

Supplementary Information

Imidazolium and picolinium-based electrolytes for electrochemical reduction of CO₂ at high pressure

Sofia Messias^a, Vitória Paz^a, Hugo Cruz^a, Carmen M. Rangel^b, Luís C. Branco^a, Ana S. Reis-Machado^{*a}

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

Table of Contents

1. Description of the high-pressure experimental set-up	3
2. Determination of Faradaic Efficiencies	4
2.1 Determination of the number of moles of products formed in the electrolysis.....	4
3. Cyclic voltammetry.....	5
4. Potential Profiles of CO ₂ reduction.....	7

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

Figure S1 shows a schematic of the experimental set-up for the CO₂ electrochemical reduction process at high pressure.

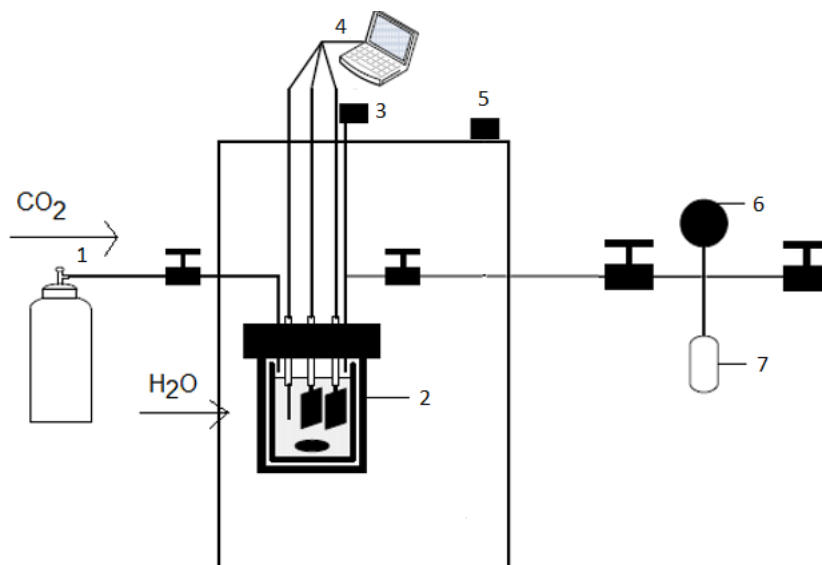


Figure S1 – Schematic diagram of the experimental set-up; (1) CO₂ cylinder; (2) electrochemical CO₂ reduction reactor; (3) digital pressure meter; (4) computer controlling potentiostat/galvanostat; (5) Temperature controller; (6) manometer; (7) sampling vessel

The experimental set-up can be divided in two main sections, reactor and sampling. The reactor is limited by the CO₂ inlet valve and the valve at the entrance of the sampling vessel. It consists of a stainless-steel reactor placed inside a temperature controlled insulated box (thermostatic air bath). The reactor is equipped with a digital pressure sensor (Omron K3JT, Omron Corporation). The sampling consists of a high-pressure sampling vessel of 50 cm³ 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.

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:

$$Q_{total} = \int Idt \quad (1)$$

As two moles of electrons are necessary, to produce one mole of hydrogen and one mole of CO, the equivalent charge Q_{H_2} and Q_{CO} passed during the electrolysis is given by equations (2) and (3):

$$Q_{H_2} = n_{H_2} \times 2 \times F \quad (2)$$

$$Q_{CO} = n_{CO} \times 2 \times F \quad (3)$$

Where F is the Faraday constant and n_{H_2} and n_{CO} are respectively the moles of hydrogen and CO formed during the electrolysis.

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

$$FE_{H_2} = \frac{Q_{H_2}}{Q_{Total}} \times 100 \quad (4)$$

$$FE_{CO} = \frac{Q_{CO}}{Q_{Total}} \times 100 \quad (5)$$

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):

$$\sum_{d=1}^3 x_i d_i \quad (6)$$

Where x_i is the molar fraction of the gas I in the mixture and d_i is the molar density of the gas, considering equation 10:

$$x_{CO_2} + x_{CO} + x_{H_2} = 1 \quad (7)$$

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:

$$ni = ni_r + ni_s \quad (8)$$

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:

$$ni_s = x_i n_{T_s} \quad (9)$$

$$ni_r = x_i n_{T_r} \quad (10)$$

Gas chromatography analysis gives the mole fraction of product *i*, *x_i* (H₂ or CO) in the sampling vessel.

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

$$n_{T_s} = PV_s/RT_s \quad (11)$$

Considering the previously determined calibrated value of the sampling zone (*V_s*), 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_{T_r}*) is given by:

$$n_{T_r} = d(P, T) \times V_r \quad (12)$$

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

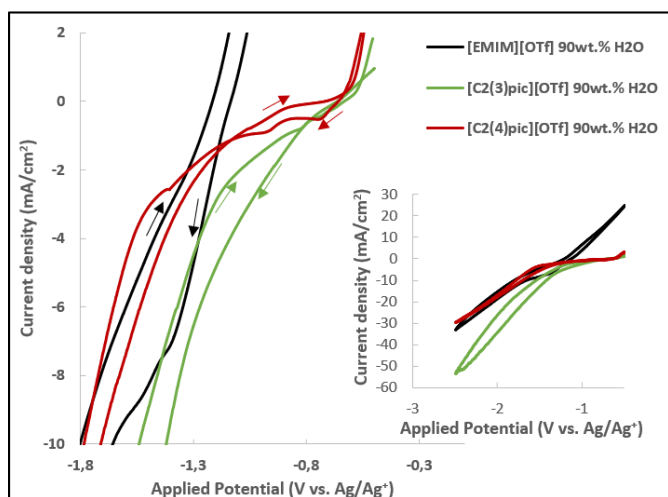
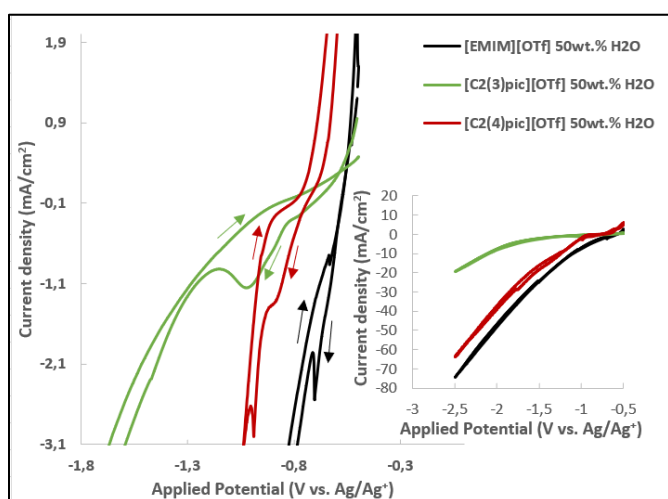
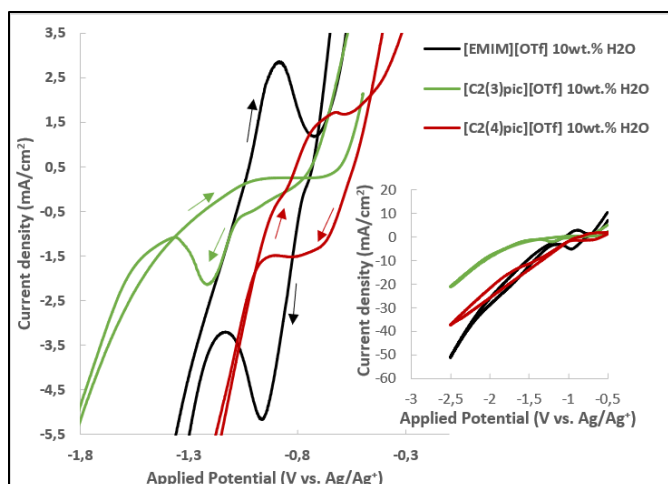
3. Cyclic voltammetry

Table S1 presents the onset potential, the oxidation peaks, and the reduction peaks for the ionic liquids with the different contents of water.

Table S1 – Onset potential, oxidation peaks and reduction peaks for the Ionic liquids with different contents of water.

	E_{onset} (V) vs. Ag/Ag⁺			E_{Ox peak} (V) vs. Ag/Ag⁺			E_{R peak} (V) vs. Ag/Ag⁺		
	[EMIM]⁺	[C₂(3)pic]⁺	[C₂(4)pic]⁺	[EMIM]⁺	[C₂(3)pic]⁺	[C₂(4)pic]⁺	[EMIM]⁺	[C₂(3)pic]⁺	[C₂(4)pic]⁺
Dry in N₂	-1.69	-0.96	-0.99	-1.18	-	-	-	-	-
Dry in CO₂	-1.30	-1.38	-0.94	-0.86	-	-	-	-	-
10wt.% H₂O	-0.81	-1.11	-0.84	-0.88	-	-0.62	-0.98	-1.22	-
50wt.% H₂O	-0.62	-1.22	-0.84	-0.63	-	-0.89	-0.70	-0.98	-0.88 ; -0.99
90wt.% H₂O	-1.17	-0.89	-1.07	-	-	-	-1.38	-	-0.73; -0.97

Figure S2 compares the CVs of different electrolytes with the same water composition.



S2 – Cyclic voltammograms on zinc cathodes at 45°C carried out at 50mV/s in the potential range of -0.5V to 2.5V vs. QRE Ag/Ag⁺ (QRE) for the ionic liquids [EMIM][OTf], [C₂(3)pic][OTf] and [C₂(4)pic][OTf] with different compositions of water in CO₂ atmosphere. a) 10wt.% H₂O; b) 50wt.% H₂O; c) 90wt.% H₂O

4. Potential Profiles of CO₂ reduction.

Potential vs time measured of the electrolysis carried out at 45°C, 10bar CO₂ atmosphere, with zinc as cathode and sacrificial anode, 10C charge passed and applied current density range of -0.65 to -0.85 mA/cm² are represented in Figure S3.

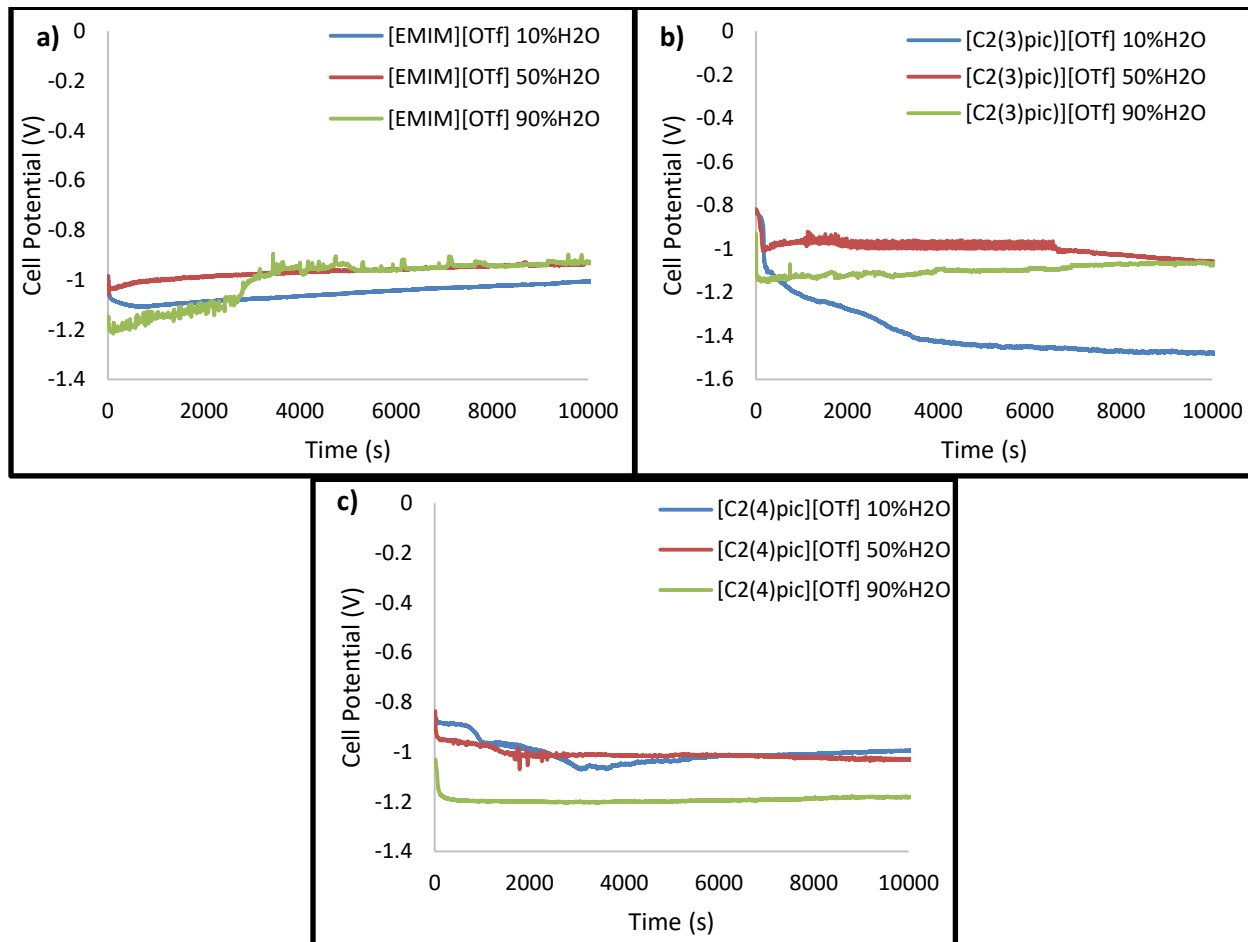


Figure S3 – Potential profiles of electrolysis carried out at 45°C, 10bar, 10 C charge passed and applied current of -0.65 to -0.85 mA/cm² using different electrolytes. **a)** [EMIM][OTf] based electrolyte; **b)** [C2(3)pic][OTf] based electrolyte; **c)** [C2(4)pic][OTf] based electrolyte

Potential vs time measured of the electrolysis carried out at 45°C, 10bar CO₂ atmosphere, with zinc as cathode and sacrificial anode, 50C charge passed and applied current density range of -7 mA/cm² are represented in Figure S4.

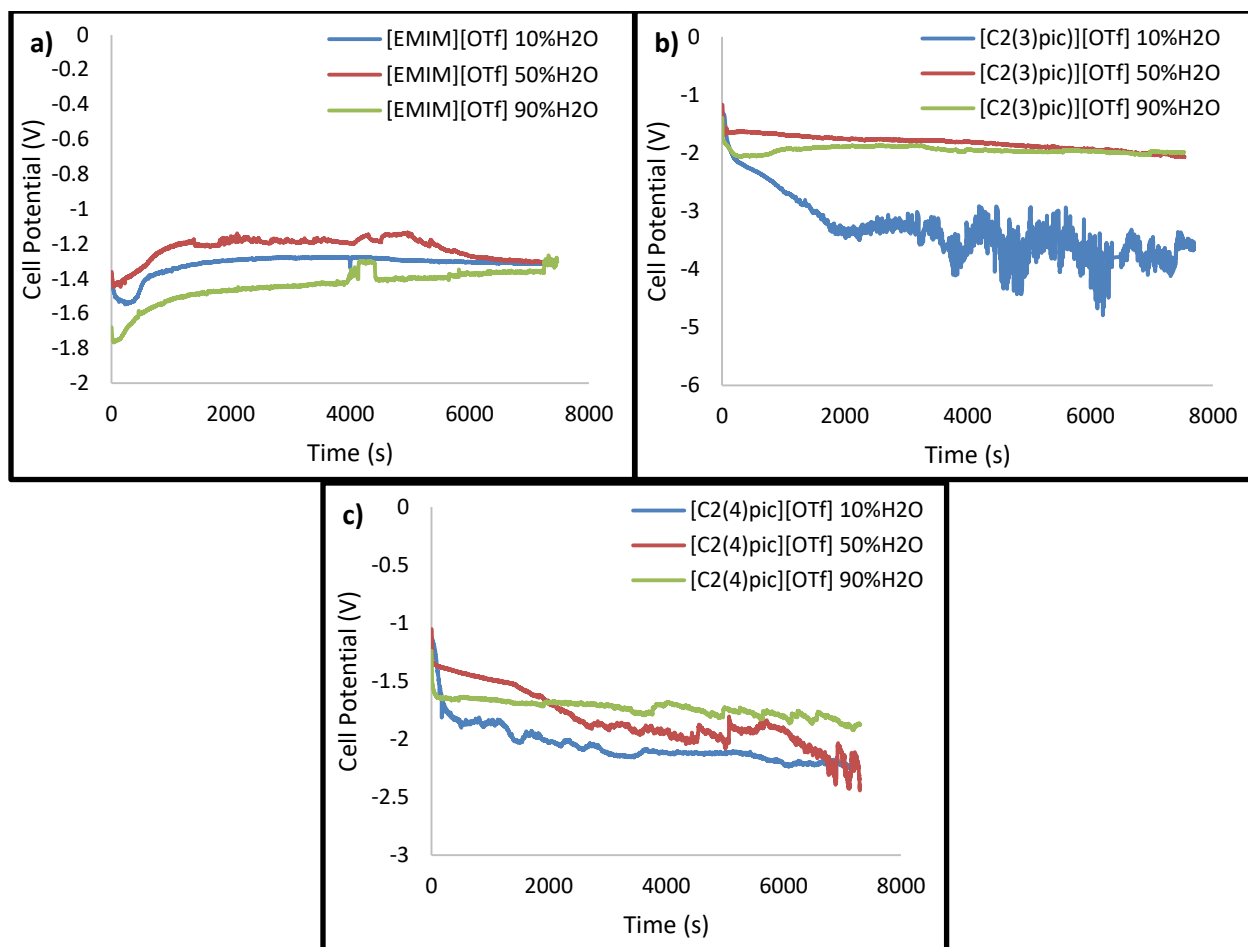


Figure S4 – Potential profiles of electrolysis carried out at 45°C, 10bar, 50 C charge passed and applied current of -7 mA/cm² using different electrolytes. **a)** [EMIM][OTf] based electrolyte; **b)** [C2(3)pic][OTf] based electrolyte; **c)** [C2(4)pic][OTf] based electrolyte