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Electrosorption behaviour of carbon nanotube and carbon nanofiber films

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Introduction

With the development of modern society, environmental issues, especially the global water crisis, have drawn a lot of attention. Water is likely to be the "oil of this century" as written by Shawn Tully in Fortune magazine [1]. It is well known that about 98% of our global water supply is either sea water or brackish water. We thus must endeavour to explore more novel, efficient, and cost effective ways to remove salts for a globally sustainable fresh water supply. In China, and other rapidly industrialising nations, the water supply crisis is aggravated due to prolonged pollution of their otherwise abundant clean water sources. It remains an arduous task to ensure modernization is facilitated against the shortage of clean water sources and other environmental and societal concerns [2]. The fundamental approaches to managing water resources focus primarily on not only enhancing water saving but also enforcing water resource management by way of tightening wastewater treatment procedures. Particularly in remote areas, due to the existing severe shortage of surface water and rainy supplies, there is a significant challenge in finding suitable drinking water for critical human and business needs. This has focused attention on inland desalination of subsurface brackish water and wastewater. Inland brackish water differs in composition from sea water, the former having lower sodium chloride levels. The disposal of the brine by-product produced from common desalting processes is the biggest problem facing inland desalination. In recent decades, the most widely used processes in desalination plants are reverse osmosis (RO), electrodialysis (ED) and thermal separations, including multistage flash distillation (MSF), multieffect distillation (MED) and mechanical vapour compression (MVC) [3]. A summary of the proportion of their usage in desalination plants is presented in Figure 4.1, adapted from Anderson [4] and Chaudhry [5]. At membrane based desalination plants, RO represents 86%, while ED only around 14%. Compared to thermal systems, membrane processes, such as RO and ED, are widely



FIGURE 4.1

Percentage of active membrane and thermal desalination plants worldwide. (Ref.[4])

adopted for desalination given their evident energy savings.

Capacitive deionization (CDI) is an electrochemically induced alternative approach for the removal of salt ions from concentrated aqueous solutions by forcing charged ions into the electrical double

layer at an electrode-solution interface when the electrode is connected to an external power supply [6-10]. CDI differs from traditional membrane processes, such as RO, which require high pressure. CDI can be accomplished without high pressure, low energy input, and low environmental toxicity. Currently most technologies are energy and cost intensive and cause secondary pollution [11]. Intensive effort has been focused on the improvement of these traditional membrane systems to be more reliable and cost effective, however; their high energy requirements still plagues the technology in many parts of the World [12]. Although some novel desalination systems, which combines desalination with renewable energy, such as solar and wind energy, to cut down the capital and driven energy investment, the input energies, such as heat and electrical energies, are still prohibitively high. RO requires, for example, 3-5 kWh/m³ for water desalination. Thus, a critical item on the international agenda is to develop new desalination technologies towards a more cost effective and secure global water supply.

CDI, also referred to as electrosorption, has a similar working principle as ED. Both operate using a direct voltage to drive ions onto an electrode, however CDI does not involve membranes. Because of the similarity in working principle, there has been some concern as to whether CDI can compete, functionally, with ED. ED is the incumbent technology and has the clear advantage of having been commercialized in the last decade with proven potential performance in the desalination field as compared with other desalination technology, such as RO. Anderson [4] broached this issue. Here they conducted a comparative analyse on these two technologies form the aspect of energy consumption. From a thermodynamic stance, assuming efficiency of 100% for ED and 70% for CDI, ED is not competitive with CDI in solutions with ion concentration within 40000 ppm.

The principle of CDI is based on imposing an external electrostatic field between two electrodes to force charged ions to migrate towards oppositely charged electrodes. The charged ions are attracted within the electrical double layer formed between the solvent and electrode interface, a schematic of which is shown in Figure 4.2. The water containing salt ions flows through a pair of charged electrodes and anions and cations migrate to anode and cathode, respectively. The ions are ideally retained within a double layer. No redox processes occur and the process can easily be reversed when the electrical field is removed or reversed.



FIGURE 4.2 Schematic of a typical CDI system

In CDI the electrosorption capacity strongly depends on the surface properties of the electrode materials, such as their surface area [13], pore microstructure [14], and pore size distribution [15,16], as well as the solution properties [11]. During electrosorption, electrodes have different preference towards different ions. Gabelich et al. [11] studied the electrosorption behaviour of carbon aerogel in different solutions and reported that ion selectivity was based on ionic hydrated radius and monovalent ions with smaller hydrated radii were preferentially removed from solution over multivalent ions. Their study also showed that a very small portion of the aerogel surface area was available for ion sorption due to the small average pore size in the carbon aerogel material. Yang et al. [12] and Ying et al. [17] reported the effect of electrical double-layer overlapping on electrosorption by carbon aerogels. Due to electrical double layer overlapping effect, a significant part of the surface area residing in micropores was not accessible to the electrolyte ions because the pore dimensions were of similar size as the thickness of the electrical double layer. Over 70% of the surface area of the carbon aerogels was attributed to micropores with strong electrical doublelayer overlapping occurring. Evidently electrode material design is very critical in determining electrosorption performance. At present, most studies employ porous carbon, including activated carbon and carbon aerogel as the electrode material [18]. However, these materials have various limitations due to their high electrical and mass-transfer resistance, and complex fabrication, low mass production, and high cost [19].

Carbon nanotubes (CNTs), an emerging member in the carbon family, have been the worldwide hotspot of study as a new electrode material due to their unique morphologies and superb properties, such as high chemical stability, high conductivity, light mass and large surface area. In the last few decades, CNTs have been successfully introduced into water applications leading to promising outcomes in the removal of heavy metals, organics, and biological impurities [20]. They have received special attention due to their exceptional water treatment capabilities and robustness to work effectively against both chemical and biological contaminants [21]. CNTs as an adsorbent medium are able to remove a wide range of heavy metal contaminant such as Cr^{3+} , Pb²⁺, and Zn²⁺, metalloids such as arsenic compounds [22-25]. In order to enhance the sorption ability of CNTs, great efforts have been focused on further enhancement, specifically towards increasing their specific surface area.

The general method for fabrication of CNTs electrodes is as follow: the as-synthesized CNTs are firstly refluxed in concentrated acid, which aims to remove residual catalyst derived from the CVD process and to introduce various functional groups into CNTs, such as carboxyl and hydroxyl groups etc., and finally to enhance the hydrophilic properties and the increase Brunauer-Emmet-Teller (BET) surface area. Then the mixture of CNTs and binder, in a certain weight ratio, is compressed under 10-30 MPa for several minutes, followed by further carbonized at high temperatures (800-1000 °C). These electrodes are finally cooled down for integration [26,27]. Unfortunately this method often sacrifices any essential and advantageous properties of the nascent CNTs; principally the electrical conductivity and the specific surface area. In this case, another type of CNTs composite electrode was proposed and developed by directly growing CNTs-CNFs nanocomposites onto a conductive film layer. Such new materials where then applies as CDI electrodes via low temperature and low pressure CVD [28-33]. This method can greatly reduce the contact resistance, avoid the loss of BET surface area and simplify the electrode preparation process.

In this chapter, we introduce some studies on a simple large area synthesis of carbon nanotube and carbon nanofiber (CNT-CNF) films and their application as electrosorption electrodes. The pore structure of CNT-CNF films is investigated and shown to be favourable for electrosorption of ions because of reduction of electrical double-layer overlapping effect. The electrosorption behaviour

including electrochemical properties, isotherms, kinetics and thermodynamics as well as ion removal selectivity in salt solutions by CNT-CNF films is also presented.

Experimental methodology

Synthesis of CNTs-CNFs film by CVD method

Graphite substrates, with a resistivity of 0.0007 Ω /cm and a thickness of 0.3 mm, were degreased and cleaned by acetone and alcohol. A 20 nm catalyst layer of Ni was deposited on the surface of the graphite substrates by a direct magnetic sputtering system (Shanghai Nanoking Co.), as shown in Figure 4.3.

Low pressure and low temperature thermal CVD (Shanghai Nanoking Co.) is used to fabricate CNT-CNF film electrodes, as shown in Figure 4.3. Acetylene is used as the carbon feedstock and hydrogen as the carrier/dilution gas. The pressure is 20 kPa. The flow rate of acetylene and hydrogen is fixed at 40 sccm and 200 sccm, respectively. The CNT-CNF growth is carried out for 30 minutes at a temperature of 550 $^{\circ}$ C. Graphite coated with nickel is used as substrate. Each Graphite plate is 70 mm wide × 80 mm long × 0.3 mm thick, and has a flow-through hole with the diameter of 6 mm (see Figure 4.3). The CNT-CNF films are grown directly and firmly anchored on the supporting graphite plate (current collector). Monolithic current collector formed from CNT-CNF films is realized.



FIGURE 4.3

The schematic diagram of CNTs-CNFs film grown on graphite plate and a digital image of CNTs-CNFs film (Ref.[31])

CDI unit cell and batch mode CDI experiment

The electrosorption unit cell shown in Figure 4.4 is employed. The assembly of one half of the unit cell is ordered as: retaining plate/rubber gasket/electrode/spacer. The retaining plate is made of polymethyl methacrylate. The spacing is 1 mm between the electrodes which is maintained by a

rectangular nylon and a rubber spacer. To investigate the total electrosorption capacity of CNT-CNF films, batch-mode experiments were conducted in a continuously recycling system including an electrosorption unit cell. In each experiment, the solution was continuously pumped from a peristaltic pump into the cell and the effluent returned to the unit cell. The solution temperature was maintained at 295 K at a flow rate around 40 mL/min. Analytical grade sodium chloride (NaCl) is used for the aqueous solutions. The relationship between conductivity and concentration is obtained according to a calibration table made prior to the experiment, which has been described in many works [32,34]. The concentration variation of different solutions is continuously monitored and measured at the outlet of the unit cell using an ion conductivity meter, as shown in Figure 4.4. The electrosorption experiments were also performed at 281 K and 291 K to explore the thermodynamic performance of CNT-CNF electrode.



FIGURE 4.4

The schematic diagram of CDI experiment with a digital image of CDI unit

Basic theory of CDI

CDI, or electrosorption, requires a direct voltage, similar with electrodialysis, to drive charged species (ions) to the electrodes. CDI is an electrochemical process that operates by adsorbing ions in the double layer formed at the electrodes by introducing a potential difference. The operational principles of CDI can be traced back to the work of Helmholtz and to the modeling of the electrical double layer by Guoy–Chapman. In a classic parallel plate capacitor, charge separation is electrostatic. Capacitance scales directly with the area of the plates, and the inverse distance of separation, as shown in Eq. (2.1):

$$C = \varepsilon_r \varepsilon_0 \frac{A}{D}$$
(2.1)

Here C is the capacitance in farads (F); A is the area of each plate in a traditional capacitor (usually metal) in square meters; ε_r is the relative dielectric constant of the material between the plates, (vacuum =1 F/m), ε_0 is the permittivity of free space (8.854 × 10⁻¹² F/m) and D is the separation between the plates, in meters (m).

Due to factors such as surface polarization, adsorption of ions, and orientation of polar molecules, the region between two different phases has a complex distribution of charge. This interface is known as a double layer. Historically, there have been three models describing the double layer. The first model was proposed by Helmholtz in 1883 [35], and describes the distribution of charges at the double layer as in the case of a capacitor: surface accumulates charge of one sign while at the solution side the opposite sign charges are accumulated. A second model developed by Guov-Chapman in 1913 took into account the electron density gradient at a charged interface, the socalled Thomas-Fermi screening distance, and its variation with distance from the surface. The consequence of this screening is that there exists a distribution of electric charge in the double layer region depending on the potential at the surface. In this model, other factors such as the Boltzmann distribution due to thermal effects (ions are not static, not temperature invariant) were also included. However, this model described ions as point charges. As a result, it predicted unrealistically high capacitance values due to extremely short distances. In 1924, Stern added to this model by assuming that the double layer can be divided in an "inner" region where ion distribution followed Langmuir's adsorption isotherm, while the region further from the surface could be roughly described with the Gouy-Chapman model. Thus, the total capacitance can be calculated as a series of inner double layer (or Helmholtz's) and diffuse layer.



FIGURE 4.5

(a) Schematic of the EDL formation within the interface between the charged solid surfaces and solution. Counter ions are specifically adsorbed at the charged surface and the fully hydrated co-ions and counter ions constitute the inner layer and diffuser layer. (b) Schematic representation of the overlapping of two EDLs in a nanopore. The electrical potential distribution adjacent to an EDL is represented by the dashed line; the solid line is the resulting electrical potential distribution because of the overlapping of the two EDLs. The EDL is composed of the inner layer and diffuse layer. A fully hydrated counter ion is held in the EDL without specific adsorption. The surface potential, diffuse potential, midplane potential and pore width are represented by φ_0 , φ_d , φ_m , and w, respectively. (Ref.[36])

Figure 4.5(a) shows a schematic representation of an electrochemical double layer (EDL) formation in a nanopore, in which the interface can be divided into an inner region (Stern layer) and an outer region (diffuse layer). In the inner layer, the ions are immobilized because they are either strongly

attracted to the surface due to electrostatic interactions, or specifically adsorbed onto the charged surface due to van der Waals force, hydrogen bonding, or other mechanisms. By definition, the inner Helmholtz plane (IHP) is assumed to be the locus of the centers of specifically adsorbed dehydrated ions [37]. On the other hand, another outer Helmholtz plane (OHP), in which the diffuse layer begins, is the locus of the closest approach of hydrated counter ions. The diffuse layer is composed of the mobile ions and their distribution depends on the electrostatic interaction and on thermal diffusion.

In the region of the diffuse layer, the relationship between the electrical potential drop and the charge density can be described by the Poisson equation for a one dimensional system;

$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\epsilon} \tag{2.2}$$

where x is the direction perpendicular to the surface, φ is the relative electrical potential in the diffuse layer, ρ is the volume charge density in the system, and ε is the dielectric constant of the medium, respectively.

The ion distribution in the region of the diffuse layer is affected by the electrical potential. According to the Boltzmann distribution, the number of ions of type i per unit volume, N_i , is expressed by:

$$N_i = N_{i0} \exp\left(-\frac{z_i e\varphi}{kT}\right) \tag{2.3}$$

In this expression, N_{i0} is the bulk concentration of ions, z_i is the valence of ion i, e is the electrical charge of the electron, k is the Boltzmann constant, and T is the absolute temperature. The volume density of charge is given as follows:

$$\rho = \sum_{i} N_i Z_i e = \sum_{i} N_{i0} Z_i \exp\left(-\frac{z_i e \varphi}{kT}\right)$$
(2.4)

By combining equations 2.3 and 2.4, the Poisson-Boltzmann (PB) equation, referred to as one of the most important equations of statistical physics, can be obtained:

$$\frac{d^2\varphi}{dx^2} = \frac{-1}{\epsilon} \sum_i z_i e N_{i0} \exp\left(-\frac{z_i e \varphi}{kT}\right)$$
(2.5)

For a symmetric electrolyte system, equation 2.5 can be reduced to the following expression:

$$\frac{d^2\varphi}{dx^2} = \frac{2zeN_0}{\epsilon}sinh\left(-\frac{ze\varphi}{kT}\right)$$
(2.6)

The classical Gouy-Chapman (GC) theory provides a description of the electrical potential distribution in the diffuse layer, but it is not an accurate representation of the EDL formation in pores because it does not take into account the effect of EDL overlapping.

As the distance between two charged surfaces decreases, the electrical potentials from the double layers begin to overlap. As shown in Figure 4.5, the net electrical potential in the region of the diffuse layer arises from the contribution of each EDL. If the thickness of the Stern layer is small compared to the pore width, it is reasonable to assume that the diffuse layer boundaries are located at x = + w/2 and x = -w/2. Therefore, the electrical potential profile, φ , between the two

surfaces can be obtained using the PB equation via the application of the following boundary conditions [7]

$$\frac{d\varphi}{dx} = 0 \text{ and } \varphi = \varphi_m \text{ at } x = 0$$
$$\varphi = \varphi_d \text{ at } x = \pm \frac{w}{2}$$

where φ_m is the electrical potential at the midplane and φ_d is the diffuse layer potential, respectively.

In the double layer, charge balance requires that:

$$\sigma_0 + \sigma_i + \sigma_d = 0 \tag{2.7}$$

where σ_0 , is the surface charge density, σ_i , is the inner layer charge density, and σ_d is the diffuse layer charge density, respectively.

When there is no specific adsorption in the inner layer, only the OHP is considered in the model, and the thickness of the inner layer corresponds to half the diameter of the hydrated counter ions. In this case, the charge density in the inner layer is assumed to be zero. Due to electro-neutrality, the magnitude of the charge density at the surface is the same as that of the diffuse layer, which is written as:

$$\sigma_0 = -\sigma_d = \left(4\varepsilon RTI\right)^{\frac{1}{2}} \left[\cosh\left(\frac{e\varphi_d}{kT}\right) - \cosh\left(\frac{e\varphi_m}{kT}\right)\right]^{1/2}$$
(2.8)

where R is the ideal gas constant (8.31 J/K \cdot mol) and I is the ionic strength.

If σ_0 is small, the connection between the surface potential (φ_0) and the diffuse layer potential (φ_d) is given by the following equation:

$$\varphi_d = \varphi_0 - \frac{\sigma_0}{c_1} \tag{2.9}$$

where C_1 is the inner layer capacitance.

By definition, the double-layer capacitance, C_{dl} , can be expressed as:

$$C_{dl} = \left(\frac{\partial \sigma_0}{\partial \varphi_0}\right) \tag{2.10}$$

In general, the EDL behavior can be considered as an electrical capacitor, which behaves as a pair of series combination of diffuse layer and inner layer capacitors. In the case that specific adsorption is absent,

$$\frac{1}{c_{dl}} = \frac{1}{c_d} + \frac{1}{c_1}$$
(2.11)

where C_d is the diffuse layer capacitance.

Discussion

Morphology of CNTs-CNFs film grown at different temperature

In the CVD processing parameters such as the temperature, pressure, carbon source, and catalyst material affect the morphology and structure of CNTs-CNFs and the subsequent macroscale film, this affects CDI performance. Among all of the factors involved, the temperature is perhaps the most significant. Hence, the effect of growth temperature on the production of CNTs-CNFs film is investigated. The growth temperature was varied from 500 to 750 $^\circ C$ at intervals of 50 $^\circ C$ maintaining the C₂H₂/H₂ flow rate at 50/200 sccm and gas pressure at 20 kPa. Figure 4.6 shows SEM images of the CNTs-CNFs fabricated by thermal CVD at different growth temperatures (500–700 $^{\circ}$ C). CNTs-CNFs are randomly distributed with different morphologies. The thickness of the grown CNTs-CNFs film on the graphite substrates ranges from about 2 mm to 6 mm. interestingly, the higher the growth temperature is, the thinner CNTs-CNFs film becomes. The diameter of the CNTs-CNFs was in the range of 100 \pm 50 nm. At 600 $^{\circ}$ C the average diameter of CNTs-CNFs decreases to 65 \pm 25 nm. At 700 $^{\circ}$ C, the diameter becomes 20 \pm 10 nm. Figure 4.6(f) shows the Raman spectra of the CNTs grown at different temperatures. The peaks imply that CNTs-CNFs are characteristic of graphite as the spectra are dominated by the underlying graphite substrate. Two peaks were located at approximately 1350 cm⁻¹ and 1580 cm⁻¹ respectively in the spectra showing typical graphite signatures [38,39]. The first-order Raman spectrum of CNTs shows strong peaks at 1580 cm⁻¹, identified as the G peak of crystalline graphite arising from zone-center E_{2g} mode and 1350 cm⁻¹ (roughly corresponding to the D-line associated with disorder-allowed zone-edge modes of graphite). The 1350 cm⁻¹ band is normally explained by relaxation of the wave vector selection rule, due to the effect of the finite size of the crystal in the material. Normally, the intensity of the 1350 cm^{-1} peak increases (i) with an increase in the amount of disordered carbon in the samples and (ii) with a decrease in the graphite crystal size. Figure 4.6(f) suggests that as the temperature increases the G peak becomes sharper, implying that the diameters of CNTs-CNFs decrease when the temperature is increased from 500 to 700 $^\circ\!\mathrm{C}$, consistent with the SEM results as well as the data from Raman spectra shown in Table 4.1. In Table 4.1, it is found that the full width at half maximum of D peak (WD) and G peak (WG) decreases with increasing growth temperature, showing the graphitization of CNTs-CNFs enhances. The G peak position shifts from 1597 cm⁻¹ (500 $^{\circ}$ C) to 1587 cm^{-1} (700 °C), which indicates decreasing of the diameter size of CNTs-CNFs and an increasingly graphitic structure at higher growth temperatures. The intensity ratio of G and D bands (I(D)/I(G)) increases from 0.83 to 1.0 with increasing the growth temperature from 500 to 600 $^\circ\!\!\!C$. Then it decreases from 1.00 to 0.78 when the temperature increases from 600 to 700 $^\circ$ C. In all cases, the I(D)/I(G) is much less than 1, suggesting that there are some defects in the CNT-CNF film though it is unclear to whether this functionally affects the fabricated CDI devices at present. However, it has been suggested that the presence of lattice defects may cause an increased ability of the electrodes to accumulate charge, which may be beneficial for charge transfer in the adsorption process



FIGURE 4.6

SEM images of CNTs-CNFs grown at (a) 500 $^{\circ}$ C, (b) 550 $^{\circ}$ C, (c) 600 $^{\circ}$ C, (d) 650 $^{\circ}$ C and (e) 700 $^{\circ}$ C, respectively, (f) the Raman spectra of CNTs-CNFs film grown at different temperatures

TABLE 4.1

Data from Raman spectra

Temperature	D	G	WD	WG	ID	IG	ID / IG
500°c	1366.40	1597.04	338.43	81.08	578.30	700.28	0.83
550°c	1348.49	1594.18	257.24	67.22	408.53	471.62	0.87
600°c	1344.25	1595.40	265.58	63.91	533.74	532.68	1.00
650°c	1339.16	1593.42	262.96	63.24	398.66	409.82	0.97
700°c	1331.76	1587.68	118.01	65.66	391.95	505.10	0.78

Morphology of CNTs-CNFs film grown at different gas flow rate

Generally, the lower growth temperature, the more amorphous carbon appears in the CNTs-CNFs composite film [28]. On the other hand, at the high growth temperature (> 600 $^{\circ}$ C), the CNTs-CNFs composite films become too mechanically fragile and are no longer suitable for electrosorption applications. Evidently a compromise is necessary. In our work, the compact CNTs-CNFs composite films are grown at 550 $^{\circ}$ C. To obtain the same film thickness, growth times of 30-60 minutes for different acetylene flow rates have been used. Figure 4.7 shows SEM images of the as-grown CNTs-CNFs composites grown at various acetylene flow rates. The CNTs-CNFs are grown non-uniformly and randomly oriented with evident tube bending and twisting. The diameter of the CNTs and CNFs is in the range of 20~500nm. At the acetylene flow rate of 10 sccm, CNTs are grown on substrates with low density and most of the sample is composed of CNTs and CNFs as well as some amorphous carbon as shown in Figure 4.7 (a). With increasing flow rate from 10 to 70 sccm, the density of CNTs increases as well as the length, while the diameter of the CNTs decreases.

Normally, the defects on CNTs-CNFs films are favor for electrosorption. To obtain the information in terms of crystallinity of CNTs-CNFs, Raman spectroscopy is employed. The Raman spectra of different CNTs-CNFs films are shown in Figure 4.7(e). All spectra are dominated by two intensity peaks at 1350 and 1595cm⁻¹, respectively. Figure 4.7(f) shows the intensity ratio of D Peak over G Peak. It is clearly noted the CNTs-CNFs film shows large defect density and small degree of graphitization with the increase of acetylene flow rate from 10 to 30 sccm. Then, it decrease when the acetylene flow rate further increase from 30 to 70 sccm. This is consistent with SEM observations.



FIGURE 4.7

The SEM image of CNTs-CNFs grown at different acetylene flow rates: (a) 10, (b) 30, (c) 650, (d) 70sccm, (e) the Raman spectra of CNTs-CNFs grown at different acetylene flow rate, (f) the intensity ratio of D peak over G peak at different acetylene flow rate. (Ref.[40])

Electrochemical characteristics of CNT-CNF films

Cyclic voltammetry (CV) is an effective tool to examine the electrochemical behavior of porous electrodes. It is useful to predict CDI performance priori to full device fabrication. Typical CV characteristic of CNT-CNF films, grown at different temperatures, is shown in the Figure 4.8(a). The measurements are examined by the electrochemical workstation in a three-compartment cell at ambient temperature. CNT-CNF film electrode, platinum plate, and saturated calomel electrode are used as the working electrode, the counter electrode, and the reference electrode, respectively. The potential sweep CV measurement is carried out in the 1 mol/L KCl solution. It can be seen that the current increases and decreases steadily with the electric potential. There is almost no deformation in CV curves from rectangular curves and no obvious oxidation/reduction peaks. Ions are adsorbed on the electrochemical reaction [41]. Moreover, the specific capacitance, C, is obtained from the CV curve using the equation shown as below:

$$C = \frac{\int i dt}{m \Delta V}$$

where i, m and ΔV are current, mass of CNT-CNF composite film and potential window, respectively. By calculation, the specific capacitance of CNT-CNF films is 28.4, 37.4, 52.7, 39.1 and 48.3F/g, corresponding to 500, 550, 600, 650, and 700 °C.

The impedance spectra of CNT-CNF film grown at different temperature, in a 1.5 mmol/L NaCl solution, are shown as Nyquist plots in Figure 4.8(b). A semicircle arc and a straight line have been observed. The high-frequency arc is ascribed to the double-layer capacitance (DLC) in parallel with the overall contact impedance generated from the electrical connection between carbon particles, and the charge transfer at the contact interface between the electrode and the electrolyte solution. At lower frequencies, the impedance plot should theoretically be a vertical line, which is parallel to the imaginary axis. However, the low frequency straight line departures from that expected, which is explained by the electrode surface in homogeneity caused by different pore distribution with different dimensions in CNT-CNF film and the existence of "constant phase element" occurs [42]. From Figure 4.8(b), it clearly shows that the semicircle arc tends to become small as well as the intercept formed by x-axis and the vertical line as the temperature increases, implying the small transfer and contact resistivity.



FIGURE 4.8

The CV curve (a) and Nyquist diagrams (b) of CNTs-CNFs grown at different temperatures

FTIR, XRD and TGA spectra of CNT-CNF film

The surface functional groups presenting on CNTs-CNFs often plays a significant role in electrosorption, which can be explored by the FTIR spectra. It determines the hydrophilicity of CNTs-CNFs films and therefore the electrosorption performance. The Infrared spectrum of the CNTs-CNFs composite film is shown in Figure 4.9(a). Some oxygenous functional groups such as carbonyl and carboxyl groups are found on the surface of CNTs-CNFs composite films. It shows three intense bands at 3433.79 cm⁻¹, 1629 cm⁻¹ and 1080 cm⁻¹, which are assigned to -O-H stretching vibration of hydroxylic groups, -C=O stretching vibration of carbonyl groups and -C-O stretching vibration, respectively. In addition, the peak at 1431 cm⁻¹ is attributed to -O-H bending vibration. Besides FTIR, three typical XRD patterns corresponding to graphical carbon are shown in Figure 4.9(b). The first peak located at 26.6°, correspond to the (002) phase. The second and third

(3.1)

peaks are located at 44° and 56.8°, corresponding to the (100) and (004) phases, respectively. To confirm the content of CNTs-CNFs, the TGA is employed. Figure 4.9(c) shows the TGA graph for the as-grown CNTs-CNFs. Thermo gravimetric (TG) and differential thermo-gravimetric (DTG) curves are indicated. From this figure, it is found that the initial burning temperature was at around 480 °C and this occurred mainly due to the presence of amorphous carbon in the CNTs mixture. The burning of CNTs themselves begins at around 500°C. There was no weight gain observed during thermal treatment, since no oxidation of the metal particles is expected to take place. The weight gain due to oxidation occurs in samples where the metal particles are exposed to or are adhered on the surface regions of the CNTs. In our case, the catalyst is completely encapsulated and is rid of any external or tip catalytic particles, as evidenced from SEM inspection, Ni catalysis are found at the tips of the CNTs and CNFs.



FIGURE 4.9 (a) FTIR, (b) XRD and (c) TGA spectra of the as-grown CNTs-CNFs film

Pore size distribution of CNT-CNF film

Figure 4.10(a) shows N_2 adsorption-desorption curves at 77 K for the CNT-CNF film. Curves are hysteretic, typical of a mesoporous material where the desorption requires definitively higher energy than adsorption [44]. The initial uptake near 0.01 P_0 (P_0 is the saturation pressure of nitrogen gas at 77 K) indicates the presence of micropores. The gradual increase of the volume adsorbed in the mid pressure range represents the development of various sizes of mesopores. The adsorption curve shows no saturation in the large pressure range, which means wide size distribution in the CNT-CNF films.

The differential surface area of the CNT-CNF films is shown in Figure 4.10(b), which demonstrates that most of the pores are smaller than 100 nm in diameter, with a bimodal distribution of pore sizes at 4 nm and 30 nm, corresponding to CNT-CNF inner cavities and confined space among the isolated CNT-CNF, respectively. Based on IUPAC classification, the pore size is divided into three groups: micropores (pore width < 2 nm), mesopores (between 2 and 50 nm), and macropores (> 50 nm). CNT-CNF films in our experiments are mainly composed of mesopores (2-50 nm) and a small portion of macropores (> 50 nm). Table 4.2 shows the BET surface area, micropore volume, total pore volume, and average pore size. It can be seen that the proportion of micropore volume in the total pore volume is about 0.3% and the average pore diameter is 8.3 nm, which confirmed CNT-CNF films in this work are mainly composed of mesopores (2-50 nm). It has been learned that The CNT-CNF film electrodes show comparable electrosorption capacity compared with carbon aerogels and activated carbon cloth (refer to Table 4.3), although surface area of CNT-CNF films is much smaller than carbon aerogels and activated carbon cloth. The optimal pore structure reduces the

overlapping effect and ensures the effective surface area of CNT-CNF films. Therefore, high electrosorption capacity of CNT-CNF films is obtained.



FIGURE 4.10

(a) N_2 adsorption and desorption isotherm at 77 K for CNT-CNF film; (b) pore size distribution of CNT-CNF film (ref. [45])

TABLE 4.2

BET surface area, micropore volume, total pore volume, and average pore size of CNT-CNF film (Ref.[28])

Surface Area (m ² /g)	Micropore Volume (cm ³ /g)	Total Pore Volume (cm ³ /g)	Average Pore Size (nm)
210.6	0.0006	0.2134	8.3

Acid treatment on CNT-CNF films

The as-grown CNTs-CNFs film electrodes are immersed into the 0.5M HCl solution to remove the deleteriously Ni catalyst. Figures 4.11(a) and (b) shows the surface morphologies of CNTs-CNFs films before and after the acid treatment. The CNTs-CNFs film before the acid treatment is more uniform than the treated samples, as shown by the inserts in Figure 4.11(a) and (b). Small Ni particles (bright dots) attach to CNTS-CNFs before the acid treatment, as shown in Figure 4.11(a). The pore sizes of such CNTs-CNFs are distributed from 4 nm to 30 nm. After acid-treatment, the CNTs-CNFs layers become coarser and show net-like structures with more mesoporous pores in comparison with the as-grown samples, as shown in Figure 4.11(b). Such networked structures provide more routes for solution entry and allow hydrated ions to easily move into the surface and subsurface of the film, making them well suited for electrosorption. Figure 4.11(c) and (d) presents the energy dispense spectra of CNTs-CNFs film before and after acid treatment while the table inserted in each figure exhibits the corresponding element analysis; Ni is partially removed by the acid treatment.

To examine the inner structure of CNTs-CNFs before and after acid treatment, the Raman spectra is employed, as presented in Figure 4.11(e) and (f). Interestingly, after the acid treatment, the half width of D peak decreases while the half width of G peak increases. Moreover, the intensity ratio of D peak (ID) over G peak (IG) increased from 0.64 to 0.77, implying the increased surface defects, which are very favorable to electrosorption.



FIGURE 4.11

SEM image, EDX spectra and Raman spectra of CNTs-CNFs before (a), (c), (e) and after (b), (d), (f) acid treatment, respectively, inset in (c) and (d) shows the element analysis table

CDI performance of CNTs-CNFs film

The removal capacity (by μ mol/g) is defined as adsorbed ion amounts per gram of the electrodes, and can be examined by the concentration change of solutions during the charging process:

Removal capacity =
$$\Delta c \times V / m$$
 (3.1)

where Δc is concentration change of the solution, V is the volume of solution flowing through the unit cell, and m is the mass of electrode. Typical CDI experiments were conducted with a solution of NaCl that has an initial conductivity around 50 μ S/cm. During batch-mode experiment with one complete recycle, the amplitude of the applied voltage is 1.2 V. Applied voltages, charge and discharge current, and conductivity transients during one charge-discharge cycle of such experiment are shown in Figure 4.12(a). Cations and anions are adsorbed onto the electrical double-layers formed at the surfaces of the CNT-CNF film electrodes during charging and are released back into the electrolyte during discharge cycles. Consequently, the salt concentration drops during charging and increases during discharging. The CNT-CNF films can be regenerated by discharging. The CDI experiments of ZnCl₂, CuCl₂, and FeCl₃ conducted with an initial conductivity around 50 μ S/cm at 1.2 V show the similar results to NaCl.

Figure 4.12(b) shows conductivity transients in NaCl during batch mode experiments at several different voltages. All charge processes are carried out for 30 minutes. Under the potential range considered salt removal increases from 4 % to 81 % (salt removal (%) = $(C_f-C_0) / C_0 \times 100\%$, where C_0 is initial conductivity and C_f is the final conductivity). Accordingly, the removal capacity, shown in Figure 4.12(c), is consistent with salt removal which is increased from 12.8 to 333.1 µmol/g when the electrical voltage increased from 0.4 to 2 V. Nevertheless, hydrolysis of water is not found when the voltage between the two electrodes is more than 1.2 V because of the existence of resistance in the whole circuit. Obviously, the salt removal capacity is dependent on the applied voltage and higher salt removal is achieved with higher voltage in the absence of electrolysis.

To investigate the recycle of removal capacity of the unit cell, repeating charge-discharge experiments are tested. The initial conductivity is 50 μ S/cm. When the conductivity returns to the initial value in the first discharge process, the second charge process starts. Figure 4.12(d) shows the transient conductivity over 5 charge-discharge cycles. Obviously, the repeatability of electrosorption process can be realized in our unit cell. In the practical experiment, removal capacity declination has not been observed in our unit cell after over 30 charge-discharge experiments.

The CNT-CNF film electrodes show comparable electrosorption capacity (56.8 μ mol/g) compared with carbon aerogels (57.0 μ mol/g) and activated carbon cloth (83.0 μ mol/g) [38], although the surface area of the CNT-CNF films is much smaller than carbon aerogels and activated carbon cloth, as shown in Table 4.3. The optimal pore structure reduces the overlapping effect and ensures the effective surface area of CNT-CNF films. Therefore, high electrosorption capacity of CNT-CNF films is obtained.



FIGURE 4.12

(a) CDI performance of CNT-CNF film electrodes in NaCl solutions: (a) one complete charge-discharge cycle; (b) effect of applied voltage on electrosorption; (c) the removal capacity dependent on electrical voltage; (d) regeneration experiment (Ref. [31, 45])

TABLE 4.3

Comparison of electrosorption capacity among different carbon electrode materials from the literatures [2]

NaCl Solution						
_	Applied	Initial	Initial	Electrosorption	Specific	
Electrodes	Voltage (V)	Conductivity	Concentration	Capacity (mg/g)	Surface Area	
		(μS/cm)	(mg/L)		(m /g)	
	1.2	100	-	3.33	400-1100	
Carbon			58.5	1.39		
aerogeis	1.2	-	140	4.51	412/602	
	1.2	-	60	0.7	-	
Carban			500	2.57		
Carbon	1.2		1000	3.71	150	
nanotubes	1.2	-	1500	4.76	153	
			2000	5.24		
	1.2	100	-	3.32	211	
CNTs-CNFs	1.2	50		1.61		
	1.2	100	-	3.87	-	
Mesoporous	1.2	51.2	-	0.68	968	
carbon	0.8	100	-	0.93	1491/1594	
	1.2	51.2	-	0.25	844	
	0.8	100	-	0.27	1491/1594	
	1.2	-	60	0.13	730	
Activated			100	6.1	1153	
Carbon			200	8		
Carbon	1.2		500	9.72		
		-	1000	10.8		
			1500	11		
			2000	11.76		
Activated				1.75	2000	
	1		F 0F			
Activated	L	-	5.85	1 69	1900	
carbon cloths-				4.68	1890	
carbon fibers				1.3	670	
Eletrospun-	1.2	-	60			
activated				3.2	550	
carbon fibers						
Graphene	2.0	50	-	1.36	222.1	

Electrosorption isotherms

To further investigate electrosorption behavior, six electrosorption experiments with different initial concentration were performed. The initial conductivities of the NaCl vary from 25 to 200 μ S/cm. Figure 4.13 shows electrosorption isotherms in the NaCl solutions. When the concentration is very dilute, the adsorbed NaCl amount inclines to zero. The removal amount of NaCl increases as the initial concentration is raised, which is due to the enhanced mass transfer rate of ions inside the micropores and reduced overlapping effect by higher concentration of solution [46]. The Langmuir

(3.2) and Freundlich (3.3) isotherms are used to simulate the experimental data for NaCl electrosorption on CNT-CNF film electrodes,

$q = \frac{q_m K_L C}{1 + K_L C}$	3.2
$q = K_F C^{1/n}$	3.3

where C is the equilibrium concentration (mg/L), q is the amount of adsorbed NaCl by CNT-CNF film (mg/g), q_m is the maximum adsorption capacity (mg/g) corresponding to complete monolayer coverage. Table 4.4 shows the determined parameters and regression coefficients R^2 , K_L and K_F of Langmuir and Freundlich isotherms, respectively. The regression coefficients of Langmuir and Freundlich isotherms are 0.998 and 0.982, respectively. From Figure 4.13, it can be seen that the Langumuir isotherm best describes the experimental data, suggesting that for modeling purposes, monolayer coverage of the CNT-CNF film surface area during electrosorption process may be assumed. The maximum adsorption capacity calculated by the Langmuir model is 12.33 mg/g for NaCl.



FIGURE 4.13 Electrosorption isotherms of CNT-CNF film electrodes in NaCl solutions (Ref. [28, 29])

TABLE 4.4

Parameters determined from isotherms of CNT-CNF film electrodes in NaCl solution (from ref. [30])

Isotherm	Model equation	Parameter	Value
Langmuir	$q = \frac{q_m K_L C}{1 + K_L C}$	q _m	12.33
		KL	0.0138
		R^2	0.998
Freundlich	$\mathbf{q} = \mathbf{K}_F C^{1/n}$	K _F	1.4371
		n	3.0154
		R ²	0.982

Electrosorption kinetics

Adsorption kinetics, which is indicative of the adsorption rate, is used to investigate the electrosorption behavior of studied CNT-CNF film electrodes. During the electrosorption, the ion concentration gradually decreases until equilibrium is reached. This progression is expected based on the large number of vacant surface sites available for electrosorption during the initial stage, and, after certain amount of time, the remaining vacant surface sites become increasingly difficult to occupy due to the repulsive forces between ions on the electrode in solution. The variation in the adsorbed amount of NaCl before reaching equilibrium is discussed kinetically using several forms of kinetic equations: first-order, second-order, and the parabolic diffusion, are presented in Eqs. (3.4)-(3.6) [47]

$$\ln\left[\frac{c_t - c_e}{c_0 - c_e}\right] = -kt \tag{3.4}$$

$$\left[\frac{1}{c_0}\right] \left[\frac{c_0 - c_t}{c_t - c_e}\right] = \mathrm{kt} \tag{3.5}$$

$$\frac{(c_0 - c_t)/(c_t - c_e)}{t} = \mathbf{k}t^{1/2}$$
(3.6)

where t and k are the electrosorption time (min) and the reaction rate constant (min⁻¹), respectively. C_0 , C_e , C_t are initial concentration, equilibrium concentration, and the concentration of adsorbate at time t (mmol/L), respectively. A linear plot of the first-order kinetic equation for this system is illustrated in Figure 4.14 with different initial concentrations of 0.6, 1, 1.8, 4.4, 6.9 and 8.6 mmol/L, respectively. The linear fitting between the concentration terms vs. time can be judged from the value of the determination coefficient in the plot, which can be regarded as a criterion for the adequacy of the selected kinetic equation. Table 4.5 summarizes the estimated coefficients of the kinetic models for electrosorption of CNT-CNF film electrodes in NaCl solution with different initial concentrations at 295 K. It can be observed that NaCl electrosorption kinetics on the CNT-CNF film is regarded as first-order rather than second-order or parabolic diffusion.



FIGURE 4.14

Linear plot of the first-order kinetic equation for electrosorption of CNT-CNF film electrodes in NaCl solutions with different initial concentrations at 295 K (Ref. [33])

TABLE 4.5

Coefficients of kinetic model equations for electrosorption of CNT-CNF film electrodes in NaCl solution with different initial concentrations at 295 K (Ref. [33])

Kinetic equation	Initial concentration (mmol/L)	Coefficient of determination (R ²)	
	0.6	0.999	
	1	0.994	
First order	1.8	0.977	
FIIST-OLUEI	4.4	0.996	
	6.9	0.993	
	8.6	0.996	
	0.6	0.956	
	1	0.919	
Second order	1.8	0.897	
Second-order	4.4	0.96	
	6.9	0.965	
	8.6	0.974	
	0.6	0.841	
Parabolic diffusion	1	0.903	
	1.8	0.548	
	4.4	0.78	
	6.9	0.885	

Electrosorption thermodynamics

The thermodynamic parameters provide in-depth information on inherent energetic changes that are associated with electrosorption. The free energy of adsorption (ΔG^0), enthalpy (ΔH^0), and entropy (S^0) changes are. The Langmuir isotherm is used to calculate the thermodynamic parameters based on equations (3.7), (3.8) and (3.9), as follows;

$$\Delta G^0 = -RT ln K_L \tag{3.7}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{3.8}$$

$$\ln(K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
(3.9)

where R is the gas constant (8.314 \times 10⁻³ kJ/molK), T is temperature (K). ΔH^0 and ΔS^0 are determined from the slope and intercept of the van't Hoff plots of $\ln(K_L)$ vs. 1/T [43]. Table 3.6 presents the thermodynamic parameters at 281, 291 and 295 K. The ΔG^0 values are negative at all testing temperatures, verifying that the electrosorption of NaCl onto CNT-CNF was thermodynamically favorable. An increasingly negative ΔG^0 implies a greater driving force of electrosorption, resulting in an increased electrosorption capacity. As the temperature increased from 281 K to 295 K, ΔG^0 decreases negatively, suggesting that the electrosorption of NaCl onto CNT-CNF is an endothermic process and the positive ΔH^0 indicates that electrosorption of NaCl onto CNT-CNF is a certain extent, by the magnitude of enthalpy change ΔH^0 . ΔH^0 of < 84 kJ/mol are typically considered as those of physisorption bonds. ΔH^0 of Chemisorption. The former is between -20 and 0 kJ/mol and the latter is between -80 and -400 kJ/mol [48]. Both of ΔH^0 and ΔG^0 suggest that electrosorption of NaCl onto CNT-CNF is driven by a largely physisorption process.

TABLE 4.6

Thermodynamic parameters for electrosorption of CNT-CNF film electrodes in NaCl solutions at 281, 291 and 295 K (from ref. [33])

Т(К)	G^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol • K)
281	-14.041		
291	-16.165	35.877	177.898
295	-16.405		

Effect of cation properties on electrosorption capacity

The effects of cation charge and size on the electrosorption capacity have been investigated in several electrosorption experiments containing different solutions. The initial concentrations of all the selected solutions were fixed at 1.5 mmol/L. The applied voltage was 1.2 V. Since the CNT-CNF can be treated as electrical double-layer capacitors, characterized via a DLC at the interface of the

carbon and the electrolyte, the DLC is a good indicator of the performance of CNT-CNF in the removal of ions and can be determined by ac impedance spectra. The DLC CL is determined by:

$$CL = 1 / 2\pi f_r R_{F_r}$$
 (3.10)

where R_F is determined by the arc diameter, the f_r is the frequency of the arc acme. Figure 4.15 shows the cation (Fe³⁺, Cu²⁺, Zn²⁺, Na⁺) concentration variation and calculated DLCs of CNT-CNF film electrodes in different solutions. The measured cation concentration variation in different solutions is consistent with the calculated DLCs in the following order:

$$Fe^{3+}>Cu^{2+}>Zn^{2+}>Na^{+}$$

Table 4.7 shows the charge, ionic radii, and hydrated radii of different cations. From Table 4.7, it can be seen that the hydrated radius of Fe^{3+} is largest while that of Na⁺ is smallest in these cations. The electrosorption preference is not completely dependent on the hydrated radii of cations. The charge of cations should play an important role during the electrosorption. CNT-CNF films in our experiments are mainly composed of mesopores. For electrode materials with such a pore size distribution, the electrical double-layer overlapping effect does not play the important role [12,17]. Cations can easily enter onto the electrode surface through these mesopores. In this case, cations with larger charge will be more easily adsorbed onto the electrode surface under the effect of electric field applied at the electrodes. As a result, trivalent Fe³⁺ ion is more effectively removed as compared with bivalent Cu^{2+} , Zn^{2+} and univalent Na^{+} . For cations with the same charge, their hydrated radii will play a main role during electrosorption. Smaller cations can pass through the pores and arrive at the electrode surface more readily. Cu²⁺ with smaller hydrated radius are preferentially adsorbed by the CNT-CNF film compared with Zn²⁺. The carbon aerogel electrode is reported to consist of a large number of pores with the size less than 2 nm [12]. The diameter of the fully hydrated ions becomes comparable to the pore size and due to strong electrical doublelayer overlapping effect it is not easy for ions to penetrate large quantities of these small pores (<2 nm) to be adsorbed on the surface of carbon aerogel electrode. It can be understood that hydrated ion radius dominantly determined the electrosorption behavior of carbon aerogel indicated by Gabelich et al. [11]. Thus, the CNT-CNF film has more preferable pore size distribution for electrosorption application in comparison with carbon aerogel [45].



FIGURE 4.15 Electrosorption capacities and DLC CL analysis of CNT-CNF film electrodes in different solutions (Ref. [31])

TABLE 4.7

Charge and radii of test cations (Ref.[49])

lon	Charge	Ionic radius (pm)	Hydrated radius (pm)
N ^{a+}	+1	95	358
Cu ²⁺	+2	72	419
Zn ²⁺	+2	74	430
Fe ³⁺	+3	60	457

The effect of anion properties on CDI performance is herein considered. The initial concentration of all the selective solutions including NaF, NaCl, NaNO₃ and Na₂SO₄ was fixed at 0.001mmol/l. The applied voltage was 1.2 V and the flow rate was 14ml/l. It was found that the comparisons of measured CDI capacities are consistent with the calculated capacitances. When the solutions have different anions and same cation (Na⁺), the CNTs-CNFs composite film electrodes show better CDI capacity for the smaller and monovalent ions as opposed to larger and divalent ions:

 $F^{-}>Cl^{-}>NO_{3}^{-}>SO_{4}^{2-}$

Cutoff pore size

If the potential is low, a further simplification can be made for the numerical solution needed to provide the surface charge density. An analytical solution for the P-B equation (Eq.2.6) for a single plane immersed in a solution of a 1:1 electrolyte is given as

$$\frac{\exp\left(\frac{e\varphi}{2kT}\right)-1}{\exp\left(\frac{e\varphi}{2kT}\right)+1} = \left[\frac{\exp\left(\frac{e\varphi}{2kT}\right)-1}{\exp\left(\frac{e\varphi}{2kT}\right)+1}\right]\exp\left(-\kappa X\right)$$
(3.11)

where κ , the Debye-Hückel parameter, is given for a symmetrical 1:1 electrolyte as:

$$\kappa = \left(\frac{2N_A l e^2}{\epsilon k T}\right)^{1/2} \tag{3.12}$$

For low electrical potentials, φ_m (Eq. (2.8)) can be obtained by substituting w/2 for X in Eq.(3.11) and using the superposition principle [12]. Inserting the expression for φ_m into Eq. (2.8), one can express surface charge density as follows:

$$\sigma_{0} = \sqrt{4\epsilon RTI} \left[\cosh\left(\frac{e\varphi_{d}}{2kT}\right) - \cosh\left\{8\left[\frac{\exp\left(\frac{e\varphi_{d}}{2kT}\right) - 1}{\exp\left(\frac{\varphi_{d}}{2kT}\right) + 1}\right] \exp\left(-\frac{\kappa W}{2}\right)\right\}\right]^{1/2}$$
(3.13)

when the pore width or the Debye-Hückel parameter κ is relatively large, the exponential term on the righthand side of Eq. (3.13) becomes very small. Therefore, the second term of the equation approaches unity and the surface charge density becomes:

$$\sigma_0 = \sqrt{8\epsilon RTI} \sinh\left(\frac{e\varphi_d}{2kT}\right) \tag{3.14}$$

The charge density predicted by Eq. (3.14) can be seen as the ideal case, in which no electrical double-layer overlapping occurs.

The square root of the bracketed expression in Eq.(2.8) or Eq.(3.13) is not always positive. Because of the overlapping of the electrical double layers, the surface charge density falls quickly with a decrease in pore width. There exists a specific width, w_m at which the value of the bracket on the right-hand side of Eq.(2.8) or Eq.(3.13) approaches zero, which means similarly that the surface charge density tends towards zero. Indeed, it is impossible to allow counter ions to move in a pore of width less than w_m . The physical significance of w_m is that the electrical double layer exists only for pore widths larger than w_m . The cutoff pore width can be obtained by setting the right-hand side of Eq.(2.8) or Eq.(3.13) to zero. In the case of Eq.(3.13), an analytical expression for the cutoff pore width can be obtained as follows:

$$w_m = \frac{2}{-\kappa} \ln \left\{ \frac{e\varphi_d [exp(\frac{e\varphi_d}{2kT}) + 1]}{8kT [exp(\frac{e\varphi_d}{2kT}) - 1]} \right\}$$
(3.15)

The cutoff pore width is essential; its size may vary from 5 to 50 Å, depending on the diffuse-layer potential and the Debye-Hückel constant, κ . Pores with widths smaller than the cutoff value do not contribute to the electrosorption of ions. The cutoff pore width of the system reflects maximum overlapping of the electrical double layers. At w=w_m, the potential profile inside the pore levels off. Furthermore, because the derivative of the potential is equal to the surface charge density, the surface charge density is zero in pores of widths equal to or smaller than the cutoff value.

Thus, we can calculate the cutoff pore size of the CNT-CNF films using this simplified model. The φ_m is obtained from the CV curve, as shown in Figure 4.8 which is approximately 0.15 V. For a symmetrical 1:1 electrolyte (ε_r) at room temperature (25°C), the κ is obtained by: $\frac{1}{\kappa} = \frac{3.04 \times 10^{-10}}{\sqrt{c}} = 4.3 \times 10^{-9}$. Table 4.8 summarizes the cutoff pore width for NaCl solutions with different concentrations. The higher the NaCl concentration, the smaller the cutoff pore size obtained. As we have shown in Figure 4.10, the CNTs-CNFs is mainly composed of mesopores (2-50 nm) which is much higher than that of cutoff pore size shown in Table 4.8, indicating a highly efficient CDI process.

TABLE 4.8

Cutoff pore width for NaCl solutions

Conductivity (µS/cm)	Concentration (mol/l) \times 10 ³	1/κ (m) × 108	Cutoff width (Å)
25	0.50369	1.355	222
50	1.0074	0.9578	157
75	1.5111	0.7820	128
100	2.0147	0.6773	111
150	3.0221	0.5530	91
200	4.0295	0.4789	79
500	10.074	0.3029	50

Conclusion

The availability of affordable clean water is one of the key technological, social, and economical challenges of the 21st century. There is a tremendous interest in the development of economically attractive desalination technologies. Over the years, a number of desalination methods have been developed among which distillation, reverse osmosis, and electrodialysis are the most commonly

known and widespread technologies. A common goal for current research is to make these technologies more energy efficient and cost effective, both for the deionization of seawater and for brackish water. Capacitive Deionization (CDI) has emerged over the years as a robust, energy efficient, and cost effective technology for desalination of water with a low or moderate salt content. The energy efficiency of CDI for water with a salt concentration below approximately 10 g/L is due to the fact that the salt ions, which are the minority compound in the water, are removed from the mixture. Instead, other methods extract the majority phase, the water, from the salt solution. Furthermore, energy release during electrode regeneration (ion release, or electrode discharge) can be utilized to charge a neighboring cell operating in the ion electrosorption step, and in this way energy recovery is possible. On the other hand, CDI with a high salt sorption capacity is determined by the porosity of carbons. However, the traditional approach for fabricating the carbon electrode would scarify the essential properties of carbon due to the usage of polymer binder.

Low temperature and low pressure CVD has been used to fabricate large area CNT-CNF film electrode for electrosorption applications toward realizing next-generation cost-effective water desalination systems. The characterization and electrosorption of CNT-CNF films have been investigated. The results showed that (i) the CNT-CNF films have an optimally networked morphology; that (ii) the pore size distribution of CNT-CNF films is favorable for electrosorption given the evidenced reduction in the electrical double-layer overlapping; that (iii) the electrosorption follows a Langmuir isotherm, indicating monolayer adsorption; that (iv) comparable electrosorption capacity with carbon aerogels and activated carbon cloth was obtained, although the surface area of CNT-CNF is much smaller; that (v) electrosorption kinetics on the CNT-CNF film in NaCl solution is regarded as first-order rather than second-order or parabolic diffusion; and finally that (vi) electrosorption of NaCl onto CNT-CNF can be ascribed to physisorption process; and (vii) CNT-CNF films have the preference to adsorb multivalent cations. For cations with same charge, the one with smaller hydrated radius will be more effectively removed; (viii) the pore distributed within CNTs-CNFs is much higher than that of cutoff pore size, which promises the high CDI performance of CNTs-CNFs.

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