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# **Supplementary Information**

# Electrochemical production of syngas from CO<sub>2</sub> at pressures up to 30 bar in electrolytes containing ionic liquid

S. Messias<sup>a</sup>, M. M. Sousa<sup>a</sup>, M. Nunes da Ponte<sup>a</sup>, C. M. Rangel<sup>b</sup>, T. Pardal<sup>c</sup> and A. S. Reis Machado<sup>a</sup>\*

a LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal b Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, 22 1649-038 Lisboa, Portugal c Omnidea, Lda, Travessa António Gedeão, Nº 9, 3510-017 Viseu, Portugal

\* Contact email: ams.machado@fct.unl.pt

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# 1. Description of the high-pressure experimental set-up

Figure S1 shows a schematic of the experimental set-up for the  $CO_2$  electro-catalytic reduction process at high pressure.



Figure S1 –Schematic diagram of the experimental set-up; a) data collection; b) electrochemical reactor c) and d) sampling e) electrolyte recirculation sections (1) computer controlling potentiostat/galvanostat; (2) anolyte inlet valve; (3) anolyte outlet valve; (4) filter; (5) anolyte compartment; (6) catholyte compartment (7) ion exchange membrane; (8) valve; (9) sampling vessel; (10) dielectric (11) valve; (12) digital pressure meter; (13) digital pressure meter; (14) filter (15) three way valve (reactor outlet/pump inlet); (16) three way valve (reactor outlet/pump inlet); (17) CO<sub>2</sub> inlet valve; (18) CO<sub>2</sub> cylinder; (19) valve; (20) sampling vessel; (21) pump A; (22) pump B; (23) pneumatic valves system of the pumps; (23) pump controller.

The experimental set-up can be divided in four main sections: reactor, recirculation facility, sampling and data collection.

The reactor zone is limited by the  $CO_2$  inlet valve and the valve at the entrance of the sampling vessel. It includes a stainless-steel reactor placed inside a Heareus oven (thermostatic air bath). The reactor is equipped with two pressure transducers for the cathode and anode compartment (WIKA'S DI32-1). The recirculation zone is limited by the three way valve connecting reactor inlet with pump outlet and the valve connecting reactor outlet with pump inlet. It includes two Isco Teledyne syringe pumps, model 500 D. The sampling zone consists of a pressure sampling vessel of 50 cm<sup>3</sup> volume equipped with a Keller manometer. It is limited by its inlet and outlet valves. The sampling vessel can be disconnected from the reactor for analysis of the gaseous products, which is carried out by gas chromatography.

#### 1.1 Operation Procedure

After assembling the electrochemical reactor, the electrolyte was pumped into each electrode compartment. The view ports were used to check that the immersed area of the two electrodes in the electrolyte were the same. Teledyne Isco syringe pumps, model 500D were used for charging the electrolyte. Heating is turned on and CO<sub>2</sub> was then introduced in the facility. Then, carbon dioxide was brought to the desired pressure, and when the reactor stabilized at the desired temperature and pressure (stabilization periods of ca. 3 hours), current was applied to the electrolysis was carried out in batch mode. A total volume of electrolyte of ca. 90 ml was used. Electrolysis were carried out under galvanostatic control with charge passed in the range of 50 C -2000 C . A potentiostat/galvanostat PGSTAT128N-Autolab 84469 was employed. After electrolysis, the system is allowed to rest for 1h-2 h before sampling, to achieve a better separation of electrolysis gaseous products from the electrolyte. Vacuum was applied to the sampling zone and the valves between the reactor and the sampling vessel were slowly opened until the pressure reached 2 bar in the sampling vessel and then closed. The sampling vessel was disconnected from the pressure facility and the gaseous mixture was analysed by gas chromatography.

In semi-continuous mode a similar procedure was followed, but the stabilization period before electrolysis was 24 h to assure saturation of the electrolyte in  $CO_2$ , due to the higher volumes of electrolyte employed. In this period, the electrolyte was recirculated for10 hours using also the Teledyne Isco syringe pumps. Then, electrolysis is undertaken at the chosen electrolyte recirculation flow rate. After the electrolysis all the electrolyte was recirculated to flow through the reactor several times so that the gaseous electrolysis products could be released in the headspace of the reactor before sampling and subsequent GC analysis (corresponding to a period of 1-2h, depending on the total volume of electrolyte and flow rate). Electrolysis were carried out at least in duplicate.

### 2. Determination of Faradaic Efficiencies

The Faradaic efficiency (FE) is defined as the ratio of the charge required to form a product to the total charge passed during the electrolysis.

The total charge passed in the electrolysis is given by the integral of current density over time:

$$Qtotal = \int Idt \quad (1)$$

As two moles of electrons are necessary, to produce one mole of hydrogen and one mole of CO, the equivalent charge  $Q_{H2}$  and  $Q_{CO}$  passed during the electrolysis is given by equations (2) and (3):

$$Q_{H2} = n_{H2} * 2 * F$$
 (2)  
 $Q_{CO} = n_{CO} * 2 * F$  (3)

Where F is the Faraday constant and  $n_{H2}$  and  $n_{CO}$  are respectively the moles of hydrogen and CO formed during the electrolysis.

Thus the respective Faradaic efficiencies can be calculated by equations (4) and (5):

$$FEH2 = \frac{QH2}{Qtotal}X100$$

$$FECO = \frac{QCO}{Qtotal}X100$$
(4)
(5)

#### 2.1 Determination of the number of moles of products formed in the electrolysis

The number of moles of products formed in the electrolysis is calculated under the following assumptions:

- the molar composition of the gaseous headspace in the reactor is the same, as the molar composition of the sampling vessel, after expansion of electrolysis gaseous headspace into this vessel.

-the molar density of the gas (d) in the reactor after expansion will be approximately equal to the average molar densities of the gases in the same conditions of temperature and pressure given by equation (6):

$$\sum_{d=1}^{3} xidi$$
 (6)

where xi is the molar fraction of the gas i in the mixture and di is the molar density of this gas, considering equation 10:

$$x_{CO2} + x_{CO} + x_{H2} = 1$$
 (7)

The number of moles of product i formed during the electrolysis will be equal to the sum of the number of moles of product i in the reactor zone  $(ni_r)$  and in the sampling zone  $(ni_s)$  after expansion:

$$ni_{=}ni_{r}+ni_{s}$$
 (8)

The number of moles of product i in the sampling zone and in the reactor zone will be equal to the mole fraction of the product plus the total number of moles in the respective experimental set-up zone:

$$ni_{s} = x_{i}n_{Ts} (9)$$
$$ni_{r} = x_{i}n_{Tr} (10)$$

Gas chromatography analysis gives the mole fraction of product i, x<sub>i</sub> (H<sub>2</sub> or CO) in the sampling vessel.

The total number of moles in the sampling vessel  $(n_{Ts})$  is given by the ideal gas law,

$$n_{Ts} = PV_s / RT_s$$
(11)

considering the previously determined calibrated value of the sampling zone (Vs), temperature of the sampling vessel (room temperature) and pressure of the sampling vessel (approx. 2 bar).

The total number of moles in the reactor  $(n_{Tr})$  is given by:

$$n_{Tr} = d(P, T) * V_r$$
 (12)

with d as aforementioned defined, and  $V_r$  is the previously determined calibrated value of the reactor zone.

#### 3. Estimation of CO<sub>2</sub> conversions

Considering the global equations:

$$CO_2 \rightarrow CO + 1/2 O_2 \quad (13)$$
$$H_2O \rightarrow H_2 + \frac{1}{2} O_2 \quad (14)$$

 $CO_2$  conversion into CO is given by equation (15):

$$CO_2 \ Conversion \ (\%) = \frac{number \ of \ moles \ of \ CO2 \ converted \ into \ CO}{number \ of \ moles \ CO_2 \ dissolved \ in \ the \ electrolyte} * 100$$
(15)

Considering equation (13) the number of moles of  $CO_2$  converted is equal to the number of CO detected in the cathodic and anodic chambers. It is calculated as described in section 2.1.

The number of moles of CO<sub>2</sub> dissolved in the electrolyte in equation (15) is estimated as the solubility of CO<sub>2</sub> in water [1] at electrolysis temperature and pressure in the recirculated electrolyte volume of 226 ml  $\pm$  5ml consisting of 90 wt. % H<sub>2</sub>O and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMOTf) 10% wt.

# 4. Determination of Energy Efficiency

Defining energy efficiency (EE) by equation (16)

$$EE = \frac{\Delta Geq \ H2 \ EF \ H2 + \Delta Geq \ EF \ CO}{nFV cell} \times 100$$
(16)

where  $\Delta G_{eq}H_2$  is the Gibbs free energy for  $H_2$  formation,  $\Delta G_{eq}CO$  is the Gibbs free energy for CO formation, n is the number of moles of electrons transferred (2 for both reactions), F the Faraday constant, EFH<sub>2</sub>, the faradaic efficiency for H<sub>2</sub> and EFCO the faradaic efficiency for CO V<sub>cell</sub> the applied cell potential. Knowing that  $\Delta G_{eq}$  is given by equation (17)

$$\Delta G_{eq} = - nFE_{cell} \qquad (17)$$

where  $E_{cell}$  is the equilibrium cell potential, equation (16) can be rewritten in function of equilibrium cell potentials to give equation (18):

$$EE = \frac{Ecell H2 EF H2 + Ecell CO EF CO}{Vcell} * 100$$
(16)

#### 5. Productions and faradaic efficiencies of electrolysis in batch mode

Table S1 presents productions of  $H_2$  produced by the corrosion of zinc (chemical  $H_2$ ), estimated electrolytic  $H_2$  and of CO. Total faradaic efficiencies, membrane crossovers, final pH of electrolysis carried out in batch mode at 45°C, 10 bar CO<sub>2</sub> pressure are also presented. Applied current was in the range of -2 mA/cm<sup>2</sup> to -3mA/cm<sup>2</sup>, and 50 C of charge passed. Electrolyte: 90% wt. of  $H_2O$  and EMIMOTf at initial pH of 3.1. Estimated electrochemical produced  $H_2$  was calculated by subtracting from 100% CO faradaic efficiencies and then deriving productions from equations (4) and (5).

Table S1 – Process parameters of electrolysis carried out in batch mode at  $45^{\circ}$ C, 10 bar CO<sub>2</sub> pressure. Applied current was in the range of -2 to -3mA/cm<sup>2</sup>, and 50 C of charge passed. Electrolyte: 90% wt. of H<sub>2</sub>O and EMIMOTF at initial pH of 3.1.

Membrane thickness (µm)	Final pH	Production (mmol/cm <sup>2</sup> )	Faradaic efficiency (%)	Crossover (%)
120	WE:6,6 CE:6.0	H <sub>2</sub> : 5.10x10 <sup>-3</sup> (E) H <sub>2</sub> : 1.31x10 <sup>-2</sup> (C) CO: 1.65x10 <sup>-3</sup>	H <sub>2:</sub> >>100 CO:23.83	H <sub>2:</sub> 12.9 CO:11.2
90	WE:6,3 CE:3.4	H <sub>2</sub> : 5.50x10 <sup>-3</sup> (E) H <sub>2</sub> : 6.50x10 <sup>-4</sup> (C) CO: 1.65 x10 <sup>-3</sup>	H <sub>2:</sub> >>100 CO:22.12	H <sub>2:</sub> 15.8 CO:6.1
75	WE:6,4 CE:3.5	H <sub>2</sub> : 5.60x10 <sup>-3</sup> (E) H <sub>2</sub> : 1.12x10 <sup>-2</sup> (C) CO: 1.35 x10 <sup>-3</sup>	H <sub>2:</sub> >>100 CO:18.07	H <sub>2:</sub> 11.9 CO:9.1

(E)- electrolytic; (C) – Chemical

The values for hydrogen generated chemically present a high experimental scatter, because chemical production of  $H_2$  depends strongly on the time in which the electrode is in contact with the acidic electrolyte. A minimal value was set for system stabilization and sampling times (see section 1.1),

however no upper limit for these time periods was ascribed, thus, they may vary among the different electrolysis.

# 6. Potential Profiles of CO<sub>2</sub> reduction in batch mode using membranes with different thicknesses.

Potentials vs. time measured of 50 C electrolysis carried out in galvanostatic mode at 10 bar  $CO_2$  and 45°C with Zn foil cathode are represented in Figure S2. After a steep initial decrease in cell potential the potential stabilizes during the remaining time of the electrolysis. The cell potential varied within the range from -3.3V - -3.0 V.



Figure S2- Potential profiles of electrolysis carried out in batch mode at 45°C, 10 bar CO<sub>2</sub>, 50 C charge passed using the electrolyte 90% wt.  $H_2O$  and EMIMOTf and membranes of 120  $\mu$ m and 75  $\mu$ m thickness.

# 7. Productions, faradaic efficiencies of electrolysis in semi-continuous mode

Flow	51 2 10 5			ILO			
rate (ml/min)	Initial pH	Final pH	Pressure (bar)	n <sub>2</sub> O concentration in the electrolyte (%wt)	Production (mmol/cm <sup>2</sup> )	Faradaic efficiency (%)	Crossover (%)
1	3.7	WE:5.7 CE:2.6	10	90	H <sub>2</sub> : 9.40x10 <sup>-3</sup> (E) H <sub>2</sub> : 6.96x10 <sup>-2</sup> (C) CO: 1.53x10 <sup>-2</sup>	H <sub>2</sub> : >>100 CO:61.99	H <sub>2</sub> : 23.8 CO: 8.4
2.5	3.8	WE:5,7 CE:2.6	10	90	H <sub>2</sub> : 7.10x10 <sup>-3</sup> (E) H <sub>2</sub> : 7.19x10 <sup>-2</sup> (C) CO: 1.83x10 <sup>-2</sup>	H <sub>2</sub> : >>100 CO:71.98	H <sub>2</sub> : 23,0 CO: 9.2
4	3.8	WE:5,9 CE:2.6	10	90	H <sub>2</sub> : 1.22x10 <sup>-2</sup> (E) H <sub>2</sub> : 1.31x10 <sup>-1</sup> (C) CO: 1.76x10 <sup>-2</sup>	H2: >>100 CO:59.16	H2: 28.4 CO: 6.8
5	3.8	WE:5,8 CE:2.7	10	90	H <sub>2</sub> : 1.05x10 <sup>-2</sup> (E) H <sub>2</sub> : 1.13x10 <sup>-1</sup> (C) CO:1.19x10 <sup>-2</sup>	H <sub>2</sub> : >>100 CO:53.24	H <sub>2</sub> : 31.5 CO: 9.20
1	3.8	WE:6.0 CE:3.1	30	90	H <sub>2</sub> : 4.60x10 <sup>-3</sup> (E) H <sub>2</sub> : 1.55x10 <sup>-1</sup> (C) CO:2.08x10 <sup>-2</sup>	H <sub>2</sub> : >>100 CO:81.80	H <sub>2</sub> : 24.7 CO: 6.9
1	3.9	WE:5,8 CE:3.0	10	50	H <sub>2</sub> : 1.76x10 <sup>-3</sup> (E) H <sub>2</sub> : 8.80x10 <sup>-2</sup> (C) CO:0.8x10 <sup>-2</sup>	H <sub>2</sub> :>>100 CO:30.66	H <sub>2</sub> : 25.0 CO: 7.6

Table S2 – Process parameters of electrolysis carried out in semi-continuous mode at  $45^{\circ}$ C. Applied current was in the range of -2 to -3mA/cm<sup>2</sup>, and 200 C of charge passed.

(E)- electrolytic; (C) - Chemical

Table S2 presents productions of hydrogen (chemical and electrolytic) and of CO, faradaic efficiencies, membrane crossovers, initial and final pH of electrolysis carried out in semi-continuous mode at 45°C. Applied current was in the range of -2 to -3mA/cm<sup>2</sup>, and 200 C of charge was passed.

It is noteworthy to mention, that in steady state, chemical production of hydrogen in electrolysis in semicontinuous, or in continuous operation, will not occur, as in steady state the electrolyte will only contact the negatively charged cathode under applied currents, where zinc corrosion does not occur.

# 8. Potential Profiles of CO<sub>2</sub> reduction in continuous mode at different flow rates.

Potentials vs. time measured for 200 C electrolysis carried out in galvanostatic mode at 45°C with Zn foil cathodes with different flow rates are represented in Figure S3. After a steep initial decrease in cell potential the potential tends to stabilize during the electrolysis. The cell potential varied within the range from -3.8 V to -2.9 V for electrolysis carried out at 10 bar and it was -3.9 V at 30 bar CO<sub>2</sub> pressure. For the same applied current and flow rate of 1 ml/min., the potential profiles of the electrolysis carried out with the electrolyte containing 50 wt. % EMIMOTf and 10 wt.% of EMIMOTf (90% H<sub>2</sub>O) are overlapped. Although, the measured cell potential is the same, the selectivities of the two electrolysis are different, as described in the main text. The selectivity for H<sub>2</sub> is higher with the electrolyte with 50 wt.% EMIMOTf.



Figure S3 - Potentials vs. time measured for 200 C electrolysis carried out in galvanostatic mode with with Zn foil cathodes, at  $45^{\circ}$ C.

# 9. References

[1] L. Kramers and S.J.T. Hangx, Subsurface mineralisation. CATO, March 2019. <u>https://www.co2-cato.org/.../20090917\_123325\_4.1-11-06\_thesis\_wp4.1\_leslie\_kramer.pdf</u>. (last accessed June 2019).