A Brief Review on High-Performance Capacitive Deionization Enabled by Intercalation Electrodes

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Owing to the advantages of cost-effectiveness, environmental-friendliness and high desalination capacity, capacitive deionization (CDI) has emerged as an advanced desalination technique. Recently, the ions intercalation materials inspired by sodium ion batteries have been widely implemented in CDI due to their exceptional salt removal capacity. They are able to extract sodium ions from the brine through intercalation or redox reactions, instead of electrostatic forces associated with the carbonaceous electrode. As a result, the ions intercalation materials have caught the attention of the CDI research community. In this article, the recent progress in various sodium ion intercalation materials as highly-efficient CDI electrodes is summarized and reviewed. Further, an outlook on the future development of ion intercalation electrodes is proposed.

1. Introduction

With the rapid population growth and economic development, the requirements for clean drinking water have grown tremendously, while the water consumption around the globe has increased at a rate of 4–8% per year in the last few decades. Meanwhile, a sharply growing amount of freshwater sources is polluted during the process of modelization, which would inevitably aggravate the global water crisis.[1–2] To face the challenge, great attempts have been devoted to explore efficient water treatment technologies, among which the desalination is envisioned to be the most feasible approach. Based on the working mechanism, the desalination technologies are generally divided into three broad categories: physical-, chemical-, and membrane-driven desalination techniques. Among these techniques, distillation emerges as the earliest commercial physical desalination technique. It is basically triggered by heat through physical methods and thereby fresh water is separated from nonvolatile solutes by evaporation and subsequent condensation.[3,4] The required energy largely depends on the latent heat of evaporation and the degree of heat recovery that can be achieved. The latent heat of water evaporation is two orders of magnitude larger than the minimum separation energy of thermodynamics, which makes thermal desalination technology inherently energy-intensive by compared to that of pressure-driven desalination.[5–7] Nevertheless, aiming to desalinate the highly-salty feed, heat-driven desalination is often required. Moreover, various improved versions of the distillation-based desalination have been developed including multistage flash distillation (MSF) and multieffect distillation (MED).[8,9] In order to offset the huge latent heat of evaporation, recent heat-driven efforts have shifted to the use of renewable energy sources, i.e., solar energy. The optimization of solar thermal desalination system and the application of solar heating membrane distillation (MD) have become popular in this research domain.[10–14] However, the distillation-based techniques are plagued by several obvious issues, such as high energy consumption, corrosion risks, high capital/operational costs, etc.[15,16] Membrane-based desalination technologies (e.g., electrodialysis (ED)[17] and reverse osmosis (RO)[18,19]), have rapidly developed into the most popular technologies in the desalination community due to their advantages of low energy consumption, easy regeneration, and high water quality. Among them, RO is the most widely employed and energy-saving desalination technique currently. It is based on the semipermeable membrane to selectively pass water molecules forced by pressure.[20–22] Ensentially, the application of RO accounts for 72% of the global seawater desalination capacity.[23] It is largely benefited from the high energy efficiency, which is achieved through high permeability and water-salt selective thin-film composite (TFC) polyamide membranes.[3,24] Furthermore, in order to allow water to pass through the membrane and thus produce purified water, RO requires excessive hydraulic pressure to generate the osmotic pressure of brine.[25,26] Unfortunately, current RO membranes and corresponding modules suffer from the mechanical stability that required to overcome the osmotic pressure encountered during the treatment of high salty solutions. Despite the utilization of TFC polyamide membranes represents a breakthrough in desalination technology in the past decade, inherent materials have limited further improvements in performance.[27,28] Meanwhile, one major drawback of the membrane-based desalination techniques is the regular...
replacement of the membrane component due to scaling or fouling, which would inevitably increase their operational and maintenance costs.

Compared with the above desalination technologies, electrochemical-assisted desalination technique is the most effective when desalinate the brackish water and low-salinity water. The obvious advantage is that avoid the use of either high pressure or high temperature. Capacitive deionization (CDI), as typical electrochemical desalination techniques, has become a new star in the desalination community due to its merits of high efficiency, low energy consumption and environmental benign.[29,30] Table 1 summarizes the energy consumption of various desalination processes which firmly confirms the advances of CDI. Actually, CDI is not only employed to achieve seawater desalination and ion separation, but also be applicable for manufacturing, agriculture and mining, which is thereby expected to be a cheap and sustainable technology.[31–33] The basic principle of CDI is that the ions in the feed solution would migrate to the oppositely-charged electrodes through the electrostatic force by imposing a low direct voltage (20 V), and stored within the EDL formed on the interface between the electrode and solution. After that, the ions could be released (or enriched) into an alternative water stream by simply removed or reversed the voltage, leading to the regeneration of electrode.[34] As compared to traditional desalination techniques, CDI exhibits remarkable advantages: i) Low energy consumption and high water recovery: the voltage across the electrodes of the CDI is below 2.0 V, indicating the only 0.6 KWh·m⁻³ of electrical energy is required which is significantly lower than that of ED and RO. Meanwhile, the water recovery of CDI can be reached as high as 85%, which is obviously higher than those of traditional desalination techniques (i.e., RO: ≈50%)[35–38]; ii) Environmental tolerance: differing from the RO and ED, the regeneration of CDI electrode does not require any additional chemicals, which could effectively reduce the risk of secondary pollution;[39,40] iii) Facile operation and minimum maintenance: the CDI device is easy to operate and requires minimum maintenance due to the low scaling or fouling risks. Most importantly, none expensive membrane is involved in CDI which would not bring any extra maintenance cost during the operation;[41,42] iv) Highly-efficient energy recovery: the required voltage of CDI is much lower than other electrode-driven desalination techniques.[43,44] On the other hand, the CDI could be directly supplied by some new energy sources, such as biomass energy and solar energy. Moreover, the electric energy released during the desorption process can be captured simultaneously and forwarded to the subsequent cycling.[45]

Despite many advances of CDI, challenges are remaining, such as parasitic reactions and low desalination capabilities, which have limited the practical application and further development of CDI. Actually, the CDI is effective for groundwater restoration, brackish water desalination and industrial wastewater regeneration. When dealing with highly-concentrated brine, the energy consumption would be increased, accompanied by the decrease of energy efficiency and salt removal capacity. Significantly, as an electricity-based desalination technique, the energy consumption related to CDI has an almost linear relationship with the amount of salt removal. When attempting to reduce energy consumption by introducing a low cell voltage, it would result in a very slow desalination rate and a longer operating durations. The side reactions taking place on CDI electrodes mainly include anodic oxidation reactions, cathodic reduction reactions, etc. The occurrence of side reactions would change the potential of zero charge (PZC) of the electrodes, causing an imbalanced potential distribution across the positive and negative electrodes, which would accelerate the water decomposition, and eventually sabotage the desalination performance of the CDI device. Besides, the side reactions also affect the pH value of the desalinated water (especially during long-term operations), leading to unsatisfied water quality. Most importantly, the intrinsic characteristics of the carbon materials (i.e., complex porous structure, inherent structural defects, self-adsorption, wettability limitations and adverse effects of side reactions), have resulted in insufficient desalination capacity.

| Table 1. Summary of the energy consumption of various desalination processes. |
|---|
| Technology | Electrode materials | Energy consumption | Energy recovery [%] | Permeate flux [m³ per day] | Ref. |
| RO | TFC cross-linked fully aromatic polyamide spiral wound | 4.35 KWh m⁻³ | 19.7–24.6 | [26] |
| | Asymmetric cellulose tri-acetate hollow fiber | 5.00 KWh m⁻³ | 60.0–67.0 | [27] |
| MSF | 21–58 KWh m⁻³ | 85% | [8] |
| MED | 5–6.5 KWh m⁻³ | 85% | [9] |
| CDI | CuFe@NiFe Prussian Blue | 0.376 KWh Kg⁻¹ | 74.7 | [60] |
| | MnHCF | 4.26 KWh Kg⁻¹ | 74.7 | [61] |
| | ZnFe₂O₄ | 0.76 KWh Kg⁻¹ | 74.7 | [78] |
| | P-NMO | 0.46 KWh Kg⁻¹ | 74.7 | [83] |
| | CuFe@NiFe Prussian Blue | 0.376 KWh Kg⁻¹ | 74.7 | [93] |
| | Ti₃C₂Tₓ, MXene | 0.24 KWh Kg⁻¹ | 5.44 | [10] |
of the carbon-based CDI. To address this issue, various cell architectures have been developed, involving membrane CDI (MCDI), flow-through CDI (FTE-CDI), CDI with flowable electrodes (FCDI), and hybrid CDI (HCDI), etc. Among these cell architectures, HCDI enabled by sodium ion intercalation (SII) electrode material has demonstrated ultra-high desalination capacity due to their superior desalination mechanisms (insertion or redox).

With the continuous development of CDI, there are two main ion storage mechanisms, namely, electrical double layer (EDL) ion storage and ion intercalation storage. Figure 1a draws the CDI process based on EDL mechanism. Basically, when a direct voltage difference is imposed on the two oppositely-positioned electrodes, cations and anions are separately forced toward the negative and positive electrode and hold by EDL, leading to the removal of salty ions. Afterwards, the electrode can be regenerated by either short-circuiting or applying an reverse voltage. Acturally, the EDL ion storage is the most important electrochemical process for desalination. After a potential difference is applied, ions are electrostatically trapped and capacitively stored in the diffusion layer formed in the pores of the carbon electrode. As shown in Figure 1c, under the combined action of electrochemical potential and electric field force, the anions and cations separate and move to the positive and negative electrodes in the solution, respectively. The ions are arranged on the side of the electrode/solution interface at a certain distance between the electrodes to form a dense EDL, which creates an internal electric field to balance the external electric field. The Gouy–Chapman–Stern model (GCS model) is proposed to explain the EDL ion adsorption. When the electrodes interacting with charged species, the EDLs are generated which composed of a dense layer (Helmholtz layer or Stern layer) and a diffusion layer. Therefore, the capacitance value can be expressed by the following formula

$$\frac{1}{C_{dl}} = \frac{1}{C_{st}} + \frac{1}{C_{d}}$$

$$C_{st} = \frac{\varepsilon}{4\pi d}$$

$$C_{d} = \frac{\varepsilon}{\lambda_{d}} \cdot \cosh \left( \frac{Z \cdot \Delta \phi d}{2} \right)$$

Where $C_{dl}$ is the EDL capacitance, $C_{st}$ is the Stern layer capacitance, and $C_{d}$ is the diffusion layer capacitance. $\varepsilon$ is the dielectric constant in the solution, $d$ is the thickness of the Stern layer, $\Delta \phi d$ is the voltage difference of the diffusion layer, $\lambda_{d}$ is the Debye length, and $Z$ is the number of ion charges. In order to improve the storage performance of EDL ions adsorption, researchers have invested massive energy to focusing on electrode materials with high adsorption capacity and sustainable ability. These characteristics are usually related to materials with high specific surface area, resonable pore size distribution, remarkable electrical conductivity and excellent chemical inert.

Despite the ion storage mechanism based on the principle of EDL is the most common phenomenon in CDI, recent outcomes have figured out that ion intercalation mechanism

![Figure 1. Schematics of CDI process based on a) EDL ion storage and b) ion intercalation storage, the working mechanism of c) EDL ion storage, and d) ion intercalation storage.](image-url)
is more conducive to improve the desalination capacity. As shown in Figure 1b, it involves the utilization of intercalation electrodes (mainly containing transition metals or conductive polymers) to collect ions from brine. The ion storage mechanism involves trapping ions to the crystallographic location of the intercalation electrodes. As shown in Figure 1d, under the action of an external electric field, the ions are attracted to the electrode/solution interface, and then enter the bulk of intercalation electrode. This process is fundamentally different from the EDL charging process that occurs in traditional carbon electrodes. Depending on the volume expansion and structural reversibility of the intercalation material, wider gap sites will produce higher cycle stability, greater ion storage capacity (higher charge storage capacity) and faster kinetics (i.e., the diffusion of ions in the host material).[32,51,52] These are due to that such electrodes have been expected to achieve significant salt adsorption capacity and definitely the highly ion selectivity.

In 2014, Lee et al. pioneered the asymmetrical HCDI configuration that utilizes Na0.7MnO2 as the SII electrode (negative electrode) and AC as the chloride ion adsorption electrode (positive electrode).[66] During the desalination process, sodium ions are chemically inserted into the NMO electrode instead of being captured by the EDL, while chloride ions are stored in the EDL formed on the surface of the AC electrode. In these “battery” materials, the ions can be chemically stored within their lattice, which is fundamentally different from the electroosmosis process that occurs at the surface of the carbon electrodes. As a result, the HCDI system has demonstrated a high desalting capacity of 31.2 mg g−1 at 1.2 V in a 580 mg L−1 NaCl solution, which has realized significant improvement compared to that of the traditional CDI system (71 mg g−1).[55] Since then, various SII electrodes were proposed, many of which were initially explored in the context of energy storage, such as FeFe(CN)6(PB),[54] Na2Ti3O7 (NTO),[55] NaTi2(P2O7) (NTP),[56] NaV2(PO4)3 (NVP),[57] Na0.7CoO2 (NCO),[58] Na0.7MnO2 (NMO),[59] polyaniline (PANI)-tube-decorated with Prussian blue analogues (PB) nanocrystals (PB/PANI composite),[60] MnHCF,[61] MoS2/rGO[62] and Ti3C2T-xMxene[63] etc.

Owing to the superior desalination capacity, the SII materials have attracted great interest in the CDI community, while the desalination capacities of these materials are greatly improved. Meanwhile, the sodium intercalation electrodes are expected to offer high charge efficiencies since the side reactions (such as anode corrosion in CDI) can be effectively restricted. Moreover, extensive studies have featured that the SII based CDI demonstrates the impressive charge storage capacity and energy-saving desalination capacity in both low and high-concentrated stream. The emergence of SII materials has greatly expanded the application range of CDI, which can not only be used for desalination, but also be extended to do water repair applications, such as the removal of heavy metals,[64,65] valuable elements (such as: lithium),[66,67] ion separation,[68,69] and water disinfection,[70] etc.

This review mainly highlights the recent progress of SII materials for CDI-related applications and provides a general understanding of their performance and advantages brought by their characteristics. Beyond that, the challenges and prospects of the SII electrodes are discussed as well.

2. Sodium Ions Intercalation Materials

In intercalation materials-based CDI systems, sodium ions are inserted into specific (nonspecific) interstitial positions or atomic planes of the electrode material. Therefore, an ideal intercalation electrode material is expected to have large ion storage capacity (to ensure sufficient desalination capacity), large gap sites (to reinforce cyclic stability) as well as fast ion storage kinetics (to promote ion diffusion). Typically, SII exhibits high crystallinity and ordered structure. In terms of the intercalation ability, most SII are capable of affording the intercalation of cations, such as Li+, Na+, K+, Mg2+, and Ca2+, etc., while a few SII, such as Mxenes, enable to be inserted by both anions and cations instantaneously. To classify the SII, various methods have been suggested, depending on the dimensions (1D, 2D, and 3D) and the characteristics of the crystal structure. In this article, the SII is discussed by chemical compositions, that is, transition metal oxides (TMO or NaTMO, TM = Mn, Ti, Fe, Ni, Co, etc.), iron pyrophosphate, prussian blue analogues, transition metal dichalcogenides and MXene. TMO have been widely investigated in sodium ion removal due to their diverse structures and easy preparation. Both iron pyrophosphate and prussian blue analogues have an open frame structure, providing abundant directions to accommodate ions. Meanwhile, they have large space for ion adjustment, which is suitable for the adsorption and separation of multivalent ions. Moreover, TMD and MXene are subjected to insert both cations and anions.

2.1. Transition Metal Oxides

Benefiting from the highly stable, tunable redox potential, abundant active site and variety, the TMO, including MnO2, TiO2, V2O5, NaMnO2 (NMO), NaCoO2 (NCO) and Na2TiO2 (NTO) etc., are extensively studied as highly-efficient electrode material for CDI.

Titanium dioxide (TiO2), as a typical pseudocapacitive material (Ti4+/Ti3+ in neutral solution), exhibits various advantages such as large capacity, rich resources, nontoxicity, good stability, and environmental friendliness,[71] which make TiO2 an excellent candidate for CDI. The TiO2 crystals exist in three natural form including anatase, brookite and rutile and several synthetic forms (such as TiO2 (B) (monoclinic) and TiO2 (H) (square), etc., relating to the different spatial arrangement of TiO6 octahedron). Previous studies have demonstrated that the crystal structure of TiO2 has a significant impact on the electrochemical/desalination behavior of TiO2. For example, Yang et al. have carried out a comparative study on the relationships between CDI performance and crystal structure of TiO2 (anatase and rutile). The results manifested that the anatase TiO2 structure is more favorable as electrode material for CDI, exhibiting a much higher desalination capacity (41.8 mg g−1 in 500 mg L−1 NaCl solution at 10 mA g−1) than that of the counterpart TiO2 electrode (rutile, 28.8 mg g−1).[72]

MnO2 is viewed as a low-cost and environmental-friendly electrodes material possessing high electrochemical activity due to the presence of active Mn3+/Mn4+ redox pair.[73] Among more than 30 polymorphisms of MnO2, tunnel structured
manganese oxides (TuMOs), constructed from MnO₆ octahedrons with various sizes and shapes, is known to have superior desalination performance. Moreover, the large tunnels in TuMOs contain positively charged cations, which could stabilize the crystal structure. Previous studies have concluded that open tunnel structures associated with TuMOs could offer excellent cation exchange properties. As a result, it would be favorable to energy storage devices. In 2018, Byles et al. systematically investigated the influence of the TuMOs’ tunnel sizes and crystal structure on their desalination performance as electrode for HCDI, as shown in Figure 2. Four types of TuMOs are investigated as HCDI electrodes, namely α-MnO₂ (2 × 2 tunnels), manganese oxide with todorokite crystal structure (Tod-MnO₂, 3xn tunnels), 2xn-MnO₂ and hybrid-MnO₂ (combination of 2xn and 3xn tunnels). After evaluation, the desalination capacities of α-MnO₂, Tod-MnO₂, 2xn MnO₂, and Hybrid-MnO₂-based HCDI are 22.1, 23.3, 27.8, and 27.3 mg g⁻¹, respectively.

Despite the high chemical stability, superior specific capacitance and high density of active surfaces of TMOs electrodes, the electrical conductivity is unsatisfied. To address this issue, Jaoude et al. proposed a simple hydrothermal strategy to realize the controlled synthesis α-MnO₂ on the surface of graphene (G), as shown in Figure 3a. In this configuration, Na⁺ are inserted into the α-MnO₂/G electrode by electrochemical reaction, while Cl⁻ is adsorbed into the graphene electrode. As illustrated in Figure 3b, the α-MnO₂/G-2 demonstrates the highest specific capacity of up to 375 F g⁻¹ among all samples, while the G/α-MnO₂/G-2-based HCDI system exhibits the highest salt removal capacity of 29.5 mg g⁻¹ at 1.2 V due to the maximum synergistic effect between G and high-crystalline α-MnO₂ (the neat G sheets mainly contribute to electrical conductivity and prevent the agglomeration of individual nanoparticles).

It is firmly believed that the desalination performance of TMOs/C nanocomposite is depending on the dispersion and particle size of TMOs. However, the weak interaction between the TMOs and carbon and inherently non-uniform distribution in the carbon matrix could results in severe particle aggregation. Luo et al. proposed a facile approach to prepare homogeneous Fe₂O₃@C composites via solvothermal carbonization by employing terephthalic acid and ferric chloride as raw materials. It is found that most Fe³⁺ are captured by H₂BDC through electrostatic action and then coordinated with a large number of carboxyl groups. This strong synergy ensures that these metal nodes are evenly distributed in the organic framework, making Fe₂O₃ uniformly present in the carbonized matrix. The results have demonstrated that the Fe₂O₃@C-5d displays a high specific capacitance of 115.6 F g⁻¹, which is significantly higher than the Fe₂O₃/GO (50.3 F g⁻¹), and NFe-Carbon (38.8 F g⁻¹) due to the uniform distribution of Fe₂O₃ as well as the superior pseudocapacitance of Fe₂O₃. Furthermore, all as-prepared composite are employed as electrode of HCDI to remove Pb²⁺. As shown in Figure 4c, it is explored that the Fe₂O₃@C-5d possess the highest Pb²⁺ adsorption capacity of 830.17 mg g⁻¹ in 500 mg L⁻¹ Pb(NO₃)₂ solution, which further evidenced that the well-dispersion of Fe₂O₃ in the carbon matrixes has a significant impact on its desalination performance.

Beside TMOs, the binary metal oxides (BMOs) have also attracted great attentions due to their good electronic conductivity, low diffusion resistance and high theoretical capacity. For instance, ferrites are deemed as protential electrode candidate for CDI originating from its high chemical stability, abundance in nature, low manufacturing cost, as well as their tunable of the composition. Yu et al. synthesized well-crystallized zinc spinel ferrite (ZFO) nanoparticles and utilized as electrode...
The ZFO-based HCDI exhibits ultra-high desalination capacity of 136.6 mg g$^{-1}$ at current density of 30 mA g$^{-1}$ and initial brine concentration of $100 \times 10^{-3}$ m and superior cycling performance (no obvious deciliation in 200 cycles). Laterly, Li et al. synthesized hollowed sea urchin-like NiCo$_2$O$_4$ nanocrystals as cathode for HCDI.[79] As verified in Figure 5a,b, the NiCo$_2$O$_4$ based HCDI system possess high salt removal capacity of 44.3 mg g$^{-1}$ and charge efficiency of 98.7%. Meanwhile, the selective removal performance of the NiCo$_2$O$_4$ based HCDI between various cations (K$^+$, Na$^+$, and Mg$^{2+}$) are also investigated. The results imply that K$^+$ is more easily inserted into the crystal layer of NiCo$_2$O$_4$, while the ionic radius has priority (K$^+$ (331 pm) < Na$^+$ (358 pm) < Mg$^{2+}$ (428 pm)). Beyond that, the salt removal capacity as high as 42.9 mg g$^{-1}$ can be achieved for the NiCo$_2$O$_4$ based HCDI after 20 cycles ($\approx 97.5\%$ capacity retention) in Figure 5c, suggesting an excellent longterm stability of the device.

2.2. Sodium Transition Metal Oxides

Sodium manganese oxide (Na$_x$MnO$_2$, NMO, $0 < x \leq 1$) exists in multiple crystal forms, i.e., 2D layered structure ($0.34 < x \leq 1$) and 3D tunnel structure ($x \leq 0.44$).[80,81] Importantly, the sodium ions diffusion and storage behavior is highly dependent upon the structure of Na$_x$MnO$_2$. In order to clarify the influence of the NMO's crystal structure on their desalination performance, Lv et al. prepared NMO with various structures (P2 group (P-NMO) as tunnel-type NMO (T-NMO) and O3 group (O-NMO) as layered NMO) and used as electrode material for HCDI.[82] In Figure 6, it is found that the salt removal capacity of NMO electrodes follows the order of P-NMO > O-NMO > T-NMO, since the T-NMO possesses the lowest desalination capacity due to its limited theoretical capacity for reversible Na$^+$ intercalation/deintercalation. In terms of O-NMO, the Na$^+$ accommodation at the octahedral site leads to a higher direct conduction activation energy of Na$^+$ between adjacent octahedral sites. Further, Na$^+$ would overcome the diffusion barrier by migrating to the tetrahedral interstitial site, resulting in enhanced desalination capacity. Besides, since Na$^+$ in P-NMO is adjusted at prismatic sites, it can directly migrate between prismatic sites through an open square path without passing through intermediate sites with lower diffusion barriers, which is the origin of the highest desalination capacity of the P-NMO.

Na$_x$Co$_2$O$_2$ (NCO), composed of the multiple CoO$_2$ plate and sodium ion layers, is another research focus in CDI because
Figure 4. a) Schematic illustration of the HF-inducing fabrication process of Fe₂O₃@C. b) CV curve of Fe₂O₃@C-5d, NFe-Carbon, c-MIL101, Fe₂O₃/GO, c) salt removal capacity of various electrodes. Reproduced with permission.[76] Copyright 2019, Elsevier.

Figure 5. a) Salt removal capacity (mg g⁻¹) and current density (A g⁻¹) with respect to cell voltage (V), b) charge efficiency, and c) cycling performance of NiCo₂O₄ at 1.2 V. Reproduced with permission.[79] Copyright 2020, The Royal Society of Chemistry.
of its stable and open framework structure for sodium ion diffusion. According to studies, the P2-type NCO could have various sodium content with different Na\(^+\)/vacancy structure. As a result, the sodium content could greatly affect the electrical conductivity and the arrangement of sodium vacancies, which ultimately become an important factor for its desalination performance as HCDI electrodes.

Na\(_x\)Ti\(_n\)O\(_2\)\(_n+1\) (NTO) with layered or tunnel structure has been widely used in SIB relating to its advantages of low cost, low toxicity, and easy preparation. Li et al. reported the synthesis of carbon@Na\(_4\)Ti\(_9\)O\(_20\) (C@NTO) core–shell nanotubes as a novel electrode for hybrid capacitor deionization (HCDI).

Furthermore, the desalination mechanism was confirmed through CV measurements, which could be expressed as follow (peaks locating at -0.22 and -0.38 V, corresponding to the reaction between Ti\(^{4+}\)/Ti\(^{3+}\))

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Na_4Ti_9O_{20} + 9Na^+ + 9e^- \leftrightarrow Na_{11}Ti_9O_{20} \tag{4}
\]

In addition to solo ions intercalation, Yang et al. proposed a new concept of dual-ions electrochemical deionization (DEDI) system that utilized NMO and BiOCl as a negative and positive electrode to achieve high-performance sodium and chloride removal through generate faradaic reaction, as shown in Figure 7a,b.[85] The DEDI system delivers a stable and reversible desalination capability of 68.5 mg g\(^{-1}\) and a charge efficiency of up to 95.8% at a current density of 100 mA g\(^{-1}\), which demonstrates an excellent desalination performance. Furthermore, the XRD tests of the electrodes before and after the desalination process were performed to get a better insight into the desalination mechanism of the DEDI, as shown in Figure 7c,d. The diffraction peaks of BiOCl became weak, while the peaks of bismuth metal emerged, indicating that the BiOCl is partially converted to Bi after chloride extraction. Meanwhile, the diffraction peaks of BiOCl reappear after salination, which indicates the recovery of BiOCl. On the other hand, the NMO electrode undergoes a similar process while its diffraction peaks are shifted to small-angle during desalination process and shifts back during salination, suggesting the reversible intercalation reaction of NMO.

Afterwards, Li et al. developed another type of DEDI system employing Na\(_{1.1}\)V\(_3\)O\(_7.9\) (NVO)@reduced graphene oxide (rGO) as a SII electrode and Ag@rGO as chloride ion intercalation electrode,[86] which realized an outstanding desalination performance that the salt removal capacity reaches up to 82.2 mg g\(^{-1}\) due to the unique band structure of NVO as well as the conductive network structure offered by rGO.

To date, TMOs have been intensively studied as electrode material for CDI-related applications (including ACDI, HCDI, and DEDI) because of their facial preparation process and structural adjustability. However, two main challenges remain for TMOs-based CDI systems, the relatively low desalination capacity, and low cycle stability, which have become the bottleneck for their practical applications.

### 2.3. Polyanionic Phosphates

Sodium iron pyrophosphate (Na\(_4\)FePO\(_4\)) with triclinic crystal structure constructed by sharing angles between metal polyhedral (FeO\(_6\) and FeO\(_4\)) and pyrophosphate P\(_2\)O\(_7\)
groups\cite{87,88} has received intensive attention in sodium ion storage due to its advantages of abundant sodium ion sites, low manufacturing cost, high thermal (chemical) stability and environmental friendliness. Kim et al. firstly introduced Na$_2$FeP$_2$O$_7$ into HCDI as the sodium removal electrode,\cite{89} and acquired a high desalination capacity of 30.2 mg g$^{-1}$ with desalination rate up to 0.081 mg g$^{-1}$ s$^{-1}$.

As a typical NASICON material, Na$_3$V$_2$(PO$_4$)$_3$ (NVP) enjoys high theoretical capacity of 117.6 mAh g$^{-1}$, yet the intrinsic poor conductivity has hindered its sodium storage applications. Recently, great efforts have been devoted to improve the conductivity of NVP by constructing a carbon layer on the surface of NVP. Zhao et al. developed three different type of carbon-coated NVP (NVP@C) with spherical, flower-like and linear shaped structures via solvothermal method,\cite{57} and further utilized as cathode for DEDI (AgCl as anode). The linear structure of NVP@C forms an ion conductor network relating to the best desalination performance. Figure 8b exhibits the CV curve of NVPW-AgCl device in 1.0 m NaCl with a scan rate of 1.0 mV s$^{-1}$. There are two distinct characteristic peaks at 0.50 and 0.36 V, which are ascribed to the extraction and reintercalation of sodium ions into the NVP electrode. As predicted, the NVPW@C|AgCl-based DEDI realizes the high desalination capacity (102.1 mg g$^{-1}$) with outstanding cycling performance (reduced from 124.0 to 98.0 mg g$^{-1}$ after 50 cycles).

In addition to crystalline polyphosphates, amorphous polyanionic phosphates is another potential candidate for HCDI.\cite{90} Dai et al. synthesized graphene-coated mesoporous amorphous FePO$_4$ nanospheres (FePO$_4$@RGO) through a one-step hydrothermal method\cite{91} for HCDI. The FePO$_4$@RGO displays a mesoporous network structure, which could promote the penetration of the electrolyte into the electrode and subsequently facilitates the diffusion of sodium ion. As a result, the desalination capacity and rate of the FePO$_4$@RGO-based HCDI are increased by 60% (50.13–85.94 mg g$^{-1}$) and 180% (0.079–0.24 mg g$^{-1}$ s$^{-1}$), while the energy consumption was reduced by 25% comparing to that of FePO$_4$.

### 2.4. Prussian Blue Analogs

The Prussian blue analogs (PBAs), a type of transition metal (iron, manganese, nickel, etc.) ferrous cyanide, has attracted much attention due to its unique open frame structure and large ion channel that allows sodium ion insertion/extraction. The PBAs can often expressed as A$_x$M[M(CN)$_6$]$_y$·zH$_2$O (0 < x ≤ 2), where A represents alkali metal ions, such as Na; M refers to transition metals, such as Fe, Co, Mn, etc.\cite{92} In 2017, Gou et al. synthesized single crystal FeFe(CN)$_6$ (PB) nanoparticles and used as negative electrode (activated carbon as the positive electrode) for HCDI.\cite{54} The PB-based HCDI displays an excellent desalination ability (up to 101.7 mg g$^{-1}$) with ultrafast ion removal rate. In order to further improve the desalination performance, the PB was coupled with reduced graphene oxide to construct a PB@NPG composite. As a result, the PB@NPG provides an improved desalination capacity of 120.0 mg g$^{-1}$.

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**Figure 7.** a,b) Schematics of working mechanism of dual-ions electrochemical deionization device, c) XRD patterns of the initial BiOCl, its state of chloride extraction, and state of chloride recovery. As-prepared BiOCl (black), chloride extraction (red), the chloride recovery (blue), # BiOCl, *Bismuth, d) XRD patterns of the as-prepared NMO, its state of sodium extraction, and state of sodium recovery. Reproduced with permission.\cite{85} Copyright 2017, The Royal Society of Chemistry.
This is attributed to the two-electron reaction of FeFe(CN)$_6$ and the large interstitial sites and tunnels of PB.

Despite the high capacity enabled by bimetallic PBAs, such as CuFe PBA, FeFe PBA, and MnFe PBA, their cycling stability is not satisfied yet. Zhao et al. proposed a feasible strategy by wrapping PBA in a strong shell (CuFe@NiFe) to improve its structural stability.$^{[93]}$ The desalination results suggest that CuFe@NiFe PBA-based HCDI promise an improved desalination capacity (54.3–71.8 mg g$^{-1}$) and cycling stability (8% reduction after 50 cycles). The enhanced desalination performance could be ascribed to the following factors: i) the unique core–shell heterogeneous structure facilitates the ion transfer and subsequently accelerates the sodium ion insertion; ii) the core–shell heterostructure effectively prevents the structural change during repeat ion intercalation and deintercalation and further improve the long term stability of the CuFe@NiFe PBA-based HCDI. Figure 9 shows the desalination and regeneration mechanism of CuFe@NiFe PBA. During the desalination process, the sodium ions are chemically inserted into the electrode, while the Fe$^{3+}$ and Cu$^{2+}$ in the CuFe PBA were reduced to Fe$^{2+}$ and Cu$^+$. In the regeneration process, sodium ions were deintercalated from the electrode, while Fe$^{2+}$ and Cu$^+$ were oxidized into Fe$^{3+}$ and Cu$^{2+}$. Thus, the overall desalination process is essentially controlled by the redox pair of Fe$^{3+}$/Fe$^{2+}$ and Cu$^{2+}$/Cu$^+$. PBAs has also been utilized towards the application of selective removal of certain ion species by using the cation hydration radius difference between ions. Singh et al. developed an symmetric two-compartment CDI, which is composed of two NiHCF electrodes with the same mass.$^{[94]}$ It has been found in CDI and other electrochemical technologies that it possess a size-based preference for cations. In this experiment, the mixed solution contains monovalent ions (Na$^+$) and divalent ions (Ca$^{2+}$, Mg$^{2+}$). Figure 10a depicts the operation of intercalated-compartments of a symmetrical desalination tank. The inset in the figure schematically illiminates the size-based repulsion of cations by the NiHCF lattice. Figure 10b realizes the concentration change of monovalent ion solution in the cyclic CDI mode, illustrating that the solution concentration is utimately relating to intercalation/de-intercalation process. It further stands out that the monovalent cations are preferentially adsorbed due to the limitations of NiHCF lattice size. Moreover, it is found that in the case of long-term selectivity, the NiHCF electrode would preferentially remove monovalent ions (Na$^+$) rather than divalent ions (Ca$^{2+}$, Mg$^{2+}$). In practical applications, the preferential removal of Na$^+$ is critical to maintain the quality of irrigation water since the high concentrated Na$^+$ would have negative impact on soil and plant growth.

Actually, cations are more important than anions in ion separation because of their higher recovery value, higher toxicity and activity. Among various cations, the removal performance of monovalent cations is generally better than that of divalent or multivalent cations. This is because multivalent cations have complex electrochemical properties and larger hydration radius than monovalent cations. Thus, intercalation materials are still in their infancy in the use of ion separation and ion removal, and more effort is required.
2.5. Transition Metal Dichalcogenides

Owing to the excellent electrochemical and mechanical properties, layered 2D TMDs has attracted a lot attentions in the field of energy storage. Typically, TMDs enjoys a layered structure with one layer of the transition metal atoms is sandwiched between two layers of sulfur atoms. It can be expressed as MX\(_2\) (where M is the transition metal (i.e., Mo, Ti, V, etc.), and X represents the sulfur group element (S, Se, Te)). Srimuk et al. developed a molybdenum disulfide/carbon nanotube (MoS\(_2\)/CNT) composite material and used as electrode of HCDI. The results shows that sodium ions can be inserted...
between MoS₂ layers, leading to incensement of the interlayer distance and the change of electronic structure, while the salt removal capacity of 25 mg g⁻¹ could be achieved in 500 × 10⁻³ M NaCl concentration.

2.6. MXenes

Recently, MXene has rapidly become a major research focus in the energy storage community due to its hydrophilic surface, large interlayer distance, and high electric conductivity.⁹⁷ Srimuk et al. first introduced Ti₃C₂-MXene into the CDI community electrode,⁹⁸ yet only 13 mg g⁻¹ desalination capacity was achieved, since the serious stacking of the multilayered Ti₃C₂-MXene.

Despite the great improvements achieved for the MXene-based CDI systems so far, the easily stacked property resulted from the weak van der Waals forces between layers has become the limitation of its further development. To address this issue, Bao et al. synthesized porous MXene by vacuum freeze drying approach.⁹⁹ By this treatment, the restack of MXene nanosheets can be alleviated. As a result, the accessibility of electrolyte in the pores is improved which favors to increase the overall capacitance. Beyond that, the porous Ti₃C₂Tₓ structure forms 3D network, which provides a multidimensional ion diffusion path for the ions. Subjecting to desalination, the porous

Figure 11. a) The schematics of asymmetric CDI system (AC//NaOH-Ti₃C₂Tₓ). b) Conductivity profiles of AC//NaOH-Ti₃C₂Tₓ, AC//Ti₃C₂Tₓ, and AC//AC in 100 mg L⁻¹ NaCl solution. Reproduced with permission.⁹⁹ Copyright 2020, American Chemical Society.

Figure 12. a) SEM images of Ti₃C₂Tₓ after ultrasonic delamination, b) TEM images of Ti₃C₂Tₓ, c) CV curves at different scan rates, d) desalination capacity at different current densities. Reproduced with permission.⁹⁹ Copyright 2020, Elsevier.
Table 2. Summary of the desalination performance of various electrodes.

| Electrode materials | Structure | $R_s/R_{ct}$ | Potential [V] | Current [mA g$^{-1}$] | Concentration [mg L$^{-1}$] | SAC [mg g$^{-1}$] | Stability | Theoretical capacitance [mAh g$^{-1}$] | Ref. |
|---------------------|-----------|--------------|---------------|-----------------|--------------------------|-----------------|----------|-------------------------------|------|
| Na$_4$Mn$_9$O$_{18}$ | 1.2       | 580          | 31.2          | 40–50           | [48]                     |
| FeFe(CN)$_6$(PB)    | 125       | 1000         | 120.0         | 77% after 100 cycles | 180  [54]                  |
| Na$_4$Ti$_9$O$_{20}$| 1.72/2.26 | 1.4          | 1000          | 66.14           | >200  [55]                  |
| NaTi$_2$(PO$_4$)$_3$| 100       | 2500         | 105           | 95% after 100 cycles | 133  [56]                  |
| NVP@C               | 100       | 1000         | 102.1         | 79% after 50 cycles | 117.6 [57]                 |
| Na$_0.7$CoO$_2$     | 2.6/1.7   | 1.2          | 500           | 34.8            | 66% after 50 cycles        | 125  [58]                  |
| Na$_2$MnO$_2$       | 3.46/22.99| 1.2          | 250           | 10.7            | [59]                       |
| PB/PANI composite   | 500       | 10 000       | 133.9         |                 | [60]                       |
| MnHCF               | 1         | 1000         | 19.1          | 72% after 280 cycles | [61]                      |
| MoS$_2$/rGO         | 1.4       | 500          | 34.2          |                 | [62]                       |
| Ti$_3$C$_2$T$_x$-Mxene| 1.2      | 1170         | 12            | 94.67% after 50 cycles | [63]                  |
| Anatase TiO$_2$     | 10        | 500          | 41.8          | over 50 cycles   | [72]                       |
| TuMOs               | 1.2       | 878          | 27.8          |                 | [74]                       |
| $\alpha$MnO$_2$/G   | –/2.3     | 1.2          | 100           | 29.5            | 98% after 4 cycles         | [75]                      |
| Fe$_2$O$_3$@C       | 2.2/6.3   | 1.0          | 100 (Pb$^+$)  | 830.17          | 93% after 10 cycles        | [76]                      |
| ZnFe$_2$O$_4$       | 30        | 5850         | 136.6         | 66% after 200 cycles | 1000.5  [78]              |
Ti$_3$C$_2$T$_x$ electrode demonstrates the salt removal capacity of 118 mg cm$^{-3}$ (corresponding to 45 mg g$^{-1}$) in 10 000 mg L$^{-1}$ NaCl solution at voltage of 1.2 V).

Actually, MXene owns a highly negatively charged surface of $-\text{OH}$, $-\text{O}$, and $-\text{F}$ groups, which may become a cationic selective cathode material reducing the effect of co-ion impaction. However, HF-etched MXene suffers from a high ion diffusion barrier and low ion storage capacity due to the small interlayer spacing. In alkaline solution, cations are easily and spontaneously intercalated into Mxene which is favor for expanding the interlayer spacing, leading to activation of the transport of charged ions. Chen et al. assembled an asymmetric CDI system, in which Na$^+$ intercalated Ti$_3$C$_2$T$_x$ (NaOH-Ti$_3$C$_2$T$_x$) and AC is employed as the cation selective cathode and anode, respectively. Most significantly, the NaOH-Ti$_3$C$_2$T$_x$ with negatively charged surface groups ($-\text{OH}$, $-\text{O}$, $-\text{F}$) enable to reduce the co-ion discharge effect. Thanks to the reduction of the expulsion of the co-ion effect and the synergistic effect, the asymmetric CDI system acquires a desalination capacity of 12.19 mg g$^{-1}$ and charging efficiency of 82.6%. Corresponding desalination mechanism is discussed in Figure 11a. After NaOH treatment, the interlayer spacing of Ti$_3$C$_2$T$_x$ increased from 9.8 to 12.1 Å, which is beneficial to the diffusion and storage of sodium ions between the layers. Figure 11b shows the conductivity distribution of three CDI systems in 100 mg L$^{-1}$ NaCl solution, manifesting the advances of AC $||$ NaOH-Ti$_3$C$_2$T$_x$ configuration.

As time goes by, Yu et al. prepared Ti$_3$C$_2$T$_x$ MXene using LiF/HCl-etching strategy and further used as the electrode for CDI. The results show that Ti$_3$C$_2$T$_x$ change from multiple layers to few layers or even a single layer after ultrasonic layering, as shown in Figure 12a,b. The CV curve of Ti$_3$C$_2$T$_x$
electrode presented in Figure 12c demonstrated a distorted rectangle shape, proving the presence of Faraday pseudocapacitance beyond EDL capacitance. Figure 10d shows that the desalination capacity is very stable at any certain current density, suggesting the good cyclic stability of \( \text{Ti}_4\text{C}_7\text{O}_{12} \) electrode. Meanwhile, the desalination capacity of the MXene-based CDI system is significantly enhanced (up to 68 mg g\(^{-1}\)) with excellent long-term stability.

### 3. Outlook and Summary

The last 5 years have witnessed the rapid development of SII electrode material for CDI related applications. The salt removal performances of various SII electrode materials are summarized in Table 2. The development of the SII electrode has brought about a major breakthrough in the desalination capacity of CDI related systems due to the superior ion intercalation desalination mechanism. Despite the great advances of intercalation electrodes-based CDI systems, several obstacles remain: i) Stability. As can be seen from Table 2, the salt removal capacity decay of intercalation electrodes, such as Na\(_{x}\)CoO\(_2\), α-MnO\(_2\)/G and ZnFe\(_2\)O\(_4\), etc., is pretty serious after few cycles. Although great efforts have been devoted to improving the desalination capacity of the electrodes, the cyclic stability of the systems is seldomly studied, which can be a serious problem for its practical applications. In addition, toxic by-products could be released from the electrode during long-term operation. Therefore, long-term test, together with the water quality monitoring should be conducted for all intercalation electrode-based systems so as to ensure their reliability; ii) Conductivity. Most of the SII electrodes suffer from problem of low conductivity, which would lead to a relatively low desalination capacity. Actually, the desalination capacity of most metal compounds (such as TMO, Na\(_{x}\)TMO\(_2\)) below the respective theoretical capacitance (referring to Table 2) due to its poor conductivity. On the other hand, the poor crystallinity reduces the capacitance either. One of the most available methods in terms of improving the conductivity of the metal compounds is to reconstruct the bulk material into an ultrathin structure, alternatively, the carbon-metal compound composite should be another solution. For example, Li et al. have demonstrated that the Na\(_{x}\)Ti\(_4\)O\(_{10}\)/GO composite electrode has achieved the desalination capacity of 41.8 mg g\(^{-1}\) which is much higher than that of pure Na\(_{x}\)Ti\(_4\)O\(_{10}\) electrode (22.0 mg g\(^{-1}\)).\(^{[102]}\) Besides, the electrical conductivity of a metal compound is ultimately depending on its nanostructure, the size of the nanosheets, and the interconnectivity between the nanoparticles. Therefore, more research attentions are needed to improve the cycling stability and the conductivity of the sodium intercalation electrode materials to meet the practical requirement for desalination. iii) Balance. At present, most intercalation materials are limited to the adsorption of cations, and there are few studies on intercalation materials that adsorb anions (such as Mo\(_2\)S\(_2\) and MXene). As a result, the unbalanced development of cathode and anode materials would hinder the further development of CDI technology. As such, more researches on cathode intercalation materials are needed. At the same time, according to different ion adsorption characteristics, an electrode material database including structure/functional design strategies can be established to comprehensively sort out the characteristics of materials, desalination performance and advantages in different ion adsorption. iv) Mechanism. Currently, great efforts have been dedicated to explore and prepare novel intercalation materials aiming to strengthen the desalination performance of CDI, few investigations are focusing on the development of advanced technique to monitor the desalination behavior of intercalation electrodes. Fortunately, with the aid of in situ characterization technology, such as in situ XRD, FTIR, and TEM, in-depth studies are presumably employed to further understand the structure-desalination activity relationship of intercalation electrodes.

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### Conflict of Interest

The Authors declare no conflict of interest.

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