



Review

Metal–organic frameworks for electrocatalysis



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ABSTRACT

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have been widely used as catalysts for their large porosities, uniform pore sizes/shapes, diversified/tunable pore surfaces, redox properties, and other unique structural features. Accompanying the urgent need for clean and sustainable technologies for energy storage and conversion, as well as the fast improvement of the chemical stability of these materials, MOFs and their composites are emerging as unique electrocatalysts for the hydrogen evolution reaction, oxygen evolution reaction, oxygen reduction reaction, carbon dioxide reduction reaction, and some other redox reactions. This review summarizes representative progress and focuses on the structure–property relationships. Combining the advantages of inorganic heterogeneous and molecular homogeneous catalysts, MOFs can serve as a promising platform for achieving high electrocatalytic performances and studying the electrocatalytic mechanisms. More attention should be devoted to designing new MOFs with high chemical stability and electric conductivity, and optimizing their crystal growth on conducting substances.

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Abbreviations: HER, hydrogen evolution reaction; OER, oxygen evolution reaction; ORR, oxygen reduction reaction; CO₂RR, carbon dioxide reduction; EOR, alcohol oxidation reaction; CV, cyclic voltammetry; LSV, linear sweep voltammetry; CPE, constant potential electrolysis; CCE, constant current electrolysis; SHE, standard hydrogen electrode; RHE, reversible hydrogen electrode; SCE, saturated calomel electrode; E_{onset} , onset potential; TS, Tafel slope; η , overpotential; j , current density; F, Faraday's constant (96,485 C mol⁻¹); m , mass loading of catalyst; TOF, turnover frequency; η_{10} , η at 10 mA cm⁻²; FE, Faradaic efficiency; $E_{1/2}$, half-wave potential; j_{lim} , diffusion-limiting current density; j_{kin} , kinetic current density; n , e⁻ transfer number; LOD, limit of detection; GC, glassy carbon; RDE, rotating disk electrode; FTO, fluorine doped tin oxide; ITO, indium doped tin oxide; CP, carbon paper; MPC, macroporous carbon; CB, carbon black; PB, phosphate buffer; Nafion, sulfonated tetrafluoroethylene based fluoropolymer-copolymer; tfe, trifluoroethanol; PXRD, powder X-ray diffraction; SEM, scanning electron microscope; XPS, X-ray photoelectron spectroscopy; DFT, density functional theory; FT-IR, Fourier transform infrared spectrometer; H₂bpdca, biphenyl-4,4'-dicarboxylic acid; H₂bim, benzimidazole; H₄cit, citric acid; H₂btta, 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole; H₂bdc, 1,4-benzenedicarboxylic acid; H₂na, nicotinic acid; tba⁺, tetrabutylammonium; H₃btc, 1,3,5-benzenetricarboxylic acid; H₃btb, benzene-1,3,5-tribenzoic acid; H₃bpt, [1,1'-biphenyl]-3,4',5'-tricarboxylic acid; H₆bht, benzenehexathiol; H₆tht, terphenylene-2,3,6,7,10,11-hexathiol; H₆tha, 2,3,6,7,10,11-triphenylenehexamine; H₄tbapy, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene; H₂anbdc, 2-aminobenzene-1,4-dicarboxylic acid; tpy, 2,2':6',2''-terpyridine; H₂dobdc, 2,5-dihydroxyterephthalic acid; H₂-salen, bis-salicylaldehyde ethylenediamine; H₂mim, 2-methylimidazole; H₂dta, dithioxamide; H₂ade, 6-aminopurine; DMF, *N,N*-dimethylformamide; tbaBF₄, tetrabutylammonium tetrafluoroborate; BmimClO₄, 1-butyl-3-methylimidazolium perchlorate; H₂dcbpy, 2,2'-bipyridine-5,5'-dicarboxylic acid; tbaOH, tetrabutylammonium hydroxide; H₂bhedta, *N,N'*-bis(2-hydroxyethyl)dithioxamide; H₂bhpdta, *N,N'*-bis(2-hydroxypropyl)dithioxamide; H₂bedta, *N,N'*-bis(2-ethyl)dithioxamide; bpy, 2,2'-bipyridine; bib, 1,4-bisimidazolebenzene; H₂adp, adipic acid; H₂maa, mercaptoacetic acid; DMC, dimethyl carbonate; bpp, 1,3-bis(4-pyridyl)propane; bib, 1,4-bisimidazolebenzene; H₂piv, 2,2-dimethylpropanoic acid; H₂pca, 4-pyridinecarboxylic acid; pcb, 2-pyridinecarbaldehyde; H₆tcpp, 5,10,15,20-(4-carboxyphenyl)porphyrin; btb, 1,3,5-tris-(4-carboxyphenyl)benzene; H₂tpyp, 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphyrine; H₂ptbc, 4-(5-(pyridin-4-yl)-4*H*-1,2,4-triazol-3-yl)benzoic acid; bpab, 1,4-bis(3-pyridylaminomethyl)benzene; 4,4'-bpy, 4,4'-bipyridine; H₄cpcp, 4,5-di(4'-carboxylphenyl)phthalic acid; H₂aa, acetic acid; H₂abts, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid); ted, triethylenediamine; RGO, reduced graphene oxide; tmbdi, 2,3,5,6-tetramethyl-benzene-1,4-di-isophthalate; H₂ptz, 5-(4-pyridyl)tetrazole; NPC, N-doped pomelo-peel-derived carbon.

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1. Introduction

As a new and unique kind of porous materials, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) are crystalline, long-range ordered arrays of metal ions and inorganic/organic ligands interconnected by coordination bonds [1,2]. MOFs are well known for their diversified and designable framework/pore structures, high porosity, high surface area, large framework flexibility/dynamism, and so on [3–6]. MOFs can also adopt heterogeneity, i.e. disordered distribution of metal ions, ligands, and/or functional groups inside the long-range ordered backbone in the solid–solution manner [7,8]. With these unique features, MOFs have been extensively studied for storage, separation, sensing, drug delivery, catalysis, and other functions [9–16]. Importantly, the pore environment and precise structure of the active site for guest binding, activation, and reaction can be straightforwardly and conveniently visualized at the atomic level using diffraction techniques, which greatly assist the study of the structure–property relationship and promote optimization/design of the material [17,18].

As heterogeneous catalysts, MOFs can possess various types of catalytic sites with coordination structures and surrounding environments, being similar to those of molecular metal complexes and proteins [6,13,14,19]. The large surface areas, high concentration and controllable arrangement of active sites, uniform pore sizes/shapes of MOFs are advantageous for high catalytic activity and selectivity [20,21]. The metal ions and organic ligands in MOFs can play multiple roles, such as acid, base, redox mediator, etc., for catalyzing various types of reactions [13,16]. Unlike gas adsorption, catalysis does not require the MOF framework to be intact after the removal of terminally coordinated guest species. During the catalysis process, the coordinating guest species can be exchanged by reactant molecules/ions.

1.1. Electrochemical reactions, catalysis, and measurements

Electrochemical reactions are an important type of chemical reactions. Many chemical reactions occur with electrons transferred directly between molecules/ions/atoms, which are called oxidation–reduction or redox reactions. Redox reactions can be separated into two half reactions at two electrodes, i.e. the oxidation reaction at the anode and the reduction reaction at the cathode, but connected by an external electric circuit and an intervening electrolyte (salt bridge and/or ion selective membrane can be included). For a spontaneous chemical reaction, an electric current is produced to serve as a battery, which unifies the random electron transfer directions to the same direction, and transforms the chemical energy to electrical energy rather than thermal energy. When a nonspontaneous chemical reaction is caused by an externally supplied current, the system is called electrolytic cell, which transforms electrical energy to chemical energy. Note that besides redox reactions, many other types of reactions can be operated in electrochemical devices.

As they are directly correlated with energy storage and conversion, electrochemical devices such as batteries, fuel cells, electrolytic cells, and supercapacitors have attracted immense

attention in recent years [22–31]. These devices involve many types of half reactions, such as the hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER), oxygen reduction reaction (ORR), carbon dioxide reduction (CO₂RR), sulfur reduction and sulfide oxidation, metal oxidation and metal ion reduction, etc. Some of these half reactions, such as HER, HOR, OER, ORR, CO₂RR, etc. have intrinsically slow reaction kinetics, meaning that large overpotentials and excess energy are required to drive them or they can provide much lower potentials and energies than the theoretical values. As an important half reaction of hydrogen fuel cell and the reverse reaction of HER, HOR needs the unique activity of Pt for adsorption and dissociation of hydrogen molecules [32]. ORR and CO₂RR also face the problem of the reaction selectivity, which leads to insufficient utilization of energy and undesired products. To overcome these problems, highly efficient and selective catalysts are demanded.

The performances of electrocatalysts can be evaluated by many parameters, such as the onset potential (E_{onset}), overpotential (η) at a specific current density (j), Tafel slope (TS), exchange current density (j_0), turnover frequency (TOF), Faradic efficiency (FE), product selectivity, and/or stability/durability. E_{onset} indicates the distinguishable starting point of the half reaction, but reading out the value is usually subjective. Obviously, η at j is more objective, and η_{10} (η at 10 mA cm^{-2}) is widely used as a standard for evaluating the HER and OER performances and durability of electrocatalysis systems, because the approximate current density expected for a 10% efficiency solar-to-fuel conversion device under 1 sun illumination is 10 mA cm^{-2} [33]. The relationship between η and j can be described by the Tafel equation

$$\eta = A \ln(j/j_0)$$

where A is the TS, and $1/A$ reflects the electron transfer rate. The Tafel equation can be very powerful in helping to discern catalyst mechanism but generally difficult to analyze. j_0 is the current at equilibrium or j at $\eta = 0$, which is a measure of intrinsic kinetic activity, but the value obtained by the Tafel plot tends to have large error. TOF represents the rate of product generation per catalytic active site, which is more relevant with the involved mechanism rather than the electrode performance, because the concentration and amount of active sites cannot be easily increased in electrocatalysis [34]. Supposing that all the current is used for the electrochemical reaction, the theoretical TOF value can be simply calculated by

$$\text{TOF}_{\text{theoretical}} = j / (n \times F \times m / M)$$

where n is the number of electrons involved in reaction, m is the mass loading of the catalyst (mg cm^{-2}), and M is the molecular weight of the catalyst unified with one active center per formula unit. Nevertheless, the electrolysis current is usually not just used for the desired reaction, especially under short-term measurements (reactions on the substance, catalysts and other species, rather than the reactant). Therefore, the real TOF value should be calculated based on the amount of reaction product. The relationship between theoretical/real TOF values and FE can be expressed by

$$\text{FE} = \text{TOF} / \text{TOF}_{\text{theoretical}} \times 100\%$$

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