Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Increased hydrogen partial pressure suppresses and reverses hydrogen evolution during Pd catalyzed electrolysis of CO_2

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Contents

S1. Experimental Section

S1.1 Chemicals and materials

$KHCO_3$ (99.7%) and 5 wt.% Pd/C were purchased from Merck. Fumion FAA-SOLUT-10 ionomer solution (10 wt.% in NPM) was purchased from Fumatech GmbH. Titanium foil 0.89 mm (99.7%) and graphite conductive adhesive were purchased from Alfa Aesar. CeTech GDS810 carbon paper was purchased from fuel cell store. CMI-7000 cation exchange membrane (CEM) was purchased from Membranes International inc. A dimensionally stable anode (DSA) was acquired from Magneto Special Anodes B.V. Milli-Q water was used for all solutions and water based cleaning procedures. All chemicals were used as received without further purification.

S1.2 Preparation of Pd/C electrode

Ti foil was cut into pieced of 30 mm by 40 mm and cleaned by boiling in 1M oxalic acid solution for 2 hours and consecutive rinsing with water. Carbon paper was cut into 20 mm by 30 mm pieces and attached to the Ti foil with graphite based conductive adhesive. The adhesive was cured at 60°C for 1 hour. This formed the electrode backbone,

Catalyst ink was prepared by mixing 50 mg Pd/C (5 wt.% Pd) with 2 ml isopropanol and 0.5 ml Fumion. The mixture was sonicated for 30 min. 200 μL of catalyst ink was adsorbed into the carbon paper of the electrode backbone. The loaded electrode was then dried in an oven at 60°C for 1 hour.

S1.3 Electrochemical setup

It is vital that pressure in the electrochemical cell is controlled accurately. The pressure in the catholyte and anolyte should be equal during the experiment, but also during pressurization and depressurization, as any difference leads to transmembrane pressure drop, potentially damaging the membrane. The setup, shown in Figure 1, minimizes transmembrane pressure drop.

Feed gas to the catholyte is mixed before entering the reactor. The gas on the anolyte side is pure argon. The gas ratio and flow is controlled via mass flow controllers (MFCs a1 and c1-c3). Pressure safety valves (PSVs) are in place to prevent over-pressurization. The pressure in the catholyte is controlled via MFC-c2, which is adjusted based on the set pressure. The pressure in the anolyte follows the pressure in the catholyte, via backpressure regulator a1 (BPR-a1). The BPR (Pressure Control Solutions) senses the pressure in the catholyte compartment and uses this as a set-point for the pressure in the anode compartment. By ensuring that the gas flow to the anolyte compartment is always larger than the gas flow to the catholyte compartment, equal pressure is maintained, also during pressurization. The gas phase is operated in continuous mode and the liquid phase in batch mode.

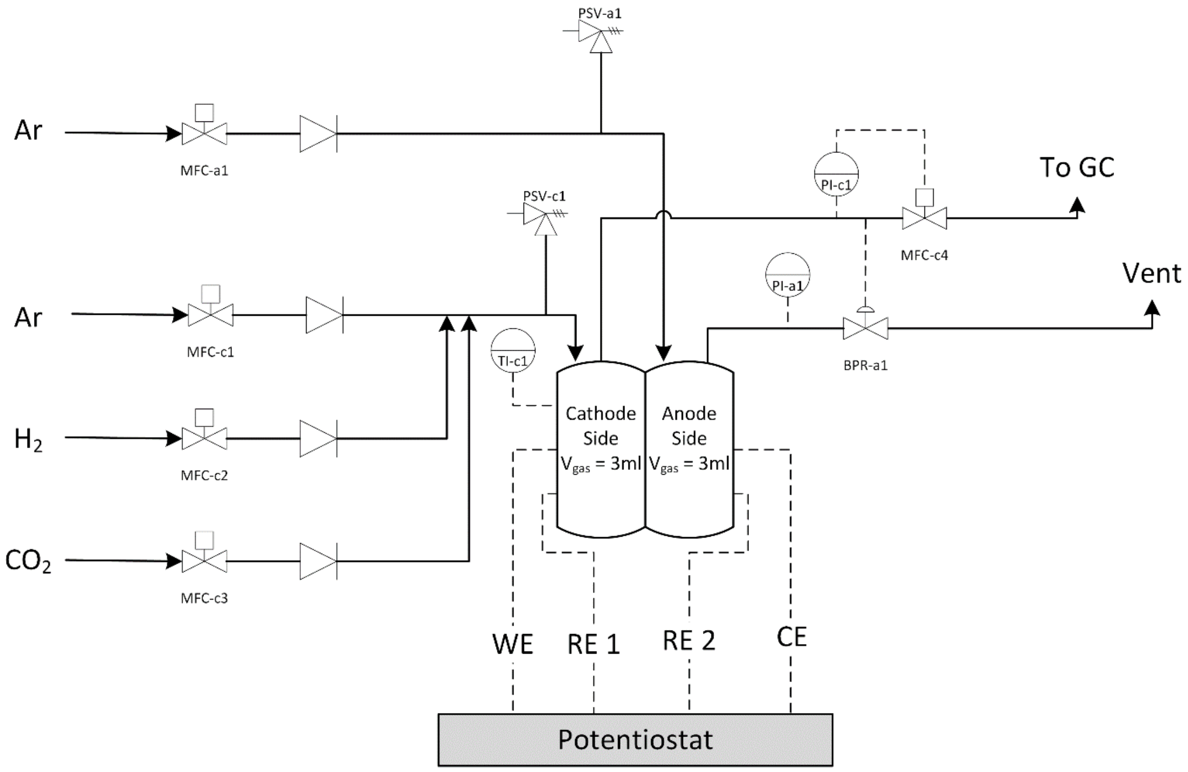

Figure 1: Flow diagram of electrochemical setup

S1.4 Operating regime

To measure catalyst behaviour accurately, the applied conditions are such that mass transport effects in the catholyte are minimized. The gas supplied to the catholyte is sparged though a fine, small glass fritte, which assures abundant small bubbles. The small bubbles facilitate mass exchange of CO_2 and H_2 between the gas phase and electrolyte. The maximum transfer of hydrogen to the electrode surface was quantified, by anodically polarizing a Pt electrode and measuring the current, whilst varying the hydrogen partial pressure. Mass transfer of hydrogen was found to be not rate determining for the CO_2 hydrogenation reaction. CO_2 mass transfer effects were evaluated, by changing the flow rate of pure CO_2 and assessing the average rate to formate. Only when the CO_2 flow was zero, there was a significant effect, as shown in Figure 2. Therefore, mass transfer effects play no significant role in the experiments and data is representative for catalyst behaviour in the kinetically limited regime.

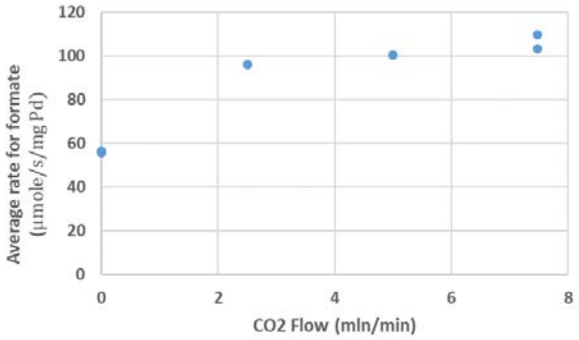

Figure 2: Variation of CO_2 flow at 1 bar to asses effects of mass transfer

S1.5 Repeatability of electrode performance

Pd/C electrodes are known to deactivate under electrochemical CO_2 reduction conditions. This deactivation is mostly reversible, with the exception of a small initial deactivation.[1] Therefore, the electrode was first used in a standard experiment and the accompanying data was omitted. Between experiments, the electrode was regenerated by 30s anodic polarization at 1.3V vs RHE. That resulted in reproducible results, as shown in Figure 3. The standard deviation over the faraday efficiency is 2.7 percent point.

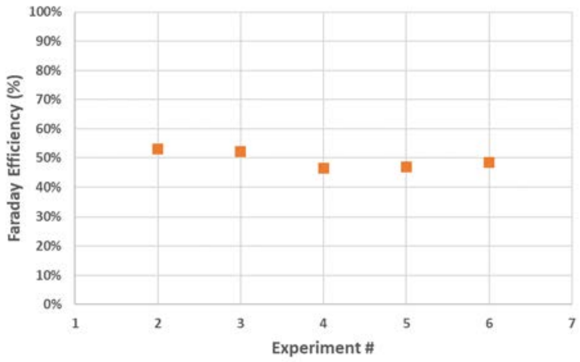

Figure 3: Repeatability assesmnent of Pd/C electrode for CO_2 reduction in 1M $KHCO_3$ at 1 bar.

S1.6 Error analysis and statistics

Based on the repeatability experiments (S1.5) a 95% confidence interval was calculated. For other measurements, an estimate of the error was made based on that value. The 95% confidence interval values for the rate to H_2 and rate to $HCOO^-$ in the repeatability experiment were scaled linearly to the measured value in other experiments.

An F-test analysis was performed to determine which model would describe the trends in Figure 2 and Figure 3 best. For Figure 2 (rate to H_2 as function of p_{H2}) it was found that a linear two-parameter model gave a significantly better fit than a one-parameter model (99.5 % confidence), but that a three-parameter model did not significantly improve the fit. For Figure 3 (rate to $HCOO^-$ as function of p_{H2}) a two-parameter model did not give a significantly better fit than a one-parameter model.

S1.7 Evaluation of performance under elevated H_2/CO_2/Ar pressure

The electrochemical cell was assembled with the Pd/C electrode as working electrode (WE) and DSA as counter electrode (CE). A CEM was used in all experiments. Both anolyte and catholyte were 6 ml 1M $KHCO_3$ solution. Total gas flow to the catholyte was kept constant at 5 mln/min, gas flow to the anolyte was 10 mln/min and total pressure during electrolysis was kept at 7 bara.

Pressurization of the reactor takes approximately 20 min, which is enough time to equilibrate the gas and liquid phase. Depressurization takes about 1 minute. During (de)pressurization, no potential is applied, but hydrogenation does occur to some extent. The amount of formate produced during this period was quantified by only performing pressurization and depressurization. In data analysis that amount of formate was subtracted from the total amount of formate produced, therefore the data in this publication accurately represents the processes that occur during pressurized electrochemistry.

All potentials were measured versus an Ag/AgCl (3M KCl) reference electrode and were converted to the Reversible Hydrogen Electrode (RHE) scale. Equilibrium pH is dependent on the CO_2 pressure in the cell, hence was calculate based on this equilibrium.

The RHE is defined as the thermodynamic equilibrium potential of the hydrogen evolution reaction at 1 bar H_2 partial pressure under experimental (electrolyte) conditions. On the RHE scale, the thermodynamic driving force for formate production is unaffected by p_{H2}, as evident from equation S13. The thermodynamic driving force for hydrogen evolution is affected by p_{H2} as per equation S14. Since H_2 participates in the hydrogen evolution reaction, but not in the formate formation reaction, it is impossible to maintain the same thermodynamic driving force to both reactions when varying p_{H2}.

S1.8 HPLC analysis and gas chromatography

After an experiment, the formate concentration in the catholyte was determined with HPLC. A Hiplex-H column was used in a Agilent Technologies 1200 series HPLC, with 5 mM H2SO4 in milli-Q as eluent. The column was at 65°C and eluent flow was 0.6 ml/min. Formate was detected with a Refractive index detector (RID) and retention time was 14.8 minutes.

Occasionally, the gas catholyte off-gas was analyzed with on-line GC analysis. The GC was an Interscience compact GC equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). The TCD was used for CO detection and no significant amounts (<0.2% FE) were formed during experiments. The FID was used for methane and higher hydrocarbon detection; no significant amounts of hydrocarbons were detected.

When no hydrogen pressure was applied to the system, the produced hydrogen could be measured by GC and an overall charge balance checked. Although the GC is not optimal for measuring H_2 in the experimental concentration range, the charge balance closure never fell outside the 93%-103% range. Analysis of the gas phase is the largest contributor to the error in charge balance closure, due to errors in the GC measurements and relatively large amount of volume in piping, control features and safety features compared to the reactor volume.

Note that reported H_2 evolution rates are calculated by difference from charge flow and formate production (measured by HPLC).

S1.9 Carbonaceous equilibrium

During sparging of the 1M $KHCO_3$ electrolyte with CO_2, equilibrium is reached between CO_2, HCO_3^-, CO_3^{2-}, H^+ and OH^-. The equilibrium is calculated through equations S1-S5, being Henry's law (S1), equilibrium reaction HCO_3^-/CO_2 (S2), equilibrium reaction CO_3^{2-}/ HCO_3^- (S3), ionization of water (S4) and the charge balance (S5). Table 1 shows the values of the equilibrium constants. Table 2 presents the calculated equilibrium composition of initially 1M $KHCO_3$ in contact with a gas phase containing 1 bar or 3 bar partial pressure of CO_2.

$$[CO_2] = H \cdot p_{CO_2} \tag{S1}$$

$$\frac{[HCO_3^-]}{[CO_2][OH^-]} = K_1 \tag{S2}$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-][OH^-]} = K_2 \tag{S3}$$

$$[OH^-][H^+] = K_w \tag{S4}$$

$$[K^+] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \tag{S5}$$

Table 1: Values of equilibrium constants

H	0.034 mol / (L · bar)
K_1	$4.44 \cdot 10^7$ L/mol
K_2	$4.66 \cdot 10^3$ L/mol
K_w	$1.0 \cdot 10^{-14}$ mol^2/L^2

Table 2: Calculated equilibrium composition of catholyte, for p_{CO2} = 1 bar and p_{CO2} = 3 bar.

P_{CO2} (bar)	1	3
pH (-)	7.82	7.34
$[H^+]$ (mole/L)	$1.52 \cdot 10^{-8}$	$4.54 \cdot 10^{-8}$
$[CO_2]$ (mole/L)	0.034	0.102
$[HCO_3^-]$ (mole/L)	0.99	1.00
$[CO_3^{2-}]$ (mole/L)	0.00	0.00

S2. References

[1] X. Min, M. W. Kanan, *J. Am. Chem. Soc.* **2015**, *137*, 4701–4708.