A REVIEW ON ELECTRODE MATERIALS USED IN CAPACITIVE DEIONIZATION PROCESSES FOR WATER TREATMENT APPLICATIONS

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ABSTRACT: *Capacitive deionization (CDI) is a promising technology of water desalination that is inexpensive and easy to process, used for heavy metals removal and water purification. It is considered a new method, with a convincing technique, applied for the removal of ionic charged species from aqueous solution. CDI has been extensively explored within recent years, and validated on various desalination applications due it its absorption capability of ions on a polarized surface, throughout the pores of electrodes used in CDI application. The structure of the electrodes used, which facilitates the entry ions and electron transfer rate throughout the pores, before storing the salt ions within the pores are among the important factor in determining the performance of CDI. Therefore, in this review, we critically scrutinize the electrode materials used in CDI technology. This review is crucial to understand which materials is the best for CDI improved performance.*

Key word: Capacitive Deionization (CDI), electrosorption, Porous Carbon Electrodes, Activated Carbon, Carbon Nanotubes, Carbon Aerogels, Graphite, Graphene Sponge.

1. INTRODUCTION

Capacitive deionization (CDI), which is also called electrosorption system, offers great advantages in water treatment application and desalination technology. Among its advantages are simple process, low production cost and power consumption, simplicity in the renovation and system maintenance compared to other traditional desalination techniques [1-5]. Moreover, it does not use any chemicals, environmental friendly, no membranes applied as well as easy to operate. The CDI mechanism is based on imposing the voltage (1~2 V) between the electrodes in order to force the charged ions to move towards the oppositely charged electrodes, as shown in Fig. 1. Anions the negative charge ions are removed from the water and stored in the positively charge electrode, meanwhile, cations the positive ions are stored in the negatively charge electrode. Ions can be attracted within the electrical double layers (EDL) formed between the bulk solution and electrode interface. For the next cycle, the absorbed ions can be released from the electrodes into the bulk solution, by cutting off and change the polarity of the electrodes [2].

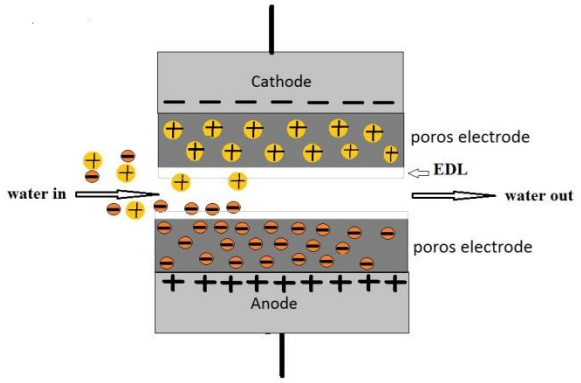

Figure.1: Schematic diagram of CDI system.

There are a numbers of factors affecting CDI performance, such as the electrode materials used, the applied voltage between the electrodes, solution conditions such as pH, flow rate and ion concentration in the solution [3]. Farmer et al. [4] compared four different voltages (0.6, 0.8, 1.0 and 1.2), and found that increased of ion application voltage increases the removal efficiency significantly. This is could be due to the increase of free electric charge on the electrode surfaces as voltage increases [5]. However, Lee *et al.* [6] tried to avoid the electrodialysis of water, and they found that applied voltage must have an upper limit. It has found for standard potential of the water electrolysis that the most effective voltage is 1.23 V, since then, most of the researchers applied a voltage of 1.2 V in their experiments [9,13,28].

Most of the research [7] reveals that the electrode used in CDI technology plays an important role towards improving its ion removal efficiency, it is reported that electrodes can be made from any electrically conductive porous material such as graphite and carbon. However, the choice of electrode materials depend on many criteria such as low cost, high degree of porosity in order to provide lower resistance path for the ions transport, high specific surface area materials to provide high absorption for the ions, and the availability of materials. In the literature, the activated carbon (AC) is so far has fulfilled the entire criteria of being a good substance for electrode. AC is a low cost material and available in abundant volume with high specific surface area which ranges from 1000 to 3000 m2/gram [8].

It is found that if the pore size of the electrode materials is greater than 10 nm, the amount of adsorbed ions remains constant. Meanwhile, for the overlapping pores size at between 0.6 and 10 nm, to some extent it would result in good adsorption capacity with EDL area [9]. The macro pore size can facilitate rapid transport of ions towards the interior side of the bulk material that can act as a reservoir of the ion diffusion buffer. This is to ensure a short distance between ion and electrode and enhanced the adsorption capacity [10]. In addition, when the average pores size is less than the minimum dimensions of ions in the solution, no absorption can occur. An ideal adsorption situation can be obtained only when the average size of the electrode pores are slightly greater than the size of ions. The actual size of an ion also plays the most important role that determines the transport phenomena in both bulk electrolyte solutions and in the course of electroadsorption processes [11].

In recent years, carbon-based materials, such as carbon cloth, carbon aerogels, carbon nanotubes (CNTs), carbon sheets, and mesoporous carbon are the usual materials used for electrode in CDI technology. Recently, most researchers are

looking for a method to increase the surface area of the electrodes as this assist the removal efficiency of ions in the CDI. Therefore, in this review, the role of electrode materials towards the performance of CDI is critically reviewed. This study provide the electrode materia'ls capacity towards improving CDI performance for water treatment applications.

2. ELECTRODE MATERIALS FOR CAPACITIVE DEIONIZATION SYSTEM

Over the past few decades, substantial research has been focused to improve the performance of CDI [12]. Since 2009, they have begun to utilize different materials as electrode in order to improve the performance and to increase the efficiency of ions removal [13]. Most of the research efforts have focused on the development of new electrode materials and the improvement of its properties [14].

Among the electrode materials that are being developed for CDI application are activated carbon [15], carbon aerogels [12,33], nanostructured carbon cloth [17], graphene [18], carbon nanotubes and nanofibers [19]. In general, for the materials to be used as electrode in CDI they should be a conductive porous material with high surface area which will result in excellent absorption of fluids as well as able to absorb and remove odor.

3. Electrode From Activated Carbon For Capacitive Deionization System

The first CDI system was a system that flew through the electrode made from an active carbon powder (ACP) [20]. The ACP is widely used as an adsorbent for color and organic impurities. Even though, before the CDI system was introduced, the ACP had already been used as an adsorbent in water treatment [16].

The conductive carbon materials for electrochemical systems began in the 20^{th} century [21]. The AC is produced from carbonaceous raw materials such as different wood or nutshells at the temperatures of 800-1000 ^{o}C for physical activation while for chemical activation at the temperature of 400-700^{o}C [22].

In 1966, Caudle *et al.* [23] were the first to use electrodes from the ACP water desalination system. Since then, there the use of ACP as electrodes in the electrochemical systems increased rapidly. ACP is a materials that is electrically and thermally unique, good for corrosion resistance, have low density, low coefficient of thermal expansion, low elasticity, conductive, low cost, and available in high purity at large quantity [24]. Due to these properties, the ACP placed up to the top list for the use for electrochemical electrodes and the conductive additive [25], likewise, it also produces a carbon material for various structures [26]. This advantage will give variety of carbon range of several hundreds to more than 3000 m^2/g surface area.

The pores sizes of the ACP have been divided into three groups: microporous, which has openings less than 2 nm, macroporous, has openings greater than 50 nm, and mesoporous, that has a range of diameter between 2-50 nm. For various porous carbon materials production, the pore size and the pore structure can be synthesized by different synthetic routes. The limitation of ACP electrode with pores size less than 0.58 nm, the Cl^- ions cannot enter the ACP electrode. In addition, the existence of oxygen-containing surface groups on the ACP prevented the Cl^- ions from entering the pores [27].

4. Electrode From Activated Carbon Cloths For Capacitive Deionization System

Activated carbon cloths (ACC) are of another material extracted from natural sources, such as wood [28], coconut shells [29], coal [30], and starch [31]. ACC has a high specific surface area (1000-1980 m2/g) and their price are cheap [32], therefore, they become targets for the use in CDI as electrodes [33]. Ryoo *et al*. [34] used ACC for electrode in CDI technology, the ACC was composited with titanium, aluminum, zirconium and silicon to enhance the ion removal in the CDI system. After that, there are many works that uses ACC with other materials to improve the CDI performance [35].

The distinctive side of the ACC is its outstanding properties, such as fast adsorption rate, narrower pore size distribution, more exposed adsorption surface, and flexibility, when compared with other AC and ACP [36]. However, the limitation of using pure ACC in CDI is that it has low removal efficiency as compared with composited ACC such as ZnO-ACC composites [37]. Therefore ACC composited with other materials is more preferable to be used in CDI for enhancing ion removal.

5. Electrode From Carbon Nanotubes For Capacitive Deionization System

CNTs has been applied in various fields, such as in aerospace [49], medical [38], and energy storage device [39]. In other aspects, CNTs is also applied in water treatment technology [40], For the last 10 years, CNTs as an electrode material is successfully introduced to the CDI system, it has received greater attention because of its exceptional ability in the capacity of water desalination process. These are due to its high aspect ratio, thermal stability and electrical conductivity of the CNTs itself [41]. The CNTs electrode has shown a good and comparable electrosorption ability for NaCl solution [42]. Heena *et al.* [43] in 2013 tried to improve the CDI electrodes by making electrodes from CNTs with 2 to 3 graphitic walls.

In 2015, Chung *et al.* [44] used pristine CNTs (p-CNTs) in their experiment, the p-CNTs were mixed with nitric and sulfuric acids (1:3) for 1hr at 95oC, they found that acid-treated (a-CNTs) effectively improves the electrical conductivity of the CNTs. After the addition of oxygen functional group to the surface a-CNTs, these physical changes associated with acid treatment increased the availability of active sites that is useful for adsorption and improved the ion adsorption on the CNTs surface [45].

These changes led to better performance of CNTs electrode for CDI application in terms of ion removal efficiency and capacity as compared to p-CNTs. The limitation of CNTs is their poor dispensability, where it is difficult to interact due to hydrophobic nature and its strong van der Waals forces [46]. This sometimes limits its ability as a good adsorption material, further work on functionalization need to be carried out to improve the dispensability of pure CNTs.

6. Electrode From Carbon Nanotubes & Activated Carbon For Composite Capacitive Deionization System

Lu *et al.* [47] fabricated CNTs-AC composite electrode with a simple method for the production of high performance supercapacitor. In the meantime, CNTs-AC binary composite electrode is also useful for an improve capacity of ions removal in water treatment application. Shi *et al.* [48] were also manufacturing CNTs-AC composite electrodes in their work the commercial CNTs and AC were mixed with phenolic resin as a pressed binder at different proportions of CNTs. It was carbonized at 600oC in an N2 atmosphere before used as CDI electrodes. Their results demonstrated that this compound electrode containing 10 wt% CNTs exhibited the best performance with greater than 90% ions removal efficiency[49].

7. Electrode From Carbon Nanotubes & Graphene Composite For Capacitive Deionization System

The composite CNTs and graphene has shown extraordinary electrical characteristics. The electrosorption behavior of a single and double-walled commercially available nanotubes with graphene have been studied to utilize them as potential materials for electrodes in CDI technology [50]. Pan et al [51] studied a comparison between their electrosorptive behaviors of SWCNTs and DWCNTs with graphene-based electrode. The graphene oxide powder was prepared by hummers' method, meanwhile the CNTs was immersed in 1 mol/L of HNO3 solution before fabricating the electrode. The experimental results revealed that the specific electrosorptive amount of SWCNTs and DWCNTs with graphene were higher than that of pure graphene-based electrode.

In 2012 Zhang *et al* [52], made graphene-CNTs (G-CNTs) composites as an electrode for CDI prepared by modified exfoliation method. In the meantime Wimalasiri and Zou [53] in 2013 studied the G-CNTs composite by using only single-walled CNTs combined with graphene oxide nanosheets in aqueous solution for CDI electrode application [54]. The composite electrode of G-CNTs confirmed to be favorable electrode material that can be used in the CDI system [49]. However, it still has a limitation which is the G-CNTs electrode has small surface area~480 m2/g Ghosh et al. [55] and low range of salt adsorption.

8. Electrode From Graphene Sponge For Capacitive Deionization System

Many studies have reported the fabrication of three-dimension (3D) graphene-based structures [56]. In 2014, Yan et al [57] carried out the first work to prepare the graphene sponge (GS) with a high surface area and homogenous graphene distribution within the sponge. The electrosorption of GS reached the high value of the 4.95 mg g-1. Pan et al. (2015) [58], produced the graphene oxide sponge (GOS) by freeze-drying process, which was developed as an electrode for CDI. GO solution was frozen by placing them in a freezer at -18oC for 48 hours, then freeze-dried at -53oC, at sublimation pressure below 10 Pa for 72 hrs. The GS was then annealed at 800oC under nitrogen flow for 3hrs. The electrosorption of electrode GOS has high capacity of 14.9 mg g-1 when the initial NaCl concentration was 500 mg L-1. The resulting GOS shows a porous structure that has a high specific surface area of 356.0 m2 g-1. Another trial was done by Xu *et al.,* [58] by doping nitrogen with GS, where nitrogen-doped graphene sponge (NGS) was used as a CDI electrode. The result showed that NGS have an enhanced specific surface area of 526.7 m2 g-1 and pore size of 3.13 cm3 g-1 [57]. Meanwhile, in 2016 Simon Drieschner *et al* [59] have fabricated graphene foams (GF) with high capacitance (165 mF cm-3) by chemical vapor deposition.

CONCLUSION

Even after five decades of progress, there are still many challenges of understanding the desalination process, as well as, finding an improved materials structure and increased surface area, to be applied for the construction of the electrode. So far, the research is still ongoing in order to improve the performance and to increase the surface area of the electrode by using the carbon of all kinds, as well as, mixing with other materials, to produce more satisfactory results for water desalination. In addition, besides the improvement of performance, it relied upon giving high quality and increased in quantity of clean water. Researches are still on going to test various types of carbon, and added materials, to increase the porosity of carbon with cheaper cost of raw materials to play an important role of increasing CDI efficiency and reducing energy consumption.

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