].

In addition, clathrates can prevent impurity solutes in an electrolyte from interfering in the electrochemical reduction of CO_2. We show that butylated hydroxytoluene (BHT), a widely used radical scavenger for the chemical stabilization of THF and many other chemicals, does not interfere with electrochemical processes performed in clathrate electrolytes. A similar effect should occur with other impurities as well. Thus, clathrates allow us to increase the CO_2 concentration in the electrolyte at ambient pressure, and render impurities ineffective that would otherwise interfere with the electrochemical reduction of CO_2.

2. Materials and methods

2.1. Materials

Potassium bicarbonate ($KHCO_3$, ≥99.99%, Sigma-Aldrich 431583), copper sulfate (97%, Mallinckrodt 4848), sulfuric acid (98%, Fisher Scientific A300C-212), tetrahydrofuran with and without butylated hydroxytoluene (BHT) (Fischer Scientific T397 with 125 ppm BHT and T427SK with no BHT), and carbon dioxide (CO_2, 99.995%, Corp Brothers) were used as received. Deionized water (18.2 MΩ, Milli-Q water purification system) was used to prepare electrolyte solutions. Copper foam electrodes measuring 2 cm^2 were prepared ex-situ as previously described [27].

2.2. Formation of clathrate hydrates

An electrolysis for a minimum of 12 h with continuous Argon (Ar, 99.999%, Corp Brothers) was purging. $10\%_{mass}$ THF was then added to this purified solution. THF stabilized with BHT was chosen due to the increased safety profile and smaller concentration of reactive peroxides. This solution was used for control and clathrate experiments. Clathrate hydrates formed under continuous purging with carbon dioxide in a pure carbon dioxide environment at around 1.015 bar (absolute) under mechanical stirring at roughly 130 rpm, and chilling at 274.5 K for 6–24 h in a custom batch reactor. Clathrate hydrates were experimentally confirmed to contain around 9 times as much CO_2 as the control solution.

2.3. Electrochemistry

Bulk electrolysis were performed in a H-type, gas tight, well stirred, two-compartment electrochemical cell separated by a proton-exchange membrane (Nafion 117, DuPont) using a Pine Research Instrumentation AFCBP1 bipotentiostat. The proton-exchange membrane was stored in electrolyte solution for a minimum of 12 h before use. A standard electrode configuration was used consisting of copper foam as working electrode and a custom-made Ag/AgCl reference electrode separated from a platinum (Pt) mesh as counter electrode. All potentials reported are referenced to an Ag/AgCl electrode (+190 mV vs SHE).

The electrochemical cell was lowered into a circulating water bath for temperature control with care taken to prevent contamination of the Nafion membrane. Clathrate experiments were performed at 2.0 °C and control experiments were performed at 4.0 °C to insure the absence of clathrates. Prior to each experiment, the electrolyte was purged for a minimum of 30 min with CO_2 at a flow rate of at least 20 mL/min. All experiments were repeated at least 3 times.

2.4. Gas product quantification

One milliliter aliquots of catholyte compartment headspace were injected into a Buck Scientific 910 gas chromatograph (GC). Aliquots were collected after 30 min of electrolysis to quantify the concentration of gaseous products. Removal of THF and other possible contaminants from the GC columns was confirmed before each run. Concentration levels measured by the GC were averaged across aliquots. Partial current and Faradaic efficiency of each gaseous product were determined from the ratio of measured product concentration to concentration expected for 100% Faradaic efficiency from the total charge passed during a typical electrolysis experiment. Owing to the honeycomb structure lined with dendritic protrusions of the copper foams, Faradaic efficiencies are reported rather than current efficiency because of the difficulty in measuring total surface area of the foams.

2.5. Liquid product quantification

Liquid products from the electroreduction of CO_2 were quantified using 1D ^1H NMR. ^1H spectra were recorded on Bruker Avance DRX-400 (400 MHz) and Avance 600 (600 MHz) spectrometers. The THF and water peaks were suppressed by a modified version of the WET solvent suppression technique [28].

3. Results and discussion

In this work, a copper foam electrode with electrodeposition time of 15 s was chosen for its best compromise of mechanical stability and pore network with expected intermediate diffusion distance for CO_2 [27]. Electrolysis experiments were performed in an H-type cell under potentiostatic conditions at three applied voltages (−1.0 V, −1.3 V, −1.7 V vs Ag/AgCl). The Cu-foam electrodes were mechanically stable in that the porous structure remained intact during preparation, handling, and electrochemical experiments. The electrolyte fluid was filtered yielding a somewhat moist filtrate of clathrate hydrate crystals with the appearance of snow. The filtrate's mass was 14% of the total fluid's mass. Despite this rather small clathrate concentration, the clathrate hydrate fluid was measured to contain around 9 times as much CO_2 as the control solution. We confirmed that only H_2 is formed using the THF-containing electrolyte without CO_2. Thus as expected, THF was electrochemically inert under our reduction conditions [29]. Formic acid, H_2, and CO were found to be the major products produced while CH_4 and higher hydrocarbons ($>C_2$) were minor products. Fig. 1 shows the FEs of gaseous and liquid products from electro-reduction of CO_2 at the Cu-foam electrode in non-clathrate and clathrate electrolytes. One can generally observe that the H_2 production is lower when clathrates are present as compared to when they are not present in the electrolyte. Instead, more carbonaceous products were formed. The total FE approached 100% for all measurements except when the applied voltage was −1.7 V. At this voltage, it is possible that a liquid product formed in an amount below the detection limit of our NMR measurements. At −1.7 V, FEs for the products formed are similar regardless of the presence or absence of clathrate hydrates in the electrolyte.

Faradaic efficiencies of CO_2 reduction products and HER at three different voltages (−1.7 V, 1.3 V, −1.0 V) are shown in Fig. 1. These values are scaled by a correction factor that accounts for the scavenging of radical protons by BHT (a stabilizer included in THF). The scaling factor was determined by running reductions with and without BHT to quantify the decrease in the HER with BHT present. At −1.7 V, the FEs of the major products (upper plots of Fig. 1) are comparable regardless of the presence or absence of clathrates. In contrast, the FE of the major products diverges significantly at −1.3 V. For example, the FEs of CO (20% vs. 5%) and methane (~1% vs. 0.2%) are higher when clathrates are present whereas FEs of C_2 products are unchanged. Any change in the FE of formic acid with and without clathrates present