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Electroreduction of CO₂ to CO paired with 1,2-propanediol oxidation to lactic acid. Towards an economically feasible system.

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Abstract

In industrial electrochemical processes it is of paramount importance to achieve efficient, selective processes to produce valuable chemicals while minimizing the energy input. Although the electrochemical reduction of CO₂ has received a lot of attention in the last decades, an economically feasible process has not yet been developed. Typically, the electrochemical reduction of CO₂ is paired to water oxidation, forming oxygen, but an alternative strategy would be coupling the CO₂ reduction reaction to an oxidation in which a higher-value product is co-produced, significantly improving the economic feasibility for CO₂ reduction as a whole. Importantly, both reactions need to be chosen wisely, to ensure their compatibility and to minimize the voltage requirements for the redox system. In this study, as an example of this approach, we demonstrate such a match - the electroreduction of CO₂ to CO, paired with the electrooxidation of 1,2-propanediol to lactic acid. Combining these reactions decreases energy consumption by ca. 35%, increases of product value of the system, and results in combined faradaic efficiencies of up to 160% when compared to the CO₂ reduction reaction in which oxygen is formed in the anode.

Introduction

Electrochemical CO₂ conversion offers an attractive strategy for the conversion of a greenhouse gas into valuable chemicals and fuels¹. However, the high overpotentials required² to drive the conversion of a highly thermodynamically and kinetically stable molecule such as CO₂, together with the low selectivity³⁻⁴ of the process, has stalled the upscaling of this reaction⁵. Electrochemical methods are potentially interesting from an industrial point of view due to the low temperatures and pressures required. That said, physical restrictions, such as mass transport limitations, make the processes commercially unfavorable. However, these limitations can be minimized by the utilization of continuous flow electrochemical set-ups⁶. Such reactor concepts yield several further advantages when compared to batch reactors, such as improved mixing between phases and control of heat transfer.

Numerous studies have focused on improving the electrochemical performance and steering the selectivity and efficiency of CO₂ reduction by studying the effect of several parameters such as the nature and/or structure of the catalyst⁷⁻⁸, the nature and/or pH of the electrolyte⁹ and the potential distribution¹⁰, among others¹¹⁻¹³. Despite these efforts, the conversion of CO₂ in an aqueous electrolyte appears to be economically unfeasible⁵. In aqueous systems, the reduction of water to¹⁴ competes with that of CO₂, decreasing electron efficiency and making the process less economically attractive. Additionally, the counter reaction in these systems is usually the oxidation of water to oxygen, a product with limited value when produced on a large scale. A strategy to make electrochemical processes more economically viable is the combination of two different reactions which both produce high added value products in one reactor, such as the well-known chloralkali process¹⁵, where the formation of chlorine gas occurs on

the anode, and sodium hydroxide is formed on the cathode. The combination of two different reactions allows for the production of two different value-added chemicals, which can be efficiently separated since they are formed in different compartments. More importantly the energy demand of the system is decreased with this approach.

The aim of this study was to demonstrate an economically feasible, paired electrochemical process which maximizes energy efficiency by utilizing the energy input for the formation of valuable products on both sides of the electrochemical cell. Specifically, this study is focused on the continuous electrochemical reduction of CO₂ to CO in the cathodic compartment, and the oxidation of 1,2-propanediol (PDO) to lactic acid mediated by 4-acetamido-(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (ACT-TEMPO), in the anodic compartment. The selection of these two redox processes is driven by the interest in our labs for biomass valorization as well as CO₂ utilization¹⁶. Lactic acid is the key building block for polylactic acid¹⁷, a promising bio-based polymer that is replacing existing oil-based polymers in a new generation of sustainable and eco-friendly plastics. In our study, 1,2-propanediol, is used as a starting material, and can be easily produced via hydrogenolysis of glycerol¹⁸. Glycerol is the main side product of biodiesel production, and is therefore abundant and cheap¹⁹⁻²⁰.

From the perspective of electrochemical lactic acid production, the carbon footprint of the process can be reduced in comparison to the formation of lactic acid via the thermochemical processes. The sustainability of the system can be further improved if the source of energy is renewable.

The principle of paired electrosynthesis has been demonstrated for a limited set of reactions such as the oxidative condensation of

syngaldehyde with the reduction of CO_2 to CO^{21} or the reduction of nitrate with the oxidation of ammonia²². This study serves as an example of further possibilities of paired systems and their potential to improve the electrochemical processes in terms of productivity and efficiency.

Experimental

The electrochemical measurements were carried out with a Autolab potentiostat (PGSTAT20) connected to a micro-flow cell purchased at ElectroCell. The cathode was a gold plate (Alfa Aesar, 99.9%) with a surface area of 10 cm^2 . The working electrode was electropolished before each experiment by cyclic voltammetry (100 cycles) between -2 and $+2 \text{ V}$ vs Ag/AgCl in a 0.5 M KHCO_3 (Sigma Aldrich, 99.7%) solution. The anode electrode was a carbon felt (Fuel cell store) with a surface area of 10 cm^2 . Two leak free Ag/AgCl electrodes (Innovative Instruments LF-1-100) were used as reference electrode (RE), one situated in the cathodic compartment and the second one in the anodic compartment. All potentials in this work are reported against Ag/AgCl . The currents reported were normalized per geometric area.

In addition, an electrode consisting of $15 \text{ nm Au}/\text{C}$ nanoparticles deposited on a carbon cloth (10 cm^2) was also used as working electrode. Gold nanoparticles were synthesized by the citrate reduction method²³. Briefly, the reduction of tetrachloroauric acid (HAuCl_4) was initiated by trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) by injecting a specified amount of trisodium citrate solution into a heated tetrachloroauric acid solution which was vigorously stirred with a Teflon coated magnetic bar. The color of the solution changed gradually from transparent light yellow, to colorless, to dark black, and finally to the characteristic wine red which indicates the formation of gold nanoparticles. The heating was stopped after 30 minutes, then the gold nanoparticle dispersion was kept at room temperature under stirring. The electrodes were prepared by deposition of the catalyst material on carbon cloth coated with a microporous layer. Catalyst were prepared by sonicating Au/C nanoparticles in MilliQ water (30 ml), Nafion solution (1 $\mu\text{L}/\text{mg Au}$), carbon black (Vulcan XC 72) (3 $\text{Au}:2 \text{ Carbon}$) and isopropylalcohol (30ml) for 15 min. The resultant solution was sprayed onto the gas diffusion layer (Carbon cloth) with a loading of $1 \text{ mg}/\text{cm}^2$. The characterization of the Au nanoparticles used in this study can be found in figure S1.1 in the supporting information, section 1.

The experiments were conducted in galvanostatic mode, applying a certain current to the working electrode (cathode) and monitoring the potential obtained at the cathode (E_{cathode}) using an Autolab potentiostat (PGSTAT20). The anode potential (E_{anode}) and the cell voltage (E_{cell}) were also monitored by the use of two multimeters.

The experiments were carried out in a flow cell (ElectroCell) with two compartments separated by an anionic exchange membrane (Fumasep FAA-3-PK-130). The catholyte consisted of a 0.5 M KHCO_3 solution where pure CO_2 (Linde 2.7) was bubbled through with a flow rate of 9 l/h , while the anolyte consisted of a $0.5 \text{ M KHCO}_3/0.5 \text{ M K}_2\text{CO}_3$ buffer solution which contained 20 mM ACT-TEMPO (abcr, 98%) as a mediator and $20 \text{ mM 1,2-propanediol (PDO)}$ (Sigma Aldrich, >99.5%) as a reactant. The anolyte and the catholyte (200 mL each) were both recirculated through the electrochemical cell with a flow rate of 25 l/h . The selection of the catholyte was motivated by the extensive use of bicarbonates

solutions during electrochemical reduction of CO_2 . The anolyte buffer solution was chosen due to the higher alcohol oxidation performance of ACT-TEMPO redox pair at $\text{pH } 10$.

The gaseous products produced at the cathode during the reduction of CO_2 were sampled every 15 minutes and analyzed using an Interscience (Trace GC, Supelco carboxen 1010 PLOT column, FID detector) gas chromatographer (GC). The liquid products obtained during the reduction of CO_2 and the oxidation of 1,2-propanediol were collected every 15 minutes and analyzed by an Agilent (1260-Infinity, Amminex HPX-87H column, RID detector) High Performance Liquid Chromatograph (HPLC) system.

Results and Discussion

Figure 1 shows an overview of the electrochemical process for the reduction of CO_2 to CO paired with the oxidation of 1,2-propanediol to lactic acid (LA) and pyruvic acid (PA), mediated by ACT-TEMPO . A detailed image of all the components of the micro flow cell employed and the complete set-up used for this study can be found in figure S.2 in the supporting information, section 2.

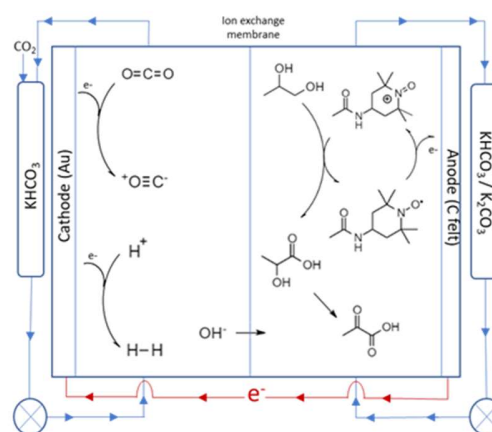
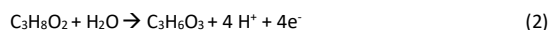


Figure 1: Schematic representation of the electrochemical reactions involved in the process.

Figure 1 shows a schematic representation of the reactions involved in the electrochemical system. The cathodic reaction is the reduction of CO_2 to CO on a Au electrode in a 0.5 M KHCO_3 solution saturated with CO_2 . The anodic reaction consists of the reversible redox reaction of ACT-TEMPO which serves as a mediator for the oxidation of 1,2-propanediol to lactic acid and further oxidation to pyruvic acid. This reaction is similar to the method described in the literature for 5-(hydroxymethyl)furfural to furandicarboxylic acid.²⁴ The anodic reaction took place on a carbon felt electrode in a $0.5 \text{ M KHCO}_3/0.5 \text{ M K}_2\text{CO}_3$ buffer. The use of an anolyte solution of $\text{pH } 10$ was motivated by the maximum oxidation rate of alcohols obtained in previous studies for ACT-TEMPO ²⁵⁻²⁶. The oxidation of 1,2-propanediol mediated by ACT-TEMPO is reported for first time in this study. A discussion about the advantages of ACT-TEMPO mediated oxidation of 1,2-propanediol in comparison to the direct

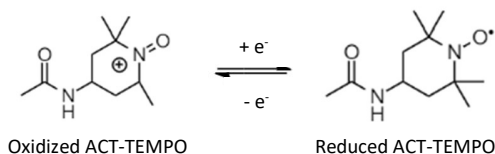
oxidation of 1,2-propanediol on noble metal electrodes can be found in section 3 of the supporting information.

The studied reactions listed below:



The molecular structures for the redox pair of the mediator used for the anodic reaction (ACT-TEMPO) are shown in scheme 1.

Scheme 1. Molecular structures of 4-Acetamido TEMPO in the oxidized and the reduced state.



Cyclic voltammetry was carried out, to characterize the electrode surface (in the absence of the reactant) and to characterize the electrochemical reaction (in the presence of the reactant). Figure 2a shows the cyclic voltammetry of a gold plate electrode in the absence (black line) and in the presence (orange line) of CO_2 . The onset potential for the reduction reaction occurs at slightly less negative potentials in the presence of CO_2 , and higher current densities were measured when compared to the reaction in the absence of CO_2 . However, these slight potential changes might be associated with a small change in pH when CO_2 is present in the solution. Both CO_2 reduction and hydrogen evolution reaction (HER) occur in the same potential range. Thereby, the current associated with CO_2 reduction can be hindered by HER, which occurs at a faster rate. Figure 2b shows the cyclic voltammetry of a carbon felt electrode in the presence of ACT-TEMPO and absence of 1,2-propanediol (black line), and in the presence of both ACT-TEMPO and 1,2-propanediol (orange line). When 20 mM of 1,2-propanediol is present in the solution, the oxidation peak observed between 0.5 and 1.5 V has a higher current density than in the presence of only 20 mM of ACT-TEMPO while the reduction peak is diminished. The increase of the oxidation peak in the presence of PDO can be explained by the direct oxidation of PDO on the surface of the electrode and by the fact that oxidized ACT-TEMPO is regenerated faster when reacting with PDO. When PDO is present, the amount of reduced ACT-TEMPO in the vicinity of the electrode increases due to the fact that PDO favors the reduction of oxidized ACT-TEMPO. On the other hand, the reduction peak shows a lower current when PDO is present in solution. This behavior can be explained due to the lower concentration of oxidized ACT-TEMPO which is being consumed by PDO.

In order to achieve an efficient paired process, it is of paramount importance to select a current which is favorable for the reactions in both compartments of the electrochemical cell. For instance, in the current example, a current density of 80 mA/cm^2 would efficiently convert PDO into lactic acid at the anode, but at such a high current density the hydrogen evolution reaction would dominate at the cathode, and CO selectivity would be poor. To investigate the influence of applied current and find an optimum, a

range of matching current densities of the anodic and cathodic reactions (2, 7, 15, 30 and 50 mA/cm^2) was selected to perform the galvanostatic electrolysis. This was based on the results obtained when performing cyclic voltammetry at the cathode in the presence of CO_2 and at the anode in the presence of PDO and ACT-TEMPO. For every experiment, the cathode was selected as a working electrode.

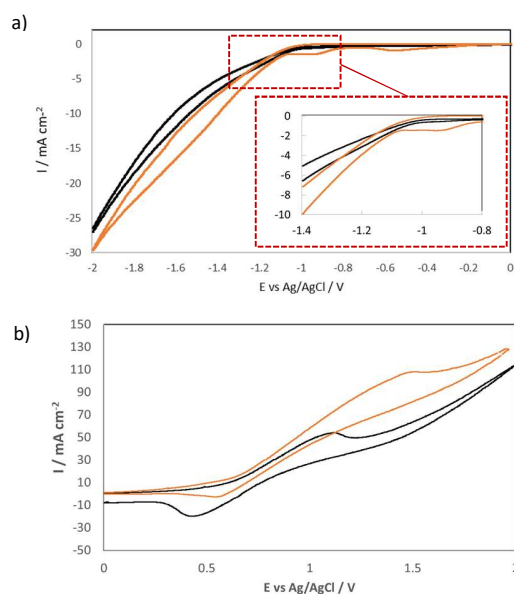


Figure 2: a) Cyclic voltammetry of Au plate electrode in a 0.5 M KHCO_3 solution in the absence (black line) and in the presence (orange line) of CO_2 . The insert displays the potential range where the onset potential for CO_2 reduction and HER is located. b) Cyclic voltammetry of carbon felt electrode in the presence of 20 mM ACT-TEMPO (black line) and in the presence of 20 mM ACT-TEMPO and $20 \text{ mM 1,2-propanediol}$ (orange line). Scan rate= 0.05 V/s

When electrolysis experiments were performed at -2 and -7 mA/cm^2 (data not shown) no CO was detected at the cathode by gas chromatography. Detectable amounts of CO were measured when higher current densities were applied.

Figure 3 shows the faradaic efficiency of CO obtained on a gold plate electrode when different current densities (-15 , -30 and -50 mA/cm^2) were applied to the cathode. The highest selectivity for CO formation was achieved when -15 mA/cm^2 was applied to the cathode. Importantly, the faradaic efficiency for CO decreases over time, being half of the initial value after one hour of electrolysis. However, it is possible to completely recover the activity of the gold electrode for CO formation if cyclic voltammetry is carried out prior to performing further electrolysis. The recovery procedure consist of cycling between -2 and $+2 \text{ V vs Ag/AgCl}$ at a scan rate of 1 V/s . After 100 cycles, the performance of gold plate returns to the initial values of ca. 76% faradaic efficiency for CO formation (see Figure S.4 in the supporting information, section 3). Surendranath et al.³ attributed the deactivation of gold electrodes to the adsorption of metal impurities (from even high purity reactants) on the surface of the electrode.

The faradaic efficiencies of all the reduction and oxidation products obtained when -15 mA/cm^2 was applied are shown in Figure 4. The formation rate of CO in mol/min/cm^2 can be found in the supporting information (see Figure S.4).

Since the current applied to the electrochemical cell served for the oxidation and for the reduction reactions, a summation of the total faradaic efficiency, based on all the targeted products obtained in the cathode (CO and formic acid) and in the anode (lactic acid and pyruvic acid), was calculated and also plotted in figure 4 (yellow bars). In this manner, a total of 200% faradaic efficiency can theoretically be obtained if the efficiencies of the reduction and the oxidation products are combined. A more detailed explanation of how the faradaic efficiency was calculated can be found in the supporting information, section 8.

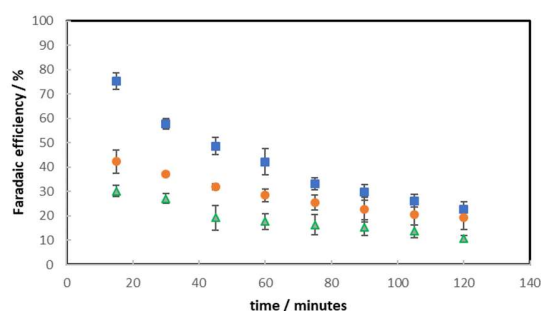


Figure 3: Faradaic efficiencies for CO production on Au electrode in a 0.5 M KHCO_3 solution during electrolysis at -15 mA/cm^2 (blue squares), -30 mA/cm^2 (orange circles) and -50 mA/cm^2 (green triangles).

During electrolysis experiments performed in a paired manner at -15 mA/cm^2 , CO and formic acid were detected in the catholyte as reduction products. The faradaic efficiency of formic acid (ca. 3%) was stable during the 2h of electrolysis. However, the faradaic efficiency of CO decreased over time, being ca. 75% after 15 minutes of electrolysis and ca. 22% after 2 hours. Accordingly, the faradaic efficiency of hydrogen formation due to the competitive hydrogen evolution reaction increased over time. Interestingly, when the electrolysis was performed using 15 nm Au/C nanoparticles deposited on carbon felt as a cathode, a lower electrode deactivation for CO formation was observed (See Supporting information, Figure S.6, section 6), with the faradaic efficiency for CO being ca. 76% after 15 minutes of electrolysis, and ca. 46% after 2 hours. Numerous studies have shown the different performance of Au nanoparticles²⁷⁻³⁰ compared to Au plate electrodes highlighting the importance of the structure and geometry of the electrode surface. The performance of CO_2 reduction can be improved by the use of different Au nanoparticles in terms of size, loading and/or by the use of oxide-derived Au electrodes. Zhu et al. studied the size effect of monodispersed Au nanoparticles¹³, finding that the edge sites are active for CO evolution and the corner sites are more active for the competitive HER. Thereby, by changing the size of the gold nanoparticles it is possible to tune the amount of edge sites and hence increase the selectivity for CO. Chen et al. showed that the formation of gold nanoparticles resulting from the reduction of a gold oxide film

yields high selectivity for CO at low overpotentials and more importantly, perseverance of activity for 8 hours³¹.

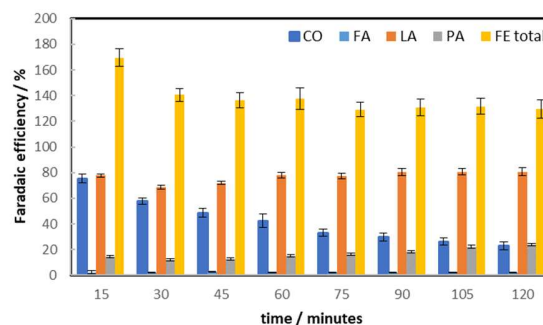


Figure 4: Faradaic efficiencies obtained during the electrochemical reduction of carbon dioxide (CO_2) to carbon monoxide (CO) and formic acid (FA) on a gold plate cathode in a 0.5 M KHCO_3 solution, and faradaic efficiencies obtained during the electrooxidation of 20 mM of 1,2-propanediol (PDO) to lactic acid (LA) and pyruvic acid (PA) with 20 mM of ACT-TEMPO as a mediator on a carbon felt anode in a $0.5 \text{ M KHCO}_3/0.5 \text{ M K}_2\text{CO}_3$ buffer solution. The electrolysis was carried out for 2 hours at 15 mA/cm^2 . Electrolyte flow rate = 25 l/h. CO_2 flow rate = 9 l/h. The total faradaic efficiency (yellow bars) indicates the summation of the faradaic efficiency of CO, HCOOH, LA and PA.

The oxidation products (lactic acid and pyruvic acid) produced in the anolyte during electrolysis at -15 mA/cm^2 when the reaction was carried out in a paired fashion, were analyzed by HPLC and their faradaic efficiencies are summarized in Figure 4. It should be noted that 1,2-propanediol is oxidized to lactic acid, which is consequently oxidized to pyruvic acid³². Lactic acid was formed with a relatively constant faradaic efficiency over time, oscillating between 77% and 80%, while the faradaic efficiency for pyruvic acid slightly increased over time, from ca. 14% after 15 minutes of electrolysis and ca. 23% after 2 hours. The conversion degree of 1,2-propanediol toward lactic acid and further oxidation to pyruvic acid was calculated and plotted in figure S.7 in the supporting information, section 7.

The combined faradaic efficiency of the anodic and cathodic processes, which is based on the summation of the faradaic efficiencies obtained for CO and formic acid formation (cathodic process) and lactic acid and pyruvic acid formation (anodic process) during the paired electrolysis, was calculated to be ca. 160% after 15 minutes of electrolysis, and ca. 130% after 2 hours (see figure 4, yellow bars).

Importantly, crossover of species from the anolyte to the catholyte and vice versa were not detected.

Figure 5 shows the potentials measured during the electroreduction of CO_2 and during the electrooxidation of 1,2-propanediol mediated by ACT-TEMPO when -15 mA/cm^2 was applied. In general terms, all the potentials measured were relatively constant during the 2 hours of electrolysis. The cathode potential oscillated between -1.75 and -1.85 V vs Ag/AgCl. The anode potential was stable during the whole measurement at 0.55 V vs Ag/AgCl. The cell voltage slightly oscillated between 2.53 and 2.63 V. The theoretical cell voltage was calculated according to $E_{\text{cell}} = E_{\text{anode}} + E_{\text{cathode}}$, with E_{anode} being the potential measured between

the anode and a reference electrode situated close to the anode, and E_{cathode} being the potential measured between the cathode and a reference electrode situated close to the cathode. The theoretical cell voltage for this system, excluding the losses, was calculated to be between 2.3 and 2.43 V. A multimeter was connected between the anode and the cathode to measure the real cell voltage. Therefore, by subtracting the cell voltage calculated for the system from the cell voltage measured by the multimeter, a resistive loss in the membrane and in the solution of ca. 0.2 V was detected. It is important to note that the employed electrochemical cell has two extra compartments for the two reference electrodes required for this study, making the distance between electrodes relatively large. The losses in the cell can be further optimized by designing an electrochemical reactor with an optimized geometry and a shorter distance between electrodes.

Importantly, when the electrochemical reduction of CO_2 is carried out with the optimal conditions to form oxygen as the counter reaction, and thereby using a platinum anode, a much higher cell voltage is measured (ca. 4V) (See Figure 6). While the cathode potential showed a slightly higher value (ca. -1.95 V vs Ag/AgCl) than in the paired process (ca. -1.85 V vs Ag/AgCl), the anodic potential was considerably higher (ca. 1.7 V vs Ag/AgCl). An increase of ca. 1.2 V is observed when comparing the anodic

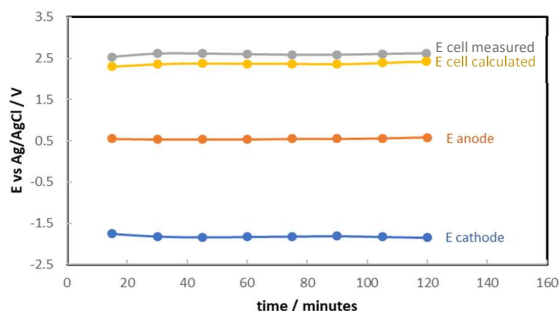


Figure 5: Potentials measured during the electroreduction of CO_2 at -15 mA/cm^2 on Au plate cathode in a 0.5 M KHCO_3 solution and electrooxidation of 1,2-propanediol mediated by ACT-TEMPO on a carbon felt electrode in a $0.5 \text{ M KHCO}_2 / 0.5 \text{ M K}_2\text{CO}_3$ buffer solution. The line joining the data points is intended as a guide.

potential measured on a platinum electrode for the oxidation of water (ca. 1.7 V) with the anodic potential measured on a carbon felt electrode for the oxidation of 1,2-propanediol (ca. 0.5 V). The increase in anode potential is the main cause of a higher cell voltage, since resistive loss in the non-paired process is comparable to the resistive loss in the paired process (ca. 0.2 V), and the cathode potential in the non-paired electrosynthesis is only 0.1 V higher than in the paired process. In summary, in the paired process, a 1.4 V lower cell voltage was measured, resulting in a 35% reduction in electrical energy requirements.

It is important to highlight that the conditions reported in this study can be further optimized for a continuous paired reaction. It is necessary to perform a more detailed study of all the possible parameters that can influence the performance of the electrochemical reactions in a continuous flow, such as the influence of the flow rate, the temperature and the use of gas diffusion electrodes among others. Moreover, the anodic reaction

was not performed in a continuous flow system, since PDO was not constantly fed into the reactor. Thereby, the conditions for the anodic reactor can also be further optimized. In addition, further optimization of the electrochemical reactor can be achieved by selecting an optimal cell geometry and the optimal area of the electrodes employed to ensure a more efficient performance of the reactions.

Nevertheless, using the current conditions, the paired electroreduction of CO_2 and electrooxidation of 1,2-propanediol presents several advantages when compared to the electroreduction of CO_2 with electrooxidation of water. One of these is the formation of two products with an added value, namely CO and lactic acid. In addition, the oxidation of 1,2-propanediol occurs efficiently on cheap carbon felt electrodes,

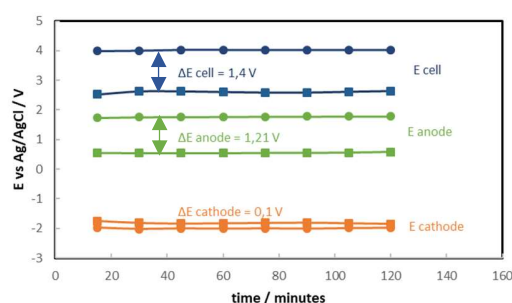


Figure 6: Potentials measured during the paired electrolysis (electroreduction of CO_2 at -15 mA/cm^2 on a Au plate cathode in 0.5 M KHCO_3 solution paired with the electrooxidation of 1,2-propanediol mediated by ACT-TEMPO on a carbon felt electrode in $0.5 \text{ M KHCO}_2 / 0.5 \text{ M K}_2\text{CO}_3$ buffer solution) (squares) and during the non-paired electrolysis (electroreduction of CO_2 at -15 mA/cm^2 on a Au plate cathode in 0.5 M KHCO_3 solution paired with the electrooxidation of water on a Pt electrode in $0.5 \text{ M H}_2\text{SO}_4$ solution) (circles). The line joining the data points is intended as a guide.

whereas the oxygen evolution reaction requires expensive anode materials, such as platinum or iridium oxide. In addition, the lower cell voltage required to drive the reactions when CO_2 reduction is paired with 1,2-propanediol oxidation (paired) compared to water oxidation (non-paired) makes the process more economically attractive, as the higher overpotential that is required is one of the main barriers to commercialization of the technology.

Techno-economical evaluation

In order to get more insight into the economic viability of the paired reaction compared to the non-paired reaction, a rudimentary techno-economic evaluation has been carried out. The results are summarized in Figure 7. The techno-economic comparison is limited in scope, covering only the key cost indicators which are expected to be significantly different for the paired and non-paired reaction. This includes cost of stack (anode, cathode, membranes and cell) and cost of energy (kWhr/kg product). Other costs which are expected to have a limited impact for both the paired and non-paired reaction are considered out of scope for this study. These include capital cost components such as power electronics, feed and product management systems, building infrastructure,

instrumentation, and operating cost components such as mediator, energy for separation and purification of products (downstream processing). A detailed explanation of all the equations and assumptions used for the economic model can be found in the supporting information, section 9.

For the preliminary economic evaluation of the process, two cost indicators were used in this study: the operational expenditure (OPEX) and the capital expenditure (CAPEX).

Figure 7a-b shows the OPEX costs of the reaction. These have been estimated in accordance with the performance parameters obtained during experimentation, such as cell voltage, faradaic efficiency and current density. An 80% Faradaic efficiency was assumed for both reactions, CO₂ reduction to CO and 1,2-propanediol oxidation to lactic acid.

The energy consumption for the amount of CO produced (see Figure 7a) was calculated for the paired and non-paired processes. A price of 0.04 €/kWh³³ was assumed as the energy price for the energy consumption calculation. When CO is formed during the non-paired electrolysis, the energy consumption per kilogram of CO produced is 1.5 times higher than the energy consumption per kilogram of CO during the paired process. This difference is primarily a result of the fact that the cell voltage needed to drive the reaction is higher than the one measured for the paired process, being 1.4 V lower.

An additional parameter to evaluate the OPEX of the process is the product value, which is illustrated in Figure 7b. This was estimated assuming a price for racemic lactic acid of 1500 €/ton³⁴, a price for CO of 500 €/ton³⁴ and a price for oxygen of 0 €/ton (as the electrolysis is carried out at ambient conditions, the oxygen formed is not pressurized, thus is of little value). The cost of PDO (900 €/ton) was subtracted from the product value of lactic acid. In the non-paired reaction, low oxygen is formed on the anode, therefore CO is the only valuable product. This gives the system a total product value of only 0.06 €/kWh. However, when the reduction of CO₂ is paired with the oxidation of 1,2-propanediol, a total product value of ca. 0.22 €/kWh was calculated, a fourfold increase over the non-paired system.

The capital investment was also evaluated in terms of the material of the electrodes and the type of membrane used for the two systems. This includes the cost of stacks containing anode, cathode, membrane and cell structure. A breakdown of these costs is explained in the supporting information, section 9. Other costs³⁵ such as the cost of feed and product management system, and the power electronics, which contribute towards to total capital investment for building an overall production unit, were assumed to make a similar contribution towards the CAPEX for the two cases and were not included in the comparison. An important parameter that can considerably influence the CAPEX is the price of the anode material. Figure 7c illustrates the cost per kg of CO produced depending on the anode material as a function of the current density of the system. For the studied paired electrolysis, carbon felt was used as anode, while for the non-paired process, a platinum electrode was used, as this is common for oxygen production. The price of carbon felt ranges from 27 and 180 €/m² (based on supplier quotes), while the price of platinum varies between 1000 and 1200 €/m² (based on a supplier quote for Pt gas diffusion electrode with 0.2 mg/cm² loading). The CAPEX was

calculated assuming anode, cathode and membrane life expectancy of 5 years, and electrochemical cell life expectancy of 10 years, in both cases.

From figure 7c it can be concluded that the use of a platinum electrode nearly doubles the CAPEX per kg of CO formed in comparison to the use of carbon felt in the paired process. For instance, at the current density at which these investigations were performed (15 mA/cm²), the capital cost per kg of CO produced is 1.81 €/kg for platinum, and 0.93 €/kg for carbon felt.

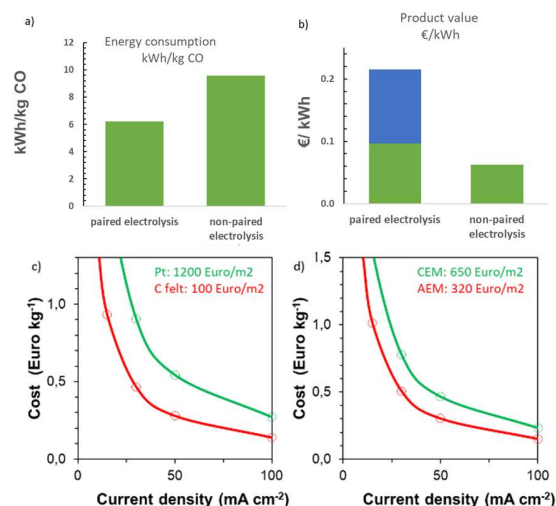


Figure 7: Techno-economical comparison of paired and non-paired electrolysis. a) Energy consumption per kg of CO produced. b) Product value per kWh of CO (green) and lactic acid minus the cost of the reactant 1,2-propanediol (blue) c) CAPEX cost per kg of CO depending on the anode material used (platinum in green and carbon felt in red) as a function of the current density. d) CAPEX cost per kg of CO depending on the exchange membrane used (cation exchange membrane in green and anion exchange membrane in red) as a function of the current density. CAPEX cost shows stack costs including anode, cathode, membrane and cell.

In addition, the type of the membrane used also plays a role in the capital cost estimation. In the paired process, an anion exchange membrane can be used since the electrolytes in both compartments are alkaline in nature. Contrarily, in the non-paired process the optimal conditions to produce oxygen is at acidic conditions. Thereby, the use of a cation exchange membrane is required. Figure 7d shows the cost associated per kg of CO formed, depending on the membrane used as a function of the current density of the system. The price of an anionic exchange membrane is ca. 320 €/m² (quote from supplier Fumatech), while the price of a cation exchange membrane is around double that at 650 €/m² (quote from supplier FuelCellStore). This results in a CAPEX per kg of CO formed 1.25 times higher for the non-paired system.

Based on this preliminary cost evaluation, it can be reasoned that a pairing strategy can significantly improve the overall business case for CO₂ reduction. To maximize this, it is of paramount importance to select the optimal pairing reaction, as this study demonstrates.

Conclusion

The electrochemical reduction of carbon dioxide to carbon monoxide paired with the electrochemical oxidation of 1,2-propanediol to lactic acid mediated by ACT-TEMPO has been experimentally investigated and the economics of the coupled reactions has been assessed. This work showcases a novel approach towards cost effective electrochemical CO₂ reduction. Faradaic efficiencies of ca. 80% for CO and lactic acid formation have been observed, leading to a combined faradaic efficiency for the paired process of ca. 160%. The reaction has been compared to a benchmark case in which cathodic CO₂ reduction is coupled to anodic oxygen evolution. This non-paired electrolysis leads to a cell voltage 1.4 V higher than the cell voltage measured during the paired electrolysis. This higher cell voltage is mainly due to the higher anodic potential required for oxidation of water compared to the potential required to oxidize 1,2-propanediol. A preliminary economic viability study has shown the economic feasibility of the paired electrolysis. It showed a significant cost reduction for CO production when CO₂ reduction is coupled to 1,2-propanediol oxidation in comparison to the non-paired process. Several parameters can have a significant effect the total cost of the reaction. Firstly, the utilization of the electrons in both reactions, allowing the formation of two added value products with the same energy use, results in almost a 4 fold increase in product value per kWh. In addition, the lower cell voltage required to drive the paired reaction, leads to a decrease of 35% in energy consumption. In terms of the CAPEX cost, the biggest influences arises from the use of a cheaper anode material and membrane for the paired electrolysis. This makes the paired process economically more attractive. The preliminary economic assessment performed in this study already indicates the economic attractiveness, of the paired process, in terms of cost reduction, even bearing in mind that the has been data obtained at a low stage of process development.

In summary, by pairing two redox reactions which both produce value added chemicals, and which give an overall system which requires lower potential, a substantial reduction in energy consumption can be achieved. With this approach, the electrochemical reduction of CO₂ might ultimately become an economically feasible system.

Supporting Information

Characterization of Au/C nanoparticles, experimental set-up, oxidation of 1,2-propanediol to lactic acid mediated by ACT-TEMPO, recovery of the gold electrode, formation rate of CO on Au plate and Au nanoparticulated electrodes, Faradaic efficiencies obtained on nanoparticulated gold electrode, conversion of 1,2-propanediol and formation of lactic acid and pyruvic acid, Faradaic efficiency calculation, techno-economic evaluation.

This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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