

Electronic Supplementary Information (ESI)

Three-dimensional hierarchical porous carbons with a bimodal pore arrangement for capacitive deionization

Xiaoru Wen,^a Dongsong Zhang,^{*a} Liyi Shi,^{a,b} Tingting Yan^a, Hui Wang^b and Jianping Zhang^b

^a *Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, China.*

Fax: 86 21 66134852; E-mail: dszhang@shu.edu.cn

^b *Department of Chemistry, Shanghai University, Shanghai 200444, China.*

Characterization

The morphologies of the samples were observed by the transmission electron microscopy (TEM, JEOL JEM-200CX) and field emission scanning electron microscopy (SEM, JEOL JMS-700F). The X-ray diffraction (XRD) measurements were performed with a Rigaku D/MAX-RB X-ray diffractometer by using Cu K α (40 kV, 20 mA) radiation and a secondary beam graphite monochromator. The Raman spectra were recorded on an in-equipped with an optical microscope at the room temperature. For excitation, the 514.5 nm line from an Ar⁺ ion laser (Spectra Physics) was focused on the sample under the microscope with an analyzing spot of about 1 μ m. Nitrogen adsorption-desorption measurements were performed at 77 K with a Micromeritics ASAP 2020 instrument. Prior to the measurements, the samples were degassed overnight at 493 K in a vacuum line. The specific surface area and pore

volume were calculated with the Brunauer-Emmett-Teller (BET) method and the mesopore size distribution was estimated with desorption braches based on Barrett-Joyneer-Halenda (BJH) model. The maropore size distribution was obtained by the Hg porosimetry analysis (AutoPore IV 9510).

Electrochemical Performance Measurements

The working electrodes for electrochemical evaluations were prepared as follows. A mixture of the prepared material, acetylene black, and polytetrafluoroethylene with a weight ratio of 80: 10: 10 was ground together to form a homogeneous slurry. Finally, the mixed slurry was coated onto the graphite paper and then dried at 120 °C overnight.

The electrochemical performance was tested by the cyclic voltammetry (CV) , Electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GC), which were conducted in a same three-electrode cell in which the prepared carbon electrode, a graphite sheet, and a saturated calomel electrode (SCE) acted as the working electrode, counter electrode, and reference electrode, respectively. All the experiments were carried out at the room temperature.

The CV and GC tests were performed on the CHI-660D and Land CT2001A, respectively. Here, the specific capacitance (C_m) was calculated from the CV curve according to the following equation¹:

$$C_m = Q / 2m\Delta V \quad (1)$$

Where m is the mass of the activated substance, ΔV is the range of the potential, and Q is the integrated area of the CV curve, respectively.

The EIS measurements in a frequency window of 10 mHz to 100 kHz were also conducted on the CHI-660D. The amplitude of the alternating voltage was 5 mV around the equilibrium potential (0 V).

Additional Discussion

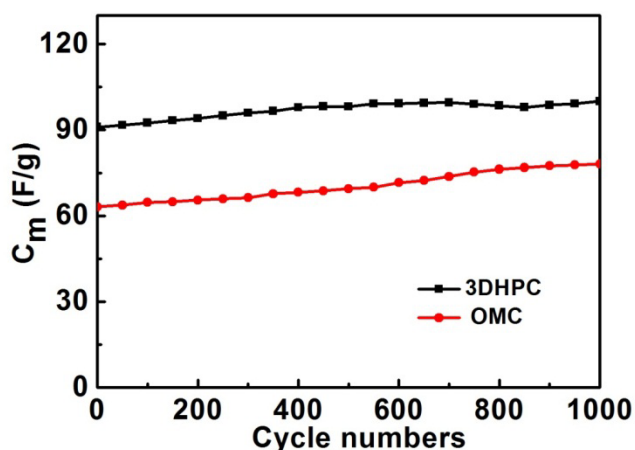


Fig. S1 The specific capacitances vs. cycle numbers of the 3DHPC and OMC electrodes.

To investigate the stability of 3DHPC and OMC electrodes, the CV cycles were conducted in a 1 M NaCl aqueous solution at a scan rate of 10 mV/s and the dependence of corresponding specific capacitances on the cycles was plotted in Fig.S1. Clearly, no capacitance decay is found within 1000 cycles indicating the good stability of the 3DHPC electrode as well as the OMC one. The slight increase of the specific capacitance can be observed for both electrodes and it means that the long time cycling should favor the access of ions to the more inner space, which may result in a much larger available surface area for the electrosorption². The excellent cycle performance renders the electrode can be further used with a stable desalination performance during the CDI process. In addition, the 3DHPC electrode exhibits much superiority on the specific capacitance during the cycles and such result suggests that the 3DHPC electrode displays a much better electrosorption capacity than the OMC

one. The improved desalination capacity combining with good stability make the 3DHPC as a promising CDI electrode for the water desalination.

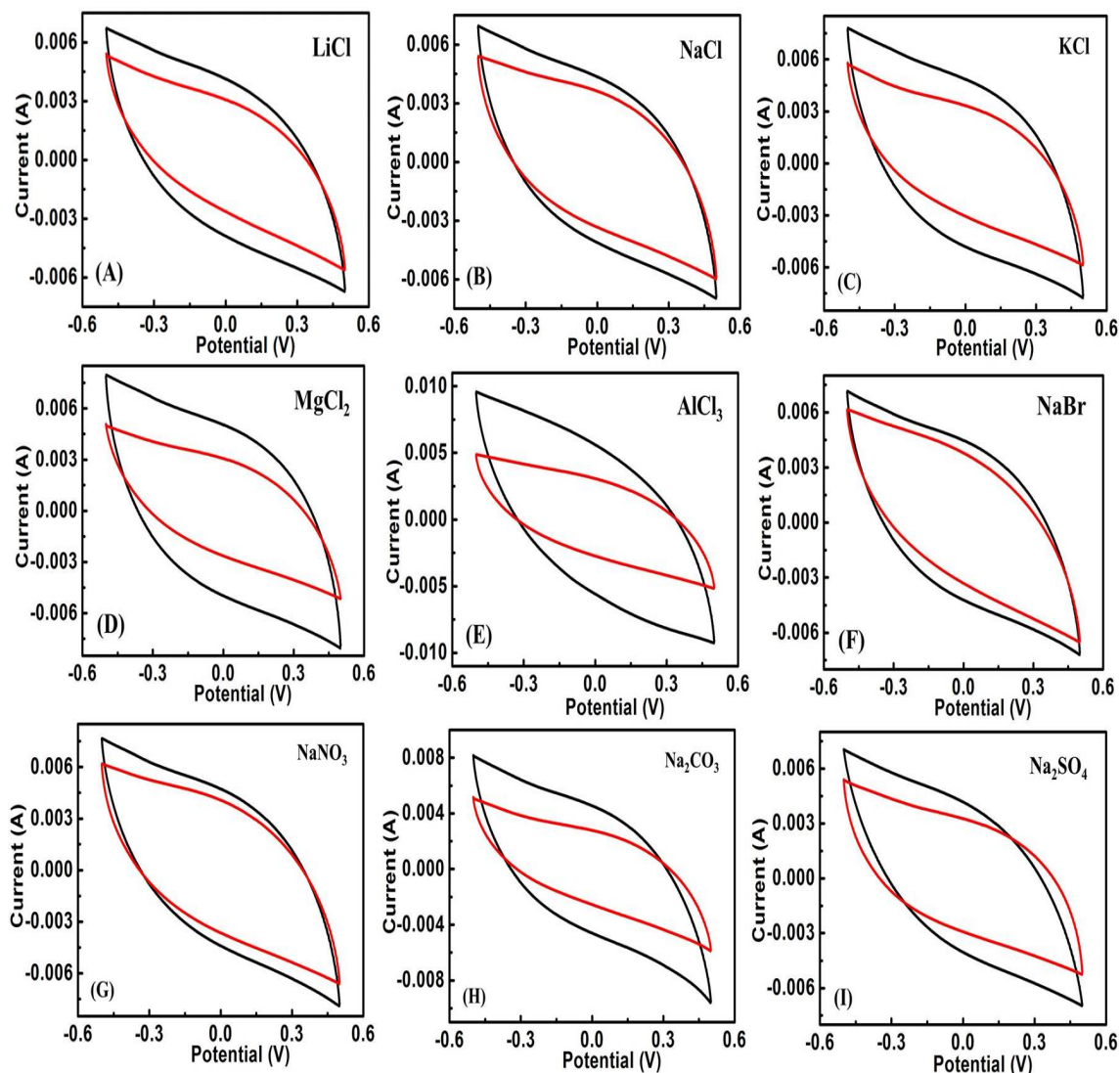


Fig. S2 CV curves for the 3DHPC (black line) and OMC (red line) electrodes in 0.5 M salt solutions with various cations and anions at a scan rate of 10 mV/s.

To reveal the relationship between the pore structure and ion species, the CV measurements were carried out in the salt solutions with various cations (Li^+ , Na^+ , K^+ , Mg^{2+} , and Al^{3+}) and anions (Cl^- , Br^- , NO_3^- , CO_3^{2-} , and SO_4^{2-}). Fig. S2 shows the resultant CV profiles of the 3DHPC and OMC electrodes in 0.5 M aqueous solutions at a scan rate of 10 mV/s. Clearly, all the CV curves related to various ion sizes and

valences are symmetrical without any Faradic reactions appeared in the chosen potential range, indicating the pure capacitive behavior coming from the double electric layer formation during the CDI process^{3, 4}. Moreover, the 3DHPC electrode obtains an enlarged area of the CV profiles in any chosen ion solution, which indicates an increased specific capacitance. The evidently different CDI behaviors of the OMC and 3DHPC electrodes mainly result from the different pore arrangements.

References

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