Continuous conversion of CO_2 to alcohols in a TiO_2 photoanode-driven photoelectrochemical system

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ABSTRACT

BACKGROUND

The recycling of CO_2 by photo-electrochemical reduction has attracted wide interest due to its potential benefits when compared to electro-, and photo-catalysis approaches. Among the different available semiconductors, TiO_2 is the most employed material in photo-electrochemical cells. Besides, Cu is a well-known electrocatalyst for alcohols production from CO_2 reduction.

RESULTS

In this study, a photo-electrochemical cell consisting on a TiO_2 photoanode Membrane Electrode Assembly (MEA) and a Cu plate are employed to reduce CO_2 to methanol and ethanol continuously under UV illumination (100 $mW \cdot cm^{-2}$). A maximum increment of 4.3 $mA \cdot cm^{-2}$ in current between the illuminated and dark conditions is achieved at -2 V vs. Ag/AgCl. The continuous photo-electrochemical reduction process in the filter-press cell is evaluated in terms of reaction rate (*r*), as well as Faradaic (*FE*) and energy (*EE*)

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efficiencies. At -1.8 V vs. Ag/AgCl, a maximum reaction rate of r= 9.5 μmol·m^{-2}·s^{-1}, *FE*= 16.2 % and *EE*= 5.2 % for methanol, and r= 6.8 μmol·m^{-2}·s^{-1}, *FE*= 23.2 % and *EE*= 6.8 % for ethanol can be achieved.

CONCLUSIONS

The potential benefits of the photoanode-driven system, in terms of yields and efficiencies, are observed when employing a TiO_2-based MEA photoanode and Cu as dark cathode. The results demonstrate first the effect of UV illumination on current density, and then the formation of alcohols from the continuous photoreduction of CO_2. Increasing the external applied voltage led to an enhanced production of methanol, but decreases ethanol formation. The system outperforms previous photoanode-based systems for the CO_2-to-alcohols reactions.

KEYWORDS: Photoelectrocatalysis; CO_2 reduction; TiO_2; Cu; methanol, ethanol.

1. INTRODUCTION

The concentration of CO_2 in the atmosphere has increased to worrying levels in recent years, mainly due to fossil fuels burning. This has accelerated research activities to obtain value added products from residual CO_2, instead of discard it as a residue.[1] There are different possibilities to convert CO_2 into valuable products. Among the different technologies available, the electrochemical reduction of CO_2 has attracted great interest due to the potential economic and environmental benefits. This technology, apart from allowing CO_2 dissociation at ambient conditions using electricity, is also an excellent alternative to store the intermittent energy produced from renewables in the chemical

bonds.[2] Moreover, the integration of a light source in electrochemical reduction devices (a photoelectrochemical approach, PEC) has attracted an increasing interest recently because it may allow avoiding the interconnections between devices, reducing, in principal, system capital costs and electricity losses.[3] Compared to photocatalysis, the applied bias can cause band bending and help the oriented transfer of the photogenerated electrons, decreasing the recombination of the photogenerated electron-hole pairs. Besides, photocatalytic materials with unfavorable band positions for CO_2 reduction and H_2O oxidation can be still used in photoelectrocatalytic systems when applying an external bias.

There are different electrode configurations for the PEC systems on dependence on which electrode (i.e., anode, cathode or both) acts as photoelectrode.[4] Photocathode-dark anode has been the most employed configuration.[5-9] In this case, a *p*-type semiconductor is employed as photocathode and a metal as anode. Unfortunately, with the *p*-type semiconductors two-electron products are usually obtained and the system efficiency is low. On the other hand, CO_2 reduction in a photoanode-dark cathode PEC is a simpler configuration and depends on the photoanode and the cathode activity independently[10-12], and offers the advantage of reducing the external energy requirements of the process.[13] In this configuration, H_2O oxidation in the photoanode provides electrons and protons for CO_2 reduction in the cathode compartment. Besides, the negative potential voltage generated in the photoanode by the light, supplies an additional negative potential for CO_2 reduction in the cathode.[4] Another PEC photoelectrodes configuration is the combination of a photocathode for CO_2 reduction with a photoanode to deals with H_2O oxidation (as

represented in Figure 1).[13-15] In contrast to the previous configurations, the main advantage is that with some pairs of materials an external electrical energy supply for the redox reactions may, ideally, not be needed. However, in most cases, the voltage generated by the light source is not enough and a continuous external power supply is required.[16, 17]

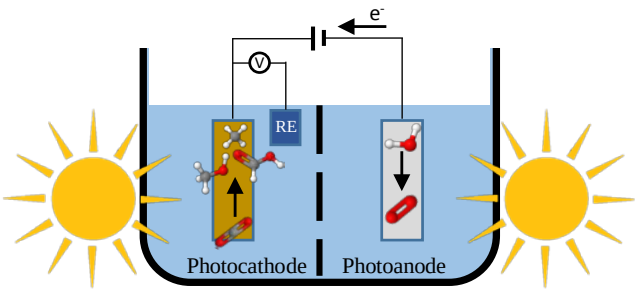

Figure 1. PEC cell in a phocathode-photoanode configuration. Edited from [2].

Moreover, the formation of alcohols from CO_2 has received increasing attention due to their proper integration in the actual fuel infrastructure, besides been considered an advantageous energy storage and a precursor to synthesize other products. [18-20] Methanol (CH_3OH) is considered an excellent energy intermediate due to the stable storage properties and its high energy density. In addition to the application as a fuel, CH_3OH is an intermediate to other bulk chemicals employed in everyday life products like plastics and paints. [21] Ethanol (C_2H_5OH) is an important raw material with high heating value usually employed in disinfectants and organics material.[22] It can also replaces fossil fuels in a key sector such as the transport industry.[23] Thus, both products offer an alternative to deal with climate change,

reducing our dependence on fossil fuels and allowing CO_2 recycling in a neutral carbon cycle. [18, 24]

TiO_2 is the most employed semiconductor in photo-assisted processes.[25-28] It is a *n*-type semiconductor that possesses a wide band gap (3.0 eV) and mainly absorb UV light. [29] This semiconductor has been considered a cheaper and more environmental friendly material [30] since the first report in 1979.[25] Besides, Cu has demonstrated to possess the capacity to produce hydrocarbons and alcohols from CO_2.[31] In particular, previous works from our group employed a Cu plate for CO_2 electroreduction, with a reaction rate of CH_3OH of r= 8.7 $\mu mol \cdot m^{-2} \cdot s^{-1}$ and a *FE*= 4.6 % at -1.3V vs. Ag/AgCl. These values were subsequently enhanced by using Cu oxide [31, 32] and metal-organic frameworks (MOFs)-based electrodes at different experimental conditions in continuous operation mode. [18, 31-33]

Thus, the aim of the present work is coupling a TiO_2-based photoanode in an electrochemical filter press cell for the continuous conversion of CO_2 to alcohols (i.e. CH_3OH and C_2H_5OH) in order to reduce the requirements of external energy, and so reduce energy consumption. A Cu plate is used as dark cathode for designing a reliable photoanode-dark cathode configuration for CO_2 photoreduction. The specific objectives are as follows: (1) to prepare and optimize a TiO_2-based photoanode, (2) to adapt an electrochemical cell for the PEC conversion of CO_2 to alcohols, and finally (3) to analyze the effect of voltage on process performance. The results are considered a step further in the development of continuous CO_2 conversion processes under the sun.

2. EXPERIMENTAL SECTION

2.1. TiO_2 photoanode preparation

A TiO_2 photoanode is fabricated by air-brushing an ink composed by a mixture of TiO_2 (Sigma Aldrich, P25), Nafion (Alfa Aesar 5wt%) as binder and isopropanol (99.5%, Sigma Aldrich) as vehicle, with a 70:30 wt% TiO_2/Nafion ratio in a 3 wt.% of solid in the final isopropanol dispersion onto a Toray carbon paper (TGP-H60). An ultrasound bath is used to homogenize the mixture. The TiO_2 loading varies from 1 to 3 $mg \cdot cm^{-2}$. The TiO_2 photoanode is coupled by hot-pressing with a Nafion membrane (Nafion 117), previously activated in HCl for 30 minutes and rinsed with deionized water before use, forming a Membrane Electrode Assembly (MEA) able to enhance H^+ transport, reducing mass transfer limitations. [33, 35]

2.2. Photoelectroreduction cell and experimental conditions

The continuous PEC reduction of CO_2 is carried out using a commercial filter press cell reactor (Electrocell, Denmark), employing a Cu plate as cathode and the prepared MEA as photoanode, which also separates the cell compartments. A 1 M KOH aqueous solution is used as catholyte and anolyte and a cold UV LED light (100 $mW \cdot cm^{-2}$) to illuminate the photoactive area (10 cm^2) of the TiO_2 photoanode. In the cathode side, there are two inputs: the catholyte and the CO_2 gas; and one output: the catholyte with the reaction products (liquid and gaseous). The Cu plate works as working electrode, the TiO_2 phoelectrode as counter electrode and Ag/AgCl as reference electrode. The CO_2 reduction is conducted at ambient conditions. Figure 2 shows a scheme of the experimental setup, while Figure 3 shows a detailed view of the cell configuration. The experimental system

includes four tanks for inlet and outlet electrolyte solutions, two peristaltic pumps to circulate the liquid at a flow rate of 10 ml·min^{-1}, two pressure indicators and mass-flow controllers to fix the CO_2 inlet flow rate at 180 ml·min^{-1}. Moreover, a potentiostat (AutoLabPGSTAT 302N) is used. The PEC behavior of the TiO_2 photoanodes is evaluated in a one-compartment glass at a scan rate of 50 mV·s^{-1} after 20 cycles with and without light illumination.

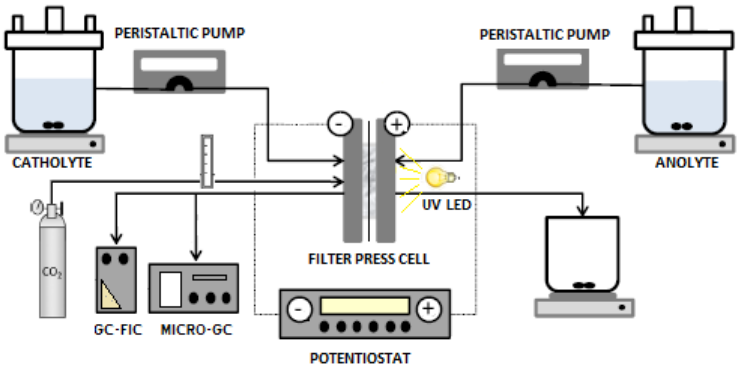

Figure 2. Experimental system for the continuous PEC reduction of CO_2. Edited from [36].

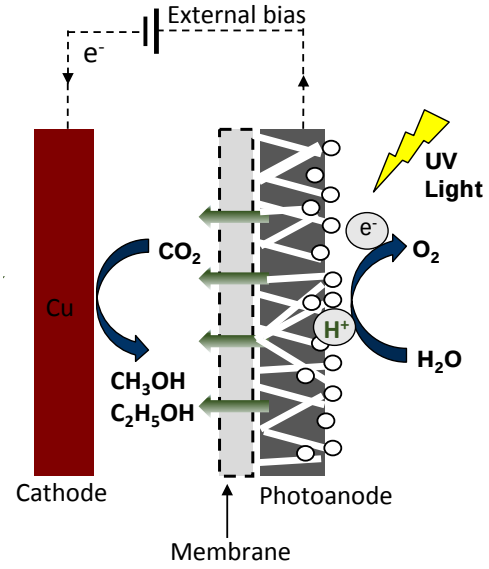

Figure 3. Detail of the PEC cell configuration. Edited from ref. [32].

Continuous experiments in the PEC cell are performed by duplicate during 50 minutes. Both liquid and gas samples are taken every 10 minutes, and a final average concentration is calculated for each test. The values that are two times lower/higher than the average value are discarded in order to calculate the reaction rate (r) and the Faraday efficiency (FE) with an error less than 10%. The values are normalized to reacting CO_2 (inlet-outlet) in the system and adjusted to a FE= 100%. To collect the gaseous samples, the experimental system is pressurized to 0.2 bar for its subsequent analysis in an in-line gas microchromatograph (3000 Micro GC, Inficon). Liquid samples are analysed in a gas chromatograph (GCMSQP2010 Ultra Shimadzu) equipped with a flame ionization detector (FID). The reaction rate shows the formation rate for every product per unit of

area and time (μmol·m^{-2}·s^{-1}) and the *FE* is defined as the selectivity of the reaction to form each products, calculated according to the Ec 1:

$$FE\ (\%) = \frac{z \cdot n \cdot F}{q} x100\ \ [Ec\ 1]$$

where z is the theoretical number of e^- exchanged to form the desired product, *n* is the number of moles produced, *F* is the Faraday constant (F = 96,485 C·mol^{-1}) and *q* is the total charge applied in the process. Moreover, the energy efficiency, *EE*, which indicates the total energy used toward the formation of the desired products can be calculated according to the following equation (Ec 2):

$$EE\ (\%) = \frac{E_T}{E} xFE\ \ [Ec\ 2]$$

Where *E* is the real potential applied in the system and E_T the theoretical potential needed for the formation of CH_3OH (-0.58 V vs. Ag/AgCl) and C_2H_5OH (-0.53 V vs. Ag/AgCl).

3. RESULTS AND DISCUSSION

3.1. Photoelectrochemical behavior of the TiO_2 photoelectrode

Figure 4a shows the photocurrent response of the TiO_2 photoanode MEA during on-off illumination cycles in a one-compartment glass under 100 mW·cm^{-2} of UV illumination at -1.8 V vs. Ag/AgCl in the presence of CO_2, while Figure 4b shows the current densities observed with and without illumination in cell when CO_2 is continuously bubbling in a potential range between -1.2 V and -2 V vs. Ag/AgCl and a TiO_2 loading of 3 mg·cm^{-2}, where an optimal reduction of CO_2 to alcohols can be expected. [34, 37, 38] It should be noted

that the TiO_2-based photoanodes showed no changes in response (current) during on-off cycles when illuminated with a visible LED light (100 $mW \cdot cm^{-2}$).

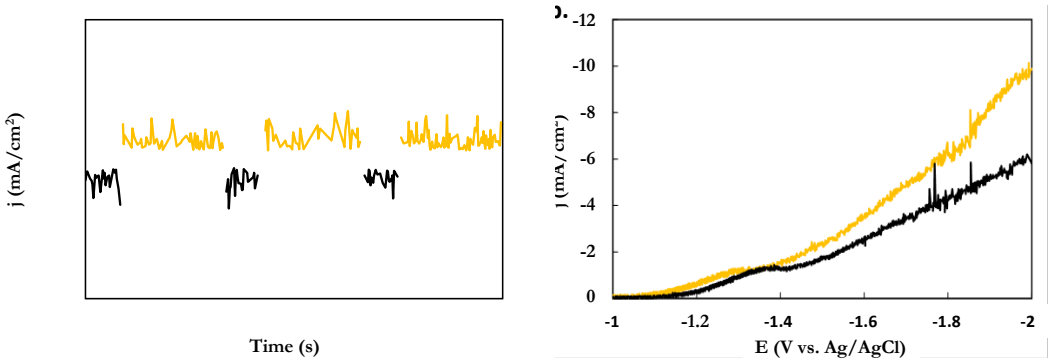

Figure 4. (a) On-off cycles for the TiO_2 photoanode MEA in the dark (black) and under UV illumination (yellow) with CO_2 at -1.8 V vs. Ag/AgCl and, (b) *j-E* characteristics of the TiO_2 MEA photoanode in the dark (black) and under UV illumination (yellow) with CO_2.

First, the current density of the system under UV light results larger than in the dark conditions in on-off cycles (Figure 4a) at -1.8 V vs. Ag/AgCl. Then, figure 4b shows that the increase in current density under UV light illumination can be observed in all the potential range evaluated. The variation in current density between the illuminated and dark conditions represents the highest attainable photocurrent in the system. Of course, increases in current density are associated to higher voltage values, getting a maximum increment of j= 4.3 $mA \cdot cm^{-2}$ under UV illumination (j= 9.9 $mA \cdot cm^{-2}$) respect to the dark experiment at -2 V vs. Ag/AgCl (j= 5.6 $mA \cdot cm^{-2}$), although this high potential could not

be beneficial for alcohols production. [36] These results may be taken as a first indication for an enhanced PEC process performance as evaluated hereafter.

3.2. Process performance of the TiO_2/Nafion/Cu plate system

The products obtained for the continuous CO_2 reduction PEC reduction employing a TiO_2-based MEA as photoanode and a Cu plate as cathode are alcohols (i.e. CH_3OH and C_2H_5OH) together with CO and C_2H_4. Their formation, and so process performance, is evaluated in terms of *r* and *FE*. Figure 5 initially shows an example of the evolution of *j* during the experimental time (UV illumination).

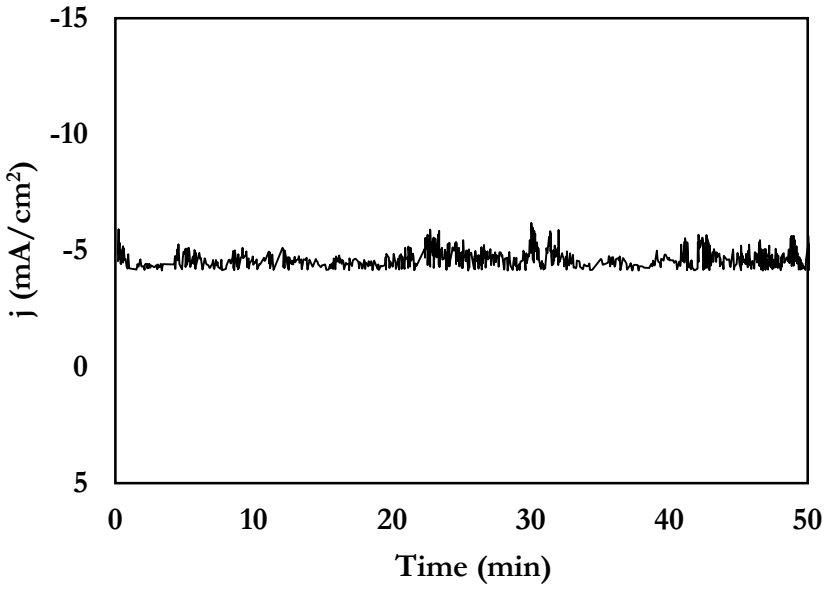

Figure 5. PEC activity, *j*, with time at -1.8 V vs. Ag/AgCl.

As can be observed, the system presents a pseudo-stable activity after 50 min of operation in the continuous liquid-liquid CO_2 PEC conversion. The small fluctuations observed are

commonly caused by the direct input of CO_2 gas into the cathode compartment, as well as the production of gaseous products (bubbles) on the electrode surface. The results also give an idea of the stability of the system, although, of course, longer-term tests would be needed in order to assess the feasibility of the system for real applications.

Among the different key variables of the process, the TiO_2 catalyst loading can have a remarkable impact on process performance. [35]. In principle, the higher the semiconductor surface, the greater the photocurrent generated as more electrons are excited in the photoanode.

Therefore, figure 6 shows the *FE* values at three different TiO_2 catalyst loadings in the MEA (i.e.1, 2 and 3 $mg \cdot cm^{-2}$).

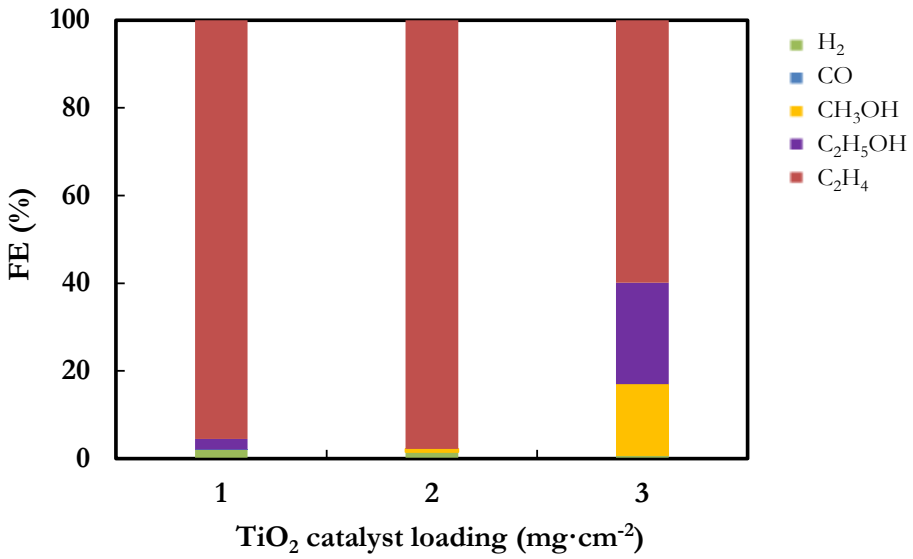

Figure 6. Effect of TiO_2 loading in the photoanode.

As observed, 3 mg·cm^{-2} seems to be the optimum for both, CH_3OH and C_2H_5OH formation, with a *FE* value of 16.2 % and 23.2%, respectively, in comparison to the value observed at 1 mg·cm^{-2}, where no CH_3OH was detected and a C_2H_5OH *FE* value of 2.4 % can be achieved. At higher catalyst loadings than 3 mg·cm^{-2}, Seger et al. [34] found that the light absorption limits the photocurrent generation due to particle agglomeration which hampers the accessibility of the light to the catalytic surface. Consequently, a TiO_2 loading of 3 mg·cm^{-2} is recommended to get the best performance in the developed TiO_2 photoanode MEA-driven system for CO_2 PEC conversion and is applied hereafter.

Then, the values for alcohols (i.e. CH_3OH and C_2H_5OH) formation in a voltage range from -1.2 to -2 V vs. Ag/AgCl are presented in Table 1, while Figure 7 shows the *FE* to all liquid and gas-phase products detected as a function of the applied voltage.

The values in Table 1 are normalized by the total charge *q* (C) passing through the system in order to properly analyze the PEC activity. The values are also compared with our previous findings for the electrochemical conversion of CO_2 (in the dark) using a Cu plate.[31]

Table 1. Production rates, *r*, for alcohols at different *E* employing a Cu plate as cathode.

E (V)	**j (mA·cm^{-2})**	**q (C)**	**r (µmol·m^{-2}·s^{-1})**		**r · C^{-1} x10^{-8}**	
			CH_3OH	**C_2H_5OH**	**CH_3OH**	**C_2H_5OH**
-1.2	0.1	6	-	19.3	-	321.6
-1.4	1.6	21.6	-	13.9	-	64.3
-1.6	1	20.7	-	14.9	-	71.9
-1.8	5.9	102	9.5	6.8	9.3	6.6
-2	9.8	117.6	24	-	20.4	-
-1.3*	10.8	584.8	8.7	-	1.5	-

-1.5*	16.6	894.2	23	-	2.6	-

*Cu plate cathode-Pt anode. Q/A= 2 ml·min^{-1}·cm^{-2} in an electrochemical system. [31]

First, the data shows that the current densities values in the PEC system are significantly reduced (for a comparable production of alcohols) to those at a Cu plate and a Pt anode in an electrochemical system (in the dark), which might initially indicate an enhancement in energy efficiency. Then, the reaction rate values, *r,* show similar ranges for CH_3OH for the same voltage level in electrochemical and PEC experiments. The $r \cdot C^{-1}$ values obtained in this work, however, are clearly superior in PEC (r= 9.3 µmol·m^{-2}·s^{-1}·C^{1} for CH_3OH at -1.8 V vs. Ag/AgCl) in comparison to those achieved in the electrochemical experiments (r= 2.6 µmol·m^{-2}·s^{-1}·C^{1} for CH_3OH) at similar voltage level, showing the benefits of the PEC. The PEC system seems also to be beneficial for the formation of C_2H_5OH, which requires a higher number of electrons and C-C coupling. This enhancement of CO_2 reduction to alcohols can be generally associated with two phenomena: first, the cathode potential becoming more negative (higher supply of e^-) and then, the large amount of H^+ generation from water the photo-electrolysis, that seem to be available for CO_2 conversion to alcohols in the cathode. [11] The *FE* to both alcohols notably decrease at -2 V vs. Ag/AgCl, which can be ascribed to an enhanced formation of C_2H_4 (Figure 7).

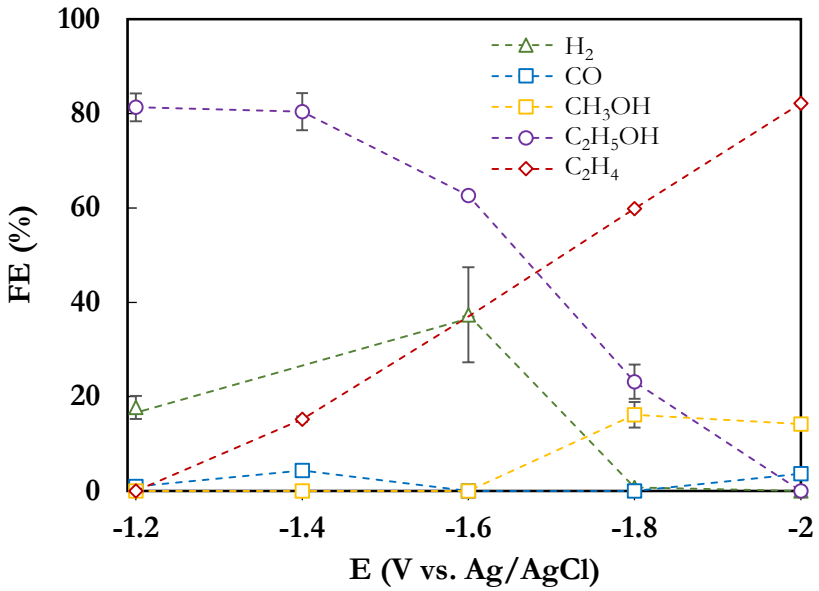

Figure 7. *FE* for all liquid and gas-phase products obtained at different *E*.

The highest *FE* to CH_3OH is achieved at –1.8 V vs. Ag/AgCl, *FE*= 16.2 %. In the other hand, the *FE* to C_2H_5OH is negatively affected by increases in *E*, going from *FE*= 81% at -1.2 V to 23.2 % at -1.8 V vs. Ag/AgCl, in agreement with the values shown in Table 1. These *FE* values towards C_2H_5OH, exceed those previously reported for other promising Cu-based systems, such as Cu-based MOF materials supported on GDEs (*FE*~ 6% at -10 $mA{\cdot}cm^{-2}$ in $[Cu_3(\mu_6\text{-}C_9H_3O_6)_2]_n$). [36]

Besides, the formation of C_2H_4 can be expected in the potential range tested, as previously found in our group for the gas-phase CO_2 reduction at Cu-based surfaces, achieving a *FE*= 91% to C_2H_4 at -2.1 V vs. Ag/AgCl [33] as also reported by other authors. [39, 40] Overall, an applied voltage of -1.8 V vs. Ag/AgCl is preferred for the formation of both alcohols.

Furthermore, Table 2 summarizes *EEs* achieved for alcohols as a function of the applied potential.

Table 2. Energy efficiency (*EE)* for CH_3OH and C_2H_5OH.

	EE (%)						
E(V) vs. Ag/AgCl	-1.2	-1.4	-1.6	-1.8	-2	-1.3*	-1.5*
CH_3OH	-	-	-	5.2	4.1	2	1.4
C_2H_5OH	35.9	30.4	20.7	6.8	-	-	-

*Cu plate cathode-Pt anode. Q/A=2 $ml \cdot min^{-1} \cdot cm^{-2}$ employing an electrochemical system. [31]

As observed, a maximum *EE* for CH_3OH can be obtained at -1.8 V vs. Ag/AgCl (*EE*= 5.2%), while lowering the voltage applied seems beneficial for C_2H_5OH production (*EE*= 35.9% at -1.2 V vs. Ag/AgCl). These results are clearly superior to the maximum *EE* values obtained in Cu plate-based system for the electrochemical reduction of CO_2 (in the dark).

Finally, the best performance results obtained at -1.8 V vs. Ag/AgCl are compared (in terms of *r* and *FE*) with previous reports for alcohols production in photoanode-dark cathode PEC systems in Table 3. As observed, the formation of CH_3OH and C_2H_5OH achieved using a TiO_2 photoanode MEA- Cu cathode configuration from this work are, in general, higher than those previously reported for CH_3OH production, and are only exceeded by the value recorded by Hasan et al.[41] with a cathode of Pt and a photoanode of Cu-RGO-TiO_2/ITO, It should be also taken into account that others variables (i.e. reaction medium, cell configuration, experimental conditions, etc.) may affect the results. Besides, the *FE* to C_2H_5OH achieved in this work clearly surpass others in literature (except the results from Hasan et al. [41]) employing the PEC configuration.

Table 3. Production of alcohols from CO_2 in a photoanode-dark cathode configuration.

Cathode	Photoanode	Light source/ Intensity	E (V vs. Ag/AgCl)	j ($mA \cdot cm^{-2}$)	r ($\mu mol \cdot m^{-2} \cdot s^{-1}$)	FE (%)	Ref.
Cu plate	TiO_2	UV LED (λ =365; 100 $mW \cdot cm^{-2}$)	-1.8	5.9	CH_3OH: 9.5 C_2H_5OH: 6.8	CH_3OH: 16.2 C_2H_5OH: 23.2	[This work]
Cu	TiO_2	AM 1.5G (100 $mW \cdot cm^{-2}$)	-0.7	1.36	-	CH_3OH: 1.1	[43]
Pt-Cu/CF	TiO_2	300 W Xe arc lamp (320 nm<λ>410 nm)	-1.95	-	CH_3OH: 0.41 C_2H_5OH: 1.25	CH_3OH: 5 C_2H_5OH: 29	[4]
Pt	Cu-RGO-TiO_2/ITO	150 W Xe arc lamp	-0.56	1.31	CH_3OH: 525.16	CH_3OH: 32.5	[41]
Pt-RGO	Pt-TNT*	300 W Xe-arc lamp	-1.95	-	CH_3OH: 0.14	CH_3OH: 5	[10]
Pt-RGO	Pt (5%)-TNT	300 W Xe arc lamp (320 nm<λ>410 nm)	-1.95	-	CH_3OH: 0.21 C_2H_5OH: 0.78	-	[12]
Pt-RGO	Pt-TNT	300 W Xe arc lamp (320 <λ>410 nm)	-1.95	-	CH_3OH: 2.43 C_2H_5OH: 3.75	-	[42]

*TNT: TiO_2 nanotubes.

4. CONCLUSIONS

Coupling light to electrochemical devices for CO_2 conversion is an interesting approach to obtain value added products under the sun, solving the issues related to global warming at the same time. When the continuous photoelectrochemical transformation of CO_2 is carried out in a filter-press cell employing a TiO_2 MEA photoanode, a maximum increase

of 4.3 $mA \cdot cm^{-2}$ in current density is observed under UV illumination, denoting the potential benefits of the developed photoanode-driven system for an enhanced energy efficiency. Methanol and ethanol, as well as hydrogen, carbon monoxide and ethylene, are detected as liquid and gas-phase products in the system employing a Cu plate as cathode. At -1.8 V vs. Ag/AgCl, the maximum production of methanol is 9.5 $\mu mol \cdot m^{-2} \cdot s^{-1}$, the Faradaic efficiency is 16.2 % and the energy efficiency 5.2 %. In case of ethanol, a reaction rate of 6.8 $\mu mol \cdot m^{-2} \cdot s^{-1}$, a Faradaic efficiency of 12.1 % and energy efficiency of 6.8 % can be achieved for a TiO_2 loading of 3 $mg \cdot cm^{-2}$ in the photoanode. In general, methanol production results are enhanced at higher voltages, while ethanol production seems to be negatively affected. All in all, the developed TiO_2 photoanode-driven system is able to enhance the production of alcohols from CO_2 under UV light, reducing the energy required in the process compared to an electrochemical system.

5. ACKNOWLEDGEMENTS

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