Electrochemical Generation of Syngas from Water and Carbon Dioxide at Industrially Important Rates

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ABSTRACT:

The electrochemical production of syngas would enable production of chemicals and transportation fuels from carbon dioxide, water and renewable energy, but a suitable process at the moment does not exist. In this paper we consider two options for syngas production: i) CO₂ electrolysis to produce CO, water electrolysis to produce H₂ and then mixing the CO and H₂ to yield syngas; and ii) the simultaneous co-electrolysis of CO₂ and H₂O in a single electrolyzer. The results show that both processes can produce syngas at industrially important rates. In this paper we demonstrate CO₂ electrolysis at 100 mA/cm², i.e., about 1100 turnovers/sec, and water electrolysis at 8 A/cm² at 2.0 V/cell, with about 80,000 turnovers/sec. Both systems are stable for a thousand hours or more, i.e., billions of turnovers. We also demonstrate simultaneous CO and H₂ production in a single electrolyzer. These results demonstrate that syngas can be produced at industrially important rates via electrolysis.

KEYWORDS: syngas; electrolyzer; anion exchange membrane; CO₂ conversion; carbon dioxide utilization

1 INTRODUCTION:

Minimizing the release of carbon dioxide (CO₂) greenhouse gas to the environment, while still providing the liquid fuels and other hydrocarbons that current civilization relies on, will require the large scale commercialization of processes analogous to photosynthesis. Water and carbon dioxide will need to be combined with renewable energy from carbon-neutral sources, such as wind or solar, to produce hydrocarbons in a sustainable manner [1-10]. Initially, this CO₂ will come from high CO₂ concentration sources such as steel mills, cement furnaces, and ethanol fermenters. Ultimately, it may become necessary to capture CO₂ from ambient atmosphere in order to reduce global concentrations to early industrial levels. Several routes have been discussed in the literature, as summarized in our recent review [10]. In this paper we will discuss a route that we have been exploring: CO₂ electrolysis to CO [10-23], water electrolysis to produce H₂ [24-26], or an electrolyzer that simultaneously does both water and CO₂ electrolysis. The produced CO and H₂ are either mixed to form syngas or produced directly

at the desired syngas ratio in a single reactor, so that the syngas can then be converted to fuels and chemicals via well-established industrial processes (such as the Fischer Tropsch [27] process.)

We are not the only group working on this topic. Indeed, our recent review article [10] cited 323 previous literature contributions, and there are several excellent reviews [28-53]. In this paper we wish to review our own work on the topic. One is referred to the review articles [10], [28-53] for descriptions of the work from earlier investigations.

This paper will concentrate on describing two advances. First, we will review our latest work on proton exchange membrane (PEM) water electrolyzers, in which we obtained power densities in excess of 50 W/cm^2 using only 0.25 mg/cm^2 of IrO_2 as the anode catalyst [25, 28, 29]. In comparison, present commercial PEM electrolyzers typically use loadings of 4-8 mg/cm^2 of Platinum Group Metal (PGM) and achieve much lower power densities [54-58]. Second, we will review our demonstration of electrolysis of CO_2 into CO and O_2 with unexpectedly high selectivity and low overpotential at ambient temperature and pressure [10-22]. The latter result is due in part to the unexpected suppression of the competing water electrolysis reaction by the unique organic cationic “Helper Catalysts” employed [10-22].

Both electrolysis processes have been demonstrated at membrane current densities of at least 100 mA/cm^2 , which is an industrially relevant rate comparable to that of commercial chlor-alkali electrolyzers.

2 METHODS

2.1 PEM H_2O Electrolyzers

The water electrolysis experiments were performed in 50 cm^2 single cell hardware (Fuel Cell Technologies, Albuquerque, New Mexico, USA) using a graphite based quad-serpentine cathode flow field (Poco Graphite, Inc. Decatur, Texas,) and a modified Ti anode quad-serpentine flow field (Giner, Inc., Auburndale, Massachusetts, USA). All catalyst coated membranes (CCMs) were a construction of nanostructured thin film (NSTF) electrodes, laminated under suitable conditions of heat and pressure in a purposely built linear high pressure laminator onto a perfluorosulfonic acid (PFSA) polymer electrolyte membrane (3M Company, St. Paul, MN, USA) with a uniform lot of Pt-NSTF cathode electrodes (Pt loading $0.25 \text{ mg}\cdot\text{cm}^{-2}$, unless otherwise noted), and the anode electrode as described below. The cells were assembled using in-house prepared CCMs, sintered and platinized Ti gas diffusion layers (GDLs) (Giner, Inc.,) and CHR® (Saint-Gobain Performance Plastics, Merrimack, New Hampshire, USA) Teflon™ (DuPont, Wilmington, DE, USA) reinforced gaskets. Gasket thickness was adjusted to match the desired cell compression level of the GDLs. All cells were assembled with bolts torqued to $12.5 \text{ N}\cdot\text{m}$. The performance tests were performed on in-house built test stands consisting of a 10 kW TDK Lambda ESS power supply (Minato-ku, Tokyo, Japan) with a Fluke 45 A voltmeter with 1.0 MHz sampling capability (Everett, Washington, USA), Ismatec IDEX REGLO-CPF Digital pumps (ISM 321) equipped with RH1.CKC pump heads (Cole-Parmer GmbH, Wertheim, Germany), and controlled via in-house developed LabView (National Instruments, Austin, Texas, USA) drivers and control software. Water was fed to cells on the anode side at the rate of $1.25 \text{ cm}^3\cdot\text{s}^{-1}$ preheated to 85°C to enable a controlled cell temperature of 80°C . Cell temperature was controlled by Love Controls PID temperature controllers (Dwyer Instruments, Inc., Michigan City, Indiana, USA) and cartridge heaters inserted directly into the cell's body. Polarization curves were run from 1.35 V/cell to 2.0 V/cell at 50 mV steps and 300 s per step. Polarization curves were typically taken every 12 hours, before and after $2.0 \text{ A}\cdot\text{cm}^{-2}$

galvanostatic polarizations. Galvanostatic polarizations were performed by holding 100 A of total current and measuring the voltage response; results shown are the hourly average of this voltage.

2.2 CO₂ Electrolyzers

2.2.1 Chemicals

Hydrochloric acid (HCl), sulfuric acid (H₂SO₄), and two “ionic liquid” salts of the 1-ethyl-3-methyl imidazolium (EMIM⁺) cation, namely the chloride (EMIM-Cl) and the bisulfate, EMIM-HSO₄, were purchased from Sigma Aldrich and used as received. The salts EMIM-HCO₃, (EMIM)₂SO₄, and EMIM-H₂PO₄ were synthesized at 3M and Dioxide Materials’ laboratories by dissolving EMIM-Cl in ethanol, adding KHCO₃, K₂SO₄, or KH₂PO₄ in ethanol, filtering off the KCl precipitate, and then removing the ethanol under vacuum. The ionic liquids were diluted by or dissolved in deionized water (18.2 MΩ, Millipore) with 50 vol. % (for liquids) or 50 wt. % for solids. HCl and H₂SO₄ were diluted to the desired concentration with deionized water.

2.2.2 Preparation of electrodes

A silver (Ag) cathode for CO₂ reduction was prepared as follows: A cathode ink is made by mixing 30 mg of catalyst nanoparticles with 0.1 ml deionized water (18.2 MΩ, Millipore) and 0.2 ml isopropanol (3032-16, Macron). The mixture is then sonicated for 1 minute. The cathode ink is spray painted onto a gas diffusion layer (Sigracet 35 BC GDL, Ion Power) covering an area of 2.5 cm X 2.5 cm. Ag/Ni bimetallic electrodes with different ratios were also prepared for the purpose of syngas production. An IrO₂ anode was prepared in a same way.

2.2.3 Electrochemical testing: liquid cells

To produce CO with high selectivity, we conducted the experiments in two types of cell as shown in Figure 1: (a) liquid cell [19]; and (b) solid cell. The liquid cell was assembled as described in Rosen et al. [19], Brushett et al. [59], and Whipple et al. [60]. The cell consists of a multicompartiment cell. Ag and IrO₂ were used as cathode and anode, respectively. The active area was 1 cm². Various ionic liquids with EMIM⁺ cation and different anions were tested as helper catalysts and fed to the liquid chamber in the cathode. CO₂ was fed to the gas chamber in the cathode at 10 sccm. 0.5 M H₂SO₄ was used as the anolyte and fed to the liquid chamber in the anode. The cell was run at 50 mA/cm², and the gas product from cathode was analyzed by gas chromatography (GC.) EMIM-Cl was chosen to study the effect of concentration on the conductivity and the CO selectivity. The conductivity of EMIM-Cl solution was measured using a conductivity meter.

Figure 1 Schematic of liquid electrolyte cell and solid electrolyte cell [14].

2.2.4 Electrochemical testing: solid state cells

The solid cell was assembled by sandwiching a proprietary Dioxide Materials membrane between a silver cathode on carbon paper and an iridium oxide anode on carbon paper with a metal loading of about 2 mg/cm^2 . The whole assembly was mounted in Fuel Cell Technologies 5 cm^2 fuel cell hardware with serpentine flow fields. Water was fed into the anode at a rate of 0.1 sccm , and CO_2 was fed to the cathode at 20 sccm . A certain current was applied to the cell, and the cell voltage and the CO selectivity were measured after the cell had been running for 30 minutes.

2.3 Direct syngas production in a single cell

In order to produce syngas from the liquid cell (Figure 1a,) we tested the effect of pH of the EMIM-Cl solution on the CO selectivity (Figure 4). The pH of the EMIM-Cl solution was adjusted using 6 M HCl , and the CO selectivity at 25 mA/cm^2 was determined by GC. Two experiments were designed to produce syngas in a solid cell (Figure 1b). One approach was to use Ag/Ni bimetallic catalyst for the cathode while running H_2O in the anode; the other approach was to run H_2SO_4 in the anode while using Ag as the cathode catalyst.

3 RESULTS

3.1 H_2 from water splitting, using proton exchange membrane electrolyzers

PEM membranes using proton (H^+) conduction have high ionic conductivity, but the PGM catalysts needed for operation in acidic media are expensive, so efforts are made to reduce the necessary catalyst loading. Most recent investigators [55-58, 61-63] have used catalyst loadings above 1 mg/cm^2 , although there is one recent report using lower loadings [54].

In the work described here we concentrated on electrolyzers with anode catalyst loadings of only 0.25 mg/cm^2 . The work used proprietary oxygen evolution reaction (OER) catalysts comprised of thin semi-continuous films of iridium catalyst deposited on nanoscopic whiskers of nonconductive, electrochemically stable perylene red (PR) pigment, thus forming a hydrophilic

nano-structured thin film (NSTF) catalyst for the water electrolyzer anode [24, 64-67]. This whisker-like catalyst material can be laminated and imbedded into the ion exchange membrane of solid polymer electrolyte electrochemical cells, such as PEM water electrolyzers. The thin continuous metallic layer provides high conductivity and high mass-specific catalytic activity with low platinum group metal catalyst loading. The nonconductive perylene red substrate allows for high dispersion of catalytically active centers and at the same time avoids the carbon corrosion that occurs at OER potentials with carbon-supported catalysts. The combination offers catalyst stability typically associated with unsupported PGM blacks, while allowing for high electrochemical surface areas typical of supported catalysts.

Figure 2 Example of NSTF based CCM in electrolyzer cell. The cell and operating conditions as indicated in the graph and experimental section (standard operating conditions), the anode Ir-NSTF catalyst is modified for high current operation. Data obtained at 80 °C and ambient pressure.

Error! Reference source not found. shows a polarization curve and a power curve for a PEM water electrolyzer with 0.25 mg/cm² of IrO₂ on the anode and 0.25 mg/cm² of platinum on the cathode at 80 °C. Notice that the cell runs at about 8 A/cm² at a potential of 2 V (almost 75% efficiency based on higher heating value of hydrogen). By comparison, Rozain et al. [55] demonstrate currents of about 1.5 A/cm² at similar conditions, with IrO₂ loadings of 1.5 mg/cm². Skulimowska et al. [58] also report currents of 1.4 A/cm² at IrO₂ loadings of 2 mg/cm². Siracusano et al. [56, 57] find that heating the cell to 90 °C increases the current to 4 A/cm² at IrO₂ loadings of 1.5 mg/cm². Similarly, a recent paper by Rozain et al. [54] shows initial currents of 1.6 A/cm² at IrO₂ loadings of 0.23 mg/cm².

Notice that **Error! Reference source not found.** shows the highest current observed so far at a 2 V potential, and uses some of the lowest catalyst loadings. Further, the above described H₂O electrolyzer is stable. An earlier version of the system using the more common Nafion 115 perfluorosulfonic acid based (PFSA) PEM membrane demonstrated 5000 hours of operation at current densities of 2 A/cm² (20,000 turnovers/sec) and cell voltages of about 1.85 V with an average voltage loss rate of only 6.8 µV/h. This corresponds to about 3x10¹¹ total turnovers.

We also have demonstrated current densities over 19 A/cm^2 and an operating power density in excess of 50 W/cm^2 . To our knowledge this is the highest power density ever reported in a PEM electrolyzer.

3.2 CO from electrochemical CO_2 splitting

CO_2 has low solubility in acidic water solutions, which limits mass transport and reaction rates. In contrast, CO_2 has high solubility in alkaline solutions, due to the reaction with hydroxides to form bicarbonates and carbonates, but these species tend to poison commercial anion exchange membranes, as discussed above. The authors have recently developed anion exchange membranes that have high anionic conductivity and good tolerance for the presence of bicarbonates from CO_2 [13, 14].

An early breakthrough, described in Rosen et al. [19], was the addition of an organic cationic co-catalyst, such as 1-ethyl-3-methyl imidazolium (EMIM^+), which forms a weak complex with CO_2 , thus reducing the overpotential for the rate-limiting step of transferring an electron from the negative electrode to CO_2 , as illustrated in Figure 3.

Figure 3 CO_2 reduction facilitated by weak $\text{CO}_2\text{-EMIM}^+$ complex formation [19].

A further unexpected benefit is that certain “Helper Catalysts” like EMIM^+ (Fig. 3) appear to block access of hydronium (“ H^+ ”) ions to the negative electrode, suppressing the normal hydrogen evolution reaction (HER) of water electrolysis[22, 23], and thus greatly increasing the selectivity toward CO production on silver catalysts. The competing cathode half-cell reactions are shown below.

Figure 4 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMIM⁺BF₄⁻)

The initial investigations described in our previous work [19] were conducted in liquid catholyte cells using the “ionic liquid” salt EMIM⁺BF₄⁻ (Figure 4) as the source of the EMIM⁺ “Helper Catalyst” [11]. These systems showed an initial 98% selectivity toward CO product. However, the selectivity was found to decrease over time, apparently due to slow hydrolysis of the BF₄⁻ anion, which produced corrosive HF and made the catholyte more acidic. As a result, a series of alternative EMIM⁺ salts with more hydrolytically stable anions were tested, as shown in Table 1.

Table 1 CO selectivity with different ionic liquids in 1 cm² liquid cell

Ionic liquids	Current density/ mA/cm ²	CO Selectivity %	Notes
EMIM-Cl	50	97.08	Commercially available
EMIM-HSO ₄	50	12.22	Commercially available
(EMIM) ₂ SO ₄	50	95.39	Synthesized in house
EMIM-HCO ₃	50	97.44	Synthesized in house
EMIM-H ₂ PO ₄	50	45.83	Synthesized in house

The tests with the various anions showed that as the catholyte becomes more acidic, the higher concentration of H^+ increases the competing hydrogen evolution reaction, thus increasing the production of H_2 and decreasing the selectivity toward CO.

A study versus concentration of the Helper Catalyst EMIM-Cl in aqueous catholyte with a silver cathode catalyst demonstrated high selectivity over a wide range of concentrations, as shown in Figure 5. The baseline was a 50 wt% aqueous solution of EMIM-Cl, which has a concentration of approximately 3.6 M. Selectivity greater than 90% was observed with 0.5-3.6 M EMIM-Cl. Slightly higher selectivity was observed at higher concentration and higher current. Since EMIM-Cl is noticeably more viscous than water, there appears to be a trade-off between viscosity (ion mobility) and ion concentration (number of charge carriers.)

Figure 5 CO selectivity vs. concentration of EMIM-Cl[20]

3.3 Direct syngas production from a single electrolyzer by tuning the pH of the catholyte

As indicated above, the preferred H_2/CO ratio for syngas is typically from 1/1 to 4/1, corresponding to a CO selectivity of 50% to 20%. The study above using acidic EMIM⁺ counterions suggests that one way to tune the CO selectivity and H_2/CO ratio of the reaction is to increase the acidity of the catholyte, thus increasing the rate of the hydrogen evolution reaction. The data in Table 2, in which the pH of an EMIM-Cl catholyte solution was adjusted by the addition of HCl, shows this to be the case. However, the data at pH = 1 shows that it is necessary to control both the pH and the current density in order to keep the produced syngas mixture at the desired H_2/CO ratio.

Table 2 50 wt% aqueous EMIM-Cl catholyte, pH adjusted by addition of HCl

pH	Cathode Potential (V)	Current Density (mA/cm ²)	CO Selectivity (%)	H ₂ /CO
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6.6	-1.2	25	99.1	0.009
2	-1.34	25	98.2	0.02
1.5	-1.34	25	98.7	0.01
1.2	-1.25	25	85.0	0.18
1.1	-1.27	25	34.4	1.9
1.1	-1.2	20	23.6	3.24
1.1	-1.25	24	33.5	1.99
0.5	-0.88	25	0.9	103.94
0.5	-1.24	50	18.6	4.38

3.4 Switching to a solid electrolyte cell design

While the initial development on the CO₂ electrolyzer was done primarily using a Helper Catalyst like EMIM-Cl in a liquid catholyte [11, 16, 18-20, 23], this was accompanied by some problems, such as high cell resistance due to the electrolyte fluids, as well as occasional “flooding” of non-catalyst regions of the cathode carbon fiber paper gas diffusion layer with electrolyte, which increased hydrogen evolution and thus reduced the CO selectivity. A decision was made to switch to a solid electrolyte cathode cell, similar to the cells used in the PEM water electrolyzer described above [13, 14, 16].

3.5 Development of improved anion conducting membranes

In the process of implementing a solid catholyte cell design, a series of proprietary new anion exchange membranes were developed [13, 14]. Cells using these membranes have demonstrated CO selectivities comparable to those achieved in the liquid catholyte cells, along with higher current densities and more stable performance. Some examples are shown in Table 3 below. A current density of 100 mA/cm² at a cell voltage of 3 V was achieved with membrane DX4-13, and 300 mA/cm² was demonstrated at 2.8 V with DX5-13. In all cases the selectivity was above 90% at 3 V potential.

By comparison, Aeshala, et al. [68] observe only about 20 mA/cm² and 25% selectivity at a similar potential, Delacourt et al. [69] observes only 20 mA/cm² and 60% selectivity, Genovese et al. [41, 70, 71] observe only 20 mA/cm² at 12% selectivity, and Media-Romos et al.[72] observe 25 mA/cm² and 80% efficiency in the presence of an imidazolium salt similar to the ones described in our patents.

Figure 6 shows stable selectivity and cell voltage over 250 hours of operation at 100 mA/cm² for one of these solid catholyte cells. At our catalyst loadings, a current of 100 mA/cm² corresponds to about 1100 turnovers/sec, and the data in Figure 6 corresponds to about 4 billion turnovers. In other runs we have run for up to 1000 hours, corresponding to about 15 billion turnovers.

Table 3. GC analysis of gas products from a 5 cm² solid cell with anion exchange membrane.

The current is the total current in the 5 cm² cell.

anion exchange membrane	Cell potential (V)	Current (mA)	CO selectivity (%)	H ₂ /CO
DX4-13	2.66	200	79.9	0.252
DX4-13	2.75	300	91.4	0.094
DX4-13	2.97	500	92.3	0.084
DX5-13	2.80	1500	93.8	0.066

Figure 6 Stable operation of a solid catholyte cell over 250 hours.

3.6 Producing syngas in a solid catholyte cell – bimetallic catalysts

One approach to directly producing a syngas mixture from a single cell would be to use two electrocatalyst metals on the cathode, one for each of the desired reactions. Ag catalyzes reduction of CO₂ to CO, while Ni and Pt promote hydrogen evolution. Ni is a good catalyst for the HER in neutral or alkaline media, while Pt catalysts are easily poisoned by the CO, so Ni is the logical choice. Table 4 shows the results from using a cathode catalyst ink containing various ratios of Ag/Ni nanoparticles. As the table shows, a syngas mixture in the desired composition range was obtained with an Ag/Ni ratio of 1/4 and a cell voltage of 3 V. The

reported current is the total current in a 5 cm² membrane cell.

Table 4. GC analysis of gas products from a 5 cm² solid cell using Ag/Ni bimetallic catalysts.

Ag/Ni ratio	current (mA)	Cell potential (V)	CO selectivity (%)	H ₂ /CO
0/1	100	2.7	0.00	
	200	3	0.00	
1/2	200	2.8	52.61	0.90
	300	3.1	52.63	0.90
1/4	200	2.8	18.85	4.30
	300	3	37.01	1.70

3.7 Syngas production by tuning the pH at the cathode/membrane interface

In the examples described above, the anode half-cell reaction was typically the “water splitting” oxygen evolution reaction (OER.) Deionized water was typically supplied to the anode. (Humidified CO₂ gas was provided to the cathode, to prevent dry out of the membrane.) However, circulating a sulfuric acid solution on the anode side of the anion exchange membrane was found to influence the pH on the cathode side of the membrane, thus increasing the HER and decreasing the CO selectivity into the desired syngas range of 20-50%. In theory, anions migrate from cathode to anode through an anion exchange membrane in an electrolyzer, while cations transport from anode to cathode if cations are present at the anode. Here we fed H₂SO₄ to the anode so that protons could diffuse to the cathode, thus tuning the pH of the cathode/membrane interface and producing syngas. An example is shown below in Figure 7. A current density of 100 mA/cm² was applied to the cell. With 0.1 M H₂SO₄ at the anode, the selectivity was still as high as 90%. Further increasing the concentration of H₂SO₄ to 0.3 M, the selectivity decreased to 40%. The selectivity was quite stable at each concentration.

Figure 7 Adjusting syngas composition by acidifying the anode side of the anion exchange membrane.

4 SUMMARY

In this review we have explored the recent technologies that enable the production of syngas at industrially relevant rates. These technologies support two strategies for syngas production: the tandem production of H₂ and CO in separate electrolyzers, and the simultaneous production of H₂ and CO at a fixed ratio in a single electrolyzer.

The authors have shown that concomitant use of novel NSTF catalysts and PEMs allows for water electrolysis at extremely high current densities. Additionally, the use of ionic liquid co-catalysts for highly selective reduction of CO₂ to CO strongly suppressed the hydrogen evolution reaction. Eventually this CO₂ reduction technology eschewed the ionic liquids in order to operate in the present leaner and more efficient solid-state design that employs a novel anion-exchange membrane. If these two technologies were to operate in two tandem electrolyzers, this would permit the mixing of their output gases at any desired ratio as a way of generating syngas.

If it is more advantageous to the intended application for syngas to be efficiently produced in a single electrolyzer, then the technologies that the authors have demonstrated also enable this. The authors have shown that the careful manipulation of the pH on either side of the anion exchange membrane, as well as the use of bimetallic catalysts on the cathode, both permit high-capacity syngas generation at the desired CO percentage range.

The electrolyzer technologies presented here are capable of running at industrially-relevant current densities of 100 mA/cm² and often higher. Furthermore, repeated tests have shown long-term performance of these systems with negligible degradation or loss of function in the novel components such as the anion-exchange membrane. Our ambition is that these efficient and robust technologies will enable high-volume syngas generation in a variety of applications.

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