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Application of Polyaniline Modified Graphite Electrodes for Capacitive Deionization of Aqueous NaCl Solutions

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Polyaniline/graphite composite electrodes were used as the electrodes of capacitive deionization apparatus and the electrodeposition conditions of polyaniline film were studied in order to optimize the capacitive deionization unit. The results showed that the potential -0.85 V for potentiostatic method or current 0.5 A for galvanostatic method was suitable for the electrodeposition of polyaniline film by the measurement of the conductivity of aqueous NaCl solution. Meanwhile, the capacitive deionization unit could be regenerated easily.

Key Words: Polyaniline (polyaniline), Electrodeposition, Capacitive deionization unit, Conductivity, Adsorption.

INTRODUCTION

Porous electrodes are important in many physico-chemical processes such as electrochemical cells, batteries and supercapacitors[1-3]. Another important example is capacitive deionization (CDI) or "electrosorption desalination", in which ions are removed from an aqueous stream by applying a potential difference across two juxtaposed electrodes[4-10]. The ions removed from the aqueous solution are stored on the internal surface areas inside of the porous electrodes, resulting in the reduction of ion concentration and conductivity of an effluent product stream compared to the inflowing solution, which can continue until the polarization layers reach their final ion adsorption capacity. At the same time, ions can be released back into solution by reducing or even reversing the applied voltage and a product stream concentrated in ions is obtained. Capacitive deionization removes ions by charge separation and therefore may avoid the scaling problems commonly associated with membrane and distillation processes. Also, this approach could offer an attractive, energy-efficient alternative to thermal and membrane desalination processes.

To obtain a large ion adsorption capacity, it is important that a large surface area is created and thus typically materials such as porous activated carbons are used that have internal surface areas of the order of 103 m^2/g. Capacitive deionization unit with high-surface-area carbon electrodes has been considered for desalination since 1960s[11-14]. However, the pores of carbon electrodes are easily blocked, leading to the quick decay of production capacity, which limits its application. Therefore, it is needed to develop a better high surface area material as electrode material. As a

conducting polymer, polyaniline (PAni) can absorb ions because of its porosity as well as its high specific areas, stability and relatively high electrical conductivity and can be used as electrode material by deposited onto the solid surface.

Herein, the conducting polymer polyaniline deposited onto the surface of the graphite electrode can be used as capacitive deionization (CDI) electrodes for capacitive deionization of aqueous NaCl solutions. The graphite has a layer structure and good electrical and thermal conductivity. Therefore, the laminar recombination with the polymer and the reduction of the electrical conductivity infiltration threshold value can be realized by the composition of graphite and polyaniline film. Different deposition conditions of polyaniline film, such as potential and current were investigated and the optimal preparation technique was proposed. The results showed that the electrode had good reproducibility and can be used in capacitive deionization.

EXPERIMENTAL

Aniline was purified by repeated distillation with zinc dust and stored under nitrogen gas. Other reagents were of analytical grade and were used as received. All the solutions were prepared with double distilled water.

The electrochemical experiments were performed with a DJS-292 Potentiostat. The working electrode was graphite electrode (30 mm wide × 100 mm long × 0.2 mm thickness) and a platinum sheet and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in the paper were presented in the SCE scale. The polyaniline films were formed on the graphite working electrode at different potential *versus* SCE or different current in solutions of 0.5 M aniline + 2.5 M H_2SO_4.

A typical CDI unit consisted of two electrodes attached in series (in terms of solution flow). Each electrode consists of two parallel graphite electrode plates separated by a 1.52 mm gap for solution flow.

Aqueous NaCl solution was pumped in by a W375020 peristaltic pump from the bottom and exited from the top of the stack. The maximum voltage used in these experiments was 1 V with an applied flow rate of 100 mL/min. The conductivity of aqueous NaCl solutions before and after the absorption process was measured by the Thermo Orion Model 125Aplus Conductivity Meter.

Regeneration of the CDI unit was conducted in closed-loop operation and began immediately after the absorption phase. The distilled water was pumped through the shorted-out CDI unit. Pumping was initiated at the same flow rate as the absorption stage. When the conductivity reached an asymptotic level, the pump was shut off. The final conductivity of distilled water was recorded before and after the regeneration phases.

RESULTS AND DISCUSSION

Effects of deposition potential of polyaniline film on electrosorption capacity: In the process of depositing polyaniline film by potentiostatic method, the deposition

potential should be adjusted to optimize the amount and nature of the deposited polyaniline film which will be employed subsequently as CDI electrodes for the deionization of aqueous NaCl solution. Fig. 1 shows the change of conductivity value of aqueous NaCl solution with time before and after passing the electrodes obtained by different deposition potential of polyaniline film. As can be seen, the CDI electrodes prepared by constant potential -0.85 V shows the best absorption capability compared to -0.9 and -0.8 V and the change value of conductivity of NaCl aqueous solution arrives at 0.10 ms cm^{-1} when the purification time is 80 min. In this experiment, the potential -0.85 V was chosen for the electrodeposition of polyaniline film.

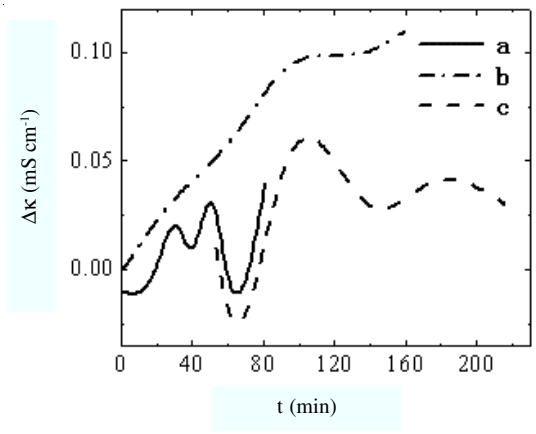

Fig. 1. Change value of conductivity of purified water with time under the different deposition potential of polyaniline film. The deposition potential of polyaniline film was (a) -0.9 V, (b) -0.85 V and (c) -0.8 V, respectively

Effects of deposition current of polyaniline film on electrosorption capacity: In addition to the deposition potential, the electrodeposition current also has great effect on the morphology of polyaniline film, which subsequently influences the adsorption capacity of the CDI unit. The change of conductivity value of aqueous NaCl solution with time before and after passing CDI unit prepared by different deposition current is shown in Fig. 2. It can be seen that with the increase of time, the change value of conductivity increases, indicating that the three CDI unit all have the adsorption ability to some extent. When the desorption time reaches 1 h, the change value of conductivity of aqueous NaCl solution after passing the polyaniline capacitor electrode obtained by constant current 0.5 A is the largest. That is to say, the CDI unit with polyaniline film deposited by 0.5 A exhibits the best purification capacity and too high or too low current is not good for the deposition of polyaniline film. The reason may be that at too low current, the polymerization of aniline can not occur, whereas too high current leads to the generation of gas, which influences the performance of polyaniline film. Therefore, the polyaniline film deposited by constant current 0.5 A shows the best adsorption capacity.

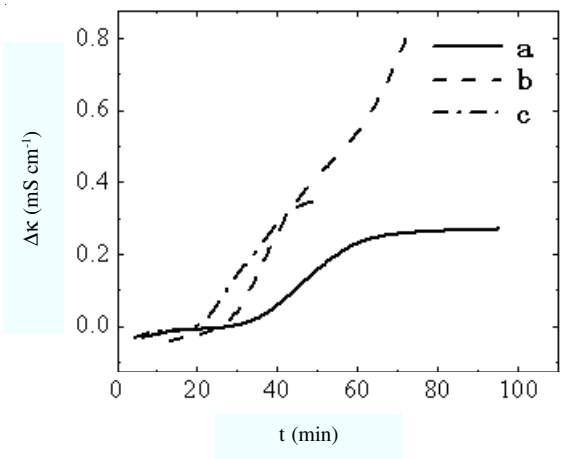

Fig. 2. Change value of conductivity of purified water with time under the different deposition potential of polyaniline film. Deposition current: (a) 0.4 A; (b) 0.5 A; (c) 0.7 A

Process of adsorption and regeneration: In order to understand the working process of the CDI unit well, the experiments of electro-adsorption and regeneration process were carried out and the change of conductivity with time is shown in Fig. 3. As can be seen, the curve of electro-adsorption process (Fig. 3A) is different from that of regeneration process (Fig. 3B). Shortly after the voltage was applied on capacitance electrodes, the conductivity of the aqueous NaCl solution after passing the CDI unit decreased quickly. It should be noted that the conductivity of aqueous NaCl solution before passing the capacitance was 9870 μS/cm. With the increase of absorption time, the conductivity decreased and it reached 9050 μS/cm after the purification was 2 h and the conductivity no longer changed until 3 h, which indicated that the adsorption saturated. Afterwards, the regeneration process of the CDI unit was studied and the distilled water was passed the CDI unit. The conductivity of the distilled water increased from 20-461 μS/cm in a very short period of time after passing the CDI unit. Then, the conductivity of the distilled water began to decrease gradually. The rate of decline of conductivity slowed down with the increase of the

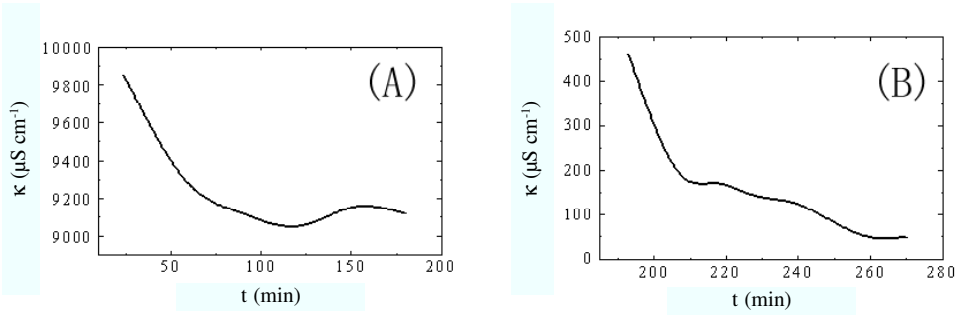

Fig. 3. Change of conductivity of distilled water with time during the process of adsorption (A) and regeneration (B) of the CDI unit

time (Fig. 3B). After 80 min of the back flushing, that is to say, the time increased from 180-260 min, the conductivity of the distilled water after passing the CDI unit was 49 μS/cm, close to the conductivity of the distilled water before passing the CDI unit. The results showed that the obtained CDI unit had good reversibility and there was no extra energy or substance needed except for the shorted-out of the CDI unit and then the distilled water was passed.

Conclusion

The deionization ability of CDI unit consisted of graphite electrodes deposited by polyaniline film was studied. The result showed that the deposition potential and current of polyaniline film had great effect on the adsorption ability of the electrode and the capacitance electrode prepared by the constant potential -0.85 V for potentiostatic method or constant current 0.5 A for galvanostatic method showed the best purification ability. Moreover, the electrode could be regenerated easily when the ion adsorption saturated and only the shorted-out of the CDI unit and the passing of distilled water were needed.

REFERENCES

1. E. Avraham, B. Yaniv, A. Soffer and D. Aurbach. *J. Phys. Chem. C*, **112**, 7385 (2008).
2. J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon and P.L. Taberna, *Science*, **313**, 1760 (2006).
3. M.D. Stoller, S. Park, Y. Zhu, J. An and R.S. Ruoff, *Nano Lett*., **8**, 3498 (2008).
4. B.B. Arnold and G.W. Murphy, *J. Phys. Chem*., **65**, 135 (1961).
5. Y. Oren and A. Soffer, *J. Appl. Electrochem*., **13**, 473 (1983).
6. J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala and J.F. Poco, *J. Appl. Electrochem*., **26**, 1007 (1996).
7. K.S. Spiegler and Y.M. El-Sayed, *Desalination*, **134**, 109 (2001).
8. K.-K. Park, J.-B. Lee, P.-Y. Park, S.-W. Yoon, J.-S. Moon, H.-M. Eum and C.-W. Lee, *Desalination*, **206**, 86 (2007).
9. H. Li, Y. Gao, L. Pan, Y. Zhang, Y. Chen and Z. Sun, *Water Res*., **42**, 4923 (2008).
10. P.M. Biesheuvel, *J. Colloid. Interface Sci*., **332**, 258 (2009).
11. D.D. Caudle, J.H. Tucker, B.B. Cooper, B.B. Arnold and A. Papastamataki, Research and Development Progress Report 188; US Department of the Interior (USDI): Washington, DC (1966).
12. A.M. Johnson, A.W. Venolia, J. Newman, R.G. Wilbourne, C.M. Wong, W.S. Gillam, S. Johnson and R.H. Horowitz, R and D Progress Report 516 (USDI Publication 200 056); Office of Saline Water: Washington, DC (1970).
13. A.M. Johnson and J. Newman, *J. Electrochem. Soc*., **118**, 510 (1971).
14. M. Matlosz and J. Newman, *J. Electrochem. Soc*., **133**, 1850 (1986).

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