

Reaction Chemistry & Engineering

Linking fundamental chemistry and engineering to create scalable, efficient processes

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Reis-Machado, S. Messias, M. M. D. Sousa, M. Nunes-da-Ponte, C. M. Rangel and T. Pardal, *React. Chem. Eng.*, 2019, DOI: 10.1039/C9RE00271E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ARTICLE

Electrochemical production of syngas from CO₂ at pressures up to 30 bar in electrolytes containing ionic liquid

Received 00th January 20xx,
Accepted 00th January 20xx

Sofia Messias^a, Miguel M. Sousa^a, Manuel Nunes da Ponte^a, Carmen M. Rangel^b, Tiago Pardal^c and Ana S. Reis Machado^{*a}

DOI: 10.1039/x0xx00000x

Electrochemical CO₂ reduction in a reactor that can operate up to 100 bar and 80°C with a configuration similar to a electrolyser for hydrogen production alkaline like, suitable to be used industrially is reported for the first time. The effect of pressure in the co-electrolysis of CO₂ and water was studied. The successful scale-up from a batch previously reported process to electrodes of ca. 30 cm² geometrical area (30 fold factor) that combines the use of pressure and an ionic liquid-based electrolyte is presented. Also for the first time, the potential of the system under study to achieve high conversions of CO₂ to avoid a purification step of syngas from unreacted CO₂ is shown. An inexpensive commercial foil of the common metal zinc was employed. Semi-continuous operation yielded syngas productivities in the range of 0.02-0.04 mmol/cm²h at ca. -1.2V vs. QRE Ag/Ag⁺. When an electrolyte consisting of 90 wt.% H₂O and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate 10 wt.% was used, selectivities for CO in the range of 62% to 72% were obtained, at 10 bar pressure, whereas selectivities of 82% were obtained at 30 bar pressure. H₂/CO ratios in the range of 1/1 to 4/1 at 10 bar pressure suitable for the synthesis of a variety of fuels, such as hydrocarbons, methanol, methane and chemical building blocks were observed. An energy efficiency of 44.6% was calculated for a H₂/CO ratio of 2.2 suitable for the synthesis of methanol.

Introduction

Carbon Capture and Utilization Technologies (CCU) are being intensively investigated, such as power to Gas [1-2] and power to Liquid [3] to produce fuels and chemical building blocks from CO₂. In a recent report [4] it was shown that CCU has the technical potential to change the paradigm of a chemical production based on fossil resources to renewable energy, reducing annual GHG emissions by up to 3.5 Gt CO₂-eq in 2030. In these technologies, hydrogen is produced in an electrolyser using renewable electricity and water. In a second step, hydrogen and CO₂/CO are reacted to synthesize hydrocarbons, or other fuels and chemical building blocks. Some of these technologies are already commercial, such as the George Olah plant producing renewable methanol in Iceland, others are being tested at a pilot scale, or ready for scale-up. Technologies presently with lower maturity that offer the potential of being very energy efficient and cost-effective are also being actively researched, namely electrochemical reduction of carbon

dioxide, with or without simultaneous reduction of water to hydrogen.

While water electrolysis is already at a commercial stage CO₂ – water co-electrolysis has still a number of challenges to overcome [5] including low productivities, before it can be deployed industrially. Some of these challenges are a consequence of the stability of the CO₂ molecule and the need to apply high overpotentials to reduce it electrochemically, leading to processes with poor energy efficiencies. Electrochemical CO₂ reduction has been studied in gas phase, where gaseous CO₂ is fed to the cathode through gas diffusion electrodes (GDE) and in liquid phase, where CO₂ dissolved in the liquid electrolyte contacts the electrode. A figure of merit of this technology is productivity. One of the process-intensifying parameters that since the pioneer work in electrochemical CO₂ reduction has been recognized to improve productivities is pressure [5-12]. However, this variable has been seldom studied [13], due to the challenge of designing a configuration of an electrochemical reactor able to operate at pressures higher than atmospheric pressure. The aforementioned studies were conducted in liquid phase laboratory cells with configurations not suitable for industrial deployment. Gas phase electro-reduction is in a higher maturity development stage than liquid phase configurations, most probably due to the ease of finding commercial laboratory prototypes for research. Dufek et al. [14] have used a customized commercial PEM (Proton Exchange Membrane) electrolyser cell and implemented a pressurized system for continuous reduction of CO₂ in gas phase into syngas using an Ag GDE electrode and an aqueous electrolyte using

^a LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

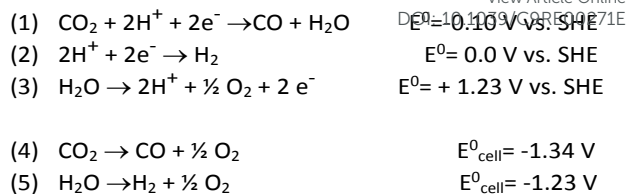
^b LNEG, National Laboratory of Energy and Geology, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

^c Omnidea, Lda, Travessa António Gedeão, Nº 9, 3510-017 Viseu, Portugal

† Contact e-mail: ams.machado@fct.unl.pt

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

conventional inorganic supporting salts. When CO production was compared with the production at atmospheric pressure a five-fold increase in CO production was observed. This is a configuration that can be scaled-up for an industrial application. In our previous study [15] CO₂-water co-electrolysis to produce syngas was investigated combining operation at high pressure (30 bar), at 45°C and the use of an ionic liquid (IL)-based electrolyte. Room temperature ILs are salts that usually comprise an organic cation and are liquid at temperatures below 100°C. Some classes of ILs present wide electrochemical windows, good conductivities, thermal and chemical stability, negligible volatility and anti-corrosion properties [16]. Due to their remarkable properties, they have been recognised among the most promising materials for electrochemical CO₂ reduction [17]. Their main advantages are not only as CO₂ absorption media, allowing to overcome the low solubility of CO₂ in aqueous electrolytes, but also their role as co-catalysts by stabilizing the reaction intermediate CO₂^{•-} radical anion. The use of ILs for this application has been reviewed by Alvarez-Guerra et al. [18] The first work combining operation at high-pressure and an IL-based electrolyte was the work of Zhao et al. [19]. To our knowledge there are no further reports of combined use of pressure and an IL-based electrolyte besides the work of Zhao et al. and our previous work. In this latter work, a single compartment test bed with no separator was employed, where a sacrificial zinc anode was used to avoid the oxidation at the anode of the reduced products originated at the cathode. The electrolyte consisted of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMOTf) and 10 wt. % of water. Bimetallic cathodes of zinc and copper of ca. 1 cm² geometrical area were developed that showed electrochemical activity for syngas production with high selectivities, tunable H₂/CO ratio and low energetic requirements. Both of the aforementioned studies used electrochemical cell configurations in liquid phase not suitable for industrial use, and to our knowledge no configuration able to be scaled-up for industrial use has been described in the literature. In this work for the first time, the electrochemical CO₂ reduction in a reactor that can operate up to 100 bar and 80°C with a configuration similar to an alkaline electrolyser for hydrogen production, suitable to be used industrially is reported. In this purposely built high pressure electrochemical cell, the catholyte is separated from the anolyte by a protonic exchange membrane and the sacrificial anode of our previous work was replaced by a commercial anode available in the market, optimized for oxygen evolution in aqueous media. The present development study addresses co-electrolysis of CO₂ and water to produce syngas in aqueous electrolyte containing IL. To take advantage of the properties of ILs as i) CO₂ absorption media ii) supporting electrolytes and iii) co-catalysts [20] an electrolyser with a liquid phase configuration able to operate at high pressure needed to be implemented. The cathodic and anodic reactions and respective standard electrode potentials are indicated by equations (1-3) and the global equations for syngas production (4-5) are given together with the equilibrium cell potential E⁰_{cell} in standard conditions [21-22].



The main objective of this work was to investigate the effect of pressure and the scalability of the process. Electrolysis were carried out at a much lower pressure than in our previous study (10 bar), but also at 30 bar, due to the interest of this operating pressure for coupling with other pressurized processes, such as Fischer-Tropsch. Operation in batch mode is also compared with operation in semi-continuous mode.

Zinc-based catalysts are promising cost effective catalysts for electrochemical syngas production from CO₂, due to the high selectivity of this common, inexpensive metal towards CO. Thus, a commercial zinc foil was used as cathode to develop the process. Although more advanced catalysts are known from the state of the art [23-26], the goal was to understand the influence of some process parameters of liquid phase electrochemical CO₂ reduction using non-conventional electrolytes, before aiming at better performances.

Zinc is a metal very prone to oxidation in air, in contact with moisture and with aqueous electrolytes. Rosen et al. [27] demonstrated that nanostructured and bulk Zn catalysts are structurally stable at potentials more negative than -0.7 V vs. RHE in aqueous neutral electrolytes. Chemical oxidation occurred at more positive potentials. In our previous study [15] using an electrolyte with a high content in IL, (1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIMOTf) and 10 wt. % of water) no corrosion currents were observed in the working potential range of -0.4 V- -1.9 V vs. RHE both for the bimetallic cathodes and for the pure metals copper and zinc. In particular, near 100% selectivities for CO were obtained for the zinc cathode at 30 bar in a slightly acidic electrolyte. As the target is to produce syngas, the possibility of varying H₂O concentration in the electrolyte to tune the H₂/CO ratio was examined in the present work. As comparison an electrolyte consisting of 90 wt. % water, where the IL can play essentially the role of supporting electrolyte and co-catalyst and an electrolyte with 50 wt. % water were tested. It is known that the size and nature of the ions of the supporting electrolyte influence the selectivity of electrochemical CO₂ reduction [28]. For instance, it was recognized that Cl⁻ inhibits H₂ evolution. A selectivity of 93% for CO was obtained with a zinc cathode, when an 0.5 M NaCl aqueous electrolyte (pH 4.5) was used[23]. One disadvantage attributed to the use of ILs is their cost. The price of ILs can be 10 or 20 times higher than conventional solvents [29], but as ILs can be recycled, their cost should be considered as an investment cost. Nevertheless, the present work investigates electrolytes with a lower content in IL, namely, 10 wt. % and 50 wt. % than the electrolyte used in our aforementioned previous study (90 wt.% IL) with the aim of gathering data for the optimization of the CapEx of the process.

Results and discussion

Cyclic Voltammetry Characterisation

Cyclic voltammograms (CVs) with a zinc cathode carried out at 45°C in 10 bar argon atmosphere and 10 bar CO₂ atmosphere are presented in Fig. 1. The onset potential of electrochemical reactions was evaluated considering a cut-off current of -1 mA/cm² [30]. CVs in argon atmosphere with dried IL as electrolyte were undertaken to show the electrochemical stability of the IL under the conditions of temperature, pressure and cathode used. In these conditions, the onset potential for the reduction of residual water present in the IL is -1.7 V vs. QRE Ag/Ag⁺. Then, the cathodic current starts to increase until eventually reductive degradation of the EMIM cation at more negative applied potentials starts to occur. When the CV is taken in argon atmosphere with the electrolyte composed by 90 wt.% of H₂O and EMIMOTf acidified to pH 3.5 with H₂SO₄, zinc oxide reduction starts at the onset potential of -0.76 V vs. QRE Ag/Ag⁺, reaching a maximum at -0.83 V vs. QRE Ag/Ag⁺. The current starts to increase again at -1.01 V vs. QRE Ag/Ag⁺, where protons reduction predominantly occurs. In the CV taken under CO₂ atmosphere, it can be verified that oxidative currents increase, due to the drop in pH of the electrolyte as a consequence of CO₂ dissolution [31]. The onset potential is at -1.17 V vs. QRE Ag/Ag⁺ and current density increases continually, showing thus a different behaviour, than the CV taken in argon. It can also be observed that cathodic current densities are very similar, when taken in argon and in CO₂ atmosphere. However, an increase of current density was clearly observed in the CV obtained with the electrolyte composed by 50 wt.% of H₂O and EMIMOTf acidified to pH 3.5 with H₂SO₄. A similar behaviour is observed as for the electrolyte with 90 wt.% of H₂O, but the onset potential is reached at the much less negative value of -0.62 V vs. QRE Ag/Ag⁺. Another remarkable difference is that for this electrolyte composition no significant zinc corrosion currents are observed, illustrating the anti-corrosion properties of ILs [16]. Thus, cyclic voltammetry shows that the Zn cathode does not suffer corrosion at potentials more negative than -1.17 V

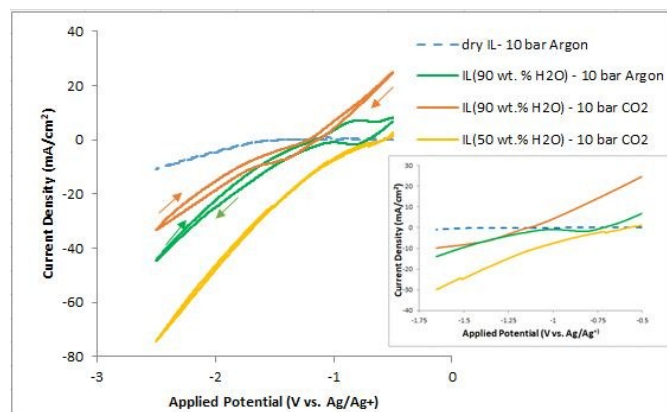


Figure 1 – Cyclic voltammograms on zinc cathodes at 45°C carried out at 50 mV/s in the potential range of -0.5 V to -2.5 V vs. QRE Ag/Ag⁺. Dashed blue curve –dry IL in 10 bar argon; brown curve- IL+90 wt.% H₂O in 10 bar CO₂; green curve – IL+90 wt.% H₂O in 10 bar argon; yellow curve IL+50 wt.% H₂O in 10 bar CO₂.

and -0.62 V vs. QRE Ag/Ag⁺ in the electrolyte containing 90 wt.% of H₂O and 50 wt.% of H₂O respectively. DOI: 10.1039/C9RE00271E

The use of this simple catalytic system with the electrolyte containing 90 wt.% of H₂O implies current densities in the range of -2 to -5 mA/cm², when applied potentials are in the low overpotential region (<-1.17 V < -1.3 V vs. QRE Ag/Ag⁺), whereas for the electrolyte containing 50 wt.% of H₂O currents of ca. 17 mA/cm² are obtained for an applied potential of -1.3 V vs. QRE Ag/Ag⁺.

Electrolysis in batch mode

Galvanostatic electrolysis were carried out in batch mode at 45°C, 10 bar CO₂ atmosphere using the two compartment electrochemical reactor and the electrolyte consisting of 90 wt.% H₂O and EMIMOTf acidified to pH 3.5 with H₂SO₄. Applied currents were in the range of -2 to -3 mA/cm² and 50 C of charge was passed. Commercial protonic exchange membranes of the same type, but with different average thicknesses were tested, namely with 120 μm, 90 μm and 75 μm. Calculated faradaic efficiencies considering total H₂ detected were well above 100%. Bearing in mind that corrosion of zinc does not occur during electrolysis in the applied current range, this can be explained by the production of H₂ by a chemical pathway due to the corrosion of zinc in acidic medium during stabilization periods. This was experimentally confirmed by sampling the headspace of the reactor after a stabilization period, without applying current. The gaseous products resulting from electrolysis are CO and H₂. As bulk metallic zinc is known to reduce CO₂ essentially to CO [32–34] other products containing carbon that are eventually produced at very low concentrations are not considered in this work. Thus, electrochemically produced H₂ was calculated by subtracting from 100% CO faradaic efficiencies and then deriving the productions. Table 1 presents total average productions of electrolytic H₂ and CO and faradaic efficiencies of CO detected in the cathodic and in the anodic compartments. The calculation of productions and faradaic efficiencies are described in detail in ESI. This table also shows average crossovers of H₂ and CO of the different membranes in the conditions tested. Membrane crossover was defined as the molar percentage of the gas produced in the cathode compartment that was detected in the anode compartment in respect to the total number of moles found in the cathode and the anode. Fig. 2 depicts the productions of electrolytic H₂ and CO in the aforementioned conditions. Total quantities of H₂ detected produced chemically and electrochemically are indicated in Table S1 of ESI. From Fig. 2 it can be observed that the thicknesses of membranes tested have no significant influence on both H₂ and CO productions. As expected, hydrogen exhibited higher crossovers than CO, due to the higher diffusivity of the former gas. When CO₂ dissolves into the electrolyte, it exerts a buffer effect. The pH of the electrolyte at 45°C and 10 bar can be estimated to be near 3.5, that is the pH of water with dissolved CO₂ at this temperature and pressure [31]. However, during electrolysis the pH of the catholyte near the cathode tends to increase due to the consumption of protons to generate CO and H₂ and on the other

Table 1 – Process parameters of electrolysis carried out in batch mode at 45°C, 10 bar CO₂ pressure. Applied current was in the range of -2 mA/cm² to -3mA/cm², and 50 C of charge passed. Electrolyte: 90 wt. % of H₂O and EMIMOTf at initial pH of 3.1.

Membrane thickness (μm)	Final pH	Production (mmol/cm ²)	CO Faradaic efficiency (%)	Crossover (%)
120	WE:6.6 CE:6.0	H2: 5.10x10 ⁻³ CO: 1.65x10 ⁻³	CO:23.83	H2: 12.9 CO:11.2
90	WE:6.3 CE:3.4	H2: 5.50x10 ⁻³ CO: 1.65 x10 ⁻³	CO:22.12	H2: 15.8 CO:6.1
75	WE:6.4 CE:3.5	H2: 5.60x10 ⁻³ CO: 1.35 x10 ⁻³	CO:18.07	H2:11.9 CO:9.1

hand, the pH of the anolyte tends to decrease near the anode due to water oxidation. Table 1 also shows the average pH of the electrolyte after electrolysis in the catholyte (WE) and in the anolyte compartments (CE) both measured at atmospheric pressure. It can be observed that the pH of the catholyte increased after electrolysis due to the presence of carbonates and bicarbonate and zinc corrosion species in the electrolyte [15]. The pH of the anolyte decreased due to the production of protons by water oxidation.

The protonic membrane with 120 μm thickness was selected to study the process in semi-continuous mode, due to the ease of manipulation of a more robust membrane. The cell potentials measured with the protonic exchange membranes were in the range of -3.3V to -3.0 V (Fig. S2 of ESI). Electrolysis were also carried out in the same conditions, but in the single compartment test bed (data not shown). CO productions of the order of magnitude of 10⁻² mmol/cm² were obtained. Although a comparison of two different reactor configurations and with distinct anodic reactions (zinc oxidation and water oxidation) is difficult, it can be verified that there is a loss in productivity, with a change to the two compartment configuration in batch mode. This is most probably due to mass transfer limitations.

Electrolysis in semi-continuous mode

Galvanostatic electrolysis were carried out in semi-continuous mode at 45°C, 10 bar CO₂ atmosphere using the two compartment electrochemical reactor with the selected protonic exchange membrane. Electrolysis were carried out, as previously, at 10 bar CO₂ pressure but also at 30 bar CO₂ pressure. The electrolyte used consisted of 90 wt. % H₂O and EMIMOTf acidified to pH 3.5 with H₂SO₄. For comparison an electrolyte consisting of 50 wt.% H₂O and EMIMOTf acidified to pH 3.5 with H₂SO₄ was also used. Applied currents were in the range of -2 to -3 mA/cm² and 200 C of charge was passed. Table 2 presents total average productions of electrolytic H₂ and CO, faradaic efficiencies for CO detected in the cathodic and in the anodic compartments and average pH of the electrolyte before and after electrolysis measured at atmospheric pressure. Electrolytic H₂ productions were calculated in the same way as already described for batch electrolysis. Total quantities of H₂ detected produced chemically and electrochemically are indicated in Table S2 of ESI. Table 2 also shows average crossovers of H₂ and CO in the conditions tested. The crossovers

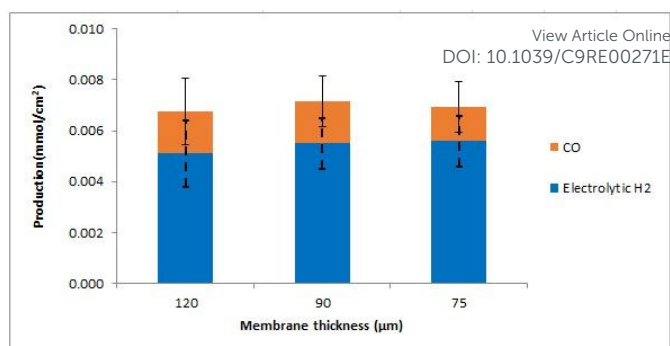


Figure 2 – Syngas production in batch mode at 45°C, 10 bar, with applied currents of -2 to -3 mA/cm² and 50 C charge passed using the electrolyte 90 wt.% H₂O and EMIMOTf at initial pH of 3.1 and membranes of different thickness. Electrolytic H₂: blue bar, dashed error bar; CO: brown bar, continuous error bar.

of hydrogen are higher than those observed in the batch operation mode due to the longer stabilisation periods (see ESI). Crossovers of CO are similar for both modes of operation. It can also be observed that without the buffering effect of CO₂, the pH of the catholyte increased due to consumption of protons at the cathode and the pH of the anolyte decreased due to the production of protons at the anode.

In Fig. 3 the productions of electrolytic H₂ and CO obtained in 200C electrolysis are presented for the different operation modes. The results of the batch electrolysis (50C) were extrapolated for 200C electrolysis, assuming a constant productivity. It is noteworthy to mention, that in steady state, chemical production of hydrogen in electrolysis in semi-continuous, 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. It can be observed that for 10 bar electrolysis CO production is higher in semi-continuous mode and presents a maximum at a flow rate of 2.5 mL/min decreasing at the higher flow rates tested. This is due to the decrease in the residence time of CO₂ at the surface of electrode, influencing the H₂/CO ratio. Hydrogen production follows the opposite trend showing a minimum at a flow rate of 2.5 ml/min. The order of magnitude of production/cm² of CO in the two compartment reactor with electrodes with a scale-up factor of ca. 30 fold increase in electrode area is the same as in the single compartment reactor in batch mode showing no loss in productivities. At 30 bar pressure and at 1 ml/min flow rate the production of CO corresponds to the maximum production of CO at 10 bar. This fact can most probably be explained by the increase in CO₂ solubility in the electrolyte and consequent enhanced availability at the surface of the electrode. The increase in EMIMOTf concentration in the electrolyte yielded less CO, when compared with electrolysis in 10 wt. % EMIMOTf (90 wt. % H₂O), in the same conditions (Fig. 3). The higher current densities for this electrolyte composition observed in Fig. 1 are thus ascribed to enhanced hydrogen evolution. This is certainly the result of the interplay of different variables, such as CO₂ solubility [35], conductivity/viscosity [36] and mesoscopic and nanoscopic organization of the electrolyte [17]. Without this type of data, predictions concerning performance

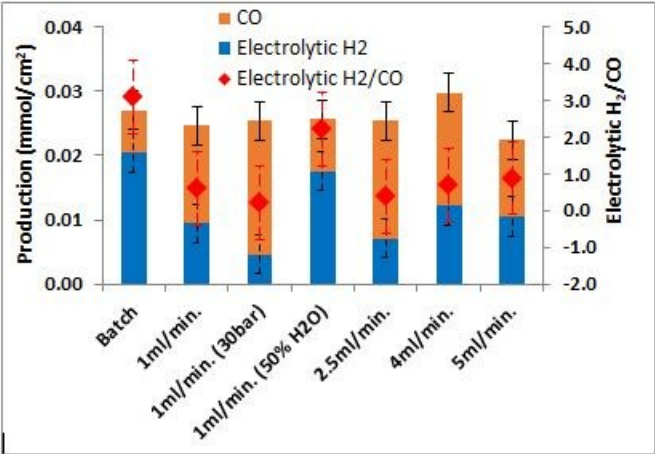


Figure 3 – Syngas production in batch and semi-continuous mode at 45°C, 10 bar, 200 C charge passed in different operation modes, pressure and electrolyte composition. Values for the batch electrolysis were extrapolated to 200C. Electrolytic H₂: blue bar, dashed error bar; CO: brown bar, continuous error bar; electrolytic H₂/CO ratio: dashed red error bar. When not specifically indicated, 10bar pressure was used and the electrolyte composition was 90 wt. % H₂O with EMIMOTf.

of electrolytes are difficult to make and experimental testing is necessary.

Many approaches to control the H₂/CO ratio have been followed [37]. Using the flow rate as a control parameter, water concentration in the electrolyte as it is proposed here, or a specific bimetallic electrode proposed in our previous work, or by other authors [15,38] are approaches that can be easily implemented industrially. Preferred H₂/CO ratios for syngas for applications in hydrocarbon synthesis, dimethyl ether, methanol, methane are typically from 1/1 to 4/1, corresponding to a CO selectivity of 50% to 20%. It can be observed that in some of the conditions tested the present process yields syngas compositions in this range.

Fig 4 shows the faradaic efficiencies for the different operation modes. In semi-continuous mode, selectivities for CO are significantly increased, when compared with batch selectivity

for CO at 10 bar. At 30 bar selectivities reach ca. 80%. The cell potentials of electrolysis carried out in semi-continuous mode were in the range of -3.5 V to - 3.9 V (Fig. S3 of ESI). Cell potentials become more negative with increasing CO selectivity. Considering the selectivity for a flow rate of 1 ml/min. at 10 bar, that yields a syngas composition corresponding to the H₂/CO ratio of 2.2 suitable for methanol synthesis, an energy efficiency of 44.6% was calculated (see ESI).

Productivities of electrochemical reduction of CO₂ are not frequently reported, because reaction selectivity is often not constant during electrolysis. Hatsukade et al. [39] reported a maximum productivity for CO of 0.09 μmol/cm²h at ca. -1.3V vs. RHE in electrolysis carried out at 25°C and atmospheric pressure with an Ag foil cathode of 99.998 % purity, a Pt anode, with an anion exchange membrane Selemion in continuous mode. As electrolyte 0.1 M KHCO₃ was used. Sastre et al. [40] obtained a maximum productivity for CO of 50 μmol/cm²h at -1.05 V vs. RHE in electrolysis carried out at 20°C and atmospheric pressure in continuous mode. The cathode used was Ag nanoparticles supported on graphitic carbon nitride (g-C₃N₄), the anode was a Pt gauze and a Nafion 117 membrane was employed. As electrolyte 0.1 M KH₂PO₄/K₂HPO₄ buffer was used. In the present paper, productivities of ca. 0.02-0.04 mmol/cm²h at ca. -1.2V vs. QRE Ag/Ag⁺ were obtained, several orders of magnitude higher than the ones obtained with a noble metal cathode and of the same order of magnitude as the porous aforementioned electrode. However, in the literature, systems using other types of porous electrodes and IL-based electrolytes are reported [38] that have achieved current densities several orders of magnitude higher than the ones obtained in this work, showing the need for a better catalytic cathode. Comparing productivities obtained in this work in semi-continuous operation with productivities in our previous work for the zinc cathode [15], it can be verified that in the latter work, productivities of one order of magnitude higher were obtained, due to the higher quantities of solubilized CO₂ in the electrolyte with a higher content in IL (90 wt.%). This is also in accordance

Table 2 – Process parameters of electrolysis carried out in semi-continuous mode at 45°C. Applied current was in the range of -2 to -3mA/cm², and 200 C of charge passed

Flow rate (ml/min)	Initial pH	Final pH	Pressure (bar)	H ₂ O concentration in the electrolyte (wt. %)	Production (mmol/cm ²)	CO Faradaic efficiency (%)	Crossover (%)
1	3.7	WE:5.7 CE:2.6	10	90	H ₂ : 9.40x10 ⁻³ CO: 1.53x10 ⁻²	CO:61.99	H ₂ : 23.8 CO: 8.4
2.5	3.8	WE:5.7 CE:2.6	10	90	H ₂ : 7.10x10 ⁻³ CO: 1.83x10 ⁻²	CO:71.98	H ₂ : 23.0 CO: 9.2
4	3.8	WE:5.9 CE:2.6	10	90	H ₂ : 1.22x10 ⁻² CO: 1.76x10 ⁻²	CO:59.16	H ₂ : 28.4 CO: 6.8
5	3.8	WE:5.8 CE:2.7	10	90	H ₂ : 1.05x10 ⁻² CO: 1.19x10 ⁻²	CO:53.24	H ₂ : 31.5 CO: 9.20
1	3.8	WE:6.0 CE:3.1	30	90	H ₂ : 4.60x10 ⁻³ CO: 2.08x10 ⁻²	CO:81.80	H ₂ : 24.7 CO: 6.9
1	3.9	WE:5.8 CE:3.0	10	50	H ₂ : 1.76x10 ⁻³ CO: 0.8x10 ⁻²	CO:30.66	H ₂ : 25.0 CO: 7.6

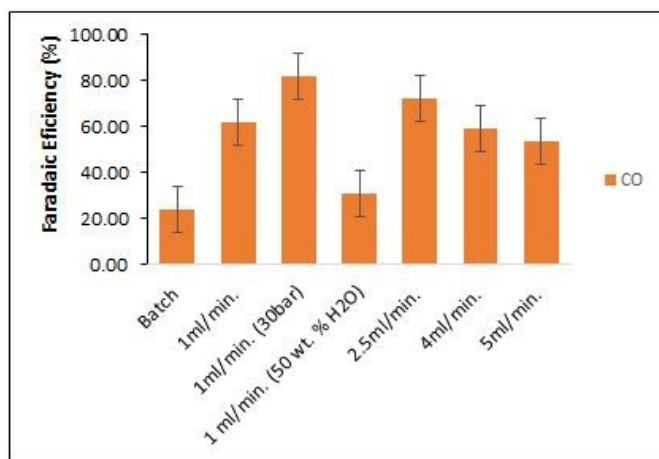


Figure 4 – Faradaic efficiencies of CO obtained at 45°C. Applied current was from -2 to -3 mA/cm², and 200C of charge passed. Values for the batch electrolysis were extrapolated to 200C. When not specifically indicated, 10 bar pressure was used and the electrolyte composition was 90 wt. % H₂O and EMIMOTf.

with the lower onset potential observed in these conditions (-1.00 V vs. QRE Ag/Ag⁺) when compared with the onset potential of the present work for the electrolyte with 90 wt.% H₂O (-1.17 V vs. QRE Ag/Ag⁺).

Fig. 5a) and b) represent CO₂ conversions (see ESI) into CO vs. charge passed and time respectively. The conversions obtained were extrapolated for total CO₂ conversions yielding a time of 73 h and a charge of 26314C. In the system under study it is not foreseen inactivation issues. Thus total CO₂ conversions are most probably within reach. Considering the nature of the cathode employed in this work and the duration of the electrolysis, the conversions obtained compare very well with the 23% conversion of the scale-up study of Jeanty et al. [41] in gas phase using an Ag GDE after electrolysis of a couple of hundred hours.

Conclusions

A process for producing green syngas to be powered by renewable energy operating at near room temperature and high pressures was successfully scaled-up from our previous reported batch process to an electrode size of ca. 30 cm² geometrical area (ca. 30 fold factor) without loss in performance. Pressures used in these work were only up to 30 bar. Pressure shows the most significant influence on CO selectivity and CO productivities. The combination of high pressure, the use of ionic liquid-based electrolytes for electrochemical CO₂ reduction in liquid phase has allowed achieving productivities of the same order of magnitude of some porous electrodes and much higher than those reported in the literature using noble metal catalysts, with strict purity requirements. A syngas composition H₂/CO in the range of 1/1 to 4/1 suitable for the synthesis of several fuels and chemical building blocks can be obtained using an inexpensive commercial foil of a common metal such as zinc. However, it presents the drawback of yielding limited current densities not appropriate for a commercial application, since costs decrease significantly as current densities increases. Further

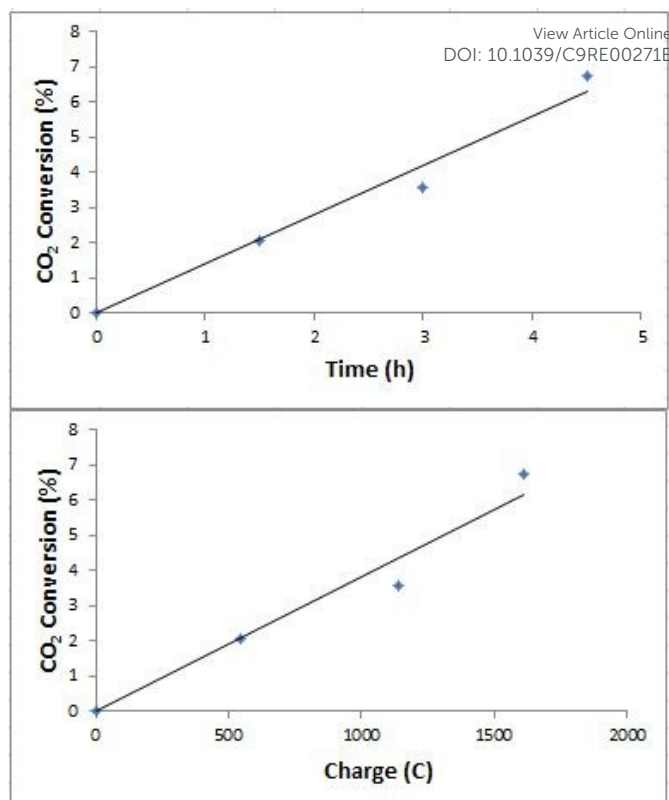


Figure 5 – CO₂ conversions of electrolysis carried out in semi-continuous mode with a flow rate of 2.5 ml/min. at 45°C, 10 bar vs. a) charge passed; b) time.

investigations are necessary for reliably estimating the costs of this technology. In terms of scalability, the potential is there to operate facilities at the MW power scale similar to water splitting electrolyzers for H₂ production [42]. Work will continue with the integration of more performant zinc-based electrodes in the system under study. As expected, semi-continuous operation mode yielded higher productivities as a consequence of more efficient mass transport, when compared with the batch operation mode. The process will be further adapted for a flow-by operation mode. A further research effort is necessary to develop membranes customized for a CO₂ electrolyser with enhanced protonic conductivities, minimizing crossovers.

The present work shows the potential of the system under study to achieve high conversions of CO₂ to avoid a purification step of syngas from unreacted CO₂. This additional step adds-up to process costs and decreases energy efficiencies. The electrochemical cell configuration will be improved further, as the distance between the electrodes, and consequently the ohmic drop has not been optimized. This work also shows the potential for process intensification, in terms of productivities and of further integration with CO₂ capture, since relatively low concentrations of IL were used. This can in principle be achieved as ionic liquid are also being used as CO₂ capture agents at pilot scale [43]. Taking advantage of the tunable properties of ionic liquids, there is large room for designing ionic liquids optimized simultaneously as electrolytes and co-catalysts for syngas production, contributing to significant improvements in the energy efficiency of the process. As designer solvents there is also a wide scope for development of low toxicity compounds customized for a specific application.

Experimental

Materials and reagents

Carbon dioxide (N45 purity 99.995%) and Argon Alphagaz 1 were purchased from Air Liquide. 1-Ethyl-3-methyl-imidazolium trifluoromethanesulfonate (triflate) > 99% purity was purchased from Iolitec and dried overnight before use.

Cyclic voltammetry

Cyclic voltammetry was carried out using an PGSTAT128N-Autolab 84469 potentiostat. A three-electrode system was used. The working electrode was a commercial zinc foil. The same material was also used as sacrificial anode. An Ag/Ag⁺ quasi-reference electrode (QRE) was employed. It consists of a cylindrical piece of high purity Ag of 1.5 mm diameter. Before each experiment the silver rod was mechanically polished with silicon carbide emery paper 220 µm thoroughly washed in distilled water and dried before immersion in the electrolyte. All voltammograms were performed in a potential range from -0.5 V to -2.5 V vs. Ag/Ag⁺ QRE at 45° C, and a scan rate of 50 mVs⁻¹. The two first cycles were discarded. The electrochemical cell used is described in detail elsewhere [15].

Electrolysis

To be able to compare results obtained with cells with different configurations, electrolysis were carried out in a single compartment test bed and in a two compartment reactor. The probability of silver affecting catalysis, when electrolysis are carried out in the single compartment test bed is very low. In

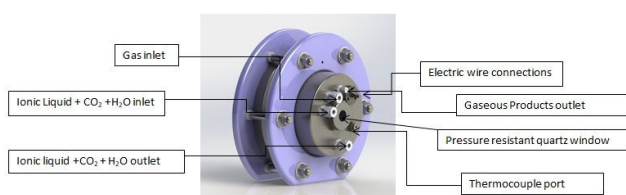


Figure 6 – 3D design of the two compartments electrochemical cell.

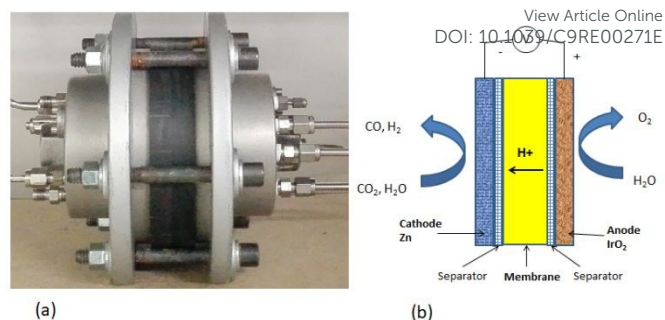


Figure 7 – a) View of the electrochemical reactor; b) Scheme of the electrode membrane assembly. Components are not on scale.

fact, energy dispersive X-ray spectroscopy (EDS) analysis of the cathodes after electrolysis did not detect Ag on the cathode. The two compartment electrochemical reactor is a two electrode system and the Ag/Ag⁺ QRE was not used.

Electrolysis in a single compartment test bed

The same set-up as the one used for cyclic voltammetry was employed. The working electrodes were zinc foils of 1.2 cm² geometrical area and 1 mm thickness. The electrolytes consisted of mixtures of 1-ethyl-3-methyl-imidazolium triflate (EMIMOTf) and water (90 wt. % and 50 wt. %) contained in a glass beaker; 5 ml of EMIMOTf were used. After assembling the electrochemical reactor, CO₂ was introduced. A CO₂ purge was carried out to remove air from the system. Then, carbon dioxide was again introduced and the reactor was brought to the desired pressure. After temperature stabilization, current was applied to the electrodes and electrolysis was carried out. Detailed electrolysis, sampling procedures and analysis are described elsewhere [15].

Electrolysis in the two compartment reactor

A detailed description of the pressure facility, and the electrolysis procedure is given in ESI.

The electrochemical reactor was designed and built for this work. This reactor can be operated from room temperature up to 80°C, and work at pressures in the range of atmospheric pressure up to 100 bar. It consists of a cylindrical stainless steel electrochemical cell with an inner volume of 170 cm³ divided by an ion exchange membrane and equipped with 2 cm diameter pressure resistant quartz view windows to the cathode and anode compartments. Protonic exchange membranes with average thicknesses of 120 µm, 90 µm and 75 µm were used. They were conditioned before electrolysis following the instructions of the manufacturer. The electrochemical cell is a two electrode system. The working electrode used was a commercial zinc foil and the anode was a commercial IrO₂/Ti mesh purchased from DeNora. Fig. 6 shows a 3D scheme of the electrochemical cell, showing gas inlet/outlet ports, liquid inlet/outlet ports, electric wire connections, thermocouple port and quartz view windows. The dimensions of the electrodes were 6 cm x 6 cm x 0.1cm. The electrodes are placed on an insulating polymer support on each side of the membrane. Between the electrode and the membrane there is a polymeric

separator mesh. Fig. 7 a) shows a view of the electrochemical reactor and Fig. 7b) depicts a scheme of the electrode-membrane assembly.

After assembling the electrochemical reactor, the electrolyte was pumped into the reactor. CO₂ was then introduced in the facility. Teledyne Isco syringe pumps, model 500D, were used for charging the electrolyte and for recirculating it, when electrolysis were conducted in semi-continuous mode. Then, carbon dioxide was brought to the desired pressure, and when the reactor stabilized at the desired temperature and pressure, current was applied to the electrodes and electrolysis was initiated.

Electrolysis were carried out under galvanostatic control. A potentiostat/galvanostat PGSTAT128N-Autolab 84469 was used. 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 and then closed. The sampling vessel was disconnected from the pressure facility and the gaseous mixture was analysed by gas chromatography. Electrolysis were carried out at least in duplicate.

Gas Phase Analysis

Gaseous products were analysed with a 3000 MicroGC from Agilent equipped with a TCD detector. A molecular Sieve 5A, 10 m x 0.32 mm column with a Plot U 3 m x 0.32 mm pre-column that can analyse H₂, N₂, O₂, CO and CH₄ with argon as carrier gas was used. A Plot U de 8 m x 0.32 mm with Plot Q de 1 m x 0.32 mm as pre-column that can quantify CO₂ and other hydrocarbons was employed with helium as carrier gas. Compositions were determined by comparison with calibrated gaseous mixtures of known compositions supplied by Air Liquide.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was performed under the project "SunStorage - Harvesting and storage of solar energy", with reference POCI-01-0145-FEDER-016387, funded by European Regional Development Fund (ERDF), through COMPETE 2020 - Operational Programme for Competitiveness and Internationalisation (OPCI), and by national funds, through FCT - Fundação para a Ciência e a Tecnologia I.P.

Notes and references

- 1 H. Blanco and A. Faaij, *Renew. Sustain. Energy Rev.* 2018, **81**, 1049–1086.
- 2 M. Bailera, P. Lisbona, L. M. Romeo and S. Espotolero, *Renew. Sustain. Energy Rev.* 2017, **69**, 292–312.
- 3 P. Schmidt, V. Batteiger, A. Roth, W. Weindorf and T. Raksha, *Chem. Ing. Tech.*, 2018, **90**, 127–140.
- 4 A. Kätelhön, R. Meys, S. Deutz, S. Suh, and A. Bardow, *Proceedings of the National Academy of Sciences*, 2019. www.pnas.org/cgi/doi/10.1073/pnas.1821029116-accessed June 2019
- 5 J.P. Jones, G.K.S. Prakash and G.A. Olah, *Isr. J. Chem.*, 2014, **54** 1451–1466.
- 6 S. Nakagawa, A. Kudo, M. Azuma, and T. Sakata, *J. Electroanal. Chem.* 1991, **308**, 339–343.
- 7 A. Kudo, S. Nakagawa, A. Tsuneto and T. Sakata, *J. Electrochem. Soc.*, 1993, **140**, 1541–1545.
- 8 K. Hara, A. Tsuneto, A. Kudo and T. Sakata, *J. Electrochem. Soc.* 1994, **141**, 2097–2102.
- 9 K. Hara, A. Kudo and T. Sakata, *J. Electroanal. Chem.*, 1995, **391**, 141–147.
- 10 M. Todoroki, K. Hara, A. Kudo and T. Sakata, *J. Electroanal. Chem.*, 1995, **394**, 199–203.
- 11 K. Hara, A. Kudo and T. Sakata, *J. Electroanal. Chem.* 1997, **421**, 1–4.
- 12 K. Hara and T. Sakata, *Bull. Chem Soc. Jpn.*, 1997, **70**, 571–576.
- 13 A. S. Reis-Machado, A. V. M. Nunes, M. Nunes da Ponte, *The Journal of Supercritical Fluids*, 2018, **134**, 150–156.
- 14 E. J. Dufek, T. E. Lister, S. G. Stone and M. E. McIlwain, *J. Electrochem. Soc.* 2012, **159**, F514-F517.
- 15 T. Pardal, S. Messias, M. Sousa, A. S. Reis-Machado, C. M. Rangel, D. Nunes, J. V. Pinto, R. Martins and M. Nunes da Ponte, *J. CO₂ Util.*, 2017, **18**, 62–72.
- 16 C. Verma, E. E. Ebenso, and M.A. Quraishi, *Journal of Molecular Liquids*, 2017, **233** 403–414.
- 17 D. Faggion Jr., W. D. G. Gonçalves and J. Dupon, *Front. Chem.* 2019, **7**, 102, doi: 10.3389/fchem.2019.00102
- 18 M. Alvarez-Guerra, J. Albo, E. Alvarez-Guerra and A. Irabien, *Energy Environ. Sci.* 2015, **8**, 2574–2599.
- 19 G. Zhao, T. Jiang, B. Han, Z. Li, J. Zhang, Z. Liu, J. He and W. Wu, *J. Supercrit. Fluids.*, 2004, **32** 287–291.
- 20 B.A. Rosen, A. Salehi-Khojin, M.R. Thorson, W. Zhu, D.T. Whipple, P.J.A. Kenis and R.I. Masel, *Science*, 2011, **334**, 643–645.
- 21 D. J. A. Lange's, *Handbook of Chemistry*, 15th ed., McGraw-Hill, NewYork, 1999, p. 165.
- 22 D.R. Lide, *CRC Handbook*, 84th ed., CRC Press, BocaRaton, Florida, 2003.
- 23 F. Quan, D. Zhong, H. Song, F. Jia, and L. Zhang, *Mater. Chem. A*, 2015, **3**, 16409-16413.
- 24 B. Kumar, J. P. Brian, V. Atla, S. Kumari, K. A. Bertram, and R. T. White, J. M. Spurgeon, *Catal. Today*, 2016, **270**, 19–30.
- 25 X. Mao, and T. A. Hatton, *Ind. Eng. Chem. Res.*, 2015, **54**, 4033–4042.
- 26 M. Jia, C. Choi, T. Wu, C. Ma, P. Kang, H. Tao, Q. Fan, S. Hong, S. Liu, Y. Soo, Y. Jung, J. Qiua and Z. Sun, *Chem. Sci.*, 2018, **9**, 8775-8780.
- 27 J. Rosen, G. S. Hutchings, Q. Lu, R. V. Forest, A. Moore, and F. Jiao, *ACS Cat.*, 2015, **5**, 4586–4591.
- 28 K. Ogura, J. R. Ferrell, A. V. Cugini, E. S. Smotkin and M. D. Salazar-Villalpando, *Electrochem. Acta*, 2010, **56**, 381-386.
- 29 M. Ramdin, T. W. de Loos, and T. J.H. Vlught, *Ind. Eng. Chem. Res.* 2012, **51**, 8149–8177.
- 30 F. Endres, Douglas MacFarlane and Andrew Abbott, *Electrodeposition from ionic liquids*, Wiley-VCH, 2008.
- 31 M. Chuang, M. Johannsen, Characterization of pH in Aqueous CO₂-Systems International Symposium on Supercritical Fluids: new trends in supercritical fluids: energy, materials, processing, 2009, 18-20 May, Arcachon, France. (<https://www.isasf.net/fileadmin/files/Docs/Arcachon/poste>

[rs/p4-P46%20ISSF2009_Johannsen_P46.pdf](#) accessed June 2019)

- 32 S. Ikeda, A. Hattori, M. Maeda, K. Ito and H. Noda, *Electrochem.* 2000, **68**, 257–261.
- 33 S. Ikeda, A. Hattori, K. Ito and H. Noda, *Electrochem.* 1999, **67**, 27–33.
- 34 Y. Hori, K. Kikuchi, S. Suzuki, *Chem. Lett.* 1985, 1695–1698.
- 35 M. E. Zakrzewska and M. Nunes da Ponte, *J. Chem. Eng. Data*, 2018, **63**, 907–912.
- 36 J. Shi, F. Shi, N. Song, J.-X. Liu, X.-K. Yang, Y.-J. Jia, Z.-W. Xiao and P. Du, *J. Power Sources*, 2014, **259**, 50–53.
- 37 S. Hernández, M. A. Farkhondehfar, F. Sastre, M. Makkee, G. Saracco, and N. Russo, *Green Chem.*, 2017, **19**, 2326–2346.
- 38 Z. Liu, R.I. Masel, Q. Chen, R. Kutz, H. Yang, K. Lewinski, M. Kaplun, S. Luopa and D.R. Lutz, *J. CO₂ Util.* 2016, **15**, 50–56.
- 39 T. Hatsukade, K. P. Kuhl, E. R. Cave, D. N. Abram and T. F. Jaramillo, *Phys.Chem.Chem.Phys.*, 2014, **16**, 13814–13819.
- 40 F. Sastre, M. J. Muñoz-Batista, A. Kubacka, M. Fernández-García, W. A. Smith, F. Kapteijn, M. Makkee, and J. Gascon, *ChemElectroChem*, 2016, **3**, 1497–1502.
- 41 P. Jeanty, C. Scherer, E. Magoria, K. Wiesner-Fleischer, O. Hinrichsen, and M. Fleischer, *Journal of CO₂ Utilization*, 2018, **24**, 454–462.
- 42 M. Carmo, D. L. Fritz, J. Mergel and D. Stolten, *International Journal of Hydrogen Energy*, 2013, **38**, 4901–4934 .
- 43 A. S. Reis-Machado and M. Nunes da Ponte, *Current Opinion in Green and Sustainable Chemistry* 2018, **11**, 86–90.

View Article Online
DOI: 10.1039/C9RE00271E

