The study of capacitive deionization behavior of a carbon nanotube electrode from the perspective of charge efficiency
Haibo Li, Sen Liang, Mangmang Gao, Guolong Li, Jin Li and Lijun He

ABSTRACT

In this work, the capacitive deionization (CDI) performance of a single-walled carbon nanotube (CNT) electrode has been studied from the point view of charge efficiency theory. It is revealed here that the charge efficiency of a CNT electrode is strongly dependent upon the cell voltage and solution concentration. Either the high cell voltage or the low ionic strength results in a high charge efficiency, implying that CDI is expected to be a promising technique for an aqueous solution with low ionic strength. Additionally, it is found that the high decay constant and high electrical double-layer capacity are beneficial to enhance electrosorption performance.

Key words | capacitive deionization, charge efficiency, electrosorption

INTRODUCTION

The outstanding physico-chemical properties of carbon nanotubes (CNTs) have stirred interest for a variety of practical applications in photonics, electronics and chemistry (Jiang et al. 2002; Lu et al. 2005; Wang et al. 2006; Apul et al. 2013; Wei et al. 2015). Capacitive deionization (CDI) is based on an electrochemical process for producing potable water from saline water with low energy, low cost and low environmental impact (Oren 2008; Li et al. 2008, 2009; Tao et al. 2011). Remarkably, it targets removal of the salt ions, which are only a small fraction of the feed solution. As a result, compared with most traditional desalination technologies, CDI requires less energy to operate and the electrodes are easily regenerated. The basic concept of CDI is the electrical-potential-induced surface adsorption of ions on to electrodes through the formation of electrical double layers at the water–electrode interface and, therefore, the process needs low voltage to operate, and does not require any harsh chemical cleaning process. Principally, the ion adsorption capacity is directly related to the specific surface areas (SSA) and bulk conductivity of the electrodes. The SSA is responsible for providing the space for accommodating ions, and the superior conductivity facilitates ion diffusion (Li et al. 2010; Zhang et al. 2012). Therefore, CNTs with hundreds of SSA and excellent conductivity are often selected as the starting materials to make electrodes for CDI (Zhang et al. 2006; Zhan et al. 2010; Li et al. 2011).

It is well known that CDI is a dynamic electrochemical process which can be described by the Gouy–Chapman–Stern (GCS) double-layer model. The model considers an inner, or Stern, layer and a diffuse ion cloud described by the equilibrium Poisson–Boltzmann equation for ions as ideal point charges (Bazant et al. 2004; Broglioli 2009). The previous studies on electrode characterization focus on electrode charge (or capacitance), often only at low cell voltages and for one value of the ionic strength, which is very limited to reasonably evaluate the CDI performance of an electrode. Besides this, the current response during the CDI process is often ignored, thereby losing some useful information. Recently, Biesheuvel and his colleagues introduced a very useful parameter, called charge efficiency ($A$), into CDI processes to optimize the electrode material, and this shows great potential (Biesheuvel et al. 2009). Principally, the $A$ derived from the GCS model is defined as the ratio of equilibrium salt adsorption to electrode charge. Ideally, the $A$ equals 1 if counterion adsorption can fully compensate for the electron charge. However, in reality, it is often far less than 1 due to the influence of co-ions impaction. Thus, the value for $A$ as a function of voltage and ionic strength is an excellent probe to test models for the structure of the double layer inside the CNT.

Up to now, the charge efficiency dependent on CNT-based CDI has not yet been investigated; therefore, it
is necessary to perform this study. The aim of this study was to calculate and explore the charge efficiency of CNT-based CDI by varying the experimental conditions, involving cell voltage and ionic strength. As a counterpart, the corresponding current response will be investigated as well. Further, a comparison will be made between the CNT and an activated carbon (AC) electrode of charge efficiency under the same experimental conditions to demonstrate the advances of the CNT electrode in the CDI process.

**MATERIAL AND METHODS**

**Materials and preparation**

Single-walled CNTs (SWCNT) were purchased from Nano-tech Port Co., Ltd (Shenzhen, China) with detailed specifications, such as length (5–15 μm), ash percentage (≤2 wt%), surface area (>400 m²/g), purity (≥90%) and diameter (<2 nm). CNTs, with graphite as the conductive material and polytetrafluoroethylene (PTFE) as binder, were mixed and used to fabricate the electrode, and their percentages in the final electrode were 70%, 20% and 10%, respectively. Ethanol (10–20 mL) was added dropwise into the mixture and then put into an ultrasonic bath for 2 h. Subsequently, the mixture was pressed on to the graphite sheet then assembled into a CDI device. Each electrode was 80 mm wide × 100 mm long × 0.2 mm thick, and had a hole with the diameter of 4 mm as a water inlet or outlet. For comparison, a commercial AC (Kejing, China) was used to fabricate an electrode by the same approach. The desalination performance of both the AC electrode and the CNT electrode will be investigated by compared with respect to charge efficiency.

The surface morphologies of SWCNT electrodes were examined using a JEOL JSM-5100 scanning electron microscope (SEM). The pore-size distribution and Brunauer–Emmett–Teller (BET) SSA were deduced from the N₂ physical adsorption measurement data that were obtained with an ASAP 2010 accelerated surface area and porosimetry system (Micrometitics, Norcross, GA, USA).

**CDI experiment**

Batch-mode experiments were conducted in a continuously recycling system including a CDI unit cell (shown in Figure 1), with a conductivity monitor and current recorder. It should be noted that a nylon spacer as insulator was inserted between the two carbon electrodes to avoid short circuit. In each experiment, the solution was continuously pumped by a peristaltic pump into the unit cell and the effluent returned to the feed tank. Analytically pure sodium chloride (NaCl) was used for the aqueous solutions and the solution volume and temperature were maintained at 50 mL and 298 K, respectively, with an initial concentration of 4.1 mM (500 μS/cm in conductivity) or 8.2 mM (1,000 μS/cm in conductivity). The relationship between conductivity and concentration was obtained according to a calibration table made prior to the experiment, which has been described in our previous works (Li et al. 2009; Zhan et al. 2010). A direct voltage of 0.2–1.6 V was applied between electrodes. The hydrolysis of water was constantly monitored by a pH meter. It should be noted that hydrolysis of water was not found when the voltage between the two electrodes was more than 1.2 V because of the existence of high resistance across the whole circuit. The variation of conductivity and current was recorded simultaneously and independently.

**Theoretical**

As discussed elsewhere (Biesheuvel et al. 2009; Zhao et al. 2010), the concept of charge efficiency is derived from an assumption. If each electron charge is fully charge-balanced by counterion adsorption, the transfer of one electron from one to another electrode is accompanied by the removal of precisely one salt molecule out of the bulk solution. However, in the actual case, the co-ions are simultaneously expelled from the double layer accommodating the adsorbed ions, which has a negative impact on the charge efficiency. Ideally, if the counterion adsorption can fully compensate for the electron charge, the charge efficiency would be close to 1. Therefore, the charge efficiency (A) is a very useful tool to evaluate how much the electrical voltage contributes to the adsorption and is experimentally defined as

\[
A = \frac{F \times \Gamma}{\sum}
\]
where $F$ is Faraday constant (96,485 C/mol), $\Gamma$ (adsorption capacity, mol/g) is calculated from the adsorption curve where the concentration (mg/L) is a function of time, and $\Sigma$ (charge, C/g) is obtained by integrating the current. Thus,

$$\Gamma = \frac{(C_t - C_0) \times V \times 10^3}{58.5 \times M}$$  \hspace{1cm} (2)

$$\Sigma = \frac{\int i dt}{M}$$  \hspace{1cm} (3)

where $C_t$ and $C_0$ are the final and initial concentration (mg/L), $V$ (L) is the volume of test solution, and $M$ (g) is the mass of total electrodes.

RESULTS AND DISCUSSION

Typically, the adsorption capacity of the electrodes is directly related to their SSA, pore-size distribution and bulk conductivity. High SSA and reasonable pore-size distribution can promise a huge space to accommodate ions during adsorption, while high conductivity is beneficial to decrease the contact resistivity. Figure 2 depicts the pore-size distribution of CNT. The BET SSA and total pore volume of CNT is 448.06 m$^2$/g and 0.556 cm$^3$/g, respectively. The average pore diameter of 5 nm confirms that the CNTs are mainly composed of mesopores (2–50 nm). Such a mesoporous network structure is further confirmed by the SEM image in the inset of Figure 2. This ensures a low mass-transfer and allows hydrated ions to easily enter through the pores of the CNT electrode, which is very helpful for the ion adsorption (Leonard et al. 2009).

Figure 3(a) and 3(b) shows the typical conductivity and current transient in CDI, respectively. The inset in Figure 3(b) illustrates the current transient within 60 s at the initial stage of experiment. It should be noted that all of the experiments were run a sufficient amount of time (1–2 h) to reach equilibrium, indicating no more ions could be adsorbed onto electrodes. Clearly, Figure 3(a) illustrates that the conductivities dramatically decrease once the electrical voltage is applied. As expected, a high voltage results in a high adsorption capacity due to the high electrostatic force. As time goes by, the conductivities do not vary with time and CDI reaches saturation. The current response in Figure 3(b) follows a similar tendency as the conductivity response during the charge process. In a simplified model, the equivalent circuit of the CDI process is analogous to the combination of electrode resistivity ($R_s$) with electrical double capacitor ($C_d$), where the $R_s$ is connected with $C_d$ in series. With a constant charging potential, the current transient follows the equation: $e^{-\tau/R_s C_d}$, where $\tau$ represents the exponential decay constant, which can be obtained from the current

![Figure 2](https://iwaponline.com/wst/article-pdf/71/1/83/470072/wst071010083.pdf)

**Figure 2** | Pore-size distribution of CNT and corresponding SEM image (inset). The y-axis (it is often used as differential form) and x-axis represent the pore volume and pore size, respectively.

![Figure 3](https://iwaponline.com/wst/article-pdf/71/1/83/470072/wst071010083.pdf)

**Figure 3** | (a) Conductivity and (b) current responses in the CDI unit. Inset in (b) gives the current variation within 60 s.
response curve. Thus, \( \tau \) is 247.46, 366.1 and 632.45 s, corresponding to 1.0 V, 1.2 V and 1.4 V, respectively. Furthermore, the \( R_s \) and \( C_{dl} \) at cell voltage of 1.0, 1.2 and 1.4 V are calculated as 44.46, 52.27 and 67.82 \( \Omega \) and 5.57, 7.01 and 9.33 F, respectively. Obviously, the double-layer capacity, \( C_{dl} \), is greatly increased by increasing the cell voltage from 1.0 to 1.4 V, together with decay constant \( \tau \), confirming that the high cell voltage is beneficial to enhance the CDI performance of the CNT electrode.

In the regeneration process, or so-called discharge process, a short circuit is employed without imposing a reverse voltage because reverse voltage is not easy to control and may reverse electrosorption. The conductivity shows a rapid increase when the voltage is removed and a slower increase after several minutes (Figure 3(a)). According to Equation (1), from the equilibrium salt adsorption capacity \( \Gamma \) obtained from Figure 3(a) and the equilibrium charge \( \Sigma \) derived from Figure 3(b), it is easy to get the charge efficiency \( \Lambda \). Figure 4(a)–(c) shows \( \Sigma \), \( \Gamma \) and \( \Lambda \) as functions of voltage and ionic strength in CNT-based CDI, respectively. It can be observed that all of them increase with the increase in cell voltage, while the increase in ionic strength results in a negative impact on \( \Lambda \), which is consistent with the result reported by Zhao et al. (2010, 2012). In their work, both the theoretical and experimental analyses prove that the CDI is expected to be most promising for an aqueous solution with low ionic strength. A brief qualitative explanation is given below.

Ions in the diffuse electrical double layer reach equilibrium between the diffusion and electrostatic force, which could be reasonably described by the Poisson–Boltzmann equation and the Gouy–Chapman solution for ion concentrations and potential. At a long distance from the electrode the charge is completely held, so that the electric field is present only inside the diffuse electrical double layer. The relation between the surface charge density \( \sigma \) and the potential difference \( \phi \) between the electrode and the bulk solution is given by

\[
\phi = \frac{2k_B T}{e} \sinh^{-1}\left(\frac{\sigma}{\sqrt{8CN_Ae_0e_rk_B T}}\right)
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( e \) is the electron charge, \( N_A \) is the Avogadro constant, \( e_0 \) is the electric constant, \( e_r \) is the relative dielectric constant and \( C \) is the concentration; the equation is valid for a symmetric, monovalent electrolyte such as NaCl (Brogioli 2009). To better describe the experimental results, Brogioli (2009) rewrote Equation (4) in terms of electrical double-layer effective thickness \( L \) as \( \phi = L \sigma / e_0 e_r \), with \( L \) defined as \( L = \lambda_s \sinh^{-1}\left(\sqrt{\chi / C}\right) \), where \( \lambda_s = 2k_B T e_0 e_r / e \sigma \) and \( \chi = \sigma^2 / (8N_A e_0 e_r k_B) \) Therefore, the electrical double-layer thickness \( L \) is directly related to the electrostatic forces and diffusion. Obviously, the electrical double-layer thickness is...
inversely proportional with the solution concentration. Specifically, with the lower concentration, the electric field can extend to a longer distance since the solution is less effective in holding the charge. Once the concentration changes, the ions move toward the new equilibrium, resulting in a dynamic change in the length $K_B$.

Taking CDI with an initial concentration of 4.1 mM at 1.2 V for example, $\Gamma$ is $\sim 22.37 \mu$mol/g and $\Sigma$ is $\sim 10.33$ C/g, which are calculated from Equations (2) and (3). Thus $\Lambda$ is calculated to be $\sim 0.21$. Accordingly, the effective SSA should be 39.24 m$^2$/g, which is $\sim 8.76\%$ of the measured BET SSA of the CNT. The reason for the low charge efficiency is suggested to be co-ions impaction, weak adhesion between CNT and substrate, and low surface area. Basically, it should be realized that the charge dose not equal the salt adsorption, because the electron surface charge is compensated for in the diffuse layer by an adsorption of counterions as well as by a depletion of co-ions. Consequently, the charge efficiency is less than unity. Actually, in our experiment, in order to get rid of residual catalyst residing inside the CNT from preparation, the CNT was immersed in 1 M HNO$_3$ for at least 1 hour. Therefore, the oxygen functional groups, such as carboxyl and hydroxyl, would be introduced on the surface of the CNT, leading to a strong affinity between the charged ions and the CNT electrode. In this case, the co-ions impaction cannot be neglected. Also, PTFE which serves as binder has a large negative impact on the surface area and conductivity of CNT and thereby negatively contributes to charge efficiency.

As discussed above, CDI is envisioned to be a very energy-efficient water desalination technology, especially when the ionic content is relatively low. Herein, we performed a comparative study between CNT and AC electrode of the charge efficiency at an initial ionic strength of 0.85 mM to demonstrate the advance of CNT over AC in the application to CDI. Figure 5(a)–(c) depicts the adsorption capacity, charge and charge efficiency with respect to cell voltage in CNT- and AC-based CDI, respectively. According to Equations (1)–(3), it is rational to obtain the corresponding adsorption capacity, charge and charge efficiency for CNT and AC electrodes, respectively. In both CNT and AC electrodes, it is found that the $\Lambda$ increases with an increase in cell voltage, as do the results of Figure 4(c), confirming the behavior of $\Lambda$ predicted by the GCS theory (Biesheuvel et al. 2009; Zhao et al. 2012). Furthermore, the charge efficiency of the CNT electrode is higher than that of the AC electrode at each cell voltage, even two times higher when considering the high cell voltage, demonstrating the high energy efficiency of the CNT electrode over the AC electrode.

CONCLUSIONS

In conclusion, the charge efficiency of two oppositely positioned CNT electrodes can be determined from the total salt adsorption and electrode charge as reached at
equilibrium. It is found that the charge efficiency of the CNT electrode is associated with cell voltage and ionic strength. The high cell voltage and low ionic strength account for high charge efficiency. On the other hand, the CNT electrode shows higher charge efficiency than that of the AC electrode, confirming that the CNT electrode is preferable over the AC electrode when applied to CDI. Thus, the charge efficiency is proved to be a very useful parameter to evaluate the capacitive performance of porous electrodes in the CDI process.

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REFERENCES


Oren, Y. 2008 Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). Desalination 228, 10–29.


