

Assessing the CO₂ Capture and Electro-Reduction in Imidazolium-Based Ionic Liquids: Role of the Ion Exchange Membrane

Original

Assessing the CO₂ Capture and Electro-Reduction in Imidazolium-Based Ionic Liquids: Role of the Ion Exchange Membrane / Gallone, Mario; Fortunati, Alessia; Hernández, Simelys. - In: CATALYSTS. - ISSN 2073-4344. - 15:4(2025). [10.3390/catal15040318]

Availability:

This version is available at: 11583/2998661 since: 2025-03-30T09:27:21Z

Publisher:

MDPI

Published

DOI:10.3390/catal15040318

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Article

Assessing the CO₂ Capture and Electro-Reduction in Imidazolium-Based Ionic Liquids: Role of the Ion Exchange Membrane

Mario Gallone ¹, Alessia Fortunati ^{1,2} and Simelys Hernández ^{1,*}

¹ CREST Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy; mario.gallone@polito.it (M.G.); alessia.fortunati@iit.it (A.F.)

² Istituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy

* Correspondence: simelys.hernandez@polito.it

Abstract: The electrochemical CO₂ reduction (eCO₂RR) to valuable chemicals offers a promising method to combat global warming by recycling carbon. Among the possible products, syngas—a CO and H₂ mixture—is especially valuable for industrial reactions. The use of Room Temperature Ionic Liquids (RTILs) electrolytes presents a promising pathway for eCO₂RR because of the lower overpotential required and the increased CO₂ solubility with respect to the aqueous ones. Ensuring a constant CO/H₂ production is essential, and it relies on both the catalyst and reactor design. This study explores eCO₂RR in RTIL mixtures of 1-butyl-3-methyl imidazolium trifluoromethanesulfonate (good for CO₂ conversion) and 1-butyl-3-methyl imidazolium acetate (good for CO₂ capture), with various amounts of water as a proton source. We evaluated syngas production stability across different electrochemical cells and ion exchange membranes after determining the appropriate electrolyte mixture for a suitable CO/H₂ ratio near 1:1. The two-chamber cell configuration outperformed single-cell designs by reducing oxidative RTILs degradation and by-products formation. Using a bipolar membrane (BPM) in forward mode led to catholyte acidification, causing an increase of HER relative to eCO₂RR over time, confirmed by Multiphysics modeling. Conversely, an anionic exchange membrane (AEM) maintained constant syngas production over extended periods. This work offers guidelines for syngas generation in RTIL-based systems from waste-CO₂ reduction, which can be useful for other green chemical synthesis processes.

Keywords: electrochemistry; CO₂ reduction; CO₂ capture; ionic liquids; syngas; membrane; sustainability



Academic Editors: Consuelo Alvarez-Galvan, Marisol Faraldos and Belén Bachiller-Baeza

Received: 20 February 2025

Revised: 16 March 2025

Accepted: 17 March 2025

Published: 26 March 2025

Citation: Gallone, M.; Fortunati, A.; Hernández, S. Assessing the CO₂ Capture and Electro-Reduction in Imidazolium-Based Ionic Liquids: Role of the Ion Exchange Membrane. *Catalysts* **2025**, *15*, 318. <https://doi.org/10.3390/catal15040318>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Increasing CO₂ atmospheric concentration (from 280 ppm during the pre-industrial era to 426 ppm reached in 2024) is a crucial threat to humankind, leading to global warming. To face this challenge, many efforts have been dedicated to valorizing waste CO₂ to obtain value-added products. Electrochemistry plays a pivotal role since CO₂ can be reduced to other chemical species, such as CO [1–3], HCOOH [4–6], CH₄ [7–9], C₂H₄ [10–13], and CH₃OH [14–16] via the electrochemical CO₂ reduction reaction (eCO₂RR). In particular, the simultaneous production of CO and H₂, defined syngas, is a crucial reagent for industrially relevant reactions [17–23]. When investigating the conversion of CO₂ dissolved in the liquid electrolyte, aqueous-based electrolytes suffer from low CO₂ solubility (30 mM) [17], leading to sluggish reaction kinetics and competing side reactions, like the H₂ evolution

reaction (HER). Therefore, organic solvents such as acetonitrile [18] (CH_3CN) are used, enabling a higher CO_2 solubility (0.02 mol%) [19], but usually entailing low conductivity and lack of stability under electrochemical conditions because of electrode passivation or solvent degradation. However, overcoming these challenges requires the development of electrolytes that provide improved CO_2 transport, stability, and tailored interactions with reaction intermediates. In this scenario, Room Temperature Ionic Liquids (RTIL) have been studied as effective electrolytes for eCO_2RR applications [20–24]. RTILs are molten salts at ambient conditions. Their ionic nature makes RTILs very conductive. However, due to the strong ionic interactions between the cations and the anions, they usually suffer from high viscosity. Thus, dissolving RTILs in an organic solvent (e.g., CH_3CN or 3-methoxypropionitrile, 3-MPN) is a good strategy for obtaining highly conductive electrolytes. RTILs offer superior CO_2 solubility and a wider electrochemical stability window compared to other non-aqueous electrolytes, making them the ideal choice for CO_2 capture and conversion applications; they act as co-catalysts by interacting with CO_2 and stabilizing the intermediate $\text{CO}_2^{\bullet-}$ radical anion (generally considered to be the rate-determining step for CO_2 activation), lowering the eCO_2RR overpotential [25,26]. Imidazolium-based RTILs have shown excellent CO_2 capture properties [19], and high conversion efficiencies [27,28]. The capture properties are related to the ability of the imidazolium cation to release a proton, forming a highly reactive carbene species; this carbene can interact with CO_2 , forming a Bmim- CO_2 complex. The ability to form the carbene species is controllable by choosing the right anion, as highlighted by the work of Fortunati et al. [29,30].

Not only the electrolyte or the electrocatalyst design [31,32], but the reactor setup also plays an important role [33,34]. The electrochemical configurations (e.g., the type of electrochemical cell employed) strongly influence the outcome of the process. A single-compartment cell is a simple, easy-to-operate setup commonly used in lab experiments exploiting RTILs. It requires a few amount of electrolyte and bypasses the anolyte optimization process. However, coexistence in the same cathodic and anodic processes environment can lead to undesired oxidation/reduction of the cathodic/anodic products. Besides, the electrolyte should be optimized to be simultaneously suitable for eCO_2RR at the cathode and Oxygen Evolution reaction (OER) at the anode [35,36]. Instead, the membrane is a decisive parameter when using two-compartment cells (e.g., H-type cells) [37]. For aqueous-based eCO_2RR applications, a bipolar membrane (BPM) is generally preferred to enhance the CO_2 single-pass conversion (SPC) with respect to an anionic exchange membrane (AEM). CO_2 forms (bi)carbonate anions in water, which migrate from the catholyte to the anolyte through the AEM and re-oxidizes at the anode, causing CO_2 loss [38].

The present work studies mixtures of imidazolium-based RTILs, with and without adding water as a proton source, as electrolytes for eCO_2RR to syngas on Ag by using laboratory-scale electrochemical cells. Based on a recent work of some of us [30], we selected 1-butyl-3-methyl imidazolium trifluoromethane sulfonate ([Bmim] $[\text{CF}_3\text{SO}_3]$), which promotes highly selective CO production, and 1-butyl-3-methyl imidazolium acetate ([Bmim] $[\text{CH}_3\text{CO}_2]$), which is a good CO_2 capture RTIL and promotes HER. Hence, the synergistic effect of the two anions was exploited here to achieve a tunable and constant CO/H_2 ratio during syngas production [39–42]. The system's selectivity and stability towards syngas evolution depended on configuration parameters such as electrolyte composition and electrochemical cell employed. In the case of the two-compartment H-cell configuration, the role of the membrane employed in the reaction outcome was studied experimentally and with COMSOL 6.1 (COMSOL Srl, Brescia, Italy) Multiphysics modeling.

This work provides guidelines to control the CO/H_2 ratio and stability in RTIL-based electrolytes by exploiting their CO_2 capture and cocatalyst features. Moreover, we

(i) highlight the necessity to take into account the eventual degradation processes of the RTILs, avoidable by separating the anode and cathode chambers; (ii) most importantly, we warn the reader that BPM is not always the right choice when talking about eCO₂RR. This work paves the way for developing sustainable integrated RTILs-based technologies for synthesizing fine chemicals (for example, via carbonylation [43,44], hydroformylation or thermocatalytic processes for methanol production), requiring different CO/H₂ ratios (from pure CO to CO/H₂ = 2 to 0.5), starting from syngas electrochemically generated from CO₂ [45,46].

2. Results

2.1. Electrolyte Preparation

Electrolytes were prepared by mixing two different ILs, i.e., [Bmim] [CH₃CO₂] and [Bmim] [CF₃SO₃] (The chemical structures of the RTILs are depicted in Figure 1), in 3-MPN. Different amounts of H₂O were added to the mixture to act as a proton source for eCO₂RR and HER. In principle, controlling the CO/H₂ ratio should be possible by varying the water content. Mixtures of 1.6 M of [Bmim] [CF₃SO₃] and 2.4 M of [Bmim] [CH₃CO₂] in 3-MPN were used to maximize the conductivity of each IL component (see Figure S1 in the Supplementary Materials). Then, different volumetric percentages of H₂O were added to the original solution, namely 20%v/v, 10%v/v, 5%v/v, and 1%v/v, until a total volume of 50 mL (see molar compositions in Table 1). The different mixes were named based on the water addition (%v/v). MIX0% stands for the electrolyte without any further addition of water (besides water traces < 110 ppm are present, see Section 4.1), while MIX20% contains 20%v/v of H₂O. Logically, the molarity of the ILs decreases with the increase in water content. The ratio between triflate's and acetate's molarities was kept constant at 2.

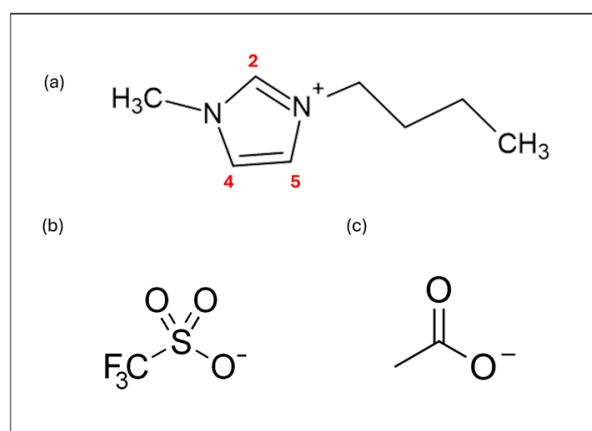


Figure 1. (a) 1-butyl-3-methylimidazolium cation. The three carbons of the imidazolium ring are indicated in red. The proton on C2 is the acidic site. Its acidity also depends on the nature of the anion [30]. (b) Triflate ([CF₃SO₃][−] or OTf) anion. (c) Acetate ([CH₃CO₂][−] or OAc) anion.

Table 1. Molar composition of the electrolytes.

Name	H ₂ O (%v/v)	H ₂ O (mL)	H ₂ O (mmol)	Added H ₂ O (M)	[SO ₃ CF ₃] (mmol)	[SO ₃ CF ₃] (M)	[CO ₂ CH ₃] (mmol)	[CO ₂ CH ₃] (M)	[Anion] (mmol)	Conductivity (mS/cm)
MIX20%	20	10	550.0	11.0	48	0.96	24	0.48	72	21.7
MIX10%	10	5	275.0	5.5	54	1.08	27	0.54	81	18.8
MIX5%	5	2.5	137.5	2.75	57	1.14	28	0.57	85	16.1
MIX1%	1	0.5	27.5	0.55	59	1.19	29	0.59	88	12.7
MIX0%	~0.2	0	~3	0	59	1.20	30	0.60	89	11.6

2.2. RTIL-Based Electrolyte Electrochemical Characterization

The activity towards $e\text{CO}_2\text{RR}$ of the electrolyte mixtures was studied in a single compartment cell (Figure S2A, Supplementary Materials) via Linear Sweep Voltammetry (LSV) between 0 and -2.5 V vs. Ag/AgCl with a scan rate of 10 mV/s. In N_2 -saturated electrolytes, the onset potential shifts toward more positive values for higher water contents (Figure 2a), because of higher HER activity due to the increased concentration of protons. With water traces (MIX0%), a more negative onset potential was observed in the CO_2 -saturated rather than the N_2 -saturated, indicating that the $e\text{CO}_2\text{RR}$ is favorably promoted in the RTIL-based electrolyte. This phenomenon was observed for any mixes with water content until 5%. Conversely, analogous onset potentials were reported in the N_2 - and CO_2 -saturated MIX20%, indicating that the HER is a non-negligible process at 20% water concentration in the electrolyte (see Figure 2b and inset). The positive shift of the onset potential in the presence of CO_2 evidences the reactivity of the electrolytes towards $e\text{CO}_2\text{RR}$. In N_2 -saturated electrolyte, every mixture is electrochemically stable until an applied potential of -2 V vs. Ag/AgCl, up to 5% v/v , where the water content becomes high enough to shift the onset potential due to the HER. For more negative potential, the electrochemical reduction of the ILs in the electrolyte began to be the primary Faradaic process.

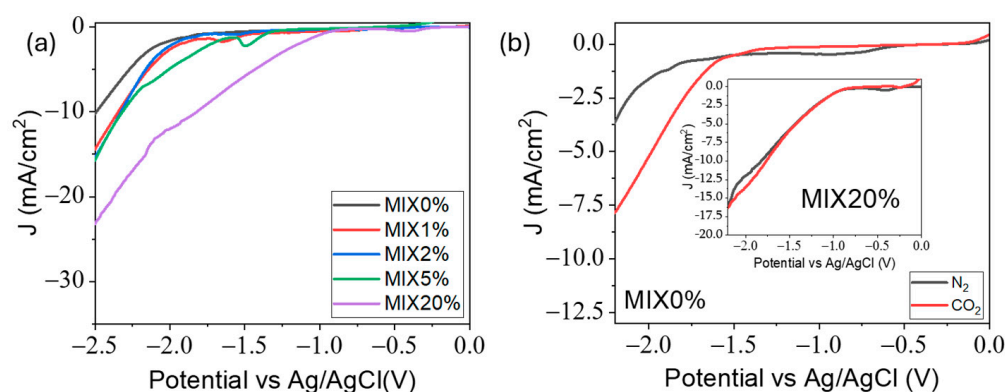


Figure 2. (a) LSV in N_2 of electrolytes with increasing concentration of H_2O . (b) LSV MIX0% in N_2 and CO_2 . In the inset of (b), the LSV both in N_2 - and CO_2 -saturated atmospheres MIX20% is reported. iR compensation is applied to avoid any conductivity-related bias. Reduction peaks visible in MIX5% and MIX1% are probably related to impurities (since the peak is absent either in MIX0% or MIX2%). However, the assignment of this undefined redox phenomenon is beyond the scope of the manuscript.

2.3. CO_2 Electrolysis Tests

Electrolysis tests were conducted in a single-compartment cell and an H-type (Figure S2B, Supplementary Materials) cell to assess the cell configuration's influence on selectivity and the CO and H_2 production stability in the RTILs-based electrolytes with different water contents. Figure 3 reports the Faradaic Efficiency (FE) of the principal gaseous products during 90 min CP experiments in the single cell at -20 mA/cm². These results suggest that water is the leading proton donor for HER and $e\text{CO}_2\text{RR}$. Indeed, by lowering the H_2O content in the electrolyte, the FE shifts towards mainly CO production. However, even with traces of water in the electrolyte (no added water for MIX0% and 1.6 M Bmim OTf), the $e\text{CO}_2\text{RR}$ occurs, while the HER is significantly suppressed. Fortunati et al. recently showed that a stronger Lewis base anion (as acetate) turns the C2 proton of the imidazolium cation more acidic. Thus, if released, this proton can serve as a co-proton source for the reaction together with the low amount of water present in the electrolyte.

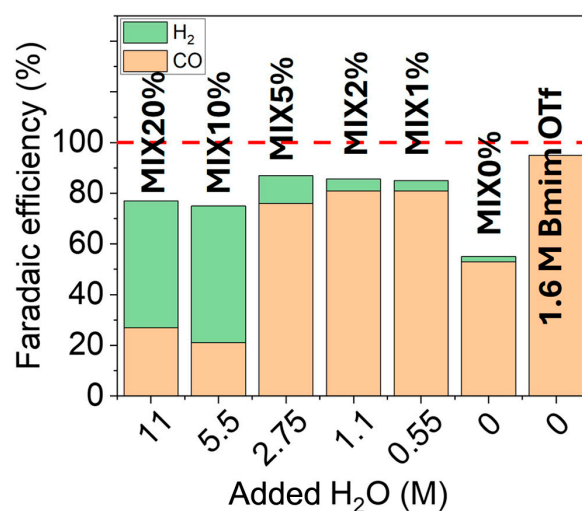


Figure 3. Dependence of Faradaic Efficiency toward H₂ (green) and CO (orange) for different electrolytes during chronopotentiometry in single cell at -20 mA/cm^2 for 90 min.

Moreover, the total Faradaic efficiency decreases following a decrease in water content and applied current (Figure S3, Supplementary Materials). These results may be attributed to the products' partial reoxidation and the possible presence of other Faradaic processes, such as the degradation of ILs. When a polycrystalline Ag plate is employed as a working electrode, the three detectable reduction products are CO and HCOO⁻ (from eCO₂RR) and H₂ (from HER). However, as pointed out by the pioneering work of Hori [40], in the potential range explored, in an aqueous system, the selectivity towards CO production on Ag is one order of magnitude higher than HCOO⁻. Moreover, previous work from our group using similar electrolytes and catalysts [30] highlighted how the Ionic Liquid here employed (e.g., Bmim OTf and Bmim OAc) are selective towards producing CO and H₂, respectively. No other liquid products (such as HCOO⁻ or alcohols) were detected significantly either by HPLC or GC-MSD. Kroon et al. [47] employed theoretical calculations to predict that cation radicals may form at cathodic potential, causing imidazolium dimerization through C2 hydrogen. Cation dimerization during the reaction is supported by the evident color change in the solution, from pale yellow to dark brown, especially at low water content in the electrolyte (Figure S4, Supplementary Materials). Besides, CH₄ and C₂H₄ were detected when potentials over -2 V were applied in a single-compartment electrochemical cell, and the concentration of these products increased with the applied potential and with the ILs molarity in the mixture (Figure S5, Supplementary Materials), thus suggesting both to be IL's degradation products. Hence, the electron count is probably closed by a reductive mechanism of Ionic Liquids degradation, as reported by Kroon et al. However, since these RTIL cathodic degradation mechanisms are radical-involved mechanisms, it is difficult to make an exact count to obtain an efficiency value, and this is beyond the scope of the present paper. To confirm this hypothesis, a CP ramp ranging from -5 mA/cm^2 to -90 mA/cm^2 was conducted in an inert N₂ atmosphere (Figure 4), continuously analyzing the outlet gases to confirm whether the C-based products are generated even without CO₂. CH₄ and C₂H₄ were detected, while CO was absent, confirming that methane and ethylene are formed as IL degradation products. CO started forming when the electrolyte was saturated with CO₂, and a sudden decrease in the cathodic potential, $E(\text{we})$, happened. Since no variation was detected on the anode potential, $E(\text{ce})$, after CO₂ saturation of the electrolyte, we hypothesized that the RTILs degradation occurred via oxidation at the Pt anode (placed close to the cathode in the single-compartment cell). Moreover, Ag is known to be selective towards CO production, and only a few works report CH₄ and C₂H₄

production under specific mass transport conditions, further excluding any CO₂ reduction origin of those products under the tested conditions [48,49]. As a final note, LSVs carried out before and after electrolysis for the MIX0% showed significant difference (while minor changes occurred for MIX20%, see Figure S6A,B, Supplementary Materials), indicating that the electrolyte degradation strongly depends on IL concentration, being higher at lower water contents.

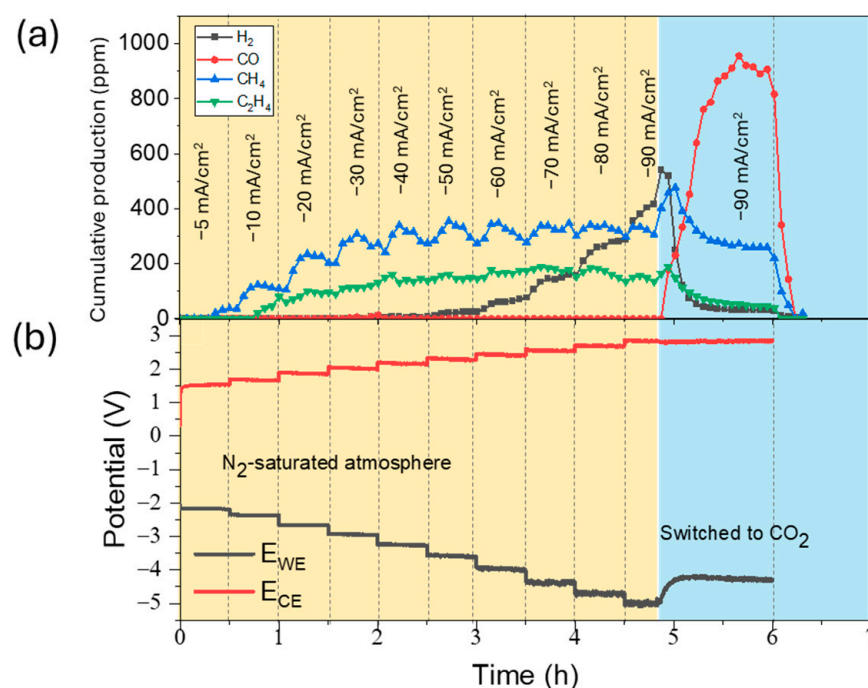


Figure 4. (a) gas products collected in single cell during $t = 6$ h step-electrolysis experiments at different current densities in N₂-saturated electrolyte (yellow region) and CO₂-saturated electrolyte (blue region); (b) Potentials measured at the Working Electrode (we) and Counter Electrode (ce) during the current ramp from $j = -5$ mA/cm² to $j = -90$ mA/cm². Potential is referred to Ag/AgCl electrode.

Previous experimental evidence showed that the separation between the catholyte and the anolyte is of utmost importance, even at the expense of higher cell potential. In this way, the electrolyte degradation at the anode can be prevented, consequently preserving the RTIL-based electrolyte's stability and the syngas' purity out-stream and suppressing the evolution of unwanted side products such as CH₄ and C₂H₄. By changing the experimental setup from a single-cell to an H-cell, the membrane employed to separate the cathodic and anodic compartments becomes the primary concern.

From the data obtained in the single cell, MIX20% was selected as the most suitable electrolyte for syngas production, allowing a total CO:H₂ ratio close to 1:1. In the single cell, despite the initial high CO selectivity, HER generally increased during operation becoming the primary faradaic process at the end of the test (Figure S7, Supplementary Materials), probably due to the RTIL-electrolyte partial oxidation. To overcome this limitation, the co-electrolysis experiments were performed in an H-type cell (see the Section 4.3) with MIX20%, and the obtained FE values are summarized in Figure S8 (Supplementary Materials). In this configuration, the membrane dramatically influences selectivity over time. When using a bipolar membrane, the CO production was rapidly suppressed, arriving at zero after a few minutes of operation (see Figure 5a). The system's selectivity becomes stable only when an anionic membrane is employed (Figure 5b). This phenomenon can be ascribed to the proton production at the interface layer of the BPM, which makes the system more selective towards HER. As detailed in the Section 2.4, a descriptive COMSOL model has been built

to confirm this hypothesis. Moreover, adding 20% of water to the ILs-based electrolyte also reduced the possibility of the imidazolium cation to act as a proton source and ensured a higher electrolyte stability.

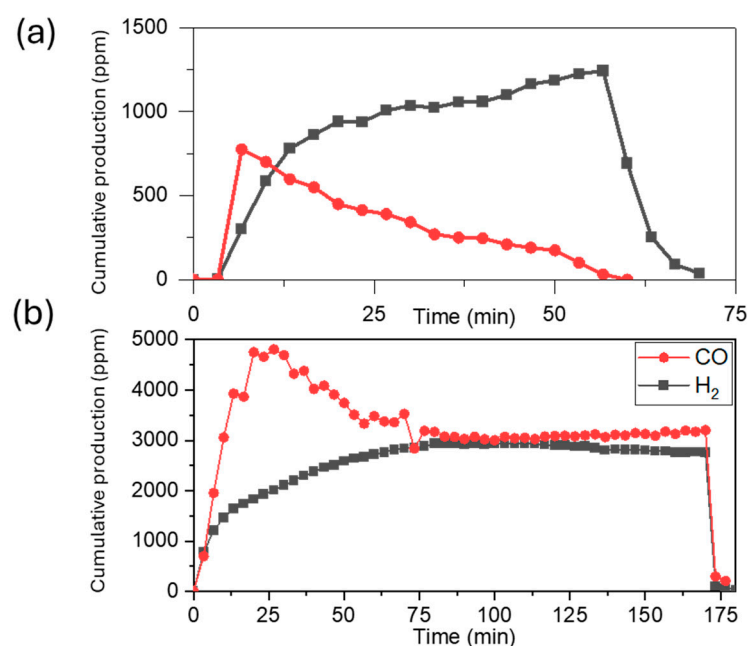


Figure 5. (a) Gas production profile obtained with MIX20% during 1 h electrolysis at -20 mA/cm^2 in H-type cell equipped with BPM and KOH 0.5 M as anolyte. (b) Gas production profile obtained with MIX20% during 3 h electrolysis at -20 mA/cm^2 in H-type cell equipped with an AEM and KOH 0.5 M as anolyte.

On the other hand, catholyte and anolyte cross-over is a severe issue when a two-compartment cell (e.g., H-cell or Flow cell) is employed, and organic electrolytes can exacerbate such phenomena by destabilizing the polymeric matrix of the membrane. To investigate such phenomena, two samples of the anolyte (KOH aqueous solution) and two samples of the catholyte, were collected before and after several hours of chronopotentiometry with the AEM, and were analyzed by IR spectroscopy. As shown in the Figure S9 (Supplementary Materials), the two anolyte spectra are similar, which confirms the absence of ILs crossover from the catholyte to the anode compartment. Indeed, no peaks related to the RTILs nor the 3-MPN organic solvent are present in the anolyte after 3 h of test: only the vibrational modes of water (between 3000 and 3000 cm^{-1}) related to O-H bonds stretching, and the sharper peak (around 1600 cm^{-1}) related to the H-O-H scissoring vibration are visible. Similarly, Figure S10 (Supplementary Materials) compares the two catholyte spectra before and after the test, demonstrating no appreciable aqueous KOH cross-over during the reaction. The broad O-H band in the region between 3000 and 3500 cm^{-1} is not visible in the catholyte's IR spectra at the end of the chronopotentiometry, suggesting that the anolyte crossover is not a severe issue in the proposed setup.

2.4. Computational Modeling

To explain the experimental results shown in Figure 5, we developed a simplified 1-dimensional COMSOL Multiphysics model. In particular, the model aims to validate the following hypothesis: (i) Water is the main proton source for HER; (ii) Protons in the C2 position of the imidazolium cations of the ILs can act as additional proton sources for CO_2 reduction when the water concentration is low; (iii) the use of a Bipolar Membrane determines unstable syngas production due to increased proton concentration at the cath-

ode during operation. The structural model included the Ag surface (cathode) as a point electrode, a diffusion layer of 100 μm , and the bulk electrolyte (as a point concentration reference). Since the density of [Bmim][CH₃SO₃] is equal to 1.2135 kg/L at 292.95 K and CO₂ molality in [Bmim][CH₃SO₃] is 0.4927 mol/kg at 293.2 K [50], then we assumed a CO₂ solubility in [Bmim] of 0.60 mol/L, equivalent to 600 mM. This CO₂ concentration was then set at the bulk electrolyte, while [H⁺] and [OH⁻] were generically assumed to be 0 mM, and [CH₃SO₃⁻], [CO₂CH₃⁻], and [H₂O] bulk concentrations were taken from Table 1. For simplicity, no further species were included in the model. Anode and, consequently, anodic reactions were not considered since the focus was on the catholyte chamber of the H-cell experimentally employed.

As heterogeneous reactions at the cathode, CO and H₂ formation were considered, with kinetic parameters, charge transfer coefficients, and equilibrium potentials retrieved from Ref. [51] (see Table 2). The CO exchange current density from Ref [51] was multiplied by a correction factor of 5 to match experimental results. Instead, the kinetic parameters evaluated from our own experimental study were not used due to the significant mass transfer limitations occurring in our system (due to varying H₂O content). The proton source for CO₂ reduction and Hydrogen Evolution was either [Bmim⁺] protons (at low water content in the electrolyte, see Equations (1) and (2)) or H₂O itself (Equations (3) and (4)). CO and H₂ current densities were then modeled via Butler-Vomer equations, including a specific dependence on CO₂ (for eCO₂RR) and H⁺/H₂O surface concentrations (for HER, depending on the proton source). This mass transfer factor was normalized by a reference concentration of 1 M. The actual conductivity of the bulk electrolyte (data in Table 1) was used in the model.

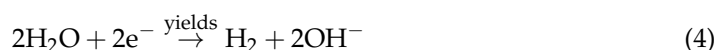
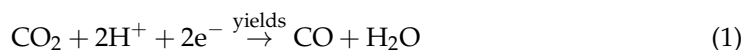
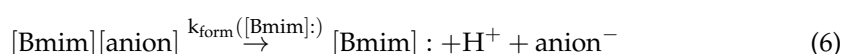


Table 2. Kinetic parameters included in the model.

	j_0 (mA/cm ²)	α	E^0/V vs. RHE	Reference
H ₂	$6.36 \cdot 10^{-2}$	0.14	0	[51]
CO	$2.01 \cdot 10^{-3}$	0.35	-0.11	[51]

Regarding chemical equilibria reactions at the bulk electrolyte, water self-ionization (Equation (5)), and release of C2 proton (Equations (6) and (7)) were included, assuming the reaction rates reported in Table 3, where values on ionic liquids are taken from our recent density functional theory study [29]. In Equation (7), we set a frequency factor of 1 fs⁻¹. Given the previous considerations, H⁺ and OH⁻ evolution within the electrolytes followed Equations (8) and (9).



$$[\text{H}^+] = A \exp\left(\frac{-\Delta G([\text{Bmim}] :)_{\text{SO}_3\text{CF}_3}}{k_B T}\right) [\text{SO}_3\text{CF}_3] + A \exp\left(\frac{-\Delta G([\text{Bmim}] :)_{\text{CO}_2\text{CH}_3}}{k_B T}\right) [\text{CO}_2\text{CH}_3] \quad (7)$$

$$R_{H^+} = kw_1[H_2O] - kw_2[H^+][OH^-] + k_{form-SO_3CF_3}[SO_3CF_3] + k_{form-CO_2CH_3}[CO_2CH_3] \quad (8)$$

$$R_{OH^-} = kw_1[H_2O] - kw_2[H^+][OH^-] \quad (9)$$

Table 3. Homogeneous reaction rates.

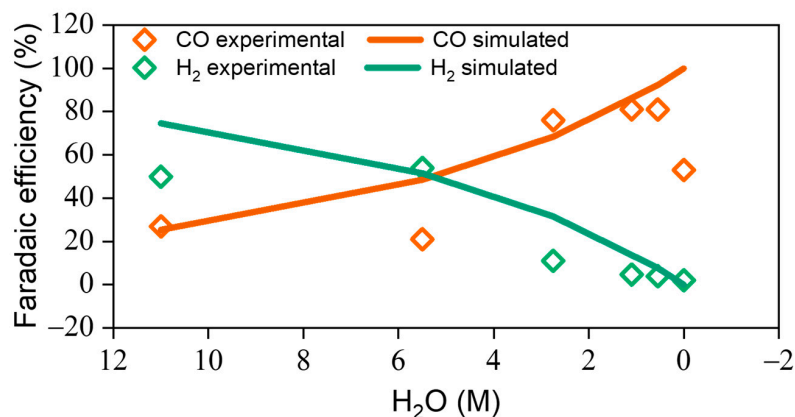
Constant	Value	References
kw1 (mol/m ³ s)	2.4·10 ⁻²	[17]
kw2 (m ³ /mol s)	2.4·10 ⁶	[17]
ΔG([Bmim]:)SO ₃ CF ₃ (eV)	1.03	[29]
ΔG([Bmim]:)CO ₂ CH ₃ (eV)	2.24	[29]

The diffusion coefficients and charges reported in Table 4 were used to solve the Nernst-Planck equation. Regarding diffusion coefficients, values estimated in water for H⁺, OH⁻, and H₂O were multiplied by a correction factor obtained as $\frac{D_{CO_2}([Bmim][PF_6])}{D_{CO_2}([H_2O])}$. Diffusion coefficients for [CH₃SO₃⁻] and [CO₂CH₃⁻] were assumed to be 0.1·10⁻⁵ cm²/s, while their charges were set to -1 |e|⁻.

Table 4. Diffusion coefficients assumed in the model.

Species	Diffusion Coefficient (cm ² /s)	Charge (e ⁻)	Solvent	Reference
H ⁺	9.311·10 ⁻⁵	+1	Water	[17]
OH ⁻	5.273·10 ⁻⁵	-1	Water	[17]
H ₂ O	2.57·10 ⁻⁵	0	Water	[52]
CO ₂	1.91·10 ⁻⁵	0	Water	[17]
CO ₂	2.9·10 ⁻⁶	0	[Bmim][PF ₆]	[53]

By running a stationary simulation assuming the molar compositions in Table 1 and an applied current density of -20 mA/cm², the model returns values of Faradaic efficiency toward H₂ and CO well aligned with the experimental results in Figure 3. As shown in Figure 6, H₂ selectivity is close to zero at low water content, suggesting the need for H₂O to sustain hydrogen production. Instead, a high selectivity toward CO is observed with very low water content, strengthening the hypothesis of [Bmim] C2-H as an additional proton source for the eCO₂RR.

**Figure 6.** Experimental (scatters) and predicted (lines) faradaic efficiencies values for H₂ (green) and CO (orange) for the 5 ILs mixtures with water addition and only water traces (close to 0 concentrations), at -20 mA/cm² applied current density.

To qualitatively investigate the role of the bipolar membrane in tuning the H_2/CO ratio, we included in the model an artificial proton source at the electrode (H^+ flux of $0.5 \text{ mol}/(\text{m}^2\text{s})$) to resemble the water splitting occurring at the BPM. As evident from the time-dependent study shown in Figure 7, after an initial CO_2 reduction activity, the diffusion of H^+ from the membrane to the cathode leads to high H_2 and negligible eCO_2RR activity (Figure 7a). Indeed, a very high H^+/CO_2 concentration ratio is observed at the surface. Instead, by employing the anion exchange membrane (i.e., without any proton flux, Figure 7b), H^+ concentration does not increase, as confirmed by the H^+/CO_2 ratio around 0.

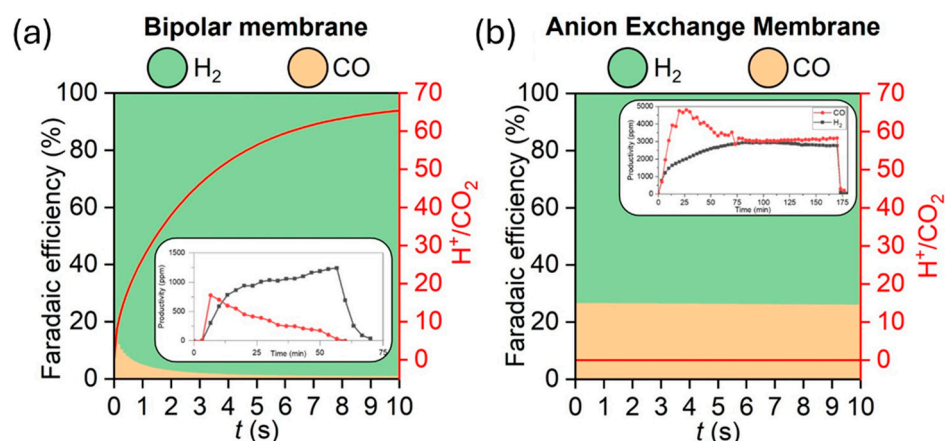


Figure 7. Time-dependent FE toward H_2 (green) and CO (orange) depending on the cell membrane, (a) Bipolar (BPM) and (b) Anion Exchange (AEM). Experimental reports are given as inset. Red curves indicate H^+/CO_2 surface ratio.

3. Discussion

Our study suggests that several phenomena are responsible for the instability in syngas evolution in RTIL-based electrolytes. The anodic degradation of the RTILs during electrolysis in a single-compartment cell is a severe issue that determines the generation of side products like CH_4 and C_2H_4 and, thus, the unreliable determination of eCO_2RR products in single cells. Electrolysis experiments have evidenced acetate anion as the main cause of degradation by-products. Acetic acid electrolysis on Pt at oxidative potential follows a mechanism known as Kolbe reaction. This mechanism leads to the cleavage of the C-C bond of acetic acid with the subsequent coupling of two CH_3^\bullet radicals to form ethane. Ethylene is reported to be a non-Kolbe product—coming from a side mechanism of the Kolbe reaction [54]. However, the absence of ethane as a gaseous byproduct indicates the existence of another degradation mechanism that has led to the evolution of CH_4 and C_2H_4 . The reactivity of acetic acid towards electrolysis on Pt anode leading to a similar Kolbe mechanism supports what is reported in Figure 3, where MIX0% displayed a total FE lower with respect to 1.6 M Bmim OTf. This phenomenon can be explained by the presence in MIX0% of the acetate anion coming from Bmim Acetate. The hypothesis is that when the Pt anode is immersed in the electrolyte within a single cell, the presence of acetate anions increases the probability of radical species formation, thereby raising their concentration. This makes the electrolyte chemically less stable, even at the cathodic interface. When only Bmim OTf is employed as electrolyte, the anion degradation doesn't occur, and the total FE, which is close to 100%, accounts for only the eCO_2RR to CO and HER. The remaining percentage of FE can then be explained by the previously cited cation degradation reported and calculated by Kroon et al. [47] However, the mechanism of anodic RTILs degradation requires additional studies, which will be discussed in a follow-up manuscript. Regarding the identity of the proton source, the selectivity towards HER

rises dramatically by increasing the amount of water in the electrolyte. Besides, eCO₂RR still happens even in electrolytes containing very low amounts of H₂O, such as MIX0% and 1.6 M [Bmim] [CF₃SO₃], indicating that C2 of the imidazolium cation can serve as an additional proton source. This hypothesis is supported by COMSOL modeling, which shows good agreement with the experimental data (Figure 6). Nearly 100% of Faradaic efficiency toward CO is predicted even when the model assumes the absence of water and the equilibrium reaction in Equation (6), confirming the reliability of the RTIL C2-H as an alternative proton source.

Experimentally, we note that in the case of 1.6 M [Bmim] [CF₃SO₃], the total FE is over 90%, confirming the hypothesis that the IL with the [CF₃SO₃][−] anion is less prone to degradation than with the [CH₃CO₂][−] one. CO production remains stable when no [CH₃CO₂][−] anion is present in the electrolyte. Under this condition, no other Faradaic process can occur at the Ag surface other than eCO₂RR, and the protons coming from the imidazolium cation are selectively employed for CO evolution. When only [CF₃SO₃][−] anions are present, the electrode-electrolyte interface is more hydrophobic due to the presence of the -CF₃ moiety; thus, less water is present at the surface. Given the high CO selectivity reported, the hypothesis that H from C2 can act as a proton source for eCO₂RR is further confirmed. Cation degradation to release C2-H may be an issue regarding the system's long-term stability since this eventually led to a change in electrolyte composition. Moreover, imidazolium cations at the electrode interface, when losing the proton in C2 position, can form a carbene species that poisons the Ag surface [30], hindering eCO₂RR. These processes can be avoided by adding H₂O to the electrolyte. Proton evolution from H₂O is easier and more favorable than the IL cation disruption.

Regarding the electrochemical setup, changing from a single cell to an H-type cell is crucial to avoid IL oxidative degradation. However, the membrane employed to separate the anodic and cathodic chambers also plays a crucial role in the outcome of the process. When MIX20% was tested in the H-type cell equipped with BPM, syngas was produced, but the CO/H₂ ratio was not stable due to the rapid suppression of eCO₂RR at the Ag interface. After 1 h of −20 mA/cm² chronopotentiometry, the system's selectivity switched towards HER. Conversely, in the same electrolytic condition but equipping the H-cell with an AEM, the CO/H₂ ratio reached a steady state after 1.5 h, and the syngas productivity was maintained for up to 3.5 h, after which the system was still fully functioning.

Moreover, as pointed out in Figure 5b, once the stability of the gas evolution is obtained, the syngas composition can be easily tuned by varying potentiometric parameters (Figure S8, Supplementary Materials). This gives a potent tool for online syngas production with on-demand CO/H₂ that can be exploited to perform coupled organic reactions that require different syngas compositions. Carbonylation reaction usually requires only the presence of CO as reactant; by contrast, high-pressure and high-temperature hydroformylation require syngas with CO:H₂ equal to 1:1.

To explain the cause of syngas instability caused by BPM, Figure 8 depicts a scheme of the process hypothesized to happen at the membrane. BPM comprises a cation exchange layer (CEL) and an anion exchange layer (AEL) pressed together [37,55]. When a bias is applied to the system, water splitting occurs at the interface, and H⁺ and OH[−] are produced in the catholyte and the anolyte, respectively (if the membrane is operated in forward bias mode, with the CEL facing the cathode). This phenomenon causes progressive acidification of the catholyte with a consequent progressive switching of the selectivity towards HER. The diffusion coefficient of the two electroactive species can also be considered in this scenario. H⁺ displays a diffusivity almost ten times more than CO₂; this would further explain the reason for the total suppression of eCO₂RR with time (Table 4). This hypothesis is strongly supported by COMSOL modeling. In fact, from Table 4 it is evident how the diffusion of H⁺

from the bipolar membrane completely takes over CO_2 adsorption at the surface, leading to almost 100% selectivity to H_2 during a -20 mA/cm^2 chronopotentiometry. Instead, when the AEM is in place, j_{CO} and j_{H_2} become stable after a short time due to an effective depletion of H^+ from the catalytic surface.

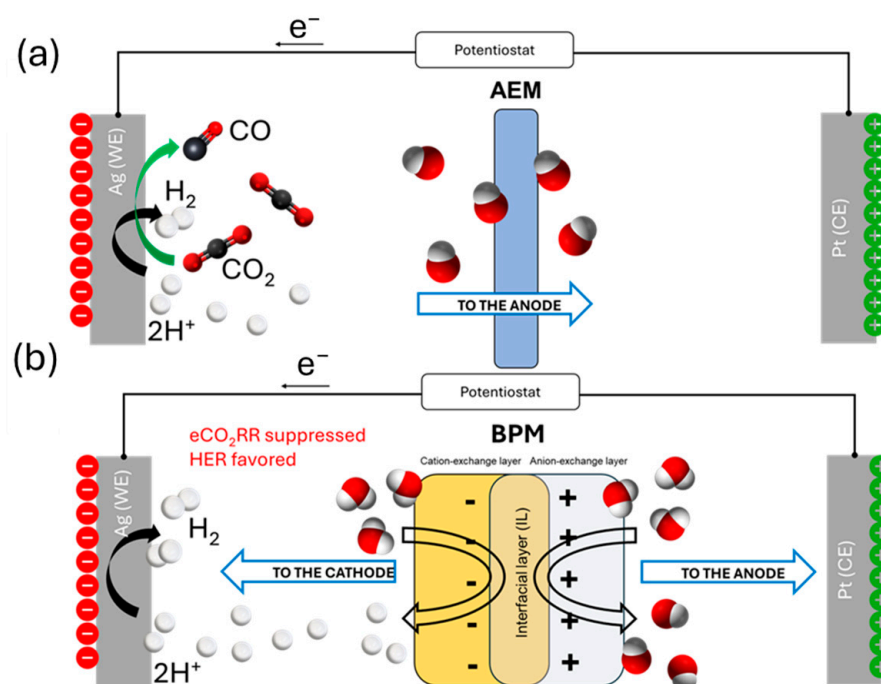


Figure 8. (a) Scheme of the process using an AEM membrane; (b) schematic of the process proposed as the cause of syngas production instability when a BPM is employed. Water splitting at the interface layer happens, and protons migrate from the membrane to the cathode, switching selectivity toward HER.

4. Materials and Methods

4.1. Chemicals

The Ionic liquids (ILs) employed, i.e., 1-Butyl-3-methylimidazolium acetate ([Bmim] [CH₃CO₂]) and 1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim] [CF₃SO₃]) were synthesized by IoLiTec GmbH (Heilbronn, Germany) (high purity grade) and were used without any further purification ([Bmim] cation purity > 99.4%, Triflate anion purity > 99.9%, water content in [Bmim] [CF₃SO₃] < 110 ppm, Acetate anion purity > 98%, water content in [Bmim] [CH₃CO₂] < 0.6%). The organic solvent employed, 3-methoxypropionitrile (3-MPN), was purchased from (Merck KGaA, Darmstadt, Germany). Double-distilled Milli-Q water ($R > 18.2 \text{ M}\Omega$, 25°C) was obtained using a Millipore Direct-Q 3 UV system (Merck KGaA, Darmstadt, Germany) and employed as the protic solvent.

4.2. Characterizations

Conductivity measurements were made by using a VWR pHenomenal MU 6100 H Multi-Parameter instrument (VWR International Srl, Milano, Italy), and the results are shown in Figure S1 in the Supplementary Materials. The ATR-IR spectra of the anolytes and catholytes (in shown in Figures S9 and S10) were collected in the range between 400 and 4000 cm^{-1} with 4 cm^{-1} resolution, using a Bruker TENSOR 27 spectrometer (Bruker Italia Srl, Milano, Italy).

4.3. Electrochemical Tests

The electrochemical characterization was carried out using a single-compartment electrochemical cell. Linear Sweep Voltammetry (LSV) curves were collected in a single cell with a scan rate of 10 mV/s and are reported hereafter applying the iR drop correction; the uncompensated resistance (R_u/Ω) was measured for each electrolyte via single-frequency (100 mHz) impedance measurement (ZIR). Chronopotentiometries (CPs) were conducted in both a single and an H-type cell. An Ag foil, Ag/AgCl (KCl sat.) and Pt mesh were employed as working electrode (WE), reference electrode (RE) and counter electrode (CE), respectively. Gas inlet/outlet in the cells allowed the outgassing and the saturation of the electrolytes with N_2 and CO_2 . During the CPs, the gas was continuously fed into the cell at a constant rate of 20 NmL/min using a mass flow controller (Bronkhorst EL-FLOW, Bronkhorst, Ruurlo, The Netherlands), and magnetic stirring was maintained to favor the convection of electroactive species towards the electrode-electrolyte interface. In the H-type cell, either a Fumasep BPM membrane or an FAA 3 (thickness 130) μ m peek-reinforced AEM were used. An aqueous solution of 0.5 M KOH was employed in the H-type cell as anolyte. All electrochemical measurements were conducted using a Biologic SP-300 potentiostat (supplied from BioLogic, Seyssinet-Pariset, France) and EC-Lab software version 11.50 (released 4 May 2023) for data collection and analysis. The online detection of gaseous products during eCO_2RR was done through a Varian 490 micro-gas chromatograph. Further details are provided in the text. All potentials (E) are referred to the Ag/AgCl reference electrode.

5. Conclusions

In this work, we investigated different conditions and setups to achieve a tunable syngas production with a constant CO/H_2 ratio. Starting with the electrolyte, we showed how an RTIL-based electrolyte enhances eCO_2RR activity. By selecting the proper mix of RTILs, it is possible to balance the two competing reactions (eCO_2RR and HER) to produce syngas with a CO/H_2 ratio constant over time. This is thanks to the specific choice of the RTILs employed: one (Bmim OAc) is more indicated for the capture and consequently HER, while the other one (Bmim OTf) is selective towards eCO_2RR to CO. Water is the preferred proton source for HER; however, eCO_2RR can occur even in low-water-concentration electrolytes (few ppm), suggesting that the acidic proton at C2 position of the imidazolium ring can act as well as a co-proton source for CO_2 reduction. These data have shown good agreement with modeling results through COMSOL Multiphysics.

When choosing the most suitable cell for the reaction, a two-compartment cell (e.g., H-cells or flow cells) is the best solution. When a single cell was used, it was impossible to maintain the two processes equally stable, with the HER overcoming the eCO_2RR in a short time. Although in previous works it was possible to produce CO stably in a single cell with $FE_{CO} > 90\%$ with Bmim OTf in 3-MPN as the electrolyte, herein, the addition of Bmim OAc led to oxidative phenomena of the RTIL-based electrolyte at the anode, with a negative effect in the eCO_2RR . Indeed, while controlling the potential at the cathode, the anodic potential can increase to values that may degrade the RTILs, producing by-products such as ethylene and methane, which can be wrongly attributed to the eCO_2RR and reduce the purity of the produced syngas.

The usual average higher cell potential of H-cells due to high ohmic resistances can be avoided using flow cells or better-designed H-cells with a low distance between the electrodes, even if a few works have implemented such a setup to work with RTILs-based electrolytes. Separating the anodic chamber from the cathodic chamber would prevent issues related to the degradation of products and enable the choice of the anodic reaction to lower the overall cell potential further. Besides, we have demonstrated the

importance of choosing the right membrane. When a BPM was employed, we observed constant acidification of the catholyte due to water splitting at the CEL, which makes HER favored with time, in agreement with our modeling data supporting such a mechanistic hypothesis. An anionic membrane is preferred in this IL-based system to obtain stable syngas production for hours without losing catalytic activity [45].

A trade-off between the different phenomena in a specific electrochemical cell should be found to optimize the production of the target product. We demonstrated that a stable syngas production could be obtained while exploiting the advantage of the mixture of Bmim OAc and Bmim OTf as electrolytes, i.e., high CO₂ solubility and co-catalytic effect, by using a two-chamber electrochemical cell with an AEM. Depending on the application, the syngas CO/H₂ ratio can be controlled by changing the electrolyte's water/ionic liquid ratio. The known issue of the loss of CO₂ from the catholyte by bi/carbonates crossover through the anionic membrane should be mitigated differently. For instance, the bi/bicarbonates (being oxidized to CO₂ in the anode) can be recovered by caustic washing with KOH of the anodic outgas, producing a bicarbonate solution that can be recirculated and reused as catholyte or by a pressure swing absorption process to separate the CO₂ to be recirculated in the gaseous form. The best option should be selected based on techno-economic considerations beyond this work's scope. Herein, we offer guidelines for syngas generation in RTIL-based systems from waste-CO₂ reduction, which can be helpful for the development of novel green chemical synthesis processes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15040318/s1>: Figure S1. Conductivity trend of 3-MPN solutions prepared starting from a mix of 1.6 M [Bmim][SO₃CF₃] and 2.4 M [Bmim][CO₂CH₃] solutions and adding variable amounts of H₂O. Raw data in Table 2; Figure S2. Schematic representation of (a) the single cell and (b) the H-cell employed for the electrochemical measurements; Figure S3. Cumulative Faradaic Efficiency (FE) obtained with 90 min Chronopotentiometry (CP) in a single-cell configuration for different electrolytes and applied currents in CO₂-saturated electrolytes; Figure S4. MIX0% before (left) and after (right) three 90 min CPs at $j = -20, -40, -50$ mA/cm² in a single-compartment cell; Figure S5. Productivity (in mmol) of (a) CH₄ and (b) C₂H₄ for different electrolytes and potentials vs. (Ag/AgCl) in a single cell and N₂-saturated electrolyte; Figure S6. Linear Sweep Voltammetry (LSV) collected in CO₂-saturated electrolyte before and after three 90-min CPs at $J = -20, -40, -50$ mA/cm² in single-compartment cell; Figure S7. Time evolution of H₂ and CO productivity (in ppm) during chronopotentiometry at $j = -20$ mA/cm² CP for the MIX20% electrolyte in a single-compartment cell configuration; Figure S8. FECO (in orange) and FE_{H₂} (in green) obtained in an H-cell equipped with AEM at different potentials with the MIX20%. Figure S9. IR spectra of the anolyte (0.5 M KOH aqueous solution) before and after 3 h electrolysis at -20 mA/cm² in H-type cell equipped with an AEM. Figure S10. IR spectra of the catholyte (MIX20%) before and after 3 h electrolysis at -20 mA/cm² in H-type cell equipped with an AEM.

Author Contributions: M.G. designed the methodology, performed the experimental investigation, and wrote the initial draft of the manuscript. A.F. contributed to the experimental investigation and conceptualization of results. S.H. conceptualized the results, conceived the project, provided the resources and funding, and reviewed and edited the final manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: Projects INTERFACE-E53D23003280006 and SUNCOCHEM-862192 by European Commission.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The European Commission supported this work through Next Generation EU, Mission 4 Component 2 Investment 1.1 CUP E53D23003280006 under the PRIN 2022 project Interface and the European Union's Horizon 2020 Research and Innovation Action program under

the SunCOChem project (Grant Agreement No. 862192). We thank Federico Dattila for the support with the modelling work and conceptualizing the results. The ionic liquids were supplied by Iolitec Ionic Liquids Technologies GmbH, Heilbronn, Germany.

Conflicts of Interest: The authors declare no competing interests.

References

1. Monteiro, M.C.O.; Philips, M.F.; Schouten, K.J.P.; Koper, M.T.M. Efficiency and selectivity of CO₂ reduction to CO on gold gas diffusion electrodes in acidic media. *Nat. Commun.* **2021**, *12*, 4943. [[CrossRef](#)] [[PubMed](#)]
2. Marcandalli, G.; Goyal, A.; Koper, M.T.M. Electrolyte effects on the faradaic efficiency of CO₂ reduction to CO on a gold electrode. *ACS Catal.* **2021**, *11*, 4936–4945. [[CrossRef](#)] [[PubMed](#)]
3. Cuatto, G.; Zoli, M.; Gallone, M.; Guzmán, H.; Castellino, M.; Hernández, S. Standardization of Cu₂O nanocubes synthesis: Role of precipitation process parameters on physico-chemical and photo-electrocatalytic properties. *Chem. Eng. Res. Des.* **2023**, *199*, 384–398. [[CrossRef](#)]
4. Rotundo, L.; Garino, C.; Priola, E.; Sassone, D.; Rao, H.; Ma, B.; Robert, M.; Fiedler, J.; Gobetto, R.; Nervi, C. Electrochemical and Photochemical Reduction of CO₂ Catalyzed by Re(I) Complexes Carrying Local Proton Sources. *Organometallics* **2019**, *38*, 1351–1360. [[CrossRef](#)]
5. Franco, F.; Cometto, C.; Nencini, L.; Barolo, C.; Sordello, F.; Minero, C.; Fiedler, J.; Robert, M.; Gobetto, R.; Nervi, C. Local Proton Source in Electrocatalytic CO₂ Reduction with [Mn(bpy-R)(CO)₃Br] Complexes. *Chem. A Eur. J.* **2017**, *23*, 4782–4793. [[CrossRef](#)]
6. Franco, F.; Cometto, C.; Vallana, F.F.; Sordello, F.; Priola, E.; Minero, C.; Nervi, C.; Gobetto, R. A local proton source in a [Mn(bpy-R)(CO)₃Br]-type redox catalyst enables CO₂ reduction even in the absence of Brønsted acids. *Chem. Commun.* **2014**, *50*, 14670–14673. [[CrossRef](#)]
7. Wang, Y.; Chen, Z.; Han, P.; Du, Y.; Gu, Z.; Xu, X.; Zheng, G. Single-Atomic Cu with Multiple Oxygen Vacancies on Ceria for Electrocatalytic CO₂ Reduction to CH₄. *ACS Catal.* **2018**, *8*, 7113–7119. [[CrossRef](#)]
8. Shen, J.; Kortlever, R.; Kas, R.; Birdja, Y.Y.; Diaz-Morales, O.; Kwon, Y.; Ledezma-Yanez, I.; Schouten, K.J.P.; Mul, G.; Koper, M.T.M. Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilized cobalt protoporphyrin. *Nat. Commun.* **2015**, *6*, 8177. [[CrossRef](#)]
9. Weng, Z.; Jiang, J.; Wu, Y.; Wu, Z.; Guo, X.; Materna, K.L.; Liu, W.; Batista, V.S.; Brudvig, G.W.; Wang, H. Electrochemical CO₂ Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution. *J. Am. Chem. Soc.* **2016**, *138*, 8076–8079. [[CrossRef](#)]
10. Li, F.; Thevenon, A.; Rosas-Hernández, A.; Wang, Z.; Li, Y.; Gabardo, C.M.; Ozden, A.; Dinh, C.T.; Li, J.; Wang, Y.; et al. Molecular tuning of CO₂-to-ethylene conversion. *Nature* **2020**, *577*, 509–513. [[CrossRef](#)]
11. Hori, Y.; Murata, A.; Takahashi, R.; Suzuki, S. Enhanced formation of ethylene and alcohols at ambient temperature and pressure in electrochemical reduction of carbon dioxide at a copper electrode. *ChemInform* **1988**, *19*, 17–19. [[CrossRef](#)]
12. Dinh, C.-T.; Burdyny, T.; Kibria, M.G.; Seifitokaldani, A.; Gabardo, C.M.; de Arquer, F.P.G.; Kiani, A.; Edwards, J.P.; De Luna, P.; Bushuyev, O.S.; et al. CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **2018**, *360*, 783–787. [[CrossRef](#)] [[PubMed](#)]
13. Zhan, C.; Dattila, F.; Rettenmaier, C.; Bergmann, A.; Kühl, S.; García-Muelas, R.; López, N.; Cuenya, B.R. Revealing the CO coverage-driven C–C coupling mechanism for electrochemical CO₂ reduction on Cu₂O nanocubes via Operando Raman spectroscopy. *ACS Catal.* **2021**, *11*, 7694–7701. [[CrossRef](#)] [[PubMed](#)]
14. Yang, H.; Wu, Y.; Li, G.; Lin, Q.; Hu, Q.; Zhang, Q.; Liu, J.; He, C. Scalable Production of Efficient Single-Atom Copper Decorated Carbon Membranes for CO₂ Electroreduction to Methanol. *J. Am. Chem. Soc.* **2019**, *141*, 12717–12723. [[CrossRef](#)]
15. Lu, L.; Sun, X.; Ma, J.; Yang, D.; Wu, H.; Zhang, B.; Zhang, J.; Han, B. Highly Efficient Electroreduction of CO₂ to Methanol on Palladium–Copper Bimetallic Aerogels. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 14149–14153. [[CrossRef](#)]
16. Albo, J.; Sáez, A.; Solla-Gullón, J.; Montiel, V.; Irabien, A. Production of methanol from CO₂ electroreduction at Cu₂O and Cu₂O/ZnO-based electrodes in aqueous solution. *Appl. Catal. B* **2015**, *176–177*, 709–717. [[CrossRef](#)]
17. Bohra, D.; Chaudhry, J.H.; Burdyny, T.; Pidko, E.A.; Smith, W.A. Modeling the electrical double layer to understand the reaction environment in a CO₂ electrocatalytic system. *Energy Environ. Sci.* **2019**, *12*, 3380–3389. [[CrossRef](#)]
18. Siritanaratkul, B.; Eagle, C.; Cowan, A.J. Manganese Carbonyl Complexes as Selective Electrocatalysts for CO₂ Reduction in Water and Organic Solvents. *Acc. Chem. Res.* **2022**, *55*, 955–965. [[CrossRef](#)]
19. Cadena, C.; Anthony, J.L.; Shah, J.K.; Morrow, T.I.; Brennecke, J.F.; Maginn, E.J. Why Is CO₂ So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300–5308. [[CrossRef](#)]
20. Feng, J.; Zeng, S.; Feng, J.; Dong, H.; Zhang, X. CO₂ Electroreduction in Ionic Liquids: A Review. *Chin. J. Chem.* **2018**, *36*, 961–970. [[CrossRef](#)]

21. Sun, L.; Ramesha, G.K.; Kamat, P.V.; Brennecke, J.F. Switching the reaction course of electrochemical CO₂ reduction with ionic liquids. *Langmuir* **2014**, *30*, 6302–6308. [[CrossRef](#)] [[PubMed](#)]
22. Li, Y.; Li, F.; Laaksonen, A.; Wang, C.; Cobden, P.; Boden, P.; Liu, Y.; Zhang, X.; Ji, X. Electrochemical CO₂ reduction with ionic liquids: Review and evaluation. *Ind. Chem. Mater.* **2023**, *1*, 410–430. [[CrossRef](#)]
23. Parada, W.A.; Vasilyev, D.V.; Mayrhofer, K.J.J.; Katsounaros, I. CO₂ Electroreduction on Silver Foams Modified by Ionic Liquids with Different Cation Side Chain Length. *ACS Appl. Mater. Interfaces* **2022**, *14*, 14193–14201. [[CrossRef](#)] [[PubMed](#)]
24. Coskun, O.K.; Dongare, S.; Doherty, B.; Klemm, A.; Tuckerman, M.; Gurkan, B. Tailoring Electrochemical CO₂ Reduction on Copper by Reactive Ionic Liquid and Native Hydrogen Bond Donors. *Angew. Chem. Int. Ed. Engl.* **2023**, *63*, e202312163. [[CrossRef](#)]
25. Brennecke, J.F.; Gurkan, B.E. Ionic liquids for CO₂ capture and emission reduction. *J. Phys. Chem. Lett.* **2010**, *1*, 3459–3464. [[CrossRef](#)]
26. Anderson, J.L.; Dixon, J.K.; Brennecke, J.F. Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: Comparison to other ionic liquids. *Acc. Chem. Res.* **2007**, *40*, 1208–1216. [[CrossRef](#)]
27. Papisizza, M.; Yang, X.; Cheng, J.; Cuesta, A. Electrocatalytic reduction of CO₂ in neat and water-containing imidazolium-based ionic liquids. *Curr. Opin. Electrochem.* **2020**, *23*, 80–88. [[CrossRef](#)]
28. Reche, I.; Gallardo, I.; Guirado, G. Electrochemical studies of CO₂ in imidazolium ionic liquids using silver as a working electrode: A suitable approach for determining diffusion coefficients, solubility values, and electrocatalytic effects. *RSC Adv.* **2014**, *4*, 65176–65183. [[CrossRef](#)]
29. Dattila, F.; Fortunati, A.; Zammillo, F.; Guzmán, H.; López, N.; Hernández, S. Descriptors for Electrochemical CO₂ Reduction in Imidazolium-Based Electrolytes. *ACS Catal.* **2024**, *14*, 16166–16174. [[CrossRef](#)]
30. Fortunati, A.; Risplendi, F.; Fiorentin, M.R.; Cicero, G.; Parisi, E.; Castellino, M.; Simone, E.; Iliev, B.; Schubert, T.J.S.; Russo, N.; et al. Understanding the role of imidazolium-based ionic liquids in the electrochemical CO₂ reduction reaction. *Commun. Chem.* **2023**, *6*, 84. [[CrossRef](#)]
31. Zhang, X.; Guo, S.-X.; Gandionco, K.A.; Bond, A.M.; Zhang, J. Electrocatalytic carbon dioxide reduction: From fundamental principles to catalyst design. *Mater. Today Adv.* **2020**, *7*, 100074. [[CrossRef](#)]
32. Singh, M.R.; Clark, E.L.; Bell, A.T. Effects of electrolyte, catalyst, and membrane composition and operating conditions on the performance of solar-driven electrochemical reduction of carbon dioxide. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18924–18936. [[CrossRef](#)] [[PubMed](#)]
33. Marcandalli, G.; Monteiro, M.C.O.; Goyal, A.; Koper, M.T.M. Electrolyte Effects on CO₂ Electrochemical Reduction to CO. *Acc. Chem. Res.* **2022**, *55*, 1900–1911. [[CrossRef](#)] [[PubMed](#)]
34. Liang, S.; Altaf, N.; Huang, L.; Gao, Y.; Wang, Q. Electrolytic cell design for electrochemical CO₂ reduction. *J. CO₂ Util.* **2020**, *35*, 90–105. [[CrossRef](#)]
35. Xi, W.; Xi, W.; Yang, P.; Yang, P.; Jiang, M.; Jiang, M.; Wang, X.; Wang, X.; Zhou, H.; Zhou, H.; et al. Electrochemical CO₂ reduction coupled with alternative oxidation reactions: Electrocatalysts, electrolytes, and electrolyzers. *Appl. Catal. B Environ.* **2024**, *341*, 123291. [[CrossRef](#)]
36. Jiang, N.; Zhu, Z.; Xue, W.; Xia, B.Y.; You, B. Emerging Electrocatalysts for Water Oxidation under Near-Neutral CO₂ Reduction Conditions. *Adv. Mater.* **2022**, *34*, 2105852. [[CrossRef](#)]
37. Tufa, R.A.; Chanda, D.; Ma, M.; Aili, D.; Demissie, T.B.; Vaes, J.; Li, Q.; Liu, S.; Pant, D. Towards highly efficient electrochemical CO₂ reduction: Cell designs, membranes and electrocatalysts. *Appl. Energy* **2020**, *277*, 115557. [[CrossRef](#)]
38. Hernández, S.; Farkhondehfar, M.A.; Sastre, F.; Makkee, M.; Saracco, G.; Russo, N. Syngas production from electrochemical reduction of CO₂: Current status and prospective implementation. *Green Chem.* **2017**, *19*, 2326–2346. [[CrossRef](#)]
39. Rosen, J.; Hutchings, G.S.; Lu, Q.; Rivera, S.; Zhou, Y.; Vlachos, D.G.; Jiao, F. Mechanistic Insights into the Electrochemical Reduction of CO₂ to CO on Nanostructured Ag Surfaces. *ACS Catal.* **2015**, *5*, 4293–4299. [[CrossRef](#)]
40. Hoshi, N.; Kato, M.; Hori, Y. Electrochemical reduction of CO, on single crystal electrodes of silver Ag(111), Ag(100) and Ag(110). *J. Electroanal. Chem.* **1997**, *44*, 283–286.
41. Hori, Y. Electrochemical CO₂ Reduction on Metal Electrodes. In *Modern Aspects of Electrochemistry. Modern Aspects of Electrochemistry*; Springer: New York, NY, USA, 2008; pp. 89–189. [[CrossRef](#)]
42. Mahyoub, S.A.; Qaraah, F.; Chen, C.; Zhang, F.; Yan, S.; Cheng, Z. An overview on the recent developments of Ag-based electrodes in the electrochemical reduction of CO₂ to CO. *Sustain. Energy Fuels* **2019**, *4*, 50–67. [[CrossRef](#)]
43. Jensen, M.T.; Rønne, M.H.; Ravn, A.K.; Juhl, R.W.; Nielsen, D.U.; Hu, X.-M.; Pedersen, S.U.; Daasbjerg, K.; Skrydstrup, T. Scalable carbon dioxide electroreduction coupled to carbonylation chemistry. *Nat. Commun.* **2017**, *8*, 489. [[CrossRef](#)] [[PubMed](#)]
44. Ponsard, L.; Nicolas, E.; Tran, N.H.; Lamaison, S.; Wakerley, D.; Cantat, T.; Fontecave, M. Coupling Electrocatalytic CO₂ Reduction with Thermocatalysis Enables the Formation of a Lactone Monomer. *ChemSusChem* **2021**, *14*, 2198–2204. [[CrossRef](#)]
45. Miró, R.; Fernández-Llamazares, E.; Godard, C.; Bernardos, M.D.d.L.; Gual, A. Synergism between iron porphyrin and dicationic ionic liquids: Tandem CO₂ electroreduction–carbonylation reactions. *Chem. Commun.* **2022**, *58*, 10552–10555. [[CrossRef](#)]

46. Biswas, A.N.; Xie, Z.; Xia, R.; Overa, S.; Jiao, F.; Chen, J.G. Tandem Electrocatalytic–Thermocatalytic Reaction Scheme for CO₂ Conversion to C₃ Oxygenates. *ACS Energy Lett.* **2022**, *7*, 2904–2910. [[CrossRef](#)]
47. Kroon, M.C.; Buijs, W.; Peters, C.J.; Witkamp, G.-J. Decomposition of ionic liquids in electrochemical processing. *Green Chem.* **2006**, *8*, 241–245. [[CrossRef](#)]
48. Dutta, A.; Morstein, C.E.; Rahaman, M.; López, A.C.; Broekmann, P. Beyond Copper in CO₂ Electrolysis: Effective Hydrocarbon Production on Silver-Nanofoam Catalysts. *ACS Catal.* **2018**, *8*, 8357–8368. [[CrossRef](#)]
49. Shiratsuchi, R.; Nogami, G. Pulsed Electroreduction of CO₂ on Silver Electrodes. *J. Electrochem. Soc.* **1996**, *143*, 582–586. [[CrossRef](#)]
50. Kumelan, J.; Kamps, Á.P.-S.; Tuma, D.; Maurer, G. Solubility of CO₂ in the ionic liquids [bmim][CH₃SO₄] and [bmim][PF₆]. *J. Chem. Eng. Data* **2006**, *51*, 1802–1807. [[CrossRef](#)]
51. Bui, J.C.; Kim, C.; Weber, A.Z.; Bell, A.T. Dynamic boundary layer simulation of pulsed CO₂ electrolysis on a copper catalyst. *ACS Energy Lett.* **2021**, *6*, 1181–1188. [[CrossRef](#)]
52. Wang, J.H. Self-Diffusion Coefficients of Water. *J. Phys. Chem.* **1965**, *69*, 4412.
53. Moya, C.; Palomar, J.; Gonzalez-Miquel, M.; Bedia, J.; Rodriguez, F. Diffusion coefficients of CO₂ in ionic liquids estimated by gravimetry. *Ind. Eng. Chem. Res.* **2014**, *53*, 13782–13789. [[CrossRef](#)]
54. Liu, S.; Govindarajan, N.; Prats, H.; Chan, K. Understanding the reaction mechanism of Kolbe electrolysis on Pt anodes. *Chem Catal.* **2022**, *2*, 1100–1113. [[CrossRef](#)]
55. Habibzadeh, F.; Mardle, P.; Zhao, N.; Riley, H.D.; Salvatore, D.A.; Berlinguette, C.P.; Holdcroft, S.; Shi, Z. Ion Exchange Membranes in Electrochemical CO₂ Reduction Processes. *Electrochem. Energy Rev.* **2023**, *6*, 26. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.