CHEMISTRY A European Journal



Accepted Article

Title: The role of organic components in electrocatalysis for renewable energy storage

Authors: Gejun Liu, Haipeng Bai, Bo Zhang, and Huisheng Peng

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201803322

Link to VoR: http://dx.doi.org/10.1002/chem.201803322

Supported by ACES



The role of organic components in electrocatalysis for renewable energy storage

Gejun Liu, Haipeng Bai, Bo Zhang* and Huisheng Peng*

G. Liu, H. Bai, Prof. Dr. B. Zhang, Prof. Dr. H. Peng State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science and Laboratory of Advanced Materials, Fudan University, Shanghai 200438, China

The first two authors contributed equally to this work.

*Correspondence and requests for materials should be addressed to Huisheng Peng (penghs@fudan.edu.cn) (H. P.) and Bo Zhang (bozhang@fudan.edu.cn) (B. Z.)

Abstract: CO₂ electroreduction and water splitting are known as two promising strategies to convert renewable intermittent electric energy into chemical energy. Thus, the three half reactions i.e., CO₂ reduction reaction, hydrogen evolution reaction and their counter reaction, the oxygen evolution reaction in above two electrolytic processes have arisen wide research interest. The organic polymer electrocatalysts or electrocatalysts containing organic compositions play important roles in these catalytic processes. It is shown that the organic molecules can efficiently catalyze the reactions themselves and also modulate the active sites towards high selectivity and efficiency. Roles of the organic molecules in conducting polymers, the metal complexes and the framework materials are extracted on above three half reactions and the comprehensive review will serve as guidelines for future research and aid in design of electrocatalysts related to organic molecules.

1. Introduction

The global sustainable development requires sufficient energy supplement. However, the present energy system based on non-renewable fossil fuels does not meet this requirement in long term. Great efforts have been made to develop alternative energy supply and kinds of electrical supply from renewable energy like wind energy, solar energy, and hydroenergy is thought to be appropriate candidate. Although these clean energies are renewable, there are still great obstacles in the practical application. Among all challenges, the storage and transport of these intermittent electric energy are particularly difficult and costly. Converting these intermittent electric energies into chemical energies stored in energy-rich chemicals using electrochemical processes is a desirable strategy to make full use of collected renewable energy. And the most desired two processes are CO_2 electroreduction and water splitting.

Carbon compounds like coal, natural gas and petroleum are widely used as the carriage of energy in most industrial systems. The consuming of carbon compounds produces vast CO₂ emission and has caused and will continue to cause climate challenges^{1, 2}. Electrochemically converting CO₂ into valuable carbon-based fuels is a promising pathway to meet the demands of both intermittent energy storage and CO_2 reducing ^{3,4}. However, CO₂ is a notoriously inert chemical and the conversion of CO₂ into fuels is kinetically and dynamically sluggish. Multi-products are produced in CO₂ reduction reaction (CO₂RR), such as carbon monoxide (CO), formic acid (HCOOH) or formate (HCOO^{-}) , oxalic acid $(\text{H}_2\text{C}_2\text{O}_4)$ or oxalate $(\text{C}_2\text{O}_4^{2-})$, formaldehyde (CH_2O) , methanol (CH₃OH), methane (CH₄), ethylene(CH₂CH₂), ethanol (CH₃CH₂OH) and so on. There are still several crucial challenges in CO_2RR . Firstly, as shown in (eqn (1) - (6)), the multiple proton coupled electron transfer to CO₂ requires large overpotential to overcome the energy barrier. Although, with the help of electrocatalysts, the overpotential drops obviously, the energy requirement is still too high. Secondly, the selectivity of catalysts towards specific product still impedes the CO₂RR. The competing reaction i.e., hydrogen evolution reaction (HER) (eqn (7)) in CO_2RR is unavoidable, especially in protic solvents. Consequently, the produced gas is mixture of multi gases which is not favored for the high cost in gas separation. Thirdly, the current reduction efficiency is still too low for industrial application and the short catalytic life could cause enormous cost in catalyst supplements.

Besides CO₂ electroreduction, water splitting is also a promising pathway to the storage of intermittent electric energy. Water is the most readily available feedstock on the earth and its reduction product, the H₂, offers better gravimetric energy density. As a high energy density chemical, H₂ is widely used in industrial process as feedstock or fuel, meanwhile, H₂ is also applicable in fuel cell system. Thus, water splitting is an appropriate pathway for energy conversion from intermittent electric power to easily stored chemical energy.

The two desirable electroreduction reactions mentioned above, i.e., the CO₂RR and HER, are generated in the cathode of an electrolytic process. To supply the electrons necessary for the reduction of the feedstock into fuel, a concurrent oxidation reaction is required and the oxygen evolution reaction (OER) (eqn (8)) is generated in the anode of both electrolytic reactions, simultaneously. In an electrolytic reaction, half reaction in anode can dramatically affect the energy efficiency of the system and electrolytic efficiency, and thus affect the energy conversion ratio of the generated electric energy. To promote the efficient extraction of electrons from water to facilitate the electrolytic reaction, highly active OER catalysts are required⁵. Consequently, all the three half-reactions, i.e., CO₂RR, HER and OER, are crucial in the storage of renewable energy using an electrolytic method.

 $CO_{2} + e^{-} \rightarrow CO_{2}, E^{0} = -1.90 V (1)$ $CO_{2} + 2 H^{+} + 2 e^{-} \rightarrow CO + H_{2}O, E^{0} = -0.53 V (2)$ $CO_{2} + 2 H^{+} + 2 e^{-} \rightarrow HCO_{2}H, E^{0} = -0.61 V (3)$ $CO_{2} + 4 H^{+} + 4 e^{-} \rightarrow HCHO + H_{2}O, E^{0} = -0.48 V (4)$ $CO_{2} + 6 H^{+} + 6 e^{-} \rightarrow CH_{3}OH + H_{2}O, E^{0} = -0.38 V (5)$ $CO_{2} + 8 H^{+} + 8 e^{-} \rightarrow CH_{4} + 2 H_{2}O, E^{0} = -0.24 V (6)$ $2 H^{+} + 2 e^{-} \rightarrow H_{2}(7), E^{0} = 0 V (7)$ $2 H_{2}O \rightarrow 4 H^{+} + O_{2} + 4 e^{-}, E^{0} = 1.23 V (8)$

Regarding the electrocatalysts, current research focuses primarily on metal and their alloys, metal-containing compounds and kinds of specific polymers. Over the research interests, the organic components play important roles in both the metal-containing compounds and polymer catalysts. The organic molecules are indispensable to electrocatalysts for unique catalytic property and efficient regulating ability. Kinds of organic polymers like polypyrrole (PPy) were reported to possess catalytic activity and some were reported to be the support of the catalysts. The organic components in metal complexes and compounds were also regarded to affect the catalytic performance and they are often ideal for fine tuning reactivity *via* synthetic modifications of the ligands. Meanwhile, the framework materials like Metal Organic Frameworks (MOFs) catalysts and Covalent Organic Frameworks (COFs) catalysts containing organic ligands are potentially good catalysts for their programmable structures⁶. By changing the metal center or the organic molecular species, the catalytic performance can be modulated as desired.

As the consequence of organic components in catalytic performance, it is essential to find out the mechanisms of organic components in an electrolytic process. Although there have been some excellent reviews about the effects of organic component in electrocatalytic process⁷⁻¹⁰, there is still no review focusing on the effects on the electroreactions mentioned above for renewable energy storage. In this review, we summarize the roles of organic components in conductive polymer, the metal complexes and framework materials catalysts in their catalytic performances in CO₂RR, HER and OER.

2. The role of organic components in CO₂RR

The rapid advance of industrial activities has caused enormous emission of CO_2 and thus broken the ideal scenario that the CO_2 produced on earth should be balanced with which is consumed. Meanwhile, unlimited usage of fossil fuel does not meet the requirement of sustainable development. Efforts have been made to develop clean energy to prevent the sluggish of energy consuming manufacturing industry. However, the present ways to store or transport generally intermittent electric energy are not promising due to the high cost. Electrochemically converting atmospheric CO_2 into valuable carbon-based fuels or industry feedstock is of great importance to satisfy both the storage of intermittent renewable electricity and reducing greenhouse gas net emissions. Therefore, electrochemically converting CO_2 into useful materials seems to be necessary, indeed critical for sustainable development.^{7, 11, 12}

The most commonly explored electrocatalysts for CO_2RR are transition metal elements and their associated compounds. This is probable because these metals have vacant orbits and active *d* electrons, which are believed to be able to energetically facilitate the bonding between the metal and the CO_2 molecule. Meanwhile, the organic components in the electrocatalysts were found to influence the catalytic performance like catalytic activity, product selectivity and catalytic stability dramatically. Furthermore, some organic compounds were also reported to be capable to electroreduce CO_2 . Hence, we highlight the effects of organic component in CO_2RR and three classes of organic components are discussed. The first class is conducting polymers being used as catalysts or catalysts supports. The widely used metal complexes are classified as the second species and the influence of organic components of these complex is studied. For the similar component of both metallic and organic molecular and highly regulated pore structure, the MOFs and COFs materials are classified as the third class.

2.1 Conducting polymer

Conducting polymers are generally used as catalysts directly or as support of the heterogeneous electrocatalysts of CO₂RR. These polymers usually contain nitrogen functionalities that possess catalytic activity or complex metal cations or anchor metal nanoparticles either within the polymer backbone or the pendant chain^{13, 14}. The organic polymers rich in nitrogen like polymers based on bipyridine, benzimidazole and polyaniline(PANI) are the most studied polymer catalysts or catalyst supports for CO₂RR. The metal-free and nitrogen-rich imidazole, porphyrin and their derivate catalysts were reported to be applicable in CO₂RR. Smith¹⁵ synthesized two organic polymers based on repeating benzimidazole and pyridine-bipyridine units, respectively. They proved the CO₂ reduction activity by comparing the CV curves of the two nitrogen-rich polymers in CO₂ saturated acetonitrile containing 1% water. Aydin et al.¹⁶ developed a PPy polymer catalyst and used this catalyst for CO₂RR under high pressure in CH₃OH at an overpotential of - 0.4 V vs. Ag/AgCl. The Faradic efficiency (FE) of HCHO, HCOOH, and CH₃COOH were 1.9, 40.5, and 62.2%, respectively. Another nitrogen-rich polymer i.e., the PANI was used as CO₂RR catalysts and showed selectivity mainly towards organic acid. Köleli et al.¹⁷ developed a PANI catalyst and the CO₂RR was carried out in methanol solution at - 0.4 V vs. SCE. They achieved the FE of 12 and 78% for HCOOH and CH₃COOH respectively. They also applied the bulk PANI electrode in a high pressure cell to reduce CO₂ to HCOH¹⁸. Ogura et al. developed a Prussian blue laminated PANI electrode and used it for the CO₂RR under high pressure¹⁹. By this modified electrode, CO₂ was reduced at 0.8 V vs. Ag/AgCl in aqueous H₂SO₄. The reaction products were CH₃CHOHCOOH, CH₃COOH, HCOOH, CH₃OH, and CH₃CH₂OH. In these cases, the contained nitrogen functionalities were thought as the active sites as they were capable of adsorbing and activating CO₂ molecules. The use of bare conducting polymers may be favorable for the practical application because the costs are relatively low according to the current technologies.

Although conducting polymers are capable to reduce CO_2 , the catalytic property is generally unsatisfactory for limited product species and distribution. The metalpolymer catalysts combined the advantages of conducting polymer and metal catalyst and were reported to be efficient in CO_2RR . Using non-electrochemical methods like adsorption, solvent casting and chemical reduction deposition techniques or electrochemical methods like electrochemical synthesizing dissolved monomers, polymers can be coated onto conducting metal supports to fabricate metal-polymer electrodes²⁰. The electrochemical synthesis is preferred for its controllable loading amount^{21, 22}. The polymers were reported to affect the catalytic selectivity and stability. Kinds of metals have been incorporated in metal-polymer electrodes and the copper-polymer catalysts were preferred in CO₂RR for their ability to produce multi-carbon products. Grace²³ fabricated Cu₂O nanoparticles decorated PANI matrix (PANI/Cu₂O) catalyst using cyclic voltammetry and constant current technique (**Figure 1 a-d**). Well-defined Cu(I) species was detected in the catalyst surface during the CO₂RR in 0.1 M tetrabutylammonium perchlorate and CH₃OH electrolyte. The H adatoms form and subsequently transfer to CO₂ through the polymer film to form the products. The main products were HCOOH and CH₃COOH with FE of 30.4% and 63.0% at a potential of - 0.3 V vs. SCE (**Figure 1 e**).

Generally, the reduction product distribution for a specific catalyst is fixed, and it is interesting that the PPy was reported to change the product distribution. Ayd 1^{24} and colleagues investigated the effects of PPy on Cu catalyst in a CH₃OH/0.1 M LiClO₄/H⁺ electrolyte system. The coating of this conducting polymer caused a shift of the product distribution to hydrocarbons, especially to CH₄ (as shown in **table 1**) and they obtained FE of CH₄ (25%) and HCOOH (20%) under their established optimum values of mentioned parameters. The morphology of the catalyst was well maintained, and there were no changes or damages visible in the cauliflower structure of polymer film before and after electrolysis *via* SEM measurements.

Besides affecting the product distribution, the PANI and PPy based catalysts can drive CO_2 reduction beyond CO without the help of Cu, Ru, or Ir which were reported to be the only known materials that can drive CO_2 reduction beyond CO. Ogura et al.,²⁵ investigated the CO_2 reduction property of Pt [1,8-dihydroxynaphthalene-3,6-disulfonatoferrate(II)] complex-immobilized PANI/Prussian blue-laminated electrode. The major product was not CO but C₃H₆O₃, CH₃COOH, HCOOH, CH₃OH, and CH₃CH₂OH. The numerous reduced products were ascribed to the roles of PANI and the metal complex that render CO₂ chemically active by combining the electrophilic carbon atom. The activated CO₂ was hydrogenated and converted to organic acids and alcohols by the reaction with H atoms. They concluded that the HCOH was the

precursor of the organic acids (except formic acid) and alcohols and the insertion of CO₂ into intermediated was crucial for multi carbon production.

Being directly used as catalysts, the metal-free nitrogen-rich polymers can primarily reduce CO₂ into organic acids and aldehydes. They may provide both efficient electron transport channels and reduction active sites. The electron transport channels stemed from their inherent conductivity and the active sites were usually nitrogen-containing groups as they were capable of adsorbing and activating CO₂ molecules. However, the current studies based on metal-free conducting polymers as CO₂RR catalysts showed obvious drawbacks. Firstly, the product species are mainly primary reduction products and the more thoroughly reduced products like CH₄ and C₂H₄ are rarely available. Secondly, the selectivity towards specific products remains unsatisfied. Thirdly, the production efficiencies of most such catalysts are still too low for real applications. When metal catalysts are introduced, the active sites of conducting polymers will be suppressed by metal active centers with higher activity and efficiency. In most metalpolymer composite catalysts, the polymers are no longer the active sites. However, the conducting polymers can still influence the catalytic performance of metal catalysts like the product distribution and species. The influences of conducting polymers on metal active centers may provide a new strategy to modulate the reduction products. However, the current selectivity still need to be optimized urgently to avoid the additional product separation processes.

2.2 Metal complex

The metal complexes are widely used in electrocatalytic processes for their tunable metallic center and ligand species to achieve different reduction conditions like multielectron or multi-proton for different products and high reduction efficiency. The active catalytic center can be produced in the reduction process either by reducing the metal center or by reducing the ligand scaffold⁹. In a metal complex catalyst, both the reduced metal ions and the ligand scaffold can be used to store multiple reducing equivalents to facilitate the CO₂RR.

Pyridine-transition metal complexes represent one of the most thoroughly studied classes of molecular catalysts towards CO₂RR to date as they offer the ability to not only stabilize the reduced metal centers but also accept reducing equivalents within the

7

ligand π system, allowing for the storage of multiple reducing equivalents across the entire molecule9, 26, 27. Costentin and colleagues28 synthesized iron tetraphenylporphyrin molecular catalyst and used it for CO₂ electroreduction to produce CO. The phenolic groups were introduced in all ortho and ortho' positions of the phenyl groups and were found to considerably speed up catalysis of this reaction by the electrogenerated Fe(0) complex for a high local concentration of protons associated with the phenolic hydroxyl substituents. The Fe molecular catalysts manifested a CO FE above 90% through 500 000 000 turnovers over 4 h of CO₂RR at an overpotential of 465 mV with no apparent degradation. Meanwhile, Weng et al.²⁹ reported a (Cu(II)-5,10,15,20-tetrakis-(2,6molecular Cu-porphyrin complex dihydroxyphenyl)porphyrin) that can be used as a heterogeneous electrocatalyst with high activity and selectivity for reducing CO₂ to hydrocarbons in aqueous media (Figure 2). The partial current densities and TOFs for CH₄ and C₂H₄ ethylene were 13.2 and 8.4 mA·cm⁻², and 4.3 and 1.8 molecules site⁻¹·s⁻¹ at - 0.976 V vs. RHE, respectively. The Cu centers and built-in OH groups in the porphyrin structure were thought as two indispensable factors for the distinct electrocatalytic performance of the catalyst and this was proved via a series of control experiments.

The formation of CO is the first step of CO₂RR and Co(II)-porphyrin electrocatalysts were reported to be effective CO production catalyst and Hu et al. carried out a comprehensive study of the Co meso-tetraphenylporphyrin (CoTPP) in CO₂RR under both homogeneous and heterogeneous conditions^{30, 31}. The former homogeneous condition employed N,N-dimethylformamide as solvent while the later heterogeneous conditions were carried out in an aqueous medium. The CoTPP performed poorly as homogeneous electrocatalyst and showed low product selectivity and efficiency. Interestingly, when the CoTPP was located on carbon nanotubes and used as a heterogeneous catalyst, a high CO selectivity of > 90% was achieved at a low overpotential (Figure 3). This may be a result of the local environment created by the aqueous solution and the organic ligand. This catalyst revealed different working mechanisms in homogeneous and heterogeneous conditions. Under homogeneous conditions [Co^ITPP] reacted only slowly with CO₂ in DMF according to steady state voltammetry, while [Co⁰TPP]²⁻ as a much stronger reductant was capable of mediating the catalytic CO₂ reduction, although with a low FE. However, once CoTPP became immobilized on CNTs or similar carbon materials, [Co^ITPP]⁻ may serve as the active species with a remarkably enhanced activity in aqueous solution.

The Co-phthalocyanine-based CO₂RR catalyst was also reported by Zhang et al.¹ They developed a catalyst with a combined nanoscale and molecular approach. The introduced cyano groups to the Co phthalocyanine molecule uniformly anchored on carbon nanotubes can enhance the catalytic performance on the molecular level (**Figure 4 a and b**) for the reduction of CO with the FE of 95% and can be stable for 10 h (**Figure 4 c and d**). The electron-withdrawing cyano groups can facilitate the formation of Co(I) which was considered as the active sites for reducing CO₂. High reduction activity was also achieved with a turnover frequency of 4.1 s⁻¹ at the overpotential of 520 mV in a near-neutral aqueous solution.

Besides Co complexes, the rhenium (Re) complexes were also reported to be selective toward CO during CO_2RR^{32} . A dipyridylamine ligand with a pendant pyrrole (*N*-(3-*N*,*N*'-bis(2-pyridyl)propylamino)pyrrole, PPP) was used to prepare Re(I) complex i.e., Re(CO)₃(k^2 -*N*,*N*-PPP)Cl. The reduction was carried out on a glassy carbon electrode with poly[Re(CO)₃(k^2 -*N*,*N*-PPP)Cl] film prepared *via* electrochemical polymerization of the pyrrole moiety. The resulted catalyst exhibited electrocatalytic activity for the reduction of CO₂ to CO.

Combining the advantages of both high-active metal centers and the regulating ability of incorporated molecular ligands, the metal complexes show promising advantages in CO_2RR . Benefited from the non-bulk distribution of metal atoms, this kind of catalysts shows relatively high reduction efficiency when evaluated by turnover frequency. Meanwhile, the reduction conditions of metallic centers can be modulated as desired like multi-electrons or multi-protons for specific product species and, as a result, selectivity of specific product like CO is high. However, the production of multi-electron reduction products is still superficial. Consequently, although the precise control of reduction conditions for high industrial added value products like C_2H_4 and C_2H_5OH are still not established.

2.3 Framework materials

The MOF and COF materials are similar in their component and structures. They both possess metallic core, organic bone and highly ordered porous structures. The porous materials were reported to be efficient CO₂RR catalysts for the combination of the

advantages of both molecular and heterogeneous catalysts. The framework materials are potentially good catalysts for the following reasons. Firstly, the manipulation of the catalytic active centers is feasible. Secondly, the diverse ligands allow the modulation of pore sizes and structures³³. Thirdly, the expected function can be introduced into the catalysts by simply modulating functionalized ligands. Up to now, several kinds of MOFs were reported to be efficient to produce CO in CO₂RR.

It is feasible to modulate porous, electrode-immobilized, networks of molecular catalysts using MOF chemistry and it was proved by Hod et al.³⁴. The resulting thin film catalysts from a material with functionalized Fe-porphyrins as catalytically competent, redox-conductive linkers *via* electrophoretic deposition possessed high effective surface coverage of electrochemically addressable catalytic sites (~ 1015 sites \cdot cm⁻²) (**Figure 5 a**). The well-defined nanoscale porosity of the MOF facilitated access of the solvent, reactant, and electrolyte to the surfeit of catalytic sites and resulted in production of CO and H₂ (**Figure 5 b**). However, their CO selectivity was relatively low. Indeed, the CO production is a mature process, and many catalysts have been reported for producing CO with selectivity over 90%.

Besides Fe MOFs, the Co-based MOFs were also reported to be selective towards CO. Kornienko et al.³⁵ introduced thin-film catalysts of nano-sized Co-porphyrin MOFs $(Al_2(OH)_2TCPP-Co)$ (TCPP-H₂ = 4,4',4'',4'''-(porphyrin-5,10,15,20-tetrayl)tetrabenzoate)) as atomically defined and nanoscopic materials (**Figure 6 a**). The catalytic centers were Co(I) reduced from Co(II) which was proved *via in-situ* spectroelectrochemical measurements during the course of the reaction. The catalyst was proved efficient and selective towards CO in aqueous electrolytes. Although the selectivity towards CO production was only about 76%, the catalytic performance was stable over 7 h with a TON of 1400 per-site (**Figure 6 b**). Furthermore, the integrity of the organic units throughout the catalytic process was certified and the plate-like morphology had been maintained.

The Co-porphyrin COFs catalysts for highly efficient CO production were also reported by Lin et al.³⁶. They developed modular optimization of COFs with building units of Co-porphyrin catalysts and linking of organic structures through imine bonds. The morphologies of the activated COF samples showed aggregation of only one kind of crystallite with rectangular rod-shaped morphology (~50 nm in length). The catalytic

10.1002/chem.201803322

active center was Co and the electronic structure was influenced by the COFs environment. The catalysts exhibited high FE (90%) toward CO and turnover numbers (up to 290, 000 hour⁻¹) at pH of 7 at an overpotential of -0.55 V (**Figure 7**). Impressively, they achieved high catalytic activity that was 26-folds than that of molecular Co complex, and the catalyst was stable without degradation over 24 h. They used X-ray absorption spectroscopy to reveal the influence of the COF environment on the electronic structure of the catalytic cobalt centers and founded that the COF environment could directly modulate the electronic properties of molecular centers coupled into the extended lattice. The interaction between the metal and COF lattice could furnish a Co center with a more delocalized electronic structure, a network-solid analog to no innocent ligand behavior in molecular systems.

Some other framework materials were also reported to be able to produce CO₂ reduction products beyond CO. A Cu rubeanate MOFs (CR-MOFs) was found to have high HCOOH selectivity in aqueous condition, in fact the only CO₂ reduction product³⁷. The CR-MOFs catalyst also possessed high stability. Meanwhile, the Cu-based COFs catalysts were also fabricated to reduce CO₂ to alcohols and showed stable electrocatalytic performance³⁸.

Compared with the metal complexes, the advantages of framework materials are originated from the well-ordered pores that represent efficient gas molecular storage structures. With tunable metal centers and ligands with different sizes and functional groups, the framework catalysts can be designed for different products. Furthermore, the high stability and turnover frequency of framework catalysts are impressive, which can be attributed to the restrained metal active center and probable single-atom catalytic property. However, there are still obstacles in the development of framework catalysts for CO₂RR. Until now, the modulating of metal centers and ligands failed to generate efficient pathways for the other products beyond CO and HCOOH. The hypodynamic production of multi carbon products on framework catalysts may be a result of unfavorable adsorption of bridge-bound CO intermediate on metal-active centers of framework catalysts. The metal-active centers were found to be crucial to C-C coupling.

3. The role of organic components in HER

As an earth-abundant source, water is the most available and cheap industrial feedstock.

Its reduction product H_2 is thought as the cleanest energy and environmental protective fuel because its combustion production is only water. Up to now, the Pt group noble metals are reported as the best HER catalysts but impeded by its high cost and implicate process procedure. The numerous needs for H_2 call for economical and efficient HER catalysts. The organic molecule catalysts or organic molecule containing catalysts are thought to be an appropriate substitute for noble metal catalysts. To be consistent with the above part, the role of organic components is studied in three aspects, i.e., the conducting polymers, the metal complexes and the framework materials.

3.1 Conducting polymer

Conducting polymers such as PANI, PPy, 3,4-polyethylenedioxythiophene (PEDOT) and polythiophene (PTh) can be expected as probable HER electrocatalysts, mainly due to their good electrical and proton conductivity, high stability, low price, easy access, and ability to store charges. The conductivity of catalysts is found to be a key factor in catalytic process to ensure electron transport, but many efficient electrocatalysts for HER like MoS₂ show poor conductivity³⁹. Thus conducting polymers are considered to be promising matrix that can both stabilize the catalysts and enhance the conductivity. In addition, conducting polymers could show catalytic activities without other components.

Conducting polymers integrated with metallic catalysts are most widely used, in which polymers act as support and conductor. In a metal-polymer catalytic system, the polymer was reported to affect the catalytic performances. The PPy is widely used in catalyst modification for the high conductivity, large electrochemical surface area and good stability. Wang et al.⁴⁰ reported a PPy/MoS_x copolymer film as HER catalyst fabricated by one-step electrochemical copolymerization. In their experiment, small tafel slope of 29 mV·dec⁻¹, positive onset potential of 0 V *vs*. RHE, and high exchange-current density of 56 mA·cm⁻² were observed and the catalytic performances were comparable to commercial Pt/C catalysts. They concluded that the high activity of PPy/MoS_x was attributed to the outstanding conductivity of PPy that offered large electrochemical surface area, the good interface of PPy/MoS_x film to the substrate electrode and high S ratio that provides more active S edge sites. The absence of Py and the interaction with (NH₄)₂MoS₄ made S rich to form catalysts with high S to Mo ratios and produced more active sites. The optimal ratio of Py to (NH₄)₂MoS₄ was 250:1.

Abrantes et al.⁴¹ fabricated Ni-P (phosphorus content at about 20%) deposited PPy film. Higher catalytic surface area played an identical role again in improving electrocatalytic activity towards HER. The Ni-P loaded PPy composite was active for nitrite oxidation except HER, indicating the promising application of such composites in cathodic reactions and anodic reactions, in which polymers worked as electron transfer channel and assistant inactive substrate, respectively.

Some works studied the role of PPy from another view. HER performances of pure and PPy-coated GdNi₄Al intermetallic alloy were investigated. The PPy-coated GdNi₄Al showed smaller tafel slope and better activity than pure alloy, as PPy coatings slowed the generation and growth of oxides to maintain metallic conductivity⁴². Mo et al.⁴³ analyzed the influence of different morphologies of PPy, and the electrode modified by PPy fibrils showed higher electrolysis current density than PPy cauliflower. PPy fibrils re-doped with various metal complexes further increased current densities, PPy(Ni-EDTA) electrode exhibited the best among Fe-complex (PPy(Fe(CN)₆³⁻)), Ni-complex(PPy(Ni-EDTA)) and Cu-complex (PPy(Cu-EDTA)) as investigated.

Conducting polymers could be mixed with metallic catalysts simply or integrated at the molecular scale. In some cases, metal-dispersed polymers act as effective substitutes. Early works focused on simple mixtures of polymers and metal particles. Pandey and Lakshminarayanan⁴⁴ prepared Pd nanoparticle-dispersed PEDOT thin film on the gold substrate as HER electrocatalyst in acid medium. The size of Pd-PEDOT clusters was around 200 nm, Pd was embedded in PEDOT matrix and the amount of Pd in Pd-PEDOT film was measured to be about 15%. The low percent Pd catalyst showed improved catalytic activity than Pd disk, in which electron path provided by the PEDOT could be regarded as a major factor. On the basis of the Heyrovsky-Volmer mechanism, the HER operates according to eqn(9), in which Pd_s and H_s represent the surface states, and Pd_b and H_b represent the bulk states of Pd and hydrogen, respectively. The CV results showed two peaks while bulk Pd electrodes showed one peak, indicating that the Pd-PEDOT disk electrode gained more surface active sites for adsorption as nanoparticles.

 $Pd_sH_s + Pd_b \rightarrow Pd_s + Pd_bH_b$ (9)

Navarro-Flores et al.⁴⁵ incorporated Ni into PPy and PANI to enhance electrocatalytic

activity. PPy and PANI worked as 3D matrices to control structures of Ni catalyst layers. The 3D Ni/conducting polymer layers with 3D HER zone on glassy carbon surface showed higher HER activity than Ni electrodeposited on a 2D substrate (Figure 8), rather than electronic effect, mainly resulted from the increased active surface area of 3D composite, leading to an increase of active sites. The active area included two regions, i.e., the contacting parts between Ni and electrolyte and the embedded polymer matrix. Different deposition time and order were studied and the small amounts of Ni with the thick pre-deposited PANI layer offered better catalytic activity, while Ni/PPy with lower porosity than Ni/ PANI suffered from hydrogen accumulation at the Ni/PPy interface at high overpotentials. Makhloufi et al.^{46, 47} also synthesized modified PPy electrode by electrochemical cementation of Cu. The Cu-modified PPy acted as proton reduction electrocatalyst with enhanced performance. In another work, they coated Cu-Al sheet by immersing PPy electrode in CuSO₄ solution, and the catalyst showed better activity than bulk Cu. The works studied the influence of polymer properties and contacting modes, and got rid of noble metals. However, the role of polymers in metal electrocatalyst system is controversial, as conducting polymers are less conductive materials compared with metal, and they show poor conductivity in the potential window of HER. To investigate the problem, Aydın et al.⁴⁸ demonstrated that PANI, PPy and aniline/pyrrole copolymer (PANI-PPy) coated Pt electrodes showed more negative potential values and higher activation energies in HER than Pt blank. But the negligible gap of activation energies between Pt and polymer coated ones supported the possibility to utilize the adsorption ability of polymer on the other catalysts. Based on these studies, it is more possible that the mixtures of metal and conducting polymers may be worse than equal amounts of metal, but polymers could be regarded as effective supports to reduce the metal and reach comparable activity.

In other cases, metallic catalysts were linked to the polymer backbone and showed improved activity and stability. Yang et al.⁴⁹ coated PPy-ferrocene monosulfonate (PPy-FMS) on Pt/PVDF membrane. The PPy-containing catalytic ferrocene worked as HER catalyst in 1.0 M H₂SO₄, ferrocene was attached to PPy and exhibited stable performance, and more open structures in the PPy coatings lead to better stability. The activity of metallic catalysts and stability of PPy coatings were simultaneously realized through chemical bonds, in place of physical mixture in a number of studies. However, they still fell back on Pt/PVDF substrate. Feng et al.⁵⁰ fabricated a nanosheet structured core-shell PANI-Co(OH)₂ Ni electrodeposition on foam through and

electropolymerzation. The composite electrocatalyst possessed a large specific surface area, and the porous network accelerated the electrolyte diffusion (Figure 9 a). The Co(OH)₂ was bonded with PANI through synergistic coupling. The synergistic effects were shown by density functional theory to change the absorption energy of H atoms and accelerate the HER. It was further verified by experiments that the electron delocalization formed between the hydroxide d orbitals and the polymer π -conjugated ligand (Figure 9 b). The shifted electronic state of $Co(OH)_2$ improved the activity of catalyst in alkaline solution, which showed an onset potential of ~ 50 mV, a tafel slope of 91.6 mV·dec⁻¹, and a small overpotential of 90 mV at current density of 10 mA·cm⁻ ², and could maintain over 100, 000 s. All of the electrochemical performances of Co(OH)₂@PANI nanosheets/Ni foam were improved apparently compared with Co(OH)2 nanosheets/Ni foam, PANI/Ni foam, and Ni foam, which could be attributed to the lower H and water adsorption energies of Co(OH)₂@PANI structure. This work viewed the improvement of catalytic performance from a deeper electron orbital perspective, and the prepared HER catalyst which got rid of noble metal showed impressive performance.

Besides conducting polymers, non-conducting polymers also play important roles in electrocatalytic effects. Winther-Jensen et al.⁵¹ reported electrocatalyst composed of PEDOT (conducting polymer) and polyethylene glycol (PEG) family (non-conducting polymer) that showed higher performance than pure PEDOT, and the catalytic performance was notably improved after 24 h electro process in the 1 M H₂SO₄ electrolyte, which may be ascribed to coordination between PEG and H_3O^+ . The PEDOT was vapor-phase-polymerized in the presence of PEG to attain structural integration. In contrast, PEDOT-polymethylvinylether composite exhibited no catalytic activity, as PMVE showed poor ion-coordinating ability. Non-crystalline 3PEG5000 copolymer was adopted instead of PEG to fabricate PEDOT-PEG composites with different crystallinity. The crystallinity of composites was found to affect the watersplitting property dramatically. A more effective electrode was developed on a goldcoated porous teflon membrane with PEDOT-PEG layer (Figure 10 a), which could be stable over 80 days at the constant potential (Figure 10 b). Likewise, the new-designed electrode showed overpotential comparable to Pt (Figure 10 c) and the increasing catalytic activity after 72 h of immersion (Figure 10 d) mainly due to the enhanced diffusion of active species caused by swelling. In general, the Pt-free polymer based electrocatalysts showed impressive hydrogen evolution activity and gave a new way to

understand the role of non-conducting polymer in HER.

However, Gu et al.⁵² argued that the substrates worked as hydrogen evolution catalyst rather than PEDOT-PEG films. The vapor-phase-polymerized PEDOT-PEG films were fabricated on three different common substrates, including gold, glassy carbon and titanium. The HER overpotential decreased apparently compared to the previous work, while the potential was only close to the substrate but cannot be more positive. The results did not negate the effect of swelling to enhance proton diffusion, as surface area and ion channels increased, but indicated that diffusion assist the substrate rather than PEDOT to exhibit HER performance, so the hydrogen evolution took place on the substrate. The porosity of polymer film was possibly increased when immersed in acid, and ultimately reached saturation, hence the performance improved with time (**Figure 11**).

More studies reported that the hydrogen evolution occurred on the substrate or the interface of polymer and substrate. In 1982, Bard et al.⁵³ showed that electrochemically conducting PPy films deposited on platinum or tantalum were highly ionic conductive, which made it possible for hydrogen and oxygen evolution reaction on the substrates. Schultze et al⁵⁴. studied the proton migration and water diffusion of PANI coated on metal substrates, and demonstrated that the HER/OER took place at the interface of PANI and metals. It was further found that poly-N-methylpyrrole (PNMePy), poly-3-Methylthiophene, and poly-bithiophene on gold/palladium substrates transferred from insulator to conductor during oxidation. The intercalation of anions along with the solvent resulted in swelling of polymer films and promotion of ionic conductivity. Ouyang et al.⁵⁵ reported that the amount of counter anions doped in PNMePy was a key factor of H⁺ penetration. Maksymiuk et al.⁵⁶ verified that a polymer mixture of PNMePy and poly(4-styrenesulfonate) (PSS) covered on gold could enhance H⁺ transport and facilitate hydrogen evolution at low concentration of H⁺, while HER could be hindered by higher proton concentration. As mentioned above, the reduction of H⁺ in HER is more likely to take place on the metal substrate rather than polymer films.

Efforts have been made to improve the conductivity and stability of conducting polymers *via* the design of derivatives and new polymerization methods, because the two properties were thought as major parameters of conducting polymers.⁵⁷ it was found that the reduction of water at neutral pH was poor on the PEDOT cathode even

at an overpotential of 100 mV. In 1 M NaH₂PO₄ (pH = 4), the overpotential for measurable proton reduction was of the order of 100 mV and at 1 M H₂SO₄ (pH = 1), and the overpotential was reduced further. However, the use of PEDOT as electrocatalysts was limited because it was totally reduced at 0.9 V vs. SCE in which state the PEDOT was also almost non-conducting. The poor conductivity of common polymers in the potential window of HER has restrained the development of the field seriously. The synergetic influence of non-conducting polymers has not been investigated sufficiently. One of the most promising solutions could be the exploration of new methods to integrate the polymer and active catalysts, as most studies just stopped on dispersed catalysts in polymer supports. A lot of efforts should be made to bring the superiority of two components into full play in the future.

3.2 Metal complex

The metal complexes with tunable metallic center conditions are applicable in HER. As typical HER catalysts, Co and Ni are also adopted to make metal complexes for HER. Dong et al.⁵⁸ prepared a 2D supramolecular polymer (2DSP) single-layer sheet by Langmuir-Blodgett method (**Figure 12 a**), with a thickness of 0.7 - 0.9 nm, on the order of square millimeters in area. The free-standing 2DSP sheet showed hydrogen generation activity with the tafel slope of 80.5 mV·dec⁻¹, onset potential of 110 mV and overpotential of 333 mV at 10 mA·cm⁻² in 0.5 M H₂SO₄ (**Figure 12 b**). The structure of the 2DSP sheet contributed to electrocatalytic performance, as the large surface area and thin monolayer made more active sites exposed. The complex comprised of triphenylene-fused nickel bis(dithiolene), and a *p*-conjugated monomer named 1,2,5,6,9,10-triphenylenehexathiol (THT) was used as the key building block. The novel structure of 2DSP provided a new view to fabricate HER electrocatalysts, but the performance need to be further enhanced.

Co porphyrin is one of the most widely studied electrocatalysts for HER. Kellett et al.^{59,} ⁶⁰ designed Co porphyrin electrocatalysts for hydrogen production from water. The water-soluble porphyrins, meso-tetrakis (N,N,N-trimethylanilinium-4-yl)porphyrin chloride (CoTMAP), meso-tetrapyrid-4-ylporphyrin (CoTPyP) and mesotetrakis(Nmethylpyridinium-4-yl)porphyrin chloride (CoTMPyP), were tested at a potential of - 0.95 V vs. SCE at a Hg-pool electrode in 0.1 M trifluoroacetic acid. The complex on a glassy-carbon electrode showed electroactivity around Co(II)/Co(I) potential. Hu et al.⁶¹ reported a variety of Co-porphyrin complexes with hydrogen evolution activity. Co difluoroboryl-diglyoximate complexes [Co(dmgBF₂)₂] and [Co(dpgBF₂)₂] were active at potentials as positive at - 0.55 V and - 0.28 V vs. SCE respectively in acidifying CH₃CN. The complexes of [Co(Tim^{Ph/Me})Br₂]Br and [Co(Tim^{Ph/Me})(CH₃CN)₂](BPh₄)₃ with more positive Co(II/I) redox potentials were less active and stable for HER. Co(I) was proposed as the active species under acidic condition, which can be protonated to form Co^{III}-H hydride intermediate, and the intermediate could regenerate Co(II) and generate H₂ simultaneously.

The structures of metal complexes seem favorable to HER, as the numerous exposed active sites may lead to low overpotentials, the convenient combination of non-metallic elements may cause high activity, and the stable molecular structure may contribute to high stability. However, there are still large vacancies in further enhancing the properties. The metal complexes applied in HER show distinct trends in using Co or Ni as active center and need to be clarified by a more systematic study. The other metal complexes should be also carefully explored. In addition, most complexes are active in particular potentials, and the detailed electrochemical performances have not been revealed yet.

3.3 Framework materials

In recent years, MOFs have been exploited to be suitable electrocatalysts or their precursors for HER. The porous materials with several unique advantages like high flexibility, large specific surface area, and tunable pore channels that are expected to enhance HER activity. To integrate the advantages of MOFs and functional materials, Dai et al.⁶² anchored molybdenum polysulfide (MoS_x) on Zr-MOF (UiO-66-NH₂) by facile solvothermal method and prepared efficient HER catalysts. The MOF-based MoS_x showed an overpotential of 200 mV at 10 mA·cm⁻², a tafel slope of 59 mV dec⁻¹, an onset potential of nearly 125 mV, and maintained performance after 5000 CV sweeps. The modified activity could be ascribed to the improved electron transport, high surface area of MOFs and increased number of active sites due to the combination of MoS_x nanosheets and the MOFs. Hod et al.⁶³ used a mesoporous MOFs films, NU-1000, which was grown solvothermally on conductive glass, as scaffolds to deposit a hybrid Ni-S electrocatalyst. Compared with the MOF-free Ni-S, the hybrid materials showed a decreased kinetic overpotential by more than 200 mV at a current density of 10

Accepted Manuscript

 $mA \cdot cm^{-2}$, indicating a significantly enhanced performance for HER. The MOFs was explored as proton conductor to modify the immediate chemical environment of the sulfide-based catalyst. However, note that the MOF scaffold did not exert its cocatalytic effect although the initial aim was to boost the electroactive surface area.To overcome the low electrical conductivity of MOFs, polyoxometalate (POM) ions with redox nature are combined. Nohra et al.⁶⁴ lead up the application of MOFs as electroactive catalysts in hydrogen production. Polyoxometalate-based MOFs (POMOFs) with triangular 1,3,5-benzene tricarboxylate linkers, tetrahedral *\varepsilon*-Keggin and Zn(II) ions were synthesized by hydrothermal reaction. The reported $\varepsilon(\text{trim})_{4/3}((\text{TBA})_3[\text{PMoV}_8\text{MoVI}_4\text{O}_{36}(\text{OH})_4\text{Zn}_4][C_6\text{H}_3(\text{COO})_3]_{4/3}6\text{H}_2\text{O})$ and $[\varepsilon(\text{trim})]_{\infty}((\text{TBA})_3[\text{PMoV}_8\text{MoVI}_4\text{O}_{37}(\text{OH})_3\text{Zn}_4][C_6\text{H}_3(\text{COO})_3]8\text{H}_2\text{O})$ based POMOFs showed remarkable HER activity, with the turnover number of 120, 000 and 260 mV anodic shift. The performance of new POMOF catalysts could be attributed to the structure of the POMOFs, but not extensive porosity, and the confinement effect also made contributions. Qin et al. ⁶⁵ fabricated two polymolybdate-based MOFs (POMOFs) $([TBA]_3[\varepsilon-PMo^V_8Mo^{VI}_4O_{36}(OH)_4Zn_4][BTB]_{4/3} \cdot xGuest)$ named NENU-500 and NENU-501 ([TBA]₃[*ε*-PMo^V₈Mo^{VI}₄O₃₇(OH)₃Zn₄][BPT]) (BTB = benzene tribenzoate, TBA^+ = tetrabutylammonium ion, BPT=[1,1'-biphenyl]-3,4',5-tricarboxylate) as active electrocatalysts for HER (Figure 13). Combining the redox activity of a POM and the porous structure of a MOF, NENU-500 showed an overpotential of 237 mV at the catalytic current density of 10 mA \cdot cm⁻², an onset potential of 180 mV and a tafel slope of 96 mV·dec⁻¹ in 0.5 M H₂SO₄. In addition, both the prepared POMOFs catalysts NENU-500 and NENU-501 maintained the catalytic performance after 2000 cycles.

The MOF-derived catalysts have played an important role in the field of HER due to their unique porous structures in nature. Indeed, the calcined MOFs are recognized for high-performance catalysts like metal carbide; non-calcined MOFs suffer from poor conductivity, and they have been enhanced by combining POM ions. Although a lot of achievement has been made, there is still room to further improve the performance of MOFs.

4. The Role of organic components in OER

As a reaction involves 4 successive electron transfer steps, the OER is much more complicated than HER and some CO_2 reduction reactions. OER suffers from slow

kinetics and high overpotentials and is thus considered to be a bottleneck in the reaction efficiency. Developing wally OER catalysts becomes imperative in the production of chemical fuels from electricity. Kinds of precious metal oxides like IrO₂ and RuO₂ are so far the most efficient OER catalysts. Limitations arise from the use of precious metals involved catalysts cost, strenuous catalyst synthesis and unstable performances, and these limitations impeded their large-scale applications. Up to now, many promising organic-metal composite catalysts based on Mn, Fe, Co, Ni and Cu have been developed for water oxidation for their outstanding activity, stability and low cost. In this part, the role of organic components is also studied in three aspects, i.e., the conducting polymers, the metal complexes and the framework materials.

4.1 Conducting polymer

Low-cost efficient catalysts for the OER are crucial for the large-scale application of renewable energy technologies. As a result, the noble metal-free or even metal-free catalysts are well anticipated. Conducting polymers are promising candidates for their tunable components *via* simple processing strategy. A metal-free OER catalyst was proposed by Zhang et al.⁶⁷ by wrapping pure CNTs with electrochemically inert polymers (i.e., poly(ethylene-alt-maleic acid), poly(vinyl alcohol), poly(vinyl acetate), poly(ethylene glycol)) with polar oxygen-containing groups (i.e., -COOH, -OH, - COOCH₃, -O-) *via* non-covalent interactions. The as-fabricated catalyst showed great OER property on par with the commercial noble RuO₂ catalyst. The OER process did not destroy the CNT structure, and they retained the graphitic structure integrity. The great OER activity was attributed to a synergistic effect of intrinsic topological defects in the CNTs as the main active centers and the coated polymer layer as a co-catalyst for improved OER energetics.

Besides bulk conducting polymer catalysts, the nanomaterials are also expected for their high surface areas, rich exposed active sites and high reaction efficiencies. As reported, well-defined PPy/ionic liquid (IL) nanoparticles with diameters of 24–44 nm were fabricated by chemical oxidation polymerization for OER based on the complexation of water-soluble polymers and metal cations (**Figure 14 a**)⁶⁸. The asprepared PPy/IL catalyst with the IL containing 1-allyl-3-methylpyridinium cation and tetrachloronickelate anion complex. The catalyst possessed a tafel slope of 53 mV·dec⁻¹ and achieved a current density of 10 mA·cm⁻² at potential of 583 mV that

corresponded to an overpotential of 392 mV (Figure 14 b-e). The reported catalytic activity was at par with or even superior to the transition metal oxide based electrocatalyst in terms of onset potential for O_2 evolution as well as overpotential.

Besides the direct use of conducting polymer as catalysts, the polymer can also play a role as catalyst modifier and support. For saline water splitting, Venkatkarthick et al.⁶⁹ developed a membrane-protected anode, using anionic backbone of sulfonated polystyrene-block-(ethylene-ran-butylene)-block-polystyrene polymer (S-PSEBS) over the anode (IrO₂/Ti) (**Figure 15 a and b**). The polymer coating was uniform without cracks, and IrO₂ surface was completely covered with S-PSEBS polymer layer. It electrostatically repelled the chloride ions from the electrode surface and thereby enhanced the OER rather than the chlorine evolution. The oxygen evolution efficiency of the designed electrode was nearly 95% when the electrode was modified with a perm-selective membrane which was much better than the bare IrO₂/Ti electrode. The polymer membrane can not only protect the catalyst for longer catalytic life but also affect the catalytic selectivity, which may provide a general design strategy for better catalyst (**Figure 15 c and d**).

The polymer as catalyst support was reported to be multi-functional. The nitrogencontaining molecule, as stated before, was applied in CO₂RR and also showed versatility that was reported to affect the OER catalyst performance. An OER catalyst of PANI/MWCNT supported CoFe₂O₄ nanoparticles was synthesized by Liu et al.⁷⁰ (**Figure 16 a**). The PANI was found to provide more active sites to attach CoFe₂O₄ NPs and improved the synergistic effect between the CoFe₂O₄ and MWCNT and further promoted the electrical conductivity and stability of the catalyst. The fabricated catalyst showed high OER activities at an overpotential of 314 mV at 10 mA·cm⁻² current density. In 1 M KOH and at a scan rate of 5 mV·s⁻¹, the tafel slope was 30.69 mV·dec⁻¹. Furthermore, the catalyst showed good catalytic life for at least 40 h at 540 mV *vs*. Ag/AgCl (**Figure 16 b and c**).

Similarly, IrO₂ nanoparticles were electrodeposited into poly(pyrrole-alkylammonium) films by oxidative electro polymerization of a pyrrole-alkylammonium monomer to fabricate nanocomposite anode OER catalyst⁷¹. The electrocatalytic activity of IrO₂ nanoparticles was well maintained when incorporated in the polymer matrix and even enhanced due to the nanostructure of polymer matrix. The pyrrole metal complex was

also fabricated by Cao et al.⁷² for OER. They reported a conducting PPy coated $MnCo_2O_4$ catalyst ($MnCo_2O_4@PPy$) and revealed that the PPy provided a conductive network for fast electron transfer that can help to overcome the poor electronic conductivity of $MnCo_2O_4$. Meanwhile, the coupling between the PPy layer and $MnCo_2O_4$ promoted the transfer of electrons from PPy to $MnCo_2O_4$. The OER activity of $MnCo_2O_4@PPy$ was even comparable to that of the commercial RuO_2/C (20 wt%).

Impressively, electrochemically inert conducting polymers rich at polar oxygencontaining groups could be stable at a positive potential and showed good OER property. The incorporated noble or non-noble metal catalysts can further enhance the catalytic property and the interface of conducting polymer and metal particles played crucial roles in the performance of the composite catalysts. The metal polymer composite catalysts were reported to be comparable to classical pure noble catalysts, which provided an efficient substitute to reduce the cost in anode OER catalysts in renewable energy conversion.

4.2 Metal complex

Benefited from the multi-functional organic components, the metal complex catalysts are also applied in OER. Transition metal complexes, including mononuclear, binuclear, and multinuclear complexes of Mn, Ru, Ir, Fe and Co have been applied in OER and were reported to be able to stabilize the catalysts in the reaction processes in strong acid, neutral and alkali electrolytes.

For acid electrolyte, Rigsby et al.⁷³ simulated the Ru-based water oxidation catalysts with bispyridylpyrazolate (bpp) ligand bridged binuclear Co(III) complexes. The Co_{III}Co_{III} bridging-peroxo complexes overcame the thermodynamic instability and kinetic lability of non-bridging complexes and showed water oxidation activity in acid (pH = 2.1). Cyclic voltammograms showed the decay of reversible feature at 1.22 V with a new feature at 0.17 V, indicating the presence of Co(tpy)₂^{2/3+}. Bozoglian et al.⁷⁴ demonstrated the electrochemical activity for OER of Ru-Hbpp (in,in-{[Ru(II)(trpy)(H₂O)]₂(µ-bpp)}³⁺ (trpy is 2,2':6',2''-terpyridine, bpp is bis(2-pyridyl)-3,5-pyrazolate)) catalyst. Five different oxidation states were observed with the help of electrochemical analyses and UV-vis spectroscopy. The structure and electronic properties of catalyst helped oxygen atoms be properly oriented to form O-O bonds.

In a neutral condition, Han et. al.⁷⁵ fabricated a water-soluble Ni meso-tetrakis (4-N-methylpyridyl) porphyrin complex that can electrocatalyze water oxidation to O₂ in neutral aqueous solution (pH = 7.0) with the onset potential of ~ 1.0 V *vs*. NHE. They proved the fabricated Ni porphyrin catalyst was a real molecular electrocatalyst with Ni(IV) species produced in the electro process for water oxidation with a TOF of 0.67 s⁻¹ at 20 °C. Meanwhile, a macrocyclic Ni (II) complex homogeneous catalyst was also reported to be robust by Zhang et al.⁷⁶. The water oxidation in neutral aqueous solutions using the oxidatively robust 2,7-[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine ligand (BPMAN) based dinuclear Cu(II) complex was carried out by Su et al.⁷⁷ with the structure shown in **Figure 17**. Their calculations suggested that the O-O bond formation took place by a cooperative interaction between two Cu^{III} centers rather than by a nucleophilic attack of water on the high-oxidation-state Cu^{IV}=O moiety.

Series works reported metal complexes for alkali water oxidation. Shoshanna⁷⁸ and colleagues developed an efficient, inexpensive and robust homogeneous Cu-bipyridine-hydroxo complex electrocatalyst. At solutions at pH values of 11.8 - 13.3, the overpotential of the catalyst was 750 mV with a turnover frequency of 100 s⁻¹ and the catalyst resting state was the simple monomeric (bpy)Cu(OH)₂ complex. Meanwhile, Zhang et al.⁶⁶ also synthesized Cu complex for alkali water oxidation with polypeptide ligand that assembled into triglycylglycine macrocyclic ligand (TGG⁴⁻) complex of Cu(II), i.e., [(TGG⁴⁻)Cu^{II-}OH₂]²⁻. Although their overpotential was ~ 520 mV in 0.25 M phosphate buffer (pH = 11), the catalyst exhibited high stability and activity toward water oxidation with a high turnover frequency of 33 s⁻¹. It was revealed that the initial oxidation to Cu(III) was followed by further oxidation to a formal Cu(IV) with formation of a peroxide intermediate, which underwent further oxidation to release oxygen and close the catalytic cycle.

Similar to Cu(IV) species considered as the active centers of OER, the high-valencestate metals are thought to be essential in water oxidation reactions. Wasylenko et al.^{79, 80} reported a series of Co(II) complexes exhibiting water oxidation activity. Under alkaline conditions, $[Co(Py5)(OH_2)](CIO_4)_2$ (Py5 = 2,6-(bis(bis-2pyridyl)methoxymethane)pyridine) could be stabilized to the $[Co^{III}-OH]^{2+}$ state after proton-coupled electron-transfer (PCET), and Co(III) was further oxidized to Co(IV), which finally catalyzed the oxidation of water. The complex showed an overpotential of 500 mV at pH 9.2. The $[Co^{II}(pz_4depy)(OH_2)]^{2+}$ (pz_4depy = 2,6-bis(1,1-di(1*H*- pyrazol-1-yl)ethyl)pyridine) showed similar structure and property to the $[Co(Py5)(OH_2)](ClO_4)_2$. To study the PCET procedure of two complexes, the interconversion of $[Co^{III}-OH]^{2+}$ and $[Co^{II}-OH_2]^{2+}$ can occur in PCET. Wang et al.⁸¹ also reported Ni-based alkali water oxidation catalyst and they demonstrated a complex of Ni and glycine as an efficient water oxidation catalyst with a modest overpotential of 475 mV. It was stable for prolonged periods of at least 10 h, and can achieve an activity of 4 mA·cm⁻² at pH 11 solution with a FE of $60 \pm 5\%$. The catalytic species was reported to be heterogeneous Ni-hydroxide formed by electrochemical oxidation. This Ni species could achieve a current density of 4 mA·cm⁻² and persisted for at least 10 h.

The active sites with high valence states are imperative in OER. Generally, most metal ions used in OER could not be stable under both strong acidic and alkaline conditions. The organic ligands make it feasible to fabricate OER catalysts with high valence state metals that are applicable in aqueous solutions with different acid-base properties. The acid-base resistance properties of metal complex catalysts make it possible to meet the needs of the various conditions of renewable energy conversion reactions as anode reaction catalysts. However, although many non-noble metal complexes are applicable in OER, their catalytic performances still need to be improved.

4.3 Framework materials

Framework materials such as MOFs and COFs are attractive as OER and the other catalysts for their highly ordered structures, large porosities and diversified pore surfaces. The great OER property of MOFs was reported to be comparable to Pt/C catalysts. Sohrabi et al.⁸² reported a composite from CoP-based MOF and MWCNTs. Ultrastable Zr₆ clusters and tetrakis (4-carboxyphenyl) porphyrin Co(II) were used to produce porous coordination networks with 3D nanochannels. They expressed that their composite exhibited better OER and ORR performances than the commercial Pt/C catalyst. The stability of the catalyst was investigated, and the results indicated that the structure of the catalyst remained faultless during the electrochemical reaction. The Coporphyrin COFs on MWCNTs ((CoP)n-MWCNTs) for water oxidation were reported by Jia et al.⁸³. A catalytic current density of 1.0 mA·cm⁻² was achieved with an overpotential of 290 mV in alkaline media. The π - π stacking interaction might drive the formation of the thin layer of Co-porphyrin COFs around the MWCNTs.

Besides the great catalytic activity, the MOFs were also reported to be durable. Lu et al.⁸⁴ prepared a Co MOFs i.e., $[Co_2(\mu-Cl)_2(bbta)]$ (MAF-X27-Cl in the guest-free form with H₂bbta = 1*H*,5*H*-benzo-(1,2-d:4,5-d')bistriazole) as OER catalyst (**Figure 18 a**). The catalyst possessed ultrastability that could retain its crystallinity in both s0.001 M HCl and 1.0 M KOH aqueous solution for at least 1 week. The OER performance increased gradually from 508 to 387 mV at 10 mA·cm⁻². During OER process, $[Co_2(\mu-OH)_2(bbta)]$ (MAF-X27-OH in the guest-free form) was resulted from the replacement of Cl⁻ by OH⁻. They confirmed that the surface hydroxide ligand can accelerate the OER process. However, it was not possible for inorganic metal and metal oxide/hydroxides catalysts for their oxidized metal surfaces under OER environments (**Figure 18 b**).

Apart from the single metal MOFs, multi-metal MOFs are also admired. A series of Fe/Ni MOFs including Fe-BTC, Ni-BTC and Fe/Ni-BTC (BTC = 1,3,5benzenetricarboxylic acid) were synthesized and explored for OER by Wang et al.⁸⁵ (Figure 19). The catalysts showed a low onset overpotential at 170 mV for synergy effect of heterogeneity and porosity of the system. The MOFs were electrochemically deposited into a Ni foam to form thin films inside, and the prepared electrode showed high electrocatalytic activity with a low overpotential of 270 mV at 10 mA·cm⁻², small tafel slope of 47 mV \cdot dec⁻¹, high efficiency and great stability for more than 15 h (Figure 19 b and c). Besides, the synergistic effect between Ni and Fe was also been applied to prepare 2D MOFs nanosheet-based hybrids⁸⁶. Inert Fe-MOF nanoparticles were deposited onto the 2D MOFs nanosheets, and the obtained Ni-MOF@Fe-MOF catalyst can reach the optimal overpotential of 265 mV at 10 mA \cdot cm⁻², while the overpotential of Ni-MOF was merely 370 mV. Notably, demonstrated by TEM and Raman results, the active species of the catalyst should be interconnected with abundant NiO nanograins (about 5 nm) formed during OER process, and homogeneous mesopores promoted mass transport.

Recently, based on Fe/Ni dual-MOFs, Li et al.⁸⁷ prepared rod-like trimetallic MOFs (Fe/Ni/Co(Mn)) by solvothermal methods with tuned molar ratios of metallic elements. The optimal sample (i.e., Fe/Ni_{2.4}/Co_{0.4}- Material of Institute Lavoisier -53) exhibited enhanced OER activity, which can reach the overpotential of 219 mV at 10 mA·cm⁻² and 236 mV at 20 mA·cm⁻² with tafel slope of 52.2 mV·dec⁻¹. Fe-MIL-53 or Fe/Mn(Co)-MOFs without Ni showed lower performances, indicating that Ni served as active sites, and Fe and Co promoted the OER activity by the synergy effect.

The multifunction MOFs catalysts were also reported by Jahan et al.⁸⁸. They reported a tri-functional catalyst for HER, OER, and ORR based on assembled graphene oxide (GO) and Cu-MOFs. GO was able to improve the electrical conductivity of MOF hybrid, which contributed to rapid charge transfer. Compared with the physical mixture of the Cu-MOF and GO, the composite of GO-incorporated Cu-MOFs showed much better electrochemical performances. They concluded that the high catalytic activities of the composites were attributed to the synergistic effects of framework porosity, larger bond polarity and catalytically active copper in the MOF hybrid.

Two-dimensional MOFs attract increasing attentions for OER recently, and several studies reported high performances through different methods. Huang et al.⁸⁹ synthesized 3D pillared-layer MOF as OER catalyst, during continuous scans in KOH electrolyte, the pillar ligands were selectively removed to form 2D nanosheets of MOFs, which showed the overpotential of 211 mV at 10 mA·cm⁻². The wrinkled 2D structure with high performance can also be transformed from 3D structure in the electrolyte saturated with O₂, but much slower. Jia et al.⁹⁰ designed and fabricated a nickel phthalocyanine-based 2D MOF (NiPc-MOF) with four-fold symmetry, which can grow on several supports to form a thin film and reach the overpotential of 250 mV. Besides, Hai et al.⁹¹ prepared NiFe-bimetal 2D MOFs nanosheets through a simple ultrasonic oscillation method, and the NiFe MOFs showed the overpotential of 260 mV at 10 mA·cm⁻². Similarly, the 2D MOFs were ultrathin so that mass transport can be easier and electron can transfer fast, and the high specific surface area also contributed a lot to the high performances above.

Benefited from the unique structure, noble metal-free and transition metal-containing framework catalysts have been reported to possess high efficiency and durability. However, the reported catalysts still cannot substitute the classical noble metal catalysts due to the relatively complicate synthesis and process.

5. Summary and outlook

Electrochemistry presents an attractive and viable strategy for renewable energy storage. The electrocatalysts play vital roles in the process of CO_2RR , HER and OER. In addition, the organic molecules are indispensable due to their unique catalytic properties and high capability of modulating catalysts.

When introduced into a catalytic system, the organic molecules can efficiently catalyze the reactions themselves and also modulate the active sites towards high selectivity and efficiency. As for the modulation of active sites, organic components influence the electronic structures, help to expose more sites, protect the metal species or act as intermediate. The conducting polymers like PANI and PPy are usually used as the electrode, and they can serve as both active sites and electronic transmission channels. Besides bulk polymer electrode, the organic molecules are also commonly used to modulate the active sites especially in the metal complexes and framework materials. The property of the ligand molecules that are electro-providing or electron-withdrawing can influence electron structures of the metal catalytic centers and further influence the electron concentration, bond length, lattice parameter and other features that are crucial to the electrocatalytic property. As a result, the activity, selectivity and durability can be modulated.

Conducting polymers are applicable for catalysts directly or catalyst supports, and they can provide both efficient electron transport channels and reduction active sites. Among them, nitrogen-rich polymers like PPy and PANI are used as metal-free CO₂RR catalysts. However, they suffer from low selectivity, low efficiency and strict electrolyte. When a metal-active center is introduced, the reduction active sites shift from organic to metallic parts typically with higher reduction efficiencies. The reduction of CO₂ on polymer catalysts or polymer-supported catalysts needs to be enhanced in product species, selectivity and efficiency. Conducting polymers serve as effective supports for the HER in most time, and PPy has been mostly explored. Currently, the electrical conductivity is still the main limitation for the performance of the composite based on the typical mixture of polymer and active metal catalyst. The future efforts should be focused on the molecular interaction between conducting polymer and metal to improve the performance remarkably. In the case of the OER, electrochemically inert conducting polymers rich in polar oxygen-containing groups are applicable in OER as catalysts or supports. Non-noble metal polymer catalysts may represent a mainstream direction for high efficiencies and low costs.

Metal complexes show high reduction efficiencies in CO₂RR due to good distributions of metal-active centers. However, although the catalyst states are programmable ideally, and the metal complex can potentially be used to produce a variety of reduction products, it remains unavailable yet. Currently, only the CO production efficiencies are comparable to metal catalysts, and the efficiencies for the other products are still too low. The further efforts should be made on the development of multi-electron reduction products for high industrial value. The structures and compositions of metal complexes are critical for the HER activity, and it is necessary to reveal the underlying rules and design new active complexes. The active sites with high valence states are imperative in the OER. Generally, most metal ions used in the OER could not be stable in strong acidic, neutral and alkaline aqueous solutions. Fortunately, the organic ligands make it feasible to fabricate non-noble metal OER catalysts with high valence states. However, the catalytic performances of most metal complexes still cannot satisfy the industrial application.

Framework materials like MOFs and COFs are efficient catalysts as they possess various active centers, tunable pore sizes and ligand functions, and admirable catalytic durability. For the CO₂RR, the high stability and turnover frequency of framework catalysts are impressive, but they failed to generate efficient pathways to make products beyond CO and HCOOH. The unfavorable formation of multi-carbon products may be ascribed to the weak C-C coupling on the single metal atom center, which needs a systematic study in the following work. The porous structure can help to enhance the HER activity and durability because of the improved electron transport, large surface area, high active site number and modified chemical environment. The MOF hybrid materials do show higher performances compared with the MOF-free counterparts. However, the further improvement for the MOF hybrid catalyst is limited by poor conductivity, which can be one of the promising directions. The framework materials are also efficient OER catalysts with comparable properties with noble metal catalysts. The stabilities of organic bone structures are the key for the stable catalytic performance. More interests will be attracted to further enhance the catalytic properties aiming at real applications with low costs in synthesis and processing.

Our mapping of the roles of organic moieties in CO_2RR , HER and OER suggests that the organic molecules contributed to many effective catalysts. Considering their intrinsic advantages, the organic molecules can and will play more important roles at economic and effective synthesis of the catalysts and renewable energy storage.

Acknowledgement

This work was supported by the Ministry of Science and Technology of China (2016YFA0203302), National Natural Science Foundation of China (21634003, 21503079, 51573027, 51403038, 51673043, and 21604012) and the Science and Technology Commission of Shanghai Municipality (16JC1400702, 15XD1500400, and 15JC1490200).

Conflict of interest:

The authors declare no conflict of interest.

Keywords: renewable energy, organic, electrocatalyst

References

- X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang and H. Wang, *Nat. Commun.*, 2017, 8, 14675.
- 2. H. Bai, Y. Zheng and R. Yang, *Mater. Design*, 2016, **99**, 145-154.
- 3. K. Malik, S. Singh, S. Basu and A. Verma, *Wires. Energy Environ.*, 2017, **6**, e244.
- Y. Yang, S. Ajmal, X. Zheng and L. Zhang, *Sustainable Energy Fuels*, 2018, 2, 510-537.
- 5. A. R. Parent and K. Sakai, *ChemSusChem*, 2014, 7, 2070-2080.
- 6. Q. Yang, Q. Xu and H. L. Jiang, *Chem. Soc. Rev*, 2017, **46**, 4774-4808.
- 7. J. Qiao, Y. Liu, F. Hong and J. Zhang, Chem. Soc. Rev., 2014, 43, 631-675.
- 8. Y. Oh and X. Hu, Chem. Soc. Rev., 2013, 42, 2253-2261.
- N. Elgrishi, M. B. Chambers, X. Wang and M. Fontecave, *Chem. Soc. Rev.*, 2017, 46, 761-796.
- 10. Y. H. Qian, I. A. Khan and D. Zhao, *Small*, 2017, 13.
- S. Gao, Z. Sun, W. Liu, X. Jiao, X. Zu, Q. Hu, Y. Sun, T. Yao, W. Zhang, S. Wei and Y. Xie, *Nat. Commun.*, 2017, 8, 14503.
- 12. S. Gao, Y. Lin, X. Jiao, Y. Sun, Q. Luo, W. Zhang, D. Li, J. Yang and Y. Xie, *Nature*, 2016, **529**, 68-71.
- 13. S. Ponnurangam, I. V. Chernyshova and P. Somasundaran, *Adv. Colloid. Interface Sci.*, 2017, **244**, 184-198.
- 14. S. Sinha, E. K. Berdichevsky and J. J. Warren, Inorg. Chim. Acta, 2017, 460,

63-68.

- 15. R. D. L. Smith and P. G. Pickup, *Electrochem. Commun.*, 2010, **12**, 1749-1751.
- 16. R. Aydin and F. Köleli, Synth. Met., 2004, 144, 75-80.
- 17. F. Köleli, T. Röpke and C. H. Hamann, Synth. Met., 2004, 140, 65-68.
- 18. R. Aydin and F. Köleli, J. Electro. Chem., 2002, 535, 107-112.
- 19. K. Ogura, J. Electrochem. Soc., 1998, 145, 3801-3809.
- 20. B. I. Podlovchenko and V. N. Andreev, Russ. Chem. Rev., 2002, 71, 837-851.
- 21. P. Santhosh, A. Gopalan and K. Lee, J. Catal., 2006, 238, 177-185.
- 22. J. M. Kinyanjui, J. Hanks, D. W. Hatchett, A. Smith and M. Josowicz, J. *Electrochem. Soc.*, 2004, **151**, D113.
- A. N. Grace, S. Y. Choi, M. Vinoba, M. Bhagiyalakshmi, D. H. Chu, Y. Yoon,
 S. C. Nam and S. K. Jeong, *Appl. Energy*, 2014, **120**, 85-94.
- 24. R. Aydın, H. Ö. Doğan and F. Köleli, *Appl. Catal. B: Environ.*, 2013, **140-141**, 478-482.
- K. Ogura, N. Endo and M. Nakayama, J. Electrochem. Soc., 1998, 145, 3801-3809.
- M. Wang, T. Weyhermuller, E. Bill, S. Ye and K. Wieghardt, *Inorg. Chem.*, 2016, 55, 5019-5036.
- M. Wang, J. England, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2014, 53, 2276-2287.
- C. Costentin, S. Drouet, M. Robert and J. M. Savéant, *Science*, 2012, **338**, 90-94.
- Z. Weng, J. Jiang, Y. Wu, Z. Wu, X. Guo, K. L. Materna, W. Liu, V. S. Batista,
 G. W. Brudvig and H. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 8076-8079.
- G. RamÍRez, M. Lucero, A. Riquelme, M. Villagrán, J. Costamagna, E. Trollund and M. J. Aguirre, J. Coord. Chem., 2006, 57, 249-255.
- 31. X. M. Hu, M. H. Ronne, S. U. Pedersen, T. Skrydstrup and K. Daasbjerg, *Angew. Chem. Int. Ed Engl.*, 2017, **56**, 6468-6472.
- K.-C. Cheung, P. Guo, M.-H. So, L. Y. S. Lee, K.-P. Ho, W.-L. Wong, K.-H. Lee,
 W.-T. Wong, Z.-Y. Zhou and K.-Y. Wong, *J. Organomet. Chem.*, 2009, 694, 2842-2845.
- D. N. Bunck and W. R. Dichtel, Angew. Chem. Int. Ed Engl., 2012, 51, 1885-1889.
- I. Hod, M. D. Sampson, P. Deria, C. P. Kubiak, O. K. Farha and J. T. Hupp, ACS Catal., 2015, 5, 6302-6309.

- N. Kornienko, Y. Zhao, C. S. Kley, C. Zhu, D. Kim, S. Lin, C. J. Chang, O. M. Yaghi and P. Yang, *J. Am. Chem. Soc.*, 2015, **137**, 14129-14135.
- S. Lin, C. S. Diercks, Y. B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R.
 Paris, D. Kim, P. Yang and O. M. Yaghi, *Science*, 2015, 349, 1208-1213.
- 37. R. Hinogami, S. Yotsuhashi, M. Deguchi, Y. Zenitani, H. Hashiba and Y. Yamada, *ECS Electrochem. Lett.*, 2012, **1**, H17-H19.
- 38. J. Albo, D. Vallejo, G. Beobide, O. Castillo, P. Castaño and A. Irabien, *Chemsuschem*, 2016, **10**.
- Y. Jiang, X. Li, S. Yu, L. Jia, X. Zhao and C. Wang, *Adv. Funct. Mater.*, 2015, 25, 2693-2700.
- T. Wang, J. Zhuo, K. Du, B. Chen, Z. Zhu, Y. Shao and M. Li, *Adv. Mater.*, 2014, 26, 3761-3766.
- 41. L. Abrantes and J. Correia, *Electrochim. acta*, 2000, **45**, 4179-4185.
- 42. A. Jukic and M. Metikoš-Hukovic, *Electrochim. Acta*, 2003, **48**, 3929-3937.
- 43. X. Mo, J. Wang, Z. Wang and S. Wang, Synth. Met., 2004, 142, 217-221.
- 44. R. K. Pandey and V. Lakshminarayanan, J. Phys. Chem. C, 2010, 114, 8507-8514.
- 45. E. Navarro-Flores and S. Omanovic, *J. Mol. Catal. A: Chem.*, 2005, **242**, 182-194.
- 46. L. Makhloufi, H. Hammache, B. Saidani, N. Akilal and Y. Maloum, *J. Appl. Electrochem.*, 2000, **30**, 1143-1150.
- 47. L. Makhloufi, H. Hammache and B. Saidani, *Electrochem. Commun.*, 2000, **2**, 552-556.
- 48. R. Aydın and F. Köleli, *Progress in Organic Coatings*, 2006, 56, 76-80.
- 49. C. Yang, J. Chen, G. F. Swiegers, C. O. Too and G. G. Wallace, *Synth. Met.*, 2005, **154**, 69-72.
- J. X. Feng, L. X. Ding, S. H. Ye, X. J. He, H. Xu, Y. X. Tong and G. R. Li, *Adv. Mater.*, 2015, 27, 7051-7057.
- 51. B. Winther-Jensen, K. Fraser, C. Ong, M. Forsyth and D. R. MacFarlane, *Adv. Mater.*, 2010, **22**, 1727-1730.
- 52. C. Gu, B. C. Norris, F.-R. F. Fan, C. W. Bielawski and A. J. Bard, *ACS Catal.*, 2012, **2**, 746-750.
- 53. R. A. Bull, F. R. F. Fan and A. J. Bard, *J. Electrochem. Soc.*, 1982, **129**, 1009-1015.
- 54. B. Pfeiffer, A. Thyssen and J. W. Schultze, J. Electroanal. Chem. Interfacial

Electrochem., 1989, 260, 393-403.

- 55. J. Ouyang and Y. Li, J. Appl. Poly. Sci., 1996, **59**, 1827-1832.
- 56. K. Maksymiuk and K. Doblhofer, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 745-750.
- 57. B. Winther-Jensen and D. R. MacFarlane, *Energy Environ. Sci.*, 2011, 4, 2790.
- R. Dong, M. Pfeffermann, H. Liang, Z. Zheng, X. Zhu, J. Zhang and X. Feng, Angew Chem. Int. Ed. Engl., 2015, 54, 12058-12063.
- 59. R. M. Kellett and T. G. Spiro, *Inorg. Chem.*, 1985, 24, 2373-2377.
- 60. R. M. Kellett and T. G. Spiro, *Inorg. Chem.*, 1985, 24, 2378-2382.
- 61. X. Hu, B. M. Cossairt, B. S. Brunschwig, N. S. Lewis and J. C. Peters, *Chem. Commun.*, 2005, 4723-4725.
- X. Dai, M. Liu, Z. Li, A. Jin, Y. Ma, X. Huang, H. Sun, H. Wang and X. Zhang, J. Phys. Chem. C, 2016, 120, 12539-12548.
- I. Hod, P. Deria, W. Bury, J. E. Mondloch, C. W. Kung, M. So, M. D. Sampson,
 A. W. Peters, C. P. Kubiak, O. K. Farha and J. T. Hupp, *Nat. Commun.*, 2015, 6, 8304.
- B. Nohra, H. El Moll, L. M. Rodriguez Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. Ngo Biboum, J. Lemaire, B. Keita, L. Nadjo and A. Dolbecq, J. Am. Chem. Soc., 2011, 133, 13363-13374.
- J. S. Qin, D. Y. Du, W. Guan, X. J. Bo, Y. F. Li, L. P. Guo, Z. M. Su, Y. Y. Wang,
 Y. Q. Lan and H. C. Zhou, *J. Am. Chem. Soc.*, 2015, 137, 7169-7177.
- M. T. Zhang, Z. Chen, P. Kang and T. J. Meyer, J. Am. Chem. Soc., 2013, 135, 2048-2051.
- Y. Zhang, X. Fan, J. Jian, D. Yu, Z. Zhang and L. Dai, *Energy Environ. Sci.*, 2017, 10, 2312-2317.
- A. Chinnappan, H. Bandal, S. Ramakrishna and H. Kim, *Chem. Eng. J.*, 2018, 335, 215-220.
- R. Venkatkarthick, S. Elamathi, D. Sangeetha, R. Balaji, B. Suresh Kannan, S. Vasudevan, D. Jonas Davidson, G. Sozhan and S. Ravichandran, *J. Electroanal. Chem.*, 2013, 697, 1-4.
- 70. Y. Liu, J. Li, F. Li, W. Li, H. Yang, X. Zhang, Y. Liu and J. Ma, *J. Mater. Chem. A*, 2016, **4**, 4472-4478.
- 71. Y. Lattach, J. F. Rivera, T. Bamine, A. Deronzier and J. C. Moutet, *ACS Appl Mater Interfaces*, 2014, **6**, 12852-12859.
- 72. X. Cao, W. Yan, C. Jin, J. Tian, K. Ke and R. Yang, *Electrochim Acta*, 2015, 180,

788-794.

- 73. M. L. Rigsby, S. Mandal, W. Nam, L. C. Spencer, A. Llobet and S. S. Stahl, *Chem. Sci.*, 2012, **3**, 3058.
- F. Bozoglian, S. Romain, M. Z. Ertem, T. K. Todorova, C. Sens, J. Mola, M. Rodriguez, I. Romero, J. Benet-Buchholz and X. Fontrodona, *J. Am. Chem. Soc.*, 2009, 131, 15176-15187.
- 75. Y. Han, Y. Wu, W. Lai and R. Cao, *Inorg Chem*, 2015, 54, 5604-5613.
- M. Zhang, M. T. Zhang, C. Hou, Z. F. Ke and T. B. Lu, *Angew Chem. Int. Ed. Engl.*, 2014, 53, 13042-13048.
- X.-J. Su, M. Gao, L. Jiao, R.-Z. Liao, P. E. M. Siegbahn, J.-P. Cheng and M.-T. Zhang, *Angew Chem. Int. Ed. Engl.*, 2015, 54, 4909-4914.
- 78. S. M. Barnett, K. I. Goldberg and J. M. Mayer, *Nat. Chem.*, 2012, 4, 498-502.
- 79. D. J. Wasylenko, H. M. Tatlock, L. S. Bhandari, J. R. Gardinier and C. P. Berlinguette, *Chem. Sci.*, 2013, 4, 734-738.
- 80. D. J. Wasylenko, C. Ganesamoorthy, J. Borau-Garcia and C. P. Berlinguette, *Chem. Commun.*, 2011, **47**, 4249-4251.
- D. Wang, G. Ghirlanda and J. P. Allen, J. Am. Chem. Soc., 2014, 136, 10198-10201.
- S. Sohrabi, S. Dehghanpour and M. Ghalkhani, J. Mater. Sci., 2018, 53, 3624-3639.
- 83. H. Jia, Z. Sun, D. Jiang and P. Du, *Chem. Mater.*, 2015, 27, 4586-4593.
- X.-F. Lu, P.-Q. Liao, J.-W. Wang, J.-X. Wu, X.-W. Chen, C.-T. He, J.-P. Zhang,
 G.-R. Li and X.-M. Chen, J. Am. Chem. Soc., 2016, 138, 8336-8339.
- L. Wang, Y. Wu, R. Cao, L. Ren, M. Chen, X. Feng, J. Zhou and B. Wang, ACS Appl. Mater. Interfaces, 2016, 8, 16736-16743.
- K. Rui, G. Zhao, Y. Chen, Y. Lin, Q. Zhou, J. Chen, J. Zhu, W. Sun, W. Huang and S. X. Dou, *Adv. Funct. Mater.*, 2018, 28, 1801554.
- F. Li, Q. Shao, X. Huang, and J. Pamg, *Angew Chem. Int. Ed. Engl.*, 2018, 130: 1906-1910.
- 88. M. Jahan, Z. Liu and K. P. Loh, *Adv. Funct. Mater.*, 2013, 23, 5363-5372.
- J. Huang, Y. Li, R. K. Huang, C. T. He, L. Gong, Q. Hu, L. Wang, Y. T. Xu, X.
 Y. Tian, S. Y. Liu, Z. M. Ye, F. Wang, D. D. Zhou, W. X. Zhang and J. P. Zhang, *Angew Chem. Int. Ed. Engl.*, 2018, **57**, 4632-4636.
- 90. H. Jia, Y. Yao, J. Zhao, Y. Gao, Z. Luo and P. Du, *J. Mater. Chem. A*, 2018, **6**, 1188-1195.

91. G. Hai, X. Jia, K. Zhang, X. Liu, Z. Wu and G. Wang, *Nano Energy*, 2018, 44, 345-352.



Figure 1. (a-d) FE-SEM images of PANI/Cu₂O films at different magnifications showing the homogeneous Cu₂O particles in PANI matrix and (e) FE of HCOOH and CH₃COOH *vs.* applied potential. The applied time was 30 min for each experiment. Reprinted with permission from ref. 23. Copyright 2014, Elsevier.



Figure 2. Synthetic routes and structures for Cu-porphyrin molecular catalysts. Reprinted with permission from ref. 29. Copyright 2016, American Chemical Society.



Figure 3. (a) The structure of CoTPP and the production process of synthesizing MTPP-CNT catalyst, (b) SEM image of CoTPP-CNT composite and (c) the selectivity towards CO and H_2 of CoTPP-CNT. Reprinted with permission from ref. 31. Copyright 2017, Willy.



Figure 4. (a) TEM image of Co-phthalocyanine catalyst, (b) element distribution of C, N and Co, (c) product distribution of Co-phthalocyanine *versus* application potential and (d) the long-term catalytic performance of Co-phthalocyanine. Reprinted with permission from ref. 1. Copyright 2017, Nature Publishing Group.



Figure 5. (a) The structure of Fe-porphyrins MOFs and (b) its production selectivity towards CO and H₂. Reprinted with permission from ref. 34. Copyright 2015, American Chemical Society.



Figure 6. (a) The structure of Co-porphyrin MOFs and (b) its selectivity towards CO and H₂. Reprinted with permission from ref. 35. Copyright 2015, American Chemical Society.



Figure 7. (a) The structure of Co-porphyrin COFs catalysts and (b) the turnover numbers of COFs *vs.* time. Reprinted with permission from ref. 36. Copyright 2015, American Association for the Advancement of Science.

Accepted Manuscrii



Figure 8. (a) Deposition of Ni on a pre-deposited PPy layer and (b) co-deposition of Ni and PPy. Reprinted with permission from ref. 45. Copyright 2005, Elsevier.



Figure 9. (a) HRTEM image of Co(OH)₂@PANI nanosheets/Ni foam (inset: SAED pattern of the PANI layer), (b) and (c) XPS spectra of Co in Co(OH)₂@PANI nanosheets/Ni foam and Co(OH)₂ nanosheets/Ni foam, respectively. Reprinted with permission from ref. 50. Copyright 2015, Willy.



Figure 10. (a) Schematic of PEDOT-based air electrode, (b) LSV of PEDOT-PEG after 0, 2, 4, 6, 9, 12, 24, 48, and 72 h, (c) Pseudo-steady-state measurement of proton reduction on PEDOT-PEG (blue curve) compared to Pt-coated (grey curve) and (d) long-term performance of PEDOT-PEG. Reprinted with permission from ref. 51. Copyright 2010, Willy.



Figure 11. Long-term HER performance of PEDOT-PEG film on gold, titanium, and glassy carbon (GC). The solid lines represent HER performance on bare substrates. Reprinted with permission from ref. 52. Copyright 2012, American Chemical Society.



Figure 12. (a) Synthesis of a 2DSP single-layer sheet at an air/water interface and (b) polarization plots of the 2DSP sheet and blank electrode. The inset shows the tafel plot. Reprinted with permission from ref. 58. Copyright 2015, Willy.



Figure 13. (a) The schematic of HER catalyzed by POMOFs, (b) comparison of $\varepsilon(\text{trim})_{4/3}$, $\varepsilon_2(\text{trim})_2$, and $[\varepsilon(\text{trim})]_{\infty}$ at a scan rate of 2 mV/s and (c) crystal structures of the three $\varepsilon(\text{trim})_{4/3}$ POMOFs. Reprinted with permission from ref. 65. Copyright 2015, American Chemical Society.



Figure 14. (a) The synthesizing diagram of PPy/IL catalyst, (b) the polarization curve obtained in 1 M KOH, (c) tafel plot, (d) potentiostatic analysis performed at a constant potential of 590 mV and (e) cyclic voltammetry performed at scan rate of 20 mV \cdot s⁻¹. Reprinted with permission from ref. 68. Copyright 2018, Elsevier.



Figure 15. (a) The structure of S-PSEBS, (b) SEM image of S-PSEBS coated IrO₂/Ti electrode, (c) oxygen and chlorine evolution current efficiency of IrO₂/Ti electrode as a function of current density in 0.5 M NaCl and pH 8.3 at 30 °C, and (d) oxygen and chlorine evolution current efficiency of S-PSEBS coated IrO₂/Ti electrode as a function of current density in 0.5 M NaCl and pH 8.3 at 30 °C. Reprinted with permission from ref. 69. Copyright 2013, Elsevier.



Figure 16. (a) The process for the preparation of the $CoFe_2O_4/PANI-MWCNTs$ and application in OER, (b) Nyquist plots of the $CoFe_2O_4/PANI-MWCNTs_{1:20}$ (40 wt%), $CoFe_2O_4/MWCNTs$ (40 wt%) and $CoFe_2O_4$ being recorded at the overpotential of 0.50 V *vs*. Ag/AgCl, and (c) chronoamperometric measurement in N₂-saturated 0.1 M KOH at 540 mV *vs*. Ag/AgCl (inset, polarization curves of $CoFe_2O_4/PANI-MWNTs_{1:20}$ (40 wt%) before and after 1000 cycles). Reprinted with permission from ref. 70. Copyright 2016, Royal Society of Chemistry.



Figure 17. (a) The structure of the dicopper (II) catalysts, and (b) ORTEP view (thermal ellipsoids set at 50 % probability) of the cation of copper complex catalyst. The counter anions and hydrogen atoms are omitted for clarity. Reprinted with permission from ref. 77. Copyright 2014, Willy.



Figure 18. (a) Three-dimensional coordination network and pore surface structures of Co COFs and (b) LSV curves of MAF-X27-OH and MAF-X27-Cl at pH of 7. Reprinted with permission from ref. 84. Copyright 2016, American Chemical Society.



Figure 19. (a) Design and synthesis of Fe/Ni-BTC MOFs and thin films, (b) LSV curves of as fabricated MOFs and (c) tafel slops of as-prepared MOFs. Reprinted with permission from ref. 85. Copyright 2016, American Chemical Society.

Table 1. FE of CO ₂ reduction products with film thickness on a PPy-coated Cu
electrocatalyst in a CH ₃ OH/0.1 M LiClO ₄ /1.5 \times 10 ⁻³ MH ⁺ at a potential of 3.0 V and
pressure of 20 bars. The reduction time was 3 h.

Film thickness (µm)	FE (%)				
	CH4	C_2H_4	CO	НСООН	CH ₃ COOH
0.5	21.1	2.2	10.2	24.2	36.3
0.9	23.2	2.3	12.9	21.1	38.2
1.4	25.5	3.1	15.1	19.8	40.2
2.1	25.2	3.1	18.2	18.2	34.1
5.4	25.1	3.1	20.2	18.7	20.1

Frontispiece

This review highlights the roles of organic components in electrocatalysts for renewable energy storage electroreactions, i.e., CO₂ reduction reaction, hydrogen evolution reaction and their counter reaction, and oxygen evolution reaction. It is found that organic molecules can and will play more important roles at economic and effective synthesis of the catalysts and renewable energy storage.





Gejun Liu is currently carrying out her M.S. studies in macromolecular chemistry and physics in the group of Prof. Huisheng Peng in the Laboratory of Advanced Materials at Fudan University. She received her B.E. in materials science and engineering from Northwestern Polytechnical University in 2016. Her work focuses on the electrocatalysts.



Haipeng Bai obtained his B.S. in environmental science and M.S. in materials engineering in School of Natural and Applied Science at Northwestern Polytechnical University. Currently he is carrying out his Dr. studies major in polymer physics and chemistry in the group of Prof. Huisheng Peng in the Department of Macromolecular Science at Fudan University. His research interests focus on the electrocatalysts.

57



Bo Zhang is currently a professor in the Department of Macromolecular Science at Fudan University. He received his B.E. in optical information science and technology at Northwestern Polytechnical University in China in 2006, and Ph.D. in chemical engineering and technology at East China University of Science & Technology in 2011. He started as a lecturer at the East China University of Science & Technology in 2011 and then worked at University of Toronto as a visiting scientist from 2015 before joining Fudan University in 2017. His research centers on electrocatalysts.



Huisheng Peng is currently a professor in the Department of Macromolecular Science and Laboratory of Advanced Materials at Fudan University. He received his B.E. in polymer materials at Donghua University in China in 1999, M.S. in macromolecular chemistry and physics at Fudan University in China in 2003, and Ph.D. in chemical engineering at Tulane University in the USA in 2006. He then worked at Los Alamos National Laboratory before joining Fudan University in 2008. His research centers on smart fibers for energy and electronics.