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## Introduction

Energy production from fossil fuels results in critical environmental contaminations due to the emission of the greenhouse gas CO<sub>2</sub> into earth's atmosphere.<sup>1</sup> While CO<sub>2</sub> acts as a pollutant, it is also a cheap and abundant C<sub>1</sub>-feedstock for carbon-based chemicals if efficient pathways for its conversion are established.<sup>2</sup> Especially, the development of sustainable production processes by means of electrocatalysis are a promising pathway to efficiently activate CO<sub>2</sub> and allow for the utilization of electricity from renewable sources like wind or photovoltaics.<sup>3</sup> While electrochemical CO<sub>2</sub> reduction was previously shown, the hampered mass transport and low water solubility of CO<sub>2</sub> render this process still inefficient and instead facilitate the formation of H<sub>2</sub>.<sup>4,5</sup> In addition, the metal–substrate binding strength (H<sup>+</sup> vs. CO<sub>2</sub>), and electron transfer kinetics at the material surface, are among the key factors for the selectivity of the electrocatalytic CO<sub>2</sub> reduction.<sup>6,7</sup> While low-coordinated Cu nanoparticle sites facilitate HER, up to a certain extent, nanostructuring of Cu particles was shown to favor CO<sub>2</sub> reduction over HER.<sup>8–11</sup> General design principles leading to more efficient electrochemical CO<sub>2</sub> reduction catalysts, however, are not yet available.<sup>12</sup> Notably, the capability of a catalyst to show either

# Bio-inspired design: bulk iron–nickel sulfide allows for efficient solvent-dependent CO<sub>2</sub> reduction†

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The electrocatalytic reduction of carbon dioxide (CO<sub>2</sub>RR) to valuable bulk chemicals is set to become a vital factor in the prevention of environmental pollution and the selective storage of sustainable energy. Inspired by structural analogues to the active site of the enzyme CODH<sub>Ni</sub>, we envisioned that bulk Fe/Ni sulfides would enable the efficient reduction of CO<sub>2</sub>. By careful adjustment of the process conditions, we demonstrate that pentlandite (Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub>) electrodes, in addition to HER, also support the CO<sub>2</sub>RR reaching a peak faradaic efficiency of 87% and 13% for the formation of CO and methane, respectively at 3 mA cm<sup>-2</sup>. The choice of solvent, the presence of water/protons and CO<sub>2</sub> solubility are identified as key-properties to adjust the balance between HER and CO<sub>2</sub>RR in favour of the latter. Such experiments can thus serve as model reactions to elucidate a potential catalyst within gas diffusion electrodes.

HER or CO<sub>2</sub>RR activity usually depends on the process conditions applied. *E.g.* Cu and pyrite (FeS<sub>2</sub>) were both reported to facilitate H<sub>2</sub> generation as well as CO<sub>2</sub> reduction at various conditions and further support the Janus-faced character of both processes.<sup>13–17</sup>

Contrary to artificial catalysts,<sup>18–20</sup> nature has developed sophisticated machineries to allow for an efficient CO<sub>2</sub> reduction. *E.g.* the carbon monoxide dehydrogenase<sup>21</sup> allows for selective reduction of CO<sub>2</sub> to CO at –0.52 V vs. NHE and ambient pressure with turn over frequencies of up to 700 molecules per h.<sup>22–24</sup>

The efficient enzymatic reactivity is related to its unique [Ni–4Fe–5S] cluster (Fig. 1a), a finely enzyme regulated amount of protons/water at the reactive center, as well as a directed CO<sub>2</sub> access to the low valent active sites. Furthermore, the protein scaffold of the enzyme allows for a synchronized influx of electrons and substrates enabling high enzymatic selectivity. We and others recently showed that efficient electrocatalysts

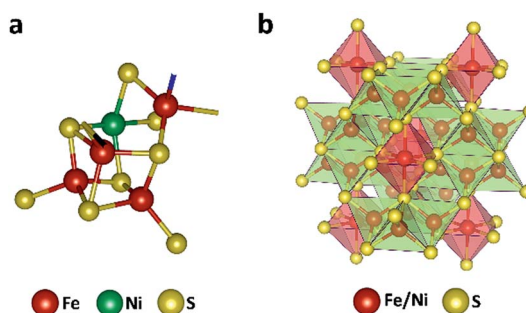


Fig. 1 Active site in the nickel-containing CO dehydrogenase (pdb: 1su6) (a) and crystal structure of the Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> (b).

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products of 3.2% at  $-1.2$  V to 5.7% at  $-1.8$  V vs. NHE. In pyridine, HER is significantly suppressed showing faradaic efficiencies for  $H_2$  of solely 60, 30 and 8% at  $-1.2$ ,  $-1.5$  and  $-1.8$  V. In addition, a clear increase of the FE for  $CH_4$  from solely 0.3 to 3.0% at  $-1.2$  V was observed. In contrast, in MeCN, DMSO, DMF and PC,  $Fe_{4.5}Ni_{4.5}S_8$  electrodes reveal a significantly altered behavior. In these solvents, the faradaic yields for HER are significantly reduced and an increased amount of  $CO_2RR$  products is observed. It is noteworthy that in MeCN and PC methane (FE 12.8% in MeCN, 8.3% in DMSO and 13.0% in PC) and ethylene (FE 0.5% in MeCN, 2.2% in DMSO and 1.4% in PC) are the major products at  $-1.2$  V vs. NHE which corroborates the finding of pentlandite being capable to hydrothermally hydrogenate  $CO_2$ .<sup>34</sup>

At very negative potentials, the CO formation capability of the material is generally increased reaching FE as high as 71% in MeCN, 42% in DMSO and 51% in PC at potentials of  $-1.8$  V. Surprisingly, the product distribution in DMF is less dependent on the potential applied showing steady methane formation (FE 23%) and smaller variations in CO formation (FE 11–30%) as compared to MeCN, DMSO and PC. While  $CH_4$  and CO are the main products from  $CO_2$  reduction, it is notable that especially in aprotic solvents  $C_2H_4$  and  $C_2H_6$  are also observed (Fig. 2c). *E.g.* FE for  $C_2H_4$  of 2.2% (DMSO), 0.7% (DMF) and 0.5% (MeCN) were observed. Likewise,  $C_2H_6$  was observed in the range of 1–1.3%, respectively. The faradaic efficiencies below 100% observed within the non-protic solvents can most-likely be assigned to high capacitive currents and poor conductivity leading to *e.g.* heat formation, gas leakage, as well as a potential partial re-oxidation of  $CO_2$  reduction products and are not necessarily an effect of the electrode behavior in the different solvents.<sup>40</sup> However, these amounts are among the highest ever reported for non-Cu containing materials (Table S4†).<sup>41</sup> We conclude that beside the proton availability and the solvent chosen, the  $CO_2$  solubility in the various solvents has a major influence on the  $CO_2RR$  by enhancing the effective concentration of  $CO_2$  at the electrode surface.

The solubility of  $CO_2$  in acetonitrile (0.27 M) was reported to be significantly higher compared to water (0.04 M) and methanol (0.16 M).<sup>42</sup> Likewise, an increased  $CO_2$  solubility is observed for DMF (0.18 M)<sup>43</sup> and PC (6.97 M)<sup>43</sup> which encourages the  $CO_2$  reduction in these solvents (Table S5†). However, the solubility of  $CO_2$  in DMSO is just 0.02 M and contradicts this hypothesis. In this regard, the proton availability which is commonly displayed by the acidity of water in a particular electrolyte or the solvent itself will influence  $CO_2RR$  and is highlighted by increased HER activity in aqueous  $KHCO_3$  ( $pK_a$  10.3) compared to MeOH ( $pK_a$  16).

### Dependency on water/proton concentration

The efficiency of  $CO_2RR$  seems to be a compromise between altered proton concentration at the electrode surface (generally caused by the water content in a given solvent) and the capability of a certain electrolyte to efficiently absorb  $CO_2$ . We thus opted to determine the influence of the water amount on the activity of  $Fe_{4.5}Ni_{4.5}S_8$  electrodes. Hence, we examined the

selectivity towards  $CO_2RR$  using MeCN electrolyte solutions with varying water concentrations (24–30 000 ppm) (Table S3†) by performing LSV (Fig. 3a).

A shift of the potential necessary to achieve a catalytic current of  $-20$  mA  $cm^{-2}$  to lower potentials ( $-2.1$  V; 24 ppm  $H_2O$  vs.  $-1.3$  V; 30 000 ppm) is observed as the water concentration in the electrolyte increases. However, gas analyses after 1 h CPC at  $-1.8$  V clearly shows that at higher water concentrations HER is facilitated and  $CO_2RR$  is suppressed (Fig. 3b). While for high water concentrations in the electrolyte, FEs of 87% (30 000 ppm) and 62% (5000 ppm) are observed for hydrogen, only 11% and 19% FE, respectively, were found for CO. Contrary, in the presence of lower water concentrations,  $CO_2RR$  becomes the dominant reaction. Here, FE for CO significantly increases to 37% (500 ppm  $H_2O$ ) and 87% (24 ppm  $H_2O$ ), respectively, concomitant with a decrease of the FE for HER to 14% and 3%, respectively.

In control experiments using Ar purged electrolytes containing 24 ppm  $H_2O$ , no formation of  $CO_2RR$  was observed (Fig. S6†). In addition, to rule out a suppressed oxidation on the anode side due to an imbalanced amount of charges passed through the system, we added conc. sulfuric acid to the acetonitrile mixture at the cathodes chamber. This allows for a fast HER reaction and allows for a comparable oxidation reaction as observed under  $CO_2RR$  catalytic condition. Similarly, no increased formation of  $CO_2$  reduction products (Fig. S7†) was observed proving the dominant reduction of  $CO_2$  rather than electrolyte decomposition. Similar results were observed when using DMSO or DMF under otherwise identical conditions. To confirm the origin of the various C-products observed, we performed a mass-selective product analysis utilizing  $^{13}CO_2$  in acetonitrile under otherwise identical electrochemical conditions. While the observed mass peak of 29 is indicative for the formation of  $^{13}CO$  from  $^{13}CO_2$  (Fig. S9†), the unaltered mass

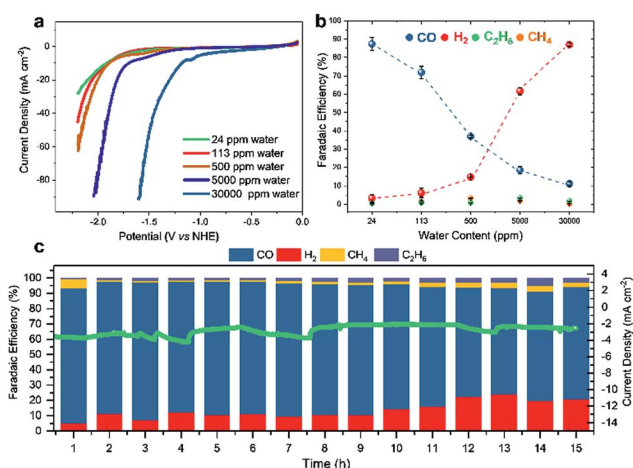


Fig. 3 Linear sweep voltammograms recorded at 5 mV s<sup>-1</sup> in MeCN with different water content and  $CO_2$  purge (a), faradaic efficiencies of  $CO_2$  reduction products in the gas phase at a constant potential of  $-1.8$  V vs. NHE from MeCN with various amounts of water (b). Long term electrolysis for 15 h at  $-1.8$  V vs. NHE with 24 ppm water including the observed faradaic efficiencies (c).



pattern of ethane suggests a different origin (Fig. S10†). We thus repeated the CO<sub>2</sub> reduction experiment in the presence of CD<sub>3</sub>CN. The resulting mass pattern and the observed mass peak at 33 clearly indicate the formation of C<sub>2</sub>D<sub>3</sub>H<sub>3</sub> and suggest that ethane originates from the hydrogenation of acetonitrile rather than reduction of CO<sub>2</sub> (Fig. S10†). Likewise, we analyzed the origin of CH<sub>4</sub> that was observed within our experiments *via* the same technique. While the MS pattern of CH<sub>4</sub> overlaps with those of the reaction matrix under the applied instrumental conditions, increase of the peak intensity at *m/z* = 17 and the missing higher mass peaks for CD<sub>3</sub>H and derivatives upon performing the experiments in CD<sub>3</sub>CN indicate that likewise CH<sub>4</sub> is formed from CO<sub>2</sub> (Fig. S11†).

Notably, fine-tuning of the water concentration in the electrolysis cell and the applied potential allows for the tailored electrochemical production of syngas (Table S4†). Markedly, for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> that were likewise found as reduction products, FE is independent of the water concentration (Fig. S1†) suggesting a different catalytic mechanism. The results clearly show that HER and CO<sub>2</sub>RR are both catalyzed by Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> electrodes and the outcome of the reduction can be tuned by the process conditions rather than by further catalyst modification.

### Durability and potential intermediates

To further investigate the Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> bulk electrodes for its capability to act as a potent electrocatalyst in CO<sub>2</sub>RR, we performed stability tests in acetonitrile (24 ppm water H<sub>2</sub>O) at an applied potential of −1.8 V over 15 h (Fig. 3c). During the electrolysis, the system operated at a constant current density of around 3 mA cm<sup>−2</sup>. While in the beginning of the controlled potential electrolysis, high faradaic efficiencies of up to 87% CO are observed, it decreases slowly with electrolysis time to 75%. In equal measure, the FE for H<sub>2</sub> increases from 8 to 21%. This change in the CO:H<sub>2</sub> selectivity can be caused by either an incremental change of the catalyst surface and hence its reactivity or an increase in water concentration over the course of the electrolysis. Notably, SEM-EDX showed only carbon deposition. The Fe:Ni:S content, however, is not affected, indicating high stability of the material. We subsequently quantified the water content after 15 h electrolysis and observed an elevated water concentration, responsible for the hampered catalyst performance. This increase most likely originates from traces of water present in the CO<sub>2</sub> stream causing accumulation of water in the electrolyte over time. To further evaluate the stability of Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub>, we performed long-time stability experiments in the presence of various amounts of water. Noteworthy, after conducting electrolysis at −1.8 V in a 5000 ppm water acetonitrile solution, the electrode is covered with a black film and correlates with the observed decrease of CO<sub>2</sub>RR activity. Energy dispersive X-ray spectroscopy (EDX) revealed a high carbon content of up to 80% at the electrode surface (Fig. S2†). While similar results were previously observed for Cu electrodes,<sup>44</sup> the exact reason of this electrode passivation, however, is not well understood and remains subject of future investigations.

*Ex situ* X-ray photoelectron spectroscopy (XPS) measurements were carried out to reveal the composition and chemical

state of the pentlandite catalysts as-prepared and after CO<sub>2</sub>RR. Both show a significant content of oxygen as it can be seen from the survey scans (Fig. S12†). Moreover, the sample after reaction bears considerably high amounts of the electrolyte residuals as indicated by intense F 1s, N 1s, and C 1s peaks. A closer investigation of the high-resolution regions of the metallic components (Fig. 4a and b) and sulfur (Fig. 5) confirms severe oxidation of the catalyst surface before and after the reaction and subsequent exposure to air. A spectral deconvolution of the Fe 2p<sub>3/2</sub> photoemission line using an Fe(III) multiplet structure<sup>45</sup> and a single FeS<sub>x</sub> peak (Fig. 4c) indicates only 18 at% of the latter.

Similarly, the Ni 2p<sub>3/2</sub> region is dominated by the Ni(OH)<sub>2</sub> structure<sup>46</sup> represented by a photoemission peak at 855.9 eV and a characteristic shake-up satellite at 861.4 eV (Fig. 4d). The peak at 853.0 eV represents a sulfide species and corresponds to ~23% of the total Ni content. XPS analysis of the sample after reaction does not display a significant change in the chemical state of Fe and Ni, although one needs to consider that both samples were measured *ex situ* and that at least partial catalyst reduction is expected under reaction conditions that can be further re-oxidized upon *ex situ* sample transfer in air. Moreover, calculation of the Fe : Ni ratio for the sulfide species, shows enrichment with nickel before and after reaction. The S 2p region of both samples shows a shape typical for Fe<sub>x</sub>Ni<sub>9−x</sub>S<sub>8</sub> materials<sup>25</sup> with a structure between 160–165 eV, characteristic of oxysulfide films,<sup>47</sup> and a mildly oxidized iron pyrite surface.<sup>48,49</sup> The structure at higher binding energy is deconvoluted in two doublets, at 168.4–169.7 and 166.1–167.3 eV, representing sulfate and sulfite species correspondingly.<sup>50</sup> The structure at higher binding energy is deconvoluted in two doublets, at 168.4–169.7 and 166.1–167.3 eV, representing sulfate and sulfite species, correspondingly. Remarkably, the amount of oxidic sulfur species increases from 17 to 50 at% after the reaction. Despite the high amount of oxidized species observed by XPS, we do not intend to identify those as active in

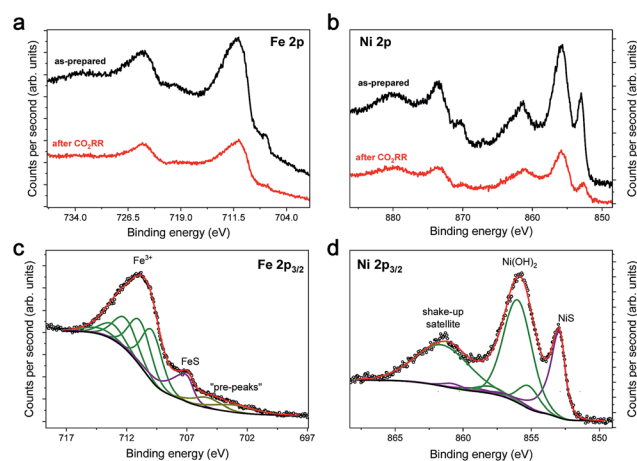


Fig. 4 (a) Fe 2p and (b) Ni 2p XPS spectra of pentlandite before and after CO<sub>2</sub>RR. Examples of the spectral deconvolution fit for the as-prepared sample are shown in (c) for the Fe 2p<sub>3/2</sub> core level and (d) for Ni 2p<sub>3/2</sub>.





Fig. 5 S 2p XPS spectra of the pentlandite before and after CO<sub>2</sub>RR (a) and spectral deconvolution exemplified for the as-prepared sample (b). The decrease in the intensity of the S signal observed after reaction is at least partially related to the overlayer resulting from electrolyte residues.

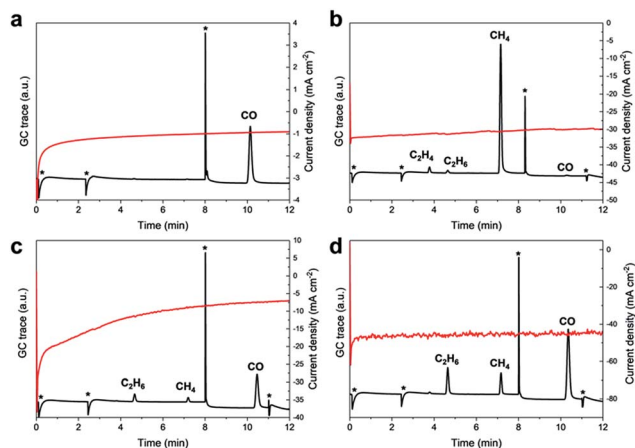


Fig. 6 GC traces and recorded current densities starting from different carbon sources like Cs<sub>2</sub>CO<sub>3</sub> (a), formaldehyde (b), oxalic acid (c) and formic acid (d).

the CO<sub>2</sub>RR. Both Fe and Ni are well known to form native oxide overlayers upon exposure to air. However, the increased amount of oxidic sulfur species is striking. We attribute it to the formation of S defect sites under reaction conditions, which are then more prone to oxidation when exposed to air. Notably, such [NiFe]-oxido-species are also found in the natural archetype Ni-dehydrogenases and are discussed as key intermediates in the enzymatic CO<sub>2</sub> reduction.<sup>51,52</sup>

As copper is one of the benchmark materials in CO<sub>2</sub>RR, we decided to compare Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> and a copper disc electrode under the same experimental conditions. CPC experiments at  $-1.2$ ,  $-1.5$  and  $-1.8$  V vs. NHE were subsequently performed in acetonitrile (113 ppm H<sub>2</sub>O) (Fig. S3†). While we observed current densities of  $-0.14$ ,  $-0.73$  and  $-3.2$  mA cm<sup>-2</sup> at  $-1.2$ ,  $-1.5$ , and  $-1.8$  V, respectively, for Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub>, Cu bulk electrodes showed significantly smaller current densities of  $-0.01$ ,

$-0.10$  and  $-0.28$  mA cm<sup>-2</sup> under otherwise identical conditions (Fig. S3†). Analysis of the gaseous products after 1 hour at  $-1.2$  V and  $-1.5$  V, revealed significant higher HER activity of Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> with FEs of 34 and 51%, respectively, for H<sub>2</sub> in comparison to those observed for Cu bulk electrodes (0 and 6%). *In lieu*, Cu revealed higher efficiency towards methane formation with FE of 20 and 9% at  $-1.2$  V and  $-1.5$  V respectively versus the observed FE of 13 and 4% for Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> electrodes under identical conditions. Likewise, the efficiency for CO at Cu electrodes (FE 39%,  $-1.2$  V; FE 9%,  $-1.5$  V) is higher than observed for Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> (FE 11.4%,  $-1.2$  V; FE 4%,  $-1.5$  V). Notably, these differences are only observed at low current densities/low potentials. At  $-1.8$  V, there is only a small difference in the product distribution. Both, Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> and Cu electrodes reveal suppressed H<sub>2</sub> formation and facilitate the CO<sub>2</sub> reduction to mainly CO (72% FE for both electrodes) and traces of methane (1% FE for Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> and 6% FE for Cu). Notably, at such high potential conditions, Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> generally reveals higher current densities suggesting faster conversion kinetics and revealing its potential (Fig. S3†).

The overall narrow product distribution of Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> pointed our attention towards potential intermediates of the CO<sub>2</sub>RR and their subsequent conversion on Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> bulk electrodes. We thus tested the reactivity of various potential CO<sub>2</sub> reaction products, such as carbonate, CO, formaldehyde, formic acid and oxalic acid under electrocatalytic conditions (at  $-1.8$  V vs. NHE) in acetonitrile containing 24 ppm water.

CPC in saturated Cs<sub>2</sub>CO<sub>3</sub> solutions (3.31 mM) in MeCN yielded exclusively CO as the major product (42% FE, Fig. 6a) and suggests that likewise, carbonates can serve as a CO<sub>2</sub> source. In the presence of oxalic acid, the major reduction product is CO (FE 3.9%) and only trace amounts of hydrogenation to afford C<sub>2</sub>H<sub>4</sub> (FE 0.05%), C<sub>2</sub>H<sub>6</sub> (FE 1.60%) is also detected. Additionally, CO poisoning experiments were performed since Fe and Ni strongly adsorb CO and usually undergo surface deactivation. CPC experiments at  $-1.8$  V vs. NHE in a solution of MeCN (24 ppm H<sub>2</sub>O, Fig. S4 and S5†) applying a continuously applied CO stream showed no obvious influence on the catalytic current and suggests no CO poisoning. Furthermore, neither gaseous nor liquid CO conversion products were detected, underlining the inertness of the Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub> electrodes towards further CO conversion. Under same conditions, a 37% formaldehyde solution afforded high amounts of CH<sub>4</sub> (FE 4.2%) and traces of C<sub>2</sub>H<sub>4</sub> (FE 0.13%) and C<sub>2</sub>H<sub>6</sub> (FE 0.10%) (Fig. 6b). Notably, only negligible amounts of CO were observed herein. It is worth to highlight that C<sub>2</sub>-reduction products are observed in the presence of oxalic or formic acid (Fig. 6c and d) although with low efficiency (FE < 1%). Our results clearly show that although the formation of alternative reduction products seems possible, they will be converted to mainly CO and methane with a minor amount of C-C coupling products.

## Conclusion

In conclusion we have shown, that Fe<sub>4.5</sub>Ni<sub>4.5</sub>S<sub>8</sub>, much like its natural congeners, [FeNi]-hydrogenase and CODH<sub>Ni</sub>, can



catalyze HER as well as CO<sub>2</sub>RR depending on the chemical environment and with seemingly comparable catalytic intermediates. In this regard, protic electrolytes such as aqueous KHCO<sub>3</sub>, methanol as well as aprotic pyridine promote HER with high faradaic efficiency. In addition, utilizing the same electrodes in aprotic solvents such as acetonitrile, dimethyl formamide, dimethyl sulfoxide and propylene carbonate with well-defined water contents, CO<sub>2</sub>RR is favored over HER. Under such conditions, CO and methane are the main products with FE of up to 87% and 13%, respectively, at moderate current densities (*ca.* 3 mA cm<sup>-2</sup>). Our experiments clearly show that controlling the availability of protons in the chemical environment of the electrocatalyst is key towards successful CO<sub>2</sub>RR. While we are aware that water is the preferred electrolyte to perform such reduction reactions, our study shows that investigating potential CO<sub>2</sub>RR electrocatalysts in non-aqueous, can lead to the discovery of novel catalysts that operate under alternative reactions conditions (*e.g.* gas diffusion electrodes or in a pure gas stream). In addition, we herein show that the materials can facilitate the hydrogenation of nitriles with simple iron and nickel-based electrocatalysts.

## Conflicts of interest

There are no conflicts to declare.

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