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Broader context

The interface interaction between electrode materials and saline water is a key process in capacitive deionization (CDI) and is the focus of growing attention in water sustainability and environmental electrochemistry. Significant effort in the past has been mainly directed to developing porous carbon materials for promoting the salt adsorption capacity and cycling stability. Unfortunately, CDI with these materials are often performed in oxygen-free saline water, which complicates quantitative evaluation of CDI performance towards practical use and thereby impedes progress in this field. More recently, evidence has pointed out that carbon materials usually experience serious performance degradation especially when saline water contains dissolved oxygen, which is recognized as simulative natural saline water environment for CDI operation. In this opinion, we highlight the significance of metal-organic framework (MOF) derivatives such as pyrolytic carbons, pyrolytic metal-containing carbons, and MOF-based hybrids as an alternative to conventionally used carbon materials, especially for CDI of oxygenated saline water. Through carefully comparing the published data regarding CDI performance (salt adsorption capacity *versus* cycling lifetime) of MOF derivatives with typical carbons, we expect that MOF derivatives with promoted CDI performance even in oxygenated saline water would be the future choice for industrial CDI application.

Metal-Organic Framework Derivatives for Promoted Capacitive Deionization of Oxygenated Saline Water

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Abstract

Capacitive deionization (CDI) using porous materials is a sustainable method for providing affordable freshwater, but the low salt adsorption capacity and poor cycling stability of benchmark carbon materials significantly limit the practical implementation. Metal-organic framework (MOF) derivatives, such as pyrolytic carbons, pyrolytic metal-containing carbons, and MOF-based hybrids, have been designed as an alternative to conventionally used carbon materials. In particular, for CDI of oxygenated saline water, which has always been a great challenge, MOF derivatives have also demonstrated enhanced salt adsorption capacity and cycling stability. MOF derivatives provide a new opportunity to significantly expand the library of advanced materials suitable for CDI technologies with improved performance.

For decades, water sustainability has been one of the most concerning topics for humans worldwide.[1] The reduction in affordable freshwater, increasing water pollution, and growing population have worsened the water supply crisis. Saline water desalination by capacitive deionization (CDI), which stores salt ions within the inner pores of porous materials,[2] is an emerging technology. The fundamental concept of CDI is defined as an electrochemical method based on the electrical double layer (EDL) principle; therefore, CDI is also known as 'electrosorption'. Theoretically, CDI has advantages over other desalination techniques, including simple operation, low cost, and environmental friendliness.

In the past 20 years, CDI has received increasing attention, and **Fig. 1** shows the record of publications and citations over this period using the keywords 'capacitive deionization' or 'electrosportion'. In particular, the concept of CDI is considerably broader than before. Currently, CDI is not only defined as an EDL capacitive desalination technology, but also includes various electrochemical deionization technologies based on ion storage/release during electrode charging-discharging cycle.[3] Increasingly more novel advanced materials are being developed and applied in CDI electrodes as alternatives to the conventional carbon materials. Some of these materials have ion trapping mechanisms that are very different from the EDL capacitive principle. To exploit these new materials, different cell structures have been developed to achieve better CDI performance, and consequently CDI variants such as membrane CDI, flow-electrode CDI, hybrid CDI, inverted CDI, rocking-chair CDI, dual-ion electrochemical deionization, and even redox flow electrochemical deionization have been derived. This period can be considered as the era of the second generation of CDI technologies, namely "*CDI-X*".

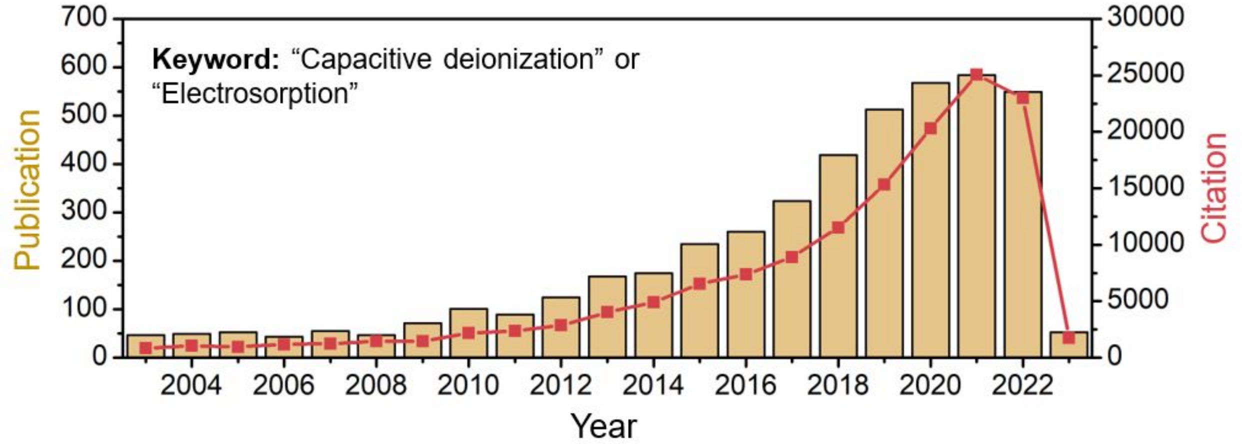

Fig. 1 Record of publications and citations over the past 20 years using the keywords 'capacitive deionization' or 'electrosportion' from the Web-of-Science (As of February 2023).

Despite progress in expanding the library of CDI materials and CDI concepts, CDI technology based on porous carbon materials remains dominant. Therefore, in this opinion, we mainly discuss the limitations of carbon-based materials in CDI, especially for oxygenated (natural) water, and further present the utilization of metal-organic framework (MOF) derivatives to promote CDI performance in oxygenated (natural) saline water. Finally, the future prospects of CDI are discussed.

Limitations of conventional carbon materials in CDI

Generally, electrode materials are the main part of a CDI apparatus.[4] The development of new-family materials has received increasing attention in the CDI community. The porosity and electrical conductivity of electrode materials significantly affect the resulting CDI performance. The past two decades have witnessed the rapid development of porous materials with high porosity and good electrical conductivity for laboratory-scale CDI.[4] Consequently, substantial effort has been devoted to the design of porous carbon materials with suitable characteristics for optimizing the CDI performance. Despite the progress in the processing or synthesis of carbon materials, most carbon materials obtained by simple processing routes exhibit poor salt adsorption capacities (SACs) because of their limited functionality, which leads to insufficient charged groups at their surfaces, a narrow pore size distribution that would lead to poor lectrolyte penetration, and low electrical conductivity.

Furthermore, the performance degradation of carbon electrodes is another concerning problem that limits the industrial application of CDI. Recent studies have demonstrated that the side reactions of carbon electrodes are the main causes of CDI degradation.[5] In particular, the carbon oxidation reaction at the anode generates considerable oxygen-containing groups and degrades the carbon framework. Additionally, oxygen reduction at the cathode produces oxidizing substances such as H_2O_2 during the charging process, which further oxidizes the carbon surface under the flow of electrolytes. As the cycle continues, more oxygen-containing groups are generated coupled with serious destruction of the pore structure of the carbon framework. Although the total charge input during the cycle may be equivalent, the formed oxygen-containing groups inhibits anion adsorption (**Fig. 2a**), leading to severe SAC deterioration. Consequently, the charge utilization efficiency decreases, which further causes a significant increase in energy consumption per removed salt. Considering the dissolved oxygen in natural saline water, the performance degeneration of carbon-based CDI is inevitable. Therefore, a strategy to address this problem should be the main concern for promoting large-scale CDI applications.

Pyrolytic carbons from MOF pyrolysis for CDI

MOFs, which are assemblies of transition metal nodes and organic linkers, are emerging as a novel family of porous materials with uncommon advantages, such as precise pore structure, ultrahigh porosity, diverse morphologies, and good oxidization resistance.[6] Although more studies have explored the potential of MOFs and MOF hybrids to circumvent the limitations of carbon materials for CDI, the poor electrical conductivity of most MOF materials limits their electrochemical performance.

Generally, the pyrolysis of MOFs creates carbonaceous porous networks (**Fig. 2b**), which is a promising method to increase the electrical conductivity, and thereby improve the CDI performance.[7] Considering the precise tuneability of MOFs in terms of composition, morphology, and structure using various synthetic methodologies, MOFs provide great platforms for conductive porous materials by pyrolysis.[8] MOF-derived carbon was reported in 2008 by Xu *et al.*,[9] demonstrating high specific surface area porous carbons from the pyrolysis of MOF-5 with furfuryl alcohol. Without an additional carbon source, our research group pioneered the investigation of the direct carbonization of ZIF-8 and reported the structural properties of MOF-derived carbon.[10] In 2014, the CDI application of porous carbon from IRMOF-1 was demonstrated by Park *et al.*[11], achieving a high SAC of 11 mg g^{-1} under three charge-discharge cycles. In the subsequent year, Pan *et al.*[7] and Chang *et al.*[12] further explored the CDI performances of porous carbons derived from ZIF-8 and MOF-5, respectively.

Following these pioneering studies, the use of MOFs and their composites as precursors to fabricate functional carbons by pyrolysis is considered a promising approach to obtain highly porous carbon-based materials.[8] The past decade has witnessed the rapid development of a series of MOF-derived carbons, resulting in various synthetic strategies for controlling their chemical compositions, morphologies, and structures. From our perspective, MOF precursors are of great importance for deriving carbon materials with unique chemical and physical properties. Typically, most MOF precursors can be divided into single particle type or assembled particle type. In addition to the direct pyrolysis of pristine MOF particles to synthesize carbon materials, pre-modification of MOF particles to engineer specific precursors can result in unusual properties in the carbon materials. For example, metal node/organic ligand changes in the MOF composition can tune the porosity, degree of graphitization, and heteroatom doping in the MOF-derived carbon.[13] The generation of hollow MOF particles forms carbon materials with huge cavities, which facilitate electrolyte penetration and buffering.[14] The core-shell motif structure on the MOF can functionalize the carbon materials with a variety of tunable nanoarchitectures.[15] Furthermore, the assembly of MOF particles into high-dimensional structures provides more possibilities for deriving carbon superstructures. Self-assembly of MOF particles forms layered MOF superstructures, which have been demonstrated to be excellent precursors for the fabrication of carbon superstructure.[16] These carbon superstructures usually exhibit better electrochemical properties than the single carbon particles. Furthermore, hybridization of MOF particles with other carbon nanomaterials, such as carbon nanotubes and graphene, forms novel carbon hybrid materials with tailored nanostructures and heterointerfaces, which usually possess the advantages of both the components.[17]

Generally, MOF-derived carbons do not only inherit the high porosities, tailored nanoarchitectures, and tunable compositions from MOFs, but also exhibit good electrical conductivity that most MOFs do not possess. MOF-derived carbons usually exhibit better CDI performance than conventional carbon materials.[7] In particular, high porosity is favorable for accommodating more salt ions, which is considered to be the key factor for determining the CDI performance of carbon-based materials mainly based on the EDL principles. However, the CDI performance of carbon materials is usually limited because the porosity cannot be increased indefinitely. Thus, the tunability of the nanoarchitectures and compositions of MOF-derived carbons is crucial for improving CDI performance.[18] The compositional control of carbon materials, such as heteroatom doping, can not only induce pseudocapacitive contributions to the CDI process, but is also beneficial for improving the surface charge, wettability, and conductivity, thereby enhancing the CDI process.[17]

Beyond carbons: Pyrolytic metal-containing carbons and MOF-based hybrids for CDI of oxygenated saline water

Although the above-mentioned MOF-derived carbons have demonstrated great potential for achieving higher SACs, they easily experience poor cycling stability in natural (oxygenated) saline water, which is similar to the performance of conventional carbon materials. Therefore, two emerging solutions have been developed to improve CDI cycling stability in oxygenated saline water.

The first solution is based on the inhibition of H_2O_2 formation by promoting the oxygen reduction reaction (ORR) at the electrode surface. As discussed previously, H_2O_2 formation *via* a two-electron ORR pathway is known to be responsible for the deterioration of the CDI cycling performance for carbon materials.[19] Therefore, if the ORR process can be improved from a two-electron pathway to a four-electron pathway, H_2O_2 formation can be inhibited and the CDI cycling stability can be improved. However, this strategy has been mainly limited by the poor ORR activity of most carbon materials. MOFs are recognized as superior precursors for fabricating metal-containing carbon materials (with nanoparticles, single atoms, *etc.*) with superior ORR catalytic performances (**Fig. 2b**). Compared to conventional methodologies based on post-modification of carbonaceous precursors with metallic species, MOFs assembled with metal nodes and organic ligands enable the derivation of metal-containing carbons with uniformly distributed and tunable active sites. Moreover, the synthesis approaches are simple. Based on this principle, our group[20] developed three dimensional nitrogen-iron-doped carbon (3D-FeNC) tubes to achieve a superior ORR activity by the layer-by-layer motif method for the synthesis of 3D interconnected MOF tubes using a Zn-containing polyacrylonitrile fiber template with subsequent pyrolysis. The resultant 3D-FeNC tubes were carefully designed as one-dimensional hollow tubes for rapid ion diffusion, while the 3D interconnected carbon framework provided long-range electronic pathways and abundant nitrogen-iron active sites for the enhanced ORR ability. The application of the 3D-FeNC tubes as a CDI electrode material in oxygenated saline water demonstrated its unprecedented CDI performance with an exceptional SAC of 40.70 mg g^{-1} and remarkable capacity retention of 93.82%, even after 200 cycles.

Another promising method to address the problem is to develop MOF derivatives with strong oxidation resistance. Generally, the MOF derivatives in the CDI field are mainly obtained by the pyrolysis of MOFs, as discussed above. The pyrolysis operation irreversibly causes undesirable structural changes and the deterioration of the original fine structure of the MOF crystals, consequently resulting in serious capacitance loss and limited ion diffusion. In contrast, similar to conventional carbon materials, most MOF-derived carbons cannot effectively overcome carbon corrosion for practical application. Therefore, their cycling lifetime is poor, especially when applied for CDI of oxygenated water. Thus, developing pyrolysis-free MOF-based hybrids may effectively circumvent these issues. The major challenge is increasing the electrical conductivity of MOFs without any pyrolysis process. In 2019, our group pioneered the use of pyrolysis-free MOFs for application in CDI.[21] In our approach, highly conductive agents, namely polypyrrole (PPy) nanotubes, were introduced into the hybrid matrix within each MOF particle (**Fig. 2c**), which served as bridges between MOF, that is, zeolitic imidazolate framework-67, particles to increase the conductivity, while retaining the high porosity and pore structure of the MOF. Consequently, the MOF/PPy hybrids exhibited a higher CDI performance than benchmark carbon materials, suggesting the potential for the direct application of MOFs in CDI electrodes. Based on this principle, increasingly more conductive agents may be explored for use in conductive MOF hybrids.[22, 23] Similar to our pioneering work, these studies are expected to exceed the performance limitations of carbon electrodes for application in CDI, while achieving good cycling stability for long-term CDI operation in natural (oxygenated) saline water.

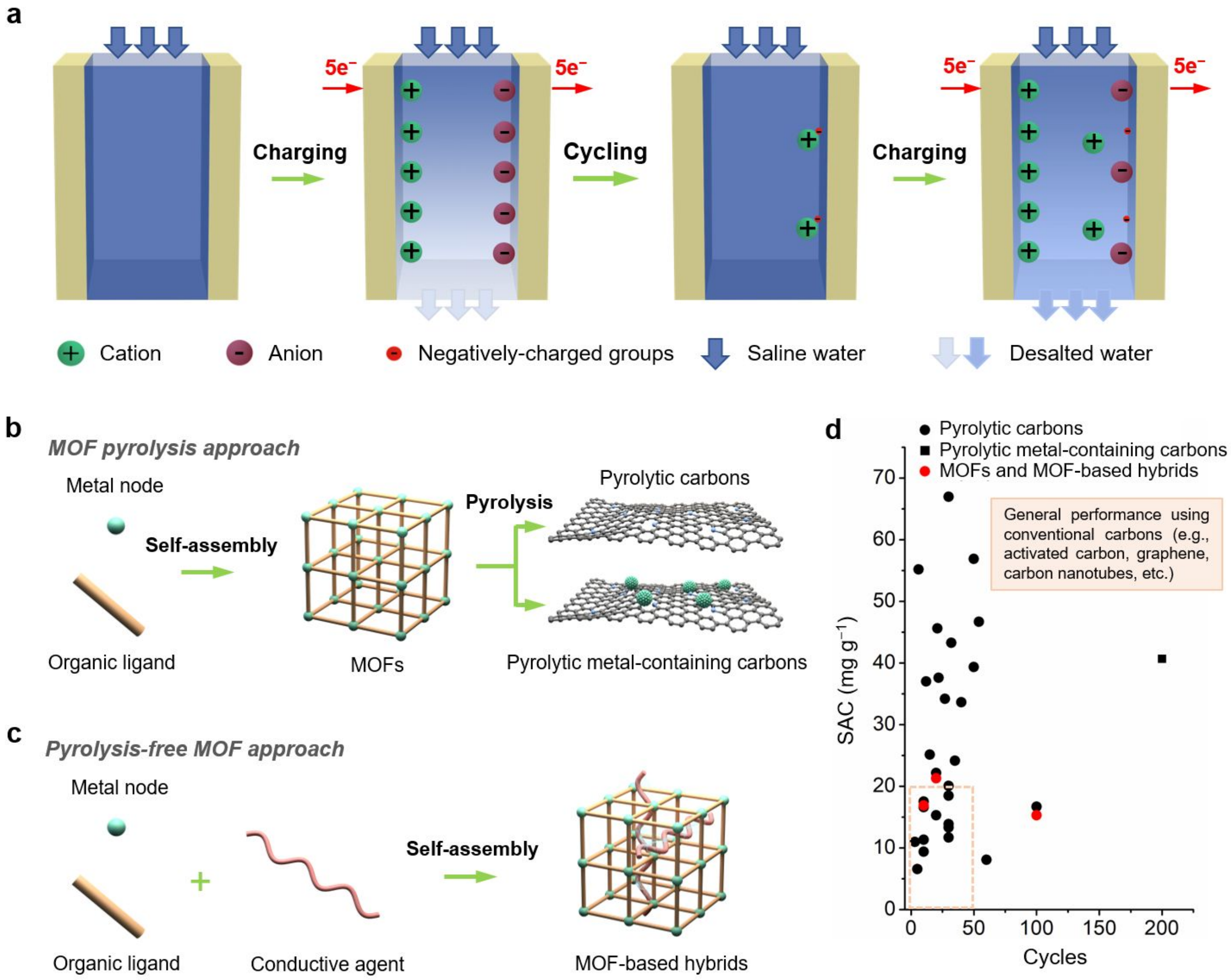

Fig. 2 Major limitations of CDI and a solution using MOF derivatives. a, Schematic of the performance

deterioration of conventional carbon materials during long-term cycling of the CDI process. **b–c**, Schematic of MOF derivatives, in which **b**) is the MOF pyrolysis approach for preparing carbons and metal-containing carbons, and **c**) is the pyrolysis-free approach for preparing MOF-based hybrids using conductive agents. **d**, Promoted CDI performance using MOF derivatives (*i.e.*, pyrolytic carbons, pyrolytic metal-containing carbons, MOFs and MOF-based hybrids) in terms of SAC and cycling stability (Ref. 18 was used for the MOF pyrolysis approach for carbons and metal-containing carbons, and Refs. 21-23 were used for the pyrolysis-free approach for MOFs and MOF hybrid materials.).

Future opportunities for MOF derivatives to expand CDI of oxygenated saline water

MOFs provide considerable flexibility to produce low-cost porous materials with various functionalities. MOF derivatives prepared by the pyrolysis or hybridization method possess good electrical conductivity that conventional MOFs do not, which results in a novel family of CDI electrodes beyond conventional carbon-based materials. We summarized the CDI performance, including SAC and cycling parameter (marked as cycles), of MOF derivatives, such as pyrolytic carbons, pyrolytic metal-containing carbons, MOFs and MOF-based hybrids (**Fig. 2d**). Typical carbons, such as carbon nanotubes, activated carbons, and graphene, mostly possess relatively low SACs (< 20 mg g^{-1}), as indicated by the dotted-line square. In addition, the cycling stability for these materials has been usually demonstrated to be < 50 CDI cycles. For oxygenated saline water, more severe performance deterioration is expected with a shortened cycling lifetime of < 20 CDI cycles. In contrast, most of the MOF derivatives exhibit larger SACs with longer cycling lifetimes. In particular, pyrolytic metal-containing carbon materials derived from MOF pyrolysis and pyrolysis-free MOFs exhibit state-of-the-art CDI performance in oxygenated saline water, exceeding the performance of the benchmark materials in terms of SAC and long-term durability for practical CDI application. Therefore, we propose that metal-containing carbon materials derived from MOF pyrolysis and pyrolysis-free MOFs may be the future direction for designing CDI materials for practical water desalination in natural (oxygenated) saline water.

However, the high production cost may be the main challenge for the large-scale implementation of MOF derivatives. Furthermore, to meet the goal of industrial application, the CDI cycles and SACs of MOF derivatives are expected to be at least 5000 cycles and >50 mg g^{-1}, respectively. Therefore, the practical application of MOF derivatives still has a long way to go. However, with the further introduction of new processing techniques and synthesis methods, the use of materials informatics to facilitate the synthesis process, and the reduction of the cost of MOF components, MOF derivatives can be further developed with significantly lower production cost, and improved CDI performance and cycling stability, which will provide new opportunities for industrial applications.

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Contributions

X.X. and Y.Y. conceived this study. X.X. drafted the manuscript, with critical revisions by L.P. and Y.Y. All the authors read and approved the final version of the manuscript.

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Competing interests

The authors declare no competing interests.

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