Engineering Sn-based catalytic materials for efficient 
electrochemical CO$_2$ reduction to formate

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The electroreduction of CO$_2$ provides a promising avenue to use renewable electricity for 
the sustainable production of chemicals and fuels. In particular, formate is attractive as a 
liquid hydrogen carrier or used directly in a fuel cell to generate electricity on demand. Sn-
based catalysts have emerged as promising catalysts, however key issues such as how to 
reduce overpotential, enhance selectivity and maximize long-term stability are still yet to 
be resolved. In this minireview, we will highlight recent key advances in developing Sn-
based catalysts, covering experimental and computational efforts on this front. Intriguingly, 
among the various strategies employed, we find that modifying the Sn oxidation state 
towards electron deficiency has been most effective. Finally, we also provide a perspective 
and outlook on future research and development on these Sn-based catalysts.
With an increase in global population coupled by a similar trend in energy consumption, carbon dioxide emissions have increased to levels that are 47% above pre-industrial levels.\(^1\) This rise in carbon dioxide concentration leads to negative environmental consequences such as global warming and climate change. The consequences and potential irreversibility have brought increased attention and urgency to abate and possibly revert the situation through carbon capture, storage and conversion.

Among them, electrochemical conversion of CO\(_2\) to chemicals allows the carbon cycle to be closed, mitigating accumulation of CO\(_2\) while sustainably producing commodity chemicals using renewable electricity.\(^2\) Formic acid is an attractive C\(_1\) product that has wide ranging applications such as a promising liquid H\(_2\) energy carrier due to its high energy density of 1.77 kWh/L, which is comparable to commercial high pressure hydrogen tanks. Furthermore, it has the added advantage of being non-toxic and has low flammability.\(^3\) Alternatively, formic acid may be also used directly in a fuel cell to generate electricity on demand.

To reduce the thermodynamically stable CO\(_2\), catalysts are needed to increase the kinetics of the electrochemical reduction reaction and achieve an appreciable yield. Most of the catalytic materials studied to date can be divided into 1) metallic such as Au,\(^4-5\) Ag,\(^6-7\) Pd,\(^8-9\) Pt,\(^10\) Zn,\(^11-12\) Cu,\(^13-15\) Ni,\(^16-17\) Fe,\(^18\) Sn,\(^19-20\) In,\(^21-22\) Bi,\(^23\) and alloys which include a combination of 2 or more of these metals,\(^24-33\) 2) non-metallics such as MoS\(_2,\)^34 carbon compounds and its derivatives such as N-doped carbon and carbon nanofibers\(^35-37\) and 3) molecular catalysts.\(^38-39\)

Among these materials, Sn is an attractive metal for CO\(_2\) reduction due to its relatively low cost compared to noble metals and its environmental friendliness due to its abundance and non-toxic nature. Sn catalysts have displayed high Faradaic efficiencies and selectivity for CO\(_2\).
conversion to formate and exhibit performance tunability through morphology and nanostructure engineering, doping and alloying.\textsuperscript{[40-47]} Product tunability to CO has also been demonstrated with similar strategies mentioned above.\textsuperscript{[48-50]} Despite these promising characteristics, Sn is limited by its low electronic conductivity and low formate selectivity at low overpotentials due to the dominance of the hydrogen evolution reaction (HER).

While there are many other excellent reviews covering the progress of Sn-based electrodes for CO\textsubscript{2} reduction,\textsuperscript{[51-54]} here we will focus on developments presented in the angle of the electronic structure of Sn. Our emphasis will be to highlight the 2 main routes of tuning the Sn electronic structure (making Sn electron-rich vs electron-deficient) and the different intermediates they stabilize. Finally, through summarizing and evaluating the existing work on the 2 routes taken, we will present perspectives for future work on this aspect.

**DFT calculations on Sn-based catalysts for CO\textsubscript{2} reduction**

Formate is the most observed product for Sn-based catalysts when used for electrochemical CO\textsubscript{2} reduction. This has been explored since its first observation by Hori et al. in 1994 where a Faradaic efficiency (FE) of 88% for formate was observed using metallic Sn at an applied potential of -1.48 vs NHE.\textsuperscript{[55]} Since then, many other works on Sn catalysts have emerged, targeting on improving its catalytic performance (selectivity and current density at low overpotentials), understanding the nature of its high selectivity towards formate and more recently, tuning its selectivity towards other CO\textsubscript{2} reduction products.

Most theoretical studies have suggested that CO\textsubscript{2} reduction to formate on Sn proceeds through the *OCHO intermediate. Yoo et al performed DFT calculations on 27 different metal surfaces and established that the free energies of *COOH and H* has a strong linear relationship while *OCHO does not show a prominent dependence (Fig. 1a).\textsuperscript{[56]} This suggests
that the conversion of CO$_2$ to HCOOH is unlikely to be through the *COOH intermediate since tuning of *COOH binding energy will also result in a shift in H* binding energy. This shift will cause an increase in HER current density, which competes with formate production.

**Figure 1**: (a) Plot of free energies of COOH* and H* relative to gas phases of H$_2$ and CO$_2$ for different transition metal (blue) and non-transition metal catalysts (red). The blue line fits the transition metal catalysts to a linear fit.$^{[56]}$ Reproduced with permission from Ref. 56. Copyright 2016 Wiley-VCH. (b) Volcano plot of formate partial current density ($J_{\text{COOH}}$) vs *OCHO binding energy at applied potential of -0.9 V$_{\text{RHE}}$.$^{[57]}$ Reproduced with permission from Ref. 57. Copyright 2017 American Chemical Society.

A separate study by Feaster et al. using a combination of experiments and DFT calculations on various transition metal catalysts, found a clear volcano trend between *OCHO binding energy and its partial current density (Fig. 1b) while *COOH does not show such a trend.$^{[57]}$ Furthermore, a large difference in HCOO$^-$ current density is observed for different metal catalysts with similar *COOH binding energy. This gives support to *OCHO as the intermediate for HCOO$^-$ production. Sn is found to be at the top of the volcano plot with optimal *OCHO binding energy, supporting its experimentally observed high selectivity towards HCOO$^-$.}$^{[57]}$
However, as noted by Yang et al., most of the DFT calculations in the literature are done on metallic Sn and may not be reflective of actual reaction conditions.\cite{52} Sn oxidizes rapidly in air to form SnO and SnO$_2$\cite{58} and metallic Sn is found to be only active for HER due to its poor stabilization of CO$_2$ intermediates.\cite{55,59} Instead, a top layer of SnO$_x$ was found to be required to stabilize the CO$_2$- free radical to enable selectivity towards formate. Hence, follow-up DFT calculations on the binding energy of OCHO$^*$ on such oxide surfaces are needed to clarify whether the actual activity of Sn arises from metallic Sn or an oxidized form of Sn.

**Operando studies of Sn-based catalysts for CO$_2$ reduction**

![Mechanism of electrochemical CO$_2$ reduction to formate on Sn/SnO$_x$ as proposed by Baruch et al.][]{60} Reproduced with permission from Ref. 60. Copyright 2015 American Chemical Society.
As discussed in the previous section, both experimental and DFT calculations found that the SnO$_x$ layer is the active catalyst site for CO$_2$-to-formate conversion. Baruch et al. investigated this using attenuated total reflectance infrared spectroscopy on Sn$_6$O$_4$(OH)$_4$ and SnO$_2$ nanoparticles and discovered that SnO$_2$ is reduced to Sn$^{II}$ oxide/oxyhydroxide at potentials more negative at potentials of -1.4 V$_{RHE}$ with a thicker steady state oxide/oxyhydroxide thickness at more negative potentials and the active species for CO$_2$ reduction is Sn$^{II}$.\textsuperscript{[60]} The CO$_2$ reaction mechanism is proposed to be firstly a reduction of SnO$_2$ to Sn$^{II}$ oxyhydroxide followed by a reaction with CO$_2$ to form a surface carbonate species (Fig. 2). This Sn carbonate forms formate upon transfer of a proton and 2 electrons.

Although the operating potentials for CO$_2$ reduction are thermodynamically unstable for Sn oxides, metastable hydrous Sn oxides are discovered experimentally to exist on the surface of Sn.\textsuperscript{[60-62]} Multiple operando studies have concluded that the practical stability of SnO$_2$ after taking into account kinetics is well beyond the thermodynamic stability window predicted by the Pourbaix diagram.\textsuperscript{[61-63]} A potential of -1.25 V$_{Ag/AgCl}$ will cause SnO$_x$ to begin reducing to metallic tin for an electrolyte of pH 8.5 and this potential increases when an electrolyte of higher pH is utilized.\textsuperscript{[62]} However, at moderately cathodic potentials, SnO$_2$ is partially reduced (Sn$^0$ or Sn$^{2+}$) and the oxide layer remains stable even after prolonged electrolysis.\textsuperscript{[62]} The potential of maximum formate FE is shown experimentally by Dutta et al. to occur where metallic Sn is predicted thermodynamically to exist.

In a separate study, Dutta et al. utilized \textit{in-situ} X-ray absorption spectroscopy and Raman spectroscopy to investigate Sn$^{IV}$ nanoparticles during CO$_2$ electroreduction and confirms that the highest FE for formate production occurs only when Sn$^{IV}$ is reduced/partially reduced to a mixed oxidation state of SnO$_x$ (1 < x <2).\textsuperscript{[61]} When the applied potential exceeds -1.5 V$_{Ag/AgCl}$...
full reduction of SnO$_2$ to metallic Sn occurs and the selectivity towards formate decreases rapidly. This reduction of SnO$_2$ to SnO$_x$ or even metallic Sn was recovered by applying an anodic potential of -0.25V$_{Ag/AgCl}$ for about 150s. However, morphology changes induced by electrochemical reduction was unable to be recovered and results in an irreversible change in catalytic activity. The optimum thickness of this SnO$_x$ layer for formate production was found to be about 3.5nm, beyond which HER will dominate.$^{[64]}$

**Tuning Sn to be electron-deficient**

Tuning Sn to be more electron-deficient has shown to be able to enhance the FE of formate production through stabilization of OCHO* intermediate, thereby reducing the energy of formation. Alloying, doping, introducing uncoordinated Sn sites and harnessing catalyst-support interactions are commonly utilized to promote Sn electron transfer, causing it to become electron-deficient.

**Alloying/ doping**

![Figure 3](image)

*Figure 3: (a) Faradaic efficiencies of Sn, CuSn, CuSn$_3$ and Cu with respect to applied potential done in a 0.1 M KHCO$_3$ pH 6.8 electrolyte.$^{[65]}$ Reproduced with permission from Ref. 65. Copyright 2019 Springer Nature. (b) Faradaic efficiencies of Pd$_x$Sn/C with different Pd/Sn ratios*
Alloying is able to tune the electronic bulk conductivity, binding strength of intermediates and surface electronic structure. Among the different metals utilized for doping and alloying, Cu and Pd shows the most promise in lower the overpotential required for formate production while retaining high FE (>90%).

Zheng et al. calculated free energy diagrams for Sn, CuSn, CuSn$_3$ and Cu and found that formate selectivity is greatly enhanced when Cu is alloyed with Sn with CuSn$_3$ having the least CO and HER activity (Fig. 3a). This improvement in selectivity is due to the electron transfer from Sn to Cu leaving Sn to be more electropositive, which weakens the binding of COOH*, H* and OCHO*. Subsequent preparation of CuSn$_3$ yielded a formate FE of 95% at a potential applied of -0.5 $V_{RHE}$.

Bi doping is found to stabilize the Sn$^{2+}$ state in SnO leading to an increased stability and introduced an additional electronic state in SnO through hybridization between Bi 6s and O 2s and 2p orbitals which increases the adsorption of *OCHO on SnO (001). Yang et al. also reported on Bi doping on SnO$_x$ nanoshells which promotes charge transfer between Sn and Bi, reducing activity of SnO$_x$ towards CO and H$_2$ while enhancing formate selectivity. This results in the Sn$_{0.8}$Bi$_{0.2}$@Bi-SnO$_x$ catalyst being able to produce formate at low applied potentials of -0.67 $V_{RHE}$. Wen et al. synthesized Sn nanosheets with Bi nanoparticles and found that the transfer of electrons from Sn to Bi leads to upshifting of Sn p and d orbitals from the fermi level, better stabilizing the HCOO* intermediate. The optimized Bi-Sn catalyst achieved a maximum formate FE of 96% at -1.14 V vs RHE.
Pd$_x$Sn nanoparticles of sizes 1-5nm with different values of x was fabricated by Bai et al. on activated carbon and is able to manipulate the proportion of high oxidation state Pd$^{2+}$ and Sn$^{2+}$ by controlling the amount of Pd incorporated.[66] When the ratios of Pd and Sn are similar (i.e. x = 1), the Pd$^0$/Pd$^{2+}$ ratio is at a minimum and this allows for the highest amount of CO$_2$ desorption. This PdSn/C catalyst is able to achieve 99% FE for formate production with only -0.43 V$_{RHE}$ of applied potential (Fig. 3b). The high selectivity towards formate is attributed to the low ratio of Pd$^0$/Pd$^{2+}$ since only PdSnO$_2$ is favourable for HC$_{OO}$* or HCOOH* formation.

Ni-N$_4$ was introduced by Xie et al. unto Sn single atom catalysts (NiSn-APC) on a hierarchical integrated electrode to promote electron delocalization from Sn atom.[70] This facilitates CO$_2$ adsorption and reduces the energy barrier for the transformation of CO$_2$ to *OCHO resulting in a FE of 86.1% compared to 70.4% of undoped Sn-single atom catalyst at -0.82 V$_{RHE}$.

A volcano correlation between Sn concentration and the formate FE was discovered by Luc et al. when AgSn bimetallic core with an ultrathin partially oxidized SnO$_x$ surface shell with different Ag/Sn ratios was investigated.[71] A higher Sn concentration leads to increased stabilization of the OCHO* intermediate caused by SnO lattice expansion. However, formate FE decreases when Sn concentration is too high due to the loss in electrical conductivity through the thickness increase of the surface SnO$_x$ shell.

**Uncoordinated Sn sites (for SnS and SnS$_2$)**

Zheng et al. performed DFT calculations on Gibbs free energy of formation ($\Delta G_{formation}$) for HCOO* and *COOH on Sn(S) with respect to sulphur content and found for low sulphur doping, $\Delta G_{formation}$ for HCOO* is reduced significantly.[72] A subsequent electrochemical reduction of SnS deposited by atomic layer deposition (ALD) was conducted to partially remove sulphur from SnS. Through introduction of these undercoordinated S sites, oxidation
state of Sn is increased and results in a formate FE of 93% at an applied potential of -0.75 V vs. RHE with a current density of 55 mA cm\(^{-2}\).\(^7\) Cheng et al. injected nitrogen into the surface of SnS\(_2\) to increase the number of active sites (through introduction of undercoordinated Sn and defect sites) and induce a partial positive charge on Sn\(^{6+}\).\(^7\) This stabilizes the CO\(_2^*\) and OCHO\(^*\) intermediate which results in 14 times higher rate of formate production when compared to pristine SnS\(_2\).

Figure 4: Linear sweep voltammetric curves of N-doped graphene, Single-atom Sn\(^{6+}\) on graphene, Single-atom Sn\(^{6+}\) on N-doped graphene done in a 0.25 M KHCO\(_3\) pH 7.1 electrolyte. Corresponding formate faradaic efficiencies for 4h for the respective samples. Inset shows amplified regions of Faradaic efficiency graph.\(^7\) Reproduced with permission from Ref. 74. Copyright 2019 Wiley-VCH.

Catalyst-support interactions

Interaction of the metal cation with supports have shown to promote CO\(_2\) reduction and have been demonstrated for other metal catalysts such as Ni.\(^7\) Zu et al. harnessed the strong bonding between Sn and the N-doped graphene support to promote delocalization of electrons and cause Sn to be more positively charged.\(^7\) This allows CO\(_2^*-\) free radical and HCOO\(^-\) to be stabilized and facilitates activation of CO\(_2\) and its subsequent protonation. The
N-doped graphene support also helps weaken the bond strength between Sn and HCOO\(^{-}\), allowing formate desorption to occur more favourably. This results in a low onset potential of 60 mV for formate production and a maximum FE of 74.3% \(\pm 1.6\) V vs. SCE (Fig. 4).

**Tuning Sn to be more electron-rich**

Tuning Sn to be more electron-rich on the other hand improves the initial stage of CO\(_2\) reduction by promoting adsorption of CO\(_2\) and CO\(_2^\cdot\). The strategies utilized to increase the electronegativity on Sn catalyst involve manipulating surface stoichiometry for vacancy creation, doping of other metal cations and inducing metal support interactions.

*Figure 5: Electrochemical performances of flame spray pyrolysis SnO\(_2\) with different feed rates of (3, 5, 7 mL/min) in 0.1 M KHCO\(_3\) pH 6.8 electrolyte. (a) Linear sweep voltammetry at scan rate of 5 mV s\(^{-1}\) (b) Faradaic efficiency of H\(_2\) vs applied potential. (c) Faradaic efficiency of CO*
Uncoordinated Sn sites (Sn and SnO₂)

Daiyan et al. prepared SnO₂ nanoparticles using flame spray pyrolysis and manipulated the concentration of oxygen hole centres and surface area by tuning the precursor feed rate due to incomplete combustion (Fig 5). These oxygen hole centres arise from the cleavage of the Sn-O-Sn or the Sn-OH links, which results in additional electrons that could be trapped in the vacancies or donated to adjacent metal sites. This results in an electron-rich catalyst surface which promotes CO₂ adsorption and lowers activation energy for the subsequent CO₂ reduction. Lei et al. confined Sn quantum sheets in graphene which lowers the Sn-Sn coordination numbers and increases the degree of disorder, resulting in dangling bonds which helps stabilize the carbon dioxide radical anion. Together with the increased conductivity from graphene, which helps electron transfer from carbon dioxide to its radical, the confined Sn quantum sheets attained a maximum formate FE of 89% at an applied potential of -1.8 V vs SCE.
Figure 6: (a) Plot of HCOO\(^-\) Faradaic efficiency and HCOO\(^-\) partial current density vs Boron content done in a 1 M KOH electrolyte.\(^{[78]}\) Reproduced with permission from Ref. 78. Copyright 2020 IOP Publishing. (b) Faradaic efficiency of HCOOH on Sn/Graphitic Carbon Nitride with different NaBH\(_4\) solution concentration (0.05M, 0.1M and 0.2M) vs applied potential done in a 0.1 M KHCO\(_3\) pH 6.8 electrolyte.\(^{[79]}\) Reproduced with permission from Ref. 79. Copyright 2019 Wiley-VCH.

Alloying/doping

Doping is able to introduce defect states (such as introducing oxygen vacancies), which increases electron transfer and suppress HER and CO production. Li et al. found that doping B into SnO\(_x\) is able to decrease the valence state of Sn\(^{2+}\) with increasing B content, due to Sn-B bond formation.\(^{[78]}\) An increase in HCOO\(^-\) FE from 40% (for pristine SnO\(_x\)) to 91% was achieved at an applied potential of -0.72 V\(_{\text{RHE}}\) for the optimized B content of 2.2% (Fig. 6a).

Mn doping into SnO\(_2\) increases the amount of oxygen vacancies and elongates the Sn-O bond which helps inhibit CO and HER production while increasing electronic conductivity and transport. This improves the formate FE from 61% to 85% with a corresponding current
density increase from 11 mA cm\(^{-2}\) to 21.2 mA cm\(^{-2}\) at an applied potential of \(-1.03 \text{ V}_{\text{RHE}}\) (for Mn-doped SnO\(_2\)) compared to \(-1.05 \text{ V}_{\text{RHE}}\) (for pristine SnO\(_2\)).\(^{[80]}\)

**Catalyst-support interactions**

Yuan et al. deposited SnO\(_2\) nanoparticles on 4 different doped nanoporous carbon supports (undoped, N-doped, S-doped, and N,S codoped) to investigate the different Sn support interactions.\(^{[81]}\) The metal supports induce a systematic Sn 3d binding energy shift towards the lower energies in the order of S-doped > N-doped > N,S codoped, suggesting that N,S codoped nanoporous carbon support has the largest metal oxide-support interaction with Sn having the highest electronegativity. The Sn deposited on N,S codoped nanoporous carbon support has the highest formate FE of 94.4% at \(-1.15 \text{ V vs RHE}\) and a formate partial current density of 56 mA cm\(^{-2}\). This enhanced performance is attributed to the negatively charged SnO\(_2\) surface which helps stabilize \(\text{CO}_2^-\) intermediate. Tian et al. fabricated Sn on graphitic carbon nitride and achieved a formate FE of 96% at \(-0.9 \text{ V}_{\text{RHE}}\) (Fig. 6b).\(^{[79]}\) This is achieved through the charge transfer from N in the support to Sn, resulting in an electron-rich Sn which promotes adsorption and activation of \(\text{CO}_2\).

**Other strategies**
Figure 7: (a) Faradaic efficiencies of C products over ultrathin SnO$_2$ quantum wires with respect to applied potential done in a 0.1 M KHCO$_3$ electrolyte.$^{[82]}$ Reproduced with permission from Ref. 82. Copyright 2019 Wiley-VCH. (b) Plot of current density (black line) and Faradaic efficiency (symbols) with respect to time for Sn porous nanowires done in a 0.1 M KHCO$_3$ pH 6.8 electrolyte.$^{[83]}$ Reproduced with permission from Ref. 83. Copyright 2017 Wiley-VCH.

Apart from tuning the electronic structure of Sn, this section discusses the other strategies that have been employed on Sn based catalysts to boost formate production. These strategies can be broadly divided into 5 strategies: Exposing active sites, catalyst nanoparticle size and loading and support pore size, addition of functional groups, bimetallic and tuning Sn oxidation states.

**Exposing active sites of catalysts**

Grain boundaries contain active sites for CO$_2$ reduction and exposing a higher surface concentration can boost the CO$_2$ reduction activity. Liu et al. fabricated SnO$_2$ quantum wires made up of individual quantum dots with grain boundaries exposed on the surface and compared them to SnO$_2$ nanoparticles of same size.$^{[82]}$ The exposed grain boundaries from
the quantum wires enhances the FE towards HCOOH formation from 61.4% of pristine SnO$_2$ nanoparticles to 87.3% at an applied potential of -1.156 V$_{RHE}$. This grain boundary enhancement is also observed by other works when porous SnO$_2$ nanofibres and nanowires are compared with SnO$_2$ nanoparticles.$^{[42, 83]}$ In a separate work on Cu-Sn bimetallic alloy, Ye et al. found that the (211) stepped surface weakens *E$_{COOH}$, resulting in a higher COOH adsorption affinity, which results in a boost in formate selectivity.$^{[84]}$

**Catalyst nanoparticle sizes and loading and support pore size**

Nanoparticle sizes of Sn based catalyst can be optimized to improve CO$_2$ reduction intermediates binding affinity. Zhang et al. investigated SnO$_2$ nanoparticles of different sizes loaded on glassy carbon (3nm, 5nm, 10nm, 200nm and SnO$_2$ foil) and found that FE for formate at an applied potential of -1.8 V increases from 60% for 3nm to a maximum of 80% at 5nm and decreases subsequently with further increase of size.$^{[85]}$ A separate study on Sn loading and particle size reveals that 0.1 mg Sn cm$^{-2}$ of 150 nm particles on glassy carbon support gives the best activity.$^{[86]}$ Loadings that are too high will result in agglomeration, decreasing the total active surface area. He et al. fabricated Sn supported on porous carbon supports and investigated the influence of pore size on the formate yield.$^{[87]}$ Micropores (pores < 2nm) is found to inhibit proton transfer and suppress HER while macropores (pore > 1 um) promotes mass and charge transport.
294 Figure 8: (a) Faradaic efficiency of HCOO⁻ for SnOₓ-multiwalled carbon nanotubes with different functional groups (COOH, NH₂, OH and pristine) under different applied potentials in CO₂ saturated 0.5 M KHCO₃ electrolyte.[88] Reproduced with permission from Ref. 88. Copyright 2019 Wiley-VCH. (b) Faradaic efficiency of HCOO⁻ for Sn deposited on different substrates (Pt, In, Sn and Cu) under different applied potentials in CO₂ saturated 0.5 M NaHCO₃ electrolyte.[89] Reproduced with permission from Ref. 89. Copyright 2018 Royal Society of Chemistry.

Addition of functional groups on catalyst surface

SnOₓ can be functionalized by with functional groups to tune chemisorption ability and surface energy. Zhang et al. investigated different functional groups (NH₂, OH and COOH) on SnOₓ nanosheets anchored on carbon nanotubes and found that functionalization with COOH provides the highest formate faradic efficiency while NH₂ gives the best CO FE.[88] In a similar strategy, Kuang et al. coupled SnO₂ with organic carbon, forming Sn-O-C linkages which enhances the adsorption and activation of CO₂, increasing formate selectivity.[90] In a first report on non-alkyl ligands, Wang et al. compared pyrazole ligands and Cl⁻ ions against
classical alkyl ligands and discovered that Sn₄Ti₆ functionalized by pyrazole and Cl⁻ have higher CO₂ reduction activity.²¹

Bimetallic systems

Alloying Sn with other metals have shown to suppress HER reaction and increase the selectivity towards C products. Alloying with Cu is most popular and have demonstrated consistent success in suppressing HER.¹⁰, ⁶⁵, ⁸⁴, ⁹² Besides alloying, depositing Sn on Cu substrates have also demonstrated similar HER suppression.²³⁻²⁴ Zhang et al. electrodeposited dendritic Sn on different substrates (Pt, Cu, Sn and In) and found Cu substrate provided the best selectivity towards formate.²⁵ The reason for the substrate dependence is determined to be due to the substrate HER activity which affects the local pH.

Sn oxidation states

A combination of Sn oxidations states (0, 2+ and 4+) have shown to be able to enhance formate selectivity.²⁶⁻²⁷ Rabiee et al. electrodeposited Sn on porous Cu hollow fibres and found that Cu is able to optimize the Sn²⁺ vs Sn⁴⁺ ratios through electron donation between Cu and Sn.²⁸ Sn with the highest Sn²⁺/Sn⁴⁺ ratio achieved a maximum formate FE of 78% at -1.2 V_RHE. A similar study by Li et al. reported a coraline structure of SnO₂/SnO and achieved the highest formate FE of 87.1% at applied potential of -1.6 V_RHE through optimizing the ratio of Sn⁴⁺/Sn²⁺.²⁹ In a first report of triple Sn oxidation state stack, Wu et al. investigates multivalent Sn in a Sn/SnO/SnO₂ configuration and found an enhanced formate FE (89.6% at -0.9 V_RHE) compared to SnO₂ and SnO/SnO₂.³⁰ Metallic Sn promotes CO₂ chemisorption, stabilizes CO₂ intermediates by regulating the electronic structure of SnOₓ and increases conductivity while combination of SnO/SnOₓ provides better HCOO⁺ adsorption. Li et al. compared SnO₂ nanosheets and Sn catalysts and found that SnO₂ suppresses CO and H₂
formation by increasing their free energy gaps of the potential limiting step, thus increasing selectivity towards formate.\cite{99}

Table 1: A summary of various strategies that have been employed for Sn-based catalysts to promote CO$_2$ reduction to formate. The table is classified according to material used, applied potential ($V_{\text{app}}$), Faradaic Efficiency (FE), Current density ($J_{\text{sc}}$), Electrolyte and reference (Ref).

<table>
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<th>Material</th>
<th>$V_{\text{app}}$</th>
<th>FE</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>Electrolyte</th>
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<td>SnO$_2$ quantum wires</td>
<td>-1.156 $V_{\text{RHE}}$</td>
<td>87.3</td>
<td>13.7</td>
<td>0.1 M KHCO$_3$</td>
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<td>1 D SnO$_2$ (wire in tube)</td>
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<td>63</td>
<td>~12</td>
<td>0.1 M KHCO$_3$ (pH 6.8)</td>
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<td>Electrochemically reduced SnO$_2$</td>
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<td>80</td>
<td>~6</td>
<td>0.1 M KHCO$_3$ (pH 6.8)</td>
<td>\cite{83}</td>
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<td>porous wire</td>
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<th>FE</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>Electrolyte</th>
<th>Ref</th>
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<td>86</td>
<td>~6</td>
<td>0.1 M NaHCO$_3$</td>
<td>\cite{85}</td>
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<tr>
<td>0.1 mg Sn cm$^{-2}$ (150nm Sn)</td>
<td>-1.4 V</td>
<td>95</td>
<td>-</td>
<td>0.45 mol L$^{-1}$ KHCO$_3$ + 0.5 mol$^{-1}$ KCl</td>
<td>\cite{86}</td>
</tr>
<tr>
<td>SnO$_2$ / 3D porous carbon</td>
<td>-0.86 $V_{\text{RHE}}$</td>
<td>92</td>
<td>29</td>
<td>0.5 M KHCO$_3$</td>
<td>\cite{87}</td>
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Addition of functional groups on catalyst
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<th>η (mV)</th>
<th>Inset Reactions</th>
<th>References</th>
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<td>SnO₂/multiwalled carbon nanotube-COOH</td>
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<td>~8.5</td>
<td>0.5 M KHCO₃ (pH 7.4)</td>
<td>[88]</td>
</tr>
<tr>
<td>SnO₂-organic carbon</td>
<td>-1.29 V</td>
<td>~17</td>
<td>0.1 M KHCO₃ (pH 6.8)</td>
<td>[90]</td>
</tr>
<tr>
<td>Sn₁₀-(Cl, pyrazole)</td>
<td>-1 V</td>
<td>57.08</td>
<td>0.5 M KHCO₃</td>
<td>[91]</td>
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<td>Bimetallics</td>
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<td>Cu₃Sn/Cu₆Sn₅</td>
<td>-1 V</td>
<td>82</td>
<td>0.1 M NaHCO₃</td>
<td>[30]</td>
</tr>
<tr>
<td>(211) Sn-Cu</td>
<td>-1.14 V</td>
<td>82.3</td>
<td>0.5 M KCl (pH 4)</td>
<td>[84]</td>
</tr>
<tr>
<td>Cu(1)Sn(4)/ nitrogen doped porous</td>
<td>-0.97 V</td>
<td>90.24</td>
<td>0.5 M KHCO₃</td>
<td>[92]</td>
</tr>
<tr>
<td>carbon cloth</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D porous Sn on Cu foil</td>
<td>-1.2 V</td>
<td>90</td>
<td>0.1 M KHCO₃</td>
<td>[94]</td>
</tr>
<tr>
<td>Dentritic Sn – Cu substrate</td>
<td>-0.95 V</td>
<td>67.3</td>
<td>0.5 M NaHCO₃ (pH 7)</td>
<td>[89]</td>
</tr>
<tr>
<td>Sn oxidation state</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnOₓ/AgOₓ</td>
<td>-0.8 V</td>
<td>~45</td>
<td>0.1 M KHCO₃ (pH 6.8)</td>
<td>[95]</td>
</tr>
<tr>
<td>Sn/ Cu hollow fiber</td>
<td>-1.2 V</td>
<td>78</td>
<td>0.5 M KHCO₃</td>
<td>[96]</td>
</tr>
<tr>
<td>SnOₓₙ(100-8)/Gas diffusion layer</td>
<td>-1.6 V</td>
<td>87.1</td>
<td>0.5 M KHCO₃</td>
<td>[97]</td>
</tr>
<tr>
<td>Sn/SnO/SnO₂ nanosheets</td>
<td>-0.9 V</td>
<td>89.6</td>
<td>0.5 M KHCO₃ (pH 7.7)</td>
<td>[98]</td>
</tr>
<tr>
<td>2D SnO₂ nanosheets</td>
<td>-1.13 V&lt;sub&gt;RHE&lt;/sub&gt;</td>
<td>94.2</td>
<td>471</td>
<td>1 M KOH (pH 14)</td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------</td>
<td>------</td>
<td>-----</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>-1.01 V&lt;sub&gt;RHE&lt;/sub&gt;</td>
<td>85</td>
<td>~17</td>
<td>0.5 M KHCO₃</td>
</tr>
</tbody>
</table>

**Perspective and outlook**

Figure 9: Pathway of formation of formate as proposed by Feaster et al. along with regions of improvement through modification of Sn electronic density.⁵⁷ Reproduced with permission from Ref. 57. Copyright 2017 American Chemical Society.

In this minireview, we have evaluated the latest developments on Sn-based catalysts for CO₂ reduction from the angle of tuning the Sn electronic structure. Tuning Sn electron density allows optimization of two key steps 1) the adsorption of CO₂ / CO₂ radical on Sn surface and 2) the stabilization of HCOO⁻ intermediate on Sn surface. Sn with a lower electron density (i.e., more electropositive) reduces the HCOO⁻ formation energy while some other studies claim it weakens the OCHO* bond, promoting the desorption of HCOO⁻. Increasing the electron density on Sn on the other hand promotes the adsorption of CO₂ (Fig. 9). From the works done so far (shown in Table 1 and Fig. 9), making Sn more electropositive (electron-deficient) and weakening the OCHO* bond appears to be more effective in lowering the overpotential required for formate production compared to increasing the electron density on Sn and thereby promoting the adsorption of CO₂. This suggests the desorption of HCOO⁻ is likely to
be the rate limiting step for formate production on Sn. It is recommended that future works on Sn be focused on further fine tuning and stabilizing the electron density of Sn for optimizing the HCOO\(^-\) desorption step.

Table 2: A summary of various strategies that have been employed for Sn-based catalysts to promote CO\(_2\) reduction to formate. The table is classified according to strategy employed, material used, applied potential (\(V_{\text{app}}\)), Faradaic Efficiency (FE), Current density (\(J_{\text{sc}}\)), Electrolyte and reference (Ref).

<table>
<thead>
<tr>
<th>Strategy employed</th>
<th>Material</th>
<th>(V_{\text{app}})</th>
<th>FE</th>
<th>(J_{\text{sc}}) (mA cm(^{-2}))</th>
<th>Electrolyte</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu alloying</td>
<td>CuSn(_3)/Carbon paper</td>
<td>-0.5 V(_{\text{RHE}})</td>
<td>95%</td>
<td>33</td>
<td>0.1 M KHCO(_3), pH 6.8</td>
<td>[65]</td>
</tr>
<tr>
<td>Pd alloying</td>
<td>PdSn/activated carbon</td>
<td>-0.43 V(_{\text{RHE}})</td>
<td>99%</td>
<td>30</td>
<td>0.5 M KHCO(_3), pH 7.4</td>
<td>[66]</td>
</tr>
<tr>
<td>Bi doping</td>
<td>Bi-SnO/Cu foam</td>
<td>-1.08 V(_{\text{RHE}})</td>
<td>93%</td>
<td>12</td>
<td>0.1 M KHCO(_3), pH 6.8</td>
<td>[67]</td>
</tr>
<tr>
<td>Bi alloying</td>
<td>Sn(<em>{0.8})Bi(</em>{0.2})/Bi-doped amorphous SnO(_x) shells</td>
<td>-0.88 V(_{\text{RHE}})</td>
<td>95.8%</td>
<td>74.6</td>
<td>0.5 M KHCO(_3), pH 7.2</td>
<td>[68]</td>
</tr>
<tr>
<td>Bi alloying</td>
<td>Bi nanoparticles on Sn</td>
<td>-1.14 V(_{\text{RHE}})</td>
<td>96%</td>
<td>60</td>
<td>0.5 M KHCO(_3), pH 7.2</td>
<td>[69]</td>
</tr>
<tr>
<td>Material/Interactions</td>
<td>Material</td>
<td>$V_{app}$</td>
<td>FE</td>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
<td>Electrolyte</td>
<td>Ref</td>
</tr>
<tr>
<td>-----------------------</td>
<td>----------</td>
<td>-----------</td>
<td>----</td>
<td>-------------------------</td>
<td>-------------</td>
<td>-----</td>
</tr>
<tr>
<td>Ni-N$_4$ alloying</td>
<td>N$_x$-Ni-Sn-N$_4$/Hierarchical integrated carbon nanosheet array</td>
<td>-0.82 $V_{RHE}$</td>
<td>86.1%</td>
<td>20</td>
<td>0.5 M KHCO$_3$, pH 7.1</td>
<td>[70]</td>
</tr>
<tr>
<td>Ag alloying</td>
<td>Ag$_3$Sn/SnO$_x$</td>
<td>-0.8 $V_{RHE}$</td>
<td>80%</td>
<td>16</td>
<td>0.5 M NaHCO$_3$, pH 7.2</td>
<td>[71]</td>
</tr>
<tr>
<td>Uncoordinated S sites</td>
<td>Reduced SnS/Au needles</td>
<td>-0.75 $V_{RHE}$</td>
<td>93%</td>
<td>55</td>
<td>0.1 M KHCO$_3$</td>
<td>[72]</td>
</tr>
<tr>
<td>N injection</td>
<td>N-SnS nanosheets</td>
<td>-0.7 $V_{RHE}$</td>
<td>93.3%</td>
<td>-</td>
<td>0.1 M KHCO$_3$</td>
<td>[73]</td>
</tr>
<tr>
<td>Metal support interactions</td>
<td>Sn/ N-doped graphene</td>
<td>-0.936 $V_{RHE}$</td>
<td>74.3%</td>
<td>11.7</td>
<td>0.25 M KHCO$_3$, pH 7.1</td>
<td>[74]</td>
</tr>
</tbody>
</table>

**Tuning Sn to be electron-rich**

<table>
<thead>
<tr>
<th>Strategy employed</th>
<th>Material</th>
<th>$V_{app}$</th>
<th>FE</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>Electrolyte</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defect engineering</td>
<td>SnO$_2$ Nanoparticles/Carbon fibre</td>
<td>-1.1 $V_{RHE}$</td>
<td>85%</td>
<td>23.7</td>
<td>0.1 M KHCO$_3$, pH 6.8</td>
<td>[76]</td>
</tr>
<tr>
<td>Confinement</td>
<td>Metallic Sn quantum sheets confined between Graphene</td>
<td>-1.14 $V_{RHE}$</td>
<td>89%</td>
<td>21.1</td>
<td>0.1 M NaHCO$_3$</td>
<td>[77]</td>
</tr>
<tr>
<td>-------------</td>
<td>--------------------------------------------------</td>
<td>----------------</td>
<td>------</td>
<td>------</td>
<td>-----------------</td>
<td>-----</td>
</tr>
<tr>
<td>B Doping</td>
<td>SnO$_x$ nanoparticles/gas diffusion layer</td>
<td>-0.72 $V_{RHE}$</td>
<td>91%</td>
<td>65</td>
<td>1 M KOH</td>
<td>[78]</td>
</tr>
<tr>
<td>Metal support interactions</td>
<td>Sn/Graphitic carbon nitride</td>
<td>-0.9 $V_{RHE}$</td>
<td>96%</td>
<td>5</td>
<td>0.1 M KHCO$_3$, pH 6.8</td>
<td>[79]</td>
</tr>
<tr>
<td>Mn Doping / O vacancies</td>
<td>Mn (11.85 wt%)-doped atomic SnO$_2$/Carbon paper</td>
<td>-1.03 $V_{RHE}$</td>
<td>85%</td>
<td>21.2</td>
<td>0.1 M KHCO$_3$, pH 6.8</td>
<td>[80]</td>
</tr>
<tr>
<td>Metal support interactions</td>
<td>SnO$_2$/N,S-codoped porous carbon support</td>
<td>-1.15 $V_{RHE}$</td>
<td>94.4%</td>
<td>56</td>
<td>0.5 M KHCO$_3$, pH 7.4</td>
<td>[81]</td>
</tr>
</tbody>
</table>
Figure 9: Plot of reported Sn-based works employing modification of Sn electronic structure as strategy. Points are divided according to making Sn electron-rich (red) and making Sn electron deficient (blue). References for works are given above every point.

To clarify these observations, more experimental and theoretical studies can be done to investigate the mechanism of formate production on Sn oxide surfaces (most of DFT done were on metallic Sn) to establish the rate limiting step. The field is still divided on the mechanisms of formate production (*COOH vs *OCHO), which would be crucial in studying and understanding the key binding intermediates during the electrochemical reduction process and further optimizing the intermediate binding energies.

Further operando measurements can be done to accurately investigate the effect on its intermediates by tuning the electron density on Sn and to further support initial studies since most of the characterizations reported were not performed under electrochemical reducing conditions. The actual state of Sn during these conditions will be imperative for future design
on Sn electrodes. Finally, the strategy of tuning the electron density could potentially be also be extended to other new metal catalysts for the purpose of engineering efficient CO₂ reduction catalysts.

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Keywords
carbon dioxide, electrocatalysis, formate, materials chemistry and renewable energy
Sn based materials are promising catalysts for facilitating the electrochemical conversion of \( \text{CO}_2 \) to formate. In this minireview, highlight recent key advances in developing Sn-based catalysts, covering experimental and computational efforts on this front. Intriguingly, among the various strategies employed, we find that modifying the Sn oxidation state towards electron deficiency has been most effective.
Uncategorized References


