ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

Research Progress of Heteroatoms-Doped Carbon-Based Materials for Capacitive Deionization

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Abstract

The shortage of fresh water resources has become one of the most concerned issues in the world. Various water treatment technologies have been developed to desalinate seawater, and capacitive deionization (CDI) has attracted wide attention as a new electro-adsorption desalination technology. However, electrode materials are an important factor affecting the performance of CDI. In recent years, considerable research progress has been made in the rational design and manufacture of heteroatom-doped carbon materials used as CDI electrode materials. In this paper, the latest research progress of heteroatom-doped graphene, carbon nanofibers and activated carbon is systematically reviewed. In addition, the challenges and possible future development in the field of CDI are briefly prospected for researchers to design carbon-based electrode materials for practical application.

Keywords

Capacitive Deionization; Heteroatoms-Doped; Carbon-Based Materials.

1. Introduction

Water is the substance on which people live. While people begin to pay attention to oil and energy, the world water crisis has also begun to seriously restrict the economic development of countries around the world. Fresh water resources in the world are not only extremely short, but also extremely uneven in geographical distribution. China, Brazil, Canada, India, the United States, Russia, Indonesia and other countries account for about 60% of the global fresh water resources. At present, 1.5 billion people in more than 80 countries around the world are always facing the dilemma of insufficient fresh water supply, and more than 300 million people in 26 countries live in a state of extreme water shortage. With the continuous growth of the world population, regional conflicts, ecological degradation, diseases and deaths against water resources will become more frequent and serious. It is estimated that in 2025, nearly 3 billion people in the world will live in a state of water shortage. 97% of the water resources on the earth are seawater resources. Desalination of seawater to obtain fresh water is a potentially effective way, which has attracted wide attention of researchers at home and abroad. At present, the existing desalination technologies mainly include reverse osmosis technology, electrodialysis technology, multistage flash evaporation technology and ion exchange technology.[1]Wait. However, these desalination technologies still have many shortcomings. For example, reverse osmosis technology must use high-pressure pump to realize water-salt separation through high driving energy, and its concentrated water chamber will also bring secondary pollution; Multi-stage flash evaporation technology needs to consume a lot of heat energy to realize the vaporization and separation of water, thus losing more energy; The ion exchange law needs complicated and expensive regeneration process, and its production cost is high. Moreover, because its regeneration needs strong acid and alkali, it is bound to destroy the environment and cause pollution. Electrodialysis technology must use extremely high voltage to force ions to move

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

directionally to achieve separation, which will bring extremely high energy consumption and cause water decomposition and low production efficiency. Therefore, the research on new desalination technology with Simple operating equipment, energy saving and Low harmfulness has become the most urgent demand in the world.

Capacitive deionization (CDI) is a new desalination technology, which has the characteristics of low cost, low working voltage, low energy consumption, Low harmfulness and environmental friendliness.[2]. Its working principle is similar to that of supercapacitor, and it is an electro-adsorption desalination technology based on the theory of electrochemical double layer (EDL) capacitance. The primitive idea is that by applying an external voltage to the porous adsorption electrode, an electrostatic field is formed between the two electrodes, so that the electric ions are forced to move to the electrode with opposite charges under the action of the electrostatic field, so as to achieve the purpose of removing the electric ions in the solution. When the adsorbed ions are close to saturation, reverse voltage or short circuit voltage is connected to both ends of the electrode to release the ions into the solution to realize electrode regeneration.[3]. Therefore, as shown in fig. 1,[4]Ions can be separated and removed by directional migration in electrostatic field.

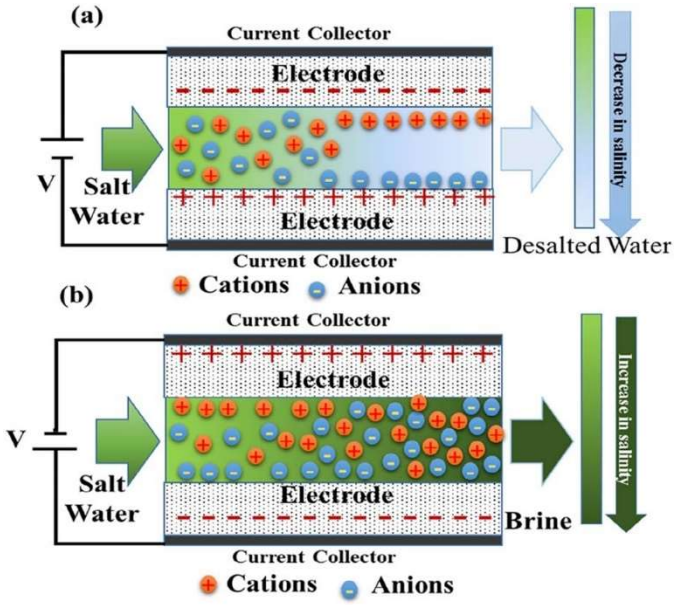

Figure 1. Schematic diagram of conventional CDI system adsorption step (a) regeneration step (b)[4].

CDI technology was first put forward in 1960s, but it didn't attract much attention at that time. Later, As a salt ion removal technology, CDI has developed from slow to fast, and its mechanism was attributed to the adsorption of EDL ions.After 20 years of development, great progress has been made in the study of seawater desalination driven by electric energy.

Desalination performance is restricted by many conditions and influenced by various parameters, Including the structure, assembly method and porous material characteristics of CDI battery. CDI battery consists of the structure of the test device, the material for absorbing salt ions and the length between two plates. The operating conditions include the voltage at both ends of the electrode, the velocity of the salt solution, the temperature of the test space, the concentration of salt ions, the acidity and alkalinity of the salt solution and different types of salt ion solutions. The characteristics of electrode materials include specific capacity, conductivity, pore size and ion available surface area[5].

Porous materials that adsorb ions at both ends are an important aspect affecting the adsorption performance of CDI. After a long period of development, some porous materials that have been studied in many aspects are carbon materials, such as graphene, carbon nanofibers and activated

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

carbon. Graphene, as a new type of two-dimensional carbon material, is a commonly used electrode in the field of CDI because of its good conductivity, large specific surface area, high specific capacitance and good chemical stability. However, graphene sheets have strong π-π interaction, usually irreversible agglomeration, and their surfaces are hydrophobic, which leads to the specific surface area and desalination performance far below their theoretical values. Carbon nanofiber is a kind of fibrous one-dimensional carbon nanomaterial, which can be obtained by electrospinning. Carbon nanofibers have attracted wide attention because of their unique continuous interconnected nanostructures and high conductivity. However, the salt adsorption capacity of CDI battery based on traditional carbon nanofibers is small, which is mainly due to its low specific surface area, poor wettability and unsatisfactory pore structure. AC has good aspects of lots of raw materials, less investment in production and low in price , which makes it a common electrode material in CDI field. However, because activated carbon is a kind of microporous carbon-rich material, it is difficult for the solution to infiltrate into the micropores of activated carbon during CDI application, which will inevitably reduce the utilization rate of activated carbon pores, and then affect the CDI performance of activated carbon. Generally speaking, an ideal electrode material should have the following characteristics: (a) larger specific surface area, which can provide more adsorption sites; (b) Appropriate pore size distribution to absorb more ions; (c) High conductivity, which is conducive to the transmission of charges; (d) Excellent hydrophilicity, which is beneficial to water adsorption; (e) High electrochemical stability. However, the number of positive and negative ions extracted by carbon materials from salt solution is certain, and the same ion effect[6]will make the adsorbed positive and negative ions re-enter the solution because of limited adsorption, so as not to adsorb as many salt ions as possible.

Therefore, some chemical or physical treatments on carbon materials have attracted the attention of many researchers to change the characteristics of the original materials and impose more abilities conducive to ion adsorption. In these treatment methods, some atoms are doped into carbon materials by physical or chemical methods to change the properties of the materials themselves, so as to obtain some abilities conducive to ion adsorption. It is found that this heteroatom doping method has a great effect on improving the adsorption of ions on carbon materials. The results show that nitrogen doping can enhance the conductivity and hydrophilicity of carbon-based materials, while phosphorus doping can fine-tune their charge and spin distribution, thus optimizing their electrochemical properties.[7]. The larger size of S is beneficial to adjust the electronic properties of carbon, which can easily polarize electron pairs, generate charge positions and significantly improve the electrochemical properties.[8]. Co-doping of N, P and S will produce more defects due to the synergistic effect between them, which will enhance the charge delocalization on C atom. Doping metal atoms can change the carbon material itself, make it have more defects, reduce its own resistance, make it have better conductivity, and at the same time make the originally hydrophobic carbon material hydrophilic and improve its wettability. The resulting defects can increase the contact area of the carbon material itself with the solution so that it can contact more ions, which will further promote the process of ions entering the carbon material from the aqueous solution.

2. Heteroatoms-doped Carbon Materials

2.1 Heteroatoms-Doped Graphene

Qian et al.[9] fabricated nitrogen-doped self-shrinking porous 3D graphene material (NSPG) by adding pyrrole monomer to graphene oxide. Compared with the macroporous structure of traditional 3D graphene, NSPG has more mesopores and nanopores, thus obtaining a great usable surface area and providing more favorable places Ion storage. Therefore, in the NaCl solution of 100mg L-1 before adsorption, the electrode showed a high desalination capacity of 13.16mg g-1. Experiments show that it is an utilizable and feasible path to enhance CDI ability by adjustingthe distribution of pore size of carbon materials by nitrogen doping to obtain larger specific surface area.

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

Xu et al.[10] reported a novel nitrogen-doped graphene sponge (NGS) by directly freeze-drying GO and then annealing in NH3 atmosphere. Because of its large specific surface area and pore volume, low charge transfer resistance, excellent pore structure and higher specific capacity, NGS was used as a CDI electrode for the first time.In 1.2 V, NaCl salt solution with 500 mg L-1 before adsorption, the electrode showed a high electric adsorption capacity of 21.0 mg g-1, which was about 1.4 times and 4.6 times that of graphene sponge GS(14.6 mg g–1) and original graphene PG (4.5 mg g-1), respectively.

Zhang et al.[11] assembled the core-shell composite with incomplete graphene oxide shell into bulk membrane by compression molding method, and then heat-treated it in NH3 atmosphere, and successfully constructed an independent membrane electrode (F-N-GPM) with network porous structure. The interconnected spherical shells provide more active sites for ion adsorption, and the doping of nitrogen further improves the hydrophilicity of the graphene-based electrode. Therefore, the electrode showed excellent desalting performance in NaCl salt solution, and the desalting capacity was 21.8 mg g-1. Even after 10 adsorption and desorption cycles, the desalting capacity remained at 95%. In addition, the electrode also showed certain desalination ability for Various salt ions, indicating their potential application in different saline solutions.

Liu et al.[12] synthesized a novel three-dimensional reduced graphene oxide (NHGH-0.2) by one-step hydrothermal treatment. NHGH-0.2 has a layered porous structure due to the synergistic effect of nitrogen doping and chemical etching, with a specific surface area of 874.9 m2 g-1. When the current density is 1 A g-1 in 6 M KOH solution, the electrode shows a specific capacitance of 303.1 F g-1, and after 1000 charge-discharge cycles, the capacitance remains at 92.8% of the initial cycle, indicating that it has good electrochemical cycle stability. in NaCl solution of 100mg L-1 before adsorption and voltage of 1.6 V, the electro-adsorption capacity of the electrode is 22.14 mg g-1.

Jing et al.[13] developed a novel reduced graphene oxide aerogel (NFGA) electrode material for CDI by combining the nitrogen-supported framework into the graphene layer. The introduced nitrogen support frame provides a more stable structure for the graphene layer and improves its electrochemical performance. The excellent specific capacitance of NFGA electrode was 235.3 F g−1 in 1.0 M NaCl solution at 5 mV s−1. After 500 cycles at 1.0 A g-1, the GCD curve remained at 98.3% of the initial cycle, indicating that it had good electrochemical cycle stability. In 1.2 V, 500 mg L−1 NaCl salt solution, the electro-adsorption capacity of the electrode is 25.76 mg g-1. After 50 cycles of adsorption and desorption, the regeneration curve has no obvious change and attenuation, indicating that the cycle stability is good. The more stable graphene structure not only enhances the desalination capacity of graphene, but also enhances its electrode regeneration ability.

Jiang et al.[14] designed a new type of nitrogen-doped porous graphene for CDI. The three-dimensional porous structure of the material provides more electrochemical active sites for ion adsorption. The three-dimensional porous structure of the material provides more electrochemical active sites for ion adsorption. Nitrogen doping improves the conductivity and reduces the charge transfer resistance, thus improving the electrochemical performance. In NaCl salt solution of 500 mg L-1 before adsorption and the voltage of 1.4 V, the electrode has an electro-adsorption capacity of 45.04 mg g-1 and a maximum salt adsorption rate of 3.0 mg g-1 min-1. In addition, after 500 cycles of adsorption and desorption, the desalting capacity is almost not attenuated, indicating that the electrode has good renewable performance.

Han et al.[15] synthesized a three-dimensional graphene (PGA) with adjustable pore size as CDI electrode. Due to the 3D layered porous structure and highly cross-linked network of graphene sheets, PGA has a large specific surface area (567.14 m2 g-1). After 30 cycles, the desalting capacity of the electrode is maintained at 20.93mg-1g-1 in NaCl salt solution of 500 mg L-1 before adsorption at a voltage of 1.6 V, indicating that the electrode has good cycle stability.

Mamaril et al.[16] reported a novel three-dimensional reduced graphene oxide (3D NFrGO) co-doped with nitrogen and fluorine by one-step hydrothermal method for removing heavy metal Cu(II). The doping of nitrogen and fluorine improves the conductivity of NFrGO, and also causes more vacancy

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

defects in electrode materials, thus improving the electrochemical performance. In 100 mg L-1 Cu(II) salt solution and at a voltage of 1.2 V, the salt adsorption capacity of the electrode is 52.4 mg g−1, and the ion removal rate is as high as 95%. In terms of metal ion removal, the desalination capacity of this electrode material is higher than that of other reported carbon-based materials.

2.2 Heteroatoms-Doped Carbon Nanofibers

Luo et al.[17] successfully synthesized an interconnected nitrogen-doped carbon nanofiber (LPCNF) with layered porous structure.This unique structure provides effective accessible surface area for ion adsorption and increases active sites. In addition, the doping of nitrogen improves the hydrophilicity of the material, adjusts the electronic structure and enhances the adsorption capacity of ions. The electrode achieved a maximum desalination capacity of 68.11 mg-1 g-1 in NaCl salt solution with 500 mg L-1 before adsorption and a voltage of 1.6 V. In addition, after 50 desalting cycles, the electrode still maintains 93.4% electrostatic adsorption capacity, which shows that the electrode has good cyclic regeneration performance.

Chen et al.[18] successfully embedded iron nanoparticles into carbon nanofibers through simple electrostatic spinning technology and then high temperature annealing, which was the first time that iron nanoparticles were applied to the anode of CDI. The existence of iron nanoparticles improves the capacity of the electrode, and the special structure of carbon nanofibers reduces the dissolution of iron nanoparticles in the reaction process, thus having good stability. Due to the synergistic effect of electric double layer and pseudo-capacitance, the electrode showed excellent electro-adsorption capacity (82.5 mg g−1) and rapid adsorption rate (20.4 mg g−1 min−1) during desalination. At the same time, after 30 cycles of adsorption and desorption, the desalination capacity of the electrode remained at 93% of the initial capacity. At present, there are few reported CDI anode materials, which will provide feasible ideas for the future development of CDI anode materials. Cyclic stability is also an aspect that we need to focus on in the practical application of CDI, and we also need to focus on how to build a reasonable structure to enhance the renewable ability of carbon-based electrode materials.

Gao et al.[19] reported a new type of sulfur and nitrogen co-doped carbon nanofibers (SCNF) by a simple co-electrostatic spinning strategy, followed by high-temperature heat treatment. The electrode is composed of disordered stacked nanofibers and co-doped with sulfur and nitrogen atoms, which shows excellent capacitance deionization performance and cycle stability. The electrode has a desalination capacity of 29.5 mg g-1 in NaCl salt solution of 500 mg L-1 before adsorption at a voltage of 1.4 V. After 23 desalination cycles, the desalination performance is almost unchanged. DFT calculation also shows the synergistic effect of co-doping strategy on enhancing the desalination capacity of Na and Cl ions.

2.3 Heteroatom-Doped Activated Carbon

Liu et al.[20] fabricated nitrogen-doped activated carbon (NAC) for the anode of CDI by high-temperature heat treatment of the mixture of activated carbon powder (ACP) and melamine. NAC shows a larger specific capacitance than ACP, and its conductivity is improved. In 50 mmol L-1 NaCl salt solution, at a voltage of 1.2 V, the electro-adsorption capacity of the electrode is 15.73 mg g-1. After 50 cycles, the retention rate of desalting capacity of the electrode can still be maintained at 79%, indicating that the electrode has good cycle stability. In addition, in the long-term CDI test, NAC anode shows stronger oxidation resistance, which also shows that the electrode can be recycled for a long time.

Zhao et al.[21] designed pyrrole-derived nitrogen-doping activated carbon (PPyN AC) by in-situ polymerization of pyrrole monomer with AC, followed by high-temperature carbonization, and used it as CDI electrode to capture rare earth elements in aqueous solution for the first time. After CDI test, the electric adsorption capacity of PPyN-AC electrode for La(III) is 23.66 mg g-1 within 25 minutes. It is worth noting that PPyN-AC electrode can selectively capture La(III) from the quaternary system

ISSN: 2414-1895 DOI: 10.6919/ICJE.202505_11(5).0025

of La(III, Fe(III), Ca(II) and Na(I) in aqueous solution. This selective extraction of single ion from aqueous solution shows us a new method to recover rare earth elements.

Hsu et al.[22] synthesized nitrogen-doping activated carbon (NAC) for the anode of CDI electrode through the combination of acid pretreatment and high-temperature nitrogen doping. Acid pretreatment of activated carbon is beneficial to the doping of nitrogen atoms, thus improving the electrochemical properties of the materials. The maximum electro-adsorption performance of asymmetric NAC30//AC battery is 24.7±1.6 mg g-1. After 100 cycles, NAC30//AC still maintains 40% of its maximum electro-adsorption performance. It is proved by experiments that this strategy of combining acid pretreatment with nitrogen doping provides a feasible method for promoting the development of activated carbon in CDI field.

3. Conclusion and Prospects

CDI is a new deionization technology that adsorbs various ions by applying electric power. Ions are brought into the charged porous electrode and stored in the porous structure of the electrode. The desalination performance of CDI is affected by many factors. Electrode material is the most important factor affecting the desalination performance of CDI. Carbon materials have become a research hotspot in recent years because of their simple preparation method, stable performance, low cost and environmental protection. By doping some nonmetallic elements (N, S, P, F, etc.) and transition metal elements (Fe, Co, Ni, Mn, etc.), more defects can be introduced into the carbon skeleton, and the specific surface area and specific capacity of the material can be improved, which is beneficial to the charge transfer process. Optimize its surface electronic structure, improve the hydrophilicity and conductivity of carbon materials, further promote the capacitive deionization process and improve the desalination capacity of carbon materials.

At present, the heteroatoms-doping of carbon materials is mainly nitrogen-doping. It is a promising modification method to develop monoatomic doping and polyatomic co-doping reasonably and efficiently to enhance the desalination performance of carbon-based materials. Although there are still many challenges, the exploration of carbon-based electrodes doped with heteroatoms continues. How to accelerate the development of CDI technology in different fields through the study of carbon-based electrode materials is a key issue to be studied in the future.

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