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A Crucial Piece to the Puzzle for the Electrochemical CO₂ Reduction toward Formic Acid

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Sn-Based Electrocatalyst Stability: A Crucial Piece to the Puzzle for the Electrochemical CO₂ Reduction toward Formic Acid

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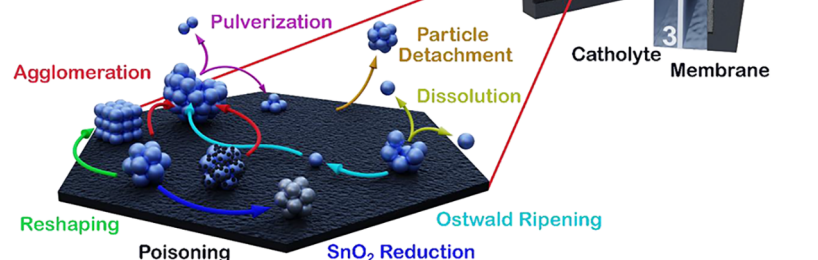
Article Recommendations



Supporting Information

Sn-based electrocatalyst degradation mechanisms

- 1 Catalyst degradation
- 2 Loss of GDE hydrophobicity, flooding, salt crystallization
- 3 Thermal, chemical and mechanical membrane degradation
- 4 Bubble formation blocking active sites



ABSTRACT: Nowadays, Sn-based electrocatalysts for the electrochemical CO₂ reduction reaction (eCO₂RR) toward formic acid have been reported to reach industrially relevant current densities and Faradaic efficiencies approaching 100%. However, electrocatalyst stability remains inadequate and appears to be a crucial piece to the puzzle, as lifetimes in the range of several thousands of hours should be reached for practical application and economic viability. Here, we provide insights into stability issues related to Sn-based electrocatalysts and electrolyzers for formic acid production. By determining the chemical and physical phenomena that occur during the electrochemical reduction reaction on the surface and bulk of Sn-based catalysts, we intend to elucidate the most common degradation mechanisms that impair long-term electrocatalytic activity of these catalysts. Moreover, highlighting the importance of correctly selected process conditions and an optimized reactor design allows us to unveil all necessary aspects for a stable Sn-based eCO₂RR toward formic acid.

Over the past decades, the electrochemical CO₂ reduction reaction (eCO₂RR) into industrially valuable products has become one of the most promising technologies to valorize anthropogenic CO₂ emission, while also providing a means of energy storage for intermittent renewable sources, such as wind and solar.^{1–3} The eCO₂RR technology benefits from the fact that it can be carried out at ambient temperature and pressure, while water and renewable electricity, from the aforementioned intermittent sources, provide a renewable feedstock.⁴ Furthermore, a variety of products, such as formic acid (HCOOH), carbon monoxide (CO), methane (CH₄), methanol (CH₃OH),

ethylene (C₂H₄) etc., can be obtained with a relatively high rate of formation,⁵ by carefully tuning the electrocatalytic cathode material, reactor configuration, and reaction conditions.^{6,7}

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According to most eCO₂RR literature and techno-economical assessments (TEAs), the eCO₂RR toward formic acid (FA), which is a two-electron process, has the potential to generate the highest revenue per mole of consumed electrons.⁸ [Note: In this paper, FA will be used to refer to both formic acid and formate, as both products can be formed during the eCO₂RR, depending on the pH.] This advantage originates from the fact that FA can be produced with high Faradaic efficiencies (FEs) on cheap and Earth-abundant metals with a high overpotential for the competing hydrogen evolution reaction (HER). Due to its strong acidic nature and reducing properties, FA is frequently used in food chemicals, pharmaceuticals, and textiles. Furthermore, FA has the potential to be used as a liquid hydrogen carrier or can be directly used in fuel cells, such as the direct formic acid fuel cell (DFAFC). However, for this process to become industrially feasible, a low-cost catalyst with excellent activity, selectivity, and stability is required.^{8–12}

Sn-based electrocatalysts have been studied extensively, due to their high selectivity toward FA, along with their low toxicity (compared to Pb, Hg, In, and Cd), non-noble nature, and ecological and inexpensive properties.¹³ A wide array of Sn-based electrocatalysts such as bulk Sn, Sn nanoparticles, Sn-based alloys and core–shell nanoparticles, Sn oxides, sulfides, and other carbon-supported Sn-based catalysts have been reported for the eCO₂RR toward formic acid.^{14–17}

Electrocatalyst stability is a crucial piece to the puzzle, as lifetimes in the range of several thousands of hours should be reached.

Currently a FE_{FA} of approximately 100%¹⁸ and current densities as high as 471 mA cm⁻² in a microfluidic flow cell electrolyzer have been achieved,¹⁹ indicating that both selectivity and productivity reach high and industrially relevant values. Furthermore, Xiang et al. recently successfully demonstrated a closed “electricity–formate–electricity” loop. Their carbon black-supported SnO₂ electrocatalyst was able to convert CO₂ to formate with a FE_{FA} of 80% at -1.43 V vs RHE, 251 mA cm⁻², and an energy efficiency (EE) of 30%, producing 0.5 M formate within 1 h. This formate solution was subsequently used as a fuel in a direct formate fuel cell (DFFC), achieving a peak power density of 92 mW cm⁻² and an EE of 30%.²⁰ Unfortunately, the stability of these state-of-the-art Sn-based electrocatalysts remains inadequate (<1000 h) and is insufficiently studied. To reduce maintenance and electrolyzer downtime due to electrocatalyst replacement (and as such lower OPEX), long-term catalyst stability is essential.²¹ The eCO₂RR toward CO is currently being tested in pilot units, since long-term stability (1200–3800 h) has already been achieved. The eCO₂RR toward formic acid is expected to also reach pilot scale once this prolonged stability has been attained. Sn-based electrocatalysts are believed to be a viable option, and electrocatalyst stability is a crucial piece to the puzzle, as lifetimes in the range of several thousands of hours should be reached.^{22,23}

■ RATIONAL ELECTROCATALYST DESIGN

In the past decades, Sn-based electrocatalysts have developed from bulk foils to rationally designed Sn-based electro-

catalysts.¹³ Even though Sn-based electrocatalysts have become more advanced in terms of morphology and composition, they have also become more prone to degradation since considerably more degradation mechanisms come into play during the eCO₂RR on these rationally designed electrocatalysts as compared to bulk Sn electrodes. Therefore, obtaining prolonged electrocatalyst stability has become even more important in order to retain the enhanced activity and selectivity attributed to these rationally designed electrocatalysts throughout long-term operation. Table S1 in the Supporting Information (SI) provides a comprehensive overview of some of the best performing Sn-based electrocatalysts for the eCO₂RR toward formic acid and their reported stability.

Looking at these state-of-the-art Sn-based electrocatalysts, only four of them have a reported stability of more than 100 h,^{24–27} while almost all of them have an excellent FE_{FA} higher than 70%. In order to select an industrially relevant Sn-based electrocatalyst for the eCO₂RR toward FA, a trade-off should be made between electrocatalyst selectivity (FE_{FA}), activity (*J*), and stability.

Wen and co-workers reported a promising and durable Bi-Sn bimetallic electrocatalyst which showed no apparent signs of degradation after 100 h. This prolonged durability has been ascribed to the strong anchoring of the Bi-Sn electrocatalyst to the carbon fabric supporting material.²⁷ A similar strategy has been reported by Kim et al., who designed a leaching resistant SnO₂/γ-Al₂O₃ electrocatalyst. In their research, they found that the strong interaction between the γ-Al₂O₃ supporting material and SnO₂ electrocatalyst attributed to retain its morphology, crystallinity, size, and electrochemical performance after 152 h of electrolysis.²⁶ Another interesting Sn-based electrocatalyst has been reported by Wu et al., to yield an excellent stability of 174 h, maintaining a FE_{FA} of 70%.²⁵ The most stable Sn-based electrocatalyst to date, to the best of our knowledge, has been reported by Yang and co-workers. Their three-compartment electrochemical formic acid cell exhibited a stable performance for more than 550 h, utilizing a Sn nanoparticle coated GDE with a FE_{FA} of 94% and a 140 mA cm⁻² activity.²⁴ While there is no obvious degradation reported for these four state-of-the-art Sn-based electrocatalysts, their stability above 1000 h remains unclear.

Most of these state-of-the-art Sn-based electrocatalysts have already been discussed extensively in other recent review articles.^{13,14,28,29} However, it should be noted that excellent electrocatalysts with a high FE_{FA}, as reported in Table S1, could not be relevant if their stability remains insufficient. In industry, electrocatalyst activity and selectivity are usually subsidiary to a prolonged electrocatalyst lifetime (stability). Furthermore, the overpotential and thus operating potential should be as low as possible in order to limit the required amount of electricity and increase the energy efficiency of the overall process.²² Finally, the electrocatalyst fabrication protocol should also be suitable for large scale application.

Despite the fact that Sn-based electrocatalysts will always be susceptible to degradation at high cathodic potentials during the eCO₂RR, rational electrocatalyst design has been shown to increase electrocatalyst lifetime. An overview of the most predominant degradation pathways (Figure 1), their causes, and possible mitigation strategies is given in the SI and summarized in Table 1.

Unfortunately, nearly all degradation pathways depicted in Figure 1 and summarized in Table 1 are considered

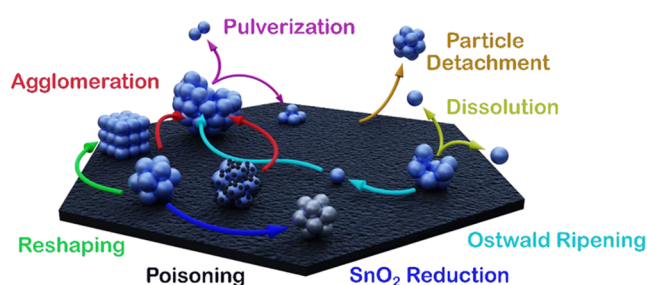


Figure 1. Overview of the most predominant degradation pathways for Sn-based electrocatalysts.

irreversible, as they bring about permanent morphological changes. The only exceptions are (partial) electrocatalyst recovery after poisoning and in situ SnO_2 reduction. Catalyst poisoning by reaction intermediates or impurities originating from the electrolyte, electrolyzer components, or CO_2 feed is partially recoverable by renewing the electrolyte solution or shortly reversing the polarity of the electrolyzer.^{30–34} The reversibility of in situ SnO_2 reduction to metallic Sn under harsh cathodic operating conditions has been studied on reduced graphene-oxide supported Sn^{4+} oxide nanoparticles ($\text{SnO}_2\text{NPs}@r\text{GO}$) (Figure 2a), by Dutta et al.³⁵ They found that SnO_2 nanoparticles, which had previously undergone complete reduction to Sn^0 , could only be partially recovered as Sn^{4+} and that their high initial selectivity was almost completely and irreversibly lost, as shown in Figure 2b.³⁵

In order to prolong electrocatalyst lifetimes, rational electrocatalyst design, to prevent or reduce catalyst degradation, will thus be of great importance. In literature, several mitigation strategies are being used and suggested,³⁶ which are discussed in more detail below.

The currently most established mitigation approach to reduce degradation mechanisms such as agglomeration, particle detachment, dissolution/leaching,³⁷ and Ostwald ripening is the particle confinement strategy.³⁸ This has also been proven in literature to some extent for Sn-based electrocatalysts.

Lei et al. reported an increased stability over 50 h for Sn quantum sheets confined in graphene, relative to 15 nm Sn nanoparticles mixed with graphene, 15 nm Sn nanoparticles, and bulk Sn which all exhibited poor stability during this

period. The confined Sn quantum sheets showed a very stable current density of 21 mA cm^{-2} at -1.8 V vs SCE , while the FE remained larger than 85%.³⁹ In order to improve electrocatalyst stability, a leaching-resistant $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ nanocatalyst was synthesized by Kim et al., and a remarkable stability over 152 h was achieved, maintaining a Faradaic efficiency of 65% toward formic acid and a current density of 21.7 mA cm^{-2} . The leaching-resistant $\text{SnO}_2/\gamma\text{-Al}_2\text{O}_3$ nanocatalyst was found to retain its morphology, crystallinity, size, and electrochemical performance after electrolysis due to the strong interaction between the electrocatalyst and its supporting material.²⁶

Recent studies^{35,40–46} indicate that a metastable oxide layer with hydroxylated structures at the interface form the active site for the selective eCO_2RR toward FA on Sn-based cathodes at reducing potentials. Therefore, in situ reduction of Sn oxides to metallic Sn is another crucial degradation pathway which should be mitigated in order for Sn-based electrocatalysts to become industrially feasible. Aside from lowering the operating potential and thus overpotential, a possible strategy to overcome this stability issue could be the co-electrolysis of CO_2 with low concentrations of oxygen (O_2) or other oxidants. He et al. revealed in their study on copper catalysts that this co-electrolysis results in an increased surface coverage of adsorbed hydroxyl species.⁴⁷ When looking at Sn-based electrocatalysts, this could be considered beneficial and possibly prevent in situ SnO_2 reduction to metallic Sn. Nonetheless, further research should be devoted to this topic to confirm this hypothesis.

Other mitigation strategies mentioned in literature include the following: (I) a modification of the electronic structure, which could prevent reaction intermediate poisoning by directly adjusting the binding energy of reaction intermediates³⁶ or result in lower overpotentials, which in turn attenuates other degradation pathways such as in situ SnO_2 reduction or pulverization. Lowering overpotentials (by means of dopants or other methods), furthermore, limits the required amount of electricity and increases the energy efficiency of the overall process. (II) Single atom fixation, which has been proven to increase electrocatalyst stability by fixing metal atoms within the support material.³⁶ Several multidentate nitrogen ligand-stabilized single-atom electrocatalysts have been reported in literature for the eCO_2RR toward CO .⁴⁸

Table 1. Overview of Major Degradation Pathways and Their Mitigation Strategies

degradation pathway	Sn-based electrocatalyst type	cause	mitigation strategy
agglomeration	nanostructures	thermodynamic driving force	particle confinement
dissolution/leaching	Sn-based electrocatalysts ^a	catholyte flow rate	particle confinement; controlling the local pH value
Ostwald ripening	nanostructures	thermodynamic driving force	particle confinement
particle detachment	nanostructures	catholyte flow rate	particle confinement
passivation/oxidation	Sn-based electrocatalysts ^a	not reported	not reported
poisoning	Sn-based electrocatalysts ^a	electrolyte impurities, gaseous pollutants in the CO_2 feed	electrolyte/ CO_2 feed purification; shortly reversing the polarity of the electrolyzer
pulverization	nanostructures	hydrogen diffusion-induced stress, operating potential	doping/lowering overpotential
reshaping	nanostructures	thermodynamic driving force	particle confinement
SnO_2 reduction	Sn oxides	operating potential	doping/lowering overpotential; controlling the local pH value

^aSn-based electrocatalysts include bulk Sn, Sn nanoparticles, Sn-based alloys and core–shell nanoparticles, Sn oxides, sulfides, and other carbon-supported Sn-based electrocatalysts.

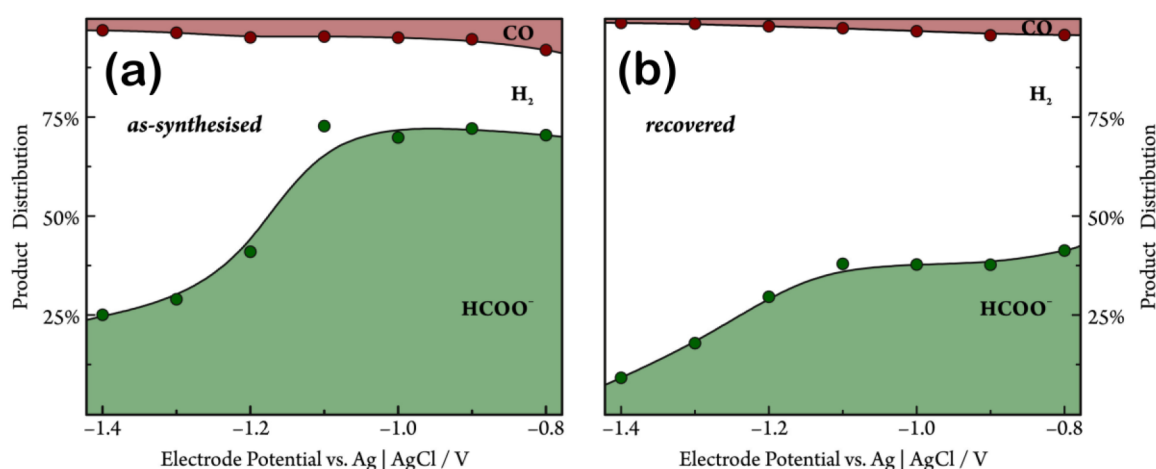


Figure 2. Product distribution of as-synthesized (a) and recovered (b) $\text{SnO}_2\text{NPs@rGO}$ electrocatalyst. Reproduced with permission from ref 35. Copyright 2018 Elsevier Ltd.

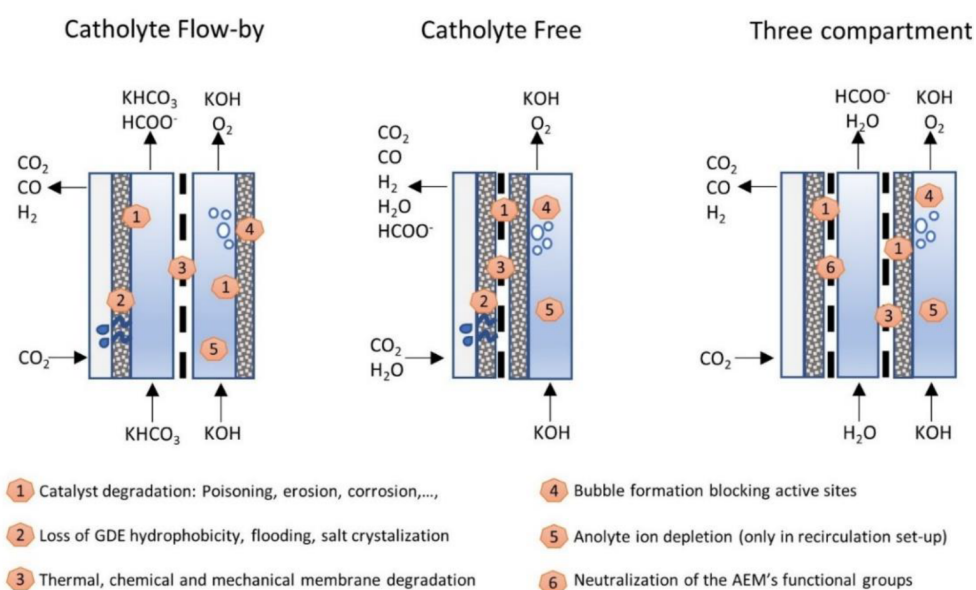


Figure 3. Degradation mechanisms of the different cell configurations of Sn based CO_2 electrolyzer.

Aside from providing a beneficial intermediate stabilization and an easy charge transfer, single-atom electrocatalysts appear to be more poisoning resistant since metallic impurities could be more easily deposited on the carbon support material rather than on the active electrocatalyst site.^{36,48}

RATIONAL REACTOR AND PROCESS DESIGN

In addition to smart catalyst design and a correct selection of process conditions, the stability of the overall process is also affected by the reactor design. In general, four components need to be considered for the achievement of a stable process, namely the gas diffusion electrode (GDE) (including cathode catalyst), membrane, anode, and electrolyte, as shown in Figure 3.

Recently, a thorough investigation on the stability of GDE's was performed by Nwabara et al. which identified four major degradation mechanism: (I) catalyst poisoning, (II) catalyst delamination, (III) loss of hydrophobicity, and (IV) formation and deposition of salt/carbonate.⁴⁹

Electrocatalyst Poisoning. A first cause for catalyst poisoning can be found in electrolyte impurities, originating from traces in the electrolyte itself or oxidation of electrolyzer components, absorbing on the catalyst surface. The absorption of these species will block active eCO_2RR sites and thereby lower the performance of the cathode. This type of degradation mechanism usually starts at the onset of the experiment, causing a gradual decrease in FE and/or current density. Additionally, the catalyst surface can be poisoned by the adsorption of reaction intermediates.³⁶ To a certain extent the process is reversible by renewing the electrolyte or shortly reversing the polarity of the electrolyzer, although the latter can also have a negative effect on the catalyst material.^{30–33} A final cause for electrocatalyst poisoning can be found in gaseous pollutions of the CO_2 feed. In their research, Luc et al. revealed the reversible nature of Sn catalyst poisoning caused by sulfur dioxide (SO_2) impurities. In the presence of 1% SO_2 , the FE_{FA} dropped because of the thermodynamically more favorable SO_2 reduction. However, contrary to Cu catalysts,

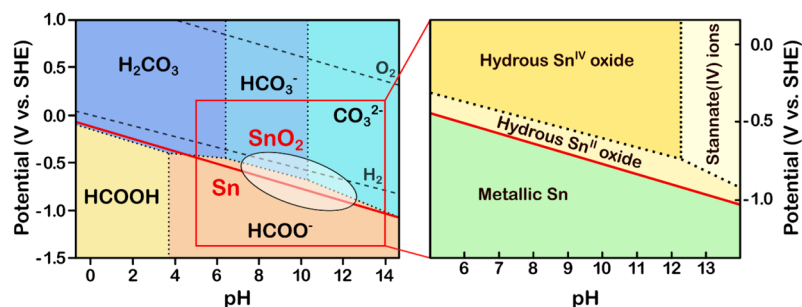


Figure 4. Combined Pourbaix diagram of Sn-water, considering the oxide phases and the carbonate–water system with the dominant carbonate species. The overlapped area highlights the conditions in which stable SnO_2 could catalyze HCOO^- from eCO_2RR . The Pourbaix diagram was redrawn from refs 35 and 57.

these SO_2 impurities caused no permanent selectivity alterations on Sn and Ag catalysts.³⁴

Electrocatalyst Delamination. The delamination of Sn particles occurs due to erosion caused by flow of catholyte across the GDE surface, resulting in loss of catalyst. This was studied using ICP-MS to determine the amount of Sn in the catholyte before and after the experiment. During these experiments a loss of 5 wt% of the Sn was observed after 6 h, accompanied by a simultaneous decrease in FE.⁵⁰ Alternatively, catholyte free electrolyzers (Figure 3) have been employed for the eCO_2RR .^{51–53} Due to the absence of catholyte in this type of electrolyzers it is assumed that erosion of Sn will be reduced to a negligible amount, however this remains to be confirmed.

Loss of Hydrophobicity, Flooding, and the Formation and Deposition of Salts. The most investigated degradation mechanisms in Sn-based electrolyzers are the loss of hydrophobicity, flooding of the GDE, and the formation and deposition of salts.^{31,49–51,54} Studies that investigated flooding in Sn based catholyte flow-by electrolyzers found that whenever a potential is applied, the hydrophobic character of the GDE is partially abolished. This phenomenon, called the electro-wetting effect, is the main cause for GDE flooding and will be more distinct when the supplied potential increases. The flooding of catholyte results in blocked pores and thereby is detrimental for the performance and stability of the GDE. However, by utilizing pressure sensors and needles valves to control the pressure difference across the GDE, it is possible to adjust the flooding's flow rate. When a negative pressure difference (i.e., when the pressure on the gas side is higher than the pressure on the catholyte side) was maintained, no flooding occurred. However, this mode of operation led to the formation of salt crystals in the pores, blocking access to the catalytically active sites and thus inhibiting the electrolyzer's stable operation. Operation at a positive pressure difference (i.e., the pressure on the catholyte side is higher than the pressure on the gas side) resulted in a stable operation of the electrolyzer (>6 h) since flooding prevented the formation of crystals. Nonetheless, the positive pressure difference allowed electro-wetting and thus GDE flooding, which ultimately (when large positive pressure difference are present) limits cell performance (*vide supra*). An optimal pressure difference could thus be found at ± 0 mbar, where the amount of flooding was minimized, yet still retaining sufficient humidity in the GDE to prevent crystallization, allowing the reactor to reach a stable (>6 h) FE_{FA} of 76% at 100 mA cm^{-2} and a final formate concentration of 11 g/L.⁵⁰

Research by Leonard et al. shows that, in addition to the electro-wetting effect, the hydrophobicity of the GDE also decreases due to the low surface tension of eCO_2RR products. Since the tendency of the organic/water mixture to wet the GDE is mainly determined by the length of the carbon chain, the risk of hydrophobicity loss will be lower when formic acid (C_1 carbon) is produced. Nonetheless the risk for GDE flooding increases at higher product concentrations, specifically for formic acid, flooding problems will occur at concentrations >50 mol% which, to this day, has not been acquired in lab experiments. However, to avoid expensive post-electrolysis purification, highly concentrated (>80 mol%) formic acid product streams are required, given that these are the desired industrial product streams, the highest reported for Sn electrolyzers being 12 mol%.^{52,55,56}

Electrolyte. Currently, aqueous electrolytes are most commonly applied in eCO_2RR due to their easy preparation, low toxicity, and easy applicability. Aqueous electrolytes can be categorized in basic, neutral, or acid conditions, and many studies have been carried out at various pH values seeking to optimize the performance of the eCO_2RR at various electrodes. As for Sn, variations in pH can directly affect the surface stability by determining the chemical state of the Sn surface, varying from Sn, SnO_2 , $\text{Sn}(\text{OH})_2$ to $\text{Sn}(\text{OH})_4$. In this sense, Lee et al. analyzed various potential versus pH combinations, considering thermodynamically stable phases of SnO_2 nanoparticles (100 nm) as shown in Figure 4.⁵⁷

Lee et al. further considered three pH conditions (8.42, 10.2, and 11.72) inside the specific range highlighted in Figure 4, to carry out measurements seeking to selectively produce formic acid. Through GC and HPLC analysis they determined that pH 11.72 resulted in the highest FE_{FA} (69.5%) for prolonged periods of testing (up to 5 h of stable reaction), on a SnO_2 nanopowder electrocatalyst. Other pH's presented a decay in activity throughout time as the bulk solution slowly became closer to neutral pH and consequently noted the reduction of SnO_2 to Sn. Therefore, when working with Sn electrodes in aqueous electrolytes, it is important to understand the direct relation of pH fluctuations and the stability of these electrocatalysts in order to ensure continuous FE's for longer periods of time.⁵⁷ Interestingly, Chiacchiarelli et al. discovered that the tendency of electrolyte to deposit on the surface of Sn-based electrodes was highly dependent on the size of cations present, noting that when replacing Na^+ for Cs^+ , deposition on the surface was severely reduced and thus increasing electrocatalyst stability by an optimized aqueous electrolyte selection.⁵⁸

Catholyte-Free Electrolyzers. In catholyte-free electrolyzers, flooding of GDE pores is less prominent simply because of the absence of a catholyte. However, since no liquid is present, the risk of salt crystallization increases. To prevent this, researchers employ humidified CO₂ to reach stable electrolyzer performance. For a Sn based electrolyzer, this was first described by Lee et al., who sparged the CO₂ with water before entering the cell. This method allowed a stable performance at 40 mA/cm² and a FE_{FA} of 90% for over 50 h, by preventing the formation of salt crystals. Furthermore, it has been shown that optimization of the amount of water in the CO₂ stream is required, as a lower water content will result in higher liquid product concentrations but increases the risk of salt deposition while an excess of water in the stream may once again result in flooding of the GDE pores.⁵²

In later research, multiple researchers investigated catholyte-free Sn electrolyzers in setups similar to the one described in Lee's paper, where the inlet CO₂ stream is sparged with H₂O by bubbling it through water.^{53,59} Alternatively, liquid water can be directly injected in the CO₂ gas stream. In this configuration, stable electrolysis can be achieved when a buildup of liquid products in the reactor is prevented, as this would increase the chances of product crossover toward the anode compartment and re-oxidation of formic acid to CO₂. By increasing the water injection flow rate, salt precipitation can be prevented.⁶⁰

■ UNIFIED STABILITY EVALUATION

So far, we highlighted the increasing importance of Sn-based electrocatalyst stability and the need for stability evaluation. This necessity for an unambiguous and standardized electrocatalyst performance and stability evaluation has also been articulated in recent literature.^{61–64} However, despite the proposal of several methods and techniques to assess stability and degradation mechanisms of electrocatalysts, a unified approach has not been implemented to this date. In our own research, we previously performed long-term (24 h) measurements to obtain an initial assessment of the electrocatalyst stability.^{60,65,66} In the following paragraphs we will discuss several well-known electrochemical evaluation methods and accelerated degradation tests that have been used for years to determine and predict the lifetime of electrocatalysts in fuel cell, water electrolyzer, and chlor-alkali electrolysis research.

Nowadays, prolonged chronoamperometric (CA) or chronopotentiometric (CP) measurements,⁶⁷ combined with ex situ characterization techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electron microscopy,⁶⁸ are becoming common practice to investigate electrocatalyst stability. However, as suggested by Birdja et al., electrocatalyst stability should preferably be reported by means of partial current density (whether or not normalized by the ECSA), for the targeted product, and not as FE, current (density), or cell potential as a function of time. The usage of partial current density as a key descriptor for electrocatalyst stability embodies the important trade-off between activity (current density) and selectivity (FE) and, furthermore, provides valuable insights into the production rate of a specific product, which is more relevant.⁶² Electrocatalyst activity, selectivity, and stability are highly dependent on the local reaction environment (local pH conditions, mass transfer, etc.),⁶⁹ and experimental parameters (duration, sampling frequency, etc.).⁶² For future eCO₂RR research, it will thus become increasingly more important to test state-of-the-art

electrocatalysts under more realistic and industrially relevant operating conditions⁶⁹ in a unified stability evaluation protocol.

Considering that long-term CA or CP measurements are very time-consuming (several days to weeks or months), accelerated degradation/durability tests (ADT) could provide a time efficient indication of electrocatalyst lifetime. However, prior to an ADT, a base stability of 48 h at >200 mA cm⁻² and a FE of >80% should be achieved. During an ADT, system durability (or part of the system) is evaluated by applying extreme conditions such as high current densities, elevated temperature or pressure, high electrolyte concentration, the introduction of CO₂ stream contaminants (N₂, NO_x, SO_x, H₂S, hydrocarbons, etc.), or potential/current cycling. ADTs have already been proven to be essential for the development of, for example, proton exchange membrane fuel cells (PEMFCs), as they enable a stability assessment of several components (such as the electrocatalyst, GDE, electrocatalyst binder, and membrane) within a short period of time.⁶⁴ By exploring ADT protocols used for other electrochemical processes such as water electrolysis, chlor-alkali electrolysis, and fuel cells, Nwabara et al. were able to validate several ADT protocols for CO₂ electrolysis.⁶⁴ In their research, two methods—(I) total charge passed and (II) electrolyte molarity—were tested. When passing the same total charge in a shorter time scale (by increasing the applied current density and thus decreasing electrolysis time), an exponential degradation rate was observed with respect to the applied current density. An increase in electrolyte molarity revealed a limiting conductivity after which cathode degradation accelerated.⁶⁴ Nevertheless, every type of electrocatalyst lifetime evaluation should be accompanied by ex situ or in situ characterization methods. In order to unravel all (Sn-based) electrocatalyst degradation mechanisms, the development and implementation of several complementary techniques, such as in situ liquid-phase transmission electron microscopy (LP-TEM),⁷⁰ operando electrochemical X-ray absorption spectroscopy (XAS) and in situ Raman spectroscopy is paramount.⁷¹

An alternative proposal for a unified stability evaluation was made by Popovic and co-workers.⁶³ Although their guidelines were mainly suggested for copper electrocatalysts, their proposed standardized tests can be extended to other electrocatalysts for the eCO₂RR. First, an initial 12–24 h electrolysis experiment with online gas product distribution (every hour) should be performed. Subsequently, start–stop conditions should be simulated by performing a 1 h electrolysis (with gas product quantification), followed by 200–1000 potential cycles from OCV to operating potential at a scan rate of 50–100 mV s⁻¹ and a final 1 h electrolysis (with gas product quantification). Both experiments should be accompanied by ex situ or in situ morphological characterizations.⁶³ To make this proposal applicable to Sn-based electrocatalysts, liquid product analysis by means of HPLC or NMR should also be performed. Finally, one could vary the method of potential cycling from triangular wave cycling to square wave cycling to increase the ADT conditions even more.

An alternative approach to perform electrocatalyst stability measurements, is to simulate electrolyzer operating conditions. Recently published gastight rotating disk electrode (RDE) setups^{72,73} can allow for the evaluation of product selectivities and (partial) current densities over prolonged measurements, while accurately controlling mass transfer to and from the surface. For membrane electrode assemblies (MEAs), the

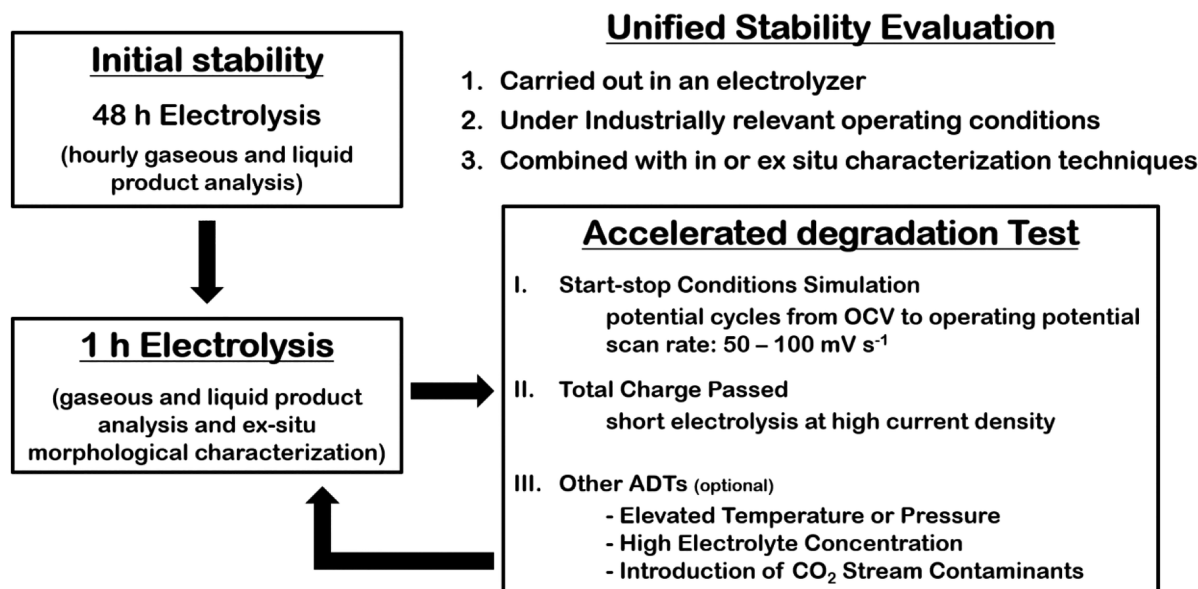


Figure 5. Unified stability evaluation protocol.

floating electrode technique can be employed to study electrode performance under high current densities.^{74,75} These techniques have been successfully used in the past to study the stability of other electrocatalytic reactions.

In addition to the above suggested approaches, the calculation of a stability number (S-number) allows for an easy quantification and comparison of electrocatalyst stability.⁷⁶ In the past, two similar metrics have independently been proposed for electrocatalyst benchmarking. Kim et al.⁷⁷ proposed an activity–stability factor (ASF), while Geiger and co-workers⁷⁶ suggested the stability number (S-number). Although both metrics were first used to describe the stability of iridium-based electrocatalysts during the oxygen evolution reaction (OER), they can easily be expanded to the eCO₂RR. For the OER on iridium-based electrocatalysts, the S-number is defined as the ratio between the amount of evolved oxygen and the amount of iridium lost into the electrolyte. Applied to the eCO₂RR toward formic acid on a Sn-based electrocatalysts, the S-number can be defined as the amount of produced formic acid molecules per Sn atoms lost into the electrolyte, making it an excellent surface area or catalyst loading independent measure, complementary to the previously discussed techniques as it does not account for all possible degradation mechanisms.

As illustrated above, several excellent figures of merit, techniques, and even standardized stability evaluation protocols, all with their own advantages and disadvantages, have already been proposed. However, in order to bring the electrocatalytic CO₂ reduction toward formic acid on Sn-based electrocatalysts toward an industrial feasibility, we propose a combination of these stability experiments, carried out in an electrolyzer under industrially relevant operating conditions, as depicted in Figure 5. Initially, a 48 h stability measurement should be performed with hourly gaseous and liquid product analysis, in order to benchmark the base (Sn-based) electrocatalyst performance (FE%, partial current density, etc.) and stability. Subsequently, several ADT protocols should be executed with a 1 h electrolysis (with gaseous and liquid product quantification) and an ex situ morphological characterization, before and after each ADT. Hereby a

benchmark electrocatalyst performance and characterization are obtained prior to subjecting the electrocatalyst to an ADT, while the post-ADT 1 h electrolysis and ex situ morphological characterization provide valuable information regarding the electrocatalyst degradation and major degradation pathways. (I) Start–stop conditions should be simulated using potential cycles from OCV to operating potential at a scan rate of 50–100 mV s⁻¹, as the eCO₂RR would preferably be powered by intermittent renewable energy sources. Furthermore, (II) a “total charge passed” ADT should be performed, multiplying the current density (as obtained during the 48 h stability measurement) in order to pass the same charge in a shorter time scale, while applying more stress to all components of the electrochemical system in order to identify their durability. Other ADTs such as elevated temperature or pressure, high electrolyte concentration, and the introduction of CO₂ stream contaminants are excellent additions to evaluate state-of-the-art Sn-based electrocatalysts under more realistic and industrially relevant operating conditions and are required once targeting pilot scale electrolyzers.

CONCLUSIONS AND OUTLOOK

Over the past decades, the electrochemical CO₂ reduction reaction (eCO₂RR) forming industrially valuable products has become one of the most promising technologies to valorize anthropogenic CO₂ emissions. According to most eCO₂RR literature and techno-economical assessments (TEAs), the eCO₂RR toward formic acid (FA) has the potential to generate the highest revenue per mole of consumed electrons. Sn-based electrocatalysts for the eCO₂RR toward FA have been studied extensively, due to their high FA selectivity, along with their low toxicity, non-noble, ecological, and inexpensive properties.

Nowadays, Sn-based electrocatalysts have been reported to reach a FE_{FA} approaching 100%. Although the reported state-of-the-art stability is still inadequate (2–550 h), industrially relevant current densities (>200 mA cm⁻²) have already been achieved, and Sn-based electrocatalysts are believed to be a viable option as proof of concept closed “electricity–formate–electricity” loops are currently being demonstrated in literature, reaching an energy efficiency of 30%. Electrocatalyst

stability appears to be a crucial piece to the puzzle as lifetimes in the range of several thousands of hours should be reached. Nevertheless, the eCO₂RR toward FA is expected to reach pilot scale, in the coming years, once this prolonged stability has been attained.

In the search for an industrial electrocatalyst, rational Sn-based electrocatalyst design has moved from bulk Sn to advanced nanostructures such as nanoparticles, alloys, core-shell nanoparticles, oxides, sulfides, etc. While this rational design has proven to be beneficial in terms of selectivity (FE) and activity (current density), it has also introduced a large array of degradation pathways.

A continuation of this rational electrocatalyst design, utilizing several mitigation strategies could prolong Sn-based electrocatalyst stability to industrially relevant lifetimes.

Furthermore, the need for an adequate stability evaluation and unified stability testing protocol has become higher than ever if we want to transpose our research from a laboratory environment to an industrial scale. In recent literature several initial attempts have been made at proposing a standardized stability evaluation protocol. However, needless to say, electrocatalyst performance (activity, selectivity, and stability) is highly dependent on the local reaction environment (local pH conditions, mass transfer, etc.), which in turn is influenced by the reactor design (configuration, GDE, membrane, anode, electrolyte, etc.) and experimental parameters (duration, sampling frequency, etc.). When assessing (Sn-based) electrocatalyst stability, one should thus consider the entirety of the system (electrolyzer design/configuration, GDE including cathode electrocatalyst, membrane, anode, and electrolyte) and not only focus on optimization of the Sn-based electrocatalyst, as instability could be introduced by components other than the Sn-based electrocatalyst.

In order to bring the electrocatalytic CO₂ reduction toward FA on Sn-based electrocatalysts toward an industrial feasibility, future research should focus on an adequate stability evaluation by means of the discussed metrics, techniques, and protocols. Excellent Sn-based electrocatalysts and CO₂ electrolyzers are currently being designed by the scientific community. Unfortunately, a crucial piece of the puzzle has been unintentionally neglected, and both Sn-based electrocatalysts and electrolyzers are being optimized side by side, potentially missing out on the joint optimum.

The need for an adequate stability evaluation and unified stability testing protocol has become higher than ever if we want to transpose our research from a laboratory environment to an industrial scale.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.1c02049>.

Comprehensive overview of some of the best-performing Sn-based electrocatalysts for the eCO₂RR toward formic acid (Table S1) and their reported stability (PDF)

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