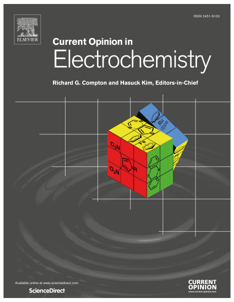

Coupling electrochemical carbon dioxide conversion with value-added anode processes: an emerging paradigm

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Coupling electrochemical carbon dioxide conversion with value-added anode processes: an emerging paradigm

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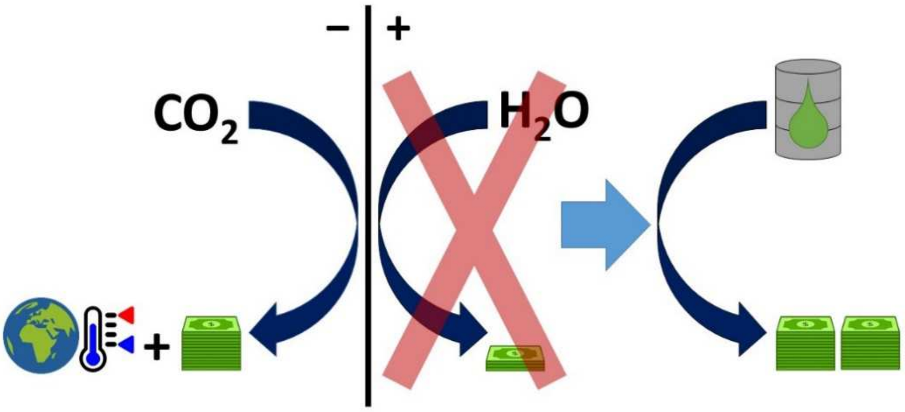
Abstract

Water oxidation (i.e., oxygen evolution) reaction is the most often used, green anodic pair of carbon dioxide (CO_2) electroreduction, mimicking the natural photosynthetic process. At the same time, it requires high energy input, and generates a product of little commercial value (i.e., oxygen). Finding appropriate alternative anode processes to be coupled with CO_2 reduction is a major undertaking. Several factors need to be considered, such as (i) the value of the product, (ii) abundance and cost of the substrate, (iii) necessary cell voltage (energy input), (iv) needed catalysts, (v) cell structure and components, (vi) ease/complexity of product analysis and separation. This opinion discusses all these aspects, and outlines the main questions to be answered through future research activity.

Graphical abstract



Keywords

Carbon dioxide valorization, flow-cell, paired electrolysis, co-electrolysis, catalysis

1. Introduction

Electrochemically converting CO_2 into valuable products allows to reduce its emission to the atmosphere and offers a possibility to store intermittent renewable energy in the form of high energy density chemicals.[1] With the simultaneous evolution of the employed catalysts, membranes and the development of continuous-flow electrolyzer cells, a remarkable advancement was witnessed in the past decade.[2] Although the long-term stable operation of CO_2 electrolyzers is yet to be achieved, electrolysis at 1 A cm^{-2} partial current density for CO or C_2H_4 production has already been presented on the laboratory scale[3–5] Based on gross-margin models, this reaction rate is already high enough for industrial implementation.[6,7] Efforts towards scale-up are ongoing in both academic and industrial laboratories, and the first multi-layer electrolyzer stack has also been demonstrated.[8] CO_2 can also be electrochemically attached to larger organic molecules, through either carbon-carbon or carbon-heteroatom bond formation. High-value products such as carboxylic acids, or carbonates/carbamates, can be formed from cheap precursors, such as furanic compounds.[9–12] Due to the high product value, production rate is of lower importance, but high selectivity and conversion are required. Hence the two different applications (i.e., small vs. large molecule products) necessitate very different cell architectures and operation conditions. In this Opinion, we only focus on CO_2 reduction (CO_2R) to small molecule products (e.g., CO, C_2H_4).

The energy efficiency of CO_2 electrolyzers however, is still low, which is rooted in the large cell voltages (i.e., typically around and over 3 V). Further development of CO_2R catalysts, cell components and electrolyzers will likely lead to a decrease in this value in the upcoming years. At the same time, it is very timely to scrutinize possible alternative anodic reactions, which can substantially increase the energy efficiency and/or the commercial value of the products formed.

Historically, CO_2R has been performed in conjunction with anodic water oxidation (i.e., the oxygen evolution reaction (OER)).[13] The reason behind this is threefold: (i) continuous-flow CO_2 electrolyzers build on the knowledge accumulated on cation- and anion exchange membrane-based (CEM and AEM, respectively) water electrolyzers, where optimized solutions are available for OER; (ii) studies on the necessary overpotential and its stability are well-documented, therefore the anode can serve as a quasi-reference electrode, (iii) no mass transport limitations occur due to the high concentration of water.

In this opinion, we summarize the different possibilities to perform CO_2R with alternative anodic processes, which in turn allows electrolyzer operation at lower cell voltage (i.e., higher energy efficiency), and/or lead to the formation of high-value anodic products. We note that such paired electrolysis process is only industrially viable, if there is a sizable market for the products, large amount of the substrate is continuously available, and the total value of the products exceeds the total production costs. Several possible avenues exist to achieve this coupling, including (i) implementation of CO_2R in already existing technologies (e.g., chlor-alkali and chlorate electrolysis, organic electrosynthesis (such as benzene to benzoquinone, epoxidation of propylene to propylene oxide)), (ii) oxidize industrial waste ("sacrificial agents") (iii) produce raw chemicals (e.g., H_2O_2) in large quantity, (iv) generate fine chemicals.[14–16] In any case, the overall CO_2 footprint and the complexity of the process have to be also considered.

Diverting from OER however, is associated with a multitude of challenges. The oxidation potential of the reactants, the optimal operation conditions (pH, temperature, pressure etc.) might differ significantly. Moreover, in most of the cases more than one product form, which necessitates proper product separation. In case of OER, the used anolyte is easily recirculated (after separating the O_2 gas), which is not a trivially viable strategy in case of other anodic reactions. Overall, pairing CO_2R with any alternative anodic process necessitate the re-consideration of the electrolysis process as whole. Some scientific, technological and economic aspects of these challenges are discussed in what follows.

2. State-of-the-art

2.1. Value-added anode processes

Several studies were published in the last decade, in which alternative anodic oxidation reactions were paired with the hydrogen evolution reaction (HER). These studies investigated the oxidation of alcohols, amines, urea, hydrazine and biomass-derived intermediate compounds, summarized in comprehensive reviews.[17,18] In Table 1. we selected some of the most appealing anode reactions, based on the compilation in Ref. [18], that might be paired with CO_2R. The low economic value of oxygen is striking, compared to all other alternatives. Notably, for some oxidation products there is no established market yet, as reflected by the large variation of reported market prices. Furthermore, the price of both the product and the precursor might change significantly if a reliable technology is introduced in the future.

The oxidation potential of any of these, typically biomass-derived, organic compounds is significantly less positive. This can save over 1 V of cell voltage (and therefore over 35% of the necessary energy input), compared to OER. On the other hand, despite the thermodynamic ease of these reactions, often high overpotentials are associated to these processes[18]. Furthermore, depending on the reaction conditions (e.g., pH, temperature, potential) various products can be made from these typically biomass-derived compounds. As a specific example, dihydroxyacetone, glyceraldehyde, glycerate or tartronate may form the electrooxidation of glycerol, just to mention some of the possible high-value products[19]. These facts together highlight the need for more active and selective catalysts, tailored for each reaction.

Table 1. Possible anode reactions that can be paired with CO$_2$R, mostly based on Ref. [18]

Reactant	**Price ($/kg)**	**Product**	**Price ($/kg)**	**E^0(V) vs. SHE**	**Production (Mt/yr)**
Deionized water	0.02-0.1†	Oxygen	0.024-0.04	1.23	2
		Hydrogen peroxide	0.56-0.58	1.78	2.8 [20]
Ethanol	0.4 [21]	Acetaldehyde	1.0	0.193	1.7 [20]
		Acetic acid	0.68-0.92	−0.334	10 [20]
		Ethyl acetate	1.21-1.8	−0.208	2.7
1,3-propanediol	2.20	Acrylic acid	2.25-2.88	0.248	5.2 [20]
1,2-propanediol	1.50-2.05	Lactic acid	1.58-1.87	−0.334	0.45
Glycerol	0.16-0.80 [21], [24]			0.041	
		Glyceraldehyde	2.11 [22]	0.35 [23]	
		Dihydroxyacetone	2.0 [24]	0.33 [25]	0.004 [26]
Benzyl alcohol	1.92-3.47	Benzaldehyde	1.18-2.11	0.193	0.09 [27]
		Benzoic acid	1.85	−0.334	0.130
Hydroxymethyl-furfural	1.03	2,5-Furan-dicarboxylic acid	32-580	−0.780	0.5
Isopropanol	1.26-1.6	Acetone	0.9-1.28	0.054	6.4
Methanol	0.3 [21]	Formaldehyde	0.37-0.74	0.465	18
Methanol	0.34-0.49	Formic acid	0.97-1.08	−0.258	0.95
Ethylene glycol	0.83-1	Glycolic acid	1.84	−0.334	0.04 [28]
Ethylene glycol	0.83-1	Oxalic acid	1.4	−0.455	0.19
Brine	0.05	Chlorine	0.25 [29]	1.36 [30]	63 [20]

†depending on the scale of purification

2.2. What has been achieved so far?

Fifteen reactions other than OER were investigated as the anodic counterpart of CO$_2$R in the recent years (Table 2.). While low current density operation is dominant, in some cases (where chlorine evolution or glycerol or urea oxidation was performed at the anode) 100 mA cm^{-2} current density was approached.[13,29,31,32] Importantly, when both OER and glycerol oxidation was studied as the anodic reaction coupled with CO$_2$R at a similar current density (~100 mA cm^{-2}), the cell voltage was only 1.5 V in the latter case, compared to the 2.3 V, necessary with OER.[13]

Table 2. Alternative anode reactions paired with CO_2R.

CER: Chlorine Evolution Reaction; DSA: Dimensionally Stable Anode; CEM: Cation Exchange Membrane; CuPc: Cu-phthalocyanine; AEM: Anion Exchange Membrane; Re(bipy-tBu)$(CO)_3$Cl: Re(4,4′-ditert-butyl-2,2′-bipyridine)$(CO)_3$Cl; TEMPO: (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl; Fe-SAs/N–C: single Fe atoms on N-doped C; Ru-complex: [Ru(bis-Mebimpy(4,4′-$((OH)_2OPCH_2)_2$-bpy)$(OH_2)]^+$; ACT-TEMPO: 4-acetamido-(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl; HMF: 5-Hydroxymethylfurfural; FDCA: 2,5-furandicarboxylic acid; FFCA: 5-formylfurancarboxylic acid; DFF: 2,5-diformylfuran; TPPNi: Nickel Tetraphenylporphyrin; CoPPc: Polymeric Cobalt Phthalocyanine; STEMPO: Silatrane-anchor modified (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl

U_{cell} /$E_{electrode}$ (V)	j (mA cm^{-2})	Cathode catalyst	Cathode product(s), FE (%)	Anode reaction	Anode catalyst	Anode product(s), FE (%)	Cell type and separator	Longest exp. (h)	Ref.
3.5	75	Ag	CO (83)	CER	DSA	Cl_2 (76)	CEM membrane electrolyzer	3	[31]
1.64	12.5	CuPc	CH_4 (8), C_2H_4 (1), $HCOO^-$ (3)	Ethanol	Pd	Acetate	AEM membrane electrolyzer	6	[33]
E_{cat} −1.8, E_{an} 2.45 vs. Ag/AgCl	~1	Re(bipy-tBu)$(CO)_3$Cl	CO (100)	Syringaldehyde o-phenylene-diamine condensation	Ce(III)/Ce(IV)	Benzimidazole-derivative	H-cell	2	[34]
E_{cat} −0.7 vs. RHE	3.7	Cu-In	CO (>70)	1-phenyl-ethanol	Pt + TEMPO	Acetophenone (95-70-36)	CEM Membrane electrolyzer	3	[35]
	18	Sn	$HCOO^-$ (85), CO	Acid orange 7	Boron-doped diamond	Carboxylic acids	CEM Membrane electrolyzer	4	[36]
E_{cat} −1.7 vs. Ag/AgCl	40-45	Sn	$HCOO^-$ (72-52)	Methyl orange	Ti/SnO_2-Sb		CEM Membrane electrolyzer	5	[37]
3	10	Sn	$HCOO^-$ (35)	SO_3^{2-}	IrO_2-Ta_2O_5/Ti	SO_4^{2-}	CEM Membrane electrolyzer	5	[38]
2	4.5	Fe-SAs/N–C	CO (100)	NaCl	RuO_2/Ti	ClO^- (99)	CEM Membrane electrolyzer	24	[39]
1.8	~ 0.06	$[(tpy)(Mebim-py)Ru^{II}(OH_2)]^{2+}$	CO (26)	Benzyl alcohol	Ru-complex	Benzaldehyde (75)	AEM separated cell	1.5	[40]
E_{cat} −1.0 vs. RHE	47	Cu	CO (1), CH_4 (7), $HCOO^-$ (2), EtOH (10), Acetaldehyd	$Br^- \rightarrow Br_2$	Pt	Bromoethanol (40)	One com-partment		[41]

			e (2), Acetate (1), Propionaldehyde (1), 1-PrOH (4)						
2.5	15	Au	CO (76-22), $HCOO^-$ (3)	1,2-propanediol	Carbon felt + ACT-TEMPO	Lactic acid (77-80), Pyruvic acid (14-23)	AEM membrane electrolyzer	2	[42]
E_{cat} −1.7 vs. Ag/AgCl	40	Bi	$HCOO^-$ (91)	Methyl orange	Ti/SnO_2-Sb		CEM Membrane electrolyzer	5	[43]
1.5	95	Ag	CO (93), $HCOO^-$ (9)	Glycerol	Pt		AEM membrane electrolyzer	1.5	[13]
1.5	13		CO (95)	Glucose					
1.5	73	Sn	CO (10), $HCOO^-$ (85)	Glycerol	Pt				
1.5	99	Cu	CO (43), $HCOO^-$ (11), C_2H_4 (24) C_2H_5OH (11), 1-PrOH (7), CH_4	Glycerol	Pt				
2.5	2	BiO_x	$HCOO^-$ (81)	HMF	NiO	FDCA, FFCA, DFF (36)	CEM membrane electrolyzer	3.3	[44]
3.8	100	TPPNi-C	CO (96)	CER	DSA	Cl_2 (80)	CEM membrane electrolyzer	5	[29]
2	2	CoPPc/CNT	CO (46)	Glycerol	STEMPO	Glyceraldehyde (83)	AEM membrane electrolyzer	3	[45]
2.5	100	Ag	CO (90)	Urea	Ni		AEM membrane electrolyzer	4	[32]

As shown in Table 2., a wide variety of products can form on both electrodes depending on the cell voltage. For example, upon the oxidation of furanic compounds, such as 5-hydroxymethylfurfural (HMF)[46] 2,5-diformylfuran, 5-formly-furan, 2,5-furan dicarboxylic acid (FDCA, an important raw chemical for sustainable plastic production [47]) can be formed.

This significantly increases the complexity of these electrocatalytic systems and anticipates that beyond the electrocatalysts, electrodes and cell design, the system construction and operation will require major development efforts to reach an industry-relevant performance.

3. Challenges to be solved

3.1. Catalyst design and development

There is no preferred anodic reaction coupled to CO_2R yet. Consequently, general electrocatalysts (such as platinum) are often used, instead of reaction-specific catalysts. As one exception, for the chlorine production studies, dimensionally stable anodes (DSAs) were employed.[29,31] Interestingly, homogeneous electrocatalysts were also investigated in a few studies.[31,33,38] These trends reflect the prematurity of the field, and therefore using tailored catalysts will bring further advancements, in achieving both high activity and constant product selectivity.

Long-term stability and durability under operating conditions is of crucial importance. In the studies collected in Table 2, the longest electrolysis experiments were pursued for a few hours. The stability of these processes, together with the possible fading mechanisms will have to be addressed on an even longer timescale (weeks, months). This includes studying catalyst poisoning (e.g., deposition of different organic species), catalyst leaching, electrode support degradation, etc. In case of CO_2R coupled with OER, the cathode deactivation leads to cell voltage increase, which affects the cathode product composition. When pairing CO_2R with anode processes where different products form depending on the anode potential, such catalyst degradation can simultaneously alter the anode and cathode product composition. This necessitates a strict operational control of the whole electrolysis process, which manifests in a complex operating environment, as discussed later.

3.2. Electrode design

In flow CO_2R cells, mostly titanium is used on the anode side as structural material (e.g., current collector, gas diffusion layer) to withstand the demanding oxidative conditions. It is, however, expensive and difficult to process, especially in comparison with stainless steel or mainly carbon. Since many of the alternative anodic reactions occur at lower potentials compared to OER (and carbon corrosion), high surface area carbon might be employed as catalyst support.[48] Carbon-based electrodes offer easily adjustable electrode porosity, thickness, hydrophilicity etc., which parameters can be optimized for the given reaction and reactant type (gas phase vs. dissolved reactants). A wide variety of carbon papers, clothes, meshes are available from different suppliers, and with the continuous development of fuel-cells[49] and gas phase electrolyzers (e.g., CO_2 electrolyzers) it is expected that this market expands further. As other alternatives, porous structures (e.g., meshes, foams) made of less corrosion tolerant metals (e.g., steel, copper, nickel etc.) might be applicable as catalyst supports in this case.

A special challenge for the electrode design is its permeability for reactant and product streams. Notably, some potential reactants/products possess viscosity orders of magnitude larger than that of water. Both fluid dynamics modeling, and careful experimental studies are necessary to find viable cell- and electrode geometries.

3.3. Cell architectures

As only a few articles were published on CO_2R paired with non-OER anode reaction, no optimized cell design emerged yet. When pairing two multi-electron and multi-proton transfer processes, a compromise has to be made between the optimal conditions for the anodic and cathodic half-reactions. As for CO_2R, microfluidic reactors (**Figure 1**A), having a continuously flowing liquid electrolyte between the cathode and the anode, are widely employed.[1,50–52] These devices allow high current density operation, but due to product mixing, some of the anodic products might be reduced on the cathode (and vice versa), causing significant efficiency losses.[13] This is a challenge even in case of OER, where the product is in the gas phase, hence most of it leaves through the porous anode and only a minor amount ends up in the liquid electrolyte. In case of liquid (or dissolved) product formation, this effect is much more pronounced.

Introducing a membrane in a microfluidic cell (**Figure 1B**) circumvents this issue, and therefore it is more suitable for paired electrolysis. In this case two separate electrolyte solutions, a catholyte and an anolyte are applied. This allows to use solutions of different composition, pH, ionic strength, etc. in the two compartments, hence optimizing the reaction conditions for the two reactions separately. This benefit however, comes at a price: the two electrolyte solutions plus the membrane add extra resistance to the cell, decreasing the energy efficiency of the process. Furthermore, the system complexity also becomes significantly higher. It is generally true for all configurations that inserting a reference electrode in the cell is important to monitor the anode potential. In our opinion, such cells might be useful tools to scrutinize the effects of reaction conditions for paired electrolysis. The industrial implementation of such processes, however, especially at high current densities, will necessitate the development of more energy efficient, and simpler setups.

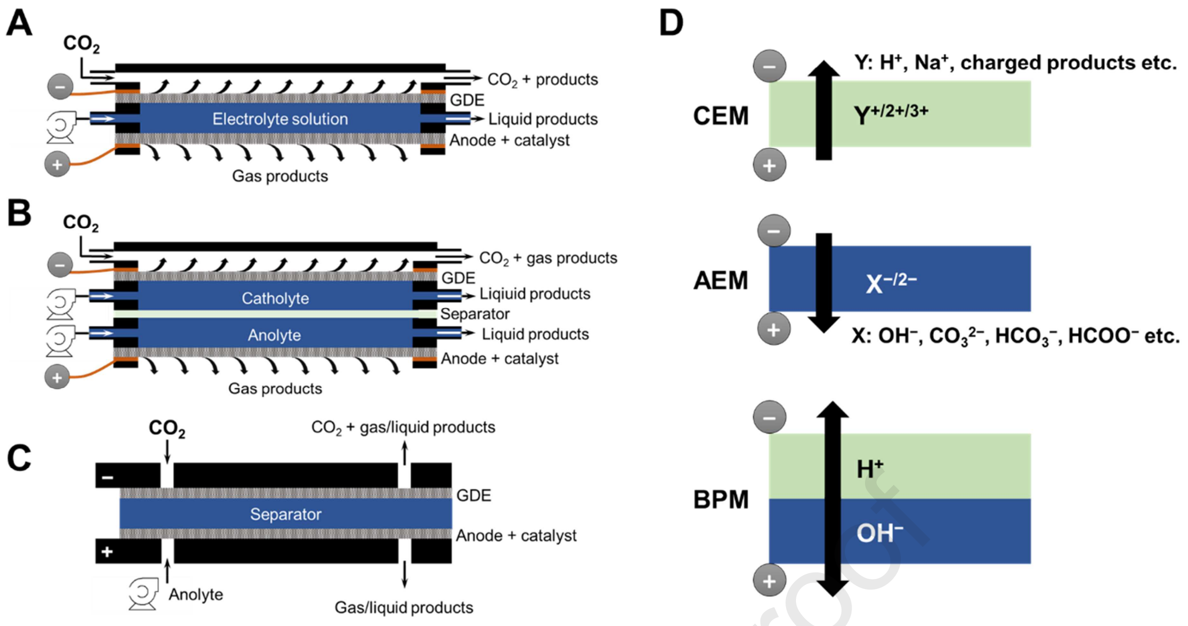


Figure 1. Typical cell configurations (A-C) and separators (D) which can be applied for paired electrolysis. (A) microfluidic electrolyzer cell with one liquid electrolyte and no further separator, (B) microfluidic electrolyzer cell with separated liquid anolyte and catholyte, (C) zero-gap electrolyzer cell with separator, without electrolyte.

Zero-gap cells offer the least complicated design. As the electrodes are sandwiched directly together (**Figure 1C**), the highest energy efficiency can be expected in this case. However, as no separate anolyte and catholyte is used, the local chemical environment of the catalysts is determined only by the membrane and catalysts chemistries, together with the operation conditions. Parameters such as the cell geometry, gas flow-rate, temperature, humidity, etc. are therefore critical in this case.

As a simple solution, a porous frit (e.g., glass) can be applied to divide the anode and cathode compartment, but the use of membrane separated cells is more appealing due to the better product separation and lower additional resistance. The use of CEMs, AEMs, or bipolar membranes (BPMs) can be envisioned (**Figure 1D,** from top to bottom, respectively). The chemical nature of the membrane is less important in microfluidic devices as the liquid electrolyte dictates the surface pH, ionic strength, etc., but in zero-gap cells it determines the local chemical environment of the catalyst layers.

Applying a CEM to separate the cell results in a highly acidic pH on both electrodes. H$^+$ ions form on the anode, and as they are the charge carriers across the membrane, they are also present on the cathode side of membrane in high local concentration (especially in a zero-gap design). This favors HER over CO$_2$R on the cathode, requiring the development of selective catalysts for the latter process functioning in acidic media, which has not been achieved yet. Using AEMs, on the other hand results in locally alkaline environment as the ion movement is the opposite in this case. This is optimal for CO_2R, but might be problematic for anode reactants which are sensitive to alkaline pH.

BPMs emerged in the recent years for CO_2R to avoid product crossing.[53–55] The typical operation of BPMs is based on water dissociation at the interface between the AEM and the CEM, and consequent OH^- and H^+ migration to the anode and cathode, respectively. This results in acidic cathode and alkaline anode pH. The alkaline anodic pH can be useful for certain processes, but the acidic pH of the cathode might necessitate the inclusion of a buffer layer between the cathode catalyst and the BPM to avoid excessive H_2 formation, complicating the cell design and operation. A reversed combination of an AEM and a CEM would lead to alkaline cathode and acidic anode pH. In this case OH^- (or CO_3^{2-}/HCO_3^-) and H^+ ions would move towards the interface of the two membranes and recombine there. The formed product must be removed from the space between the two membranes, again necessitating the inclusion of a buffer layer. Application of BPMs therefore seems challenging, but on the other hand offers the possibility to separately adjust the local pH around the electrodes. We therefore expect that combining two (or more) different membranes will play an important role in the evolution of paired electrolysis processes.

3.4. Integration and ensuring long-term operation

In the case of CO_2R coupled with OER the analysis of the anode product composition is typically neglected (see some exception in refs [56,57]), assuming the formation of pure oxygen. Because of the complex nature of paired electrolysis, online analytics becomes even more important, which necessitates the use of more sophisticated test/operational environments (**Figure 2**). The cathode part of this setup is identical to what is used for CO_2R studies with anodic OER. This constitutes of a controlled gas inlet (with optional humidification), and a product stream processing part, including water separation (or liquid product collection) units, pressure and temperature sensors and controllers, a gas-flow meter a complex gas analysis system, typically comprising of a gas chromatograph, mass spectrometer, etc.

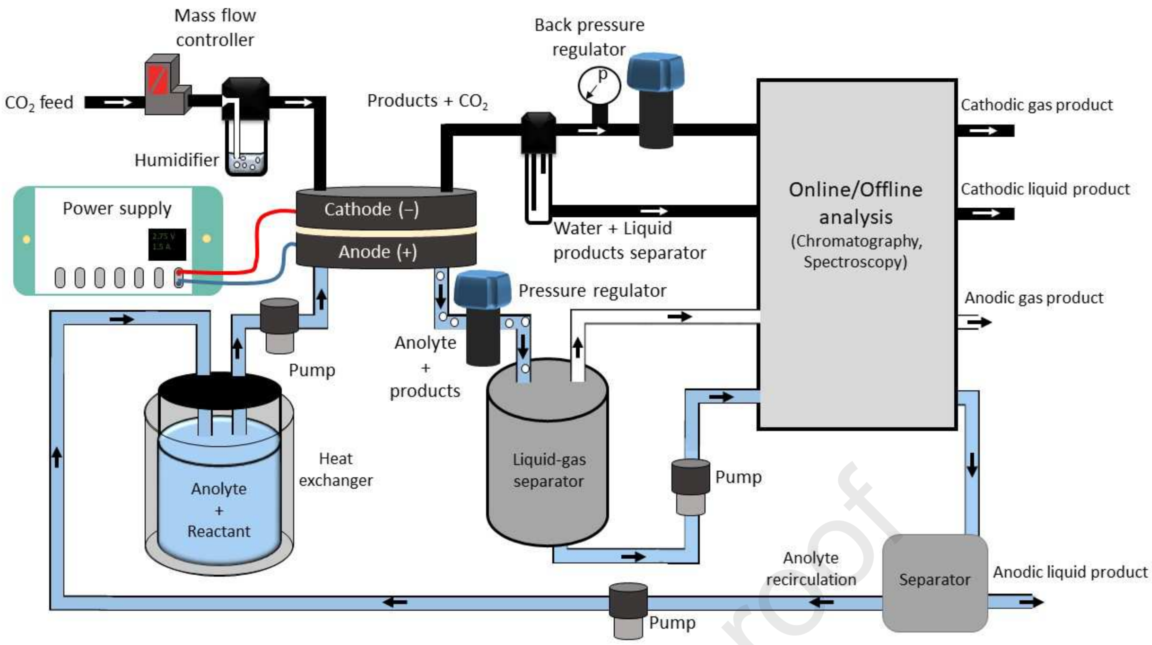


Figure 2. Exemplary operational framework for CO_2R paired with a value-added anode process in a zero-gap design. The setup can be extended to cells using liquid catholyte, by adding an extra pump to the cathode circuit.

Depending on the cell configuration, one or two (peristaltic) pumps are used to deliver the liquid electrolytes (Fig. 1A-C). Optionally, gas phase reactants can also be fed to the anode of the cell, similarly to the cathodic CO_2 feed. These fluids are tempered before entering the cell to maintain constant operational conditions. Subsequently, the anode product stream leaves the cell through a pressure regulating valve to be processed further. First, the gas products are removed, then the dissolved/liquid phase products are separated from the anolyte. The composition of the anode product stream shall be analyzed continuously to ensure proper operation. This should include online and offline methods both for the liquid and gas phases. These generally encompass gas/liquid chromatography (coupled with mass-spectrometry), NMR, FTIR and Raman spectroscopy, but other product specific spectroscopic methods can also be applied. Another engineering challenge will be to isolate the valuable products from the anolyte, which can be subsequently recirculated in the process.

4. Conclusions

Electrochemical CO_2R is a promising technology to simultaneously produce important raw chemicals and decrease the atmospheric emission of a greenhouse gas. This approach could, however, be further developed by either decreasing the energy needs by transforming organic waste streams on the anode, or by forming high-value products. Such paired electrolytic processes already attracted scientific attention in conjunction with the cathodic HER, and we expect that this will be the case with CO_2R as well. Due to the vastly different anode reactions, the cell structure, operating conditions and even the test-benches/operation frameworks have to be tailored for these processes. The system complexity is significantly increased in most cases (compared to OER), necessitating the multi-step separation and the continuous monitoring of both the anodic and cathodic products. This implies scientific and engineering challenges, but a properly designed and optimized paired electrolysis process offers the possibility of direct industrial implementation.

Conflict of interest statement

Nothing declared.

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– Highlights –

Coupling electrochemical carbon dioxide conversion with value-added anode processes: an emerging paradigm

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- Large cell voltage is needed when CO_2 reduction (CO_2R) is coupled with anodic OER,
- Alternative anode reactions can lower the cell voltage and result in useful products,
- A complex system is necessary to perform CO_2R coupled with non-OER anode reactions,
- Multi-step separation and continuous monitoring of the products is crucial.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: