Effective desalination by capacitive deionization with functional graphene nanocomposite as novel electrode material

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ABSTRACT

In this work, functional graphene nanocomposite (reduced graphite oxide-resol like material, named RGO-RF) was successfully synthesized and used as electrode in capacitive deionization (CDI) process. The porosity, morphology and electrochemical characteristics of RGO-RF were confirmed by N₂ adsorption-desorption curve, transmission electron microscopy and cyclic voltammetry, respectively. Further, the deionization performances of the RGO-RF electrode, reduced graphite oxide (RGO) and activated carbon (AC) were examined for comparison by a lab-scale CDI experimental system. It is found that the RGO-RF shows the best deionization performance among the three target materials, indicating that it is a novel electrode material which has a great potential as effective electrode for CDI. Besides, the electrosorption isotherms and electrosorption kinetics were studied, and it is found that the ion sorption behaviour of RGO-RF follows a Langmuir adsorption isotherm, implying monolayer adsorption.

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1. Introduction

Since the continuous increase of the world's population, the shortage of potable water has become one of the major issues in many countries in the past few decades [1–6]. To address this issue, extensive efforts have been devoted, involving development of new technique to reuse the wastewater and desalination of brackish water as well as the sea water. Currently, there are varieties of approaches for water purification, including ion exchange, electrodialysis, reverse osmosis and distillation, etc. [7–12]. Among all of the alternative approaches for water purification, desalination is a significant choice for producing potable water in many countries of the world, considering that 80% of our planet is occupied by the sea. However, most traditional desalination technologies are energy and capital intensive, for example, ion exchange produces secondary pollution resulting from the regeneration of resins [11] while electrodialysis, reverse osmosis [13] and distillation [14] are capital and energy intensive and require hard maintenance. Capacitive deionization (CDI), usually called electrosorption somewhere, absorbing ionic species onto the charged porous electrodes for desalination purpose, receives much attention in desalination community in recent years. Specifically, when an external direct voltage (<2 V) is imposed on the porous electrode, the electrochemical double layer would be formed in the

solution-electrode interface for holding ions. Once the external power is shorted or even reversed, the adsorbed ions would be released back to solution, resulting in the regeneration. Thus, this process shows the advantages of energy efficiency, high removal efficiency, easy regeneration and low cost over the above mentioned desalination technologies [5].

Basically, the prerequisite for the high removal efficiency of CDI is directly related to the electrode materials, which has high specific surface area for accommodating ions as well as superior conductivity for decreasing the contact resistivity. Up to date, various materials were investigated as CDI electrodes, such as activated carbon (AC), activated carbon composite materials, carbon nanotubes (CNTs), activated carbon cloth (ACC), carbon aerogel and mesoporous carbon (OMC) [5,13–28]. Based on analysing these materials, it is found that a high capacitive electrode should have large specific surface area for ionic accumulation, good electrical conductivity for effective charge holding and suitable pore size. Carbon materials have been extensively studied as electrodes, however most of them have their own disadvantages, for example, activated carbon (AC) has large surface area, the pore size is not favourable for electrosorption, and carbon nanotubes (CNTs), from the commercial application of view, are too expensive. So, it is necessary and desirable to seek and develop a new type of material as effective CDI electrodes.

Graphene, a two-dimensional carbon material with unique mechanic and electronic properties, offers promising properties, and sp² bonded carbon material, has drawn extensive attention since 2004 due to its unique physical and chemical properties [29–32]. The recent dramatic breakthrough in chemical methodology makes it

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easy to result in large-scale production which widely spans the graphene research not only carried out in laboratory, but also commercialized somewhere. As a low dimensional material, graphene has a huge theoretical specific surface area of 2600 m²/g, which is twice than that of the finely divided AC [33]. On the other hand, graphene presents an excellent electrical conductivity of 7200 S/m at room temperature [34]. These intriguing properties enable graphene to be used as electrode materials for energy storage device as well as CDI due to their similar working principle. However, although graphene was successfully proposed and developed as novel electrodes for CDI [1,35,36], the corresponding functional composites are seldom explored anywhere up to now. Because functional groups coupled with graphene have the advantage of both enlarging the specific surface area and enhancing the adsorption capability of graphene, it is worth conducting such a study to strengthen our basic understanding in application of graphene and graphene nanocomposite as electrode for CDI. In order to make the research of functional graphene deep and broadly going, functional graphene (RGO-RF) was synthesized and the electrosorptive properties were investigated for CDI.

In this work, the reduced graphite oxide-resol like material (RGO-RF) was synthesized as electrodes for CDI to examine its electrosorption performance by comparing with reduced graphite oxide (RGO) and commercial AC under the same experimental conditions. Besides, the working conditions, electrosorption isotherms and electrosorption kinetics in terms of RGO-RF based CDI were investigated as well. All of these are very important to develop new electrode materials and effective technology for desalination.

2. Experimental

2.1. Preparation of RGO and RGO-RF materials

Graphite oxide (GO) was synthesized by a modified Hummers method [37]. The detailed information was described in the Supporting Information (SI).

RGO-RF was prepared by the modified method reported by Worsley's group [38]. Typically, 2 mg/mL of GO suspension was thoroughly dispersed in deionized water by sonication for 1.5 h. Then, resorcinol (R), formaldehyde (F) and sodium carbonate catalyst (C) were added to the mixture altogether. The ratio of R:F:C was 200:400:1, according to the illustration reported [38]. Once GO was dispersed, resorcinol (1.235 g), formaldehyde (1.791 g) and sodium carbonate catalyst (5.95 mg) were added to the solution. Following, the solution was transferred to a 100 mL Teflon-lined autoclave and maintained at 85 °C for 3 days. After that, the resulting mixture was washed with acetone for 3 days in order to remove the water from the pores of the mixture. Successfully, the mixture was reduced by calcination at 900 °C under N₂ atmosphere, resulting in the reduced graphite oxide-resol like material, named RGO-RF.

2.2. Preparation of CDI electrodes

The carbon materials (RGO-RF, RGO and AC), and polytetrafluoroethylene (PTFE) as binder, were employed to fabricate the electrodes and their percentage were 80% and 20% respectively. Each electrode was about 70 mm wide × 140 mm long × 0.3 mm thick, and had a flow-through hole with a diameter of 4 mm. Ethanol (10–20 mL) was added dropwise to the mixture and then the mixture was pressed on graphite sheet and then dried for 8 h at 50 °C. Finally, the electrodes were assembled into a CDI unit cell.

2.3. Characterizations

The structures of the electrode materials were characterized by transmission electron microscopy (TEM, JEOL 3010). The X-ray diffraction (XRD) patterns of all samples were measured on a Rigaku powder

diffractometer (D/MAX-RB) using Cu K α radiation ($\lambda = 0.15418$ nm) at a scanning rate of 4°/min in $2\theta = 10\text{--}80^\circ$. Adsorption and desorption isotherms of nitrogen were measured with a NOVA 1200 gas sorption analyser at liquid nitrogen temperature (-196°C). Before the measurements, the samples were degassed under vacuum condition at 300 °C for 3 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area using adsorption data acquired at a relative pressure (P/P_0) range of 0.5–0.25. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherm based on the Barrett–Joyner–Halenda (BJH) algorithm. The micropore volume and micropore surface area were estimated by a t-plot method.

2.4. Electrochemical characterization

Cyclic voltammetry (CV) measurements of RGO-RF, RGO and AC were performed on an electrochemical workstation (CHI 600 D, Shanghai CH Instrument Company, China) with a typical three-compartment cell at ambient temperature. The as-synthesized electrode materials, a Pt wire electrode and an Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte was 1 M NaCl aqueous solution and the sweep potential range was adjusted from -1 V to 0 V (vs Ag/AgCl electrode). The capacitance was calculated from the current–voltage curves according to the following equation:

$$C = \frac{\int IdV}{v\Delta V} \quad (1)$$

where C is the specific capacitance (F/g), I is the response current (A), V is the potential (V), v is the potential scan rate (mV/s), and m is the mass of the electroactive materials in the electrodes (g).

2.5. Electrosorption experiment

Electrosorptive removal of NaCl by CDI was measured using a continuous recycling system including a CDI unit cell, a peristaltic pump, a power supply and a conductivity monitor. In a typical experiment, the NaCl with initial conductivity of 55 $\mu\text{S}/\text{cm}$ and volume of 200 mL was employed as feed solution. The mass of the electrodes was 1.5 g. The flow rate was 20 mL/min and different voltage was applied on the CDI unit. The variation of solution conductivity was monitored instantly by a multi-function conductivity meter (DDS-11A LiDa instrument). Accordingly, the correlation of conductivity ($\mu\text{S}/\text{cm}$) and concentration (mg/L) were calibrated prior to experiment.

In our experiment, the electrosorptive capacity was defined as below,

$$\text{Electrosorptive capacity (mg/g)} = \frac{(C_0 - C_t)V}{M} \quad (2)$$

where C_0 and C_t (mg/L) represent the initial and final NaCl concentrations, respectively, and V is the volume of the solution (L), and M is the mass of electrode (g).

3. Results and discussion

Generally speaking, the experimental conditions have a dramatic influence on the characters of the synthesized materials. In our experiment, hydrothermal method was used and then calcined to 900 °C directly without supercritical method, and it is found that the addition of resorcinol and formaldehyde can make the surface area of the material increase.

3.1. Morphology of RGO-RF and GO

Fig. 1 (a) and (b) shows the TEM images of GO and RGO-RF, respectively. It can be seen from Fig. 1 (a) that the GO sheets show a transparent character. In contrast to Fig. 1 (a), it is noted from Fig. 1 (b) that the RGO is fully covered by resol, incorporated with XRD pattern (Fig.S1), indicating the resol coupled with RGO very well.

The N_2 adsorption–desorption isotherm and the pore size distribution of RGO-RF, RGO and AC are presented in Fig. 2 (a) and (b), respectively. RGO-RF adopts clearly a typical type-IV isotherm with a hysteresis loop between the adsorption and desorption branches, integrated with pore size distribution, implying the existence of some mesopores which guarantees a huge space for ion accommodation in CDI process. In the case of AC, the curve exhibits a typical , which is the typical characteristic of microporous materials, illustrating that the huge BET surface area of AC is mainly contributed by the micropores and thereby it is not beneficial for ion accessing because the mesopores could be seen as the ion transportation route [25]. The detailed parameters including surface area and pore volume of RGO-RF, RGO and AC are summarized in Table 1. Notably, although the specific surface area of AC is larger than that of RGO-RF, the volume and surface area of micropores associated with RGO-RF are much smaller than that of AC except total pore volume, together with pore size distribution (shown in Fig.2 (b)), indicating the RGO-RF comprises a large fraction of mesopores (2–50 nm) which is thought to be the optimum pore size for electrosorption in CDI process. Upon this, the surface area and total pore volume of RGO-RF are much larger than the corresponding value of RGO, illustrating that the coupled resol plays a significant role in enhancing the surface area of RGO, resulting in a high electrosorption performance.

3.2. Electrochemical property

CV measurements involving the RGO-RF, RGO and AC in 1 M NaCl aqueous solution at various sweep rates (from 10 mV to 100 mV) from -1 V to 0 V were carried out to examine the electrical double layer formation, from which electrosorption capacitance was calculated (Eq. (1)). Fig. 3 (a) and (b) shows the CV curves of RGO-RF and RGO at different sweep rates and the corresponding specific capacity is presented in Fig. 4. The CV curves of the RGO are asymmetric, with two small peaks located at -0.7 and -0.3 V, respectively, indicating the presence of electrochemical reactions due to the residual functional groups as a result of incomplete reduction from GO to RGO. Upon dealing with resol, all the CV curves become symmetric (Fig. 3 (a)), regardless of the sweep rate, implying that the electrosorption process is reversible. At the mean time, the symmetric curve shows a smooth shape without presence of any peaks, illustrating that the dealt resol

Fig. 2. N_2 adsorption–desorption isotherm (a) and pore size distribution (b) of AC, RGO and RGO-RF samples at 77 K.

is beneficial to the decrease of the residual functional groups. Specifically, taking into the sweep rate at 10 mV as an example, the specific capacitance increased greatly from 112 F/g for RGO to 135.7 F/g for RGO-RF, due to a dramatic rise in the specific surface area. Likewise, the enhancement of specific surface area can account for the increase of the specific capacitance at other sweep rates. In addition, it can be seen that at each sweep rate, the specific capacitance of RGO-RF and RGO is larger than that of AC, possibly attributed to the small $V_{\text{micropore}}$ as well as $S_{\text{micropore}}$ inside the RGO-RF and RGO.

3.3. Electrosorption performances

It is known that the CDI process is closely related to the electrical voltage. In our experiment, as expected, high electrical voltage results in high electrosorptive capacity because of strong Coulombic interaction. Fig. 5 shows the electrosorption performance of RGO-

Fig. 1. TEM images of (a) GO and (b) RGO-RF.

Table 1
Pore parameters of different electrodes from the nitrogen isotherms at -196°C .

Materials	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	$V_{\text{micropore}}$ ($\text{m}^3 \text{g}^{-1}$)	$S_{\text{micropore}}$ ($\text{m}^2 \text{g}^{-1}$)	$D_{\text{pore size}}$ (nm)
RGO-RF	406.4	0.3174	0.1042	226.9	3.124
RGO	137.4	0.223	–	–	6.502
AC	836.0	0.418	0.345	754.4	2.001

RF at different electrical voltages and the inset represents the electrosorptive capacity as a function of electrical voltage. With the increase of voltage from 0.5 V to 2.0 V, the electrosorptive capacity gradually rose from 0.457 mg/g to 1.424 mg/g which is higher than the reported 23.18 $\mu\text{mol/g}$ (1.35 mg/g) [1].

Further, the impact of initial concentrations on electrosorptive performance in association with RGO-RF, RGO and AC electrodes was investigated as well. Fig. 6 shows the conductivity transient in terms of RGO-RF, RGO and AC electrodes with respect to different initial concentrations, ranging from 25 mg/L to 65 mg/L with an interval of 15 and 25 mg/L. Accordingly, the voltage was 2.0 V and flow rate of 20 mL/min. Overall, the RGO-RF presents the best electrosorption performance among three target electrodes, regardless of initial concentration. On another hand, with the concentration that increased from 25 mg/L to 65 mg/L, the electrosorptive capacity of RGO-RF electrode is gradually enhanced from 1.424 mg/g to 3.229 mg/g, illustrating that the initial concentration has a positive impact on electrosorption performance of RGO-RF. It is likewise in the case of RGO and AC electrode. Table 2 lists the electrosorptive capacity of RGO-RF, RGO and AC electrode under different initial concentrations.

Fig. 3. Cyclic voltammograms of RGO-RF (a) and RGO (b) at different sweep rates (10, 20, 30, 40, 50, 100 mV/s) in 1 M NaCl aqueous solution.

Fig. 4. Specific capacitance of RGO-RF, RGO and AC in 1 M NaCl aqueous solution at different sweep rates.

3.4. Electrosorption isotherms

To further investigate the electrosorption isotherm of as-prepared RGO-RF, batch electrosorption experiments were carried out at different initial concentrations, involving 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L, 400 mg/L and 500 mg/L with the electrical voltage of 2.0 V and flow rate of 20 mL/min. The linearized Langmuir equation (Eq. (3)) and Freundlich equation (Eq. (4)) were employed to simulate the experimental data, which are listed as below:

$$1/Q = 1/Q_m KC + 1/Q_m \quad (3)$$

$$\lg Q = \lg K + 1/n \lg C_e \quad (4)$$

where C is the equilibrium concentration (mg/L), Q is the amount of adsorbed NaCl (mg/g), Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage. K_L is Langmuir constant related to binding energy (L/mg), K_F and n are the Freundlich constants related to the capacity of adsorbent to adsorb and the tendency of the adsorbate to be adsorbed, respectively.

In order to predict the adsorption efficiency of the process, the dimensionless quantity (r) was calculated by using the following equation:

$$r = \frac{1}{1 + K_L C_0} \quad (5)$$

Fig. 5. Electrosorption of NaCl onto RGO-RF electrode at different electrical voltages. (The inset shows the electrosorptive capacity of RGO-RF).

Fig. 6. Electrodesorption of NaCl onto RGO-RF, RGO and AC electrode at voltage of 2.0 V and flow rate of 20 mL/min with different initial concentrations: (a) 25 mg/L (57 μS/cm), (b) 40 mg/L (95 μS/cm) and (c) 65 mg/L (145 μS/cm).

where C_0 and K_L are the initial concentration of NaCl and the Langmuir isotherm constant. If the value of $r < 1$, it represents favourable adsorption while greater than 1.0 represents unfavourable adsorption. The value of r at initial NaCl concentration of 25 mg/L was found to be 0.79, which indicates that the present system is favourable for adsorption.

Table 3 shows the determined parameters and regression coefficients R^2 , K_L and K_F of Langmuir and Freundlich isotherms for RGO-

Table 2

Electrodesorption capacity in association with various electrodes under different initial concentrations.

Concentration	Electrode		
	RGO-RF	RGO	AC
25 mg/L	1.424 mg/g	0.799 mg/g	0.423 mg/g
40 mg/L	2.135 mg/g	1.510 mg/g	0.612 mg/g
65 mg/L	3.229 mg/g	1.800 mg/g	1.507 mg/g

based CDI, respectively. Fig. 7 presents the experimental data as well as the fitted line. It is clearly observed from Fig. 7 that the Langmuir isotherm correlated with the experimental data very well according to the correlation coefficient (R^2). This suggested that the monolayer adsorption was primary during the electrodesorption process. Furthermore, the parameter Q_m defined as the maximum adsorption capacity is 13.245 mg/g, implying the electrodesorption limitations in RGO-RF electrode based on given experimental conditions. In addition, as introduced above, the K_L related to the free energy is always employed to calculate the affinity between the electrodesorbed species and electrode.

3.5. Electrodesorption kinetics

Adsorption kinetics is an important characteristic of the adsorption process. The electrodesorption rate of NaCl on RGO-RF was examined by studying the adsorption kinetics at different initial bias potential of 0.5 V, 1.0 V, 1.5 V and 2.0 V with a flow rate of 20 mg/L. The kinetics of electrodesorption and the electrodesorption rate of NaCl were determined by the Lagergren equation, which is often called the pseudo-first-order adsorption kinetics (Eq. (6))

$$\frac{dq_t}{dt} = k(q_e - q) \quad (6)$$

where k is the adsorption rate constant (min^{-1}), q_e and q are the amount of NaCl adsorbed at equilibrium (mg/g) and time t (min), respectively. Integrating Eq. (6) with respect to the integration conditions of $q = 0$ to $q = q_t$ at $t = 0$ to $t = t$, the kinetics rate expression becomes

$$\log(q_e - q) = \log q_e - \frac{kt}{2.303} \quad (7)$$

The adsorption kinetics was fitted with the Lagergren law by nonlinear regression using the method of least squares. The results are given in Fig. 8 and Table 4, and it is obvious that the adsorption capacity and the rate were increased greatly as the bias potential increased. The equilibrium adsorption capacity at 1.5 V was 1.002 mg/g, while adsorption capacity at 2.0 V was increased to 1.735 mg/g. However the regression coefficient R^2 is smaller than it is at 1.5 V, this maybe because of the quicker adsorption of NaCl on to the electrode at the beginning of the experiment. These results suggested that the maximum adsorption capacity for NaCl on RGO-RF electrode can be improved as the potential increased. Therefore, it was concluded that by using the RGO-RF electrodes the electrodesorption could be effectively enhanced.

Table 3

Determined parameters and regression coefficients R^2 , K_L and K_F of Langmuir and Freundlich isotherms of RGO-RF based CDI at room temperature.

Isotherm	Model equation	Parameter	Value
Langmuir	$Q = \frac{Q_m K_L C}{1 + K_L C}$	Q_m	13.245
		K_L	0.01072
		R^2	0.9925
Freundlich	$Q = K_F C^{1/n}$	K_F	2.2801
		n	0.477
		R^2	0.9546

Fig. 7. Linearized electrosorption isotherms of NaCl onto RGO-RF electrode (a) Langmuir isotherm and (b) Freundlich isotherm at 2.0 V.

4. Conclusions

In summary, the reduced graphite oxide-resol like material (RGO-RF) was successfully synthesized and used as the electrodes for capacitive deionization (CDI). The RGO-RF composites show enhanced adsorption capacity for NaCl removal as compared with RGO. The addition of resol is beneficial for the increase of the specific surface area of reduced graphite oxide (RGO), which results in high NaCl uptake. Furthermore, the electrosorptive behaviour of RGO-RF follows a Langmuir adsorption, illustrating a monolayer adsorption. The equilibrium electrosorption capacity and rate constant increased with the voltage at 1.5 V were 1.00234 mg/g and 0.05394 min⁻¹, respectively. In conclusion, compared with AC and the as-synthesized RGO, this RGO-RF material can be a candidate of electrode, which

Fig. 8. Electrosorption kinetics of NaCl onto RGO-RF at different bias potentials.

Table 4

Adsorption/electrosorption parameters of first-order adsorption kinetics for NaCl at different potentials.

Bias potentials (V)	q _e (mg/g)	K (× 10 ⁻²)	R ²
0.5	0.5039	2.929	0.94917
1.0	0.6185	3.216	0.91418
1.5	1.0023	5.394	0.96607
2.0	1.7353	4.147	0.92579

shows a promising potential for efficient CDI process in brackish water desalination and drinking water purification.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.desal.2012.05.028>.

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