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Electrochemical Production of Syngas from CO_2 Captured in Switchable Polarity Solvents

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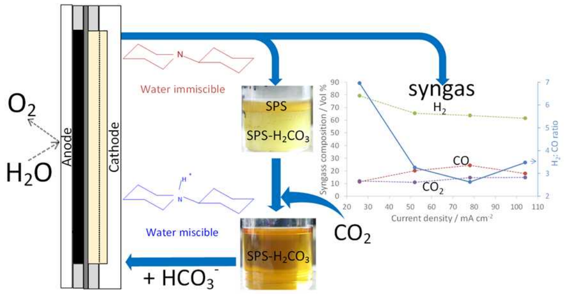
GRAPHICAL ABSTRACT



Switchable polarity solvents allowed for the first time the electrochemical reduction of captured CO_2 for an efficient production of syngas

ABSTRACT

An operational advantage that enables the deployment of technologies for the valorization of CO_2 can be achieved through the integration of the capture and conversion technologies. In that perspective, switchable polarity solvents (SPS) were assessed as re-usable capture-electrolyte media for the electrochemical production of syngas at low temperatures and pressures. A polymer electrolyte membrane cell was used to liberate captured CO_2 gas in proximity to the cathode without the addition of CO_2 gas. Due to the proximate location of release, the produced syngas had minimal CO_2 dilution with

H_2:CO ratios between 2 to 4. For the first time captured CO_2 has been reduced to CO with conversions and yields over 70 % and at current densities over 100 mA cm^{-2}.

Introduction

Exploitation of CO_2 as a feedstock is of growing research interest that goes beyond the environmental target associated with the abatement of greenhouse gas (GHG) emissions. Technology development is moving toward the generation of value from already available low-cost CO_2, which can be used as primary feedstock for the future generation of non-fossil fuels and chemicals.[1] Parallel efforts are currently underway in the development of supplementary technologies that can be classified as CO_2 capture and storage storage (CCS), and CO_2 utilization.[2, 3]

Post combustion capture of CO_2 with primary and secondary alkanolamines to trap the CO_2 as carbamates [$RNHCOO^-$] is one of the better developed CCS lines of research.[4] Over 70 years of work have gone into developing amine based CCS in hopes of it becoming industrially relevant technology.[3, 5] However, high energy consumption for the amine regeneration via carbamate decomposition to release CO_2 (the inverse of the CO_2 absorption enthalpy) is a major draw back and threatened the economic feasibility of the alkanolamine CCS process.[6] An alternative to alkanolamines are tertiary amines that can capture CO_2 as bicarbonate [HCO_3^-] and may reduce the energy demands of CCS.[6] Even still cost efficient CCS does not seem to be feasible, in the long term, without additional generation of value through the utilization of the captured CO_2 as feedstock for the production of fuels and chemicals.[2, 3] Combination of capture and utilization (CCU) thus appears to be a superior alternative to the high energy requirements of CCS.[7, 8]

Electrochemical reduction of CO_2 is one of the technologies that can be coupled with CCS to generate a diversity of value added products, which include but are not limited to alcohols, hydrocarbons, and syngas.[9, 10] However, a previous analysis of the CO_2 reduction process feasibility concluded that the two electron product, CO (or syngas) and formate, are the only products that could conceivably compete with conventional chemical production processes. Any product, requiring more than two electrode transferred per mole of CO_2, will cost more to be produced than the current market value.[11]

As a valuable product, syngas is a mixture of H_2 and CO, whose composition can be tuned for the synthesis of a variation of fuels and commodity synthetic chemicals, which can substitute fossil derived fuels without changes in the current chemical generation, transportation, and distribution infrastructure.[12] In aqueous media, and/or in the presence of water, syngas is the most favorable product from the electrochemical reduction of CO_2 to CO since the hydrogen evolution reaction (HER) cannot be completely avoided and unlike formate (the other 2e- product), separates from solution as a gas. Hence, a sustainable green chemical production could be achieved via syngas production from captured CO_2 if renewable energy sources are used to power the electrochemical reduction of CO_2.[12-15]

To date, the main technical problems identified as challenges in to scale-up the electrochemical reduction of CO_2 are:[11] 1) the low solubility of CO_2 in aqueous media and 2) mass transfer and kinetic limitations. These problems, combined, result in systems that operate at low current density ca. 20 mA cm^{-2} or less, commonly reported in the literature, and require high amounts of CO_2 gas to be continuously fed to the electrochemical reactors.[11, 16, 17] As a result, slow production rates, low conversion and additional downstream feedstock and products separation are featured. An electrochemical process' current density separates industrial feasible processes from academic curiosities as a systems capital cost and various operational costs are inversely related to the systems operational current density.

Catalyst development, electrolyzer architectures, and electrolyte formulations, have been proposed as alternatives to address the previously mentioned challenges with focus in high current efficiencies for

CO at meaningful current densities.[12, 18, 19] The work of Verma et al.[20] reported high current densities > 400 mA cm^{-2} and CO Faradaic efficiencies (FE) over 90 % when 3M KOH was used as electrolyte in a microfluidic reactor that uses Ag gas diffusion electrodes (GDE). In another work from Dufek et al.[17] a pressurized system that operates over 15 atm showed the production of syngas at current densities far in excess of 350 mA cm^{-2} with CO FE ca 90 %. While these works were able to overcome one of the most significant technology challenges for technology commercialization, both processes required continous addition of stochiometric excess of CO_2, which ended in diluted product streams.

One of the main advantages that combining carbon capture process with the electrochemical reduction of CO_2 has over standalone CO_2 reduction prcesses is that the CO_2 feed can be fed to the electrochemical reactor in an aqueous soluition in an already concentrated form. A recent work by Zhang et al.[21] reported the first attempt to electrochemically reduce CO_2 captured in a monoethanolamine medium. However, no electrochemical reduction of captured CO_2 was achieved as the system requires the continuous addition of gaseous CO_2 as source of free CO_2. It has been well established that CO_2 and no other associated form is the reducible species.[21-23] Ionic liquids, which poses other benefits toward the suppression of the HER, have also being tested as capture-electrolyte media for CO_2 reduction,[20] but the need for CO_2 gas feed remains.

Technical approach

As a technological alternative for the reduction of captured CO_2, this work proposes use of switchable polarity solvents (SPS) as a CCU technology. SPS (also reported as switchable hydrophilicity solvents SHS)[24, 25] are emerging as an extremely versatile class of materials that can shift polarity upon being exposed to a chemical agent, namely CO_2.[24] The use of SPS can be extended to many applications as solvent for chemical synthesis, floculation, water treatment and water desalination.[7, 26-28] Insoluble tertiary amines react with CO_2 to form soluble ions [HNR_3^+] and [HCO_3^-] (Sheme 1).[.4] Hence, a novel use is proposed for SPS as capture-electrolyte media for the for the electrochemical production of syngas from CO_2.

$$\begin{array}{ll}
SPS_{(org)} + CO_{2(gas)} + H_2O \rightarrow SPSH^+_{(aq)} + HCO_3^- & \text{Capture} \\
HCO_3^- + H^+ \rightarrow CO_2 + H_2O & \text{Release} \\
CO_{2(gas)} + H_2O + 2e^- \rightarrow CO_{(gas)} + 2OH^- & \text{Reduction} \\
SPSH^+_{(aq)} + OH^- \rightarrow SPS_{(org)} + H_2O & \text{Recovery}
\end{array}$$

Scheme 1. CO_2 capture and utilization cycle

1-Cyclohexylpiperidine (CHP) was tested as SPS for the capture and electrochemical reduction of CO_2 based on high CO_2 absorption capacities, up to 189.63 g/L, compatibility with polymeric systems, and expected low production cost.[29-31] As capture-electrolyte media for the utilization of CO_2, CHP presents additional ideal characteristics, such as low volatility, effective polar-to-nonolar phase transition, low membrane permeability, and compatibility with a wide range of materials.[27]

A buffer-layer-type cell with a cation exchange (CEM), inspired in the work of Delacourt et al.,[23] was used to perform the electrochemical release and reduction of captured CO_2. A scheme of the electrolysis system and a description of the membrane electrode assembly MEA are shown in Figure 1.Water oxidation occurs in the anode side of the electrochemical cell releasing O_2 gas and generating H^+ ions that are transferred through the CEM. On the cathode side H^+ ions create a localized acidic environment that in contact with the [HCO_3^-] releasing CO_2 for reduction, in-situ, and near the electro-catalyst surface. As a simple acid-base reaction CO_2 release should not limit the cathodic process maintaining an adequate CO_2 concentration on the surface of the cathode. Upon the release of CO_2 the CHP switches polarity back to water insoluble, allowing the recovery and re-utilization of the capture media. Bulk reduction experiments were performed at significant current densities > 25 mA cm^{-2}, and for the first time it was demonstrated the reduction of captured CO_2, without addition of a stoichiometric excess of CO_2 gas, for the production of syngas. As a main result non-diluted syngas can be obtained as product at low temperature and pressures.

Results and discussion

GC analysis of the prepared CHP-H_2CO_3 stock solution established that the CHP concentration in the aqueous stock solution (captured CO_2) reached a concentration of 2.7 M. Several dilutions of the stock solutions in DI water were prepared, and ionic conductivities were measured as shown in Figure 2. As the cathode electrode is separated from the CEM, ionic conductivity becomes a significant parameter in controlling electrode polarization and reaction efficiencies. With the aim to have the highest concentration of CO_2 stoichiometrically proportional to CHP), with the highest ionic conductivity, 1.25 M CHP-H_2CO_3 (20 mS cm^{-1}) was used from this point forward to perform the electrochemical reduction experiments.

Proof of concept experiments were performed at constant current density of 100 mA cm^{-2} during 30 min at 0 psig and 20 psig cathode side back pressure (self pressurized). Analysis of the produced gases demonstrated the presence of CO and an H_2 as products of the CHP-H_2CO_3 electrolysis as well as CO_2 released from the CHP-H_2CO_3 solution. Other experiments, not reported here, were performed at lower current densities where CO was not observed in the gas product. A summary of the produced gas concentrations and volumes for all the experiments reported in this paper is shown in Table S1 ESI. In the liquid stream, two phases were observed, being the top phase released CHP, and the bottom phase the aqueous solution with unreacted CHP-H_2CO_3. Hydrogen was the main product in the gas stream and low CO FE of 1.1 % and 2.9 % were observed at 0 psig and 20 psig, respectively. On the other hand, higher amounts of CO_2 were released when no back pressure was applied.

These results suggest a beneficial effect on the back pressure possibly re-dissolving unreacted CO_2, hence increasing the efficiency for CO production. During the operation the cell potential varied from ca 5.5 V to 4.5 V. High electrode polarization induced by the low ionic conductivity was then attributed to be one of the main causes for high voltage.

Addition of a supporting electrolyte was investigated to increase the ionic conductivity of the CHP-H_2CO_3 solution. $KHCO_3$ was tested as the first option. However, upon the addition of $KHCO_3$ some phase separation in the liquid phase was observed, which was associated with the release of some of CO_2 from the CHP-H_2CO_3 solution. K_2SO_4 was tested as supporting electrolyte as it has been previously proved to be a suitable electrolyte for CO_2 reduction.[17, 32] Diluted CHP-H_2CO_3 solutions with 0.2 M K_2SO_4 were prepared from the stock CHP-H_2CO_3. Hence the ionic conductivity was measured as shown in Figure 2. A 47% increase in conductivity was observed for the 1.25 M CHP-H_2CO_3 solution with 0.2 M K_2SO_4. Nevertheless, close to a 10 fold increase in the CO production and FE were obtained during the electrochemical reduction experiments.

Figure 3 shows the composition of gases produced during the electrochemical synthesis of syngas from captured CO_2 at 25 ◦C, 20 psig back pressure and current densities from 26 to 104 mA cm^{-2}. Using similar charge, experiments at various current densities were performed with electrolysis time varied accordingly. The highest CO concentration was obtained at 78 mA cm^{-2}, which corresponded to a H_2:CO ratio of 2.6 (Figure 3). It is worth noting that the amount of CO_2 released from the CHP-H_2CO_3 solution increased as the current increased (Figure S1). CO_2 release is expected to be driven by proton transfer from the anode as well as coulombic heating near the cathode surface which decomposes the CHP-H_2CO_3 acid base pair. Slow release of CO_2 at low current densities may affect the CO_2 availability for reaction and, therefore, the reaction yields at low current densities. At 104 mA cm^{-2}, higher electrode polarization, which favor hydrogen evolution over CO_2 reduction, may be one of the main causes for the decrease in the CO yield. However, a higher CO_2 release rate may have also affected the residence time of CO_2 within the electrochemical reactor causing lower CO_2 conversion. The syngas concentration profile on Figure 3 also shows that, except for the process at 26 mA cm^{-2}, the CO_2 concentration in the produced gas is lower than the amount of CO produced. For the first time it was demonstrated that syngas can be directly produced from captured CO_2 eliminating the requirement of downstream separations. As it is shown in Figure 3 this process produced syngas with commercial characteristics, 2 to 4 H_2:CO ratios, and at current densities as high as 104 mA cm^2.

Based on the proof of concept results, and published data at high pressure CO_2 reduction,[17, 33] it is clear that high pressures enhanced the CO_2 reduction efficiency. A simple parametric analysis was performed to evaluate the effect of the back pressure at a current density of 104 mA cm^{-2}. The results, which are shown in Figure 4, include the FE profiles for the experiments performed at 20 psig, and one test performed at 78 mA cm^{-2} and 40 psig. The results show that at 104 mA cm^{-2} the CO FE increased over 20% with an increase in the back pressure from 20 to 40 psig. Over 100 % increase can be observed when the FE of CO at 0 and 40 psig are compared. An 8.5% increase in the FE was also observed for the 75 mA cm^{-2} when the back pressure was increased from 20 to 40 psig. These results clearly show the beneficial effect of the back pressure in the efficiency of the electrochemical reduction of CO_2.Enhancing the contact of the released CO_2 and the electro-catalyst (CO_2 residence time) significantly favors the CO_2 reduction. Higher pressures were not tested due to design restrictions on the materials used for the electrochemical set up. However, pressure differentials as high as 87 psig have been reported for Nafion membranes.[34]

It is also observed on Figure 4 that the sum of CO and H_2 FEs are close to 100 % for all the experimental conditions. Hence no significant quantities of other CO_2 reduction products, such as formate, are expected. GC analysis of the reacted catholyte solutions (Figure S2) confirm the absence of formate, the other product most likely produced from CO_2 reduction, in detectable quantities. Moreover, the chromatograms on Figure S2 confirm no appreciable degradation of the SPS. Hence, it is rasonable to assume that the only significant products formed during the electrolysis of the CHP-H_2CO_3 solution are CO and H_2. CO_2 conversions can be calculated based on the amount of CO_2 released from the CHP-H_2CO_3 solution during the test (unreacted CO_2 +CO_2 converted to CO). The results, which are shown on Figure 5 show that CO_2 conversions and yields were as high as 71.7 % during the electrochemical production of syngas from CO_2 captured in SPS at 104 mA cm^{-2}, 40 psig, and 25 ◦C. For these conditions the measured H_2:CO ratio was 2.4. It can also be conclude from Figures 3 and 4 that operation parameters, such as current density and cathode back-pressure, can be controlled to tailor the produced syngas H_2:CO ratio in a range from 2 to 7 as an advantage for downstream conversion.[13]

A transient analysis was performed to evaluate the characteristics of the syngas product and system performance during an extended period of time (105 min). For this purpose, the system was operated at the best obtained conditions (100 mA cm^{-2}, 40 psig, and 25 ◦C), collecting samples every 15 minutes for GC analysis.The CHP-H_2CO_3 solution was kept on recirculation and without external additions of fresh solution. The results in Figure 6, show that at the beginning, while the process has not yet reached the desired operating pressure and builds an adequate concentration of free CO_2, the efficiencies for CO production are low. Close to 13% of the volume of gas collected during the first sample corresponded to air displaced from the system as electrochemically generated gas started evolving. The highest CO_2 reduction efficiency was measured for the second gas sample after stabilization of the pressure in the system. Then the relative CO yield starts decreasing, H_2 increases, possibly by the depletion of CO_2 available derived from the decrease of the CHP-H_2CO_3 concentration in the recirculated solution (Figure S3). Decrease of the CHP-H_2CO_3 concentration is enhanced by the water transferred from the anode due to electro-osmotic drag. Nevertheless, during the transient performance analysis it is also observed that the CO_2 conversion remains considerably stable, with a slight 4.3% decrease over a 90 min period (points two and four in Figure 6b). The fact that the CO_2 conversion remains stable during the operation supports the conclusion that decrease in CO yield during time is mainly caused by the depletion of captured CO_2 rather than catalyst deactivation. A continuous process feeding fresh solution and removing spent solution and the product gases may allow the continue production of syngas with stable compositions.

For this last experiment lower CO concentrations and a higher H_2:CO ratios were obtained in comparison with the results at the same conditions reported in Figures 5 and 6. Electrode aging could be one of the reasons for performance decrease. However a more detailed study of changes in the electrode surface post-reaction will be necessary to identify the real cause of activity decrease, which falls out of the scope of this paper.

Conclusions

SPS were used as capture-electrolyte media for the electrochemical production of syngas. For the first time captured CO_2 was electrochemically reduced to CO without the need to feed additional CO_2 gas to the electrochemical cell. The system greatly simplifies the electrolysis cell by eliminating the need to introduce gas efficiently to the cathode such as required with a gas diffusion electrode. The developed process allows the release and reduction of captured CO_2 in a single electrochemical cell, while the capture media can be recovered to continue the CCU cycle. A non diluted syngas stream was obtained at 104 mA cm^{-2} with H_2:CO ratios as low as 2.4 and with CO_2 conversions up to 71.7 %.

Experimental

Electrochemical reduction of captured CO_2 was performed in a 10 cm^2 (Fuel Cell technology, Inc.) cell test station customized with titanium plate current collectors (end plates) and connected to a BK Precision 1739 DC power supply (Figure 1). On the anode side Pt plated sintered titanium (Ginner, inc.), attached to a proton exchange membrane (PEM) 117 Nafion was used as electro-catalyst for water oxidation. A Master Flex C/L peristaltic pump was used to recirculate the anolyte in the anode chamber through a serpentine flow pattern engraved in the Ti current collector. In the cathode chamber, the cathode current collector was modified by removing the flow channels and replacing them with a hollow compartment that can fit a porous electrode with 10 cm^2 projected geometric area and 1.5 mm thickness. The electrode and the PEM were separated by an ultra-thin polyester fabric (178 µm). 15 mL of the catholyte solution with the captured CO_2 were recirculated to flood the cathode chamber, and into a recirculation reservoir that served as phases separator, using a bench-top Cole Parmer gear pump system. Aqueous phase was recirculated from the bottom of the phase separator while the organic phase remained at the top of the contained liquid (Figure 1 a). All the CO_2 added to the electroyzer came from the captured form and no additional CO_2 gas was added directly to the electrolyzer and/or to the capture media during operation. Once the desired current was applied the cathode side was allowed to self-pressurize by the gases produced at the cathode chamber. The pressure on the cathode side was manually controlled using a needle valve and the gases were collected in a Restek Multilayer bag, for gas chromatography (GC) analysis. Electrochemical reduction experiments were performed at different current densities from 25 to 100 mA cm^{-2}, back pressures of 0, 20, and 40 psig, and constant temperature of 25 ◦C. Temperature controller and heating units built in the cell test were used to keep the temperature constant during operation.

Electrode preparation

The cathode electrode was prepared by spraying a silver catalyst ink on a reticulated vitreous carbon (RVC) foam 80 nominal number of pores per inch of foam and 1.5 mm thick. Ag powder (1-3 µm, Alfa

Aesar) was used as the catalyst. To prepare the catalyst ink Ag powder was mixed in a solution prepared with 2-propanol (Fluka analyitical), Nafion perfluorinated resin solution (5%, Aldrich), and polytetrafluorethylene (PTFE) preparation (60%, Aldrich), to reach a final catalyst composition of 80 wt% Ag, 10 wt% Nafion, and 10 wt% PTFE. The actual catalyst loading was determined by weighing the RVC before and after painting. Several electrodes were prepared following the same procedure, which were used to perform preliminary and proof of concept experiments. However, all the results reported in this paper, after the addition of a supporting electrolyte, were obtained with the same cathode electrode, which reached an Ag loading of 25 mg cm^{-2}.

CO_2 capture

Deionized water and 1-Cyclohexylpiperidine (CHP), obtained from Alfa Aesar, were used for the capture of CO_2 in a modular gas contactor that allows continuous production of CHP-H_2CO_3 solutions.[28] In brief, The CO_2 gas and the liquid streams (water and CHP) were put in contact in a gas diffusion membrane unit with gas and liquids fed in opposite sides of the membrane. The membrane provides an enhanced mass transfer area that allows the diffusion of the CO_2 gas through the membrane and into the water-CHP mixture at efficient and controllable rates. A scheme of the apparatus used for CO_2 captured is shown in Figure S4, ESI. The CHP-H_2CO_3 solution was recirculated in the CO_2 capture system until a homogenous stock solution with a target concentration of 3 M was achieved. CO_2 capture was performed at room temperature.

Analysis

Concentration of the CHP-H_2CO_3 stock solution and catholyte were measured using an Agilent 7890 GC equipped with a 7693 auto-sampler and a flame ionization detector (FID). The gases produced during the electrochemical reduction of CO_2 were analysed in a Hewlett Packard 5890 GC equipped with two TCD detectors and two columns. A molecular sieve 5A and argon as gas carrier were used for the detection and quantification of CO, while a capillary column 2C D-poraPLOTU and helium gas carrier were used for the detection and quantification of CO_2. Finally, the volume of collected gas was measured using a Hamilton, Co. model s-1000 syringe. From the product analysis, syngas compositions, faradaic efficiencies (FE), and CO_2 conversions were determined.

Conflicts of interest

There are no conflicts to declare.

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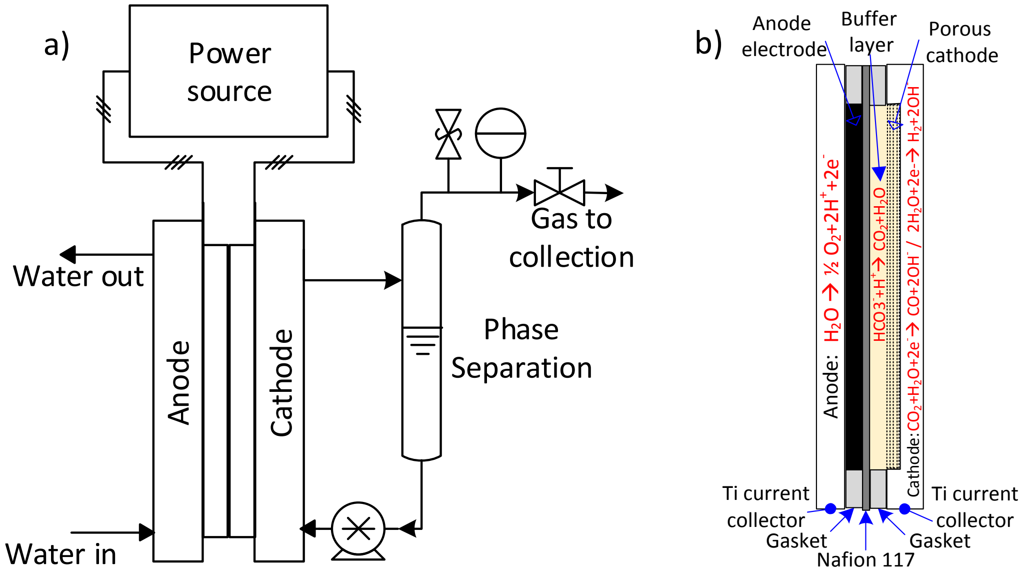

Figure 1. a) scheme of the electrolysis system for the reduction of captured CO_2, b) description of the MEA.

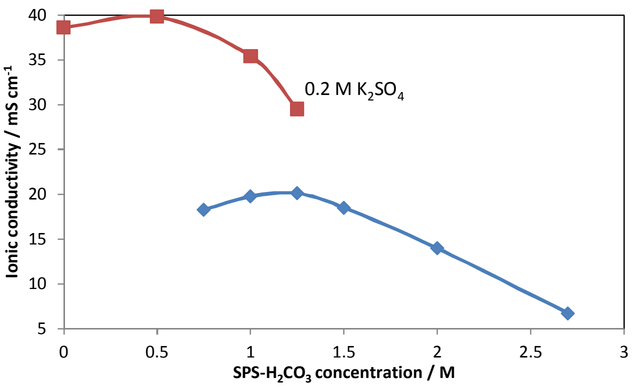

Figure 2. Ionic conductivity of CHP-H_2CO_3 solutions in the presence and absence of 0.2 M K_2SO_4.

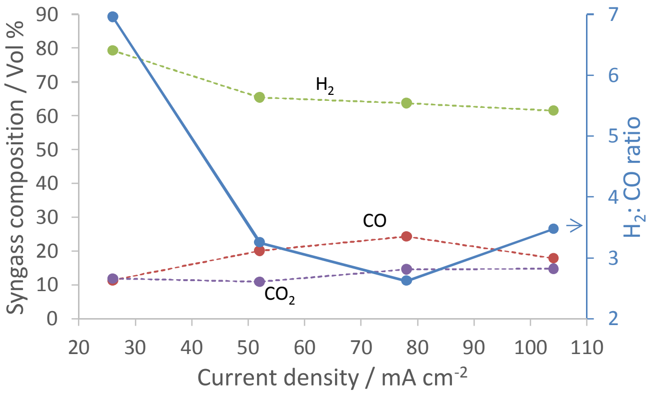

Figure 3. Composition profile and H_2:CO ratio for the syngas obtained at different current densities and at 20 psig back pressure in the cathode side.

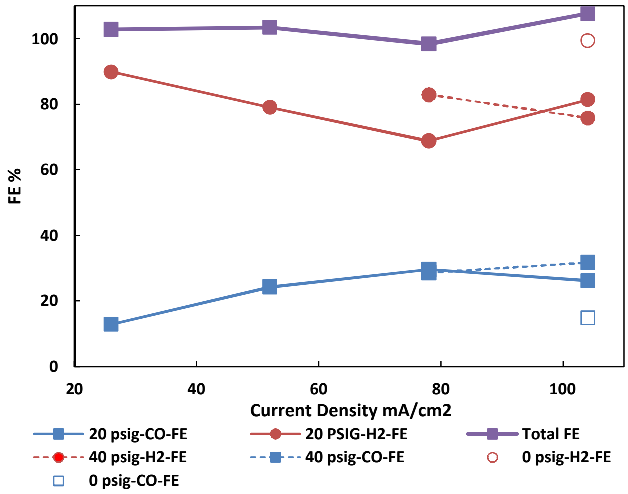

Figure 4. Faradic efficiencies of syngas produced from captured CO_2 at different current and pressures.

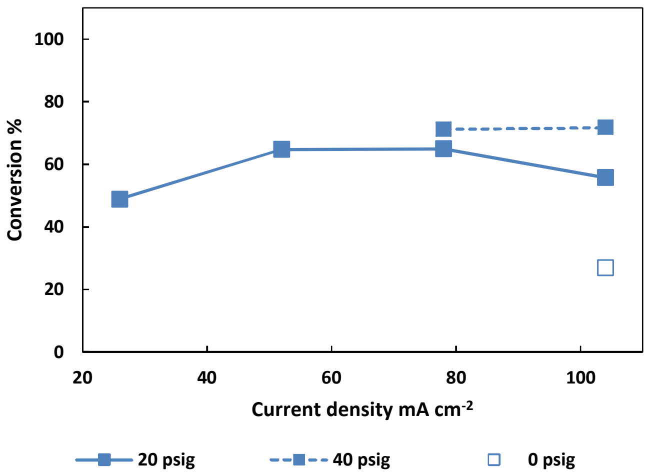

Figure 5. Conversion profiles for CO_2 released from the CHP-H_2CO_3 solution.

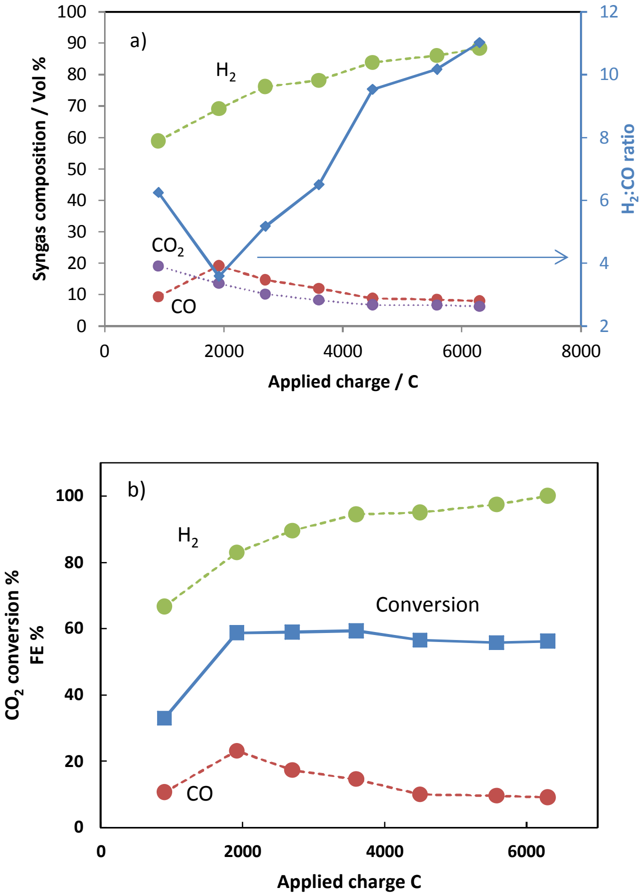

Figure 6. a) Concentration profiles of the syngas stream b) FE and CO_2 conversion.