Selective electrochemical reduction of CO₂ to formic acid in gas phase reactor with by-product recirculation

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Recirculation is a chemical engineering concept generally applied to enhance the conversion of reagents. In common applications, by-products are removed together with the desired products and only the unconverted feed is recirculated. In the concept proposed here to enhance the electrochemical reduction of CO₂ to formate or formic acid, by-products are recirculated to the reactor together with unconverted CO₂. Initial accumulation of by-products like H₂ in the reactor shifts the electrochemical formation potential of these undesired by-products to higher values and favours in this way the formation of formic acid, for which the potential is unaffected. Mathematical simulation of this recirculation process revealed formate selectivity to be substantially improved when by-products are recirculated, even at low pressure. The concept was experimentally validated in an experiment with a membrane electrode assembly reactor. In gas mixtures containing 0.07 MPa of H₂ and 0.03 MPa of CO₂, the hydrogen selectivity of the electrochemical reduction was decreased by ca. 40 % as opposed to pure CO₂. This leads to a significant increase in the formate selectivity and energy efficiency. By-product recirculation to enhance the reaction selectivity may be advantageous to other applications of electrocatalysis suffering from low selectivity of the electrocatalyst.

Introduction

To mitigate the negative effects of the rising atmospheric concentration of CO₂ on our climate, there is a need to find ways to capture CO₂ and use it as a feedstock for the production of chemicals, synthetic fuels and materials. By Carbon Capture and Utilization (CCU)¹, the carbon cycle may be closed and chemical production decoupled from fossil carbon resources.² With an increasing share of fluctuating renewable energy sources, there is also a growing need for temporary energy storage.³ When dealing with large amounts of energy, storage in gaseous or liquid fuels is technically more convenient than using batteries. A study by the European Commission revealed that climate targets for Germany could be met at a substantially lower cost with a technology mix of CCU fuels and electricity compared to full electrification.¹ This advantage of involving CCU is mainly due to the use of existing infrastructure such as pipelines, storage tanks and trailers and the availability of end-use appliances, lowering the capital expenses.

Formic acid is a candidate CCU fuel that can be obtained by electrochemical carbon dioxide reduction reaction (CO₂RR). Direct formic acid fuel cells are available, and formic acid can be

converted to hydrogen for more common hydrogen fuel cells. Formic acid is also a base chemical serving as syngas equivalent in the chemical industry, and provided it is green, it is the pivotal chemical of the 'formate bio-economy'.⁴ A techno-economic analysis by Spurgeon *et al.* projected electrochemical reduction of CO₂ to formic acid to become competitive on the fuels market.⁵

Much research effort has already been devoted to the development of electrocatalysts aiming for high formic acid selectivity at low overpotential. Most research in this area deals with liquid phase CO₂ reduction with CO₂ gas sparged into an electrolyte, often a basic bicarbonate solution. Metals such as Sn, Pb, Bi and In have been observed to reach high faradaic efficiencies for formate.^{6–10} Especially Sn(-oxide) based electrodes have been intensively investigated, as it is an earth abundant, low cost and safe metal with electronic properties near the Sabatier optimum for the *OCHO intermediate.^{11–13} The faradaic efficiency increases even further with some bimetallic catalysts, which is often ascribed to electronic synergy. Here, the second metal assists the active one in preserving a positive oxidation state needed to favour the reaction intermediate towards formate and to suppress hydrogen evolution. Examples of bimetallic catalysts are PdSn, PbSn and CuSn, reaching till 95% faradaic efficiency.^{14–16}

A major disadvantage of electrocatalytic CO₂ conversion in aqueous electrolyte is the limited solubility of CO₂ and the slow dissolution kinetics, limiting the overall reaction kinetics. When CO₂ delivery to the electrode surface is rate limiting, the

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hydrogen evolution reaction (HER) becomes prominent, since protons are abundantly available in aqueous electrolyte. This explains why formate formation is often not enhanced by increasing the cathodic overpotential and that partial current densities in liquid electrolytes are limited to a few tens of mA/cm^2 .¹¹

To increase the product yield, electrochemical cells are used where the liquid electrolyte is replaced by a solid electrolyte membrane, thus operating in the gas phase. In such a membrane electrode assembly (MEA) type system, the catalyst is usually surrounded by a thin layer of ionomer, liquid water¹⁷ and potentially some condensed formic acid.¹⁸ This layer surrounding the catalyst surface is of nm-size thickness and is thus several orders of magnitude thinner compared to liquid electrolyte reactor cells.¹⁹ Diffusion of CO_2 towards the catalyst surface therefore occurs fast, leading to high partial current densities for CO_2RR to CO of up to $250 \text{ mA}/\text{cm}^2$.¹⁸

An additional advantage of working solventless in a gas phase system is the reduced need for distillation of the formic acid product. A life cycle assessment by Thonemann *et al.* showed that the high thermal energy demand needed for formic acid recovery by distillation of a diluted formic acid solution from an electrochemical production process leads to a positive net global warming impact, thereby nullifying the carbon dioxide savings.²⁰ Gas phase, almost water-free electrochemical processes are therefore gaining popularity in this research field.^{21–24}

Lee *et al.* reported on a gas phase system producing formic acid using H_2 at the anode as the source of protons transported to the cathode through a Nafion® membrane (Fig. 1, Type I). Faradaic efficiencies towards formic acid were limited to 5–12.5%, as H_2 formation predominated.^{22,25} More recently, alkaline anion exchange membranes (AEM) have shown to increase the selectivity towards the CO_2RR as opposed to acidic proton exchange membranes (PEM) by lowering the access to protons.^{18,21,24} This type of MEA is well suited for CO synthesis,¹⁸ but poses challenges for formic acid synthesis. For example, crossover of formate to the anode is a large loss factor¹⁸ and acidification to formic acid is needed to maintain the proton balance. A centre flow compartment has been integrated into the MEA, where a liquid water flow in between an anodic PEM and cathodic AEM membrane is used to acidify formate and evacuate formic acid from the reactor cell (Fig. 1, Type II).^{21,24} Alternatively, Park *et al.* demonstrated faradaic efficiencies for formate of up to 93% in a MEA-type reactor cell using a liquid KOH anolyte, a highly humid CO_2 stream and increased reaction temperatures (Fig. 1, Type III).²⁶ If an entirely gas phase operation is desired, a MEA can be used consisting of an alkaline ionomer layer at the cathode, pressed to a PEM membrane, separating anode from cathode (Fig. 1, Type IV).²⁷ This design shows promising results for CO_2RR but remains to be explored for formic acid synthesis.

In these cell designs, H_2 remains the main by-product. An aqueous environment is needed for proton donation during formic acid formation. In this environment, at the required cell potential, avoiding the HER through catalyst design is a very

Fig. 1. MEA-type reactor cell configurations for electrochemical reduction of CO_2 . Types I and IV operate fully in the vapor phase, type II contains a liquid water flow in the centre compartment and type III contains a liquid anolyte flow.

challenging task. Therefore, additional strategies to limit this by-product formation should be explored.

Additionally, reported CO_2 conversions are often below 5%. Spurgeon *et al.* discussed the importance of recycling unreacted CO_2 , and proposed to separate unreacted CO_2 from the products and to recycle it to the reactor.⁵ In this paper we went further and investigated ways to use the recirculation concept to block undesired side reactions on the electrocatalyst while enhancing the CO_2 conversion.

Results and discussion

The process scheme of the proposed gas phase electrochemical reactor with recirculation is presented in Fig. 2. Water vapor is fed to the anode. Protons generated by water oxidation are transported through a membrane from anode to cathode compartment. Water present at the cathode mainly originates from water transport through the membrane by electro-osmotic drag. Aside from CO_2 reduction to formic acid, the cathode produces by-products, and H_2 especially. Typical products of the cathode compartment are composed of formic acid, water, unconverted CO_2 , H_2 , CO and other C-containing by-products such as methane and ethane. The cathode outlet gas stream is sent to a condenser where formic acid and water are removed by condensation. Electrocatalysts that are selective towards formic acid generally do not produce condensable products other than formic acid and water.²¹ Unconverted CO_2 and by-products are recycled to the cathode and combined with the CO_2 inlet. The pressure is regulated by a pressure release valve (P), evacuating part of the unconverted

CO₂ and by-products to avoid an excessive build-up of by-products.

Fig. 2. Gas phase electrochemical CO₂ reduction reactor with recirculation of by-products, maximizing formic acid production. The effect of recirculation on the reaction selectivity was simulated by calculating the changing partial pressures of the gases along the process steps (A to D).

Relevant half-cell reactions and corresponding standard Nernst potentials are listed in Table 1. The standard Nernst potential of the desired combination of CO₂RR with OER is -1.480 V. This is higher than for H₂ by-product formation (HER + OER), being -1.229 V.

Table 1. Half-cell reactions and standard Nernst potentials

	Half-cell reactions	Potential (V vs RHE)
Anode		
OER	$\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 (\text{g}) + 2 \text{H}^+ + 2 \text{e}^-$	1.229
Cathode		
CO ₂ RR	$\text{CO}_2 (\text{g}) + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{HCOOH}$	-0.251
HER	$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g})$	0.000
CO₂RR + OER	$\text{CO}_2 (\text{g}) + \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 (\text{g}) + \text{HCOOH}$	-1.480
HER + OER	$\text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 (\text{g}) + \text{H}_2 (\text{g})$	-1.230

First, the advantage of by-product recirculation is estimated theoretically by simulation. The concept is validated by experiments on electrochemical CO₂RR using gas mixtures simulating by-product recirculation.

Theoretical simulation

Experimental current density versus voltage (IV) curves of a Sn-nanoparticle electrocatalyst for the CO₂RR and competing HER reaction are shown in Fig. 3.²⁶ This literature data originates from a MEA-type reactor cell containing a liquid KOH anolyte flow (Fig. 1, Type III) and was deemed appropriate to demonstrate the principle behind by-product recirculation. The experimental curves were mathematically simulated through an adapted Nernst equation (Eq. 1), which was extended to include current-dependent ohmic, activation and concentration overpotentials.

$$V = V_0 + \eta_{ohm} + \eta_{Act} + \eta_{Conc}$$

$$= E^0 - \frac{RT}{nF} \ln Q + \frac{j_{total} L}{\sigma} + \frac{RT}{nF \alpha_c} \ln \left(1 + \frac{j_x}{j_{0,c}} \right) + a e^{b j_x} \quad (\text{Eq.1})$$

Eq. 1 allows to calculate the partial current densities for each reaction product at a chosen cell potential, and is dependent on the partial pressures of the individual gases.²⁸

These partial pressures were calculated at four steps in the process (Fig. 2): at the inlet (A) and outlet (B) of the electrochemical reactor, at the outlet of a condenser separating formic acid and water from the gas stream (C), and behind a pressure release valve (P) releasing a fraction of the gas (D). Iteratively re-inputting the pressures of the individual gases at the inlet of the reactor cell (A) into Eq. 1 allows to continuously recalculate the partial current densities and determine the changing faradaic efficiency towards each product over time. More details on the model, the underlying assumptions and the used symbols can be found in the Supplementary Information (SI I).

At a cell potential of 2.3 V, where the partial current density towards formate is at its maximal value, the faradaic efficiency towards formate derived from the simulated IV-curves is 86%, which matches with the experimental value of around 86% in literature.²⁶

Fig. 3. Experimental (---) and simulated (—) IV-curves for the reduction of CO₂ to formate (CO₂ reduction reaction 'CO₂RR', ●) and hydrogen evolution reaction ('HER', ■). Experimental data from Park *et al.*²⁶

On a Sn electrocatalyst, hydrogen evolution follows the Volmer-Heyrovsky mechanism.²⁹ Increasing the hydrogen partial pressure in the cathode compartment will lower the driving force for additional hydrogen formation. Although the mechanism is not entirely resolved, formic acid or formate synthesis is assumed to proceed through an oxygen-bound intermediate.¹³ Proton donation occurs from the electrolyte, either by H₂O, HCO₃⁻ or H₃O⁺ as the proton donor.¹³ It could be argued that increasing the partial pressure of hydrogen leads to an increased surface coverage of hydrogen, leaving less active sites available for the intermediate for CO₂ reduction. However, it is known that Sn has a low adsorption affinity for hydrogen and consequently a low hydrogen coverage over the entire potential range.²⁹ Enhancing the hydrogen pressure in the cathode compartment will thus not

interfere with the CO₂RR kinetics, while it will diminish the driving force for hydrogen formation. For these reasons, recirculation of the hydrogen by-product is expected to enhance the faradaic efficiency for formic acid, or formate, formation.

Recently, Kersten *et al.* experimentally explored the use of increasing the hydrogen partial pressure to suppress additional hydrogen formation on a Pd electrocatalyst in a liquid electrolyte.³⁰ A pressurized reactor vessel was used, with controlled amounts of added hydrogen gas. Raising the partial pressure of hydrogen led to a decrease of hydrogen production, while the formate production rate was maintained.³⁰ Although this approach is promising, it requires an external input of hydrogen gas. If not precisely controlled, this could result in side reactions. At a too high hydrogen partial pressure, a hydrogen oxidation side-reaction occurs on Pd. Conversely, when the hydrogen partial pressure is too low, the HER is not sufficiently suppressed. The recirculation concept proposed here, demonstrates a convenient way to automatically converge towards a steady state with increased reaction selectivity, without adding hydrogen gas.

In the simulation of the operation of the recirculation reactor, the cathode compartment was assumed to be filled with CO₂ at the start of the operation, at a given pressure which is kept constant further on. To keep the pressure constant, part of the reaction products after condensation of formic acid and water is evacuated using the pressure release valve (P). Here, it was assumed that 1% of the gas was evacuated, such that 99% was recycled and supplemented with 1% pure CO₂ make-up gas. The evolution of the gas composition at the inlet of the cathode compartment of the recirculation reactor was simulated over time using the kinetic model for the Sn catalyst (Fig. 3) (details provided in SI I). For simplicity, H₂ was considered to be the only by-product. As recirculation proceeded, there was build-up of H₂ at the inlet of the cathode compartment (Fig. 4A). At a recirculation flow rate of 200 ml/min, ca. 1000 recycles were needed to converge to a steady-state. The composition at the

inlet of the cathode compartment evolved towards a gas mixture with ca. 10% CO₂ and 90% H₂. The increasing pressure of H₂ due to recycling caused a shifting of the cathode operation point on the HER IV-curve to lower currents (Fig. 4B), decreasing in this way the electric current density serving HER.

The decreased CO₂ partial pressure should also be addressed. Depending on the reactor type, lowering the amount of CO₂ could result in diffusion limitations, where the reaction rate of CO₂ reduction is determined by the rate of diffusion of CO₂ towards the active catalytic site. When working in a MEA-type system, the diffusion distance is small. The thin layer of ionomer and/or water covering the cathode has a high permeability of CO₂, avoiding diffusion limitations up to a current density of about 200 mA/cm².¹⁸ If relying on water vapor oxidation at the anode, the operational current density is limited to lower values. This suggests that there is a margin to lower the CO₂ partial pressure, while still working outside of the diffusion limited regime. Additionally, a high CO₂ concentration leads to a more acidic aqueous environment, likely increasing the HER.³⁰ Lowering the CO₂ partial pressure is thus not necessarily detrimental to the CO₂RR and could even be beneficial.

The gain of faradaic efficiency towards formate by recycling was simulated for three different pressures in the cathode compartment: 0.2 MPa, 1 MPa and 10 MPa (Fig. 5; Table 2). At a pressure of 0.2 MPa, recirculation enhances the formate faradaic efficiency from 86% to 90.5% at the plateau. Increasing the pressure improves the faradaic efficiency further, reaching 92.0% at 1 MPa, and 93.9% at 10 MPa. This enhancement is due to the build-up of absolute H₂ pressure in the cathode compartment. At lower overpotentials, the shift of the HER IV-curve even causes additional hydrogen production to be almost completely suppressed, with a faradaic efficiency towards formate of 97.8 % at 2.1 V and 10 MPa.

As a result, recirculation leads to a significant energy saving. The specific energy consumption was estimated to drop from 3.2 kWh/kg formic acid without recirculation to 2.9 kWh/kg in a system with recirculation at a pressure of 10 MPa (Table 2).

Fig. 4. **A**, Simulated change of gas composition at the inlet of the cathode compartment with number of recycles and **B**, change of simulated IV-curves of the hydrogen evolution reaction with the number of recycles. Reaction conditions: pressure of 0.2 MPa; 99% recirculation of H₂ by-product and unconverted CO₂.

Fig. 5. Evolution of the simulated faradaic efficiency towards formate with the number of recycles at different pressures. The cell potential was maintained at 2.3 V. Reaction conditions : 99% recirculation of H_2 by-product and unconverted CO_2 . The flow rate was adjusted to reach a plateau after a similar number of recycles.

The gain of faradaic efficiency towards formate by recirculation depends on the shape of the IV-curves. This varies with the type of electrocatalyst and the reagent composition, and can be simulated by varying the values of the model parameters such as a , b and j_0 (Eq. 1). A sensitivity analysis was performed, where the model parameters were varied (SI II). Large gains in selectivity towards formate are achieved when the current serving HER increases exponentially with the reduction potential and for electrocatalysts with relatively fast kinetics for H_2 production. Earth-abundant metal catalysts are known to have this property suggesting the recirculation concept to be particularly attractive for such electrocatalyst materials.

Table 2. Simulated faradaic efficiency towards formate and specific energy consumption at different pressures. H_2O Oxidation at the anode was assumed. It was assumed that 99% of the gas is recycled, while supplemented with 1% CO_2 .

E_{cell} [V]	reactor pressure [MPa]	faradaic efficiency towards formate at steady state [%]	specific energy consumption at steady state [kWh/kg]
2.3	0.2	90.5	2.96
2.3	1	92.0	2.91
2.3	10	93.9	2.85
2.1	10	97.8	2.50

Experimental validation

Simulation suggests that by recirculating H_2 , the CO_2RR can be favoured at the detriment of the HER. In this section, this concept is experimentally validated by analysing the selectivities towards H_2 and formate formation in mixtures with various proportions of CO_2 and H_2 .

A catholyte-free electrochemical reactor setup was used, consisting of a Sn-nanoparticle on carbon cathode, a proton exchange membrane, a platinum on carbon cloth anode and a liquid KOH anolyte (Fig. 1, Type III). Gas mixtures of humidified CO_2 and H_2 were introduced into the cathode compartment at ambient pressure, ranging from pure CO_2 to 30/70 vol% CO_2/H_2 . The gas flow rate was kept constant. Detailed information on the experimental setup and product analysis methods can be found in the Supplementary Information (SI III).

For a gas flow consisting of 100% humidified CO_2 (0.1 MPa), a faradaic efficiency of 13.7% and 85.1% was obtained for formate and H_2 , respectively at a cell potential of 2.6 V. Upon increasing the fraction of H_2 in the gas mixture to 70 vol%, the faradaic efficiency towards H_2 decreases to ca. 46% (Fig. 6A).

Fig. 6. A, Faradaic efficiency towards H_2 and formate in a gas mixture consisting of pure CO_2 and a mixture of 30/70 vol% CO_2/H_2 , and **B,** partial current densities towards H_2 and formate as a function of the H_2 concentration. The reactor operated at atmospheric pressure at a cell potential of 2.6 V.

Meanwhile, the selectivity towards formate increases to ca. 21%. In this instance, the fate of 37% of the electric current is unknown. Hydrogen is presumed to be quantitatively detected. Possibly with an increasing amount of formate produced, some of it is retained inside the reactor cell, unable to leave the reactor with the gas flow in the form of an aerosol. Other possibilities are the production of other CO₂ reduction products such as methane, and the potential crossover of potassium formate or its associated acid to the anode. More research needs to be done to gain full insight into the product distributions, but the suppression of HER, which was the main purpose of this experiment, is confirmed.

The partial current density of the HER at a cell potential of 2.6 V gradually decreases upon increasing the H₂ concentration to 70 vol%, while that of the CO₂RR remains more or less constant (Fig. 6B). This leads to a decrease of the total current density with an increased concentration of H₂ (Fig. 7). This observation corresponds to what was predicted by the model simulation (Fig. 4B). The H₂ production rate decreases from ca. 242 $\mu\text{mol}/\text{cm}^2_{\text{geom.}}\cdot\text{h}$ to ca. 100 $\mu\text{mol}/\text{cm}^2_{\text{geom.}}\cdot\text{h}$, while that of formate remains constant at ca. 50 $\mu\text{mol}/\text{cm}^2_{\text{geom.}}\cdot\text{h}$ (ca. 16 $\mu\text{mol}/\text{g Sn}\cdot\text{s}$). This results in a decrease in the specific energy consumption for formate synthesis of ca. 36%.

Fig. 7. Total current density as a function of cell potential in a gas mixture consisting of pure CO₂ (—) and a mixture of 30/70 vol% CO₂/H₂ (---). The scan rate was 10 mV/s.

These observations validate that, even at a low pressure, adjusting the gas composition can effectively suppress H₂ formation and alter the selectivity in favour of CO₂RR.

This approach is not limited to formate or formic acid production and could be extended to other CCU products obtained by reaction of CO₂ with H₂O. A requirement is that the desired CCU product can be separated from the by-products in a straightforward manner, either through reactor design or a downstream separation step. Alcohols (methanol, ethanol and n-propanol), acetaldehyde and acetic acid can be separated by condensation and are possible candidates.³¹ Acetaldehyde and methanol appear promising. With a boiling point of 20.2°C and 64.7°C respectively, these molecules are volatile enough to be

vaporised inside the reactor cell, while still easy to separate from the by-products through condensation. As an example, Lucas-Consuegra *et al.* produced acetaldehyde on a copper based electrocatalyst in a gas-phase cell.³² That process may also benefit from the by-product recirculation concept.

Conclusions

A new gas phase electrocatalysis reactor system for the production of concentrated formic acid or formate from CO₂ at enhanced faradaic efficiency is proposed. Different from other recirculation concepts, gaseous by-products of the reaction are recycled to the cathode, suppressing in this way additional by-product formation.

This concept was simulated theoretically. Simulation revealed that, under the assumptions of the simulation (H₂ as the only by-product, 99% recycling, a Sn electrocatalyst), the faradaic efficiency towards formate for this specific dataset can be increased from 86% to ca. 92% at a pressure of 1MPa, lowering the specific energy consumption. At low overpotentials, hydrogen formation can be almost completely suppressed. Experiments revealed that the selectivity of CO₂RR versus HER strongly depends on the gas composition, showing a decreasing tendency to produce additional H₂ in the presence of high concentrations of H₂. The formate production rate remained unaffected by the presence of increasing amounts of hydrogen. Hydrogen recirculation provides an effective way to increase the energy efficiency of the CO₂RR, in addition to other benefits of recirculation such as an enhanced CO₂ conversion rate.

Additional research is needed to further develop this idea, including, for example, research on the influence of other by-products like CO. Different catalysts such as Pd can also be studied, as they require lower overpotentials for formic acid synthesis, leading possibly to a complete suppression of hydrogen formation at low pressures.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 The potential for CCS and CCUS in Europe. Report to the thirty second meeting of the European Gas Regulatory

- Forum 5-6 June 2019. Available from : ec.europa.eu.
- 2 A. Kätelhön, R. Meys, S. Deutz, S. Suh and A. Bardow, *Proc. Natl. Acad. Sci. U. S. A.*, 2019, **166**, 11187–11194.
 - 3 M. Victoria, K. Zhu, T. Brown, G. B. Andresen and M. Greiner, *Energy Convers. Manag.*, 2019, **201**, 111977.
 - 4 A. R. T. Morrison, V. van Beusekom, M. Ramdin, L. J. P. van den Broeke, T. J. H. Vlugt and W. de Jong, *J. Electrochem. Soc.*, 2019, **166**, E77–E86.
 - 5 J. M. Spurgeon, *Energy Environ. Sci.*, 2018, **11**, 1536–1551.
 - 6 X. Lu, D. Y. C. Leung, H. Wang, M. K. H. Leung and J. Xuan, *ChemElectroChem*, 2014, **1**, 836–849.
 - 7 J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631–675.
 - 8 B. Endrődi, G. Bencsik, F. Darvas, R. Jones, K. Rajeshwar and C. Janáky, *Prog. Energy Combust. Sci.*, 2017, **62**, 133–154.
 - 9 D. Du, R. Lan, J. Humphreys and S. Tao, *J. Appl. Electrochem.*, 2017, **47**, 661–678.
 - 10 H. R. M. Jhong, S. Ma and P. J. Kenis, *Curr. Opin. Chem. Eng.*, 2013, **2**, 191–199.
 - 11 M. B. Ross, P. De Luna, Y. Li, C. T. Dinh, D. Kim, P. Yang and E. H. Sargent, *Nat. Catal.*, 2019, **2**, 648–658.
 - 12 J. T. Feaster, C. Shi, E. R. Cave, T. Hatsukade, D. N. Abram, K. P. Kuhl, C. Hahn, J. K. Nørskov and T. F. Jaramillo, *ACS Catal.*, 2017, **7**, 4822–4827.
 - 13 C. W. Lee, N. H. Cho, S. W. Im, M. S. Jee, Y. J. Hwang, B. K. Min and K. T. Nam, *J. Mater. Chem. A*, 2018, **6**, 14043–14057.
 - 14 X. Bai, W. Chen, C. Zhao, S. Li, Y. Song and R. Ge, *Angew. Chemie - Int. Ed.*, 2017, **56**, 12219–12223.
 - 15 C. E. Moore, *ChemSusChem*, 2017, **10**, 3512–3519.
 - 16 X. Zheng, Y. Ji, J. Tang, J. Wang, B. Liu, H. Steinrück, K. Lim, Y. Li, M. F. Toney, K. Chan and Y. Cui, *Nat. Catal.*, 2018, **2018**, 55–61.
 - 17 J. M. Ahlfield, L. Liu and P. A. Kohl, *J. Electrochem. Soc.*, 2017, **164**, F1165–F1171.
 - 18 G. O. Larrazábal, P. Strøm-Hansen, J. P. Heli, K. Zeiter, K. T. Therkildsen, I. Chorkendorff and B. Seger, *ACS Appl. Mater. Interfaces*, 2019, **11**, 41281–41288.
 - 19 M. Ma, E. L. Clark, K. T. Therkildsen, S. Dalsgaard, I. Chorkendorff and B. Seger, *Energy Environ. Sci.*, 2020, **13**, 977–985.
 - 20 N. Thonemann and M. Pizzol, *Energy Environ. Sci.*, 2019, **12**, 2253–2263.
 - 21 C. Xia, P. Zhu, Q. Jiang, Y. Pan, W. Liang, E. Stavitsk, H. N. Alshareef and H. Wang, *Nat. Energy*, 2019, **4**, 776–785.
 - 22 S. Lee, H. Ju, H. Jeon, R. L. Machunda, D. Kim, J. K. Lee and J. Lee, *ECS Trans.*, 2013, **53**, 41–47.
 - 23 B. De Mot, J. Hereijgers, M. Duarte and T. Breugelmans, *Chem. Eng. J.*, 2019, **378**, 122224.
 - 24 H. Yang, J. J. Kaczur, S. D. Sajjad and R. I. Masel, *J. CO2 Util.*, 2017, **20**, 208–217.
 - 25 S. Lee, H. K. Ju, R. Machunda, S. Uhm, J. K. Lee, H. J. Lee and J. Lee, *J. Mater. Chem. A*, 2015, **3**, 3029–3034.
 - 26 W. Lee, Y. E. Kim, M. H. Youn, S. K. Jeong and K. T. Park, *Angew. Chemie - Int. Ed.*, 2018, **57**, 6883–6887.
 - 27 A. Pătru, T. Binninger, B. Pribyl and T. J. Schmidt, *J. Electrochem. Soc.*, 2019, **166**, F34–F43.
 - 28 M. Dumortier, S. Tembhurne and S. Haussener, *Energy Environ. Sci.*, 2015, **8**, 3614–3628.
 - 29 O. Azizi, M. Jafarian, F. Gobal, H. Heli and M. G. Mahjani, *Int. J. Hydrogen Energy*, 2007, **32**, 1755–1761.
 - 30 M. Blom, W. van Swaaij, G. Mul and S. Kersten, *Sustain. Energy Fuels*, 2020, **4**, 4459–4463.
 - 31 M. Y. Lee, K. T. Park, W. Lee, H. Lim, Y. Kwon and S. Kang, *Crit. Rev. Environ. Sci. Technol.*, 2020, **50**, 769–815.
 - 32 N. Gutiérrez-Guerra, L. Moreno-López, J. C. Serrano-Ruiz, J. L. Valverde and A. de Lucas-Consuegra, *Appl. Catal. B Environ.*, 2016, **188**, 272–282.