available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Review

Transition metal-nitrogen sites for electrochemical carbon dioxide reduction reaction

Chengcheng Yan^{a,b}, Long Lin^{a,b}, Guoxiong Wang^{a,c,*}, Xinhe Bao^{a,c,#}^a State Key Laboratory of Catalysis, CAS Center for Excellence in Nanoscience, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 4 September 2018

Accepted 19 September 2018

Published 5 January 2019

Keywords:

Electrochemical carbon dioxide reduction reaction

Metal-nitrogen sites

Metal-nitrogen containing macrocyclic complexes

Metal organic frameworks

Zeolitic imidazolate frameworks

Carbon material doped with metal-nitrogen sites

ABSTRACT

Electrochemical CO₂ reduction reaction (CO₂RR) powered by renewable electricity has emerged as the most promising technique for CO₂ conversion, making it possible to realize a carbon-neutral cycle. Highly efficient, robust, and cost-effective catalysts are highly demanded for the near-future practical applications of CO₂RR. Previous studies on atomically dispersed metal-nitrogen (M-N_x) sites constituted of earth abundant elements with maximum atom-utilization efficiency have demonstrated their performance towards CO₂RR. This review summarizes recent advances on a variety of M-N_x sites-containing transition metal-centered macrocyclic complexes, metal organic frameworks, and M-N_x-doped carbon materials for efficient CO₂RR, including both experimental and theoretical studies. The roles of metal centers, coordinated ligands, and conductive supports on the intrinsic activity and selectivity, together with the importance of reaction conditions for improved performance are discussed. The mechanisms of CO₂RR over these M-N_x-containing materials are presented to provide useful guidance for the rational design of efficient catalysts towards CO₂RR.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The rapid consumption of fossil fuels, together with continuously increasing population and over exploitation of forests, is the major culprit for the high atmospheric CO₂ level. Excessive CO₂ concentration will exacerbate the greenhouse effect, causing average temperature to rise and posing great challenges to global climate and environment [1]. Though notorious, CO₂ is also a potential carbon resource [2–4]. Electrochemical CO₂

reduction reaction (CO₂RR) is a promising technique for efficient CO₂ conversion. CO₂RR technique can utilize electricity generated by clean renewable energy and directly convert CO₂ into value-added chemicals (CO, formate, hydrocarbon, oxygenated compounds, etc.), making it possible to realize an ideal recycling cycle for carbon resources [5–8]. However, the undesirable energy conversion efficiency caused by a high overpotential in initiating CO₂ conversion and limited selectivity due to the competitive hydrogen evolution reaction (HER) in aque-

* Corresponding author. Tel: +86-411-84686637; Fax: +86-411-84694447; E-mail: wanggx@dicp.ac.cn

Corresponding author. E-mail: xhbao@dicp.ac.cn

This work was supported by the National Key R&D Program of China (2017YFA0700102), the National Natural Science Foundation of China (21573222 and 91545202), the Outstanding Youth Talent Project of Dalian (2017RJ03), the DMTO Project of Dalian Institute of Chemical Physics, CAS (DICP DMTO201702), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020200), and the Youth Innovation Promotion Association, CAS (2015145).

DOI: 10.1016/S1872-2067(18)63161-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 1, January 2019

ous solution discourage the near-future practical applications of CO₂RR [9–12]. Therefore, intensive research work has been focused on developing highly efficient catalysts. From early well-studied bulk metal catalysts to recent widespread metallic nanostructure/nanomaterials, researchers have done intense work on the investigation of structure-activity relationship towards CO₂RR through constructing active nanostructure for more exposed active sites, modulating nanoparticle size and active facet ratio, introducing second alloy constituent, utilizing metal-oxide interface confinement effect, etc., to optimize the catalytic performance and further confirm that the binding energy and structure of absorbed intermediates are crucial for high selectivity [13–20]. At present, Au-, Ag-, Pd- and Cu-based catalysts have been widely investigated for CO₂RR and exhibit considerable Faradaic efficiencies, yet the low mass activity and scarcity of these noble metal catalysts impede their future applications [9,21–24]. Alternatively, catalysts containing transition metal-nitrogen (M-N_x) sites, such as transition metal-centered macrocyclic complexes, metal organic frameworks and M-N_x-doped carbon materials, which show comparable or even higher activity and selectivity towards CO₂RR than noble metal counterparts, are emerging as promising candidates [25–27]. In particular, low-cost M-N_x-doped carbon materials synthesized by a facile pyrolysis of precursors containing N, C and transition metal elements, which have been widely explored as the most promising alternatives for noble metal-based catalysts in polymer electrolyte membrane fuel cells [28–30], have shown remarkable activity and selectivity towards CO₂RR and triggered a wave of research in recent years [11,31–33]. This review summarizes recent advances on the CO₂RR using a variety of M-N_x-containing materials, and practical parameters, such as synthesis protocols, characterization of active sites, and electrocatalytic performance evaluation are included, while we also discuss about the proposed reaction mechanisms and major factors that affect product distribution. We expect this review will provide practical knowledge into the rational design of improved M-N_x-containing catalysts and exploration of optimal process conditions, which are crucial in promoting the practical application of CO₂RR in the near future.

2. Metal-nitrogen containing macrocyclic complexes

Transition metal-centered macrocyclic complexes, either in

solution (homogeneous catalysis) or anchored to carbon materials/electrode (heterogeneous catalysis), have been explored as efficient catalysts for CO₂RR since the 1970s. In particular, metal porphyrins, phthalocyanines and their relative derivatives (Fig. 1) have been widely studied. Examination of product selectivity on gas diffusion electrodes (GDE) impregnated with 17 kinds of metal phthalocyanines by Matsui et al. [34] showed that with transition metals of Group VIII as the coordination center, CO was produced as the major electrolysis product and the Faradaic efficiency on Co and Ni phthalocyanines almost reached 100%; in the case of Sn, Pb or In (Group IIIA or IVA) phthalocyanines, formic acid was the major product; while methane was produced mainly on Ga, Cu and Ti phthalocyanines, with the highest Faradaic efficiencies of 30%–40%. Followed up the research work, Furuya et al. [35] interpreted such discriminative difference qualitatively by Taube's theory, i.e. the electron configurations in the metallic atom affected CO₂ activation and CO desorption, consistent with that proposed by Meshitsuka et al. Based on earlier studies, more efficient macrocyclic complexes with varying metal centers (mainly Co, Fe, Mn and Zn) and tailorable ligands are developed by structural engineering at the molecular level or constructing hybrid architecture at the nanoscopic scale [36–43].

At the potentials required for CO₂RR, the metal centers of metal phthalocyanines or other macrocyclic complexes are prone to be reduced to a low oxidation state while the macrocyclic ligand framework contributes to maintain chemical stability and store a proton and/or a reducing equivalent. Thus the intrinsic structure of active sites has been controversial all the time and intense efforts have been made to detect reaction intermediates and theoretical protocols are used to shed light on the reaction mechanisms. Savéant et al. [39,44] have done much work on improving the performance of iron tetraphenylporphyrin (FeTPP) derived molecular catalysts. Cyclic voltammetry results of the redox process of Fe oxidation state with variation of potential revealed that electrogenerated iron(0) porphyrins are active sites for CO₂RR and prepositioned phenol functionalities help improve the activity by acting as both H-bonding stabilizers and high-concentration proton donors (Fig. 2). Similarly, experimental and theoretical studies confirmed that Co center is first reduced to Co(I) and then CO₂ is adsorbed and further reduced to CO [41,42,45,46]. In a recent study, Wang et al. [47] discovered that a Cu phthal-

Fig. 1. Commonly used metal porphyrins, phthalocyanines and derivatives for CO₂RR.

Fig. 2. (a) Investigated iron porphyrins for CO₂RR; (b) Cyclic voltammograms of (A) FeTDHPP + 2 mol L⁻¹ H₂O, (B) FeTDHPP + 2 mol L⁻¹ H₂O in the presence (upper trace) and absence (lower trace) of 0.23 mol L⁻¹ CO₂ in DMF + 0.1 mol L⁻¹ *n*-Bu₄NPF₆ electrolyte at 0.1 V s⁻¹; (c) Proposed reaction pathway for CO₂RR by active iron(0) porphyrins site. Reproduced with permission [39]. Copyright 2012, The American Association for the Advancement of Science.

ocyanine based heterogeneous catalyst efficiently converts CO₂ to methane and ethylene. Interestingly, in-situ and operando X-ray absorption spectroscopy (XAS) results in Fig. 3 revealed that ~2 nm metallic copper clusters formed through the reversible oxidation state and structural changes of copper(II)

phthalocyanine serving as active centers for the production of methane.

Besides the metal center, the ligands are also crucial to improve the CO₂RR performance. Costentin et al. [39] found that the high local concentration of protons derived from all the

Fig. 3. (a) Potential-dependent Faradaic efficiency and (b) partial current densities of products towards CO₂RR catalyzed by CuPc; (c) Fitting results (red traces) of the extended X-ray absorption fine structure (EXAFS) spectra of the CuPc at different potentials in *R* space and (d) *k*-space; (e) First-shell Cu-Cu CNs of the CuPc at different potentials. The insets show the CuPc crystal structure (upper left) and a possible configuration of the Cu nanoclusters (lower right). Reproduced with permission [47]. Copyright 2018, Springer Nature.

ortho and ortho' phenolic hydroxyl substituent group of the parent FeTPP (Fig. 2a) remarkably speeded up the CO₂RR, achieving a CO Faradaic efficiency above 90% in a mixed DMF-water solvent. In a recent study, carbon electrodes covered with perfluorinated cobalt phthalocyanine (CoFPc) exhibit much higher CO₂RR performance than the parent CoPc with a maximum CO Faradaic efficiency of 93% as shown in Fig. 4a and 4b [41]. The Co(II)/Co(I) redox wave and spectroelectrochemical signal of metal-to-ligand transfer confirmed the formation of active Co(I)Pc species. They propose that the electron-deprived CoFPc promotes the desorption of associated CO and facilitates the active Co(I) regeneration, thus CoFPc is more selective and active than CoPc. Similarly, Wang et al. [42] immobilized CoPc onto carbon nanotubes and found that the introduction of electron-withdrawing cyano groups to the CoPc further improved the CO₂RR activity with much higher current density and CO Faradaic efficiency exceeding 95% (Fig. 4c and 4d).

Most macrocyclic complexes suffer from low conductivity and poor solubility in water, thus anchoring them onto electrode surface or solid supports (usually carbon materials) makes them possible to act as efficient heterogeneous catalysts towards CO₂RR in aqueous electrolytes. Non-covalent adsorption, covalently bonding and polymerization are common protocols that are used to construct hybrid catalysts [25]. Unequivocally, a proper grafting method should take a suitable support material for better electron transfer and avoid blocking catalytic sites or impeding conductivity. In a comparative study, cobalt meso-tetraphenylporphyrin (CoTPP) alone shows a poor

CO₂RR performance as a homogeneous catalyst; however, a facile immobilization of CoTPP onto carbon nanotubes remarkably facilitates the CO₂RR, resulting in a substantial enhancement with much improved CO Faradaic efficiency (>90%) and lower overpotential in aqueous medium [48]. Recently, Li et al. [43] employed an organic-inorganic hybridization strategy to construct cobalt polyphthalocyanine (CoPPc)-sheathed carbon nanotubes (CoPPc/CNT) for highly efficient CO₂RR (Fig. 5a). The thin conformal polymer coating layer achieved by in-situ polymerization of CoPc molecules helps suppress the aggregation of organic molecules and promote the exposure of more Co-N sites, and thus contributes to an excellent performance with a high CO Faradic efficiency of ~90%, considerable turnover frequency (TOF) of 4900 h⁻¹ at $\eta = 0.5$ V, and stability of >24 h, much superior to CoPc and CoPPc alone (Fig. 5b and 5c).

3. Metal organic frameworks (MOFs)

As mentioned above, polymerization of molecular catalysts on support materials is a wise way to improve the density of active sites [43,49]. However, it is not an optimal way for full accessibility of active sites due to the stacking of densely packed structure. Metal-organic frameworks (MOFs) as a class of coordination polymers with open frameworks, consist of metal ions that are linked together by organic ligands [50]. With the large availability of different metal centers, multiple organic ligands and various building blocks, the structure and functionality of MOFs can be tailored to a large extent for tar-

Fig. 4. (a) Schematic illustration for CO₂RR and (b) CO Faradaic efficiency and current density for controlled-potential electrolysis in 0.5 mol L⁻¹ NaHCO₃ over CoFPc. Reproduced with permission [41]. Copyright 2016, American Chemical Society. (c) Comparison of chronoamperograms and (d) potential-dependent Faradaic efficiencies between CoPc-CN/CNT (solid line) and CoPc/CNT (dotted line). Reproduced with permission [42]. Copyright 2017, Springer Nature.

Fig. 5. (a) Illustrated diagrams for the preparation of CoPPc/CNT; (b) CO Faradaic efficiency and (c) specific CO current and corresponding TOF values for CoPPc/CNT, CoPPc, and CoPc. Reproduced with permission [43]. Copyright 2017, Elsevier.

geted reaction [50,51]. In addition, such ordered porous structures not only promote the exposure of active sites but also facilitate mass transfer during the catalytic reaction, making MOFs ideal materials for catalysis [52,53].

Recently, following the urgent demand for efficient CO_2

conversion process and renewed interest in CO_2RR , MOFs containing Cu, Fe, Co, Re and Zn, etc., have been investigated as efficient catalysts for CO_2RR (Fig. 6) [54–59]. Similar to the case in M- N_x -containing macrocyclic complexes, MOFs suffering from low conductivity are always anchored to conductive sur-

Fig. 6. Typical examples of MOFs studied as efficient catalysts towards CO_2RR . (a) Incorporating Fe porphyrin into MOF-525 for efficient CO_2RR , the crystal structure including the chemical structure of the TCPP linker and the Zr_6 -based node were shown here. Reproduced with permission [54]. Copyright 2015, American Chemical Society. (b) Illustrated scheme for the structure of the selected Cu-based metal-organic porous materials for CO_2RR measurements. Reproduced with permission [55]. Copyright 2017, Wiley-VCH. (c) Building blocks for the $\text{Al}_2(\text{OH})_2\text{TCPP-Co}$ assembled thin-film 3D MOF for electrocatalytic reduction of CO_2 (Co, orange; O, red; C, black; N, blue; Al, light-blue; pyrrole ring, blue). Reproduced with permission [56]. Copyright 2015, American Chemical Society. (d) Highly oriented Re-based MOF thin film deposited on conductive FTO electrode for the selective CO_2 electroreduction to CO. Reproduced with permission [57]. Copyright 2016, the Royal Society of Chemistry.

faces or mixed with conductive carbon materials in CO₂RR [54,56,59]. Besides, modification or replacement of linked ligands with better electron/proton transfer ones also significantly help improve the charge/electron transfer capability [60–62]. Yamada et al. [63] first reported a Cu-containing MOF dropped on carbon paper for CO₂RR in 2012. A copper rubeanate (CR-MOF) was chosen owing to its excellent electronic and proton conductivity arising from the coalescent of a proton with the nitrogen atom and accompanying of electron transfer from Cu(II) ions. CO₂RR measurements were conducted in aqueous electrolyte and the results showed that the CR-MOF electrode endowed much lower overpotential, namely 0.2 V less than that of a Cu metal electrode, and HCOOH was the primary product with a Faradaic efficiency of 30%. Later work from Kulandainathan et al. [64] manifested that Cu₃(BTC)₂ thin film deposited on glassy carbon (GC) electrode reduced CO₂ to oxalate with a Faradaic efficiency of 51% in CO₂-saturated *N,N*-dimethylformamide containing tetrabutylammonium tetrafluoroborate. They proposed that Cu(I) formed at –0.62 V vs. Ag/Ag⁺ in the CO₂-saturated DMF solution catalyzed the reduction and the adsorbed CO₂ gas inside the pores facilitated the CO₂RR.

Yaghi et al. [65] first tried to incorporate CO₂RR-efficient Co porphyrin building units into covalent organic frameworks (COFs, a subgroup of MOFs with better conductivity due to conjugated double bonds) by organic ligands through imine bonds (Fig. 7a and 7b). They reported that COF-366-Co synthe-

sized by the connection of 5,10,15,20-tetrakis(4-aminophenyl) porphinato cobalt [Co(TAP)] with 1,4-benzenedicarboxaldehyde (BDA) displayed a high CO Faradaic efficiency (90%) when deposited on conductive carbon fabric for CO₂RR measurements. In addition, modifications through modular protocols by appropriate combinations of building units further promote the reaction activity. When biphenyl 4,4'-dicarboxaldehyde (BPDA) with longer chain was used as the strut substituting for BDA, lattice expanding results in a larger pore radius and allows for a higher CO₂ adsorption capacity and increased accessibility of the active sites. Copper porphyrin, which is catalytically inactive for CO₂RR, was used to dilute cobalt porphyrin active sites and further improve the turnover frequency of active Co sites. Consequently, COF-367-Co (1%) with only 1% Co in all metal sites exhibited an initial TOF_{EA} of 9400 h^{–1}, equivalent to a 26-fold higher than the activity of the parent Co(TAP). In another work, the same group took Al₂(OH)₂TCPP-Co (TCPP-H₂ = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate) as the linker units and assembled them into a porous thin film MOF directly grown on a conductive substrate through atomic layer deposition (ALD) technique (Fig. 7c–e) [56]. The thickness of the MOF film was optimized by precise regulation of ALD cycles and such catalytic system displayed a CO Faradaic efficiency exceeding 76% and remained stable over 7 h. Operando spectroelectrochemical measurements showed that the majority of Co(II) catalytic centers in the MOF were electro-reduced to

Fig. 7. (a) Design and synthesis of metal porphyrin-derived 2D COF; (b) TON numbers with respect to the amount of cobalt porphyrin for CO production at –0.67 V (vs. RHE) over COF-367-Co (1%), COF-367-Co, COF-367-Co, or COF-367-Cu. Reproduced with permission [65]. Copyright 2015, The American Association for the Advancement of Science. (c) The tailorable molecular structure of Al₂(OH)₂TCPP-Co; (d) Each carboxylate from Al₂(OH)₂TCPP-Co is combined with the aluminum inorganic backbone to assemble into a 3D MOF on a conductive substrate for a feasible CO₂RR system; (e) Product selectivity during CO₂ electrolysis in a potential range of –0.5 to –0.9 vs. RHE. Reproduced with permission [56]. Copyright 2015, American Chemical Society.

Co(I) and subsequently catalyzed the CO₂RR. The direct growth of the MOF onto the conductive surface is indeed an effective way for increasing the portion of electroactive sites and enhancing the charge-transport properties for MOFs materials, thus leading to a higher CO₂RR performance.

MOFs composed of metal nodes and organic linkers potentially combine the advantages of both molecular and heterogeneous catalysts. A precise manipulation of its building units allows for changes on both spatial arrangement (i.e., porous structure, topology of the structure) and electronic environment, offering a great possibility for efficient CO₂RR. Yet, the low conductivity of MOFs still restricted the exposure of electroactive sites, leading to a limited current density.

4. Carbon-based metal-nitrogen materials

Pyrolyzed metal-nitrogen-carbon materials have been widely used as promising candidates for the oxygen reduction reaction (ORR) owing to their low cost and earth-abundant components. Progress in the synthesis, characterization, ORR performance and reaction mechanisms is well summarized in related review papers [66–68]. Strasser et al. [11] firstly tried to use porous carbon materials doped with M-N_x sites, derived from the pyrolysis of nitrogen and Fe- and/or Mn-functionalized commercial carbon for CO₂RR, with CO as the major product and a trace amount of CH₄ was detected on Fe-containing catalysts (Fig. 8). Their results confirm that metal-nitrogen-carbon (M-N-C) materials are efficient in CO₂RR and have stimulated an academic research boom on carbon-based metal-nitrogen materials towards CO₂RR. In analogy to the 4-electron ORR, electroreduction of CO₂ to CO or hydrocarbons involves multiple coupled protonation/reduction steps and thereby there are some common strategies for constructing highly effective M-N_x-containing carbon materials towards CO₂RR.

Carbon-based M-N_x-doped materials are always prepared by a facile pyrolysis of mixtures composed of metal-, nitrogen- and carbon-containing precursors. During the pyrolysis, N- and C-containing precursors decomposed and transformed into N-doped carbon, while metal sites coordinated to N atoms were

simultaneously embedded into the skeleton. Thus the mixed precursors and appropriate pyrolysis parameters concerning carbonization temperature and duration time are of vital importance for constructing atomically dispersed M-N_x-containing materials [30,69,70]. Notably, to avoid the formation of metal nanoparticles which mainly promote the competitive HER, precursors with well-dispersed M-N_x structures or spatial confining metal sites are preferred and acid-leaching process is available for removing these undesirable nanoparticles. Recently, Jiang et al. [71] developed a multistep pyrolysis process to synthesize a class of single-atom catalysts on nitrogen-doped carbon nanotubes (MSA-N-CNTs) with an extraordinary high metal loading. The reconnaissance study revealed that Ni-g-C₃N₄ with Ni single atoms located in the cavity of g-C₃N₄ formed when the mixture was further pyrolyzed at 650 °C followed by the first heat treatment at 350 °C. Thanks to the strong covalent bonding between g-C₃N₄ and Ni atoms, aggregation of Ni atoms was inhibited at higher temperature (700–900 °C), giving rise to the atomically dispersed NiSA-N-CNTs. MOFs or ZIFs (zeolitic imidazolate frameworks), in which metal nodes are separated by organic linkers (especially N-containing ligands), have been used as ideal precursors to help increase the loading of atomically dispersed metal sites within the final porous carbon materials. In particular, metal residing in MOF/ZIF can be partly exchanged with other metals, thus allowing further increasing of the spatial distance of metal sites. For example, the Zn²⁺ sites in ZIF-8/ZIF-7 are replaceable with Co²⁺, Ni²⁺ and Fe³⁺/Fe²⁺ ions, and subsequently serve as perfect spacer for adjacent Co/Ni/Fe atoms to avoid the agglomeration of metal atoms during the pyrolysis. Typical work on mixed metal ZIF precursors is shown in Fig. 9 [31,70,72]. Namely, Zn atoms with low boiling point evaporated away at temperatures over 800 °C, while Co/Ni/Fe nodes are reduced in situ and anchored in the carbon skeleton with N-coordination. Li's group [70,73] has done intense work on the synthesis of single-atom catalysts by pyrolyzing ZIF-related materials, and they also found that coordination number could be regulated by pyrolyzing temperature because M–N coordination bonds were vulnerable at higher temperature. Our work on ZIF-derived M-N-C catalysts further highlights the vital role

Fig. 8. (a) Schematic structure of nitrogen atoms in different coordinated configurations in the synthesized N-C materials; (b) CO and (c) CH₄ Faradaic efficiencies on gold (black), N-C (orange), Mn-N-C (red), Fe-N-C (green) and FeMn-N-C (blue). Reproduced with permission [11]. Copyright 2015, Wiley-VCH.

Fig. 9. Schematic illustration of the synthesis of (a) F-N-C. Reproduced with permission [72]. Copyright 2017, Wiley-VCH. (b) Ni-N-C. Reproduced with permission [31]. Copyright 2018, the Royal Society of Chemistry. Copyright 2017, Wiley-VCH. (c) Co-N-C materials using Fe/Ni/CoZn bimetallic ZIF as precursors. Reproduced with permission [70]. Copyright 2016, Wiley-VCH.

of doping methods. We disclosed that introducing a second transition metal ion (Ni^{2+} or Fe^{3+}) during the crystallization of ZIF-8 could maximize the doping concentration of atomically dispersed metal sites compared with the post-synthetic ion exchange method, while post impregnation with specific metal salts (ammonium ferric citrate) helped to confine the Fe^{3+} on the surface of ZIF-8, leading to a high exposure of iron-nitrogen sites [31,32].

Similar to the rules explored in M-N_x -containing macrocyclic complexes, metal centers and their coordination state play an important role in product selectivity. Recent work on M-N_x active sites for CO_2RR revealed that Fe-N, Co-N, Ni-N, Mn-N, Zn-N and Sn-N sites are effective towards CO_2RR [31,32,73–82]. Fontecave et al. [74] examined a series of iron-based catalysts containing Fe-N sites for CO_2RR and unveiled that FeN_4 sites facilitated CO_2RR to CO and Fe-based nanoparticles favored the production of undesirable H_2 (Fig. 10a). Thus by synthetically regulating the ratio of Fe-based nanoparticles to isolated FeN_4 sites, products with controlled CO/ H_2 ratios can be obtained. In addition to the intrinsic nature of active sites, the mass transfer ability and high exposure of active sites are also crucial for the catalytic performance [83–85]. Recently, our group [32] took a post-synthetic modification strategy to prepare highly exposed Fe-N active sites through surface functionalization of ZIF-8 with ammonium ferric citrate (AFC). The C-AFC@ZIF-8 with highly

exposed Fe-N sites exhibited superior selectivity and mass activity towards CO_2RR than its counterpart derived from bulk functionalization of ZIF-8 with similar Fe loading, reaching a maximum FE_{CO} of 93.0% at -0.43 V (Fig. 10b). We also employed a post-synthetic strategy by a second pyrolysis in ammonia to further improve the performance of Fe-N sites [75]. With aid of the etching effect of ammonium at high temperature, the removal of residual Zn species and vulnerable carbon moieties further maximized the exposure of Fe-N active sites and facilitated mass transfer during the CO_2RR . Therefore, the optimal catalyst after an additional pyrolysis in ammonium showed a remarkable increase in both FE_{CO} and current density, exceeding other efficient Fe-N-C catalysts (Fig. 10c). Lin et al. [86] developed a composite material composed of pyrolyzed ZIFs and carbon nanotubes for CO_2RR , which manifests nearly 100% CO Faradaic efficiency at an overpotential of 740 mV. Moreover, when little amount of Fe was doped into the catalyst, the overpotential was further decreased to 440 mV. They ascribed such superior activity to the enhanced electron transport and expedited CO_2 transport resulted from the MWCNT support. Chen et al. [76] found that the CO Faradaic efficiency drops with decreasing Co- N_x coordination number. CoPc was loaded onto hollow N-doped porous carbon spheres (HNPCs) starting from polymer precursors by efficient coordination with abundant N sites in HNPCs support. EXAFS fitting results revealed that the Co-N coordination number is 5. $\text{Co-N}_4/\text{HNPCs}$ and $\text{Co-N}_3/\text{HNPCs}$ catalysts were obtained by pyrolyzing $\text{Co-N}_5/\text{HNPCs}$ at 400 and 600 $^\circ\text{C}$, whereas higher temperatures (800 and 1000 $^\circ\text{C}$) result in the formation of NPs. Electrochemical results display that CO Faradaic efficiency remains stable at about 90% from -0.57 V to -0.88 V vs. RHE on $\text{Co-N}_5/\text{HNPCs}$, superior to other counterparts.

As presented above, Fe-N-C/Co-N-C catalysts demonstrated impressive CO Faradaic efficiency at relatively low overpotentials; however, a drawback for future application is that the Faradaic efficiency drops rapidly accompanying an increase in the overpotential for much higher current density [11,32,73–75]. Ni-N-C materials were also examined for CO_2RR and the results showed that Ni-N-C catalysts outperformed Fe-N-C/Co-N-C counterparts at slightly larger overpotentials [77–80].

Coordinationally unsaturated Ni- N_x active sites embedded in porous carbon were synthesized by facile heat treatment of Zn/Ni bimetallic ZIF-8 at 900 and 1000 $^\circ\text{C}$. Nickel was doped during the crystallization process and the maximum loading of atomically dispersed Ni reached 5.44 wt%. CO_2RR measurements in 1 mol L^{-1} KHCO_3 electrolyte showed that FE_{CO} was kept between 92.0% and 98.0% in a higher overpotential window ranging from -0.53 V to -1.03 V (vs. RHE), and thereby CO current density increases with the applied potential and reaches $71.5 \pm 2.9\text{ mA cm}^{-2}$ at -1.03 V (vs. RHE) (Fig. 11a and 11b), breaking the limit in Fe-N-C/Co-N-C materials [31]. Based on the unsaturated coordination structure of Ni- N_x sites obtained from XAS analysis, density functional theory calculations stimulated three Ni-N active sites (NiN_3 , NiN_3V and NiN_2V_2) and free energies of major intermediates were employed to unveil the activity trend. Specifically, theoretical results revealed that the

Fig. 10. Reported Fe-N-C catalysts for CO₂RR. (a) Structure-selectivity relationships in Fe-N-C materials. Reproduced with permission [74]. Copyright 2017, American Chemical Society. (b) Enhanced exposure of Fe-N active sites through confining AFC molecule on the surface of ZIF-8, where C-AFC/ZIF-8 stands for the sample derived from pyrolysis of mechanically blended ZIF-8 and AFC mixture, while C-AFC@ZIF-8 refers to the sample synthesized through a bulk functionalization method. Reproduced with permission [32]. Copyright 2017, Elsevier. (c) Improving CO₂RR performance over the ZIF-derived Fe-N material by a second pyrolysis in ammonia. Reproduced with permission [75]. Copyright 2018, Elsevier.

free energies of *COOH (G^*_{COOH}) on coordinatively unsaturated NiN₃, NiN₃V and NiN₂V₂ were significantly lower than those on NiN₄, and the *H blockage was relatively weak on NiN₃V and NiN₂V₂ structures, confirming that the high CO₂RR performance resulted from those coordinatively unsaturated Ni-N sites (Fig. 11c and 11d).

As mentioned above, various transition metal-functionalized carbon/nitrogen precursors and different approaches were employed to construct carbon-based metal-nitrogen materials, leading to discrepancies in carbon architectures (porosity, composition and structure), M-N coordination structure and nitrogen doping state (contents and configurations). In order to understand the role of metal centers and identify a champion metal for the construction of optimal M-N_x-containing carbon materials towards CO₂RR, atomically dispersed M-N_x materials with different transition metals should be prepared by the same method, minimizing the effects of carbon and nitrogen variables. Strasser et al. [87] synthesized a family of porous carbon materials doped with active M-N_x moieties (M = Mn, Fe, Co, Ni, Cu) with transition metal salts and bipyridine-based

coordinated polymers as initial precursors for more profound understanding of reactivity trends towards CO₂RR (Fig. 12a). The CO₂RR performance greatly depended on the transition metals, both in terms of CO Faradaic efficiency and overpotential, among which Fe-N-C and Ni-N-C outperformed other metal-related porous carbon showing much improved activity while the maximum CO Faradaic efficiency was obtained at a lower overpotential on Fe-N-C ($V_{\text{RHE}} = -0.55$ V, $\text{FE}_{\text{CO}} = 65\%$) than on Ni-N-C ($V_{\text{RHE}} = -0.78$ V, $\text{FE}_{\text{CO}} = 85\%$) (Fig. 12b). DFT simulations of reaction pathways on these catalytically active M-N_x moieties agreed well with the experimental results (Fig. 12c). Consistent with the experiments, Co-N_x sites holding downhill energetics for hydrogen suffered from severe energetic barriers to CO production; while larger overpotentials were required for Ni-N_x sites to start the reaction resulting from the low H* and CO* binding energy and at larger overpotentials hydrogen evolution was hindered on Ni-N_x catalysts with much less energetic barrier for CO production. Reported work from Daasbjerg's and Li's groups [33,88] also confirmed the notable CO Faradaic efficiency of Fe-N-C and Ni-N-C with Ni

Fig. 11. CO₂RR performance of Ni-N-C and related contrast catalysts. (a) CO Faradaic efficiency over Ni-N-C samples in a potential range of −0.43 to −1.03 V vs. RHE; (b) CO partial current density measured in CO₂-saturated 1 mol L^{−1} KHCO₃ solution with a catalyst loading of 2.0 ± 0.1 mg cm^{−2} for C-Zn₂Ni₁ ZIF-8 and 1.06 mg cm^{−2} for NiPc; Free energy diagrams with implicit (solid lines) and explicit (dashed lines) solvation effect corrections for (c) the CO₂RR and (d) the HER pathways on Ni-N_x sites with different proposed Ni-N structures at 0 V. Insets: Adsorbed configurations of *COOH and *H intermediates on the NiN₂V₂ site, and the H, C, O, N, and Ni atoms were displayed in white, grey, red, blue, and purple, respectively. Reproduced with permission [31]. Copyright 2018, the Royal Society of Chemistry.

as the champion metal center even at much higher overpotentials.

5. Reaction parameters and proposed mechanisms

Despite of the intrinsic activity of the catalysts, reaction parameters such as pH value of the electrolyte and reactant CO₂ pressure also affect the selectivity and activity of CO₂RR. Sonoyama et al. [89] found that metal-*meso*-tetraphenylporphyrin (MTPP) supported on GDEs exhibited much enhanced activity with less overpotential and higher selectivity at 20 atm compared with at ambient pressure. Higher concentration and faster diffusion rate of CO₂ may account for such enhancement. Koper et al. [90] carried out a detailed pH-dependent study for an immobilized cobalt protoporphyrin catalyst, showing that at pH = 1 hydrogen evolution reaction dominated and little CO and CH₄ formed compared with at pH = 3, and further CO electroreduction to CH₄ prefers a more acidic environment (at pH = 1), as shown in Fig. 13a. The observation that CO₂ electroreduction to CO becomes much more dominate at a high pH, indicating that CO₂ activation is not sensitive to the proton concentration, which is obviously different from the competing HER. This result agrees well with the assumption that the formation of a catalyst-bound CO₂^{•−} radical anion possessing a strong

Brønsted-base character is crucial for initiating CO₂ reduction, and therefore the proton donor may be water rather than H⁺ (Fig. 13b). Analogously, Strasser et al. [91] studied the effect of pH on the CO₂RR performance of Fe-N-C catalysts, especially focusing on the selectivity of H₂, CO and methane to investigate the role of proton concentration on the catalytic reactions. CO₂RR measurements were performed in CO₂-saturated electrolyte at different pH values between 1 and 7.25. When plotting production rate versus the applied potential (vs. NHE) at different pH values (Fig. 14a), it was obvious that H₂ and CH₄ formation depended on the pH, but CO formation was independent of pH. The pH dependence observed for CH₄ and H₂ production was consistent with a rate-determining step involving a coupled-proton-electron transfer. In contrast, the unveiling pH independence for CO formation indicated a decoupled electron-proton transfer process (DEPT) in which CO₂^{•−} anion adduct was a key intermediate (Fig. 14b and 14c) similar with the mechanism proposed by Koper et al. [90,92] in Co(II)-N-C complexes. Based on the guidance of the above reaction mechanism, important catalyst design rules bearing the DEPT mechanism involve: (i) Reducing the barrier for the formation of the initial catalyst-bound CO₂^{•−} radical anion by enhancing the interaction between active sites and intermediate is an effective way to decrease the overpotential of CO₂RR;

Fig. 12. (a) A schematic local structure of the synthesized M-N_x-containing materials; (b) Applied iR-corrected potential dependent CO Faradaic efficiency for the five M-N-C catalysts; (c) Simulation results showing good accordance with experimental measurements. Middle of (c): Applied potential dependent CO production turnover frequency (TOF) over the M-N-C catalysts. Three distinct potential regions for both catalytic performances (upper and reaction pathways (lower) exhibiting different rate-determining mechanistic features. Region 1: Low overpotentials, the onset potentials of CO production correlate with the binding energy of the reaction intermediate COOH*; Region 2: Intermediate overpotentials, the TOF value of CO production at -0.6 V vs. RHE correlates with the free energy of adsorbed CO; Region 3: High overpotentials, free energy diagrams for the HER (dashed paths) and CO₂RR (solid paths) at -0.8 V vs. RHE for each M-N-C catalyst showing higher HER barriers for Ni and Cu with downhill CO₂RR barrier. Reproduced with permission [87]. Copyright 2017, Springer Nature.

Fig. 13. (a) Faradaic efficiency of CO₂ electroreduction to CO and CH₄ in 0.1 mol L⁻¹ perchlorate solution saturated with CO₂. (yellow bars: pH = 1, P_{CO2} = 1 atm; blue bars: pH = 1, P_{CO2} = 10 atm; magenta bars: pH = 3, P_{CO2} = 1 atm; black bars: pH = 3, P_{CO2} = 10 atm); (b) Proposed mechanistic pathway for the CO₂RR on Co protoporphyrin. Reproduced with permission [90]. Copyright 2015, Springer Nature.

(ii) A suitable adjustment of local pH by employing electrolyte with appropriate bulk pH and buffer capacity helps to tune the product ratio leading to optimal Faradaic efficiency; (iii) To increase the selectivity of methane or other products that requires further electroreduction of CO, a stronger binding of CO is essential [90].

6. Conclusion and outlooks

Recent advances on a variety of M-N_x sites-containing transition metal-centered macrocyclic complexes, metal organic frameworks and M-N_x-doped carbon materials towards efficient CO₂RR are summarized, including both experimental and theoretical studies. Unequivocally, these atomically dispersed metal nitrogen sites constituted of earth abundant elements with maximum atom-utilization efficiency exhibit great potential as promising alternatives for well-performed metal cata-

Fig. 14. (a) Formation rate for H₂, CO, and CH₄ in different CO₂-saturated electrolytes, black: 0.1 mol L⁻¹ HClO₄; red: 0.1 mol L⁻¹ H₃PO₄-K₃PO₄; dark yellow: 0.1 mol L⁻¹ KH₂PO₄; blue: 0.1 mol L⁻¹ KH₂PO₄-K₂HPO₄; cyan: 0.1 mol L⁻¹ KHCO₃; pink: 0.3 mol L⁻¹ KHCO₃; (b) pH dependence of CO formation rate at a constant potential on the RHE scale, the shape of which resembles that expected for a DEPT reduction; (c) Diagram of the proposed catalytic cycle of CO₂RR on Fe-N-C catalysts and metal-nitrogen molecular catalysts in a DEPT mechanism in comparison with the coupled proton-electron transfer mechanism prevailing in heterogeneous catalysis [91]. Reproduced with permission [91]. Copyright 2018, American Chemistry Society.

lysts (Au, Ag, Cu, Pd, etc.). Despite of the encouraging progress, the catalytic performance still needs to be optimized to meet the industrial requirements, and studies on unveiling the intricate reaction mechanisms are highly required for the exploration of optimal catalysts and reaction conditions. To be specific, high current density and stability are essential requirements for future application of CO₂RR, thus active sites should hold considerable turnover frequency and competitive HER should be inhibited at higher potentials in order to achieve a high performance and stability towards CO₂RR.

Though combined with conductive substrates contributes to the improved activity and selectivity towards CO₂RR on M-N_x-containing macrocyclic complexes and MOF materials, poor conductivity which leads to limited electro-active sites still remains the main challenge. In contrast, carbon-based metal-nitrogen materials derived from pyrolysis of N-, C- and transition metal-containing precursors endow excellent conductivity with improved charge/electron transfer capability. However, unlike macrocyclic complexes or MOF materials with precise active site structures, there are several functionalities (i.e., multiple N configurations and various metal nitrogen coordination states) in carbon-based metal-nitrogen catalysts, making it difficult to extract the structure-activity relationship. Therefore, careful control of synthetic strategies for structural uniformity of active sites, advanced in situ/operando characterization methods and profound theoretical simulations are

the key for understanding the role of each functionality. As illustrated above, CO and formate are major products on carbon-based M-N_x sites with few studies showing hydrocarbon or oxygenates as reduction products. Novel catalytic systems concerning M-N_x active sites that can effectively reduce CO₂ into more valuable products involving multiple proton/electron transfers still remain challenging. In addition to the intrinsic nature of active sites, a suitable adjustment of reaction conditions (pH, buffer capacity, pressure, and set-up configurations) contributes to a higher selectivity to a certain product, and a deep understanding of the CO₂RR mechanism provides inductive guidance for optimized catalytic processes in return. In brief, highly efficient, robust and cost-effective M-N_x sites manifest great potential in promoting the industrial application of CO₂RR.

References

- [1] M. Mikkelsen, M. Jørgensen, F. C. Krebs, *Energy Environ. Sci.*, **2010**, 3, 43–81.
- [2] E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, J. Pérez-Ramírez, *Energy Environ. Sci.*, **2013**, 6, 3112–3135.
- [3] M. Bui, C. S. Adjiman, A. Bardow, E. J. Anthony, A. Boston, S. Brown, P. S. Fennell, S. Fuss, A. Galindo, L. A. Hackett, J. P. Hallett, H. J. Herzog, G. Jackson, J. Kemper, S. Krevor, G. C. Maitland, M. Matuszewski, I. S. Metcalfe, C. Petit, G. Puxty, J. Reimer, D. M.

Graphical Abstract

Chin. J. Catal., 2019, 40: 23–37 doi: 10.1016/S1872-2067(18)63161-4

Transition metal-nitrogen sites for electrochemical carbon dioxide reduction reaction

Chengcheng Yan, Long Lin, Guoxiong Wang *, Xinhe Bao *

Dalian Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences

Metal-nitrogen sites constituted of earth abundant elements with maximum atom-utilization efficiency have emerged as promising catalysts for electrochemical CO₂ reduction reaction.

- Reiner, E. S. Rubin, S. A. Scott, N. Shah, B. Smit, J. P. M. Trusler, P. Webley, J. Wilcox, N. MacDowell, *Energy Environ. Sci.*, **2018**, 11, 1062–1176.
- [4] G. Yang, Z. P. Yu, J. Zhang, Z. X. Liang, *Chin. J. Catal.*, **2018**, 39, 914–919.
- [5] B. Khezri, A. C. Fisher, M. Pumera, *J. Mater. Chem. A*, **2017**, 5, 8230–8246.
- [6] L. Zhang, Z. J. Zhao, J. Gong, *Angew. Chem. Int. Ed.*, **2017**, 56, 11326–11353.
- [7] D. D. Zhu, J. L. Liu, S. Z. Qiao, *Adv. Mater.*, **2016**, 28, 3423–3452.
- [8] D. Gao, F. Cai, G. Wang, X. Bao, *Curr. Opin. Green Sustainable Chem.*, **2017**, 3, 39–44.
- [9] Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. G. Chen, F. Jiao, *Nat. Commun.*, **2014**, 5, 3242–3247.
- [10] Y. Chen, C. W. Li, M. W. Kanan, *J. Am. Chem. Soc.*, **2012**, 134, 19969–19972.
- [11] A. S. Varela, N. Ranjbar Sahraie, J. Steinberg, W. Ju, H. S. Oh, P. Strasser, *Angew. Chem. Int. Ed.*, **2015**, 54, 10758–10762.
- [12] J. Hao, W. Shi, *Chin. J. Catal.*, **2018**, 39, 1157–1166.
- [13] Y. Hori, *Electrochemical CO₂ Reduction on Metal Electrodes*, Springer, New York, **2008**.
- [14] J. Rosen, G. S. Hutchings, Q. Lu, R. V. Forest, A. Moore, F. Jiao, *ACS Catal.*, **2015**, 5, 4586–4591.
- [15] D. H. Won, H. Shin, J. Koh, J. Chung, H. S. Lee, H. Kim, S. I. Woo, *Angew. Chem. Int. Ed.*, **2016**, 55, 9297–9300.
- [16] Z. Yin, D. Gao, S. Yao, B. Zhao, F. Cai, L. Lin, P. Tang, P. Zhai, G. Wang, D. Ma, X. Bao, *Nano Energy*, **2016**, 27, 35–43.
- [17] W. L. Zhu, R. Michalsky, O. Metin, H. F. Lv, S. J. Guo, C. J. Wright, X. L. Sun, A. A. Peterson, S. H. Sun, *J. Am. Chem. Soc.*, **2013**, 135, 16833–16836.
- [18] D. Gao, Y. Zhang, Z. Zhou, F. Cai, X. Zhao, W. Huang, Y. Li, J. Zhu, P. Liu, F. Yang, G. Wang, X. Bao, *J. Am. Chem. Soc.*, **2017**, 139, 5652–5655.
- [19] F. Li, D. R. MacFarlane, J. Zhang, *Nanoscale*, **2018**, 10, 6235–6260.
- [20] F. Guan, X. M. Zhang, Y. F. Song, Y. J. Zhou, G. X. Wang, X. H. Bao, *Chin. J. Catal.*, **2018**, 37, 1484–1492.
- [21] W. Zhang, Y. Hu, L. Ma, G. Zhu, Y. Wang, X. Xue, R. Chen, S. Yang, Z. Jin, *Adv. Sci.*, **2018**, 5, 1700275.
- [22] D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang, X. Bao, *J. Am. Chem. Soc.*, **2015**, 137, 4288–4291.
- [23] J. W. Vickers, D. Alfonso, D. R. Kauffman, *Energy Technol.*, **2017**, 5, 775–795.
- [24] B. H. Zhang, J. T. Zhang, *J. Energy Chem.*, **2017**, 26, 1050–1066.
- [25] G. F. Manbeck, E. Fujita, *J. Porphyrins Phthalocyanines*, **2015**, 19, 45–64.
- [26] C. A. Downes, S. C. Marinescu, *ChemSusChem*, **2017**, 10, 4374–4392.
- [27] V. A. Sofia, J. Wen, S. Peter, *Adv. Energy Mater.*, DOI: doi:10.1002/aenm.201703614.
- [28] M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science*, **2009**, 324, 71–74.
- [29] A. Zitolo, V. Goellner, V. Armel, M. T. Sougrati, T. Mineva, L. Stievano, E. Fonda, F. Jaouen, *Nat. Mater.*, **2015**, 14, 937–942.
- [30] A. A. Gewirth, J. A. Varnell, A. M. DiAscro, *Chem. Rev.*, **2018**, 118, 2313–2339.
- [31] C. Yan, H. Li, Y. Ye, H. Wu, F. Cai, R. Si, J. Xiao, S. Miao, S. Xie, F. Yang, Y. Li, G. Wang, X. Bao, *Energy Environ. Sci.*, **2018**, 11, 1204–1210.

- [32] Y. Ye, F. Cai, H. Li, H. Wu, G. Wang, Y. Li, S. Miao, S. Xie, R. Si, J. Wang, X. Bao, *Nano Energy*, **2017**, 38, 281–289.
- [33] X. M. Hu, H. H. Hval, E. T. Bjerglund, K. J. Dalggaard, M. R. Madsen, M. M. Pohl, E. Welter, P. Lamagni, K. B. Buhl, M. Bremholm, M. Beller, S. U. Pedersen, T. Skrydstrup, K. Daasbjerg, *ACS Catal.*, **2018**, 8, 6255–6264.
- [34] N. Furuya, K. Matsui, *J. Electroanal. Chem.*, **1989**, 271, 181–191.
- [35] N. Furuya, S. Koide, *Electrochim. Acta*, **1991**, 36, 1309–1313.
- [36] Y. Wu, J. Jiang, Z. Weng, M. Wang, D. L. J. Broere, Y. Zhong, G. W. Brudvig, Z. Feng, H. Wang, *ACS Cent. Sci.*, **2017**, 3, 847–852.
- [37] J. J. Walsh, C. L. Smith, G. Neri, G. F. S. Whitehead, C. M. Robertson, A. J. Cowan, *Faraday Discuss.*, **2015**, 183, 147–160.
- [38] A. Maurin, M. Robert, *Chem. Commun.*, **2016**, 52, 12084–12087.
- [39] C. Costentin, S. Drouet, M. Robert, J. M. Saveant, *Science*, **2012**, 338, 90–94.
- [40] E. A. Mohamed, Z. N. Zahran, Y. Naruta, *Chem. Mater.*, **2017**, 29, 7140–7150.
- [41] N. Morlanés, K. Takanabe, V. Rodionov, *ACS Catal.*, **2016**, 6, 3092–3095.
- [42] X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang, H. Wang, *Nat. Commun.*, **2017**, 8, 14675–14682.
- [43] N. Han, Y. Wang, L. Ma, J. Wen, J. Li, H. Zheng, K. Nie, X. Wang, F. Zhao, Y. Li, J. Fan, J. Zhong, T. Wu, D. J. Miller, J. Lu, S. T. Lee, Y. Li, *Chem*, **2017**, 3, 652–664.
- [44] C. Costentin, M. Robert, J.-M. Saveant, A. Tatin, *Proc. Natl. Acad. Sci. U. S. A.*, **2015**, 112, 6882–6886.
- [45] I. M. B. Nielsen, K. Leung, *J. Phys. Chem. A*, **2010**, 114, 10166–10173.
- [46] K. Leung, I. M. B. Nielsen, N. Sai, C. Medforth, J. A. Shelnutt, *J. Phys. Chem. A*, **2010**, 114, 10174–10184.
- [47] Z. Weng, Y. Wu, M. Wang, J. Jiang, K. Yang, S. Huo, X. F. Wang, Q. Ma, G. W. Brudvig, V. S. Batista, Y. Liang, Z. Feng, H. Wang, *Nat. Commun.*, **2018**, 9, 415–423.
- [48] X. M. Hu, M. H. Ronne, S. U. Pedersen, T. Skrydstrup, K. Daasbjerg, *Angew. Chem. Int. Ed.*, **2017**, 56, 6468–6472.
- [49] A. R. Guadalupe, D. A. Usifer, K. T. Potts, H. C. Hurrell, A. E. Mogstad, H. D. Abruna, *J. Am. Chem. Soc.*, **1988**, 110, 3462–3466.
- [50] B. L. Chen, S. C. Xiang, G. D. Qian, *Acc. Chem. Res.*, **2010**, 43, 1115–1124.
- [51] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.*, **2009**, 38, 1450–1459.
- [52] H. Zhang, J. Nai, L. Yu, X. W. Lou, *Joule*, **2017**, 1, 77–107.
- [53] C. A. Downes, S. C. Marinescu, *ChemSusChem*, **2017**, 10, 4374–4392.
- [54] I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha, J. T. Hupp, *ACS Catal.*, **2015**, 5, 6302–6309.
- [55] J. Albo, D. Vallejo, G. Beobide, O. Castillo, P. Castaño, A. Irabien, *ChemSusChem*, **2017**, 10, 1100–1109.
- [56] N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi, P. Yang, *J. Am. Chem. Soc.*, **2015**, 137, 14129–14135.
- [57] L. Ye, J. Liu, Y. Gao, C. Gong, M. Addicoat, T. Heine, C. Wöll, L. Sun, *J. Mater. Chem. A*, **2016**, 4, 15320–15326.
- [58] Y. Wang, P. Hou, Z. Wang, P. Kang, *ChemPhysChem*, **2017**, 18, 3142–3147.
- [59] X. Jiang, H. Li, J. Xiao, D. Gao, R. Si, F. Yang, Y. Li, G. Wang, X. Bao, *Nano Energy*, **2018**, 52, 345–350.
- [60] M. Sadakiyo, T. Yamada, H. Kitagawa, *J. Am. Chem. Soc.*, **2009**, 131, 9906–9907.
- [61] Z. Zhou, N. N. Chen, Q. Luo, L. Y. Jia, J. Wang, J. Q. Tao, *J. Mol. Struct.*, **2017**, 1136, 107–111.
- [62] Y. J. Li, S. H. Zheng, X. Liu, P. Li, L. Sun, R. X. Yang, S. Wang, Z. S. Wu, X. H. Bao, W. Q. Deng, *Angew. Chem. Int. Ed.*, **2018**, 57, 7992–7996.
- [63] R. Hinogami, S. Yotsuhashi, M. Deguchi, Y. Zenitani, H. Hashiba, Y. Yamada, *ECS Electrochem. Lett.*, **2012**, 1, H17–H19.
- [64] R. Senthil Kumar, S. Senthil Kumar, M. Anbu Kulandainathan, *Electrochem. Commun.*, **2012**, 25, 70–73.
- [65] S. Lin, C. S. Diercks, Y. B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science*, **2015**, 349, 1208–1213.
- [66] C. Z. Zhu, H. Li, S. F. Fu, D. Du, Y. H. Lin, *Chem. Soc. Rev.*, **2016**, 45, 517–531.
- [67] M. X. Shen, C. T. Wei, K. L. Ai, L. H. Lu, *Nano Res.*, **2017**, 10, 1449–1470.
- [68] J. Li, F. Jaouen, *Curr. Opin. Electrochem.*, **2018**, 9, 198–206.
- [69] G. Wu, A. Santandreu, W. Kellogg, S. Gupta, O. Ogoke, H. G. Zhang, H. L. Wang, L. M. Dai, *Nano Energy*, **2016**, 29, 83–110.
- [70] P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei, Y. Li, *Angew. Chem. Int. Ed.*, **2016**, 55, 10800–10805.
- [71] Y. Cheng, S. Zhao, B. Johannessen, J. P. Veder, M. Saunders, M. R. Rowles, M. Cheng, C. Liu, M. F. Chisholm, R. De Marco, H. M. Cheng, S.-Z. Yang, S. P. Jiang, *Adv. Mater.*, **2018**, 30, 1706287.
- [72] Y. Chen, S. Ji, Y. Wang, J. Dong, W. Chen, Z. Li, R. Shen, L. Zheng, Z. Zhuang, D. Wang, Y. Li, *Angew. Chem. Int. Ed.*, **2017**, 56, 6937–6941.
- [73] X. Wang, Z. Chen, X. Zhao, T. Yao, W. Chen, R. You, C. Zhao, G. Wu, J. Wang, W. Huang, J. Yang, X. Hong, S. Wei, Y. Wu, Y. Li, *Angew. Chem. Int. Ed.*, **2018**, 57, 1944–1948.
- [74] T. N. Huan, N. Ranjbar, G. Rousse, M. Sougrati, A. Zitolo, V. Mougél, F. Jaouen, M. Fontecave, *ACS Catal.*, **2017**, 7, 1520–1525.
- [75] C. Yan, Y. Ye, L. Lin, H. Wu, Q. Jiang, G. Wang, X. Bao, *Catal. Today*, **2018**, DOI: <https://doi.org/10.1016/j.cattod.2018.03.062>.
- [76] Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, W. Chen, K. Wu, W. C. Cheong, Y. Wang, L. Zheng, J. Luo, Y. Lin, Y. Liu, C. Liu, J. Li, Q. Lu, X. Chen, D. Wang, Q. Peng, C. Chen, Y. Li, *J. Am. Chem. Soc.*, **2018**, 140, 4218–4221.
- [77] H. B. Yang, S. F. Hung, S. Liu, K. Yuan, S. Miao, L. Zhang, X. Huang, H. Y. Wang, W. Cai, R. Chen, J. Gao, X. Yang, W. Chen, Y. Huang, H. M. Chen, C. M. Li, T. Zhang, B. Liu, *Nature Energy*, **2018**, 3, 140–147.
- [78] C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu, Y. Li, *J. Am. Chem. Soc.*, **2017**, 139, 8078–8081.
- [79] K. Jiang, S. Siahrostami, T. Zheng, Y. Hu, S. Hwang, E. Stavitski, Y. Peng, J. Dynes, M. Gangisetty, D. Su, K. Attenkofer, H. Wang, *Energy Environ. Sci.*, **2018**, 11, 893–903.
- [80] X. Li, W. Bi, M. Chen, Y. Sun, H. Ju, W. Yan, J. Zhu, X. Wu, W. Chu, C. Wu, Y. Xie, *J. Am. Chem. Soc.*, **2017**, 139, 14889–14892.
- [81] Z. Chen, K. Mou, S. Yao, L. Liu, *ChemSusChem*, **2018**, 11, 2944–2952.
- [82] Y. Zhao, J. Liang, C. Wang, J. Ma, G. G. Wallace, *Adv. Energy Mater.*, **2018**, 8, 1702524.
- [83] M. Wu, K. Wang, M. Yi, Y. Tong, Y. Wang, S. Song, *ACS Catal.*, **2017**, 7, 6082–6088.
- [84] W. Wei, H. Liang, K. Parvez, X. Zhuang, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.*, **2014**, 53, 1570–1574.
- [85] W. He, C. Jiang, J. Wang, L. Lu, *Angew. Chem. Int. Ed.*, **2014**, 53, 9503–9507.
- [86] Y. Guo, H. Yang, X. Zhou, K. Liu, C. Zhang, Z. Zhou, C. Wang, W. Lin, *J. Mater. Chem. A*, **2017**, 5, 24867–24873.
- [87] W. Ju, A. Bagger, G. P. Hao, A. Sofia Varela, I. Sinev, V. Bon, B. Roland Cuenya, S. Kaskel, J. Rossmeisl, P. Strasser, *Nat. Commun.*, **2017**, 8, 944–951.
- [88] F. Pan, W. Deng, C. Justiniano, Y. Li, *Appl. Catal. B*, **2018**, 226, 463–472.
- [89] N. Sonoyama, M. Kirii, T. Sakata, *Electrochem. Commun.*, **1999**, 1,

213–216.

- [90] J. Shen, R. Kortlever, R. Kas, Y. Y. Birdja, O. Diaz-Morales, Y. Kwon, I. Ledezma-Yanez, K. J. P. Schouten, G. Mul, M. T. M. Koper, *Nat. Commun.*, **2015**, 6, 8177–8182.

- [91] A. S. Varela, M. Kroschel, N. D. Leonard, W. Ju, J. Steinberg, A. Bagger, J. Rossmeisl, P. Strasser, *ACS Energy Lett.*, **2018**, 3, 812–817.

- [92] J. Shen, M. J. Kolb, A. J. Göttele, M. T. M. Koper, *J. Phys. Chem. C*, **2016**, 120, 15714–15721.

过渡金属-氮活性位点在二氧化碳电化学还原反应中的应用

阎程程^{a,b}, 林 龙^{a,b}, 汪国雄^{a,c,*}, 包信和^{a,c,#}

^a中国科学院大连化学物理研究所催化基础国家重点实验室, 中国科学院纳米科学卓越创新中心, 辽宁大连 116023

^b中国科学院大学, 北京 100049

^c中国科学院大连化学物理研究所洁净能源国家实验室(筹), 辽宁大连 116023

摘要: 大气中过高的CO₂浓度严重影响自然界的碳循环平衡, 对全球气候和生态环境提出了严峻挑战。但同时CO₂作为一种潜在的碳资源, 可通过催化转化生成高附加值的化学品。CO₂电化学还原反应(CO₂RR)可利用太阳能、风能等可再生能源产生的电能将CO₂直接转化生成高附加值化学品和燃料, 有助于构建“碳中和”的能源循环利用网络, 具有极具潜力的应用前景。然而, 活化稳定的CO₂分子需克服一定的过电势, 且由于反应在水相中进行, CO₂RR与析氢反应互相竞争, 因此开发高效、廉价、稳定的催化剂一直是CO₂RR研究的难点。研究表明, 含有金属-氮(M-N_x)活性位的催化材料如卟啉、酞菁等大环配合物、金属有机骨架材料以及通过热解法制备的金属-氮-碳(M-N-C)材料具有优异的CO₂RR性能。本文从实验和理论两方面综述了近年来该类材料领域的相关进展, 重点介绍了金属位点种类、配体结构、载体选择对催化剂本征活性的影响, 并讨论了反应条件优化对CO₂RR性能提升的作用。结合原位表征和理论计算结果探讨了含M-N_x材料反应条件下活性位的结构及反应路径, 为合理设计和优化CO₂RR催化剂体系提供了新思路。

关键词: 二氧化碳电化学还原反应; 金属-氮位点; 含金属-氮位点的大环化合物; 金属有机骨架; 沸石咪唑骨架; 金属-氮掺杂碳材料

收稿日期: 2018-09-04. 接受日期: 2018-09-19. 出版日期: 2019-01-05.

*通讯联系人. 电话: (0411)84686637; 传真: (0411)84694447; 电子信箱: wanggx@dicp.ac.cn

#通讯联系人. 电子信箱: xhbao@dicp.ac.cn

基金来源: 国家重点研发计划(2017YFA0700102); 国家自然科学基金(21573222, 91545202); 大连杰出青年人才计划(2017RJ03); 中国科学院大连化学物理研究所DMTO项目(DICP DMTO201702); 中国科学院战略性先导科技专项(XDB17020200); 中国科学院青年创新促进会(2015145).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).