Robust and biocompatible catalysts for efficient hydrogen-driven microbial electrosynthesis

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CO2 reduction by combined electro- and bio-catalytic reactions is a promising technology platform for sustainable production of chemicals from CO2 and electricity. While heterogeneous electrocatalysts can reduce CO2 to a variety of organic compounds at relatively high reaction rates, these catalysts have limitations achieving high selectivity for any single product beyond CO. Conversely, microbial CO2 reduction pathways proceed at high selectivity; however, the rates at bio-cathodes using direct electron supply via electricity are commonly limiting. Here we demonstrate the use of non-precious metal cathodes that produce hydrogen in situ to support microbial CO2 reduction to C1 and C2 compounds. CoP, MoS2 and NiMo cathodes perform durable hydrogen evolution under biologically relevant conditions, and the integrated system achieves coulombic efficiencies close to 100% without accumulating hydrogen. Moreover, the one-reactor hybrid platform is successfully used for efficient acetate production from electricity and CO2 by microbes previously reported to be inactive in bioelectrochemical systems.

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O₂ as a sole carbon source offers an attractive platform for the sustainable production of chemicals and fuels, with the potential to avoid emitting annually 38.2 billion tons of this greenhouse gas while increasing the independence from fossil resources. Renewable energy technologies are providing new and competitive alternatives for production processes based on (bio)electrochemical reduction of CO₂ to chemicals. Assuming that these chemicals can be combusted as fuels, a carbon-neutral fuel and chemical cycle can be envisioned (cf. Fig. 1a).

A significant advantage of heterogeneous electrocatalysis processes for reducing CO₂ to C₁ and C₂⁺ compounds are high reaction rates in relatively mild reaction conditions. However, selectivity to multi-carbon compounds remains a major challenge, leading to low energy efficiencies and mixed product streams. In addition, insufficient long-term stability of the electrocatalytic performance presents a key issue that must be overcome for practical implementation. Microbial CO₂ reduction reactions, on the other hand, are highly specific, selective, and stable. Moreover, metabolic engineering approaches continuously broaden the product spectrum to include high-value chemicals of industrial relevance. Natural electron donors for microbial CO₂ reduction processes are H₂ and CO and direct supply of electrons for microbial metabolism via a cathode has been demonstrated in microbial electrosynthesis. Several industrially relevant chemicals such as methane, acetic acid, butyric acid, isobutyric acid, hexanoic acid, ethanol, isopropanol, butanol, isobutanol, and hexanol have been shown to be produced via microbial electrosynthesis from CO₂ and electricity. However, these processes currently remain limited by low direct electron uptake rates from the cathode and by a limited number of microbes that are able to directly acquire electrons from solid state electrodes for CO₂ reduction. Thus, an integrated platform that combines the advantages of rapid electrochemical reduction reactions with highly selective microbial syntheses is desirable.

The common electron donor for microbial CO₂ reduction is molecular hydrogen, which can be produced electrochemically via the well-established hydrogen evolution reaction (HER). HER is kinetically more facile than electrochemical CO₂ reduction and achieves simultaneously high current densities and selectivity. Hybrid processes have been proposed that couple the electrocatalytic H₂ production in one process to microbial CO₂ reduction in a second microbial gas fermentation step for the production of chemicals. However, such two-step processes entail the pumping and mixing of a low-soluble and explosive gas (H₂) at significant costs and safety risks.

In fact, most bioelectrochemical CO₂ reduction platforms seem to be driven by molecular hydrogen as intermediate. The cathode material of choice in these systems is commonly carbon-based due to its low price and proven biocompatibility. However, production rates in microbial electrosynthesis can be increased significantly by modifying the cathode material towards more efficient HER, e.g., by introducing transition metals, such as nickel. And while a direct integration of electro- and microbial-catalysis with H₂ as an intermediate offers the possibility to increase overall electron transfer rates, it also presents a significant challenge, because the optimal environmental conditions for both processes differ substantially. While the electrocatalytic HER is best controlled under either strong acidic or alkaline conditions and in ultra-pure electrolytes, microbial synthesis proceeds at circumneutral pH in the presence of essential media supplements (e.g. trace metals and vitamins) and with high concentrations of CO₂. Severe deactivation of inorganic catalysts by microbial growth media components was observed in previous studies as well as toxic effects towards the microorganisms caused by dissolution of the cathode material.

Due to their high electrochemical stability, transition-metal-based electrode materials were identified as particularly promising, and sustainable alternatives to Pt as catalysts for HER. Here, we select the inexpensive, earth-abundant cobalt-phosphide (CoP), molybdenum-disulfide (MoS₂), and nickel–molybdenum alloy (NiMo) as cathode materials as these show particularly promising properties at circumneutral pH and with high concentrations of CO₂. We test their biocompatibility in a directly integrated bioelectrochemical system for production of chemicals from electricity and CO₂ (cf. Fig. 1b), and characterize the electrochemical stability of the different materials under biologically relevant conditions. Using methanogenic archaea and homoacetogenic bacteria, we...
demonstrate stable and high rates of CO2 reduction to methane and acetate, respectively, at coulombic efficiencies of close to 100% and thereby a successfully integrated platform.

Results

Biocompatible hydrogen production by non-precious metal cathodes. We first characterized hydrogen production rates of cathodes with CoP, MoS2, and NiMo as HER catalysts in pure bicarbonate buffer as an approximation for a biocompatible electrolyte for microbial CO2 reduction at neutral pH. Platinum was used as the reference catalyst for the HER in all experiments.

The catalysts were prepared on planar silicon substrates of identical geometric surface areas. The resulting flat electrode surface enables direct comparison of the biocompatibility of the different materials in the integrated conditions by minimizing any convoluting effects introduced by surface roughness of the catalysts. The here presented rates were integrated over a period of 3 h to emphasize the long-term rather than initial performance.

At neutral pH in CO2-sparged aqueous solutions (0.03 M NaHCO3, pH 7), all three catalysts produced hydrogen at rates in the same order of magnitude as the benchmark catalyst platinum (see Fig. 2a and Supplementary Table 1). At all tested potentials (−0.6 to −1 V vs standard hydrogen electrode (SHE)) NiMo electrodes outperformed Pt, while the performances of the CoP and MoS2 electrodes was constantly lower than that of Pt. This trend became more pronounced with decreasing cathode potential. The highest H2 production rate of 48.0 ± 1.5 µmol h−1 cm−2 was observed for the NiMo alloy at a potential of −1 V vs SHE and a coulombic efficiency of 98.0 ± 3.1%. At the same working electrode potential, platinum achieved an average H2 production rate of 39.0 ± 1.5 µmol h−1 cm−2 at a CE of 99.0 ± 3.8%. The H2 production on CoP and MoS2 cathodes occurred at average rates of 11.1 ± 1.6 µmol h−1 cm−2 and 10.0 ± 1.1 µmol h−1 cm−2 and CEs of 94.1 ± 13.6% and 94.0 ± 9.2%, respectively. It is noteworthy that the HER performance can be significantly impacted by electrochemical conditions such as pH39,40, CO2 exposure40–42, and buffering anion concentration43,44. While a direct comparison to other state-of-the-art catalysts is challenging due to the aforementioned factors, the results clearly indicate that all tested catalysts can achieve favorable hydrogen production rates for biointegration, with the NiMo alloy presenting the most promising material under the conditions tested.

Next, the activities of the different electrodes were characterized in the presence of different microbial growth media to evaluate their sensitivity towards required microbial media additions to the electrolyte. When tested in the presence of a yeast extract-containing complex medium used for growth of homoacetogenic bacteria (homoacetogen medium, 1 g L−1 yeast extract) and a marine minimal salt medium (methanogen medium, salinity of 30 g kg−1), cf. Fig. 2b, hydrogen evolution rates by CoP, MoS2, and NiMo electrodes were not significantly affected, indicating insensitivity of the materials towards the presence of essential growth compounds. In the complex homoacetogen medium, a slightly increased current density (+10%) was observed for both CoP and MoS2 (see Supplementary Table 1), while the corresponding coulombic efficiencies were slightly reduced from 94.0% and 96.0% to 84.7% and 83.0%, respectively (see Fig. 2b). This reduction in electron recovery was likely due to unspecific reduction reactions of organic compounds (from supplemented yeast extract) on the cathode surfaces, which seems to negatively affect the selectivity for H2 of both materials under these conditions. In summary, all three cathode materials exhibited relatively high selectivity for HER and remarkably stable performance under biological relevant conditions.

Integrated bioelectrochemical synthesis of methane and acetic acid. Next, we investigated the performance of CoP, MoS2, and NiMo electrodes in integrated bioelectrochemical systems for microbial production of acetate and methane from CO2 and electricity. In this proof-of-concept study, 1 cm2 flat cathodes were introduced into H-type, two-chamber reactors that are used for microbial electrochemistry.45 A constant current of 1 mA cm−2 was applied to the cathodes while CO2 was provided as 20 vol/vol% in N2 gas atmosphere in the reactor headspace. These conditions provide an optimal environment for the selected microbial conversions, therefore excluding a limitation of the overall process by the microbial component.

In one set of experiments, the homoacetogenic bacterium Sporomusa ovata, which metabolizes CO2 and H2 to acetate (Eq. (1)), was introduced as microbial organism to investigate production of acetate as a liquid chemical. In a second set of experiments, we used the methanogenic archaeon Methanococcus maripaludis that reduces CO2 with H2 to CH4 (Eq. (2)), to investigate the production of a stable, gaseous hydrocarbon for energy storage.

$$2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$$

$$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$$

Electrocatalytically produced H2 was efficiently used by both microorganisms for CO2 reduction to acetate and methane, respectively, at high selectivity (Fig. 3, Supplementary Fig. 2 and Supplementary Table 2). Electron recovery in the respective product was near 100% in each case (see Supplementary Table 2). Figure 3 shows the production of acetate and methane in the integrated bioelectrochemical system using a NiMo cathode and S. ovata and M. maripaludis, respectively. The performance of the same system using CoP and MoS2 is summarized in Supplementary Fig. 2 and Table 2. Importantly, no H2 gas was detected (<1 vol/vol%) in the reactor headspace of each experiment throughout the entire duration of 48 h, indicating efficient and stable microbial uptake of the electrochemically produced H2 despite its low solubility in aqueous solutions. In fact, microsensor measurements46 of H2 concentration profiles in the bioelectrochemical system revealed elevated H2 concentrations only in close proximity, 50–100 µm, of the cathode surface (cf. Supplementary Fig. 3d). While the aqueous H2 concentration in abiotic, Ni–Mo cathode-containing reactors was around 220 µmol L−1, the presence and metabolism of M. maripaludis reduced that concentration to 0.2–0.6 µmol L−1 (cf. Supplementary Fig. 3a, c). Such efficient transfer of electrons from cathode into the microbial metabolism via hydrogen without the accumulation of high gas concentrations is an important feature of this directly integrated system for two main reasons: first, the use of H2 as intermediate circumvents the requirement of microbial electro-synthesis for a direct electron transfer and, therefore, extends the spectrum of microbial production hosts to possibly any gas fermenting microorganism. And secondly, the efficient H2 uptake close to the electrode surface could enable increased production rates as it is known that production rates in gas fermentation are commonly hydrogen limited15,47. Future research aiming to balance and maximize rates between inorganic HER and microbial CO2 reduction will facilitate engineering efforts to further advancing the technology29.

Notably, the cathode potentials to supply a constant current of 1 mA cm−2 for all three materials did not change significantly during the period of 48 h (cf. Fig. 3 and Supplementary Table 2). The maximum change in cathode potential was 193 mV observed for CoP in the setup using M. maripaludis, while NiMo showed the highest stability with potential changes as low as 60 mV (cf. Supplementary Table 2). An increase in reduction potential under
constant current conditions could be caused by blocking of active sites on the HER catalyst surface in the biological system. Microscopy studies did not find evidence for attachment of microbial cells to any of the tested, flat-surface cathodes (data not shown). To investigate potential surface contamination introduced through media supplements or microbial activity, XPS survey and high-resolution scans of the electrode materials were performed before and after the operation in the integrated bioelectrochemical system. All three materials showed significant accumulation of various elements after the biotic experiments (cf. Supplementary Table 3). Interestingly, however, HER activity and selectivity were retained despite these accumulations, indicating a good stability of the catalytic activity for HER even in highly supplemented electrolytes. Further, the stable selectivity for H₂ as single product conferred outright biocompatibility, and no negative effect on the tested bacteria and archaea on growth or metabolism was observed. This identifies the tested materials CoP, MoS₂, and NiMo as promising cathode materials for direct integration in hydrogen-driven bioelectrochemical systems.

**Long-term performance.** To test for robustness and long-term stability, we operated the integrated reactor system using a NiMo cathode and *M. maripaludis* for 10 days (cf. Fig. 4). When the substrate CO₂ was nearly depleted after 65 h, the reactor headspace was exchanged to remove CH₄ and to re-supply gaseous CO₂ (indicated by vertical dashed lines in Fig. 4); the growth medium was not exchanged, and both catalysts, inorganic NiMo,
and biologic *M. maripaludis* remained in the reactor. We continued this operation for a total of four cycles. The results demonstrated a repeatable and stable performance of both catalysts at consistently high coulombic efficiency for methane production from CO₂ utilizing the electrochemically produced hydrogen for a period of 10 days (see Fig. 4). Coulombic efficiencies were again close to 100% throughout the first three cycles. During the fourth cycle, a slight hydrogen accumulation in the gas phase was noted, which lowered the electron to product recovery to about 95%. This is likely due to a decrease in
microbial activity as medium supplements such as vitamins, trace elements, or reducing agent may have been depleted.

Notably, the HER performance of the NiMo cathode showed very good repeatability over multiple reaction cycles with no evidence of irreversible deactivation. Conventional HER works best at either very high or very low pH, because the concentration of proton donors and/or electrolyte conductivity is maximized\(^\text{18}\). It was shown that at neutral pH, alternative earth-abundant catalysts are able to achieve HER rates comparable to platinum or even outperform platinum-based materials\(^\text{48–50}\). Long-term stability, however, remains a major challenge in these systems. Here, the demonstrated stability over 245 h in highly supplemented electrolyte at neutral pH is therefore particularly promising.

**Microbial electrosynthesis beyond known electroactive microbes.** In previous studies, only a limited number of microbial species were identified to be able to accept electrons directly derived from a cathode for CO\(_2\) reduction in a process called direct electron transport (DET)\(^\text{21}\) while a significant number of microbes were reported to be deficient of DET\(^\text{18,21}\). As the above experiments demonstrated, the use of transition-metal-based cathodes enabled efficient direct integration of microbial electrosynthesis from CO\(_2\) and electricity via in situ produced H\(_2\), thereby circumventing the limiting necessity of a direct microbe–cathode interaction. Therefore, we hypothesized that an H\(_2\)-mediated system would enable the cultivation of any microbe capable of metabolic H\(_2\)-reduction, including microorganisms categorized as “electro-inactive”. To test this hypothesis, we used the homoacetogen *Acetobacterium woodii*, reported to be incapable of DET\(^\text{24}\), in our integrated reactor system and observed stable acetate production (see Fig. 5). Similarly to the experiments with *S. ovata* and *M. maripaludis*, hydrogen was taken up and converted into acetate at coulombic efficiency of near 100%. No toxic effects of the catalyst material towards the microorganism were observed, and, again, the inorganic cathode seemed resistant to biofouling.

Collectively, these results indicate a promising potential for the use of transition-metal-based cathodes for H\(_2\)-driven bioelectrochemical systems for production of organic chemicals. The ability to use potentially any autotrophic microorganism in such one-reactor bioelectrochemical system with electricity and CO\(_2\) as the only inputs would significantly expand the microbial platforms and their synthetic capacities for microbial electrosynthesis.

**Discussion**

Here, we demonstrated a robust and efficient, integrated bioelectrochemical platform for highly selective production of organic compounds from CO\(_2\) using earth-abundant transition-metal-based cathodes. The observed long-term stability of H\(_2\) production on CoP, MoS\(_2\), and NiMo cathodes, despite the accumulation of organic and inorganic material on the electrode surface, demonstrates the potential of this technology to be usable at industrially relevant time scales. Thus, this integrated system provides a robust and scalable pathway to combine electrochemical catalysis and the high selectivity and stability of biological systems. Moreover, the successful integration utilizing the “electro-inactive” *A. woodii* established this system as a platform for many more H\(_2\)-utilizing, CO\(_2\)-reducing microorganisms. The herein demonstrated production of acetate and methane at high selectivity, rate, and stability can be considered as an entry point for production of a range of industrially relevant chemicals. With the current rapid development of tools for genetic engineering and systems biology, it is expected that both commodity and higher value organic chemicals can be produced in the near future via this platform\(^\text{15,16,51–53}\), which is based only on an electron supply via biocompatible cathodes, electricity, CO\(_2\), and microorganisms.

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**Fig. 5** Electric production by a non-electroactive microbe. Demonstration of acetate production in a directly integrated bioelectrochemical system by the homoacetogen *Acetobacterium woodii*, known to be incapable of DET\(^\text{21}\). Electrons were supplied via a NiMo cathode at constant current density of 1 mA cm\(^{-2}\). Electrolyte was microbial growth medium modified-DSMZ-135. The product acetate was measured in the liquid phase of the reactor and is plotted as electron equivalents. Dotted line: electrons; hollow triangles: hydrogen; yellow diamonds: acetate; solid triangles: cathode potential vs SHE. Error bars represent standard deviation between biological triplicates.
Methods

Electrode fabrication. Transition-metal-based cathodes were fabricated as flat films on silicon substrates via the following methods. CoP and MoS2 were prepared as previously described using physical vapor deposition followed by phosphorylation or sulfidation, respectively40,44-45. For preparation of CoP, ~50 nm of Co was evaporated onto a clean, degenerately doped n-type Si wafer. Subsequently the samples were phosphinated at elevated temperatures in a multi-zone furnace using red phosphorus as a precursor upstream with H2 gas flowing. For preparation of MoS2, ~3.6 nm of Mo was sputtered onto a clean degenerately doped p-type Si wafer and subsequently sulfidized at 250 °C for 1 h while flowing an H2/HS2 gas mixture. Platinum and NiMo layers were prepared directly by physical vapor deposition onto clean, degenerately doped Si wafer substrates. The NiMo was achieved using dual-source, co-evaporation of Ni and Mo. The resulting NiMo were of approximate thickness of 100 nm. Based on the film thickness, planar area, and density of the crystal structure we estimate the following specific loadings: Co in CoP: 4.4 × 10−3 mg cm−2; Co: Mo in MoS2: 3.7 × 10−3 mg cm−2; Mo: Pt 2.15 × 10−3 mg cm−2; Pt and NiMo: 9.6 × 10−3 mg cm−2 NiMo.

Microbial strains and growth conditions. M. maripaludis (wild-type strain MM901) was cultured on modified DSMZ medium 141, omitting Na-acetate, yeast extract, tryptcase, Na-resazurin, and buffered with 100 mM morpholine-propanesulfonic acid (MOPS) at pH 7. S. ovata (wild-type strain DSM 3300) was cultured on modified DSMZ medium 879 omitting fructose and Na-resazurin, and buffered with 100 mM morpholine-2-(N-morpholino)ethanesulfonic acid (MES) at pH 5.9. A. woodii (wild-type strain DSM 1030) was cultured on modified DSMZ medium 135 omitting fructose and Na-resazurin, and buffered with 100 mM MOPS at pH 7. In both media, modified DSMZ879 and modified DSMZ135, the yeast extract content was reduced to 1 g L−1. Further, in all media Na2S was omitted (to avoid stripping of gas products by Na2S) and buffered with 100 mM MOPS where necessary. The media were deaerated to less than 1% dissolved oxygen and pH adjusted to those of natural environments. Cultures were incubated at 500 rpm, 30 °C and 200 rpm, 30 °C for bioelectrochemical experiments. Cells were harvested in the late exponential phase at an optical density (OD600) of 0.35–0.45, twice pelleted (5000 rpm, 5 min, 30 °C), and resuspended in fresh medium under anaerobic conditions.

For all different microbe species tested in this study and for every media employed here, no growth or production of methane/acetate was observed in the absence of either H2 or a negatively poised cathode, indicating that a small amount of yeast extract and/or other media components were not sufficient to support growth and/or product formation.

Integrated bioelectrochemical system. The bioelectrochemical reactors are custom-made, borosilicate glassy hemicylindrical gas-handles (Adams & Chittenden, Scientific Glass, Berkeley, CA, USA). The two chambers have a volume of 150 mL each and were separated by a Nafion 117 proton-exchange membrane (Fuel Cell Store Inc., College Station, TX, USA). Each cell chamber was filled with 100 mL electrolyte under a nitrogen atmosphere. Cultures were inoculated with 2% (v/v) of an exponentially growing concentrated microbial cultures were added as concentrated, washed cell suspensions to a start OD600 of 0.2 inside the cathode chamber. Each experiment was performed as a closed batch system in three independent biological replicates.

Analytical methods. The gaseous compounds methane and hydrogen were measured using a gas chromatograph (equipped with a thermal conductivity detector and a flame ionization detection detector) as described previously87. Acetate and other liquid metabolites were measured via high-performance liquid chromatography as described previously48. To allow comparison of electron uptake rates during the formation of different target products and to visualize electron to product recovery, concentrations of H2, CH4, and acetate were given as electron equivalents by multiplying the measured concentrations of the respective compound by the number of electrons required for its formation.

Coulombic efficiencies were calculated by dividing the electrons recovered in products by the electrons supplied as current at a certain time point.

Hydrogen profiles using microsensor measurements. Concentration profiles of H2 were recorded with commercially available H2 microsensors (Unisense A/S) and H2 microsensors with a sulfide frontguard. The H2 microsensors had a tip size of 20–40 μm and a sensitivity of 0.8–1.2 pA μM−1. The H2 microsensors were connected to a picoammeter, which was connected to an AD-converter connected to a computer. When profiling the microsensors were mounted in a motorized micromanipulator controlled by the software Sensortrace Pro (Unisense A/S) that also recorded the microsensor signals.

Probing in the bioelectrochemical reactors was achieved by introducing the microsensor through a hole in the rubber stopper lid, which allowed for automated movement of the sensor. To ensure anoxic conditions, the headspace was constantly flushed with anoxic gas: CO2/N2 (20/80% v/v). Except for the microsensor insertion and headspace flushing, the reactor setup was identical to the description above. Profiles were recorded from the gas phase down to the cathode surface at 500 μm steps while detailed profiles at the cathode surface were recorded with 50 μm steps. Profiling ceased when a change in the sensor signal indicated that the sensor was touching the cathode surface. In the recorded profiles, the last measurement point unaffected by cathode surface contact was defined as first point within 50 μm of the cathode surface. Recorded profiles are summarized in Supplementary Fig. 3.

Cathode surface characterization. The characterization of surface compositions of the cathodes before and after electrochemical reactions was performed via XPS. The measurements were collected on a PHI Versaprobe III instrument using a high-power mode to collect survey scans with charge neutralization enabled after Ar gas cleaning to partially remove excess organics from the surface. Acquired spectra were quantified using the Multipak software package and presented in a summary format in Supplementary Table 3.

Data availability

The authors declare that all the other data supporting the findings of this study are available within the article and its supplementary information files and from the corresponding author upon request.

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