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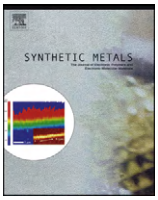

Polypyrrole nanowire modified graphite (PPy/G) electrode used in capacitive deionization

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ABSTRACT

With high specific capacitance and good conductivity, polypyrrole nanowire modified graphite (PPy/G) electrode has great promising applications in capacitive deionization (CDI). Preparation parameters of modified electrode such as concentration of supporting electrolyte solution ($LiClO_4$), concentration of monomer (pyrrole, Py), pH of polymerization medium, polymerization potential and time have significant effects on the electrode adsorption capacity of NaCl. The experimental results indicate that the optimal preparation condition of the PPy/G electrode used for CDI is 0.10 M $LiClO_4$, 0.19 M Py and pH 5.91 which was controlled by phosphates buffer solution (PBS, 0.10 M), polymerized at 0.85 V *vs* saturated calomel electrode (SCE) with polymerization time of 150 s. The obtained electrode has an area specific capacitance of 0.188 F/cm^2 determined by cyclic voltammetry (CV) method in 1.0 M $HClO_4$ at a scanning rate of 0.05 V/s. In addition, the desalination experiments of the electrode were carried out in 500 ppm NaCl solution at a working voltage of 1.4 V. The experimental results indicate that the NaCl can be removed from the feed solution by electroadsorbing of the electrode with good desalination stability and the electrode can be regenerated efficiently by its electrodesorbing.

1. Introduction

Capacitive deionization (CDI), as a non-membrane desalination technology with low-grade contamination, desalts saline solution by circulation of charge/discharge processes of capacitor electrodes. During the charge process, ions are adsorbed on the electrode under the electrostatic force and as a result, the feed solution is desalinated. Correspondingly, during the discharge process, the ions adsorbed on the electrode are released into the washing stream and thus the electrode is regenerated. In recent years, the CDI develops rapidly due to the advantages over other ordinary desalination processes on high recovery ratio of fresh water, low energy cost and no additional chemical consumed [1], and has great promising applications in desalination of brackish water, purification of drinking water, preparation of highly purified water, collection of heavy metal in electroplating wastewater, and other separation fields [2,3].

Appeared in the middle of 1960s [3], porous activated carbon was adopted as the CDI electrode material and the technology was applied for desalination of slightly alkalescent solution. Because of the low specific capacitance and high resistance, porous activated carbon made electrode has low adsorption capacity and thus high energy consumption. Not until 1996, a new kind of carbon material—carbon aerogel was developed and introduced as electrode materials, and as a result, the electrode performance was improved significantly [4]. Subsequently, CDI technology was reborn and other carbon-based electrode materials which include porous carbon aerogel–silica gel composite materials, carbon nanotubes, ordered mesoporous carbon and so on, were developed and widely adopted in CDI cells [5–10].

Normally, capacitor prepared from carbon-based materials is classified as electric double-layers capacitor (EDLC), whose capacitance mainly depends on the effective specific surface area of the electrodes. The fact that capacitance of the ordered mesoporous electrode or the porous carbon aerogel–silica gel electrode is larger than that of the active carbon electrode complies with the above principle [10,11]. Another kind of capacitor made by metal oxides, conducting polymers or their composite is called pseudo-capacitor (also electrochemical capacitor), whose specific capacitance is much higher than that of EDLC [12–23]. However, due to the high production cost and possible contamination caused

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by the metal oxides eroded into the purified water, electrodes made from metal oxides or their composites are not feasible in CDI process.

Compared with metal oxides, the conducting polymer is cheap and flexile, also with high electrical conductivity and large pseudo-capacitance [20]. So it is considered the perfect material for fabrication of pseudo-capacitor. Recent studies show that polypyrrole (PPy) can be prepared into nanowire formation, and its specific capacitance is as high as 282 F/g, which is 30% higher than that of PPy granule prepared by “soft template and characterized at 1.0 A/g in 1.0 M aqueous KCl electrolyte solution” [21].

In this paper, PPy was adopted as the electrode material, preparation conditions of the polypyrrole nanowire modified graphite (PPy/G) electrode used for CDI were tested and optimized. The desalination performances of the electrode were also characterized.

2. Preparation of the PPy/G electrode

Graphite piece with diameter of 30 mm and thickness of 2 mm was prepared by hot moulding the mixture of graphite powders (G, 90% w/w) and the phenol-formaldehyde resin (PF, 10% w/w) at the curing temperature of 150 °C and pressure of 50 MPa for 5 min. Thereafter, in order to reduce the fouling trend of electrode when “real” water samples are treated, the graphite piece is polished with 2000$^{\#}$ emery paper.

The polymerization process was carried out in a three-electrode cell with graphite piece as working electrode, another piece of graphite as counter electrode and saturated calomel electrode (SCE) as reference electrode. Polymerization of pyrrole was performed at 0.85 V *vs* SCE by potential step at room temperature in a medium containing supporting electrolyte solution ($LiClO_4$, concentration varied from 0.10 M to 0.60 M) and pyrrole monomer (concentration varied from 0.14 M to 0.24 M) at different pH values (varied from 4.50 to 8.04). Phosphates buffer solution (PBS) with concentration of 0.10 M was used to adjust pH value of the polymerization medium. Before the polymerizing reaction, the polymerization solution was deaerated thoroughly with pure nitrogen for at least 20 min. Also, after polymerization, the obtained PPy/G modified electrode was immersed in 1.0 M $HClO_4$ solution for at least 24 h to remove the monomer, oligomers, $H_2PO_4^-$ and HPO_4^{2-} from the electrode. Eventually, the electrode was reduced at −0.20 V *vs* SCE in order to dedop anions, and then immersed in deionized water for 48 h before use.

Cyclic voltammetry (CV) measurement of the PPy/G electrode is carried out in 1.0 M $HClO_4$ solution, the CV curve is recorded in the potential window ranged from −0.50 to 0.60 V *vs* SCE at scanning rate of 0.05 V/s. From the CV curves, the capacitance (C, F) and area specific capacitance (C_q, F/cm^2) are calculated by Eqs. (1) and (2):

$$C = \frac{\bar{i}}{v} = \frac{(1/(E_2 - E_1)) \int_{E_1}^{E_2} i(E)dE}{v} \quad (1)$$

$$C_q = \frac{C}{A} \quad (2)$$

where $i(E)$ is the scanning current function of the PPy/G electrode (A), E_1 and E_2 are the low limit potential and upper limit potential (V), v is the scanning rate (V/s), A is the apparent surface area of the PPy/G electrode (cm^2).

The experimental CDI cell was assembled with PPy/G electrode as anode and graphite piece as cathode. The desalination performance of CDI cell was tested using NaCl solution (500 ppm, 20 mL) as the feed. The distance between the two electrodes is set as 10 mm. A potential of 1.4 V for 3 min was applied on the CDI cell during the adsorption process, and an opposite potential of −1.4 V for 2 min during the desorption process. Conductivity of the feed solution is recorded continuously during the desalting experiments.

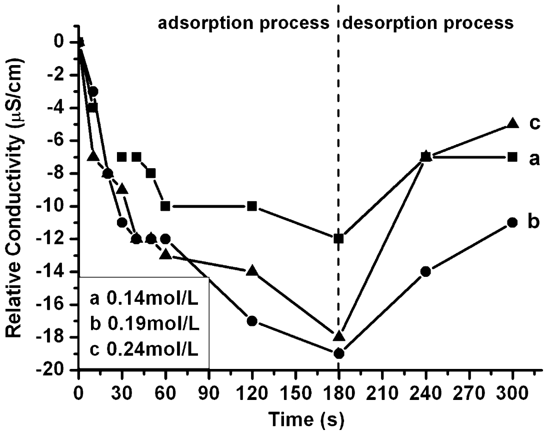

Fig. 1. Desalination performance of PPy/G electrodes prepared at different pyrrole monomer concentrations and under 0.10 M $LiClO_4$, pH 5.91 and polymerization time 150 s.

For this work, the adsorption capacity (Q, g), the desalting velocity (ψ, g/(L s)) and the regeneration ratio (η) are used to evaluate desalination performance of the PPy/G electrode, which are calculated using the following equations:

$$Q = (c_0 - c_1) \times V \quad (3)$$

$$\psi = \frac{c_0 - c_t}{t} \quad (4)$$

$$\eta = \frac{c_2}{c_0} \quad (5)$$

where c_0 is the initial concentration of NaCl solution (g/L), c_1 is the concentration after the adsorption process (g/L), c_t is the instant solution concentration at time t, c_2 is the concentration after the desorption process (g/L), V is the volume of NaCl solution (L).

3. Results and discussions

To obtain the optimal preparation conditions of the PPy/G electrode, parameters such as concentration of the pyrrole monomer, concentration of the supporting electrolyte ($LiClO_4$), pH value of polymerization medium and polymerization time were investigated. Their effects on desalination performance of the modified electrode were also tested respectively.

3.1. Concentration of the pyrrole monomer

As is known, capacitance of the PPy/G electrode mainly comes from the pseudo-capacitance of PPy [24,25], while Py monomer concentration has significant effects on the formation and capacitance of PPy. Fig. 1 illustrates the influences of Py monomer concentration on the electrode desalination performances. From the figure, it can be seen that the relative conductivity (the instant conductivity minus the initial conductivity) of the feed solution presents as V-type curve which can be divided into the adsorption process at the left side and the desorption process at the right side. During the adsorption process, ions are adsorbed on the electrodes under the electrostatic force and as a result the feed was desalted and its conductivity decreases as the process goes on. When the operating time comes to 180 s, the applied potential of the CDI cell was reversed accordingly. Under this condition, the adsorbed ions are released into the previously desalted medium and the electrodes are regenerated at the same time.

As shown in Fig. 1, the PPy/G electrode prepared at 0.19 M Py has a higher adsorption capacity than that of at 0.14 M and at 0.24 M Py. Also the specific capacitance of the PPy/G electrode prepared at 0.19 M Py is the largest under the given conditions shown in

Table 1
Specific capacitance of the PPy/G electrode prepared at different monomer concentrations.

Monomer concentration (M)	0.14	0.19	0.24
Specific surface area[a] (m^2/g)	0.026	0.015	0.0087
Specific capacitance (F/cm^2)	0.135	0.165	0.122

[a] The specific surface area is measured by BET method.

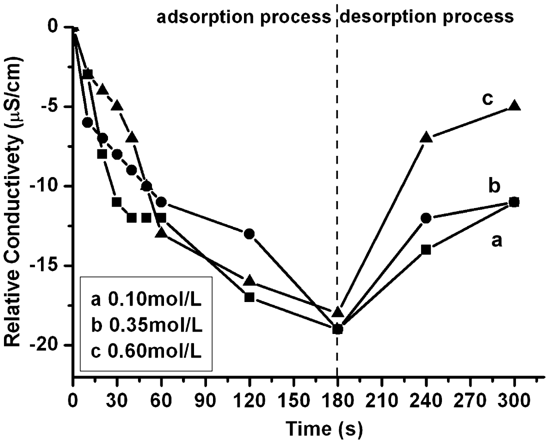

Fig. 2. Desalination performance of PPy/G electrodes prepared at different concentrations of supporting electrolyte and under 0.19 M Py, pH 5.91 and polymerization time 150 s.

Table 2
Specific capacitance of the PPy/G electrode prepared at different $LiClO_4$ concentrations.

$LiClO_4$ concentration (M)	0.10	0.35	0.60
Specific surface area (m^2/g)	0.015	0.034	0.071
Specific capacitance (F/cm^2)	0.165	0.184	0.141

Table 1. These phenomena are ascribed to the higher the monomer concentration, the thicker the PPy nanowire layer, but the higher polymerizing rate and the larger diameter of the nanowire prepared at high monomer concentration make the effective surface area of the electrode decrease [26]. So, it is believed that the effective surface area reaches the maximum value at 0.19 M Py [22] and the Py monomer concentration of 0.19 M is considered the optional one under the experimental conditions. In addition, by evaluating the regeneration ratio of electrodes prepared at different Py concentrations, a calculated regeneration ratio of 99.14% (a), 98.60% (b) and 99.36% (c) can be obtained, respectively, which means the adsorption ability of the electrode can be resumed efficiently at the given condition of desorption process.

3.2. Concentration of the supporting electrolyte

PPy nanowire prepared with ClO_4^- as the supporting electrolyte ion has a high specific capacitance and good conductivity [20], and its concentration has significant effect on the morphology of PPy nanowire, and thus the desalination performance of the electrode [27].

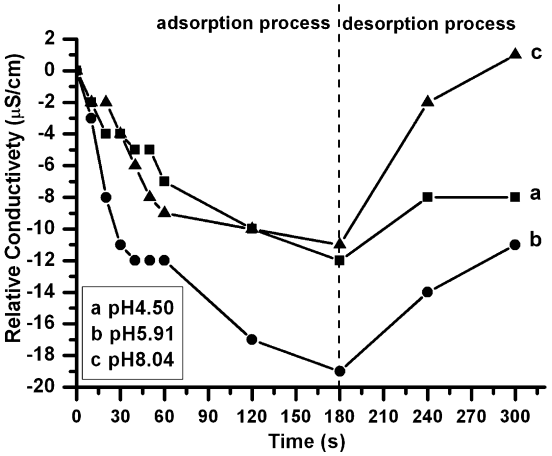

Fig. 3. Desalination performance of PPy/G electrodes prepared at different pH values of polymerization solution and under 0.10 M $LiClO_4$, 0.19 M Py and polymerization time 150 s.

Table 3
Specific capacitance of the PPy/G electrode prepared at different pH values.

pH of the polymerization solution	4.50	5.91	8.04
Specific surface area (m^2/g)	0.0020	0.015	0.068
Specific capacitance (F/cm^2)	0.133	0.165	0.185

Fig. 2 presents the influences of the $LiClO_4$ concentration on the desalination performance of the PPy/G electrode. It can be seen that the desalination performances of the electrodes present as similar V-type curves discussed in Section 3.1. The curves indicate that the adsorption capacities of the PPy/G electrodes are almost the same under the experimental condition. Table 2 also indicates that the specific capacitance of the electrode prepared at different $LiClO_4$ concentrations has no obvious difference. So, 0.10 M $LiClO_4$ solution is adopted in the following experiments. As regards to the regeneration ratio of the electrodes, the calculated ratio is as high as 98.60% (a), 98.66% (b) and 99.45% (c), respectively. This proves that the regeneration rate of the electrode is pretty good and the regeneration condition is feasible.

3.3. pH value of the polymerization solution

Fig. 3 shows the influences of pH value of the polymerization solution on the desalination performance of the PPy/G electrodes. From the figure it can be seen that the adsorption capacity, as well as the desalting velocity of the PPy/G electrode prepared at pH 5.91 is the highest among the three pH levels. However, performance of the electrode presented in Table 3 indicates that the specific capacitance of the electrode prepared at pH 8.04 is the largest, followed by pH 5.91 and pH 4.50. The adsorption capacity and the specific capacitance are determined by the effective surface area of the electrode and the electro-activity of the electrode materials. The effective surface area of the electrode gets higher with the increase of the pH, coming from the good nanowire morphology. But, the electro-activity of the electrode materials is deteriorated with the pH increase, which is caused by the overoxide of PPy at β position. As a conclusion, pH 5.91 is considered the suitable condition for the modified electrode preparation. Additionally, calculating by Eq. (5), the regeneration ratio of the electrodes is as much as 99.01% (a), 98.60% (b), 100.12% (c), respectively, which approves that the electrode adsorption ability can be regenerated sufficiently at the desorption process.

3.4. The polymerization time

Fig. 4 shows the influences of the polymerization time on the desalination performance of the PPy/G electrode. From the curves, it can be seen that the adsorption capacity and the desalting velocity of the PPy/G electrode prepared for 150 s is the highest under the given conditions. Correspondingly, the specific capacitance of the electrode prepared for 150 s is also the largest as shown in Table 4. This result is related to the larger amount of PPy nanowire produced under the longer polymerization time, which increases the adsorption capacity of the electrode. PPy degradation always

Table 4
Specific capacitance of the PPy/G electrode prepared at different polymerization times.

Polymerization time (s)	50	100	150	300	450
Specific surface area (m^2/g)	0.0013	0.0023	0.015	0.027	0.054
Specific capacitance (F/cm^2)	0.159	0.145	0.165	0.0615	0.0937

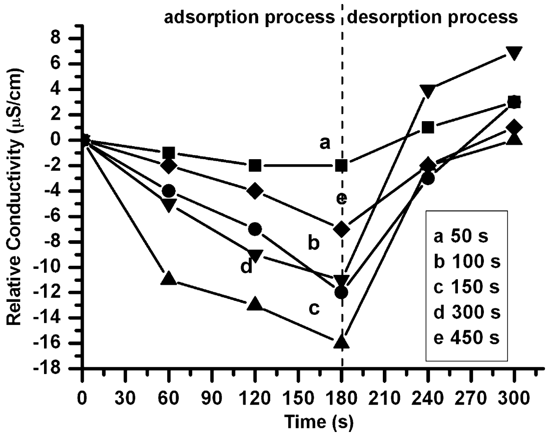

Fig. 4. Desalination performance of PPy/G electrodes prepared for different polymerization times and under 0.10 M $LiClO_4$, 0.19 M Py and pH 5.91.

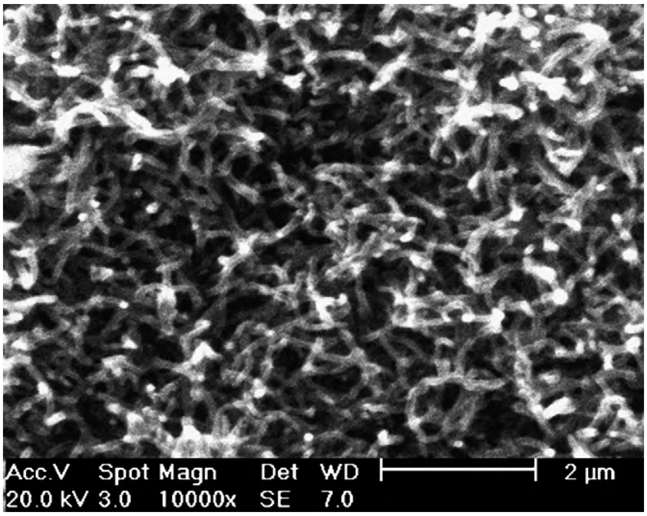

Fig. 5. SEM image of the PPy/G electrode surface.

accompanies with polymerization process which induces the lower electro-activity of PPy as mentioned above. We do think when polymerization time is longer than 150 s, the adsorption capacity and the specific capacitance decrease resulting from the degradation of PPy surpassing their increase coming from the added PPy. So, the 150 s is regarded as the optimal polymerization time. In addition, by evaluating the regeneration ratio of the PPy/G electrodes for different polymerization times, the calculated ratio are 100.31% (a), 100.31% (b), 100% (c), 100.87% (d), 100.12% (e), respectively, which means that the electrode adsorption ability can be resumed well under the given conditions.

3.5. Desalination tests

Based on the above experiments, the optimal preparation condition of the PPy/G electrode at 0.85 V *vs* SCE is obtained as 0.10 M $LiClO_4$, 0.19 M Py and pH 5.91 for 150 s. Under this condition, the SEM image of PPy formed on the modified electrode was shown in Fig. 5, in which the PPy nanowire morphology can be clearly observed and with uniform diameter.

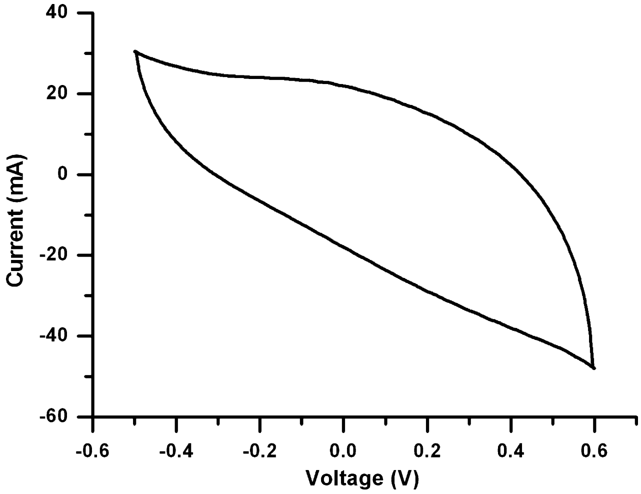

Fig. 6. Cyclic voltammetry curve of the PPy/G electrode in 1.0 M $HClO_4$ at a scanning rate of 0.05 V/s.

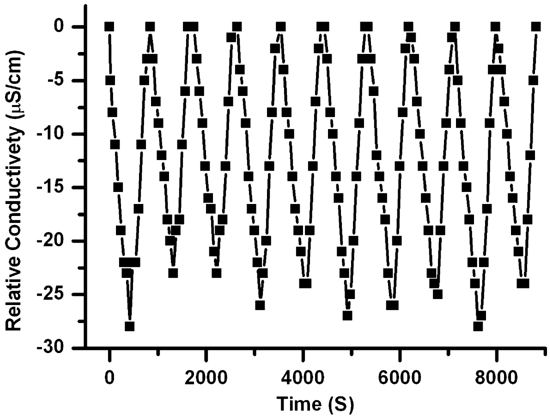

Fig. 7. The multiadsorption/desorption process of the PPy/G electrode.

Fig. 6 shows the CV curve of the PPy/G electrode prepared at the optimal condition in 1.0 M $HClO_4$ and at 0.05 V/s scanning rate. By using the CV curve and Eqs. (1) and (2), the specific capacitance of the obtained electrode can be calculated as 0.188 F/cm^2 which is higher than micro-polypyrrole (PPy) films doping with ClO_4^- (0.064 F/cm^2 at 0.005 V/s) [28]. The desalination performances of the prepared electrode are presented in Fig. 7. From the figure, it can be seen clearly that the adsorption process and the desorption process are implemented alternately during the tenth circulatory tests. By evaluating the desalination performance, conclusions can be made that the electrode adsorption capacity is stable, and the regeneration rate remains up to 99.40% for every adsorption/desorption process, which is favorable for guaranteeing the future long life of the CDI cell.

4. Conclusions

Polypyrrole nanaowire modified graphite electrode with high specific capacitance has been prepared and is used to assemble the CDI cell. Desalination performance of the electrode is characterized under the applied voltage of 1.4 V for 3 min at the adsorption process and −1.4 V for 2 min at the desorption process. The single parameter experiments conclude that the optimal preparation conditions for the PPy/G electrode are 0.10 M $LiClO_4$, 0.19 M Py and pH 5.91 at 0.85 V *vs* SCE for 150 s. The SEM image clearly shows that the prepared PPy is in nanowire morphology and with uniform diameter. The specific capacitance of the electrode is 0.188 F/cm^2 which is obtained by CV in 1.0 M $HClO_4$ at 0.05 V/s scanning rate. The desalination experiments indicate that the electrode has a stable adsorption capacity and high regeneration ratio, which promises a longer life cycle of the CDI cell.

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