

ELECTROCHEMICAL CAPACITIVE DESALINATION BEHAVIOR OF ACTIVATED CARBON FIBERS

Ming Wang, Zheng-Hong Huang, Lei Wang and Feiyu Kang

Laboratory of Advanced Materials, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Introduction

Capacitive deionization (CDI), which is ion electrosorption onto the surface of porous materials to remove ions from aqueous solutions, may serve as an energy-efficient alternative for the desalination of brackish water comparing with conventional desalination methods such as membrane separation and thermal distillation [1]. The CDI process operates at low direct voltages. Ions adsorbed are held in the electrical double layers (EDL) near charged surface of an electrode and could be released back into bulk solution by canceling the potential difference between the electrodes [1]. No additional chemicals are required for regeneration. The part of discharging energy is able to be restored for the energy recycling.

A prerequisite for the high deionization efficiency of CDI method is the demand for the high electrosorptive capacity endowed by the electrode materials. To obtain the objective, it is important that a large surface area is created and thus typical materials such as high specific surface area (SSA) materials are used. High SSA, a key factor of electrosorptive capacity, is determined mainly by the contribution of the surface area of mesopores and micropores present in carbon materials. SSA is explicitly related to pore size, thus it is especially important to understand its effect on electrosorptive capacity. The latest research in the related field of electric double layer capacitors (EDLC) has shown an anomalous increase in carbon capacitance at pore sizes less than 1 nm [2]. In CDI, the pore openings of activated carbons were controllably tuned to exhibit excellent electrochemical selectivity for ions [3]. Electrosorptive performance with modified activated carbon cloth as CDI electrodes was also investigated [4]. Up to now, more emphasis is focused on high SSA of porous carbon materials with the order of 10^3 m²/g. Activated carbon fibers (ACFs) are typical microporous materials with large surface areas and good conductivity along fiber axis. Thus they can serve as candidate for active component of CDI electrodes. The aim in present work is to identify effect of SSA on capacitive electrosorptive capacity using activated carbon materials electrodes.

Experimental

The pitch based activated carbon fibers (A5, A7, A10 and A15) were kindly provided by Osaka Gas Co., Ltd., Japan. Their BET surface areas were 500, 700, 1100 and 1600 m²/g according to the company's data. Sodium chloride and N-methyl-2-pyrrolidone were analytical grade without further purification before use. Polyvinylidene fluoride (PVDF) 761 was employed as binder. High purified graphite powder was added to enhance electrode conductivity. Graphite paper was used as current collector. The electrodes were fabricated as following procedure. 0.20 g of ACF, 0.08 g of PVDF binder and 0.12 g of graphite powder were mixed with 2 mL of N-methyl-2-pyrrolidone. A 5.0 cm × 5.4 cm graphite paper was coated with the mixture, dried in vacuum at 50 °C for 3 h and

then it was pressed by a roller squeezer to keep 0.5 mm of thickness for each plate. To thoroughly remove the solvent, the electrodes were dried again in vacuum at 130 °C for 3 h. A CDI cell consists of two parallel electrode plates separated by a 1.0 mm gap for solution flow. A sodium chloride aqueous solution was pumped into the bottom and exited from the top of the cell by a peristaltic pump at a flow rate of 6 mL/min. The voltage used in these experiments was 1.2 V. CDI process was performed in batch mode. Solution conductivity was on-line monitored with 5 seconds interval by a conductivity meter (type 308A, Leici Company). Galvanostatic cycles were tested by Land Cell Measurement.

Results and discussion

Four ACFs with different specific surface areas were selected for comparison in desalination of CDI cell. The detailed parameters ACFs shows that pore volume increases with BET SSA but the four ACFs have almost the same average pore width of 1.8 nm. The desalination performances of A5 – A15 ACFs were assessed by using the CDI apparatus to treat a sodium chloride aqueous solution with a concentration of 60 mg/L. Figure 1 shows the result of the CDI process of A5 – A15 ACFs in batch mode. The CDI process is divided into two stages: physical adsorption and electrosorption. At the beginning of an hour without applying an electric field, the change in the conductivity of the solution was recorded due to physical adsorption. After that, the CDI electrodes were put at a constant voltage of 1.2 V. At the stage of physical adsorption a common expectation was observed that the amount of NaCl adsorbed by ACFs increased in the order from A5, A7, A10 to A15, which was in agreement with the BET SSA of ACFs. Once an electric field was applied to the CDI electrodes, the conductivity of NaCl solution decreased sharply due to electrical adsorption, then the change became gradually before the electrosorption reached equilibrium. It took more time to reach equilibrium in the case of higher electrosorption. A remarkable phenomenon is that ACF with high BET surface area has low electrosorptive capability. For example, A15 had the lowest electrosorptive capability but possessed the highest physical adsorption capacity. It is noted that A7 is the most capable of adsorbing NaCl in CDI process. The order of electrosorptive capacity is A7 > A5 > A10 > A15. It seems that BET SSA is not an only determining factor for the deionization in CDI process.

The electrosorptive behavior of CDI electrodes can be more clearly understood by galvanostatic cycle measurement. The CDI cell was directly used for the measurement without solution flow. The charge/discharge curves (cell voltage against time) for A5 – A15 ACFs in a 60 mg/L NaCl solution at a constant current of 0.05 mA and a voltage of 0.5 V are shown in Figure 2. The solid line is the charge/discharge curve of A7, which demonstrates the fastest cycle with 14 minutes for one cycle. The time needed for A5 (dash line) to complete one cycle is 177 min more than twelve times that for A7. As for A10 (dot line) and A15 (dash dot line) during 6 hours, they

could not even achieve the setting voltage. The order of charge/discharge cycle is $A7 > A5 > A10 > A15$, which might reflect electrosorptivity of A5 – A7 ACFs in the CDI cell. The whole deionization could be accomplished within 30 to 60 minutes to achieve dynamic equilibrium under above mentioned condition in batch mode. In comparison with galvanostate data in the same time range of 30 minutes one could find out that A7 is much easier to being charged to the setting voltage value, while charge capability of other ACFs is much weaker. Both desalination capacity and galvanostate charge capability of ACFs are in the same order.

It is demonstrated from CDI desalination and galvanostate cycle that electrochemical capacitive desalination is not only determined by specific surface areas of porous electrode materials. Under the electrochemical circumstance electrical double layer overlapping effect should be taken into consideration [5]. According to the classic EDL theory, the EDL is composed of two layers: the inner layer and diffusion layer. The thickness of inner layer is only several Ångström, while that of diffusion layer could be about several hundreds of Ångström. In the microporous ACFs physical adsorption without application of electric field is determined mainly by SSA which contributes to the largest adsorbed quantity of NaCl for A15. However, there are two opposite influencing factors affecting electrosorptive characteristics of ACFs under electric field: the number of electrosorptive sites and EDL overlapping effect. Once CDI electrodes are applied an electric field, as the SSA increases the effect of EDL overlapping becomes stronger and ions electro-adsorbed in the EDL becomes less, which may significantly cause the loss of desalination capacity. If the SSA is too low, desalination capacity of ACFs also decreases due to the reduced adsorptive sites of carbon surface. Therefore the SSA of microporous ACFs could be optimized to achieve better electrosorptive performance. In our case, although A15 has the largest SSA, EDL overlapping effect predominates the capacitive deionization. As a result A15 shows weak electrosorptive capacity opposite to its physical adsorption. A7 is the best consequence of the balance between the number of electrosorptive sites and EDL overlapping effect.

Conclusions

The electrochemical capacitive desalination characteristics of ACFs are significantly different from their physical adsorption, the capacity of which increases with increasing the BET SSA of ACF. Galvanostate cycle measurement reflects CDI adsorptive capacity of ACFs with different SSAs. CDI capacity of microporous ACF is highly affected both by its SSA and EDL overlapping effect. High electrosorptive performance can be achieved by balancing the two influencing factors. ACF with not so high SSA (A7 in present case) possesses high CDI capacity, which suggests that ACF could be used as CDI electrode materials in large scale for practical application of CDI method.

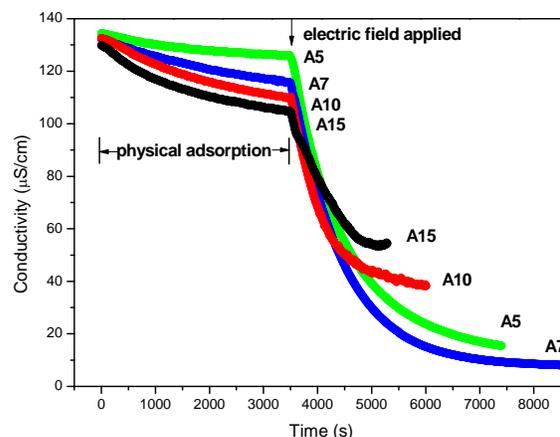


Fig. 1 Desalination behavior of ACFs with different BET SSA in flow through capacitor CDI cell.

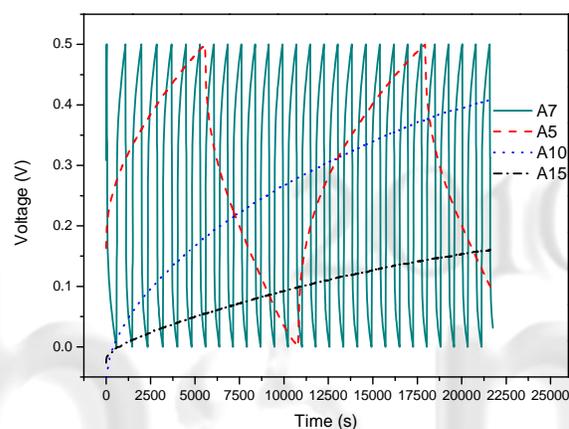


Fig. 2 Galvanostatic cycle of ACFs with different BET SSA.

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