Research progress of capacitive deionization technology

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Abstract. Capacitive Deionization (CDI), a recently developed water treatment technology, has been superior to traditional desalination processes such as reverse osmosis (RO) in terms of high environmental friendliness, simple operation, and low energy consumption. This paper reviews the progress of research into CDI technology with focus on electrode materials and factors affecting CDI such as voltage and plate spacing. It also discusses existing problems and predicts the future development direction of this technology.

1. Introduction
With the rapid development of the economy, water consumption has been rising markedly. In terms of natural resources the problem of water supply has become one that concerns the majority of the world. Developing water treatment technology is for this reason of crucial significance. Desalination, as an important part of water treatment, is drawing growing interest from researchers worldwide for its ability to effectively remove contaminated ions from seawater, brackish water and even groundwater thereby purifying water that may later be used. So far, the most commonly accepted desalination methods include the thermal process, membrane process, ion exchange, and combinations of these methods. Membrane desalination, typically reverse osmosis (RO) and nanofiltration, is disadvantageous for the need of rigorous pretreatment, high energy consumption, low water recovery, short membrane life, and emission of large volumes of high-salinity concentrated water. Thermal desalination, typically multi-effect distillation, multi-stage flashing and mechanical vapor recompression, is deficient for high energy consumption, high equipment cost, and proneness of equipment and pipelines to fouling and corrosion.

Capacitive deionization (CDI), also known as electrosorption, is currently a hotspot of desalination research for its low energy consumption, long electrode life and zero secondary contamination, displaying vast development potential in seawater desalination and advanced wastewater treatment. This paper reviews the progress in the research of CDI desalination technology with a focus on the reactor configuration, progress in electrode material, and factors affecting CDI.

2. Technical principle
The basic principle is that under an electric field, an electric double layer (EDL) forms in the micropores inside the electrode, that is to say, a double layer structure is produced near the interface between the electrode and the solution [1, 2]. During electrosorption, the solution flows between charged porous electrodes. Under the action of electrostatic interaction, ions with opposite charges migrate onto the
surface of the electrode and are fixed and stored in the EDL. Cations are stored in the negative electrode while anions are stored in the positive. The anions and cations are removed from the solution through “electrosorption”, thus desalinizing the solution. After a period of time, when the internal pores nearer the electrode material are saturated, the adsorbed ions can be released from the electrode material and the electrode regenerated by removing or reversely connecting the power supply. As such, a full CDI cycle includes both adsorption and desorption (Fig. 1).

Figure 1. Schematic representation of CDI: a) adsorption process; b) desorption process [3].

3. CDI configuration

3.1. Traditional CDI

Traditional CDI is composed of two current collectors and a water flow channel. The former causes electrons to migrate between two porous electrodes and be removed via capacitive adsorption. The latter provides a channel for water to flow through. This configuration is simple, but is not suitable for treating industrial brine waste due to its low desalinization efficiency, low energy efficiency and high proneness to fouling.

In a real-world application, traditional CDI is challenged by: a) “coion effect” during desalinization. That is, while adsorbing counter ions (ions with opposite polarity), electrodes will also repel coions (ions with the same polarity), thus reducing the current efficiency and ion adsorption and increasing energy consumption; b) during reverse voltage desorption, ions already released into concentrated water are very likely to be adsorbed again to the counter electrode, thus severely compromising the circulation effect of CDI; and c) the process features intermittent operation, low overall desalinization efficiency, and complex control. To solve these problems, a series of new reactor configurations, such as membrane capacitive deionization (MCDI), flow-electrode capacitive deionization (FCDI), and hybrid capacitive deionization (HCDI), have been developed recently.

3.2. MCDI

Membrane capacitive deionization (MCDI) was first introduced by Lee et al. in 2006, in a paper which incorporates a cation exchange membrane (CEM) before the negative electrodes and an anion exchange membrane before the negative electrode, as shown in Fig. 2. The presence of the ion exchange membranes prevents ions with the same charge from approaching the electrode, thus avoiding coion effect. This method greatly improves the efficacy of CDI by improving the charge efficiency and optimizing the ion adsorption parameters. It also improves the desorption efficiency by preventing the ions from being adsorbed again into the opposite electrode during desorption [4].

Zhao et al. compared the adsorption capacity and energy consumption between MCDI and CDI at voltage 1.5 to 3.5 V, using graphite fabric as the electrode material. At a voltage of 3.0 V, the adsorption
capacity of CDI was 4.33 mg/g while that of MCDI was 5.62 mg/g. Using CDI, the maximum unit energy consumption was 7.38 Wh/g while under MCDI, it was approximately 1.54 Wh/g, only a quarter of that under CDI [5].

![Diagram of MCDI and FCDI system](image)

**Figure 2.** Schematic representation of MCDI and FCDI system

3.3. **FCDI**

The electrodes used in both CDI and MCDI are fixed. Hence, the total adsorption capacity for one adsorption cycle is restricted by the adsorption capacity and electrode quality of the electrode material. Furthermore, both processes are noncontinuous and the electrodes have to be regenerated after they have adsorbed to saturation.

In 2013, Jeon designed a CDI process utilizing flow-electrodes (FCDI). As an improvement on MCDI, this new method prepares carbon electrode material into a slurry, which is circulated through the electrode chamber between the electrode and ion exchange membrane. An external electric field is applied to drive the ions in the raw salt solution to migrate through the ion exchange membrane before the ions are eventually adsorbed onto the pores of the suspended carbon slurry electrodes, thus removing the salt ions. One of the merits of FCDI is its continuous operation and desalination of high-salinity brine. When investigating the relationship between the salt concentration and desalination rate of flow-electrode mother liquor, Yang et al. discovered the potential use of high-concentration brine such as seawater as a flow-electrode electrolyte [6].

4. **Electrode material**

Selecting the right electrode material is key to the performance of CDI. An ideal electrode material has all the following features: a high specific surface area, good electric conductivity and iron migration, superior hydrophilicity, and high electrochemical stability. So far, activated carbon (AC), graphene (GE), carbon nanotubes (CNTs), carbon nanofibers (CNFs), and carbon aerogels (CAGs) are already widely used in CDI processes.

4.1. **AC**

Activated carbon (AC) is one of the most commonly used electrode materials [7-10]. Choi et al. fabricated a CDI assembly from AC with specific surface area of 1 260 m²/g. Under optimized operating conditions, the assembly showed a high average desalination rate of 77.8% at a voltage of 1.5V and flow rate of 20 mL/min [11].

Despite the many merits of AC, compared with other carbon materials, the low desalination efficiency and poor regeneration ability of AC associated with its low electric conductivity has made it unsuitable for direct, large-scale use as a CDI electrode. Over the recent years, however, many strategies have been developed to improve the desalination performance of AC. These mainly include
modifications by KOH, HNO$_3$, and H$_2$O$_2$. Wang et al. compared the CDI performance of KOH-treated AC and untreated AC. The experiment revealed that after treatment by KOH, a large amount of hydroxyl functional groups were added on the surface of AC. The presence of hydroxyls greatly increased the hydrophilic behavior of the treated AC. At an operating voltage 2.5 V and initial electric conductivity 1500, the desalinization efficiency of 5% KOH–AC for NaCl is 23% higher than untreated AC.

4.2. CNTs
In a carbon nanotube (CNT) carbon atoms are arranged into a one-dimensional tubular structure with a maximum tube diameter of 100 nm. The hexagonal geometry of carbon causes the electrons to be localized allowing the charge to move freely. For this reason, CNTs have superior optical and electric performance [12-15]. However, as the preparation of these tubes is a complex, costly process and the tubes themselves are hardly dispersible, when used as a CDI electrode, they are generally compounded or pretreated with other materials. Lee et al. discovered that after being acidified by a mixture of nitric acid and sulfuric acid, the CNTs became shorter and the closed structures at the end were opened. The number of oxygen-containing functional groups also increased, making the tubes more hydrophilic. As a result, the capacitance increased from 17.8 F.g$^{-1}$ to 55.8 F.g$^{-1}$. The desalinization rate at voltage 1.2 V also nearly doubled. Hou et al. managed successfully prepared a composite of multi-walled carbon nanotubes (MWCNTs) and polyvinyl alcohol (PVA) and used it in CDI for the first time. The results showed that compared with commercial AC, this material has higher hydrophilicity, a higher effective surface area, more mesopores, higher ion moving efficiency, lower energy consumption, and better adsorption performance.

Recently, atomic layer deposition (ALD) has been used to deposit TiO$_2$ nanoparticles on acid functionalized MWCNT films. Feng et al. reported upon this method, using it as a new way for high-efficiency preparation of electrodes with different properties. At an initial NaCl concentration of 40 mg·L$^{-1}$, its desalinization capacity was 5.09 mg·g$^{-1}$.

4.3. CNFs
Carbon nanofibers (CNFs) are a fibrous carbon material [16-20]. Through electrostatic spinning in conjunction with high-temperature carbonization, the diameter and surface area of the fibers can be easily and effectively controlled. The resulting nanofibers are self-supporting materials. Hence, they can be used as CDI electrodes without any binder, thus retaining the most primitive pore channel structure of the material. As CNFs have a low specific surface area, multi-channeled CNFs with desalinization capacity 1.5 times higher than untreated CNFs can be prepared by adding polymethyl methacrylate (PMMA) into the polyacrylonitrile (PAN) spinning solution. Wang et al. prepared a porous nanofiber with integral two-dimensional macrostructure by combining electrostatic spinning with polyvinylpyrrolidone (PVP) template method, which largely increased the ratio of mesopores in the material. Compared with the desalinization performance of untreated CNFs, the adsorption capacity and charge efficiency increased by 1.87 and 1.51 times, respectively. Barakat et al. compounded a composite multi-channeled CNF by mixing PAN and PMMA in different proportions (0%, 25%, 50%). The results showed that as the PMMA content increases, so does the specific surface area and adsorption capacity of the CNFs. For electrodes containing the maximum PMMA content of 50%, the desalinization rate was 89.04%.

4.4. CAGs
Carbon aerogels (CAGs) are a monolithic structure composed of 3-30 nm particles and nanoscale porous structures (smaller than 100 nm). These gels feature light mass, high porosity, and specific surface area ranging from 400 to 1 000 m$^2$. Their easy preparation and controllable pore channel structure have made them widely present in battery applications and desalinization.

Chen et al. developed a CAG with different microstructures. Optimization of the molar ratio between resorcinol and the catalyst revealed that the CAG has the best desalinization performance at a molar ratio 200 (with electrosorption capacity of 25.45 mg/g). In the CAG-loaded MnO electrode prepared by
Cheng, the number of micropores increased remarkably, with pore size typically at 0.3 – 0.4 nm. After loaded with CAG, the adsorption capacity of the electrodes for 1 000 mg/L NaCl solution increased from 18.71mg/g to 23.84mg/g.

4.5. GE
Graphene (GE) is characterized by a unique sandwich structure--which facilitates the quick transfer of ions--with a specific surface area of up to 2 600 m$^2$/g and theoretical electric conductivity of up to 7 200 S/cm. However, the actual specific surface area of GE is far lower than the theoretical value (merely 80 m$^2$/g or so), since its electric conductivity and pore structure are impaired by the lattice deficiency, interlayer stacking and agglomeration associated with redox reactions during preparation. In order to prevent interlayer stacking and agglomeration, researchers have tried to prepare three-dimensional GE by modifying the GE process equipment or GE composite electrodes via intercalation to increase the interlayer spacing of GE, reducing interlayer stacking and agglomeration, and increasing the specific surface area of the electrode.

Wang et al. obtained unagglomerated, mesopore-containing GE by adding FeCl$_2$ solution into GE dispersion solution, thermally treating it to form Fe$_3$O$_4$ nanoparticles on the GE sheet, and finally washing away the Fe$_3$O$_4$ nanoparticles with hydrochloric acid. The results showed a capacitance of 128 F.g$^{-1}$ and desalinization capacity of 10.3 mg.g$^{-1}$ (water inflow 300us.Cm$^{-1}$, voltage 1.6 V), compared with 54 F.g$^{-1}$ and 6.5 mg.g$^{-1}$ for the GE prepared without the addition of FeCL$_2$ solution. Xu et al. solved the adjacent layer contact and sheet agglomeration problem related to GE by adding nitrogen into graphene oxide (GO) through simple thermal treatment. It was also the first time that nitrogen-modified GO was used in CDI. After addition of nitrogen, the specific surface area of the electrode more than doubled that of pure GE. Its adsorption performance was 25% higher, additionally.

4.6. MOF/non-carbon materials
Metallic organic framework (MOF) is a crystal material with cyclic porous networks prepared through self-assembly by dispersing organic ligands and transition metal ions into different solutions and then mixing them together. The wide variety of transition metals and organic ligands has determined the wide variety and structural controllability of MOF. Furthermore, MOF also has a large specific surface area and pore volume. After carbonizing MOF, the resultant respective MOF-derived carbon also features a large specific surface area and pore volume, controllable pore structure, and heteroatom doping. This method has displayed considerable application potential with respect to energy storage, environmental protection, and gas separation, which has drawn much attention over the past years.

Wang et al. prepared a bimetal zeolitic-imidazolate framework (BMZIF) using Zn$^{2+}$ and Co$^{2+}$ as the central ions, and then obtained a BMZIF-derived porous carbon material (BNPC) via carbonization and acid etching. Electrochemical analysis revealed a high specific capacity, low resistivity, and good stability for the BNPC. When used as a CDI electrode, a desalinization rate of up to 16.63 mg/g was achieved at voltage 1.4 V, initial salt concentration 500 mg·L$^{-1}$, and flow rate 40 mL·min$^{-1}$.

To summarize, some electrode materials used in CDI are listed in Table 1.

5. Factors affecting the performance of CDI

5.1. Voltage
As the voltage applied to the ends of the electrode represents the adsorption driver for CDI desalinization, the desalinization performance of CDI is also dependent on the voltage applied. Many reports have proved that the salt removal rate is positively related to the voltage applied, yet excessive voltage can lead to water electrolysis. Experiments by Zhao et al. yielded the optimal operating parameters for CDI to be voltage 1.2-1.6 V, initial NaCl concentration 200-1000 mg·L$^{-1}$, and flow rate 10-40 mL·min$^{-1}$. The researchers discovered that the desalinization rate increases with increasing voltage applied at any flow rate and initial salt concentration until the voltage reaches 1.6 V and decreases when the voltage increases to 2V.
Table 1. Some Electrode material used in CDI [24-27]

| Electrode material | Surface area(m²/g) | Voltage(V) | Feed(mg/L) | Capacity(mg/g) |
|--------------------|--------------------|------------|------------|---------------|
| ACC-Ti             | 1890               | 1.0        | 5.9        | 4.5           |
| CNT-PVA            | 208                | 1.2        | 58.5       | 13.07         |
| PCNF               | 583                | 1.2        | 450        | 9.4           |
| AN-CFs             | 905.3              | 1.2        | 1000       | 16.56         |
| S-NPC              | 844                | 1.2        | 40         | 15.5          |
| CPC                | 952                | 1.2        | 1500       | 14.2          |
| N-HMGS/HGH         | 337.7              | 1.4        | 2500       | 32            |
| GO-PCNF            | 474                | 1.2        | 100        | 7.8           |
| HPG                | 1226               | 1.2        | 500        | 31.9          |
| NPCSs              | 1640               | 1.2        | 1000       | 14.91         |
| rGO/TiO2           | 0.8                | 300        | 9.1        |
| PANI/AC            | 1.2                | 250        | 3.15       |
| NG-CNFS           | 1.2                | 1000       | 14.79      |
| GO-CNT/AC          | 1.5                | 800        | 21.3       |
| MOF               | 898                | 1.2        | 1000       | 20.5          |

5.2. Electrodes
As discussed above, the electric conductivity, specific surface area, and pore size distribution of an electrode material all affect the desalinization performance of CDI. The size and wettability of the electrode also makes a difference. Lee et al. discovered that better adsorption capacity can be achieved via surface modification to change the contact angle.

5.3. Property of the salt solution
The property of the salt solution plays a critical role in the desalinization performance of CDI. In a salt solution containing various different ions, the selectivity of the electrode surface is determined by the charge, initial molar concentration, and hydration radius of the ions. Gabelich et al. discovered that electrode materials differ in pore size and structure, as well as ionic hydration radius. The selectivity of an electrode with small pores is higher for low valence ions than for high valence ions, since the pore size of the electrode is between the hydration radii of the two (0.4 nm for low valence ions and 0.6–0.7 nm for high valence ions). Hou et al. found that the dominant driver for the adsorption of high valence ions is the charge rather than the hydration radius. For ions with the same valence, however, the main determinant is their hydration radius. For example, the hydration radius of K⁺ is smaller than that of Na⁺, and it can be seen that K⁺ is more readily selected. Also, the concentration of the treatment solution will also affect the electroosorption process of CDI. Theoretically, the higher the solution concentration and the smaller the solution resistivity, the larger the effective working voltage at the ends of the electrode and, consequently, the larger the adsorption capacity of the electrode. Mossad et al. increased the concentration of NaCl solution from 500 mg/L to 3 500 mg/L, and found that as the solution concentration increases, the adsorption capacity of the electrode for NaCl increases, but the desalinization rate reduces.

5.4. Inflow rate
Huang et al. demonstrated that adsorption rate reduces with an increasing flow rate when the flow rate is 10 mL/min. The reason is that it is that the larger the flow rate, the shorter the residence time of ions in the solution between the plates. An excessive flow rate will also impact the EDL formed on the electrode surface, making the EDL unstable and thus reducing the adsorption capacity. However, excessively low flow rate could also affect the ion transport between the ions and the electrode surface during adsorption/desorption.
6. Conclusions
Remarkable progress has been made in CDI with respect to the R&D and modification of electrode materials, optimization of the structural assembly, control of desalination parameters, and size of the process equipment. However, further improvements are still necessary. These would include: a. Further optimization of the mass transfer efficiency of the electrosorption system. To solve this problem, the first step should be development and research around electrode material and electrosorption reactor structure to minimize energy loss during electrosorption; b. Integration of electrosorption with other water treatment techniques. For example, fouling can affect the desalination effect and even lead to deterioration of the system. Pretreatment is also critical; c. Long-term stable operation tests. Currently, many researches are in the laboratory stage. Ongoing operation tests are necessary to verify the high throughput operation of electrosorption reactors and put them into industrial application within the shortest time. Overall, CDI is a promising water desalination technology that can achieve high yield water recovery via its many merits. However, industrial scale application of CDI still waits upon intensive study and joint effort among research workers throughout the field.

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