Supporting Information

The Role of Mesopore Structure of Hierarchical Porous Carbons on the Electrosorption Performance of Capacitive Deionization Electrodes

Turki N. Baroud[a,b], *Emmanuel P. Giannelis*[a]*[1]

[a.] *Department of Materials Science and Engineering Cornell University,Ithaca NY 14853, USA*

[b.] *Department of Mechanical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

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Total number of tables: 4

[1] * Corresponding author. Tel: 607 255-9680. E-mail:: epg2@cornell.edu (E.P. Giannelis)

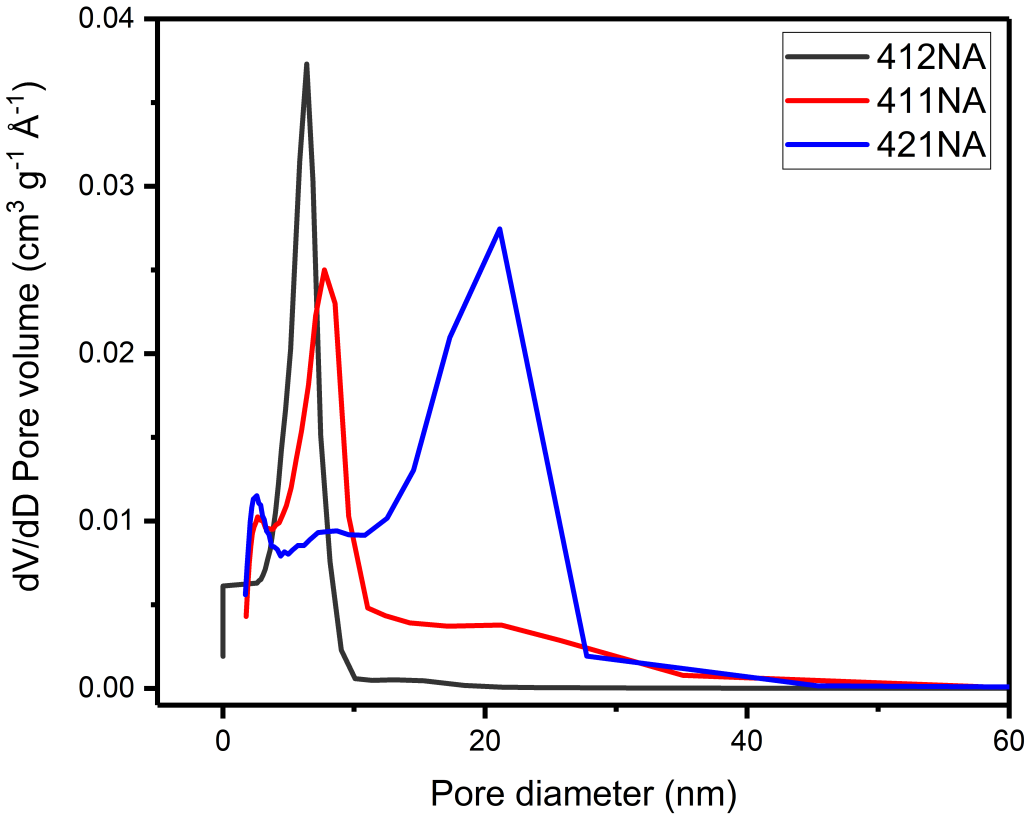

Fig. S 1 BJH pore size distributions plots of 412NA, 411NA and 421NA HPCs , obtained via nitrogen adsorption measurement at 77 K.

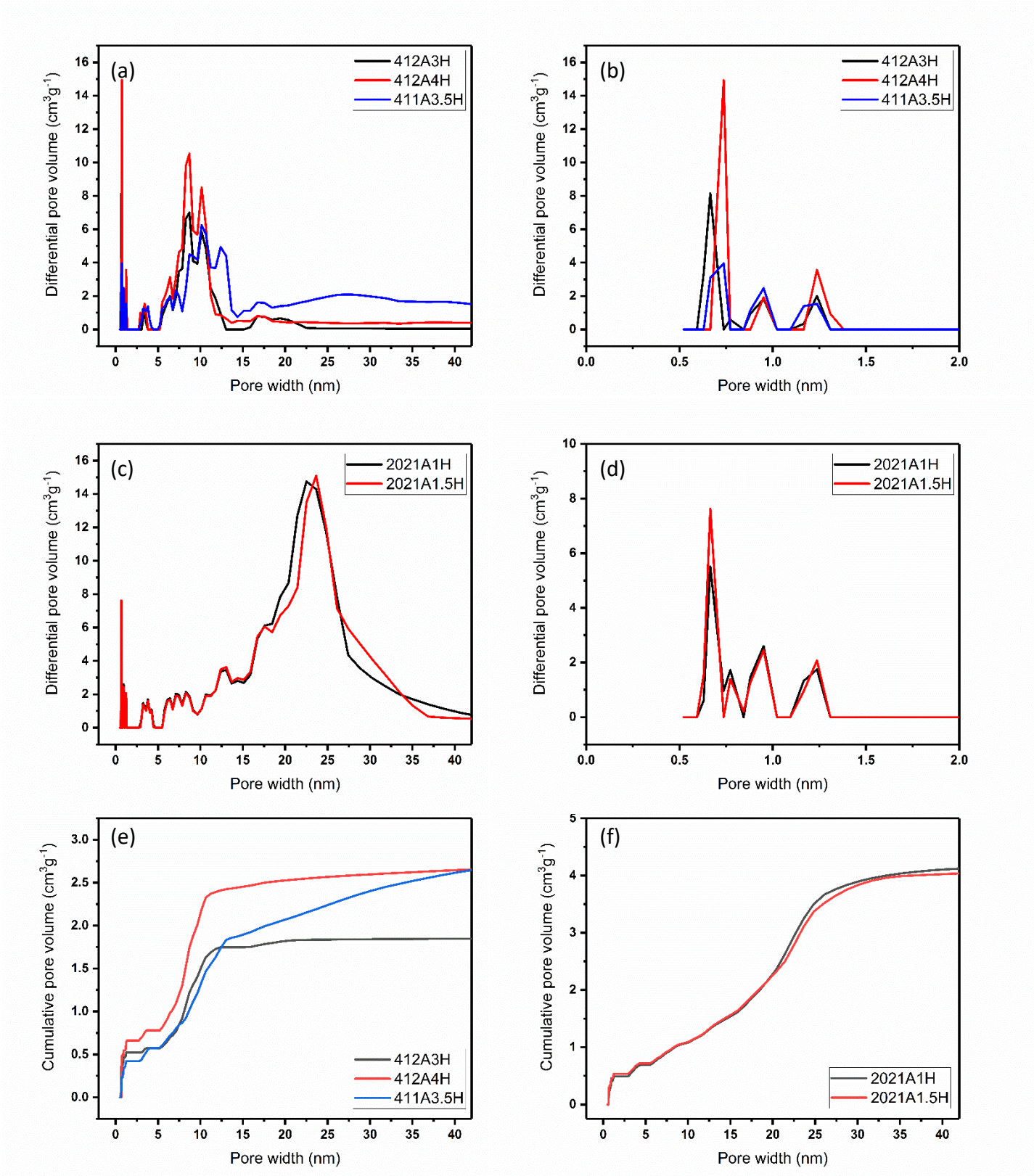

Fig. S 2 (a-c) differential pore size distribution; (e-f) cumulative size distribution of category II "activated HPCs" obtained by NLDFT.

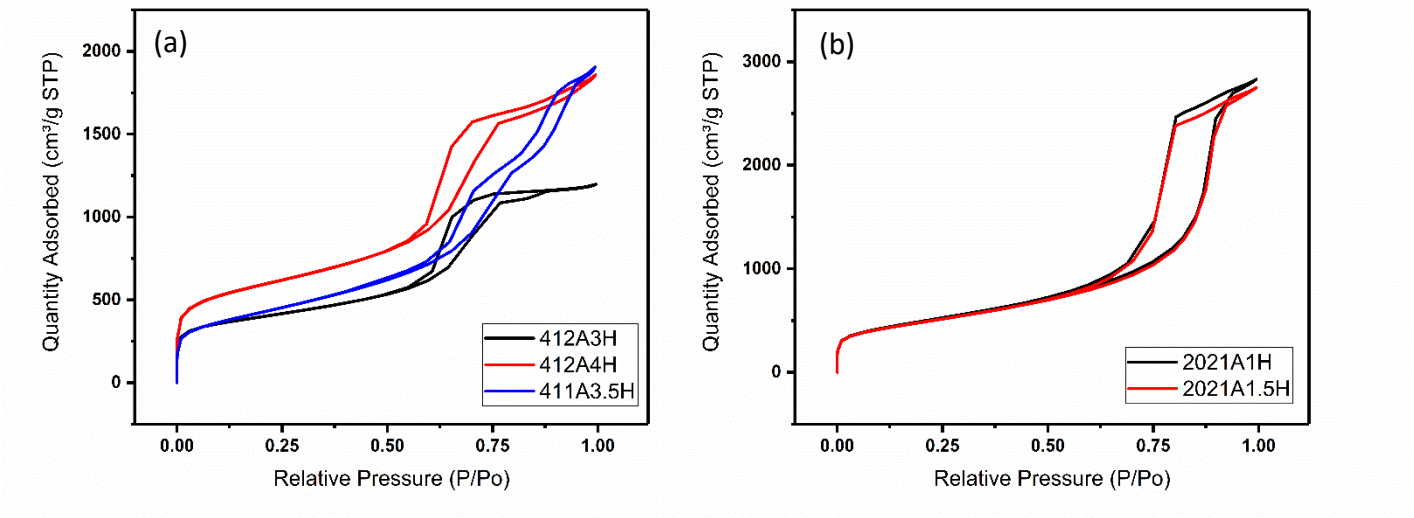

Fig. S 3 (a,b) N2 adsorption-desorption isotherms of category II "activated HPCs".

Table S 1 Surface characteristics of category II "activated HPCs" using Non-Linear Density Functional Theory NLDFT.

Carbon	Surface area S_{NLDFT} [$m^2 g^{-1}$]	Micropore surface area $S_{NLDFT(micro)}$ (for pores below 2nm) [$m^2 g^{-1}$]	Total pore volume $V_{NLDFT-T}$ [$cm^{-3} g^{-1}$]	Micropore volume $V_{NLDFT(micro)}$ (for pores below 2nm) [$cm^{-3} g^{-1}$]
412A3H	3480	2850	1.86	0.52
412A4H	4241	3256	2.7	0.66
411A3.5H	2900	2000	2.6	0.42
2021A1H	3500	2455	4.2	0.48
2021A1.5H	3795	2793	4.2	0.53

Table S 2 Atomic concentrations of various hierarchical porous carbons obtained via XPS

	Carbon	C [at. %]	O [at. %]	Si [at. %]
Category I “ Nonactivated”	411NE*	30.7	52.3	17
	412NA	93.8	6.2	0
	411NA	90.3	9.7	0
	1211NA	93.6	6.4	0
	1221NA	91.8	8.1	0
	2011NA	92	8	0
	2021NA	90.3	9.7	0
Category II “ Activated”	412A3H	92.8	7.2	0
	412A4H	95.44	4.6	0
	411A3.5H	94.6	5.4	0
	2021A1H	95.6	4.4	0
	2021A1.5H	94.2	5.8	0

(*) Non-etched carbon “NE” which refers to carbon prior to silica template etching.

Table S 3 Electrical conductivity of various hierarchical porous carbons powders[1]

	Carbon	Electrical Conductivity [S cm^{-1}]
Category I "Non-activated"	412NA	7.9
	411NA	6.5
	1211NA	2.9
	1221NA	1.5
	2011NA	3.4
	2021NA	1.6
Category II "Activated"	412A4H	3.6
	2021A1.5H	1.5

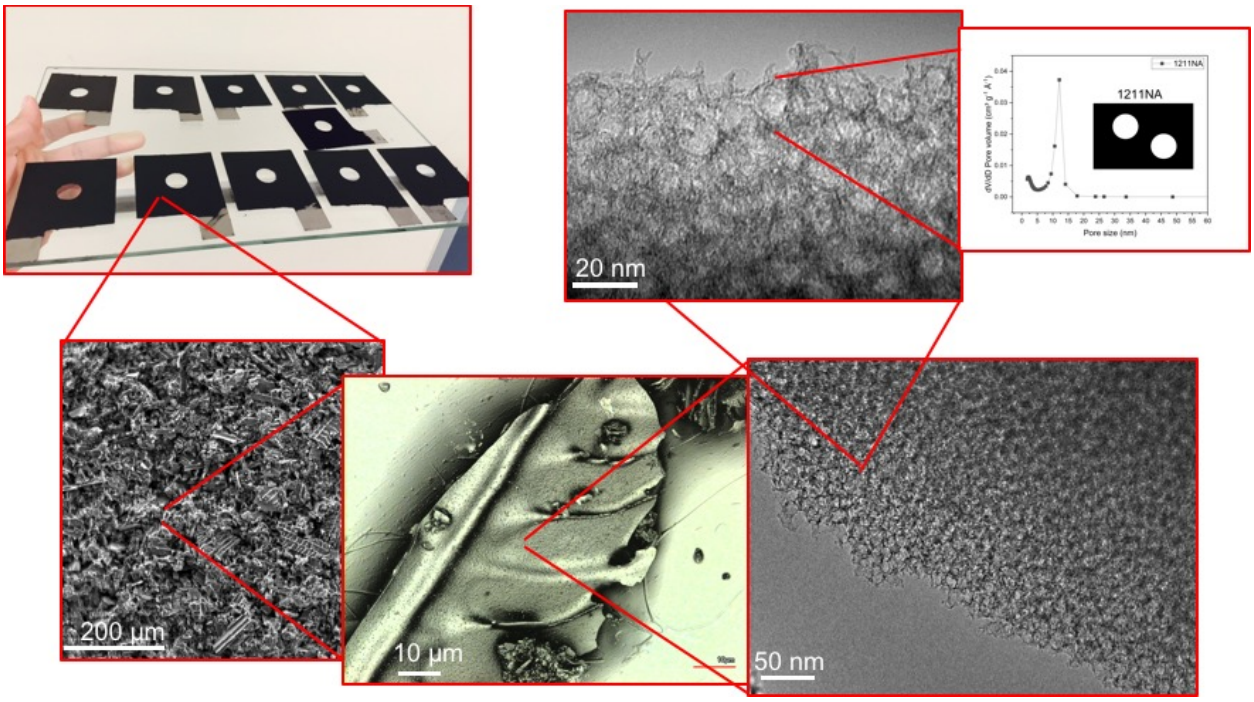

Fig. S 4 (a)Hierarchical porous carbon films coated graphite sheets as capacitive deionization electrode, (b) SEM image of the dried films, (c) optical image of single HPC particle, (d&e) TEM images of HPCs, and (f) BJH pore size distribution showing a sharp pea peak that corresponds well with silica templet.

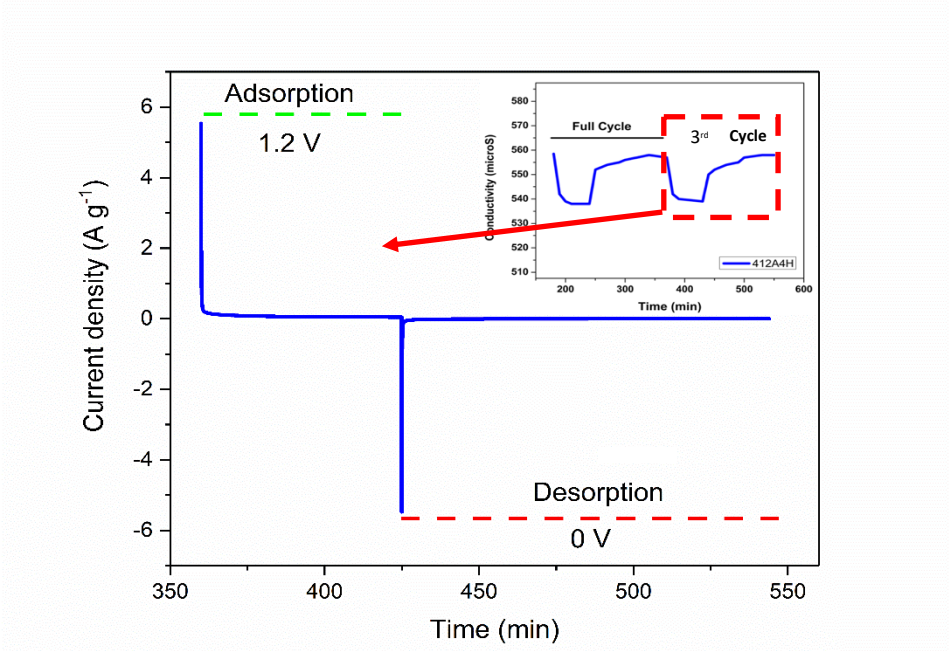

Fig. S 5 Typical profile for the current density during the adsorption and desorption cycle at 1.2 V and in 5 mM NaCl solution(3rd cycle); the inset is the typical conductivity profile during cycling.

Fig. S6 compares the pH profile of 411NA and 2021NA in 5mM NaCl solution at 1.2V. The pH of the circulated water increased dramatically from the initial value 6.9 to the final value around 10 when the potential of 1.2V was applied, before it returns back to the initial pH value at the end of adsorption cycle. No significant differences are seen in the pH profile as a result of tuning the mesopore size from 4nm up to 20nm.

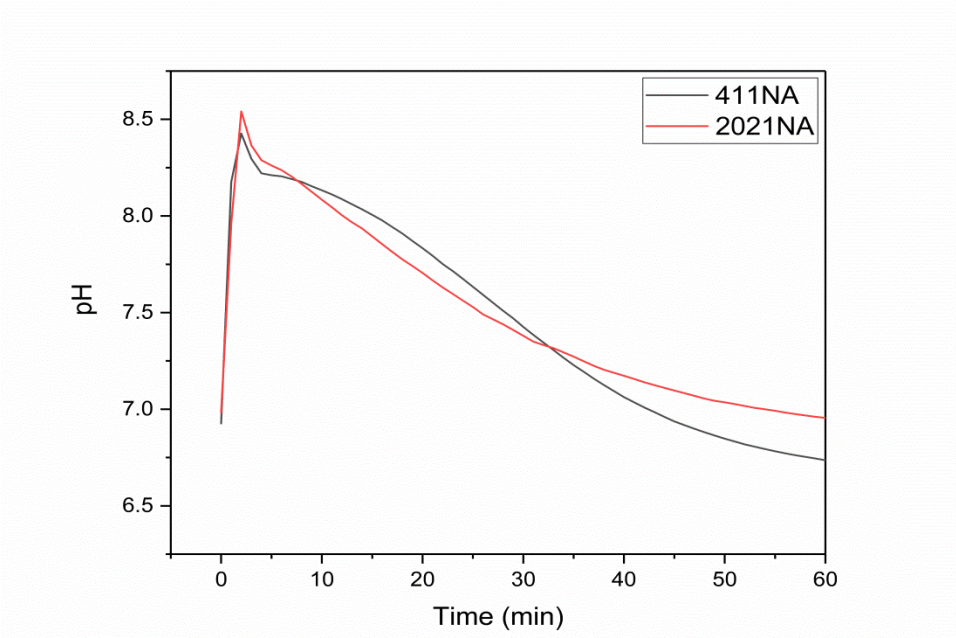

Fig. S 6 pH profile for 411NA and 2021NA HPCs during the adsorption step at 1.2 V in 5 mM NaCl solution.

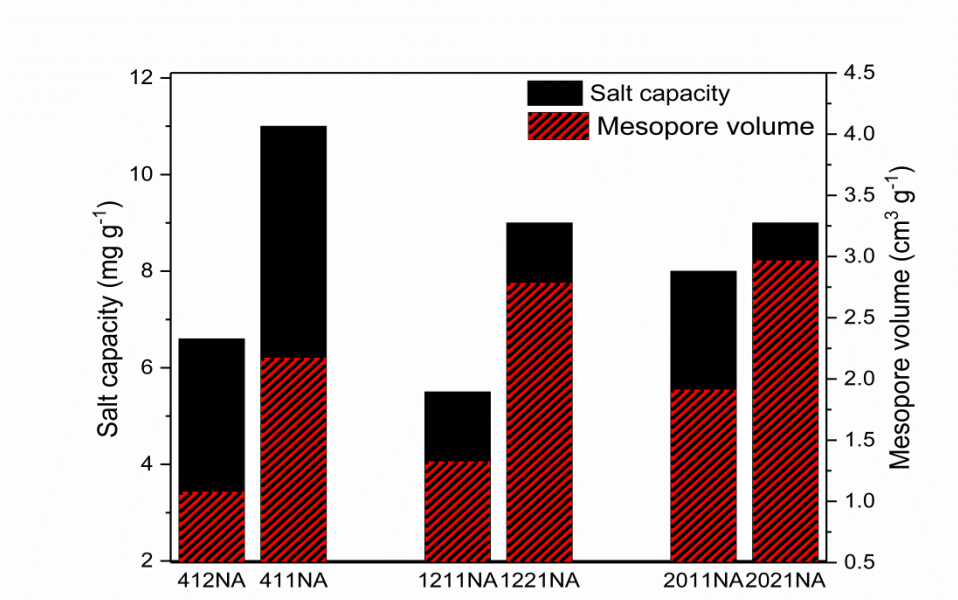

Fig. S7 The impact of doubling the mesopore volume on the salt capacity

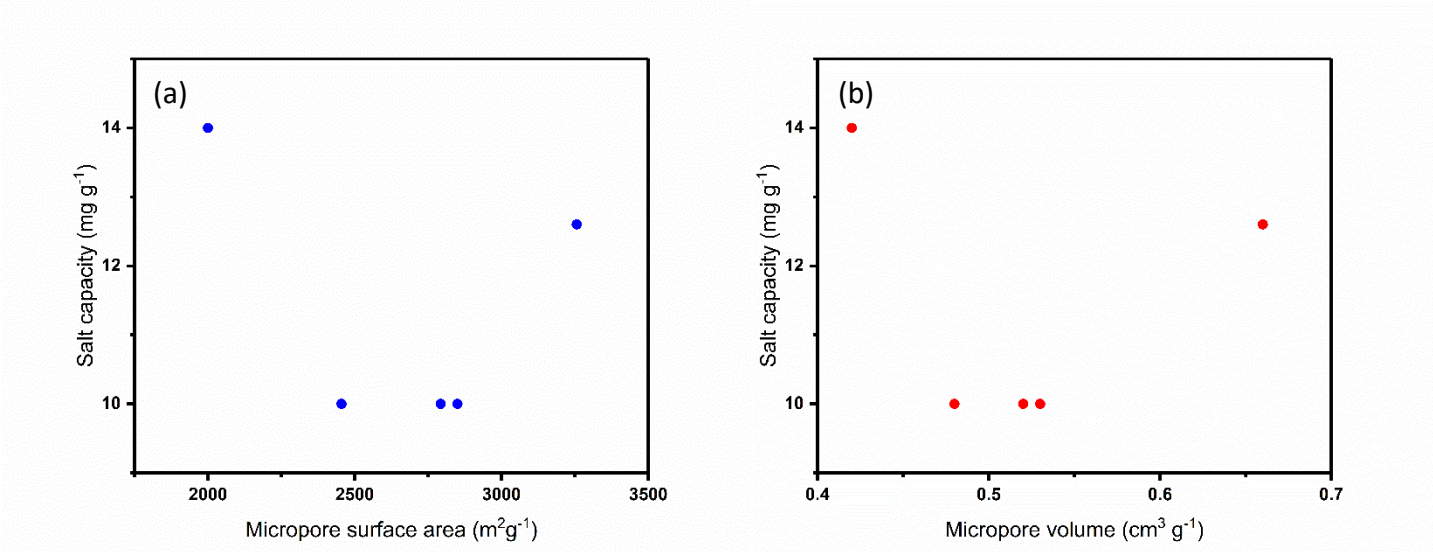

Fig. S 8 Salt capacity vs NLDFT micropore surface area (a), NLDFT micropore volume (b) of category II HPCs. All the reported values were evaluated in NaCl solution and at 1.2 V.

Table S4 illustrates the charge efficiencies of all HPCs, which were calculated according to equation 2. According to Table S3 all the HPCs demonstrate comparable charge efficiencies. Typically, the charge efficiency for CDI electrode is less than unity as the supplied charge is consumed for counter-ion adsorption and co-ion expulsion as well.

Table S 4 Charge efficiency of various hierarchical porous carbons calculated using equation 3.

Carbon	Charge efficiency
412	0.64
411	0.51
1211	0.7
1221	0.51
2011	0.60
2021	0.42
412A3h	0.58
412A4h	0.49
411A3.5H	0.54
2021A1h	0.55
2021A1.5H	0.54

Reference

(1) Sahore, R.; Levin, B. D. A.; Pan, M.; Muller, D. A.; DiSalvo, F. J.; Giannelis, E. P. Design Principles for Optimum Performance of Porous Carbons in Lithium-Sulfur Batteries. *Adv. Energy Mater.* **2016**, *6* (14), 1600134.