CO_2 Reduction Using an Electrochemical Approach from Chemical, Biological, and Geological Aspects in the Ancient and Modern Earth

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Abstract The past few decades have witnessed significant advances in our understanding of the synthesis routes and development of electrocatalysts for the reduction of CO_2 to hydrocarbons. It is also notable that the research field related to the Origin of Life theory starts to recognize the significance of electrochemical CO_2 reduction by metal-sulfide minerals as the primary step for organic carbon synthesis. In this chapter, we describe recent progress in the development of catalysts for CO_2 reduction in electrochemical systems, particularly from the viewpoint of the Origin of Life theory, and discuss the perspectives related to the evolutional origin of carbon monoxide dehydrogenases (CODHs), known as one of the most active natural enzymes for CO_2 reduction.

1 Introduction

In an attempt to mitigate the adverse effects of global warming, there has been considerable efforts to produce sustainable electricity from renewable energy sources, such as hydro, solar, wind, and geothermal power. Despite these efforts, renewable energy has inherent limitations: intermittency and fluctuation in the amount of generated energy. One possible solution for overcoming this limitation is to convert generated electricity into H_2 via electrochemical water-splitting reactions. Although electrolysis appears to be a promising solution for producing

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reliable and sustainable energy, it is highly desired that the generated H_2 is converted into liquid form for transport, a process that requires considerable energy. Although the commercialization of H_2 as an energy fuel has increased in recent years, the processing and transport of H_2, and the associated infrastructure, remain a major restriction for the widespread use of H_2 as an energy fuel. Another potential solution for the effective use of electricity generated by renewable energy would be to electrochemically convert CO_2 into hydrocarbons. Compared to H_2, hydrocarbons are more easily transformed to liquid form, and further, the infrastructure for hydrocarbon distribution, storage and utilization has been firmly established.

The past few decades have witnessed significant advances in our understanding of the synthesis routes and development of electrocatalysts for the reduction of CO_2 to hydrocarbons. CO_2 reduction catalysts are typically metals or metal alloys, such as pure metallic Cu, which is considered to be an ideal catalytic material for the production of hydrocarbons with high Faradaic efficiency (FE). However, the selective production of hydrocarbons requires an overpotential (η) on the order of 1 V to avoid the formation of H_2 gas. Furthermore, if water is oxidized to O_2 at the anode, the η for the electrochemical conversion of CO_2 to hydrocarbons increases to as high as 2 V. Such high η values are a major obstacle for improving the energy efficiency of hydrocarbon synthesis, which is a necessary prerequisite for the practical application of heterogeneous electrocatalysts in CO_2 fixation systems.

Biological systems convert CO_2 into hydrocarbons with remarkably low η and high FE through diverse enzymatic reactions. The most outstanding example is carbon monoxide dehydrogenases (CODHs), which are found in certain chemolithoautotrophic microorganisms, including acetogens and methanogens, convert CO_2 into CO with a turnover frequency as high as 45 s^{-1} [1, 2]. CODHs can also electrochemically reduce CO_2 to CO at potentials near the thermodynamic potential with the FE of nearly 100 % [1, 2]. The remarkable efficiency of CODHs for CO_2 reduction has inspired numerous scientists to determine the underlying multi-step mechanisms for developing bioinspired catalysts for carbon utilization.

The family of CODHs has evolved over billions of years, and they have used Fe, Ni, Cu and Mo as active sites. Thus, one of the fundamental issues to consider is how the active cores of CODHs, namely Fe_4S_4Ni and MoSCu, have evolved from environmentally abundant rock-forming elements and been functionalized specific for CO_2 reduction with the aid of N- and S-containing peptides. As proposed in the Origin of Life theory, the surface of bisulfide-bearing hydrothermal precipitates with trace metals, such as Ni, Cu, W and Mo, is suggested to have played a critical role in prebiotic organic synthesis by CO_2 reduction on ancient Earth [3–5]. Given those facts, seeking the evolutional transition of inactive FeS minerals to active inorganic analogs of natural enzymes is what scientists can learn from nature's trails in order to acquire the effective catalysts. In other words, in addition to determining the multi-step mechanisms by which modern-day enzymes mediate CO_2 reduction, study of the evolutionary transition of prebiotic catalysts to biotic ones and the geochemical conditions that fostered the transition may provide a new design rationale for the functional analogues of biological catalysts.

Based on the above considerations, this chapter describes recent progress in the development of catalysts for CO_2 reduction in electrochemical systems, particularly from the viewpoint of the Origin of Life theory, which concerns the early evolution of energy metabolism on ancient Earth. After briefly overviewing electrochemical CO_2 reduction by metal electrodes in Sects. 2 and 3, bioinspired approaches for catalytic CO_2 reduction are presented, and the importance of the "frustrated Lewis acid-base pair motif" for CO_2 activation is discussed in Sects. 4 and 5. In Sects. 6 and 7, recent progress on the Origin of Life theory is introduced, and the interaction between electrocatalysts and biogeochemical communities is discussed as a platform for exploring functional analogues of biological catalysts for CO_2 reduction. In Sects. 8, perspectives related to the bioenergetic evolution of CO_2 reduction and carbon assimilation are described.

2 CO_2 Reduction by Metal Electrodes

The first report in the late 19th century on the electrochemical conversion of CO_2 to organic chemicals described the reduction of CO_2 to formic acid [6]. Early electrochemical conversion studies utilized mercury and amalgam, such as zinc-amalgam and sodium-amalgam, as electrocatalysts and demonstrated the high FEs for the production of formic acid [6–12].

Since the late 1970s, researchers have searched for metal electrodes capable of acting as catalysts for CO_2 reduction. For example, Ito et al. investigated CO_2 reduction by Zn, Pb, Sn, In, and Cd metal electrodes using chromotropic acid testing and infrared spectroscopy [13] and revealed that only formate was produced by all of these catalysts during the reduction of CO_2. In 1985, Hori et al. conducted galvanostatic electrolysis at a constant current density of 5 mA cm^{-2} on various metal electrodes, including Cu, Au, Ag, Zn, Pd, Ga, Pb, Hg, In, Sn, Cd, Tl, Ni, Fe, Pt, and Ti [14, 15], and found that formate was predominantly formed at Cd, In, Sn, and Pb cathodes, whereas carbon monoxide was the primary product at Ag and Au cathodes (Table 1). Furthermore, among the examined metals, the Cu cathode was specifically active for the eight-electron reduction of CO_2 to form methane. Based on the work by Ito and Hori et al., electrode metals can be categorized into four groups: (i) metal electrodes that selectively produce formate (Hg, In, Pb, and Sn electrodes); (ii) those that mainly produce carbon monoxide (Au, Ag, Zn, and Pd electrodes), (iii) electrodes that yield hydrocarbons and alcohols (Cu electrode), and (iv) those that show no or little activity toward CO_2 reduction (Ni, Fe, Pt and Ti electrodes). Although the factors controlling the product dependence on the metals remain unknown [15, 16], the results reported by Ito et al. and Hori et al. clearly indicate that the nature of the metal electrodes influence the products formed during electrochemical CO_2 reduction.

Table 1 CO_2 reduction products on metal electrodes in aqueous solution reported by Hori et al. [14]

Metal electrode	Electrode potential	Faradaic efficiency/%		Lower limit/Upper limit		
	(V vs. SHE)	$HCOO^-$	CO	CH_4	H_2	Total
Cd	−1.66 ± 0.02	65.3/67.2	6.2/11.1	0.2	14.9/22.2	93/100
Sn	−1.40 ± 0.04	65.5/79.5	2.4/4.1	0.1/0.2	13.4/40.8	94/110
Pb	−1.62 ± 0.03	72.5/88.8	0.3/0.6	0.1/0.2	3.8/30.9	94/100
In	−1.51 ± 0.05	92.7/97.6	0.9/2.2	0.0	1.6/4.5	93/102
Zn	−1.56 ± 0.08	17.6/85.0	3.3/63.3	0.0	2.2/17.6	90/98
Cu	−1.39 ± 0.02	15.4/16.5	1.5/3.1	37.1/40.0	32.8/33.0	87/92
Ag	−1.45 ± 0.02	1.6/4.6	61.4/89.9	0.0	10.4/35.3	99/106
Au	−1.14 ± 0.01	0.4/1.0	81.2/93.0	0.0	6.7/23.2	100/105
Ni	−1.39	0.3	0.0	1.2	96.3	98
Fe	−1.42	2.1	1.4	0.0	97.5	101

3 Nitrogen-Containing Molecules as Cocatalysts for Electrochemical CO_2 Reduction

One approach for improving the catalytic activity and FF for electrochemical CO_2 reduction on metal electrodes is the utilization of nitrogen (N)-containing compounds as catalysts. In 1994, Seshadri et al. [17] reported that hydrogenated Pd electrodes electrochemically reduced CO_2 to methanol with an FE of 30 % and η of less than 200 mV in the presence of pyridine. Morris et al. [18] further studied pyridine-catalyzed CO_2 reduction with Pt electrodes by changing the catalyst concentration, temperature, and pressure, and confirmed that the reaction kinetics follow the first order with respect to both CO_2 and pyridine. Based on these experimental results, combined with density functional theory (DFT) calculations, the authors proposed the reduced activation energy for CO_2 reduction by pyridine stabilization of carbamate species, which are possible intermediates for CO_2 reduction, by the Lewis basicity of the pyridyl N and metal electrode surface. Further calculations by Keith et al. [19] indicated that the active species was a "surface-bound" dihydropyridine (DHP), rather than a pyridinyl radical in solution.

The use of ionic liquids as catalysts for CO_2 reduction has also been demonstrated as an effective approach to lower η and increase FEs. For example, Rosen et al. [20] electrochemically reduced CO_2 with an Ag cathode in an ionic liquid electrolyte and achieved an η of less than 200 mV and an FEs of more than 96 % for CO production. Notably, the authors utilized 1-ethyl-3-methylimidazolium fluoroborate (EMIM-BF_4) with the expectation that this compound would complex with CO_2 to stabilize the intermediate CO_2^- radical species. The discovery of ionic liquid-based CO_2 reduction has significantly expanded the range of materials that can function as electrocatalysts for CO_2 reduction [21–26].

Although these observations clearly indicate that N-containing molecular catalysts are effective for electrochemical CO_2 reduction in terms of the stabilization of intermediate species, the properties of the metal electrodes and their contribution to catalytic activity have not been examined in detail.

4 Cooperative Activation of CO_2 by Metals and Amino Acids in Biological Systems

The former section described the effectiveness of using homogeneous molecular catalysts for achieving high FE and low η for electrochemical CO_2 reduction. Because the electrochemical reaction proceeds at the metal electrode surface, the interaction between the metal electrodes and CO_2 and/or other reaction intermediates, in addition to the presence of N-containing compounds, should be taken into consideration when designing CO_2 reduction catalysts. One of the most sophisticated examples of the cooperative effect of metals and N-containing compounds for CO_2 reduction is the natural enzymatic system CODH [27, 28]. There are two main types of CODHs: Mo-containing CODHs, which are used by aerobic bacteria [29], and Ni-containing CODHs, which are found in anaerobic bacteria [30]. The crystal structure of Mo–CODH was first reported by Dobbek et al. in 1999 [31] at a resolution of 2.2 Å (Fig. 1, left). The active site of Mo–CODH is composed of molybdopterin-cytosine dinucleotide and S-selanylcysteine connected to a [2Fe–2S] cluster and flavin-adenine dinucleotide. The same research group determined the crystal structure of Ni–CODH in 2001 [32] at a resolution of 1.63 Å (Fig. 1, right).

To better understand the catalytic mechanisms of CO_2 reduction, a series of spectroscopic, biochemical, and structural experiments have been conducted for Ni–CODH as summarized in a review paper [33], because it catalyzes the interconversion between CO_2 and CO [2], while Mo–CODH can only catalyze the

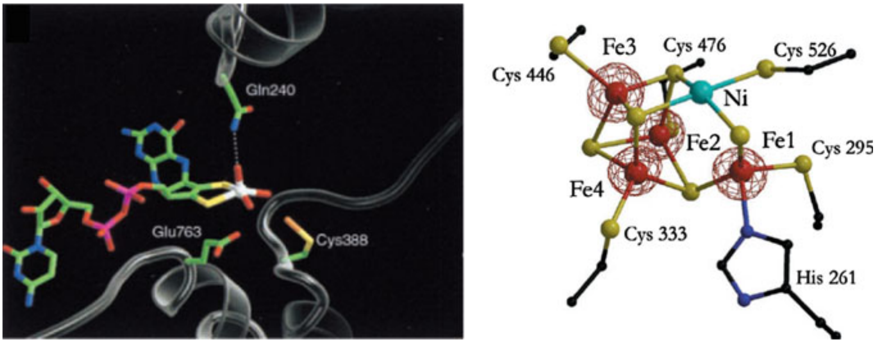

Fig. 1 Crystal structures of the active centers of Mo-containing CODH from aerobic bacteria [31] (*left*) and Ni-containing CODH from anaerobic bacteria [32] (*right*), as reported by Dobbek et al.

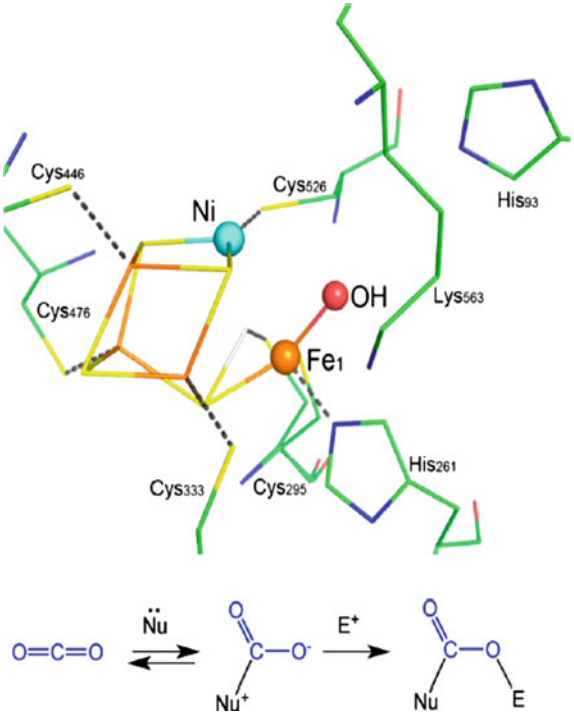

Fig. 2 *Ball-and-stick* drawing of the active site of Ni-containing CODH. A combination of nucleophilic (Nu and Ni sites in the CODH active center) and electrophilic (E, histidine 93 in CODH) interactions facilitates the reduction of CO_2 [27]

oxidation of CO to CO_2. The findings from these studies highlight the importance of nucleophilic and electrophilic interactions for the cooperative activation of CO_2 [27]. For Ni–CODH, the cooperative activation of CO_2 occurs through the nucleophilic interaction of a Ni site to a carboxylate carbon atom, and also involves electrophilic interactions of a lysine residue and Fe site with one of the carboxylate oxygen atoms [27]. These combined interactions, which is a so-called “frustrated Lewis acid-base pair motif” [34], are essential for decreasing the C–O bond order of CO_2, enabling Ni–CODH to effectively reduce CO_2 to CO without the use of strong electrophiles or nucleophiles (Fig. 2). The concept of a “frustrated Lewis acid-base pair” has been proposed for a number of enzymatic reactions in biological systems; however, few examples are applicable for the rational design of electrocatalysts.

5 Metal Sulfides as Biomimetic Catalysts

As the active sites of CODHs are composed of metal-sulfur clusters, metal sulfides are possible candidates for CO_2 reduction catalysts; however, metal sulfides have received relatively little attention as electrocatalysts for CO_2 reduction compared to electrocatalysis with metals and metal alloys. Inspired by the active sites for enzymatic CO_2 reduction in natural systems, Hidai et al. synthesized Fe–S cubane clusters, $[Fe_4S_4(SR)_4]^{2-}$ ($R = CH_2C_6H_5$ or C_6H_5), and evaluated the potential of these clusters for electrochemical CO_2 reduction in *N, N*-dimethylformamide (DMF) [35]. The addition of $[Fe_4S_4(SR)_4]^{2-}$ clusters on a mercury pool electrode resulted in an approx. 700 mV decrease in η. Although the main reaction product was oxalate, the addition of small amount of water increased the production rate of both formate and CO. Tanaka et al. synthesized a metal-sulfur cluster [36] composed of Mo, Fe and S ($[Mo_2Fe_6S_8(SEt)_9]^3$ to mimic the enzymes that found in the reductive carboxylic cycle in photosynthetic bacteria. The model reaction of α-keto acid synthesis proceeded in the presence of the cluster under acetonitrile conditions with an applied electrode potential of −1.55 V versus SCE: $RC(O)SEt + CO_2 + 2e^- \rightarrow RC(O)COO^- + EtS^-$ ($R = CH_3, C_2H_5, C_6H_5$). In addition to α-keto acid synthesis, β-keto acid synthesis was also promoted by $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$; $8PhC(O)CH_3 + 8CO_2 + 2NO_2^- + 6e^- \rightarrow 8PhC(O)CH_2COO^- + N_2 + 4H_2O$ [37]. In 2011, Kanatzidis et al. reported [38] that a chalcogel-type material, in which Fe–S cubane clusters and transition metals (Pt, Co, Ni, Sn, or Zn) were connected by Sn–S clusters, was capable of electrochemical CO_2 reduction. Notably, the CO_2 reduction efficiency in DMF tended to be higher when Ni or Co was utilized as transition metal sites. In all of these reports, the electrochemical reduction of CO_2 was conducted in an organic solvent, and the use of metal-sulfide clusters in aqueous solution has not been extensively examined, even though CODHs can catalyze the reduction of CO_2 to CO with high FE and low η under aqueous conditions [2]. To functionalize metal sulfides as CO_2 reduction catalysts, the cooperative effects of the metal centers and the surrounding N-containing molecules are an important consideration, as demonstrated in natural systems, as described in Sect. 4.

In 2014, having the idea that $FeNi_2S_4$ (violarite) has the structural similarity to the Fe_4S_4Ni active site in CODH [39], the electroreduction of CO_2 by $FeNi_2S_4$ (violarite) in aqueous solution was reported by our group [40]. Although Fe_3S_4 (greigite) inefficiently reduces CO_2, the efficiency of CO and CH_4 production was substantially improved by the substitution of Fe with Ni to form violarite. The electroreduction of CO_2 by $FeNi_2S_4$ in aqueous solution was further enhanced by modifying the surface of violarite with amine compounds, such as triethylamine and poly-allylamine hydrochloride (Fig. 3). As CO_2 reduction by CODH involves cooperative activation via both nucleophilic and electrophilic interactions [27], the enhanced activation of CO_2 reduction by substitution of Fe with Ni and the surface modification by amine compounds is of particular interest for the rational design of the efficient CO_2 reduction catalysts.

To clarify the role of Ni in the active site of CODH for the electroreduction of CO_2, Nørskov et al. [41] performed DFT calculations for a $[Fe_4S_4]$ cubane cluster with and without the substitution of Fe with Ni. The substitution of Ni in place of Fe was found to markedly decrease the activation energy for the reduction of CO_2 to CO, but the activation energy for COOH production was not affected. The authors attributed this decrease to a change in the coordination environment of the adsorbed COOH (COOH*) intermediate resulting from the Ni substitution (Fig. 4). Specifically, COOH* only binds to S sites in $[NiFe_3S_4]$ clusters, but binds to both S

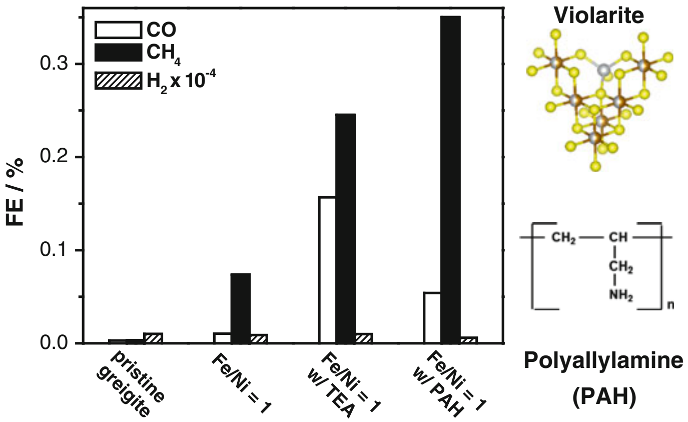

Fig. 3 Faradaic efficiencies (FEs) for CO, CH_4 and H_2 production by greigite, violarite (Fe/Ni = 1) and violarite (Fe/Ni = 1) modified with triethylamine (TEA) or polyallylamine (PAH) under a potentiostatic condition of −1.3 V versus SHE for 30 min [40]. The electrolyte pH was 5.5

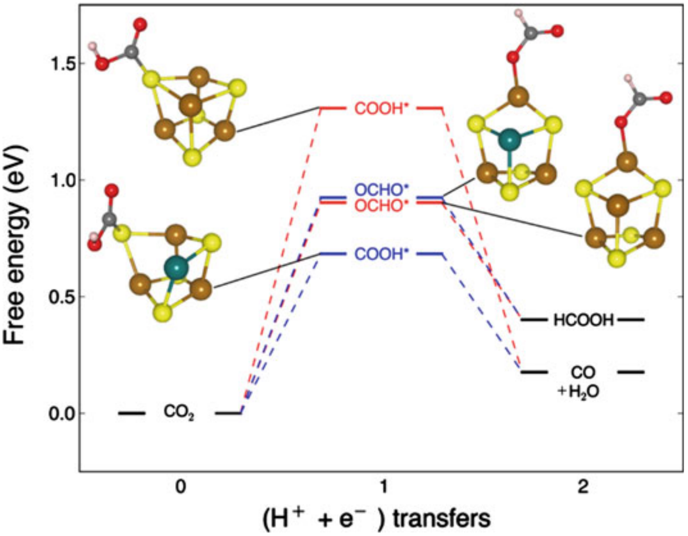

Fig. 4 Free energy diagram for CO_2 reduction on $[Fe_4S_4]^{2-}$ (*left top and right bottom*) and $[NiFe_3S_4]^{2-}$ (*left bottom and right top*) cubane complexes based on DFT calculations reported by Nørskov et al. [41]

and Fe in $[Fe_4S_4]$ clusters. Interestingly, a further decrease in the activation energy was predicted by additional Ni substitution, but only one or zero Ni-substituted cluster was predicted to be stable during the catalytic cycle. Notably, however, the computational study by Nørskov et al. did not consider the function of amino acid residues in the activation process of CO_2 reduction. As we reported previously, amine compounds play a cooperative role with Ni sites for electrochemical CO_2 reduction [40]. Therefore, a DFT study on the role of amino acids in this process is expected to provide new insights into the differences between CODH and abiotic catalysts comprised of $NiFe_3S_4$ clusters, and aid in incorporating the function of the 'frustrated Lewis acid-base pair motif' into man-made electrocatalysts.

An interesting and unanswered question is how prebiotic catalysts for CO_2 reduction evolved from readily available elements in the environments, and further, how these catalysts were functionalized to achieve low η and high FE. Concerning these points, numerous hypotheses related to chemical evolution in the prebiotic ocean and the early evolution of energy metabolism in ancient Earth have been proposed [3–5, 42]. In Sects. 6, 7 and 8, we describe the intimate relationship between processes related to the Origin of Life and electrochemistry, and discuss how these processes can help shape the design rationale for heterogeneous electrocatalysts for efficient CO_2 reduction.

6 Prebiotic Organic Synthesis by Metal Sulfides

Hydrothermal vents in the deep sea floors are surrounded by diverse ecosystems that are sustained by the chemical energy within hydrothermal fluid [43]. It is generally considered that the hydrothermal environment played a crucial role in the emergence of life on primordial earth. Although it remains a topic of debate as to whether primordial life was autotrophic or heterotrophic, the discovery of hydrothermal vents in the 1970s led researches to consider that the first species were autotrophic in nature [44]. One of the main problems of the autotrophic origin theory is the process of carbon fixation; namely, how were organic compounds continuously synthesized at hydrothermal vent? In an attempt to answer this question, Wächtershäuser proposed that CO_2 reduction proceeded at the surface of pyrite (FeS_2) [45, 46]. In this model, organic molecules synthesized on pyrite self-organized to form the first metabolizing cell. The driving force of CO_2 reduction in this system is the oxidative formation of pyrite ($4CO_2 + 7H_2S + 7FeS \rightarrow (CH_2{-}COOH)_2 + 7FeS_2 + 4H_2O$, $G^O = -420$ kJ/mol). This hypothesis is supported by the experimental observations that thiol (CH_3S^-) is formed from CO_2 in the presence of FeS [47]; acetic acid is formed from CH_3SH and CO on iron-nickel sulfide [5]; and peptides are formed from amino acids with CO and iron-nickel sulfide [48].

In contrast to Wächtershäuser's hypothesis, Russell proposed that CO_2 in ocean water reacts with H_2 contained in alkaline hydrothermal fluid in three-dimensional nano- or micro-sized cavities composed of iron sulfides [49]. The main difference between the hypotheses of Wächtershäuser and Russell is that the former considers FeS as an energy source for CO_2 reduction, whereas the latter treats FeS as a component for the reactors, with H_2, rather than FeS, acting as the electron donor for CO_2 reduction. Of note, iron sulfides, particularly Nickelian mackinawite

($FeNiS_2$), Ni-containing greigite ($NiFe_5S_8$), and violarite ($FeNi_2S_4$), are speculated to act as the "catalysts" for CO_2 reduction in the cavities proposed in Russell's model, as these materials share structural similarity to [Ni–Fe] hydrogenase, the C-cluster in CODH, and the ACS active site A-cluster, respectively [39]. Russell et al. further hypothesized that H_2, when adsorbed onto and/or absorbed into the mineral cubane sites, is dissociated into a proton, electron, and reactive hydrogen atom ($H^{\bullet}$), which then reduces CO_2 to CO [42]. Subsequently, the generated CO reacts with methane thiol (CH_3SH) produced in the Earth's crust [45] to form thioester acetyl methylsulphide, which is then hydrolyzed to acetate [5].

7 Bioelectrochemical CO_2 Reduction at Deep-Sea Hydrothermal Vents

To explain how processes related to the Origin of Life and electrochemistry are being merged, we introduce our recent findings regarding the energetics of CO_2 reduction at deep-sea hydrothermal vents. In 2010, we reported that deep-sea hydrothermal vents function as naturally occurring electrochemical fuel cells, which are powered by the reductive chemicals stored in the Earth's crust [50]. We found that natural minerals dominated by $CuFeS_2$ and FeS_2 from Black smoker chimneys in the Mariner hydrothermal field display excellent metallic electrical conduction over a 10 cm distance. In addition, we also demonstrated that deep-sea minerals promote the electrocatalytic oxidation of H_2S and H_2, as well as the electroreduction of O_2 and ferric ions. These findings led us to propose that a new type of energy propagation for CO_2 reduction and carbon assimilation occurs in the deep floor. In addition to the reductive chemicals, such as H_2 and H_2S, emitted from hydrothermal vents, we speculate that high-energy electrons from hot reduced hydrothermal fluid are directly delivered to cold oxidative seawater in the form of electrical current, with the same operation principals as electrochemical fuel cells (Fig. 5).

Based on our experimental findings, together with the hypothesis of Russell et al. that Ni/greigite may be the evolutionary origin for the $NiFe_3S_4$ cluster in CODH [39, 42], we also investigated the energetics for electrocatalytic CO_2 reduction by $FeNi_2S_4$ [40]. Through the examination of potential-dependent CO_2 reduction activity, it was found that CO_2 reduction by H_2 in hydrothermal fluids involves a strong endergonic electron transfer reaction. Therefore, a naturally occurring proton-motive force (PMF) as high as 200 mV must be established across the hydrothermal vent chimney wall. These findings are consistent with the speculation that highly alkaline hydrothermal vents in the Hadean ocean are the most likely system that supported prebiotic organic synthesis [42], as the chimney interior of these hydrothermal vents has a pH of 9–10 and the outer walls are bathed in ocean water with a pH of 5–6, generating a PMF of 180–300 mV. Of note, in addition to the PMF, steep temperature difference between hydrothermal fluid and sea water

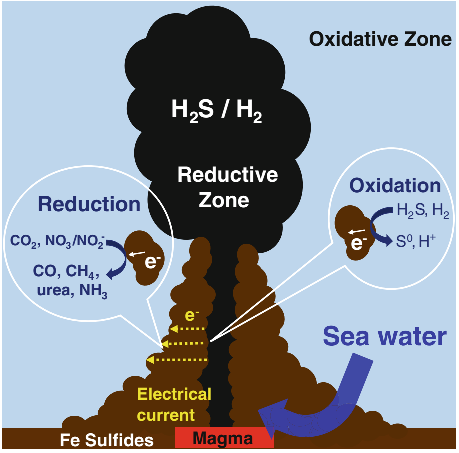

Fig. 5 Proposed model for electrical current generation in the chimneys of deep-sea hydrothermal vents [50]. Electrons generated via the oxidation of H_2S in hydrothermal fluid (*Reductive Zone*) are transported through the conductive chimney wall to sea water (*Oxidative Zone*) where they reduce Fe^{3+}, O_2, and CO_2

realized by low thermal conductivity of natural minerals resulted in the generation of high reduction energy, which is comparable to the photosynthetic CO_2 fixation center (Fig. 6) [51]. Therefore, the geochemical 'settings' of electrochemical reactors in the Hadean Ocean satisfy the thermodynamic and kinetic preconditions that are necessary to initiate the electroreduction of CO_2 to hydrocarbons. However, it is interesting to consider how prebiotic catalysts for CO_2 reduction were functionalized to achieve low η and high FE in these naturally occurring electrochemical fuel cells.

8 Evolution of Active Cores of CODHs and Challenges for the Design of Efficient CO_2 Reduction Catalysts

Finally, to help solve the questions related to the functionalization of prebiotic CO_2 reduction catalysts, here, we discuss the importance of N-containing molecules in CO_2 conversion, particularly focusing on the role of C–N bonding and N-assisted CO_2 reduction in the evolution of chemical reactions underlying the emergence of primitive life forms, and the implications of these processes in the design of electrocatalysts for the reduction of CO_2 to hydrocarbons.

As discussed in Sects. 3, 4 and 5, N-containing species functions as cocatalysts for electrochemical CO_2 reduction by either stabilizing the reduced CO_2 intermediates or directly activating CO_2 molecules by weakening the C=O bond via the concept of frustrated Lewis acid-base pair motif. We therefore speculate that

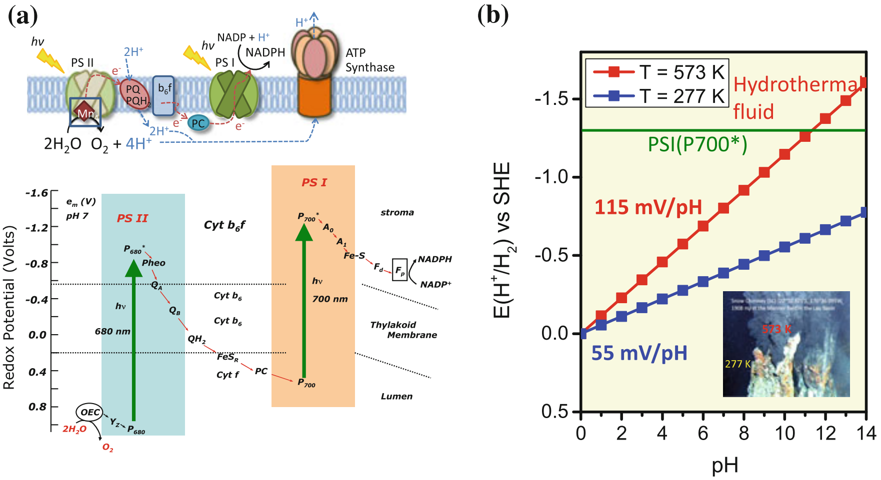

Fig. 6 **a** (*top*) The schematic image of the components of natural photosynthetic system, and (*bottom*) the energy diagram of each component; photosynthetic electron transfer chain. **b** Temperature and pH dependence of the standard redox potential of H^+/H_2 couple. Based on our results for electrochemical CO_2 reduction on violarite, a pH gradient of larger than 4 between hydrothermal fluid and ocean water is required to promote electrochemical CO_2 reduction on the surface of iron sulfide. Considering the large temperature difference between hydrothermal fluid (573 K) and ocean water (277 K), the driving force of the reaction should be high. The pH and temperature gradient between hydrothermal fluid and sea water can provide alkaline hydrothermal vent with the reduction power as high as that of photosynthetic CO_2 fixation center (PSI)

N-containing compounds in the deep-sea hydrothermal environment could aid in the conversion of oceanic CO_2 into organics or even the formation of C–N bonded compounds. From a thermodynamic perspective, the potential gradient generated from the pH, temperature, and redox disequilibrium between hydrothermal vents and acidic ocean is favorable for the reduction of nitrite/nitrate, which might exist in the oxidative ocean environment, to ammonia (E^0 = 0.897–0.875 V vs. RHE) (Fig. 6). During the reduction, in situ-formed amine-like species have the potential to coordinate with CO_2 to reduce the overpotential for CO_2 reduction and/or form C–N bonded compounds, such as urea. Of particular note is that such a C–N bond forming reaction has already been demonstrated by Shibata et al., in which urea was synthesized via simultaneous electrochemical reduction of CO_2 and nitrite/nitrate using Cu as an electrode [52, 53].

Although deep-sea electrochemical reactors are theoretically feasible to drive CO_2 reduction and C–N bond formation, determining how these inorganic minerals functioned, at least with activity comparable to their enzymatic counterparts, remains challenging. In addition, a large gap exists in our understanding of the related function of generally inactive artificial catalysts and robust bioenzymes. Russell et al. [3, 54] assumed (Fig. 7) that the mineral counterparts were the original precursors to various present-day enzymes, including [NiFe]-hydrogenases, CODH,

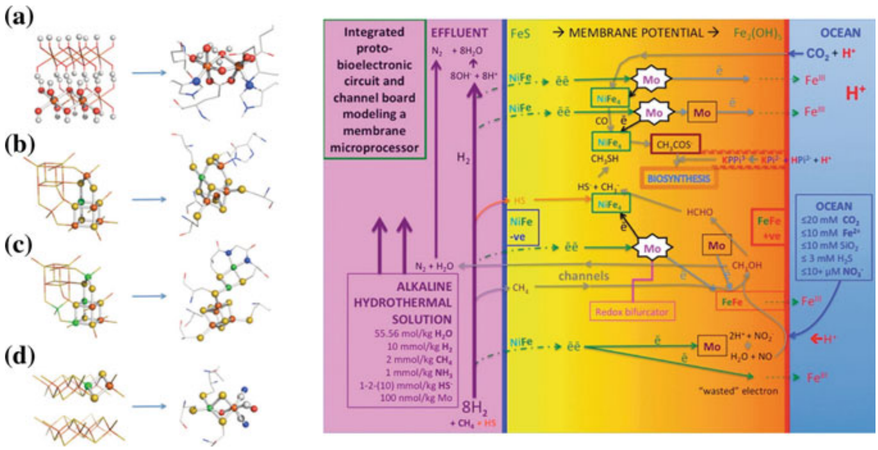

Fig. 7 *Left* Structural comparisons between transition element sulfides and oxides found in the precipitate membranes with the active sites of metalloenzymes present in the Last Universal Common Ancestor (LUCA) [39]: **a** $[Fe(OH)_2]_n$ (cf. brucite) with methane monooxygenase, **b** greigite with acetyl CoA synthase, **c** violarite with CODH, **d** nickelian mackinawite with [NiFe]-hydrogenase. *Right* The hypothetical proto-bioelectronic and proto-bioprotonic circuitry and channels in the inorganic membrane that feed the redox and proton disequilibria to the putative carbon-fixing and pyrophosphatase nano engines [54]

nitrate reductase, methane monooxygenase, methanol dehydrogenase, and pyrophosphate synthetase, acting as molecular engines. Russell et al. [3, 54] also assumed that the mineral counterparts convert redox and proton gradients to drive the endergonic reactions required for the initial stages of metabolism and ultimately life itself. This proposed theory inspired us to not only study the possible abiotic formation of C–N bonded compounds, but also to obtain insight into the design of CO_2 reduction systems from the catalytic functions of extant enzyme active centers. There should be some evolutionary reasons for the elemental strategy that nature has selected, such as energetic and kinetic priority towards some critical reactions. We speculate that C–N bonding reactions via simultaneous reduction of CO_2 and nitrite/nitrate [52, 53] may be one such critical reaction and therefore deserve detailed analysis to test the feasibility of the deep-sea emergence of primitive life theory.

The electrocatalytic formation of C–N bonds may allow for the synthesis of complex chemicals, such as urea, urethane derivatives, amides, carbamates, and isocyanate [55], by the insertion of CO_2 into other N-containing species. Such C–N bonded compounds comprise a large family of basic organic chemicals and fuels. It is expected that the coupling of different (reduced) N-compounds with CO_2-derived species may lead to the formation of various kinds of C–N bonded compounds. Although the utilization of CO_2 to synthesize such C–N bonded compounds through thermal catalysis has already been commercialized, high temperature/pressure conditions are typically required, which are energy intensive to maintain [56, 57]. We expect that better catalysts based on earth-abundant elements could be developed by understanding the bio-enzymatic functions, which could achieve the CO_2 reduction or C–N bonding with high efficiency under mild conditions.

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