High Salt Electrolyte Solutions Challenge the Electrochemical CO_2 Reduction Reaction to Formate at Indium and Tin Cathodes

Aykut Kas,[a] Paniz Izadi,[a] and Falk Harnisch*[a]

Formate is a promising product of the electrochemical CO_2 reduction reaction (eCO_2RR) that can serve as feedstock for biological syntheses. Indium (In) has been shown as a selective electrocatalyst of eCO_2RR with high coulombic efficiency (CE) for formate production at small scale at biocompatible non-halophilic that is low salt conditions. Ohmic losses and challenges on potential/current distribution arise for scaling-up, where higher salt loads are advantageous for minimizing these. Higher salt concentration within the solution or halophilic conditions also enable the use of halophilic biocatalysts. We optimized eCO_2RR with halophilic media by introducing tin (Sn) as a more sustainable alternative to In. At 3% NaCl providing a catholyte conductivity (κ_S) of 70 mS cm^{-1}, the maximum specific formate production rates ($r_{formate}$) of 0.143 ± 0.030 mmol cm^{-2} h^{-1} and 0.167 ± 0.027 mmol cm^{-2} h^{-1} were achieved at In and Sn electrocatalysts, respectively. Decrease in $r_{formate}$ and CE, in addition to higher variation between replicates was observed with further increase in NaCl concentration above 3% ($\kappa_S > 70$ mS cm^{-1}) up to 10% ($\kappa_S = 127$ mS cm^{-1}). This study sets the foundation for integrated microbial synthesis by halophiles.

Introduction

It is imperative to utilize CO_2 as feedstock to restrict global temperature increase and establish a circular economy. Various chemical, physical and biobased approaches are suggested to transform CO_2 into valuable fuels, chemicals, and building materials. Among these approaches is electrochemical CO_2 reduction reaction (eCO_2RR) that uses electric energy to convert CO_2 into valuable compounds. Albeit formation of multi-carbon compounds requires the electrochemical formation of C–C-bonds, the majority of studies reported the formation of C_1-compunds such as carbon monoxide (CO), formate/formic acid ($HCOO^-$/HCOOH), formaldehyde (CH_2O) and methane (CH_4). Formate is a valuable building block for chemical processes,[1] can serve as feedstock for microbial synthesis[2–5] and is a promising intermediate for storage of (electric) energy.[6] For achieving eCO_2RR to formate Eq. (1), metal electrocatalysts at cathodes including lead, mercury, bismuth, cadmium, copper, indium and tin are typically used.[7,8] Tin (Sn) and indium (In) based electrocatalysts possess a high selectivity for eCO_2RR to formate rather than hydrogen evolution reaction (HER, [Eq. (2)]).[9,10] We kindly refer the readers to reviews for comprehensive molecular understanding of In and Sn catalysts, their morphology and surface structures that is not in focus for this study.[9,11] Previously, highly selective and efficient eCO_2RR to formate under biocompatible mesophilic conditions (i.e., ambient T, p and neutral pH) at In was demonstrated.[12–14] Formate production rate ($r_{formate}$) and coulombic efficiency (CE) in this setup (see also Figure 1) at the cathodic potential of -1.6 V vs. Ag/AgCl, were 0.013 ± 0.002 mmol cm^{-2} h^{-1} and 64.6 ± 6.8%, respectively.[14] In a subsequent study using the similar setup and catholyte (50 mM HCO_3 buffer), higher $r_{formate}$ and CE were achieved when the cathodic potential of -2.2 V vs. Ag/AgCl was applied, reaching the $r_{formate}$ of 0.061 ± 0.007 mmol cm^{-2} h^{-1} and CE of 93.0 ± 2.4%.[13] Despite this

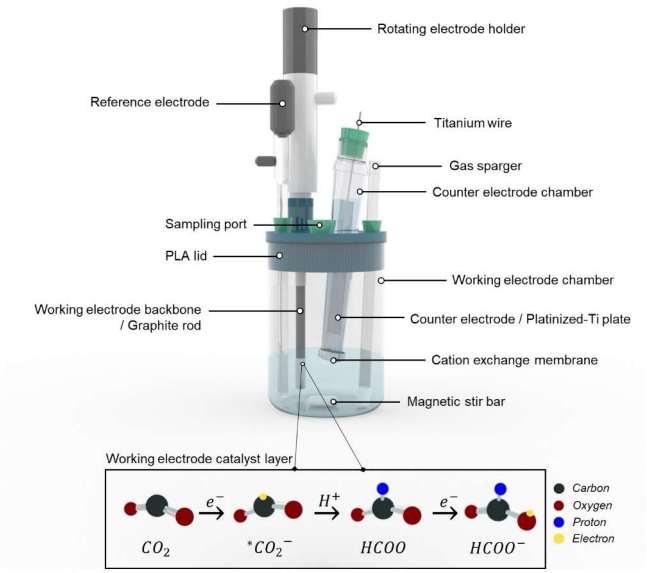

Figure 1. Electrochemical reactor and setup used throughout the eCO_2RR experiments (details see text).

[a] A. Kas, Dr. P. Izadi, Prof. Dr. F. Harnisch
Department of Environmental Microbiology,
Helmholtz-Centre for Environmental Research – UFZ,
Leipzig, Germany
E-mail: falk.harnisch@ufz.de

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excellent performance using In is no option at technical scale, as In is considered to have a high supply risk and is hence included in the EU's list of Critical Raw Materials (CRMs) since 2010.[15]

$$CO_2 + 2e^- + H^+ \rightarrow HCOO^- \quad (1)$$

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

As opposed to In, Sn is accessible, cheap and has also been widely used in eCO_2RR studies, displaying high selectivity for formate production with high CE. Sn is occasionally combined with other metals, such as Cu-Sn[16] and Pd/Sn alloy on activated carbon[17] to enhance performance, achieving near 100% CE with $KHCO_3$ buffers. Studies using only Sn as eCO_2RR electrocatalyst achieved CEs with pure Sn rods at −1.6 V vs. Ag/AgCl at 94%,[18] Sn on graphene at −1.76 V vs. Ag/AgCl reaching 89%,[19] and Sn on carbon nanofibers at −1.42 V vs. Ag/AgCl with 62% CE.[20]

Limitation of the product spectrum of the eCO_2RR to mainly C_1-compounds initiated the development of concepts that interface the eCO_2RR to a subsequent microbial synthesis, as these may lead to diversity of high-value products.[6,21–23] An exemplary demonstration of this concept for eCO_2RR to CO (and H_2) that are used for subsequent gas fermentation achieved almost 100% CE for production of alcohols.[24] Combining eCO_2RR with microbial catalysis for formate utilization allowed production of mesaconate and 2*S*-methylsuccinate by *Methylobacterium extorquens* AM-1,[25] alcohols and polyhydroxybutyrate (PHB) by *Cupriavidus necator*[26] and amino acids by synthetically modified *Escherichia coli*.[27]

Extremophiles are microorganisms that adapted to thrive in extreme conditions in their natural habitats such as low and high temperature (cryophiles and thermophiles) or high salt concentration (halophiles). Halophiles are of particular interest to be exploited by interfacing to electrochemical reactions, as highly saline conditions allow high concentrations of the supporting electrolyte that is leading to lower energetic losses.[28] Additionally, halophiles are utilized in biotechnological processes to produce specific high-value bioproducts[29,30] by synthesizing compatible solutes (e.g., ectoine, hydroxyectoine, proline) to counteract osmotic stress. Exploiting them in microbial electrosynthesis could provide a new avenue to target high-value products from waste streams, in this case starting from CO_2.

Interfacing the eCO_2RR to formate with microbial synthesis from formate, especially in situ that is in one vessel, requires developing an electrolyte composition being optimal for both microbial growth and abiotic electrosynthesis. Therefore, the optimal electrolytic conductivity (κ_S) and salt concentration favoring both microbial and electrochemical processes were investigated. This is specifically important due to the decrease in internal resistance and the required power output at higher κ_S, but decrease in saturation concentration of CO_2.[31] To investigate the effect of halophilic growth media components (buffer, mineral salt, and NaCl concentrations) on eCO_2RR to formate, the previously established reactor setup was used[12–14,32] starting from the model medium for halophiles MM63.[33] Sn and In for eCO_2RR were compared for formate production rates, CE, and electrocatalyst leaching. In particular, NaCl was investigated in this study as it is an essential compound for the growth and activity of halophilic microorganisms.[34–36]

Results and Discussion

Establishment of Sn-electrodeposition on graphite electrodes

Figure 2 shows the eCO_2RR to formate at In cathodes at −2.2 V under identical experimental conditions as the previous study.[13] Reproducible performance was observed, reaching the production rate of $r_{formate} = 0.086 \pm 0.003$ mmol cm^{-2} h^{-1} and even slightly higher coulombic efficiency (CE = 92.1 ± 0.4%). In order to allow linkage to earlier work, we performed tests on Sn at −1.6 V and −2.2 V, utilizing well-established methodology used for studying In.[12–14,32] In-catalyst setup was first established at −1.6 V[14] and later optimized at −2.2 V among a range

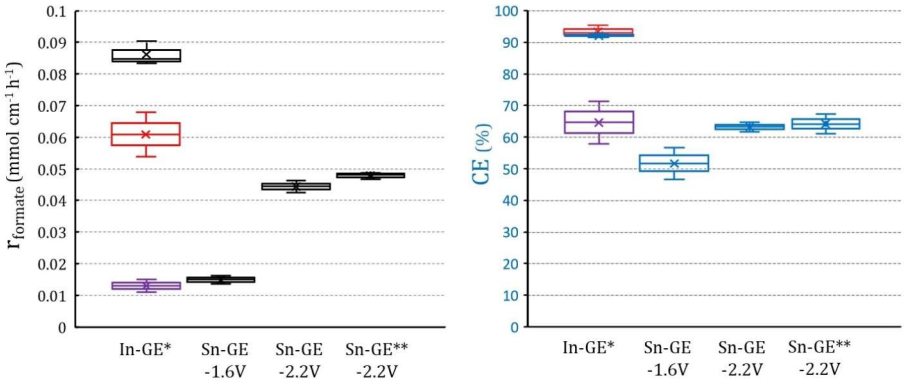

Figure 2. Specific formate production rate ($r_{formate}$) and coulombic efficiency (CE) of established In-catalyst setup (In-GE) and results with new Sn-catalyst at the graphite electrode (Sn-GE). During the eCO_2RR experiments, 50 mM $NaHCO_3$ electrolyte solution was used at the applied potentials (E_{prod}, vs. Ag/AgCl, in satd. KCl) indicated below the bar graphs ($n = 3$). * Benchmark results from our previous study using In-catalysts in the identical setup are shown in purple box plot (at $E_{prod} = -1.6$ V),[14] red box plot (at $E_{prod} = -2.2$ V)[13] and this study in black/blue box plots (at $E_{prod} = -2.2$ V). ** Electrodeposition charge (Q_{ed}) increased from 1 C to 3 C.

of potentials between −1.6 to −3.0 V.[13] Further, investigation on operating 72 h at different potentials ranging from −1.6 to −2.2 V showed that at −2.2 V highest formate concentration were achieved.[32] Therefore, for evaluating the performance of the Sn cathodes, the two exemplary potentials −1.6 V and −2.2 V were selected. When −1.6 V was applied at the Sn-cathodes, $r_{formate}$ and CE reached to 0.015 ± 0.001 mmol cm^{-2} h^{-1} and 51.7 ± 7.1 %, respectively (Figure 2). Although CE increased only to 63.2 ± 2.1 % at an applied potential of −2.2 V during experiments, $r_{formate}$ improved notably to 0.046 ± 0.004 mmol cm^{-2} h^{-1}. With Sn cathodes, $r_{formate}$ and CE values were lower than these using In cathodes in 50 mM $KHCO_3$ at the same potentials, but they were still comparable with Sn-coated carbon paper electrodes that showed approximately 63 % CE at E_{prod} = −2.0 V in 100 mM $KHCO_3$ electrolyte.[37]

As the $r_{formate}$ values achieved using Sn was not comparable with those at In electrodes, further tests were performed to improve the electrodeposition method. The impact of increasing the electrodeposition charge, which led to a thicker catalyst layer (theoretically calculated to be 3.375 µm for Q_{ed} = 3 C, Figure S1) was investigated. However, this resulted in only a slight increase in formate production and no change in CE. Therefore, electrodeposition potential of −1.0 V and 3 C charge were selected (described in Supplementary Information) for all follow-up investigations as it yielded the highest formate production rate of 0.048 ± 0.001 mmol cm^{-2} h^{-1} at a CE of 64.2 ± 3.2 % in 50 mM $NaHCO_3$ that served as a benchmark.

A reliable and reproducible electrodeposition method for Sn on graphite electrodes was established for the eCO_2RR. As it was previously established with the In electrocatalyst setup before and replicated here, results obtained in this part with Sn serve as a benchmark for the stable operation as well as performance of eCO_2RR to formate. Further optimization of the Sn-catalyst setup for scaling up or long-term operation may be of interest, as production rates certainly might be improved, e.g. by pulsed potential operational mode.[37,38]

Increasing NaCl concentration of halophilic media enhances electrochemical formate production at the cost of lower selectivity

As an initial step towards integrating eCO_2RR to formate at high salinity and its interfacing with halophilic microbial catalysis using formate, the effect of MM63 V media composition on the electrochemical processes was studied. The MM63 V medium is thereby representative of a model halophilic growth medium, as it is used for various pure culture halophilic strains.[39–43]

In the previous work with the same reactor setup, CE and $r_{formate}$ of ca. 85 % and 0.2 mmol cm^{-2} h^{-1} were achieved at the In-cathodes using 50 mM $NaHCO_3$ with the conductivity adjusted at 20 mS cm^{-1} using Na_2SO_4.[13] When MM63 V medium (without NaCl) with a similar conductivity as the carbonate buffer (κ_S = 17.9 mS cm^{-1}) was used, CE decreased to 34.0 ± 2.0 % for In, 41.4 ± 3.2 % for Sn, although $r_{formate}$ increased to 0.106 ± 0.003 mmol cm^{-2} h^{-1} for In and 0.126 ± 0.006 mmol cm^{-2} h^{-1} for Sn (Figure 3). With 3 % NaCl added to MM63 V (κ_S = 70 mS cm^{-1}), $r_{formate}$ increased to 0.143 ± 0.032 mmol cm^{-2} h^{-1} and 0.167 ± 0.027 mmol cm^{-2} h^{-1} at In and Sn electrocatalysts, respectively. Despite the increase in $r_{formate}$,

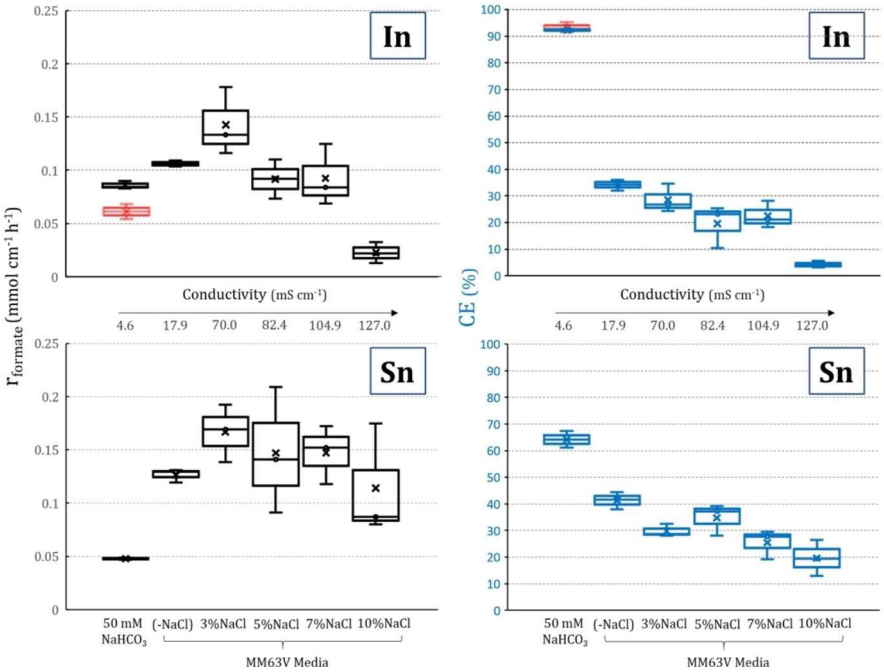

Figure 3. Specific formate production rate ($r_{formate}$) and coulombic efficiencies (CE) achieved during eCO_2RR at In-coated graphite electrode and Sn-coated graphite electrode with modified minimal media (MM63 V). A potential of −2.2 V vs. Ag/AgCl in sat. KCl was applied at the electrodes for t = 1 h at T = 30 °C (n = 3). κ_S, initial and final pH of the different growth medium experiments are summarized in Table S2. Box plots in red shows the results from[13] using the identical setup and conditions.

CEs declined to 28.4 ± 5.4 % for In and 41.4 ± 3.2 % for Sn. This increase in the $r_{formate}$ was notable, but most likely not specific to the NaCl addition. For instance the 3 % NaCl MM63 V (κ_S = 70 mS cm^{-1}) did not reach the $r_{formate}$ when conductivity-adjusted bicarbonate buffer using Na_2SO_4 (κ_S = 20 mS cm^{-1},[13] and κ_S = 21 mS cm^{-1}[32]) was used at a lower κ_S value from previous studies for 1 hour of eCO_2RR. Increasing conductivity from 4.5 mS cm^{-1} to 10 mS cm^{-1} using $NaSO_4$ led to increase in $r_{formate}$ of up to two times with In electrodes, reaching 0.136 ± 0.016 mmol cm^{-2} h^{-1}, while two fold increase was also observed simultaneously in the cathodic current.[13] This could be justified by higher HER rather than eCO_2RR, which in turn decreased the CE value. This aligns with,[44] which stated that the current density for CO or $HCOO^-$ formation could be limited given low CO_2 solubility in water at ambient conditions. Considering our case, although constant supply of CO_2 before and throughout the experiment enabled formate production to continue, it was likely that higher conductivity leading to higher current fostered HER, due to depletion of CO_2 at the cathode surface. This phenomenon might be attributed to the reaction being limited by mass transfer, and insufficient CO_2 or HCO_3^- diffusion to the electrocatalyst active sites, while H^+ could easily move to the cathode surface due to Grothuss mechanism-based transport,[45] thus becoming readily available as reactant, for instance, for HER. This could be overcome by optimizing the reactor configuration and electrode architecture, e.g., using a gas diffusion electrode (GDE) design, in which the mass transfer limitations can be tackled.[46] Additionally, it was previously shown[47] that the influence of $KHCO_3$ concentration on eCO_2RR could be due to the K^+ ions blocking the electrode surface and consequently preventing the cathodic reaction with non-polar CO_2 reactants. The larger Stokes radius of hydrated Na^+ (1.94 Å) compared to K^+ (1.34 Å) was suggested to intensify this surface blocking effect.[48]

Although acidic pH conditions at the cathode were previously reported to suppress eCO_2RR and favor HER,[49] this seems unlikely in our experiments, as minimal pH changes were observed during the one-hour operation (Table S2). After 1 hour of eCO_2RR with various halophilic media, pH increased only slightly (change was below 0.7 pH-units for all experiments). All initial pH values of the electrolyte solution/growth media, pH after reaching CO_2 saturation (also shown in Figure S3) with approximately 10 min of sparging before experiment and at the end of 1 h experiment are summarized in Table S2. In addition, elevated HER rates more likely caused a detrimental H_2 gas bubble formation that may prevent the availability of CO_2 or HCO_3^- on the cathode surface, consequently making HER more dominant reaction than eCO_2RR. Higher gas production at the cathode was visually observed both in this study and previously[13] where higher κ_S yielding higher cathodic currents.

Increasing salt concentration beyond 3 % NaCl (corresponding to 70 mS cm^{-1}) led to a decline in both $r_{formate}$ and CE, suggesting a further shift of electrons toward competing side reactions (Figure 3). This adverse effect was more pronounced for In, as $r_{formate}$ decreased below benchmarking conditions using 50 mM bicarbonate buffer electrolyte solution when NaCl concentration exceeded 5 %. The $r_{formate}$ were approximately 1.6 times higher at Sn-cathodes than at In-cathodes using both 5 % and 7 % NaCl halophilic media. Ultimately, at the highest NaCl concentration (10 %, 127 mS cm^{-1}), $r_{formate}$ reached its lowest value (0.023 ± 0.010 mmol cm^{-2} h^{-1}), with CE dropping to 4.1 ± 1.2 % at In-cathodes. Meanwhile, relatively high $r_{formate}$ of 0.114 ± 0.053 mmol cm^{-2} h^{-1} wasachieved at Sn-cathodes. Although not as thoroughly optimized as the In-cathodes, the Sn-cathodes configuration demonstrated better performance of the eCO_2RR with NaCl concentrations above 3 % using MM63 V media.

Several factors may have contributed decrease in CE, such as operational issues (described in SI. 2.2) associated with halophilic media as selectivity shifts towards side reactions, and electrocatalyst loss or inactivation through blocking of cathode surface with Na^+ ions. Cations are known to interact non-covalently with CO_2 and eCO_2RR intermediates on the cathode surface through electrostatic interactions or affect the local pH at the electrochemical interface and thus change the proton-coupled electron transfer (PCET).[50] The observed effects may potentially be also relevant for the concentration of cations present in the halophilic media. Yet, this molecular level investigation was not in focus for our current study. For achieving a high selectivity of eCO_2RR, ions in the electrolyte solution, distinct from those involved in the targeted reaction, must remain electrochemically inert without undergoing oxidation or reduction under the applied conditions. Water is the primary proton source in eCO_2RR, but buffering anions with lower pKa values might also serve as proton donors and enhance the reaction rates.[7] Additionally, adsorption of halides on the electrode surface was reported to influence charge density and selectivity surface structure and morphology during oxidation-reduction cycles.[51] In accordance with our previous findings regarding the long-term operation of the In-catalyst, the HER rates seemed to increase over time, and electrons were majorly utilized in HER rather than eCO_2RR.[32] The eCO_2RR is highly dependent on the applied potential, with the first electron transfer to CO_2 molecules being described as the rate-limiting step.[45] Previous studies with In-catalyst have shown a significant increase in both CE and $r_{formate}$ at −2.2 V compared to −1.6 V.[13,32] Even at higher overpotentials, the surprisingly high selectivity was maintained at In-catalyst with CE being 86.8 ± 16.1 % at −3.0 V, while already at −2.2 V a CE of 93.0 ± 2.4 % was reached.[13] Throughout the 72 h experiments in the previous study at −2.2 V applied potential,[32] the changes in the overpotentials of eCO_2RR or HER were negligible and unlikely to influence the selectivity shift at any stage of the experiment. Selectivity shift was more likely due to electrocatalyst unavailability or based on other mechanistic factors related to CO_2 availability rather than a thermodynamic advantage as also previously described.[13,32] Since the electrochemical cell used in our study was not designed fully gas-tight, a complete quantification of gaseous products was not conducted. Only hydrogen gas using gas chromatography and formate were observed with HPLC measurements. Although it was not desired in this study, HER could be advantageous for future integrated system. For instance, H_2 could be a source of energy in addition to formate for some microbes or synthetic

engineered strains, when microbial processes for biosynthesis and eCO_2RR are combined.[52,53]

κ_S increase affects eCO_2RR rate rather than buffer type or concentration

As shown in Eq. (3), CO_2 dissolving in aqueous solutions forms an equilibrium with carbonic acid (H_2CO_3), which dissociates into bicarbonate ions (HCO_3^-) and protons (H^+). Bicarbonate ion plays a unique role in eCO_2RR by enhancing CO_2 solubility, facilitating proton-coupled electron transfer, and acting as a reactant or intermediate.[31] Despite the decrease in CO_2 solubility at higher salt concentrations, the catholytes were saturated with CO_2 gas (Figure S3) after approximately 10 minutes.

$$CO_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} \rightleftharpoons HCO_{2(aq)}^- + H^+ \quad (3)$$

As shown above, using MM63 V medium (without NaCl) instead of 50 mM $NaHCO_3$ as catholytes led to decrease in eCO_2RR performance. Thus, the lower bicarbonate concentration seems a likely explanation for the 60% decrease in CE observed when using MM63 V media with phosphate buffer (Figure 3 and Figure 4). To determine, if the absence of bicarbonate in MM63 V medium was responsible for this variation, two further sets of experiments were performed using either a lower (50 mM HCO_3^-) or higher concentration (500 mM HCO_3^-) instead of 100 mM phosphate buffer with MM63 V (without NaCl).

Using In-cathodes, the addition of mineral salts (excluding NaCl) to the MM63 V medium or an increase in κ_S (from 4.5 to 6.4 mS cm^{-1}, a 50% increase) led to a noteworthy decrease by around 40% in both $r_{formate}$ to 0.052 ± 0.008 mmol cm^{-2} h^{-1} and CE to 54.2 ± 9.0% (Figure 4). An increase in the bicarbonate buffer concentration to 500 mM led to higher $r_{formate}$ of 0.130 ± 0.033 mmol cm^{-2} h^{-1}, where both the enhanced buffering capacity and κ_S (34.0 mS cm^{-1}) may have played a role, as also discussed previously.[13] The CE achieved using 500 mM HCO_3^- (35.1 ± 3.7% at In, 51.1 ± 8.0% at Sn) was similar to that when 100 mM phosphate buffer was used as a supporting electrolyte (34.0 ± 2.0% at In, 41.4 ± 3.2% at Sn). This suggests that the presence of bicarbonate alone does not increase the selectivity of $r_{formate}$, but also leads to decrease in CEs. Using the same reactor setup as this study, it was shown that increasing HCO_3^- concentration to 500 mM from 50 mM by keeping κ_S constant did not change formate production rates but decreased CE.[13] Presence of bicarbonate was shown to enhance the rate of eCO_2RR to CO at gold electrodes by increasing the effective CO_2 concentration near electrode surface.[54] In our case, initial HCO_3^- concentration in halophilic media as a sole parameter for improving eCO_2RR to formate did not have a high impact on the overall performance, as CE and $r_{formate}$ values remained almost stable. This was noteworthy considering the fact that MM63 V medium with 500 mM bicarbonate buffer had almost double κ_S and a high concentration of HCO_3^- compared to 100 mM phosphate buffer with MM63 V. For explaining the

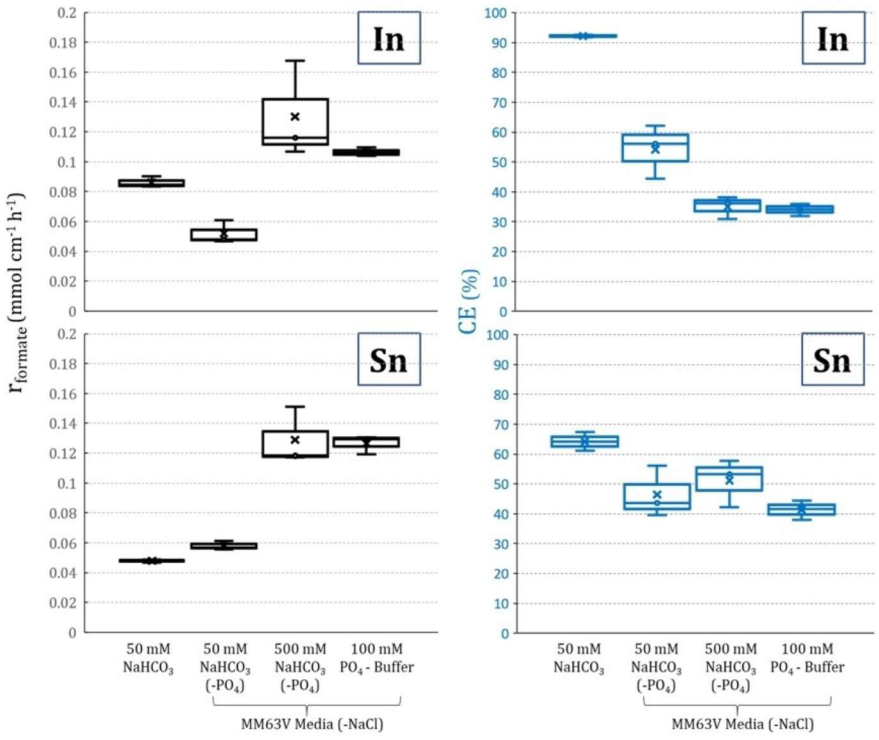

Figure 4. The effect of buffer concentration and type in MM63 V medium and 50 mM $NaHCO_3$ electrolyte solutions on eCO_2RR performance at In-coated and Sn-coated graphite electrodes., The potential of −2.2 V vs. Ag/AgCl in saturated KCl was applied for $t = 1$ h at $T = 30$ °C ($n = 3$). κ_S, initial and final pH of the different growth medium experiments are summarized in Table S2.

decrease in CE, it was previously suggested that HCO_3^- serves as a reactant for the HER as well.[55,56]

Similar to the high salt medium experiment with Sn, $r_{formate}$ was enhanced at In-cathodes to the respective value of 0.058 ± 0.003 mmol cm^{-2} h^{-1} and 0.129 ± 0.019 mmol cm^{-2} h^{-1} using 50 mM and 500 mM HCO_3^- MM63 V media. This improvement seemed to be attributed to the increased κ_S rather than the buffering capacity or the initial availability of dissolved CO_2 species when considering the similar results obtained when using 100 mM phosphate buffer and 500 mM HCO_3^-.

Catalyst loss increased with the halophilic media as electrolyte solutions

When 50 mM $NaHCO_3$ buffer or 7% NaCl MM63 V medium was provided, no formate production was monitored at the bare graphite. All charge was spent on HER, as expected for a carbon-based electrode with the applied potential more negative than −0.8 V.[57] Therefore, it was hypothesized that selectivity shift towards HER from eCO_2RR to formate at the In as well as Sn cathodes could be due to electrocatalyst loss from the graphite electrode surface. At the end of the experiments conducted under high salinity conditions (≥3% NaCl) for 1 h, the uniform electrocatalyst coating on the graphite surface (Figure S1) visually seemed to be no longer present, confirming the potential electrocatalyst loss. Therefore, potential electrocatalyst leaching to the catholyte was determined with polarography (Figure 5). The electrocatalyst loss increased almost 4 times for Sn and 8 times for In for halophilic medium (10% NaCl) in comparison to when 50 mM HCO_3 buffer was used. Overall, it did not exceed 6% in any case (Figure 5) and therefore cannot solely account for the major selectivity shift.

Contribution of the electrocatalyst loss to any selectivity shift effect was previously described as negligible,[13,14,25] where it was found to be less than 1%. However, electrocatalyst leaching seemed to be more problematic with the use of halophilic media during this study as well as during extended periods of operation up to 72 h with the identical electrochemical setup using In-catalyst.[32] Further research is required to study the electrocatalyst leaching and/or activating the catalyst during the eCO_2RR, e.g., by pulsing techniques. For instance, it was reported before that alkali metal ions can cover the electrocatalyst layer, leading to its inactivation.[47] Additionally, changes in the electrocatalyst layer and graphite backbone's surface chemistry due to inert by-product deposition, as previously reported,[11] should be considered.

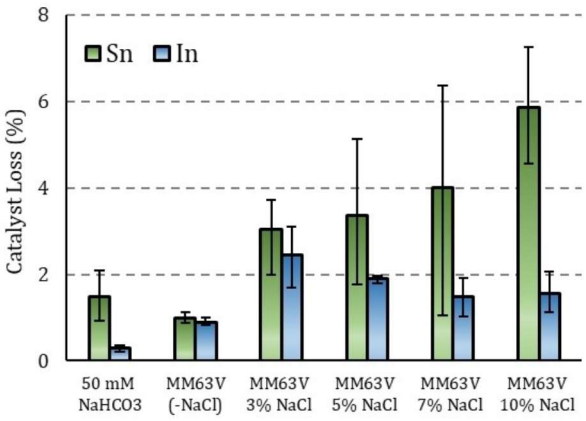

Figure 5. Measurement of electrocatalyst leaching to catholyte with polarography for Sn and In. Electrocatalyst loss (%) is calculated from the theoretical mass of electrocatalyst on graphite electrode surface based on the charge applied during electrodeposition (1.7 C for In and 3 C for Sn).

Conclusions and Outlook

In this study, we showed that it is possible to balance enhancing the performance of the abiotic eCO_2RR to formate with using halophilic media for microbial synthesis, while maintaining stability for scalability and reproducibility. To replace In with a more sustainable alternative, we introduced and systematically assessed Sn for eCO_2RR using halophilic MM63 V media with NaCl concentration varying between 0 to 10%. The performance of eCO_2RR to formate was maximized at both In and Sn electrocatalysts at 3% NaCl, with rates being increased 66% using In and 247% using Sn as electrocatalysts compared to simple buffer electrolytes (50 mM HCO_3). It was likely that excess current yielding from the increased κ_S contributed to increased hydrogen production, which in turn adversely affected the stability of the electrocatalyst and the CE of eCO_2RR. Compared to simple buffer electrolytes, addition of mineral salts and increasing NaCl concentration caused a selectivity shift to competing side reactions that affected In-cathode more unfavorably for formate production compared to Sn-cathode. Compounds in the halophilic media including NaCl and other mineral salts have been observed to adversely affect the CE of eCO_2RR to formate. Further investigation on the effects of individual cations or anions while using electrolytes other than simple buffer systems could yield important information regarding its impact on the mechanisms and hence CE. Nonetheless, overall rates of formate production through electrochemical process was also improved with the increased conductivity of the electrolyte. Impact on CE is not the most crucial factor in establishing high salt electrosynthesis since other byproducts, such as hydrogen, can also be utilized by certain microorganisms. But eventually, conducting a detailed consideration of CE for the economic feasibility of the overall process is still required. Since progress has been made in improving formate production with a model growth medium for halophiles, next step is their integration with eCO_2RR at these high salt environments and utilizing electrochemically generated formate for biosynthesis of valuable end products, which is under investigation.

Experimental Section

General remarks

All potentials are reported versus Ag/AgCl sat. KCl [0.197 V vs. standard hydrogen electrode (SHE)]. All compounds were at least of an analytical grade. The polarography standards were made in tri-distilled water, all other solutions were prepared with de-ionized water (Merck Millipore, Germany). All modified halophilic media were autoclaved before use. All eCO_2RR experiments were conducted in triplicate, and the data are presented as the mean value with their corresponding standard deviation.

Electrochemical reactor setup and operation

An established[12–14] two-chamber electrochemical cell with an in-house produced glass counter electrode chamber and 3-D printed lid was used throughout eCO_2RR experiments. Working electrode (cathode) chamber was a 400 mL glass beaker with an active volume of 50 mL. The anode (counter electrode), was placed in a glass tube and was in contact with the cathode chamber through a cation exchange membrane (CEM, fumasep FKE, FuMA-Tech GmbH, Germany) fixed with an aluminum cap. Cathode was a high-purity graphite rod (Ø = 0.635, 6 cm, C-00-RD-000121, Goodfellow, UK) coated as detailed blow with either In or Sn with a net geometric surface area of 2.5 cm^2. A rotating disc electrode (RDE) holder (CTV 101T, Tacussel, France) was used in rotating mode for electrochemical pre-treatment steps and without any rotation for eCO_2RR experiments. Plates of platinized titanium (0.05×1×7 cm, platinode, Umicore Galvanotechnik GmbH, Germany) were used as anodes. Reference electrodes (RE) were Ag/AgCl in saturated KCl (SE 11, +0.197 V vs. SHE, Xylem Analytics Germany Sales GmbH & Co. KG Sensortechnik Meinsberg, Germany) and checked before each experiment. A potentiostat (SP-50, BioLogic Science Instruments, France) was utilized to conduct the pre-treatment and eCO_2RR experiments in potentiostatic mode. A peristaltic pump (ISMATEC Reglo Analog MS-4/8, Cole-Parmer GmbH, Germany) was used to constantly recirculate anolyte into the anode compartment at a rate of 1.2 mL min^{-1}. All of the pre-treatment and eCO_2RR experiments were performed in an incubator (TH 30, Edmund Bühler GmbH – 72411 Bodelshausen, Germany) at a constant temperature of 30 °C. Components of the electrochemical reactor setup and the steps of eCO_2RR to formate are illustrated in Figure 1.

eCO_2RR experiments were conducted for 1 hour at −2.2 V. 50 mM HCO_3 buffer electrolyte solution that resembles low salt conditions was used as a benchmark within the experiments when using a new batch of materials. This enabled us to compare the performance to our previous studies.[12–14,32] Composition of MM63 V minimal medium used in high salt eCO_2RR are provided in Table S1. The pH and conductivity of the modified growth media used throughout the experiments are summarized in Table S2.

Catalyst electrodeposition

Pre-treatment of the graphite electrodes before electrocatalyst deposition was applied as previously described.[13,14] The pre-treatment and electrodeposition were carried out separately before each replicate. For electrodeposition of In, a 50 mL solution of 0.1 M $InCl_3$ in 1 M acetate buffer (pH 4.5) was used in a single chamber reactor with an applied potential of −0.9 V and a defined charge of 1.7 C. Sn electrodeposition was initially conducted as previously described at electrodeposition potential and charge of −1.0 V and 1 C, respectively.[37]

Modified method and process of establishing a procedure for Sn-coated graphite were based on the results discussed in establishment of Sn-electrodeposition part of this study and Supplementary Information. Prior to each eCO_2RR experiment, the finally prepared electrodes, were washed with deionized water. Further details of the electrocatalyst coating procedures are explained in detail in Supplementary Information.

Analytical methods

Catholyte samples of 400 μL were collected before and after 1-hour eCO_2RR experiments through the sampling port with a syringe. To detect organic compounds, liquid phase analysis was performed using an HPLC (Shimadzu Scientific Instruments, USA).

Concentration of In and Sn that leached to catholyte was determined with polarograph (797 VA Computrace, Metrohm, Switzerland) equipped with a platinum wire as the counter electrode and an Ag/AgCl in saturated KCl as the reference electrode. Differential pulse (DP) mode was used with a hanging mercury drop electrode (HMDE).[58] The external In and Sn standards were calibrated in the range of 0.906 nM to 0.906 mM (four-point calibration, $R^2 = 0.99$) and 1.08 μM to 1.08 mM (four-point calibration, $R^2 = 0.99$) respectively.

The pH and conductivity were measured with a pH electrode (InLab Micro Pro, Mettler Toledo, Switzerland) and a conductivity probe (InLab 731-ISM, Mettler Toledo, Switzerland) connected to a pH/conductivity benchtop meter (S470, Mettler Toledo, Switzerland).

Gas composition of 1-hour eCO_2RR experiments were analyzed as previously described.[12] Details of the gas phase analysis procedures are explained in detail in Supplementary Information.

Data processing and calculations

Calculations for coulombic efficiency (CE) and specific rate of formate production ($r_{formate}$) are described in Supplementary Information.

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Conflict of Interests

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: electrobiorefineries · electrochemical CO_2 reduction reaction · halophilic microorganisms · microbial electrosynthesis · secondary microbial electrochemical technologies

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RESEARCH ARTICLE

Electrochemical feeding of salt-loving microorganisms: Halophilic microorganisms are promising for bioproduction from formate. Electrochemical CO_2 reduction to formate necessitates high reaction kinetics, selectivity, and overall efficiency in saline conditions. Starting from a growth media for halophiles adjusting the concentration and composition of salts and buffers in electrolyte solutions enabled higher electrochemical production of formate.

*A. Kas, Dr. P. Izadi, Prof. Dr. F. Harnisch**