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Assessing the Electrochemical CO_2 Reduction Reaction Performance Requires More Than Reporting Coulombic Efficiency

*Paniz Izadi, Jia Song, Chandani Singh, Deepak Pant, and Falk Harnisch**

Reporting coulombic efficiency (CE) is the common way to assess the performance of electrochemical carbon dioxide (CO_2) reduction reaction (eCO_2RR) in literature, whereas its carbon conversion efficiency (CCE) is frequently neglected. Herein, the importance of reporting both efficiencies when evaluating the eCO_2RR is discussed, using Sn-based gas diffusion electrodes (GDEs) as model electrodes. It is shown that CCE can vary remarkably at a constant CE with minor operational changes. Over 120 min experiments with operational conditions being representative of numerous previous studies, the CCE is increased from ≈20% to 41% (being only 9% below the theoretical maximum). This was achieved by simply adjusting the inlet CO_2 flow rate from ≈35 to 16 mL min^{-1}, while CE was identical at both CO_2 flow rates (≈85%, 7%, and 4% for production of formate/formic acid, CO, and H_2, respectively at both conditions). Thus, it is advocated that reporting of both efficiencies, for electrons and carbon, is required for meaningfully assessing the performance of an eCO_2RR system.

1. Introduction

Electrochemical conversion of carbon dioxide (CO_2) to value-added fuels and chemicals has gained broad attention as a plausible route to effectively store intermittent renewable electric energy as well as capture CO_2. In the past decades, research on the electrochemical CO_2 reduction reaction (eCO_2RR) in aqueous solutions has focused overwhelmingly on improving the current or electron efficiency that is the coulombic efficiency (CE) sometimes also denominated as Faradaic efficiency (FE). CE was enhanced, for instance by 1) tuning the catalyst composition and morphology,[1] 2) incorporating the electrocatalyst in gas diffusion electrodes (GDE) to overcome mass transfer limits,[2] and 3) optimizing the pH and composition of the electrolyte solution and cell design (e.g., flow cell instead of H-cell).[3] Various electrocatalysts, showing promising CE, have been discovered for eCO_2RR to C_1 and C_2 products, such as formate/formic acid, carbon monoxide (CO), methane (CH_4), or ethylene (C_2H_4).[4] Simultaneously, eCO_2RR is still associated with low technology readiness levels (TRL) between 2 and 3. Factors limiting the economic feasibility of the eCO_2RR include limited energy efficiency, low carbon conversion efficiency (CCE) and overall short operational time (low stability). The electric energy consumption of eCO_2RR is mainly related to 1) thermodynamics of the reaction, i.e., its formal potential, 2) overpotentials of the half-cell reaction, and 3) $i \times R$ drop across the membrane and within the electrolyte solutions in the electrochemical cell. Thus, depending on, for instance, the electrolyte type and concentration, pH and membrane, the half-cell potential during eCO_2RR to formate ($HCOO^-$) and thus cell potential varies (**Table 1**). Using alkaline electrolytes for eCO_2RR to $HCOO^-$ appears to be optimal for achieving a low cell potential. However, the high alkalinity in the catholyte will inevitably lead to formation of K_2CO_3 and eventually $KHCO_3$, causing a waste of both, alkali hydroxide such as KOH and CO_2.

To achieve an efficient eCO_2RR, CO_2 needs to be collected and concentrated as the reactant. Most relevant is direct air capture, which utilizes alkali hydroxide system and thermal swing to release concentrated CO_2 being a process with typical cycles up to 900 °C. Hence, it requires significant energy input[5] and thus operational expenditures for providing CO_2 for eCO_2RR. Over the past decades, researchers generally have supplied excess CO_2 to the eCO_2RR system under study, aiming to obtain the maximum CE. However, most of the supplied CO_2 is not electrochemically converted using this approach, and leaves the electrochemical cell unreacted. So far, in the great majority of studies, CE was used as main, often sole criterion to assess the efficiency of the eCO_2RR, whereas CCE was paid little to

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Table 1. List of contributors to the cell voltage for an eCO_2RR system operating with alkaline, neutral, and acidic solutions, while using cation exchange membrane (CEM) or anion exchange membrane (AEM). The contributors listed here include reactions thermodynamics of cathode and anode ($E^{\circ}_{cathode}$, E°_{anode}), overpotentials ($\eta_{cathode}$, η_{anode}), and $i \times R$ drops across the electrolyte solutions and membrane. The cathodic potential ($E^{\circ}_{cathode} + \eta_{cathode}$) included here is the least negative potential reported (-1.3 V vs. SHE[14]) for eCO_2RR at 100 mA cm^{-2}. The anode overpotential is taken from the overpotential for oxygen evolution reaction (OER) with commercial RuO_2/IrO_2 (acidic anolyte) and $Ni(Fe)OOH$ (alkaline anolyte) at 100 mA cm^{-2}. The $i \times R$ drops are calculated based on the conductivity of membranes and a 5 mm thick layer of solution (conductivity used here: 1 M KOH: 201.3 mS cm^{-1}, 1 M $KHCO_3$: 96.0 mS cm^{-1}, 0.5 M H_2SO_4: 223.0 mS cm^{-1}).[15] The $i \times R$ drop across the membrane are calculated based on the area specific conductivity of the membrane soaked in the corresponding electrolyte solution and the thickness of the membrane after swelling (see also Table S3 and S4, Supporting Information).
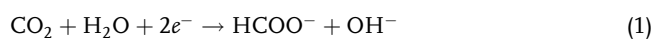
		Alkaline catholyte (pH 14)				Neutral catholyte (bicarbonate, pH 7)				Acidic catholyte (pH 0)			
		Alkaline anolyte (pH 14)		Acidic anolyte (pH 0)		Alkaline anolyte (pH 14)		Acidic anolyte (pH 0)		Alkaline anolyte (pH 14)		Acidic anolyte (pH 0)	
	Potential vs. SHE	CEM	AEM	CEM	AEM	CEM	AEM	CEM	AEM	CEM	AEM	CEM	AEM
Cathode	$E^{\circ}_{cathode}$	−1.078				−0.665				−0.252			
	$\eta_{cathode}$	−0.222				−0.635				−1.048			
Anode	E°_{anode}	0.404		1.230		0.404		1.230		0.404		1.230	
	η_{anode}	0.350[16]		0.390[17]		0.350		0.390		0.350[16]		0.390[17]	
$i \times R$ drop	Membrane	0.213[18]	0.057[19]	0.025	0.057	0.213	0.357[20]	0.025	0.357	0.213	0.102	0.025	0.102
	Catholyte	0.248				0.556				0.132			
	Anolyte	0.248[21]		0.132		0.248		0.132		0.248		0.132	
Cell potential		2.763	2.607	3.325	3.357	3.071	3.215	3.633	3.965	2.647	2.536	3.209	3.286
Drawbacks		Loss of KOH, loss of CO_2, $KHCO_3$ salt precipitation	Loss of KOH, CO_2, and $HCOO^{-[22]}$	Loss of KOH and CO_2	Loss of KOH, CO_2, and $HCOO^-$	Loss of KOH and CO_2, $KHCO_3$ salt precipitation	Loss of KOH, HCO_3^-, $HCOO^-$ and CO_2	Loss of CO_2	Loss of CO_2 and $HCOO^-$	Loss of KOH in anolyte and acidity in catholyte	Loss of acidity in catholyte		Loss of $HCOO^-$ and acidity catholyte

no attention to. A small number of studies, for instance Ma et al.[6] discussed the importance of the carbon balance in eCO_2RR using GDE reactors, and both CE and CCE values were considered for assessing eCO_2RR performance. So far, the $HCOO^-$ selective catalysts such as Sn or indium (In) showed high CE (>80%) for eCO_2RR,[7] while the value of their CCE was rather low. For instance, previous studies reported CCE of only ≈30% and ≈36% using copper (Cu)[6] and tin sulfide (SnS)[8] based electrodes, respectively. These low values of CCE could presumably be one of the reasons that eCO_2RR has not yet reached a higher TRL or even industrial applications. Recently, efforts have been made to improve the CCE by employing a highly acidic catholyte.[9] Nevertheless, strong acidic conditions may not favor the stability of the catalysts such as tin.[10]

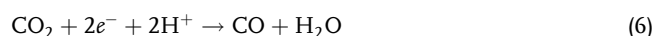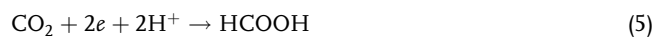Here, we show that CCE needs to be considered to the same extent as CE for reporting the efficiency of any eCO_2RR systems. Therefore, the overall components of an electrochemical set-up (such as electrolyte salt concentration and membrane type) as well as the operational conditions are crucial to the CCE.

When we consider eCO_2RR using $KHCO_3$ solution as a catholyte and Sn as electrocatalyst, the reactions depicted in Equation (1)–(4) occur, while with acidic catholyte Equation (5)–(7) are expected. Under alkaline or neutral conditions:

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^- \qquad (1)$$

$$CO_2 + OH^- \rightarrow HCO_3^- \qquad (2)$$

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- \qquad (3)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (4)$$

Under acidic conditions:

$$CO_2 + 2e + 2H^+ \rightarrow HCOOH \qquad (5)$$

$$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O \qquad (6)$$

$$2e^- + 2H^+ \rightarrow H_2 \qquad (7)$$

Considering only $HCOO^-$ as a sole carbon product of eCO_2RR, the carbon balance for two different types of membrane (cation exchange membrane (CEM), anion exchange membrane (AEM)) and acidic or alkaline anolyte solution are different. This is due to the different ions that are transported between anolyte and catholyte for assuring charge balancing (**Figure 1**).

Based on the cathode reaction in the $KHCO_3$ catholyte (Equation (1)), $HCOO^-$ formation via eCO_2RR requires one molecule of CO_2, and every $HCOO^-$ produced via eCO_2RR will produce one OH^- anion, which will react with one molecule of CO_2 available in the cathode compartment, forming a HCO_3^- anion in the catholyte (Equation (2)). Thus, every two electrons transferred consume two molecules of CO_2 (one through
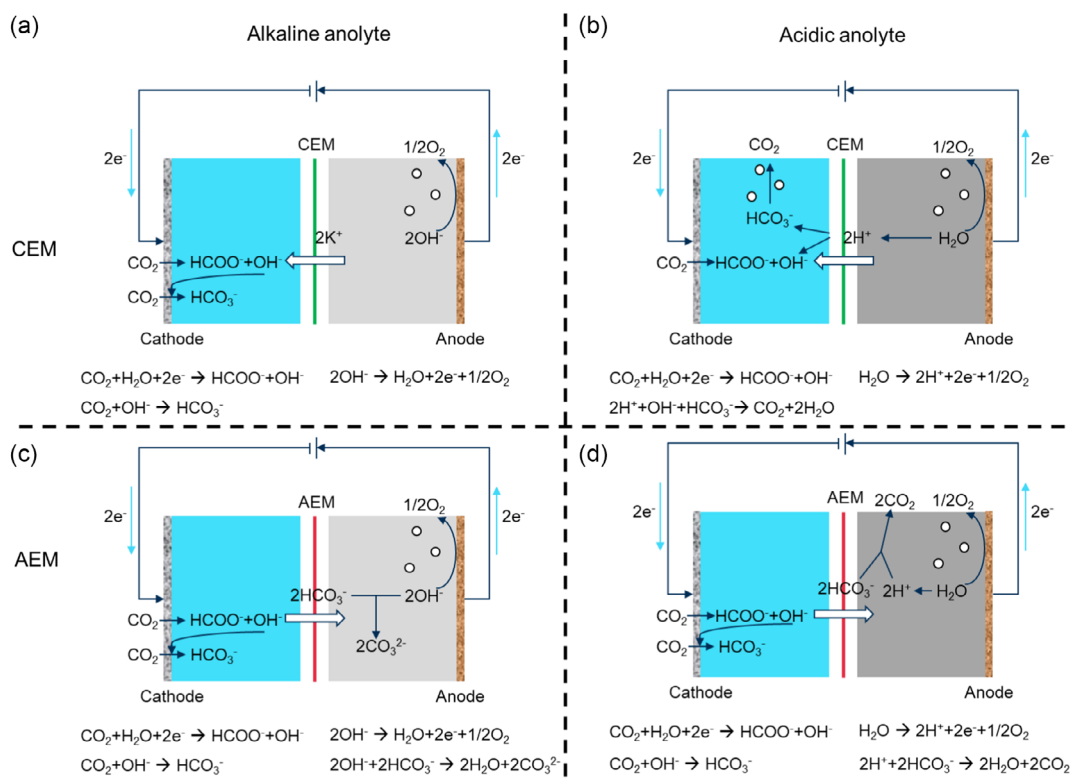
Figure 1. Schematics of carbon balance for the eCO_2RR in a $KHCO_3$ catholyte to formate ($HCOO^-$) using cation (CEM) or anion (AEM) exchange membranes with combination of acidic (dark gray) and alkaline (light gray) anolyte. a) When CEM and alkaline anolyte (KOH) are used, the ionic current is conducted through the membrane via K^+, which leads to the formation of $KHCO_3$ and HCOOK in the catholyte, b) the application of CEM and acidic anolyte leads to the transport of ionic current via H^+ through the membrane, which produces CO_2 and HCOOK. If AEM are used, the species transporting the charge balancing ionic current across membrane is HCO_3^-. In this case, the increase of $HCOO^-$ concentration in the catholyte is accompanied with the decline of HCO_3^- concentration. Depending on the anolyte used, the HCO_3^- transported from catholyte to the anolyte can either be c) alkalified by OH^- to yield CO_3^{2-} or d) acidified by H^+ to become CO_2 that is exhausted.

Equation (1) and one through Equation (2)), or in other words by generation of every molecule of $HCOO^-$ via eCO_2RR, two molecules of CO_2 are consumed. This is most often not considered in literature. When a CEM is used in an electrochemical cell, two cations (K^+ or H^+, depending on the pH of the anolyte), are transferred from anolyte to catholyte to maintain charge neutrality. Thus, the formed HCO_3^- either yields a $KHCO_3$ that may precipitate due to its low solubility, or forms CO_2 after acidification of HCO_3^- by the proton permeated from anolyte through the CEM (Figure 1a,b). This CO_2 may escape the catholyte via the tail gas, without taking part in the eCO_2RR. In all these cases, a theoretical maximum CCE of only 50% can be reached. When using an AEM, the theoretical maximum CCE is even lower. The HCO_3^- formed during eCO_2RR (Equation (2)) is transferred from catholyte to anolyte and will react either with OH^- to form CO_3^{2-}, or with H^+ to release the CO_2 to the headspace (Figure 1c,d). In acidic anolytes two HCO_3^- will react with two H^+ generated from the anodic reaction. Therefore, only one out of three molecules of CO_2 that are needed for the reaction is electrochemically converted in eCO_2RR, leading to a maximum theoretical CCE of $\approx$33%. These basic considerations already show that CCE can vary in different setups and operational conditions and, hence, it needs to be included, together with CE when reporting the efficiency for eCO_2RR.

2. Results and Discussions

In this study, efficiencies of eCO_2RR are evaluated using a setup and operating conditions being representative of previous studies (**Table 2**). In brief, the eCO_2RR on a Sn-GDE was studied (details in the Experimental Section in Supporting Information), as Sn is one of the most promising catalysts for eCO_2RR to formate.[11] For this, an inlet CO_2 flow of 35 ± 1 mL min^{-1} was applied for 120 min, while the outlet gas flow rate and composition were measured (Figure S1, Supporting Information). This value of the CO_2 flow was selected since it was almost the minimum flow rate used in previous studies (Table 2). Since the reactor was used in flow through mode by closing the outlet of the gas compartment, the overall carbon balance of the system could be determined. The effect of $KHCO_3$ concentration in the catholyte on the eCO_2RR efficiencies was examined by using various diluted $KHCO_3$ solutions, i.e., 0.5, 0.05, and 0.005 M $KHCO_3$, since the equilibrium of CO_2/HCO_3^- shifts at different $KHCO_3$ concentration, leading to change in the catholyte pH.

Before starting the eCO_2RR, all catholytes were purged with only CO_2 until reaching a stable pH, i.e., 0.5 M $KHCO_3$ to $\approx$7.5, 0.05 M $KHCO_3$ to $\approx$6.5 and 0.005 M $KHCO_3$ to $\approx$5.7 (Table S1, Supporting Information) and conductivity was

Table 2. Experimental conditions and results from previous studies on eCO$_2$RR using gas diffusion electrode (GDE) reactors.

Catalysts on GDE	Catholyte	Membrane	Anolyte	CO$_2$ inlet flow rate [mL min^{-1}]	Max. current density [mA cm^{-1}]	Cathode surface [cm^2]	Maximum CE of products [%]	Reference
Cu	1 M KHCO$_3$ 1 M KOH 5 M KOH	AEM	1 M KOH	45	150–300	2	CE$_{C_2H_4}$ = 40%, CE$_{CO}$ = 20% (the rest CH$_4$, H$_2$, etc.)	[6]
Ag	1 M NaHCO$_3$	BPM	1 M NaOH	100	200	4	CE$_{CO}$ = 50%	[23]
Cu	0.1, 1.0 and 3.0 M KHCO$_3$	AEM	1 M KHCO$_3$	50	50–700	3	CE$_{H_2}$ = 50%, CE$_{C_2H_4}$ = 30%, (the rest CH$_4$ and HCOO$^-$)	[24]
Cu	1 M KHCO$_3$/0.5 M K$_2$CO$_3$/1 M KOH	AEM/CEM/ BPM	1 M KHCO$_3$ 1 M KOH	45	200	2	CE$_{C_2H_4}$ = 43%, CE$_{EtOH}$ = 18%, (the rest CO, CH$_4$, H$_2$, C$_3$H$_8$O, HCOO$^-$, CH$_3$COO$^-$)	[25]
Cu-Sn	1 M KOH	CEM	5 M KOH	15	120	2	CE$_{CO}$ = 92%	[26]
Sn	1 M HCOOK	CEM/BPM	2 M KOH	200	100	16	CE$_{HCOO^-}$ = 80%, (the rest CO and H$_2$)	[27]
Ag	1 M KOH	–	1 M KOH	20	25–196	1.55	–	[28]
Sn	0.2 M KH$_2$PO$_4$/K$_2$HPO$_4$	CEM	0.2 M KH$_2$PO$_4$/K$_2$HPO$_4$	30–40	50	10	CE$_{HCOO^-}$ = 54%	[29]
SnO$_2$ Bi$_2$O$_3$	1 M NaOH/1 M KOH	AEM	1 M NaOH 1 M KOH	50	25–75	3.14	CE$_{HCOO^-}$ = 60%	[30]

adjusted in all experiments to ≈38 mS cm^{-1} by adding the electrochemically inert electrolyte K$_2$SO$_4$ (Table S1, Supporting Information). Although the pH of the catholytes at the beginning and throughout the experiments differed from each other, the selectivity of eCO$_2$RR to HCOO$^-$ was not affected. The CE for HCOO$^-$ production (CE$_{HCOO^-}$) (Equation (1) and (5)) in all conditions were similar at more than 85% and with a similar HCOO$^-$ production rate (r_{HCOO^-}) of ≈32 mM h^{-1} (**Figure 2**a). CO from reduction of CO$_2$ (Equation (3) and (6)) and hydrogen (H$_2$) from the hydrogen evolution reaction (HER, Equation (4) and (7)) were the other products, corresponding to an individual CE of ≈7% and 4%, respectively.

It is worth mentioning that leaching of Sn from the GDE to the solution at different catholyte pH from the beginning (Table S1, Supporting Information) and throughout the experiment (Figure S3, Supporting Information) was below the limit of detection. Despite the high CE at all conditions, being in-line with previous studies, the CCE in these experiments was low. At all conditions, the CCE was only ≈20% (Figure 2b–d). This showed that 80% of the carbon supplied to the system in the form of CO$_2$ was not electrochemically converted. In contrast, the carbon was either partially (≈60%) released via the off-gas to the atmosphere (Figure 2b–d), or fixed chemically as bicarbonate in the solution (e.g., Equation (2)). The almost identical CCE in all conditions with different KHCO$_3$ concentrations, and hence different catholyte pH, showed that release of CO$_2$ in form of gas or bicarbonate was inevitable and different pH provided did not affect the CCE.

For enhancing the CCE, the amount of CO$_2$ supply can be limited. The minimum amount needed can be calculated when considering the (fixed) current and the achieved CE. Thereby, the CO$_2$ required by eCO$_2$RR (Equation (1)) and further inevitable chemical conversion of CO$_2$ need to be considered. First, when

assuming the CE = 100% at a current of 1 A, 7.5 mL min^{-1} of CO$_2$ is required at 22 °C for eCO$_2$RR to HCOO$^-$. At the same time, the generation of OH$^-$ under alkaline conditions (Equation (1)–(4)), or H$^+$ consumption under acidic conditions (Equation (5)–(7)) that cause the chemical conversion of gaseous CO$_2$ to carbonate or bicarbonate in the liquid phase need to be considered. When now considering a minimum CE$_{HCOO^-}$ of 80% (according to the experimental results, Figure 2a) as well as carbonate or bicarbonate generation in the catholyte, a CO$_2$ flow rate of almost 15 mL min^{-1} is theoretically minimally required for eCO$_2$RR to HCOO$^-$. In practice, the CO$_2$ flow rate of minimum 16 ± 1 mL min^{-1} was also sufficient for eCO$_2$RR to HCOO$^-$ in our setup at a constant CE. In addition, this flow rate value was also confirmed by trying eCO$_2$RR at lower CO$_2$ flow rate than 15 mL min^{-1} in our setup. When the flow rate of 13 ± 1 mL min^{-1} was tried, an increase in H$_2$ evolution was observed with CE (>20%) for HER (e.g., Equation (4) and (7)), which was also discussed previously.[12] Our calculations were considering a constant CE$_{HCOO^-}$ of 80%, which of course, could vary and hence lead to minimal changes in the required CO$_2$ flow.

Thus, the CO$_2$ flow rate was further adjusted to constant 16 ± 1 mL min^{-1} for eCO$_2$RR. Since CE, CCE, and r_{HCOO^-} were similar in all the catholytes with different KHCO$_3$ concentration (0.5, 0.05, and 0.005 M) as shown before (Figure 2 - the respective CE of ≈85%, 7%, and 4% for HCOO$^-$, CO and H$_2$ production, CCE of ≈20%, and r_{HCOO^-} of ≈32 mM h^{-1}), the most diluted catholyte (0.005 M KHCO$_3$) was used for studying the effect of the decreased CO$_2$ flow rate. Interestingly, CE of the products and r_{HCOO^-} were still similar to those when a higher CO$_2$ flow rate of 35 ± 1 mL min^{-1} was used (**Figure 3**a). However, CCE increased by factor two compared to the higher flow rate (35 ± 1 mL min^{-1}), and reached ≈41%, which is already only 9% below the theoretical maximum (Figure 3b).

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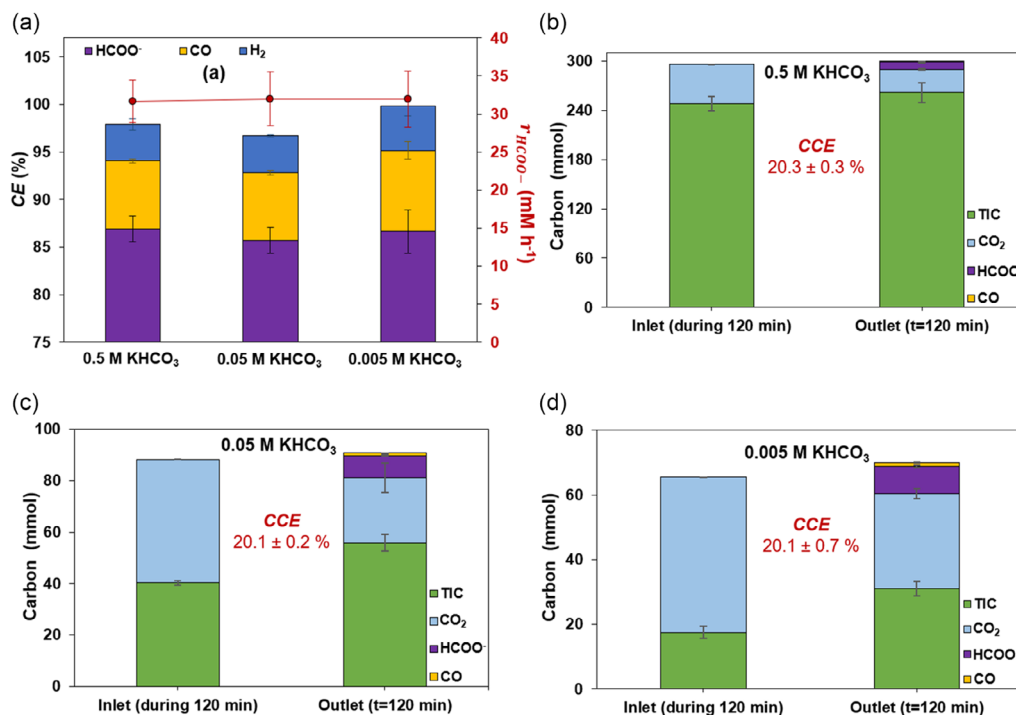SCIENCE NEWS**

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Figure 2. a) Coulombic efficiency (CE) of the eCO$_2$RR at Sn-GDE (10 cm^2) reactors and the formate (HCOO$^-$) production rate (r_{HCOO^-}) and with inlet CO$_2$ flow rate was 35 ± 1 mL min^{-1} using three different catholytes of 0.5, 0.05, and 0.005 M KHCO$_3$. Carbon balances considering inlet and outlet CO$_2$, total inorganic carbon (TIC) and products (CO and HCOO$^-$) when using catholytes of b) 0.5 M KHCO$_3$, c) 0.05 M KHCO$_3$, and d) 0.005 M KHCO$_3$. All experiments were conducted for 120 min in triplicate ($n = 3$).
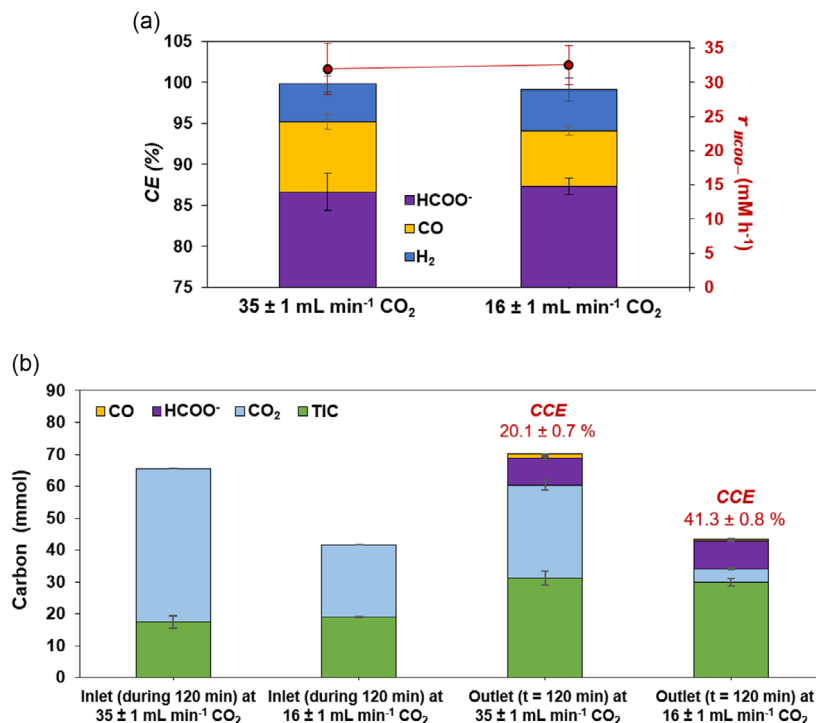

Figure 3. a) Coulombic efficiency (CE) of the eCO$_2$RR at Sn-GDE (10 cm^2) reactors and the formate (HCOO$^-$) production rate (r_{HCOO^-}) using the catholyte of 0.005 M KHCO$_3$ with the inlet CO$_2$ flow rate of 35 ± 1 mL min^{-1} and 16 ± 1 mL min^{-1}. b) Carbon balance considering inlet and outlet CO$_2$, total inorganic carbon (TIC) and products (CO and HCOO$^-$) at the CO$_2$ flow rate of 35 ± 1 mL min^{-1} and 16 ± 1 mL min^{-1}. All experiments were conducted for 120 min in triplicate ($n = 3$).

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This confirms that using a high flow rate during eCO₂RR, as performed in many previous studies (Table 2), is not necessary for achieving a high CE, but it is diminishing the CCE. At the same time, it needs to be considered that CO_2 flow rate needs to be adjusted at a value that covers the minimum requirement of CO_2 for eCO₂RR, as well as the inevitable chemical conversion of CO_2 in the liquid phase. In addition, even when using the CO_2 flow rate of $16 \pm 1\,\mathrm{mL\,min^{-1}}$, gaseous CO_2, although in smaller shares than before, was still released to the headspace ($\approx18\%$ at $16 \pm 1\,\mathrm{mL\,min^{-1}}$ compared to $\approx60\%$ at $35 \pm 1\,\mathrm{mL\,min^{-1}}$ during 120 min experiments, Figure 2 and 3). Hence, one may never achieve the theoretical maxima of 50% CCE at the same time with 100% CE, especially not at an acceptable rate. If electrochemical conversion of the CO_2 in industrial flue gas is targeted, CCE is considered as a crucial factor. Also, here, CO_2 dissolving in the solution is governed by thermodynamic principles and hence only a theoretical maximum CCE of 50% can be achieved (Figure 1). At the same time, the release of gaseous CO_2 from the reactors to the atmosphere can be technically circumvented, for instance, by adding a CO_2 recycling line to the gas compartment of the reactor.[13] In essence, we strongly advocate to report the CCE side by side to the CE when assessing the eCO₂RR, as only one of these two efficiencies tells less than half of the story.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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