Splitting water into hydrogen and oxygen is the key reaction in energy storage and conversion applications, in which the oxygen evolution reaction (OER) is kinetically very difficult due to the involved 4-electron process. Some precious metal oxides are the best electrocatalysts for the OER so far. With suitable crystal sizes/morphologies, some non-precious metal oxides/hydroxides can also exhibit good catalysis activities. However, the surface structures or active sites of these heterogeneous catalysts are very difficult to precisely characterize, preventing understanding the catalysis mechanisms. Porous coordination polymers or metal-organic frameworks (MOFs), possessing very large inner pore spaces and surface areas, as well as accurate pore surface structures that can be readily visualized by diffraction techniques, have attracted intense attention in applications related to adsorption and catalysis. However, MOFs are usually unstable in water, especially for those with open/active metal sites and in strongly acidic/basic mediums that are useful for OER. Therefore, only few MOFs have been studied as electrocatalysts for OER and their activities are usually poor.

Recently, a few MOFs showing high chemical stabilities in water and redox active open metal sites on their pore surfaces were reported. Here, we introduce recent research progresses in our research group: (1) Post-synthetic ion exchange from chloride ligand to hydroxide ligand on the pore surface in water at pH = 14, which not only drastically increases the OER performance but also provide the first experimental evidence for the intraframework O-O coupling mechanism; (2) Modular and stepwise synthesis of a hybrid MOF, which stabilizes the unstable paddle-wheel type dicobalt tetracarboxylate cluster in a chemically Fe(III) carboxylate framework and realizes very high OER performance.


Keywords: OER, post-synthetic modification, catalysis mechanism