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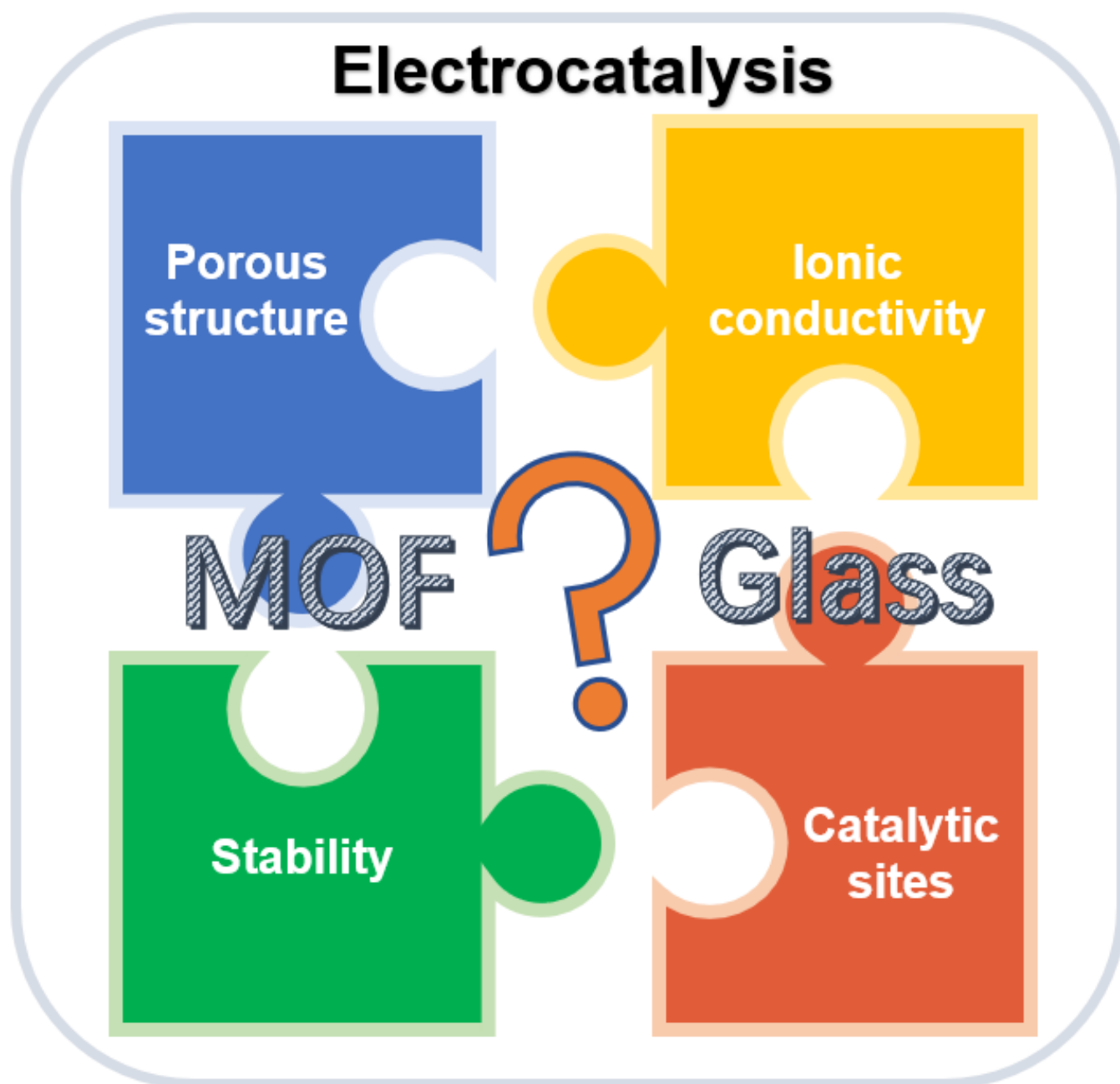
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Metal organic framework glasses: a new platform for electrocatalysis?

Yu Rao,^[a] Zongkui Kou,^[b] Xianghua Zhang^[c,d] and Ping Lu^{*[a]}



Abstract: Metal organic framework (MOF) glasses are a coordination network of metal nodes and organic ligands as an undercooled frozen-in liquid, and have therefore broadened the potential of MOF materials in the fundamental research and application scenarios. On the road to deploying MOF glasses as electrocatalysts, it remains several basic scientific hurdles although MOF glasses not only inherit the structural merits of MOFs but also endow with active catalytic features including concentrated defects, metal centers and disorder structure etc. The research on the ionic conductivity, catalytic stability and reactivity of MOF glasses has yielded scientific insights towards its electrocatalytic applications. Here, we first comb the history, definition and basic properties of MOF glasses. Then, we identify the main synthetic methods and characterization techniques. Finally, we advance the potentials and challenges of MOF glasses as electrocatalysts in furthering the understanding of these themes.

1. Introduction

Burdening from the industrial pollution and energy shortage caused by the rapid development of modern industry in the world, human beings are paying more attention to the rational use and protection of energy. The research of electrocatalysis is one of the key directions of green chemistry development^[1, 2]. The chemical reactions involved in the production and preparation of clean energy, such as oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER) and electrochemical CO₂ reduction (ECR) are relatively slow from the perspective of catalytic kinetics^[3-5]. Therefore, there is great potential for the development of highly efficient and robust electrocatalysts. Metal organic framework (MOF) glass, which is now on the rising tendency, has the huge opportunity to become one of these options. Unlike conventional inorganic, organic and metallic glasses, MOF glasses exhibit a number of unique thermophysical properties that provide new insights into the microstructure and formation mechanisms of glasses, and also show great potential for applications in catalysis^[6], battery materials^[7], gas storage and separation^[8, 9], and new optical functional devices^[10, 11]. This review briefly outlines MOF glasses and identifies their potentials and challenges for their electrocatalytic applications.

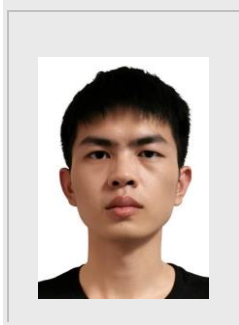
1.1. History of MOF glass

Metal-organic frameworks are organic-inorganic hybrid materials with metal nodes and organic ligand groups. Composed of inorganic and organic compounds with a well-defined crystal structure, MOF materials have the versatile topology, the easily tunable porous structure and the ultra-high specific surface area (even over 6000 m² g⁻¹)^[12]. Due to the diversity of metal ions and organic ligands, the composition and structure of MOF materials can be widely tuned to produce target materials for purposed applications. These unique properties make metal-organic skeletal materials stand out from other porous materials and are widely used in catalysis, gas storage, drug delivery and other applications^[13-15].

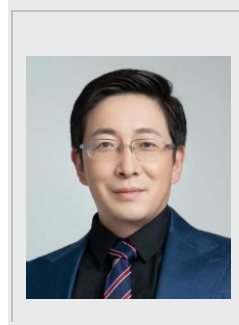
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In addition to crystalline MOF materials, the amorphization by thermal and mechanical means has been explored in MOF researches^[16, 17]. However, it was not until 2015 that there was a clear classification regarding the glassy state of MOF when some MOF materials were found to have both a molten and a glassy state^[18, 19]. A key challenge refers to that the organic ligand part of the MOF material is unstable and easily decomposed at relatively high temperature, thereby resulting in the failure of the formation of MOF glasses. Until now, only zeolitic imidazolate frameworks (ZIFs) as a subclass of the MOF material has been found to be able to form glass, which are referred to as ZIF glass. The discovery of molten and amorphous MOFs has broadened their chemical and mechanical processing options where the vitrification of MOFs allows the researchers to cast or mould glass melts into different forms, such as bulk glass, films and fibres. This opens up novel possibilities for the application of MOF glasses.

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1.2. Definition of MOF glass

In order to distinguish and clarify the definition of MOF glasses, it is firstly clear that the MOF is defined as “a coordination network with organic ligands containing potential voids”^[20]. To avoid further confusion between MOF glasses and amorphous MOFs, the term “glass” is defined as an “undercooled frozen-in liquid.”^[21] The term is thermodynamically valid, even if the glass is not formed by cooling of the melt. Long-range disorder, short-range order, and amorphous solids possessing a glass transition temperature (T_g) are necessary to form glasses.

1.3. Properties of MOF glass

1.3.1 Unordered structure

As mentioned earlier, researches on MOF glasses are mainly concentrating on ZIF glasses, which result from the collapse of the crystal structure due to the action of temperature, pressure or ball milling (mechanical forces). The long-range atoms are no longer periodically ordered in crystals, but the short range still consists of an ordered three-dimensional skeletal structure of inorganic nodes (monovalent, divalent and trivalent metal ions) and organic ligands (imidazole groups ($[Im] = [C_3H_3N_2]$)), which is similar to the silicate network structure formed by silica in oxide glass^[18, 22].

1.3.3 Glass transition temperature

Researchers have investigated the melting behaviour and kinetics, glass transition temperature and crystal melting point of MOF glasses. For example, Yue et al. studied the glass transition of ZIF crystals with the same topology and found that changing the chemical composition of the crystals can modulate the melting temperature

of the MOF glasses. T_g is related to the size of the organic ligand where larger ligands leads to a lower T_g ^[23]. The four new crystalline ZIF structures were therefore synthesized by a mixed-ligand approach and fabricated into MOF glasses by melt-quenching and cooling^[24]. The melting point of the MOF crystals and their glass transition temperature were effectively regulated. Two MOF materials are blended to make a glass, where the mixture has a single glass transition temperature, and changing the ratio of the two contents can modulate the T_g ^[9, 25]. A preliminary study of the melting process of MOF glasses by Gaillac et al. indicates that the strength of the interaction between the metal and the organic ligand is a key factor in determining the melting temperature (T_m), providing a basis for understanding the mechanism of formation of MOF glasses^[26].

1.3.3 Ionic conductivity

High ionic conductivity in MOF glasses has been established, which is mainly originated from its isotropic, lower structural density than those of crystalline. In detail, the transformation of MOF crystals into glass results in bond breakage, which creates defective sites and elevates the H^+ conductivity in MOF glasses^[27]. Due to the stable channel structure of MOF glasses and the absence of grain boundaries to hinder ion migration, the Li ion conductivity in MOF glasses is significantly increased, resulting in higher storage capacity and excellent cycling stability of lithium electrodes based on it^[7, 28].

1.3.4 Catalytic reactivity

MOF glasses inherits the intrinsic structure of MOF materials in which metal centres, organically linked ligands and void spaces have been identified as active catalytic centres. Metal centres can be easily exposed in MOF by removing the organic ligands. The introduction of functional groups such as pyridyl, amide and amino groups into the organically linked ligands of MOF can all produce basic catalytic reactivity^[29]. In addition to catalysis on metal nodes and organically linked ligands of MOF, active species can also be incorporated as guests into the open pores of MOF to generate MOF composite catalysts^[30]. These structures and properties provide a large space for the application of MOF glasses in electrocatalysis.

1.3.4 Mechanical properties

The increase in elastic modulus and hardness of MOF glass is triggered from its denser structure than the corresponding MOF crystalline^[23]. A very interesting phenomenon was disclosed in the nanoindentation test of MOF glasses where unlike inorganic glass, MOF glasses can not undergo ductile fracture while deformed with the increase of load^[31]. The fracture toughness of ZIF-62 glass has been characterized by integrating single-edge precracked beam method with molecular dynamics simulations^[32]. Compared with inorganic glasses, MOF glasses shows an obvious nanoductility. The weak Zn-N bonds were demonstrated to be responsible for low fracture toughness. However, the characterization techniques on the mechanical properties of MOF glasses is still limited by the sample size, such that a more mature preparation method of bulk samples can be developed.

1.3.5 Optical properties

Recently, a few MOF glasses have shown the high transmittance (up to 90%) in the visible and near-infrared (NIR) wavelength range where the refractive index can reach 1.56 which is close to most inorganic glasses^[10]. Moreover, the refractive index of MOF glasses can be adjusted by changing its composition. It is found that the optical absorption of Zn ZIF-62 glass is low in the NIR spectral region and doesn't have saturable absorption characteristics under 1030 nm femtosecond laser. In contrast, a NIR absorption band (1100 nm) was observed in Zn/Co ZIF-62 glass, which showed a strong nonlinear response with a modulation depth of up to 63.85%^[33].

The above achievements have contributed to our further understanding of the properties of MOF glasses. The replacement or partial replacement of organic linker ligands in MOF, the design of functional groups to modulate organic linker ligands, and the adjustment of raw material ratios in composite MOF glasses are all effective ways to modulate the properties of MOF glasses. However, compared to MOF crystals, MOF glass is still a newborn, and further research on its structure, mechanism and properties is still highly required.

2. Preparation methods of MOF glasses

MOF glasses are relatively difficult to be prepared due to the poor thermal stability of their organic ligands. As shown in **Figure 1**, the preparation of MOF glasses is rationally divided into direct and indirect preparation according to different mechanisms. Direct synthesis is mainly based on melt-quenched process, where the glass is formed directly without experiencing the crystalline state, while indirect synthesis refers to the transformation of MOF crystals into the glassy state by mechanical and/or temperature controlling means.

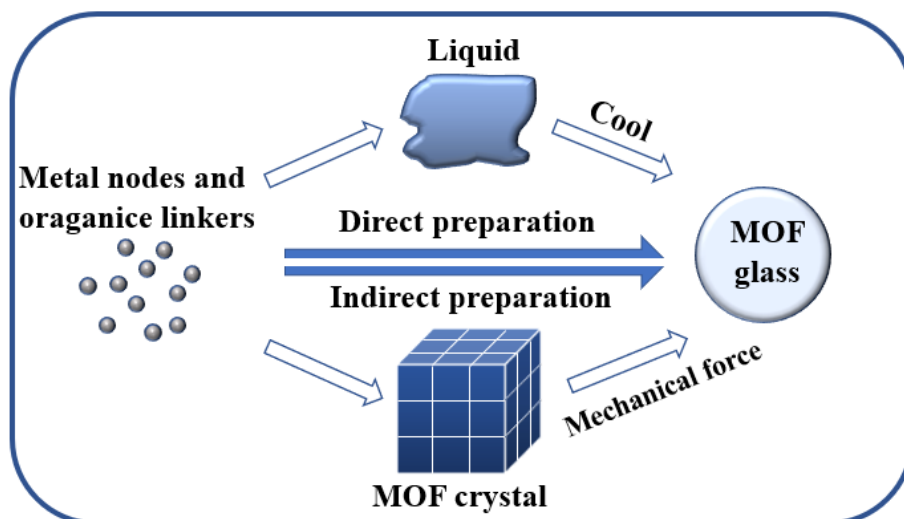


Figure 1. Schematic diagram of preparation methods of MOF glass.

2.1. Direct preparation

Melt-quenched process is the most common method of glass preparation, where the raw material is heated to a molten state, then melts is cooled at a faster rate than that of the crystallization, finally resulting in a supercooled/glassy state. In MOF materials, however, the decomposition temperature (T_d) of the typical organic ligands in the structure are between 200 °C and 500 °C^[34]. The thermal stability of MOF materials is therefore lower than that of many inorganic systems. On the path to deploying the direct preparation, the MOFs are first heated above T_m to provide a molten state. Then, rapid cooling (vitrification) takes place. Finally, melting of MOFs can be achieved by lowering T_m or raising T_d .

The melting system must allow for a certain degree of dissociation of the coordination bonds. So far, MOFs with a stable liquid state are more likely to bind metal ions with a d^{10} configuration^[27, 35]. Transition metals with a d^{10} configuration lead to lower crystal field stability energies and require relatively less energy to dissociate the coordination bonds. Of course, ligands can also be chosen from organic groups that can form weak bonds with metals, such as sulfonates, esters, amides and nitrocarbons.

2.2. Indirect preparation

MOF crystals are subjected to externally applied mechanical forces, which partially or totally disrupt the crystal structure and produce disordered structures, thus turning them into MOF glass. Mechanically induced amorphization can directly convert crystals into a glassy state through compressive, shear, and tensile stresses. Ball-milling is a common method of amorphization of ZIF materials^[36]. Controlled by the ball-milling rate and time, the amorphous material formed also retains part of its crystalline structure. However, the mechanical forces during high energy ball-milling are not only converted into potential energy of the material, but also into thermal energy. Therefore, it remains an open topic about whether the system temperature is too high during high-energy

ball milling or the increase in system temperature may lead to amorphization by melting of the particles. A more in-depth study of ball milling-induced amorphization of ZIF materials is therefore required in order to elucidate the amorphization mechanisms during ball milling.

Another process of mechanical preparation involves with the use of pressure. Pressure-induced amorphization is triggered by a sudden change from a crystalline to an amorphous state. This abrupt change is achieved by applying pressure in a temperature range below the melting point or glass transition temperature. Pressure-induced amorphization of the MOF is a result of the shear modulus of the material becoming smaller. Under mechanical stress, a further increase in mechanical load can trigger a phase change, and the elastic tensor drops below the requirement for Born stability^[37, 38]. Mechanochemical methods have been widely used, but their mechanism of action needs to be further explored.

3. Characterization of MOF glass

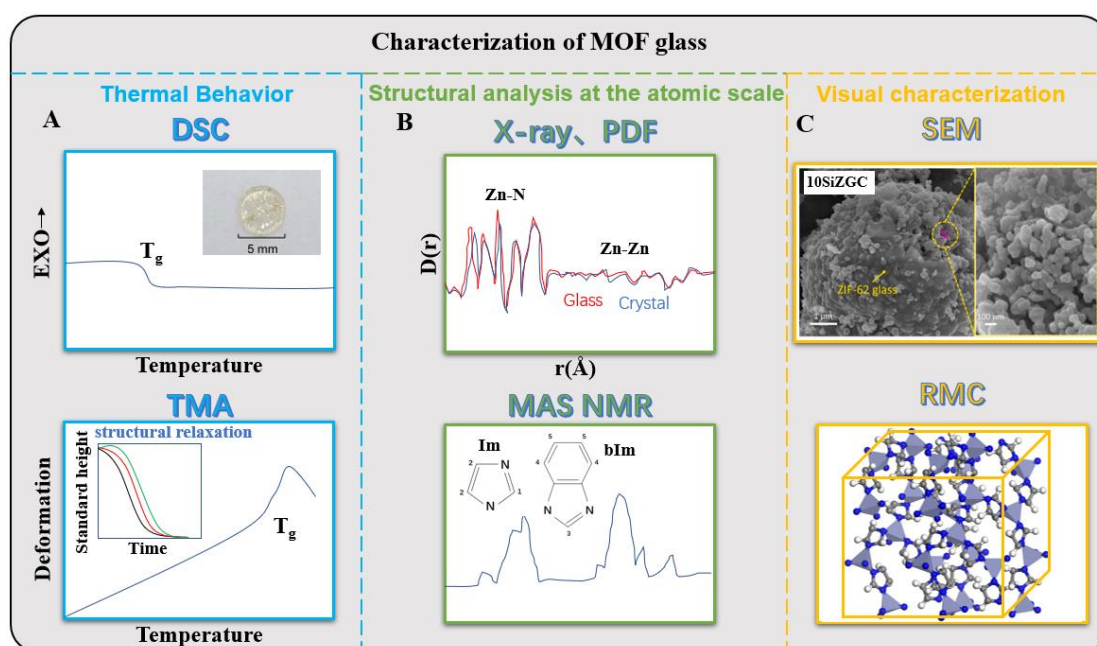


Figure 2. Common characterization methods of MOF glass. (A) Thermal analysis, Differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) can help to find the glass transition temperature. In addition, TMA can also be used to observe the structural relaxation of glass. (B) Precise atomic structure of glass are determined through with the total scattering X-ray diffraction (XRD), pair distribution function (PDF) and magic-angle spinning nuclear magnetic resonance (MAS NMR). (C) Scanning electron microscopy (SEM) images of the 10Si@cobalt-ZIF-62-glass composite (10SiZGC), SEM can characterize the microstructure, reverse Monte Carlo (RMC) can simulate the glass structure. Glass picture is reproduction from ref. [\[39\]](#) Copyright (2018), with permission from American Association for the Advancement of Science. SEM images is adapted from ref. [\[43\]](#) Copyright (2022), with permission from Elsevier.

3.1. Thermal Behavior

Thermal analysis methods fit into one of two categories (**Figure 2A**)^[21]. The first type is thermodynamic properties including such as phase transition, glass transition temperatures, decomposition temperatures, etc. The temperature-residual weight relationships, desolvation and T_g are obtained through thermogravimetric analysis (TGA). Differential scanning calorimetry (DSC) can be equipped with TGA for investigating the detailed thermodynamic and kinetic parameters of glass-forming materials, as well as identifying phase transitions and relaxation of the system^[39]. The second type that falls under the umbrella of thermal analysis is the observable

mechanical response of a material to an increase or decrease in temperature. thermal mechanical analysis (TMA) is an alternative technique to determine the dilatometric softening point and T_g .

3.2. Structural analysis

Many analytical techniques have been established to identify the structural information of glass state. There is no long-range ordered structure in the glassy state, which limits the application of ordinary X-ray diffraction technology in identifying the glass structure. However, the diffraction patterns obtained by more advanced X-ray, electron or neutron scattering techniques can obtain the short- and medium-range structural information of glass. X-ray absorption fine structure spectroscopy (XAFS) is widely used to establish short-range order, especially the local coordination environments of heavy atoms in the amorphous glasses around the metal centers^[40]. Neutron and/or X-ray diffraction (**Figure 2B**) are frequently used to evaluate middle-range correlations^[41]. While using the above technologies, precise atomic structure are determined through with the pair distribution function (PDF) and radial distribution function (RDF) analysis. Solid-state nuclear magnetic resonance (NMR), magic-angle spinning (MAS) NMR (**Figure 2B**), IR, and Raman spectroscopy are also promising methods to obtain structural changes of materials and interactions with other molecules.

3.3. Visual characterization

Macroscopic views of glasses are accessible through optical or electron microscopy. Both scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) allows to visit the microstructure of MOF glass (**Figure 2C**), mechanical deformation, and the formation of grain-boundary-free monoliths. Microzone composition can also be analyzed using energy dispersive X-ray spectroscopy (EDS). Deformation of the glass surface or the formation of a shear band under mechanical stress is precisely quantified by atomic force microscopy (AFM). Microstructures can then be theoretically simulated. Molecular dynamics (MD), density functional theory (DFT), PDF and RDF are able to provide theoretical basis and experimental data fitting. Therefore, reverse Monte Carlo (RMC) are able to obtain a visualization of glass structure model (**Figure 2C**)^[35]. However, RMC technology is also constrained by the initial model and application such that it must be zoomed in the appropriate conditions and optimized models.

4. Potential in the field of electrocatalysis

MOF glass has improved ionic conductivity, multiple catalytic sites, processability and material compounding compared to MOF crystals, which are beneficial to its application in electrocatalysis. Therefore, research on MOF glass catalysts is already underway.

4.1. Ionic conductor in the catalytic electrode

MOF glass is an excellent ionic conductive material, which could be used as ionic conductor binder in the catalytic electrode preparation. In the research on the influence of coordination polymer (CP) glass network structure on viscosity and H^+ conductivity, it was found that CP glass with wide viscosity range showed high H^+ conductivity ($> 10^{-2} \text{ S cm}^{-1}$ at $120 \text{ }^\circ\text{C}$)^[42]. The ionic conductivity of MOF glass with defects and no obvious grain boundaries is higher than that of the corresponding crystalline. For example, combination of glassy ZIF-4 with thiobis (trifluoromethanesulfonyl) imide (LiTFSI) as quasi-solid-state electrolytes (QSSEs) has exhibited high Li^+ conductivities of $1.61 \times 10^{-4} \text{ S cm}^{-1}$ at $30 \text{ }^\circ\text{C}$ and $5.96 \times 10^{-5} \text{ S cm}^{-1}$ at $-56.6 \text{ }^\circ\text{C}$, which are notably higher than the conductivity values observed in crystalline counterparts ($8.21 \times 10^{-5} \text{ S cm}^{-1}$ at $30 \text{ }^\circ\text{C}$, $4.51 \times 10^{-7} \text{ S cm}^{-1}$ at $-56.6 \text{ }^\circ\text{C}$)^[7]. The ionic conductivity of MOF glass can also be related to the electrode material application. Yue's

team recently compounded MOF glass with silicon (Si) nanoparticles to exploit their respective excellent lithium storage properties while fully realizing the synergy between the two materials, resulting in a Si@ZIF-glass composite (SiZGC) anode material with excellent performance. By combining reflow and melt quenching methods, Si nanoparticles without any surface modification were encapsulated in ZIF glass layers to obtain structurally stable composites. The composite material takes full advantage of the synergistic effect of Si and ZIF, and therefore offers a significant increase in specific capacity compared to Si, ZIF crystal and ZIF glass^[28]. When charged and discharged at a current density of 1 A g⁻¹, the capacity of the SiZGC negative electrode gradually increases and reaches 650 mA h g⁻¹ after 500 cycles (**Figure 3**).

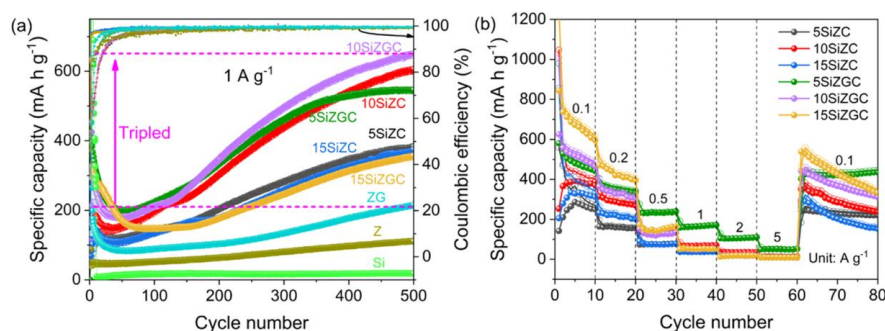


Figure 3. Electrochemical Performances. (a) The cycling performance of anodes based on different samples. (b) Rate performance of different samples at current densities of 1.0, 0.2, 0.5, 1, 2, 5 and 0.1 A g⁻¹. Chart is reproduction from ref. [43] Copyright (2018), with permission from Elsevier.

This synergistic effect is mainly due to three reasons: (1) The open and disordered network structure of the ZIF glass itself facilitates the transport and storage of Li⁺. (2) The ZIF glass layer buffered the volume expansion and pulverization of Si during the charge/discharge process, allowing Si to give full play to its high specific capacity. (3) The stable structure of the composite material fully ensures the transport of electrons and Li⁺ during the charging and discharging process, thus achieving a significant improvement in electrochemical performance^[43].

4.2. Catalytic activity

MOFs are an active class of heterogeneous catalysts with a wide range of different metal ions and organic ligands. Different metals, different ligands, and combinations of metals and ligands can all act as active centres to synergistically enhance electrocatalysis. However, in MOF glass, element doping to improve the catalytic activity may be the future direction.

Mixed metal doped MOFs exhibit superior catalytic activity. For example, Cu²⁺ were introduced into ZIF-8 to form Cu/ZIF-8 by reacting Cu(NO₃)₂, Zn(NO₃)₂, and 2-methylimidazole^[44]. Cu²⁺ is easily doped into ZIF-8 without changing its thermal stability and crystallinity. When Cu²⁺ is less than 10%, the porosity of ZIF-8 does not change. Cu/ZIF-8 are effective and reusable catalysts for the [3+2] cycloaddition of organic azide compounds to alkynes and the condensation of Friedländer and Combes. Doping ZIF-67 with Cu²⁺ significantly improves the H₂ and CO₂ absorption capacity of the material. At the same time, it can be used as a photocatalyst to degrade methyl orange^[45].

Well coordination between catalytic center and catalyst structure can greatly improve catalytic efficiency. N-heterocyclic carbene (NHC)-ligated copper single atom site (Cu SAS) embedded in MOF is reported (2Bn-Cu@UiO-67) by Chen et al. It achieve an outstanding Faradaic efficiency (FE) of 81% for the CO₂ reduction to CH₄ at 1.5 V vs. The donation of NHC enriches the surface electron density of Cu SAS and promotes the preferential adsorption of CHO* intermediates. The porous structure of MOF matrix promotes the CO₂ to 2Bn-Cu, significantly increasing the availability of each catalytic center^[46]. Liu et al. construct isolated single Pd atom

ina polyoxometalate-based metal-organic framework (POMOF). This material separate acetylene from acetylene/ethylene gas mixtures. After semi-hydro-genation, the resulting ethylene is discharged from the pores preferentially, with a selectivity of 92.6%. The combined advantages of POMOF and single Pd atom provides an effective approach for the regulation of semi-hydrogenation selectivity^[47].

In recent years, bimetallic MOF and their accessory products have shown excellent catalytic properties^[48, 49]. For example, Li et al. prepared low crystalline MOF materials by controlling the reaction of Fe/Ni ions with terephthalic acid. Because of its local crystallization and long range disorder, it provides enough active sites for catalytic reactions. As an oxygen evolution electrocatalyst, it has an overpotential of 260 mV at 10 mA cm⁻², a low Tafel slope of 35 mV dec⁻¹, and a high Faradaic efficiency of 99.5%.

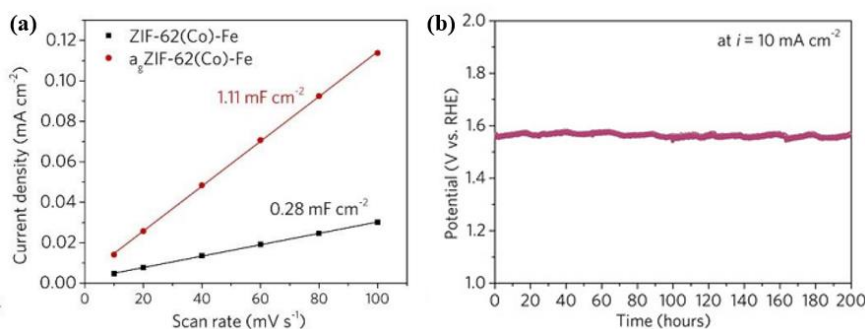


Figure 4. (a) Linear fitting of scan rates with capacitive current densities of ZIF-62(Co)-Fe and a_gZIF-62(Co)-Fe. (b) Durability of a_gZIF-62(Co)-Fe-CC assessed by chronopotentiometry under the current density of 10 mA cm⁻² in 0.1 M of KOH for 200 h at room temperature. Chart is reproduction from ref. [6] Copyright (2021), with permission from Wiley-VCH.

The introduction of metal ions into ZIF causes the Zn-Im bond to break, creating defects that favour the creation of catalytic sites in ZIF glasses. However, there are limitations in the preparation technology for the practical application of MOF materials in catalysis. Direct coating of MOF nanoparticles on substrates requires fine control of the growth process of MOF crystalline. The use of synthetic coatings with adhesives also suffers from clogging of micropores and impedes electron transfer. The researchers used the preparation of bimetallic cobalt-iron ZIF-62(Co)-Fe glass electrodes by mechanochemical coating and melt quenching. The catalytic effect of the bimetallic system was confirmed by the oxygen evolution reaction (OER) activity measured by the rotating disc electrode (RDE) technique in 0.1 M KOH aqueous solution. The vitrification treatment results in a larger electrochemical surface area and better exposure of the catalytically active centre. ZIF-62(Co)-Fe glass exhibits a much higher double-layer capacitance (DLC) value (1.11 mF cm⁻²) compared to ZIF-62(Co)-Fe (0.28 mF cm⁻²) (**Figure 4a**). The durability of ZIF-62(Co)-Fe glass was assessed by chronopotentiometry under the current density of 10 mA cm⁻² in 0.1 M of KOH at room temperature under constant stirring (**Figure 4b**). The voltage of the tested cell was relatively constant between 1.54 V and 1.57 V during 200 h operation and the leaching of metal ions is also very low^[6].

4.3. Catalytic stability

The main problem faced by the application of MOF glasses in electrocatalysis is a limited chemical stability. Electrocatalytic reactions are generally carried out in electrolyte solution, usually in a high acidity/basicity environment. However, many MOFs have been developed with high chemical stability in water and even under strongly acidic/alkaline conditions^[50, 51]. Metal ions, organic ligands and metal-ligand coordination geometry all affect the stability of MOF glass. Stable MOF materials generally fall into two categories^[52]. One is high-valency metal-carboxylate frameworks. When the ligand and coordination environment remain the same, high-priced metal ions can form stronger coordination bonds and thus a more stable skeleton. The other is low-valency metal-azolate frameworks, the most representative example of which is ZIFs^[53]. The acidic stability of ZIFs is

poor, while its base stability is good. Recently, Wang et al. synthesized a hybrid zeolitic imidazolate frameworks (HZIF-1Mo). Powder XRD pattern confirmed that HZIF-1Mo could still maintain its skeleton in aqueous solution at pH=1 after 14 weeks, and HZIF-1Mo also had high thermal stability (up to 550 °C)^[54, 55]. The development of these acid-base stable ZIFs provides a paradigm for the stability of MOF glass at different temperatures and acid-base solutions.

5. Perspectives of MOF glass in the field of electrocatalysis

The application of MOF glass in the field of electrocatalysis is gradually emerging, with great potential for catalytic reactions, electrodes and solid electrolytes. It is well known that the two most essential requirements for electrocatalytic electrode materials: (1) effective catalysis; (2) good conductivity and abundant free electrons. For MOF glasses, the metal, organic ligands, and vacancy defects present in the glass are all ideal sites to act as catalytic active centres, and utilizing all of these sites will generate a significant increase in catalytic efficiency. At the same time, the porous structure of MOF glass provides sufficient specific surface area for the reaction, which makes it easier to adsorb reactants and also accelerates the catalytic process.

In practice, MOF glasses do not have the same crystallization problems as MOF and are easy to prepare. The melt-prepared MOF glass doesn't require a binder to combine with the substrate electrode. There is also a problem for the application of MOF glasses in electrocatalysis: how to produce MOF glasses directly on the conductive current-collecting substrates to form the electrode? There is more than one way to prepare MOF glass, but MOF glass produced by mechanical means still needs to be bonded if it is to be bonded to an electrode. Mechanically bonding the MOF to the substrate electrode and then forming the glass using melt-quenched to reduce the adhesive coating is a better option. Alternatively, the MOF glass can be laminated with high-capacity materials to produce usable electrodes directly. MOF glass is stable and does not affect the exchange of ions. By making it available as a shell to wrap some catalytic materials with more restricted use requirements, MOF glass has the potential to broaden the range of other materials.

One great advantage of MOF materials is the tunability of the structure. The replacement of metals and their ligands in the MOF and the adjustment of the porosity can lead to different catalytic properties. MOF glass inherits this characteristic, but faces the limitation of having less composition available. The composition of the forming MOF glass is still dominated by ZIF, such as ZIF-4, ZIF-62, ZIF-76^[18, 56]. Recently, some new MOF glasses have been prepared by new ideas and methods. The method of ionic liquid incorporation was used to prepare IL@ZIF-8 glass, which solved the problem that ZIF-8 could not be prepared into glass^[57]. Other researchers doped ZIF-8 into ZIF-62 to prepare glass^[58]. TIF-4 MOF glass has also been prepared for selective CO₂ separation^[59]. Increasing kinds of MOF glass, which is good news for its application in electrocatalysis, and there is also research potential to develop new MOF glass materials to expand their application in electrocatalysis. There is thereby an urgent need but it is still a significant challenge to develop more kinds of MOF glass and to study its acid resistance, thermal stability, conductivity, catalytic efficiency, etc.

The aim of this review is to give both brief introduction and deep discussion to MOF glass and analyse its potentials and challenges faced in the field of electrocatalysis by zooming in several typical examples. We believe that MOF glass is bound to shine in the field of electrocatalysis in the future due to its unique properties such as high ionic conductivity, high porosity and a large number of catalytic active sites.

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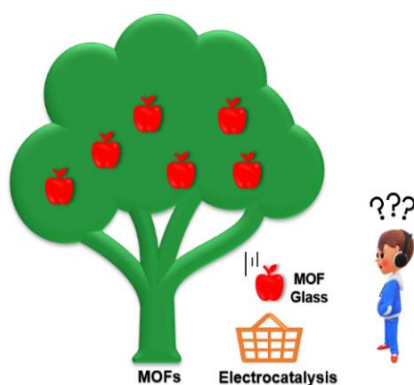
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REVIEW

The research on the ionic conductivity, catalytic stability and reactivity of MOF glasses has yielded scientific insights towards its electrocatalytic applications.



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