Electrochemical reduction of CO₂ with clathrate hydrate electrolytes and copper foam electrodes


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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ into hydrocarbons.

Typically, electroreduction of CO₂ at a metal electrode is performed in an electrolyte solution saturated with CO₂. Previous studies suggest that this reaction may be limited by the relatively low CO₂ 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 CO₂ 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 CO₂ in solution, but with limited effect; the CO₂ 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 CO₂. Compositions of water, clathrate hydrates, and electrolytes form an electrolytic fluid with a high overall CO₂ 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 CO₂ reduction. We do not yet know whether the enrichment of CO₂ 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 CO₂ and H₂ to favor the production of carbonaceous products compared to electrolyte fluids with identical chemical composition but without clathrates and therefore reduced overall CO₂ 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 CO₂ [10–13], CH₄ [14,15], N₂ [16], CO [17,18], H₂ [19] and hydrocarbons [20,21]. As much as 170 L of CO₂ gas [9] can be trapped in 1 L of clathrate hydrates, two orders of magnitude greater than the solubility of CO₂ 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 CO₂ proceeds spontaneously at
ambient pressure. Consequently, highly concentrated CO₂ 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 CO₂.

The gas stream of CO₂ does not have to be pure. Both CO₂ and N₂ mostly occupy the small clathrate cages when THF is present. The CO₂ 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% CO₂ and 70 mol% N₂ at 7 bar total pressure yields clathrates with 50 mol% CO₂ [26].

In addition, clathrates can prevent impurity solutes in an electrolyte from interfering in the electrochemical reduction of CO₂. 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 CO₂ concentration in the electrolyte at ambient pressure, and render impurities ineffective that would otherwise interfere with the electrochemical reduction of CO₂.

2. Materials and methods

2.1. Materials

Potassium bicarbonate (KHCO₃, ≥ 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 (CO₂, 99.995%, 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 CO₂ as the control solution.

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ [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 CO₂ as the control solution. We confirmed that only H₂ is formed using the THF-containing electrolyte without CO₂. Thus as expected, THF was electrochemically inert under our reduction conditions [29]. Formic acid, H₂, and CO were found to be the major products produced while CH₄ and higher hydrocarbons (>C₂) were minor products. Fig. 1 shows the FE of gaseous and liquid products from electro-reduction of CO₂ at the Cu-foil electrode in non-clathrate and clathrate electrolytes. One can generally observe that the H₂ 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, FE of the products formed are similar regardless of the presence or absence of clathrate hydrates in the electrolyte.

Faradaic efficiencies of CO₂ 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 C₂ products are unchanged. Any change in the FE of formic acid with and without clathrates present
is indeterminate. At $-1.0$ V, the FE of all carbonaceous products is 20% in the absence of clathrates compared to a FE of 80% in the presence of clathrates. While the FE of HER is suppressed to a consistent 20% at all potentials studied when clathrates are present, the FE of HER decreases from 70% to 25% with increasing overpotential in the absence of clathrates. Suppression of HER when clathrates are present allows a consistently high FE (65–75%) for all carbonaceous products at all potentials studied.

It is important to note that at $-1.0$ V, the FE of CO is 70% and the FE of gaseous hydrocarbons is 8% compared to 3.5% when clathrates are absent. While we cannot exclude the possibility that reaction mechanisms change when changing from an electrolyte without clathrates to one with clathrates, we propose that the reaction kinetics change as a consequence of an increased CO2 concentration (local super-saturation) at the electrode surface. The higher concentration of CO2 should lead to an increase in the rate of reaction for the electrochemical reduction of CO2 compared to that of HER in a manner similar to experiments performed at high pressures of CO2 [8].

THF stabilized with 100–135 ppm BHT was used in our experiments. While pure (unstabilized) THF could have been used, THF stabilized with BHT is of greater interest because of the importance of suppressing the formation of hazardous peroxides in an industrial application. Furthermore, we determined that BHT does not interfere with the electrochemical reduction of CO2 in clathrate electrolytes although it does suppress HER in electrolytes without clathrates. We quantified the effect of BHT on the FE of the HER by comparing data obtained in electrolytes containing stabilized THF (BHT present) or pure THF (BHT absent). Shown in Fig. 2 are the results obtained when the working electrode is held at $-1.3$ V or $-1.0$ V for 20 min.

Considering the small concentration of BHT (115 ppm), the probability of radical scavenging within the electrolytic double layer is very small. At more reductive potentials (e.g., $-1.7$ V vs Ag/AgCl), charge consumable by BHT is negligible as the BHT is exhausted almost immediately. At more anodic potentials we correspondingly expected BHT to survive longer. By our estimation based on BHT concentration and charge passage rate, at $-1.3$ V, 20–25 min is necessary to consume BHT at our lower potentials vs 5 min at $-1.7$ V. Experimental evidence supports this estimation. After 20 min of electrolysis at $-1.0$ V and $-1.3$ V H2 production was measured to be significantly greater with unstabilized THF as compared to stabilized THF. After 60 min of electrolysis the difference in H2 production using stabilized and unstabilized THF decreased substantially. In line with the expectation, the effect of BHT on the H2 production is not as marked for $-1.3$ V (Fig. 2 left) yet still noticeable. Interestingly, BHT in clathrate electrolytes appears to impact the H2 evolution yet not the product distribution (vide supra).

4. Summary and conclusions

We demonstrated that the presence of clathrate hydrates substantially increases the FE for the production of carbonaceous products at low overpotentials while suppressing the competing HER. Moreover, the production of heavier hydrocarbons is promoted by clathrate-containing electrolytes. Considering that the FE increases at lower overpotentials, hydrocarbon yields with over 80% FE at reduction potentials close to the thermodynamic limit are conceivable and will be explored in future studies. In addition, clathrate-containing electrolytes are a slushy fluid that can be pumped easily to deliver high concentrations of CO2. The CO2 concentration can be further increased by
increasing the clathrate content of the fluid. These features offer technological advantages that may prove to be important in industrial-scale processes that integrate capture and concentration of CO₂ with its electrochemical reduction to feedstock chemicals.

Conflict of Interest

none.

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References