Surface-treated carbon electrodes with modified potential of zero charge for capacitive deionization

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Abstract: The potential of zero charge (E_{pzc}) of electrodes can greatly influence the salt removal capacity, charge efficiency and cyclic stability of capacitive deionization (CDI). Thus optimizing the E_{pzc} of CDI electrodes is of great importance. A simple strategy to negatively shift the E_{pzc} of CDI electrodes by modifying commercial activated carbon with quaternized poly (4-vinylpyridine) (AC-QPVP) is reported in this work. The E_{pzc} of the prepared AC-QPVP composite electrode is as negative as -0.745 V vs. Ag/AgCl. Benefiting from the optimized E_{pzc} of electrodes, the asymmetric CDI cell which consists of the AC-QPVP electrode and a nitric acid treated activated carbon (AC-HNO₃) electrode exhibits excellent CDI performance. For inverted CDI, the working potential window of the asymmetric CDI cell can reach 1.4 V, and its salt removal capacity can be as high as 9.6 mg/g. For extended voltage CDI, the salt removal capacity of the asymmetric CDI cell at 1.2/-1.2 V is 20.6 mg/g, which is comparable to that of membrane CDI using pristine activated carbon as the electrodes (19.5 mg/g). The present work provides a simple method to prepare highly positively charged CDI electrodes and may pave the way for the development of high-performance CDI cells.

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1. Introduction

Many regions on the planet are facing serious shortages of fresh water. To solve this problem, various desalination technologies such as multi-stage flash distillation, reverse osmosis and electrodialysis have been developed (Anderson et al., 2010). Capacitive deionization (CDI) is an alternative desalination technology based on capacitive principle and is especially energy efficient in the treatment of low concentration streams (Suss et al., 2015). To improve the performance of CDI and broaden the scope of its application, considerable research has been conducted on the preparation of CDI electrodes (Dong et al., 2015, Hou et al., 2015, Liu et al., 2015b, Porada et al., 2015, Wimalasiri et al., 2015 and Xu et al., 2015), the optimization of the operation process (Zhao et al., 2013, Cohen et al., 2015 and Bian et al., 2015), the mathematical modeling of the CDI process (Kim et al. 2015 and Dykstra et al., 2015), membrane CDI (MCDI) (Lee et al., 2011 and Liang et al., 2013), the development of new CDI systems (Lee et al., 2014 and Gao et al., 2015a), the selective removal of ions (Seo et al., 2010, Kim and Choi, 2012 and Tang et al., 2015), etc. CDI is expected to become a low-cost and highly energy-efficient desalination technology in the future.

In a typical CDI process, water flows between two oppositely placed electrodes, and the ions in water are adsorbed into the electrodes when a cell voltage is applied. After the adsorption equilibrium is reached, the electrodes can be regenerated by short-circuiting or reversing the cell voltage to release the adsorbed ions. For CDI electrodes, the potential of zero charge (E_{pzc}) of electrodes, defined as the potential where no excess ionic charge exists in the electrode surface (Biesheuvel et al., 2015), is a key parameter because it can greatly influence the salt removal capacity, charge efficiency, and cyclic stability of CDI. The introduction of negatively charged functional groups can shift E_{pzc} to a more positive value, whereas the introduction of positively charged functional groups shifts E_{pzc} to a more negative value. The value of E_{pzc} is measurable and the ion adsorption status of an electrode

can be determined from E_{pzc} and the electrode potential (denoted by E). When $E = E_{pzc}$, the net ionic charge in the electrode is minimized. When $E > E_{pzc}$, anion adsorption occurs in the electrode. On the contrary, cations are adsorbed into the electrode when $E < E_{pzc}$. Thus, electro-adsorption occurs only when the electrode is polarized away from E_{pzc} , that is, the potential that contributes to ion adsorption is $|E - E_{pzc}|$. To enlarge the potential window for ion adsorption, E and E_{pzc} should apparently be opposite in sign. In the case of a conventional CDI anode, when E_{pzc} is positive and E is polarized from E_0 (short circuit potential) to a more positive value than E_{pzc} , the potential for anion adsorption is $E - E_{pzc}$, whereas $E_{pzc} - E_0$ is used to desorb previously adsorbed cations, and this is referred to as the co-ion expulsion effect. For CDI, the co-ion expulsion effect can result in reduced salt removal capacity and charge efficiency (Zhao et al., 2010). By contrast, choosing an anode with negative E_{pzc} can effectively avoid the co-ion expulsion effect in the anode, and anions are adsorbed instantly when a cell voltage is applied.

The cyclic stability of CDI is also closely related with the E_{pzc} of the anode. Studies have reported that the E_{pzc} of the anode gradually shifts positively as a result of anode oxidation, resulting in serious co-ion expulsion and diminished charge efficiency (Cohen et al., 2015, Bouhadana et al., 2011 and Cohen et al., 2013). Given the difficulty of avoiding the anode oxidation of carbon materials, a novel CDI system called inverted capacitive deionization (i-CDI) has been proposed to avoid the co-ion expulsion caused by anode oxidation (Gao et al., 2015a and Gao et al., 2015b). The developed i-CDI system consists of an anode with negative charges and a cathode with positive charges. A cell voltage is first applied on Q-N to desorb previously adsorbed ions during which the potential of the electrodes is gradually polarized to their E_{pzc} , and after which the electrodes are short-circuited for adsorption. The driving force of adsorption is supplied by the potential difference between the electrodes and is limited by $|E_{pzc, \text{anode}} - E_{pzc, \text{cathode}}|$. To realize the i-CDI process and obtain a broad working

voltage window, the E_{pzc} of the anode and the cathode should be as positive and negative as possible, respectively. Theoretically speaking, the more oxidized the anode is, the more negatively charged functional groups are introduced and the more positive $E_{pzc, \text{anode}}$ is. Thus, i-CDI can effectively avoid the co-ion expulsion caused by anode oxidation and exhibit excellent cyclic stability. Up to now, i-CDI performance is mainly limited by its relatively low cell voltage. Thus, optimizing the E_{pzc} of electrodes to enlarge the working voltage window of i-CDI is of great significance.

Recently, Biesheuvel et al. (2015) built a model considering fixed chemical surface charge and predicted a working range of enhanced desalination for CDI. Gao et al. (2016) demonstrated that CDI cells using surface charge enhanced electrodes can achieve an extended working voltage window and improved salt removal capacity by applying a cell voltage during the desorption process (extended voltage CDI, eV-CDI). The optimum cell voltage for desorption (V^*) at which a minimum adsorption or maximum desorption of salt occurs in a CDI cell can be predicted by amph-D model and is also closely related to the surface charge and E_{pzc} of electrodes. It can be inferred that a higher $|E_{pzc, \text{anode}} - E_{pzc, \text{cathode}}|$ value allows for a higher value of V^* , and thus a wider operating voltage window and higher salt removal capacity.

As stated above, the optimization of the E_{pzc} of CDI electrodes is very important. The E_{pzc} shift can be achieved by surface modification. Acid treatment (Cohen et al., 2011, Wu et al., 2015 and Omosebi et al., 2015), sulfonation (Qian et al., 2015), metal oxide modification (Wouters et al., 2013, Gao et al., 2014 and Liu et al., 2015c) have been used to introduce negatively charged species and positively shift the E_{pzc} of CDI electrodes. By contrast, fewer methods have been reported to introduce positively charged groups and negatively shift the E_{pzc} of CDI electrodes (Gao et al., 2015a). In the present work, commercial activated carbon is modified with quaternized poly (4-vinylpyridine) to achieve the above goal. The E_{pzc} of the

obtained AC-QPVP electrode can be as negative as -0.745 V vs. Ag/AgCl. The AC-QPVP electrode is coupled with a nitric acid treated activated carbon electrode to assemble an asymmetric CDI cell and the cell exhibits excellent i-CDI and eV-CDI performance.

2. Experimental section

2.1. Material synthesis

Before use, the commercial activated carbon (AC, Nanjing Linda Activated Carbon Co., Ltd, China) was washed with boiled water for 4 h to remove any impurities. The activated carbon and poly (4-vinylpyridine) (PVP) composite (AC-PVP) was synthesized through the polymerization of 4-vinylpyridine (96%, Aladdin Reagent Co., Ltd.) in the presence of activated carbon. Typically, 5 g activated carbon and 2 mL 4-vinylpyridine were first dispersed in 250 mL water under ultrasonication. The obtained mixture was then heated to 90 °C and 36 mg potassium persulfate was added to initiate the polymerization reaction. The reaction system was maintained at 90 °C for 24 h under nitrogen protection. AC-PVP was then recovered by vacuum filtration, washed repeatedly with ethanol, and finally dried at 80 °C for 6 h. The crosslinking and quaternization of PVP were conducted using a modified method previously reported by Fang et al. (2007). First, the obtained AC-PVP was added to 50 mL N, N-dimethyl formamide, and the mixture was preheated to 65 °C. Then, 1 g 1, 4-dibromobutane (CP, Shanghai Kefeng Chemical Reagent Co., Ltd., China) was added for crosslinking, and the mixture was stirred for 48 h in a slow current of nitrogen. After being filtrated and washed with ethanol, the mixture was dispersed into 50 mL methanol and reacted with 5.8 g 1-bromohexadecane (97%, Aladdin Reagent Co., Ltd., China) at 65 °C for 48 h. Finally, the quaternized poly (4-vinylpyridine) modified activated carbon (AC-QPVP) was washed with methanol thoroughly and dried at 60 °C for 6 h.

To introduce carboxyl groups into the surface, the activated carbon was treated in 6 M HNO_3 at 65 °C for 5 h. The obtained sample (AC- HNO_3) was then washed with water several times and finally dried at 60 °C for 6 h.

2.2. *Electrode fabrication*

To prepare the electrodes, active materials, carbon black and polyvinylidene fluoride (weight ratio=8:1:1) were mixed in N, N-dimethylacetamide (DMAc) and stirred for 12 h to obtain a slurry mixture. The graphite paper was then coated with the slurry to prepare sheet-like electrodes with a thickness of 200 μm . The electrodes were then dried at 60 °C for 12 h to remove the solvent. Finally, the electrodes were cut into pieces of $5 \times 7 \text{ cm}^2$ to be used as the electrodes for CDI. For electrochemical tests, the electrodes were cut into pieces of $1 \times 2 \text{ cm}^2$, and sealed with epoxy resin with an exposed area of $0.5 \times 0.5 \text{ cm}^2$.

2.3. *Characterizations*

The morphologies of the samples were characterized using a field emission scanning electron microscope (FESEM; FEI NOVA NanoSEM 450). The specific surface area and pore size distribution of AC, AC-QPVP and AC- HNO_3 were determined from N_2 adsorption-desorption isotherms obtained on a Micromeritics 3Flex analyzer. The chemical composition of the sample surface was analyzed using X-ray photoelectron spectroscopy (XPS; Thermo ESCALAB 250) with $\text{Al } K_\alpha$ X-ray radiation. The electrophoretic mobility of the samples was measured using Malvern Instruments Zetasizer Nano ZS90. The potential of zero charge of the electrodes was tested through differential capacitance minimum measurements in a three-electrode system consisting of a platinum foil as the cathode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and 5 mM deaerated NaCl solution as the electrolyte. The electrochemical impedance spectra were measured at a frequency of 1 Hz with a sinusoidal voltage perturbation of 5 mV and a potential increment of 5 mV. The value of E_{pzc} was determined from the minimum value of the specific

capacitance (C), which was calculated from the imaginary part of the impedance spectra (Z'') and angular frequency (ω) according to the following equation.

$$C = \left| \frac{1}{\omega Z''} \right|. \quad (1)$$

2.4. CDI tests

Single-pass CDI tests were conducted to evaluate the desalination performance of the electrodes. The CDI setup consisted of two water reservoirs, a CDI cell, a peristaltic pump, a conductivity monitor, a pH monitor and an electrochemical work station, as shown in Fig. 1. A peristaltic pump continuously pumped the NaCl solution with an initial concentration of 500 mg/L from one water reservoir through the CDI cell and into the other reservoir. The conductivity and pH of the effluent at the outlet of the CDI cell was recorded by the conductivity and pH monitor system, respectively. The concentration of the NaCl solution was calculated according to a calibration equation of concentration versus conductivity. The half-cycle time was set to 600 s, and the flow rate of the solution was maintained at 8.67 mL/min. The thickness of dried electrodes is about 30 μm , and CDI cells were assembled with two electrodes separated by 130 μm thick silicon rubber spacers. Salt removal capacity (Γ , mg/g) was calculated according to Eq. 2:

$$\Gamma = \frac{\Phi \times \int (C_0 - C_t) dt}{m} \quad (2)$$

where C_0 and C_t refer to the constant influent and changing effluent concentration, respectively (mg/L); Φ is the volume flow rate of the NaCl solution (mL/s); m refers to the total mass of the two electrodes in a CDI cell (g, 0.28-0.38 g).

The CDI cell which consists of the AC-QPVP and AC-HNO₃ electrodes was denoted by Q-N. The inverted CDI and CDI performance of Q-N was investigated. For the i-CDI tests, a cell voltage was first applied across Q-N for ion desorption (i.e., the AC-HNO₃ electrode

works as the anode and the AC-QPVP electrode works as the cathode), and the electrodes were then short-circuited for adsorption. For the CDI tests, a cell voltage was first applied on Q-N for adsorption (i.e., the AC-QPVP electrode works as the anode and the AC-HNO₃ electrode works as the cathode), and the cell voltage was then reversed for desorption. For comparison, an MCDI cell consisting of pristine AC electrodes (denoted by MCDI) was assembled, and the performance of MCDI was tested under the same operation condition as that of the CDI tests for Q-N. A CDI cell consisting of two pristine AC electrodes was also assembled and denoted by AC-AC. To investigate the CDI performance of AC-AC, a cell voltage was applied for adsorption, and the electrodes were then short-circuited for desorption.

3. Results and discussion

3.1. Characterization of materials

The morphologies of AC, AC-QPVP and AC-HNO₃ were characterized by FESEM and are presented in Fig. S1. The modification didn't significantly change the granular morphology of AC. However, the figure shows that much fewer fine particles are found on the surface of AC-QPVP than on AC and AC-HNO₃, indicating that some of them were bonded by QPVP.

XPS was conducted to characterize the surface functional groups of the samples and the obtained N 1s and O 1s spectra are presented in Fig. 2. The N1s spectrum of AC shows no obvious peaks in the spectral region of N 1s, indicating that few nitrogen atoms exist in the surface of AC. After the modification by QPVP, the ratio of surface nitrogen atoms in AC increased from 0.28% to 1.13%, as shown in Fig. S2 (Supplementary material), and the N 1s core-level spectrum of AC-QPVP can be deconvoluted into two peaks at 398.8 and 401.7 eV, which are attributed to C-N in unquaternized pyridine ring and C-N⁺ in quaternary amines,

respectively (Gu and Jia, 2013). Moreover, the fraction of C-N⁺ is as high as 89%, demonstrating that most of the nitrogen atoms in the pyridine rings are quaternized.

After nitric acid treatment, the surface oxygen atoms of AC increased from 11.2% to 15.6% (Fig. S2). The O 1s core-level spectra of AC and AC-HNO₃ can be fitted by three components at 531.7, 532.7 and 533.8 eV. The component at 531.7 eV is attributed to the oxygen double bonded to carbon (C=O) in esters and carboxylic acids. The peak at 532.7 eV is assigned to the oxygen in phenol, alcohol, aliphatic ether and ketone. The peak at 533.8 eV corresponds to the oxygen in aryl ethers (Ph-O-Ph) and the oxygen single bonded to carbon (O=C-O) in carboxylic acids and ethers (Fan et al., 2013). The oxygen in carboxyl groups contributes to both the peak at 531.7 and 532.7 eV. The deconvoluted O 1s spectrum of AC shows that the dominating peak is located at 533.8 eV and that the peak at 531.7 eV is relatively weak, indicating that the peak at 533.8 eV mainly corresponds to the oxygen in aryl ethers. After the modification, the intensity of the peak at 533.8 eV greatly decreases, whereas the peak at 531.7 eV becomes the dominating peak, indicating that nitric acid treatment converts some of the oxygen in aryl ethers to the oxygen double bond in carboxylic acids. Thus, the XPS results demonstrate that quaternary ammonium cationic groups and carboxyl groups are successfully introduced into the surface of AC-QPVP and AC-HNO₃, respectively.

The zeta potential of samples at different solution pH is shown in Fig. 3a. The point of zero charge (pH_{pzc}) of AC is about pH 2.0, and the surface charge of AC-HNO₃ remains negative over the whole pH range (2.0–10.0). The point of zero charge of AC-QPVP is about pH 8.8, which means that the surface charge of AC-QPVP remains positive over a wide pH range (2.0–8.8) and becomes negative at pH >8.8. The pH value of sea water and drinking water is between 6 and 8. The zeta potential results indicate that AC-QPVP and AC-HNO₃ have positive and negative surface charges in this pH range, respectively. Thus, negatively

charged species are prone to adsorption in AC-QPVP whereas the electrosorption of positively charged species are most likely to occur in AC-HNO₃. The E_{pzc} of the electrodes prepared from AC, AC-QPVP and AC-HNO₃ is determined from the minimum values of their normalized differential capacitance curves, as shown in Fig. 3b. The E_{pzc} of AC electrode is about 0.605 V vs. Ag/AgCl. Compared with the AC electrode, the E_{pzc} of the AC-QPVP electrode is negatively shifted to -0.745 V vs. Ag/AgCl and that of the AC-HNO₃ electrode is positively shifted to 0.820 V vs. Ag/AgCl. The results of E_{pzc} are consistent with that of the zeta potential, given that E_{pzc} and pH_{pzc} are negatively correlated (McCafferty, 2010). The E_{pzc} results demonstrate that the electrodes have the same sign of surface charge as their corresponding active materials.

3.2. *i-CDI performance*

To investigate the CDI performance, the AC-QPVP and AC-HNO₃ electrodes were assembled into an asymmetric CDI cell (denoted by Q-N). First, the i-CDI performance of Q-N was tested. A cell voltage was applied across Q-N for ion desorption (i.e., the AC-HNO₃ electrode works as the anode and the AC-QPVP electrode works as the cathode), and the electrodes were then short-circuited for adsorption. As stated previously, the working voltage window of i-CDI is limited by $|E_{pzc, \text{anode}} - E_{pzc, \text{cathode}}|$. Thus, the i-CDI working voltage window of Q-N can be theoretically as high as 1.565 V according to the E_{pzc} results. The cell voltage applied here is up to 1.4 V, and the NaCl concentration curves exhibit no desorption peaks at the start of the adsorption step, as shown in Fig. 4a, indicating that the working voltage window of Q-N for i-CDI can reach 1.4 V (Gao et al., 2015b). When a cell voltage is applied across Q-N, the concentration of the NaCl solution increases sharply to the maximum value and then falls back to the influent level, indicating that ions are desorbed from the electrodes. During the discharge process, the electrodes are short-circuited and cations are adsorbed into the AC-HNO₃ electrode, whereas the anions are adsorbed into the AC-QPVP

electrode, leading to a decrease in the concentration of the NaCl solution. As the electrodes gradually reach charge balance, the NaCl concentration of the electrolyte gradually increases to the influent value. Fig. 4b and Fig. 4c shows the calculated salt removal capacity and passed charge, respectively. It can be seen that the salt removal capacity and passed charge both increase with the cell voltage as a result of increasing driving force. The salt removal capacity at 1.4/0 V can be as high as 9.6 mg/g, and that at 1.2/0 V is 8.7 mg/g. The calculated salt adsorption capacity equals to the salt desorption capacity. However, compared with the adsorption process, more charge was passed during the desorption process and lower charge efficiency was obtained. The big difference of charge and charge efficiency during the adsorption and desorption processes can be attributed to the higher leakage current during the desorption process caused by parasitic reaction (Fig. S3).

The cyclic stability of AC-AC and i-CDI was investigated at the cell voltage of 0.8/0 V and 1.4/0 V. The plots of conductivity vs. time measured during cycling are presented in Fig. S4 and Fig. S5. Fig. 5 shows the adsorption curves of AC-AC and i-CDI at the 5th and 100th cycles at the cell voltage of 0.8/0 V. For AC-AC, a desorption peak appears at the start of the adsorption process after the cell was cycled 100 times, indicating that serious co-ion expulsion occurred in the electrodes as a result of the positive shift of $E_{pzc, anode}$ caused by anodic oxidation. Accordingly, the salt removal capacity of AC-AC decreases from 5.1 mg/g at the 5th cycle to 2.6 mg/g at the 100th cycle. For i-CDI, the maximum driving force for adsorption is $|E_{pzc, anode} - E_{pzc, cathode}|$. Thus, positive shift of $E_{pzc, anode}$ resulting from anodic oxidation would not cause co-ion expulsion in i-CDI. Fig. 5b shows that no desorption peak appears at the start of the adsorption process after the cell was tested for 100 cycles, demonstrating that i-CDI can effectively avoid the co-ion expulsion effect during a long-term cycling process. Despite this, the salt removal capacity of i-CDI still shows a certain decay (i.e., 7.1 mg/g at the 5th cycle and 5.0 mg/g at the 100th cycle). When i-CDI was cycled at

1.4/0 V, the decay of salt removal capacity and current becomes more drastic (Fig. S5). After the cyclic test, resistance of the CDI cell exhibits a significant increase and the resistance increase mainly occurred in the AC-HNO₃ anode (Fig. S6). The increase of cell resistance may be caused by anodic oxidation, given that surface oxidation and introduction of negatively charged functional groups not only can positively shift the E_{pzc} but also can decrease the electrical conductivity and specific area of carbon materials (Seredych et al., 2008 and Rangel-Mendez and Streat, 2002). The cyclic test results reveal that although i-CDI can effectively avoid the co-ion expulsion effect caused by the positive shift of $E_{pzc, anode}$, deterioration of anode such as the increase of anode resistance can still negatively affect the salt removal performance. Therefore, choosing a stable anode for i-CDI is as important as that for conventional CDI.

3.3. *eV-CDI performance*

For CDI cells using surface enhanced electrodes, extended voltage working voltage windows can be achieved by applying a voltage during the desorption process (Gao et al. 2016). The optimum cell voltage for desorption (V^*) should be a value around $|E_{pzc, anode} - E_{pzc, cathode}|$, which is 1.565 V in this work and higher than the theoretical water decomposition voltage (1.23 V). Therefore, for eV-CDI tests, a cell voltage was first applied on Q-N for adsorption (i.e., AC-QPVP works as the anode and AC-HNO₃ works as the cathode), and then the cell voltage was simply reversed for desorption (i.e., the AC-HNO₃ electrode works as the anode and the AC-QPVP electrode works as the cathode). During the adsorption process, the E_{pzc} of the electrodes are both outside their working domains, and this can effectively reduce the co-ion expulsion effect. Moreover, as a reversed cell voltage was applied, the ions in the electrodes were depleted and the potential of the electrodes was polarized to a value near their E_{pzc} during the desorption process. In this case, the electrodes themselves can provide a certain driving force for ion adsorption, as verified by the results of

i-CDI. Thus, Q-N is expected to exhibit high charge efficiency and salt removal capacity. Given that these effects are similar to MCDI using reverse voltage during desorption (Biesheuvel et al., 2011), MCDI using pristine AC electrodes was assembled and tested for comparison. The desalination performance of MCDI and Q-N is presented in Fig. 6. Fig. 6a shows that the NaCl concentration at the outlet of MCDI and Q-N both drops rapidly to the minimum value and then gradually increases, but the rate of increase is much slower than that of AC-AC (Fig. S7), indicating that MCDI and Q-N can adsorb more ions. Fig. 6e shows the calculated salt removal capacity and charge consumed at various cell voltages and indicates that the salt removal capacity of Q-N is even a little higher than that of MCDI. The salt removal capacity of Q-N at 1.2/-1.2 V is as high as 20.6 mg/g. The charge efficiency of Q-N is lower than that of MCDI, but still stays above 68%, which is much higher than that of AC-AC (below 50%, Fig. S7). Corresponding to the high salt removal capacity and charge efficiency, Q-N exhibits a high salt removal rate, as shown in Fig. 7. From Fig. 7a, it can be seen that Q-N reaches a peak (3.8 mg/g/min) in salt adsorption rate at the cell voltage of 1.2/-1.2 V. The average salt adsorption rates (ASAR) of Q-N, MCDI and AC-AC were calculated based on the total time of adsorption and desorption processes and presented in Fig. 7b. The ASAR of Q-N is the highest among the three CDI cells and is two times higher than that of AC-AC. When the cell voltage is 1.2/-1.2 V, the ASAR of Q-N can reach 1.0 mg/g/min. It should be noted that the ASAR of Q-N can be further improved by optimizing the cell configuration and operating parameters.

4. Conclusions

An inexpensive positively charged AC-QPVP composite material was synthesized for CDI. The CDI cell consisting of the AC-QPVP and AC-HNO₃ electrodes (Q-N) exhibits excellent i-CDI (1.4/0 V, 9.6 mg/g) and eV-CDI (1.2/-1.2 V, 20.6 mg/g) performance. Compared with AC-AC, Q-N also exhibits enhanced stability in the i-CDI cyclic tests. The

good electro-adsorption performance of Q-N is mainly attributed to the optimized E_{pzc} of the electrodes. For i-CDI, the significant difference between the E_{pzc} of the AC-QPVP electrode and that of the AC-HNO₃ electrode allows for a high cell voltage. For eV-CDI, the E_{pzc} of the electrodes in Q-N are both outside their working potential domains during the adsorption process; thus, co-ion expulsion can be effectively avoided. In addition, when a cell voltage is applied during the desorption process, the electrodes themselves can provide extra driving force for ion adsorption, thereby leading to rapid electro-adsorption and high salt removal capacity. This work demonstrates that excellent CDI performance can be achieved through the simple modification of inexpensive commercial materials. The asymmetric CDI system (Q-N) established here has great potential for practical applications. Moreover, the AC-QPVP prepared in this work should facilitate the development of positively charged electrode materials for CDI.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://www.sciencedirect.com>.

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Fig. 1. CDI setup consisting of two water reservoirs, a CDI cell, an electrochemical workstation and a conductivity meter.

Fig. 2. (a) N 1s XPS spectra of AC and AC-QPVP. (b) O 1s XPS spectra of AC and AC-HNO₃.

Fig. 3. (a) Zeta potential of AC, AC-QPVP and AC-HNO₃. (b) Normalized differential capacitance curves of the electrodes prepared from AC, AC-QPVP, and AC-HNO₃.

Fig. 4. Inverted CDI performance of Q-N: (a) changes in NaCl concentration over time, (b) salt removal capacity, (c) charge passed and (d) charge efficiency.

Fig. 5. Adsorption curves at the 5th and 100th cycle of (a) AC-AC and (b) i-CDI.

Fig. 6. The first row: NaCl concentration changes of (a) MCDI and (b) Q-N at different cell voltages. The second row: the current of (c) MCDI and (d) Q-N. The third row: (e) the specific salt removal capacity and charge, and (f) charge efficiency of MCDI and Q-N at different cell voltages.

Fig. 7. The instantaneous salt removal rate of Q-N (a) and the average salt adsorption rates (ASAR) of Q-N, MCDI and AC-AC (b) at different cell voltages. For ASAR, the “min” refers to the total time of the adsorption and desorption processes.