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Supporting Information of

Synthesis of Hard Carbons from Argan Shell for Na-Ion Batteries

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Additional details of experimental condition

Synthesis of hard carbon from cellulose and lignin

We prepared hard carbon from cellulose and lignin by two different processes: standard and HCl-washing processes (**Figure S1a**). A standard process is as follows: the cellulose and lignin powders were heated in a horizontal tube furnace at a heating rate of 5 °C min^{-1} and held at 800 °C for 1 hour under argon stream. The products are denoted herein after as Cellulose-800 and Lignin-800.

The HCl-treatment process is intended to compare with argan materials. Cellulose and lignin powders were treated with 2.0 mol dm^{-3} hydrochloric acid aqueous solution. For the treatment, the cellulose and lignin powders were dispersed into the hydrochloric acid and aged for 20 h at 60 °C. The powder was separated by filtration and washed with deionized water until pH 6.5-7.0 of filtrated water to remove remained HCl. The resultant powder was dried at 110 °C for 1 h under argon atmosphere. Following carbonization/pyrolysis conditions are the same as the process for argan shown in **Figure S1b**. In this process heating temperatures was 800 °C, and the hard carbons prepared at the temperatures are denoted as as Cellulose-800W and Lignin-800W.

Electrochemical tests of cellulose and lignin hard carbons

The cellulose and lignin hard carbons synthesized were mixed with sodium polyacrylate, PANa, (MW: 2,100,000 – 6,200,000, Kishida Chem., Co., Ltd.) at the weight ratio of 95:5 with deionized water. The resulting slurries were uniformly pasted onto aluminum foil, and then dried at 150 °C for 12 h in a vacuum. The mass loading of active materials was approximately 1.2-2.0 mg cm^{-2}. The electrochemical measurements were conducted by using 2032-type coin cells consisting of the hard carbon electrode, a separator (glass fiber filter, ADVANTEC), electrolyte solution (battery grade, Kishida Chemical Co., Ltd.), and sodium metal (Kanto Chemical, Co., Ltd.) as a counter electrode. The coin cells were assembled in a glove box filled with argon. The battery-grade electrolyte solution used in this study was 1 mol dm^{-3} of $\mathrm{NaPF_6}$ ethylene carbonate (EC) : diethyl carbonate (DEC) (1:1 v/v), supplied by Kishida Chemical Corporation. Galvanostatic charge/discharge cycling tests were carried out in the voltage range between 0.0 and 2.0 V, using a battery cycler (TOSCAT-3100, Toyo System Co., Ltd.) at a current rate of 25 mA g^{-1}. All chemicals were handled in an argon-filled glove box to avoid air exposure and contamination from atmosphere.

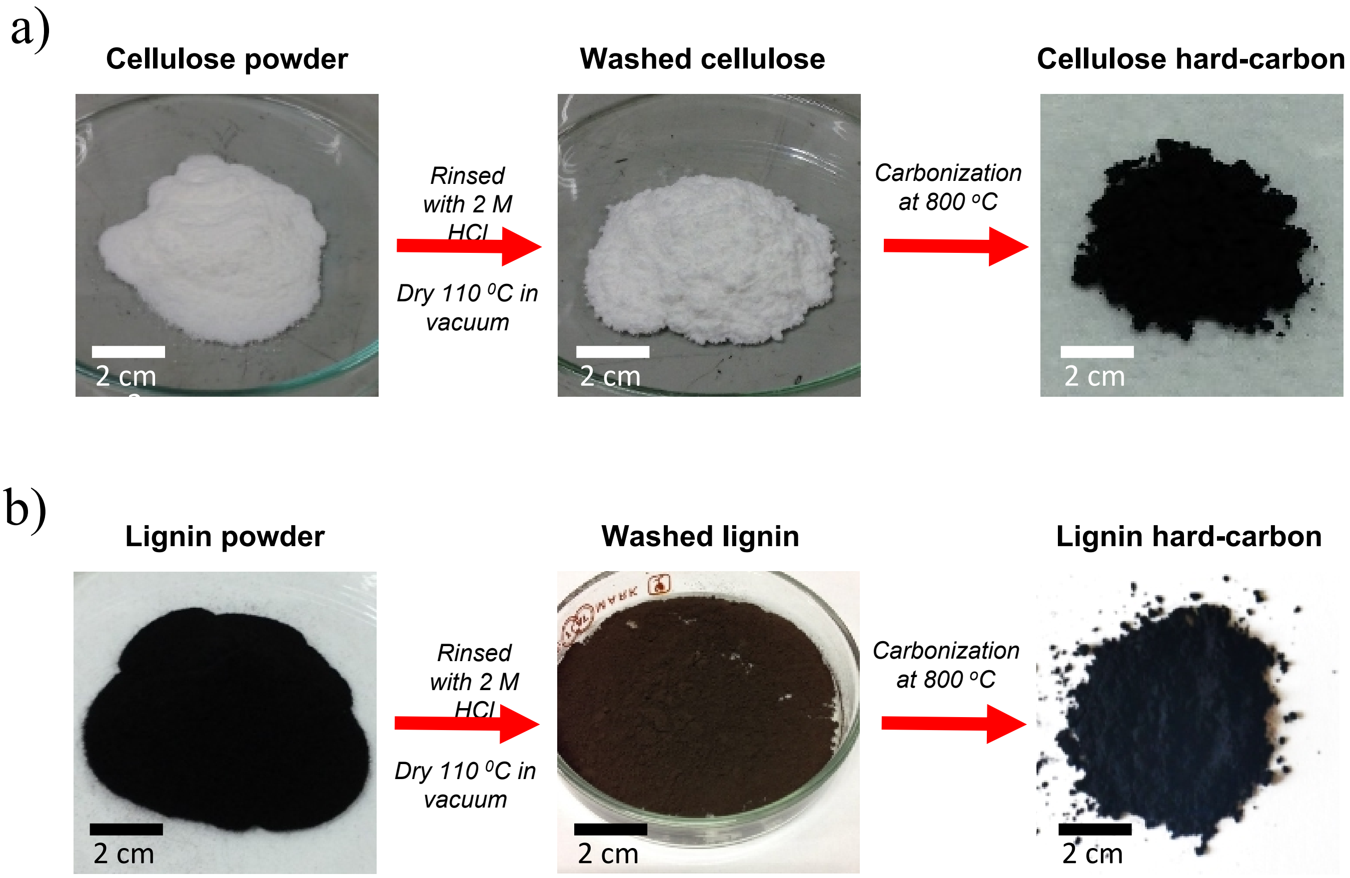

Figure S1: Cellulose and lignin materials synthesis processes with and without HCl treatment at 800 °C.

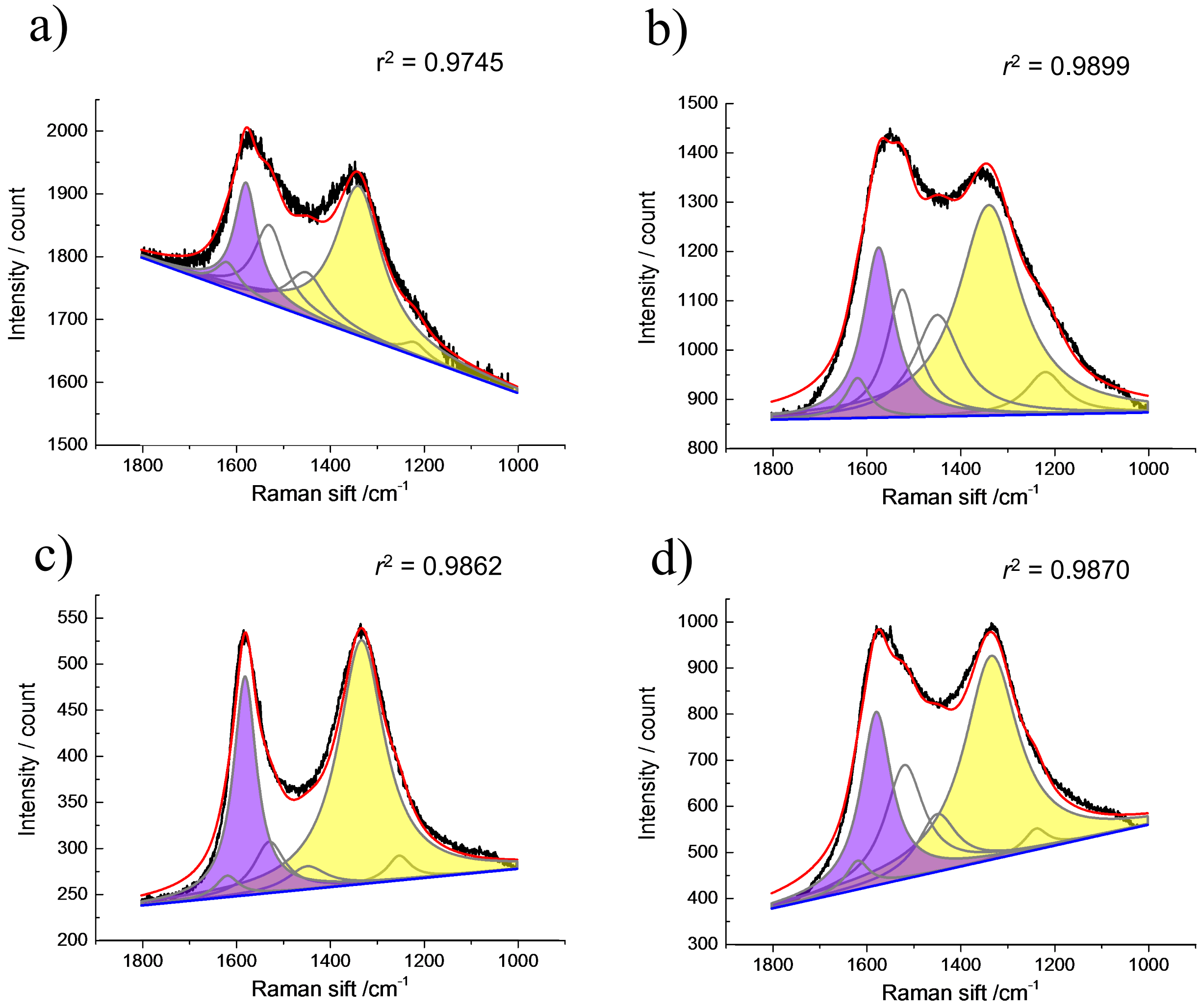

Figure S2: Fitted Raman spectra profiles of a) Argan-800, b) Argan-1000, c) Argan-1200, and d) argan-1300. The fitting was done with Fityk 0.9.0 software program using Lorentzian function.

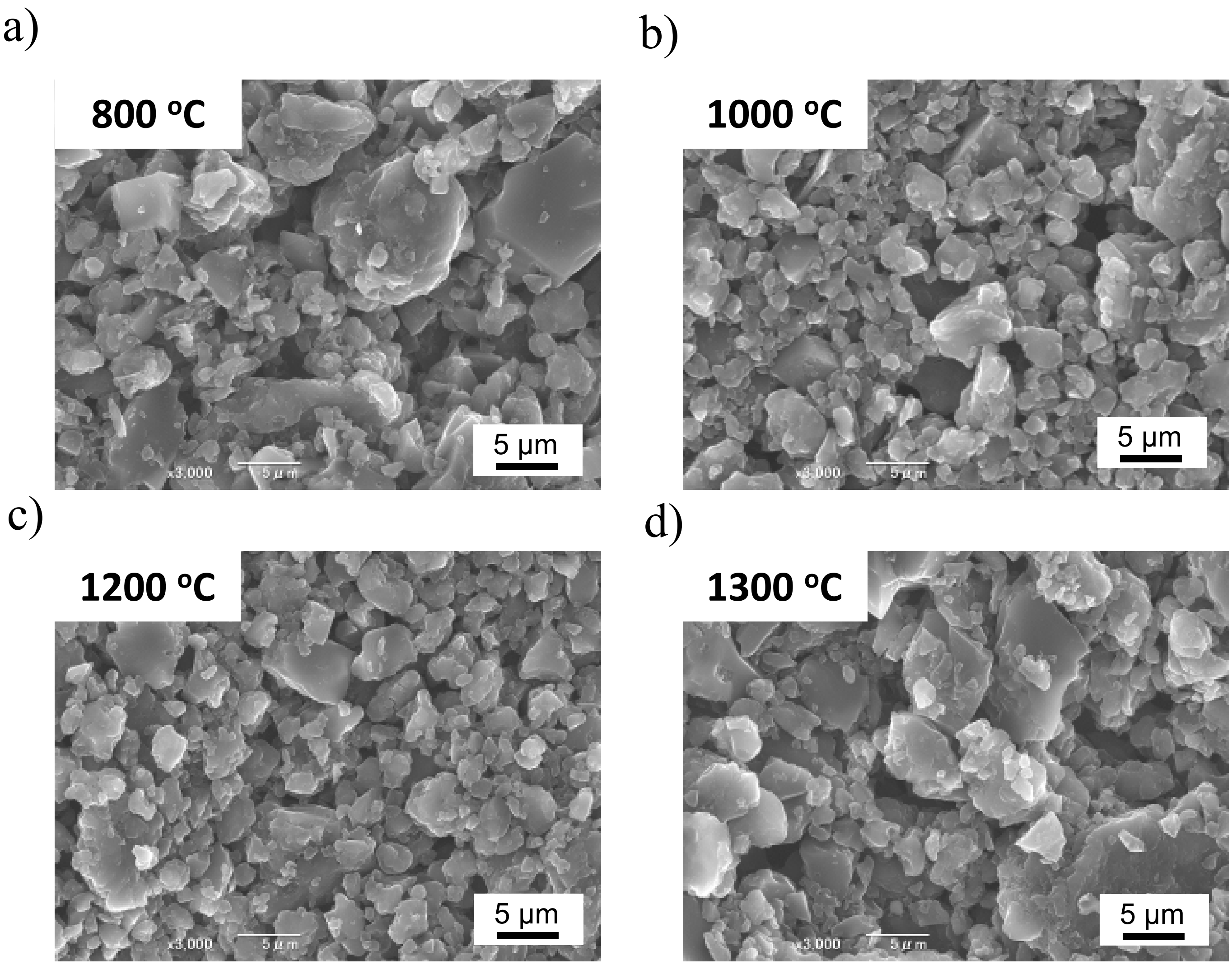

Figure S3: Electrode morphology observed by SEM of a) Argan -800, b) Argan-1000, c) Argan-1200, and d) Argan-1300.

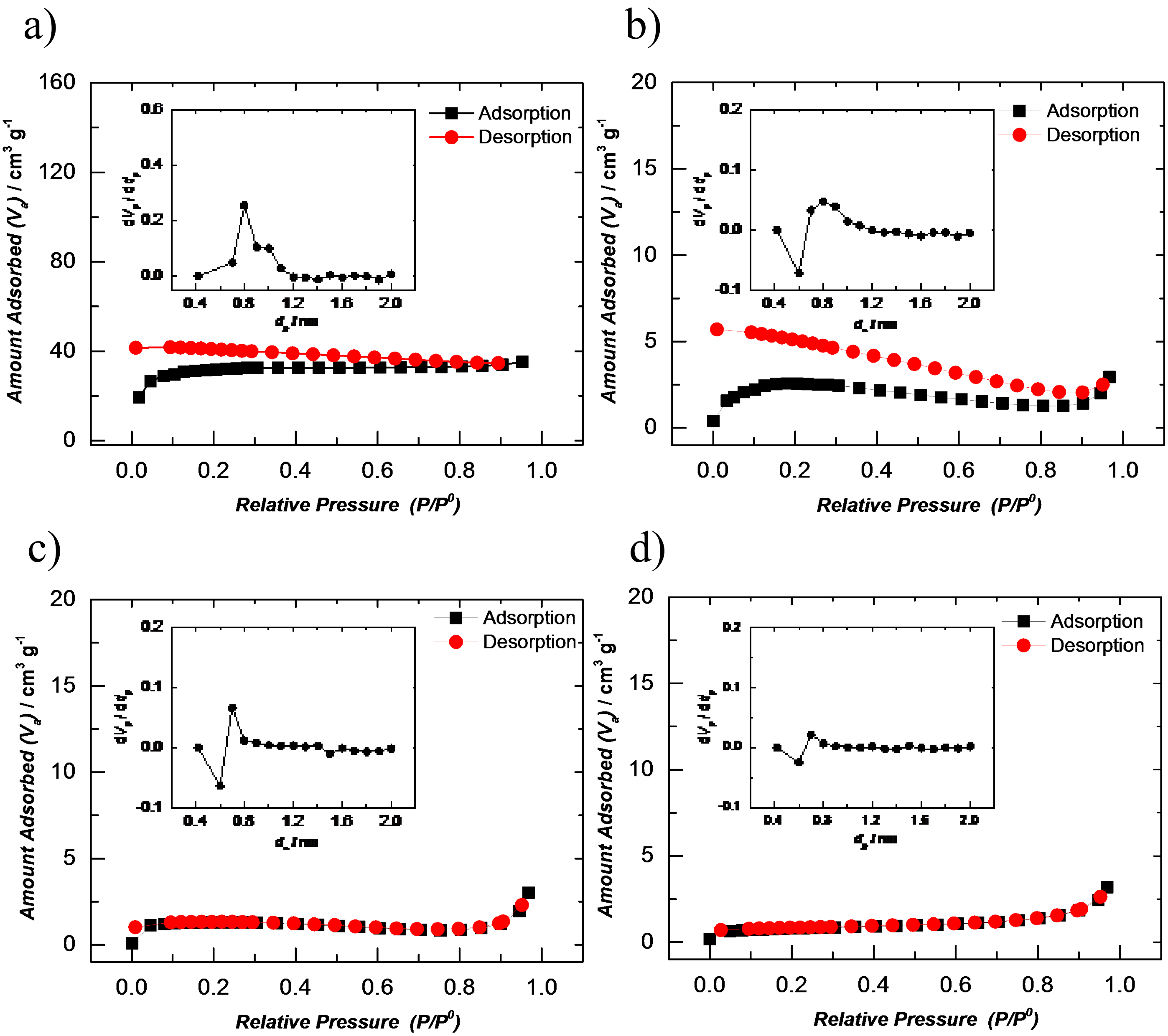

Figure S4: N_2 adsorption−desorption isothermal curve of a) Argan-800, b) Argan-1000, c) Argan-1200, and d) Argan-1300. The insert is corresponding pore size distribution.

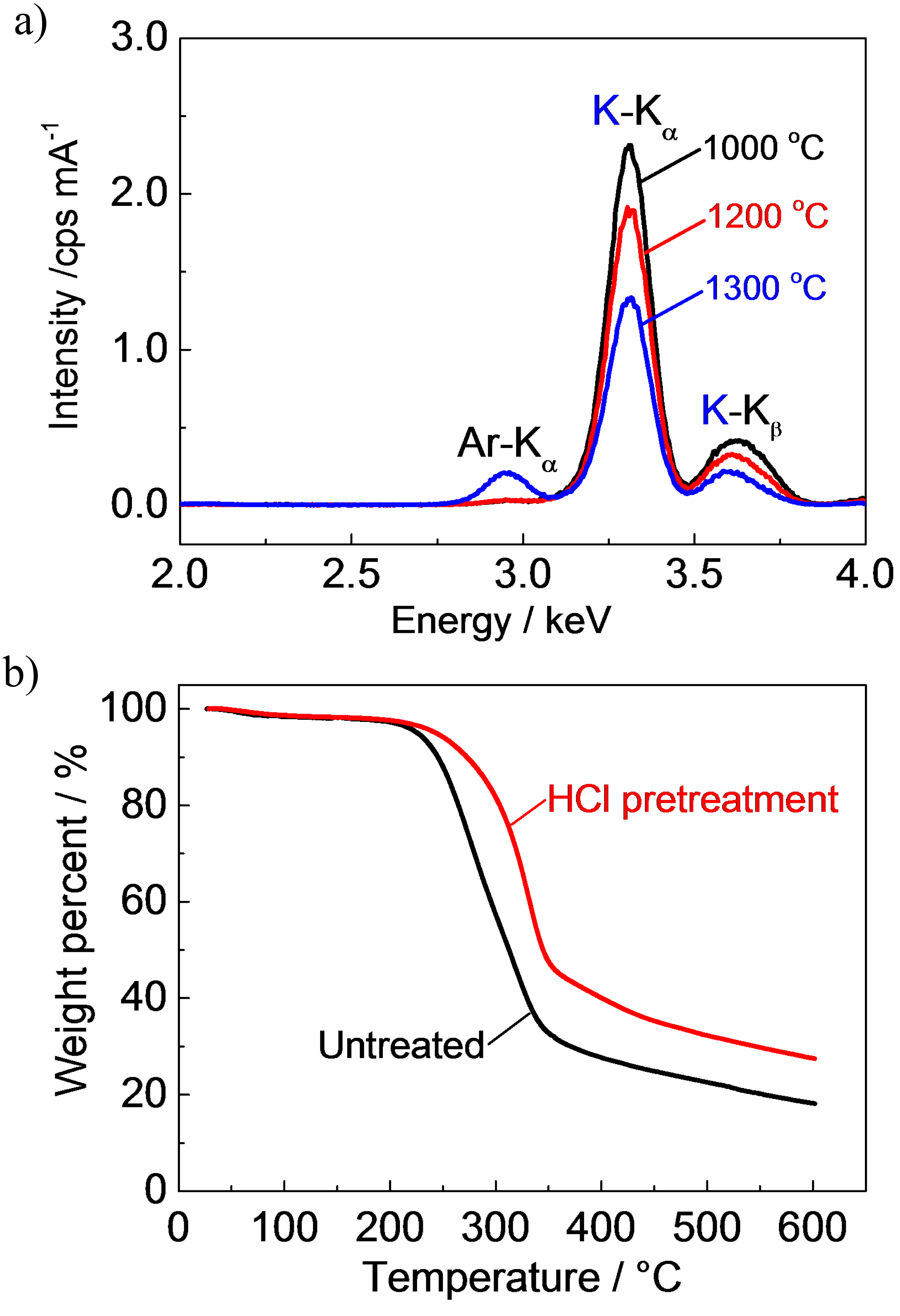

Figure S5: a) XRF spectra of untreated Argan-1000 (black curve), Argan-1200 (red curve) and Argan-1300 (blue curve). b) TGA analysis of untreated (black curve) and HCl washed (red curve) Argan raw materials before carbonization.

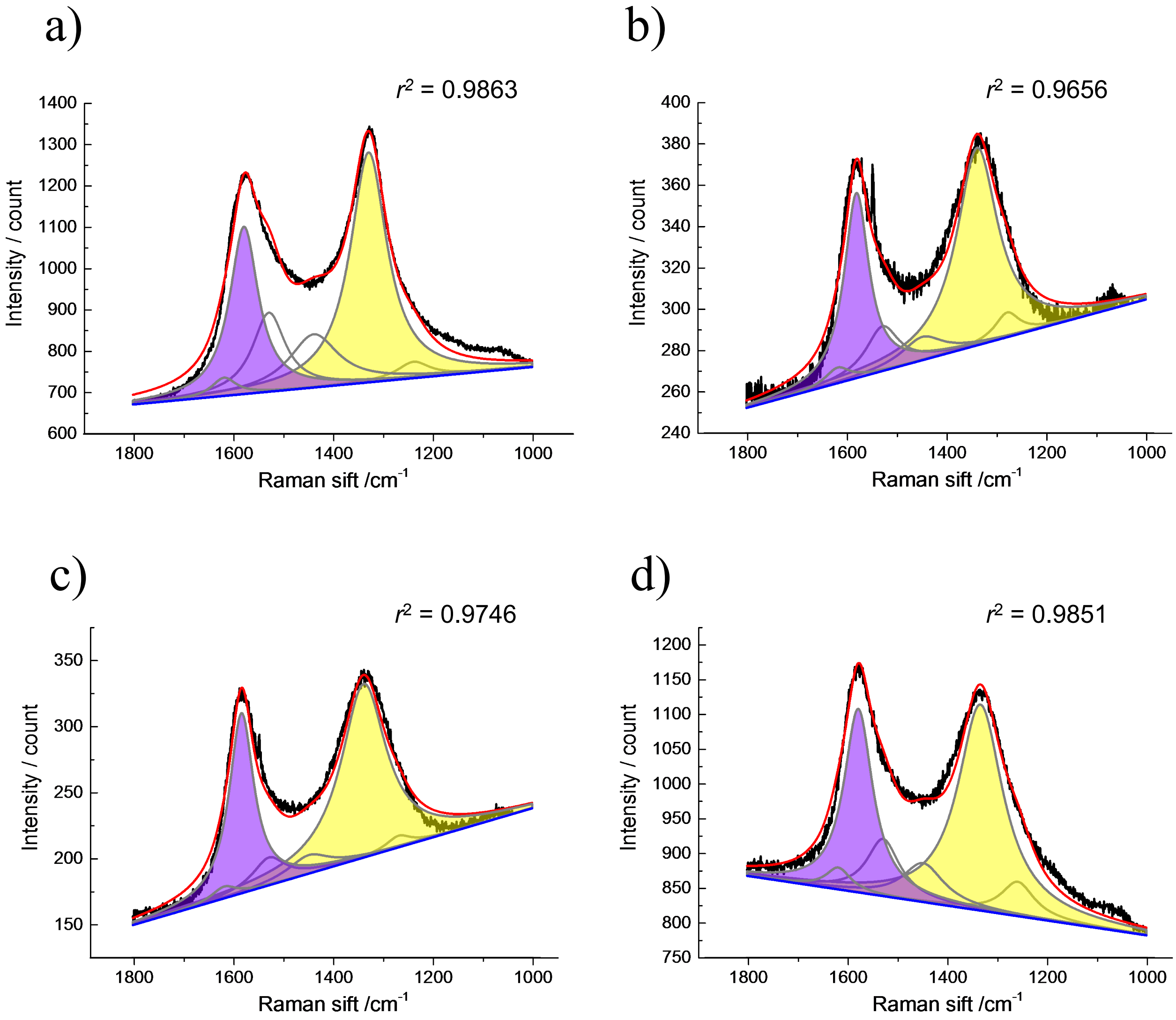

Figure S6: Fitted Raman spectra profiles of HCl washed argan materials a) Argan-800W, b) Argan-1000W, c) Argan-1200W, and d) Argan-1300W. The fitting was done with Fityk 0.9.0 software using Lorentzian function.

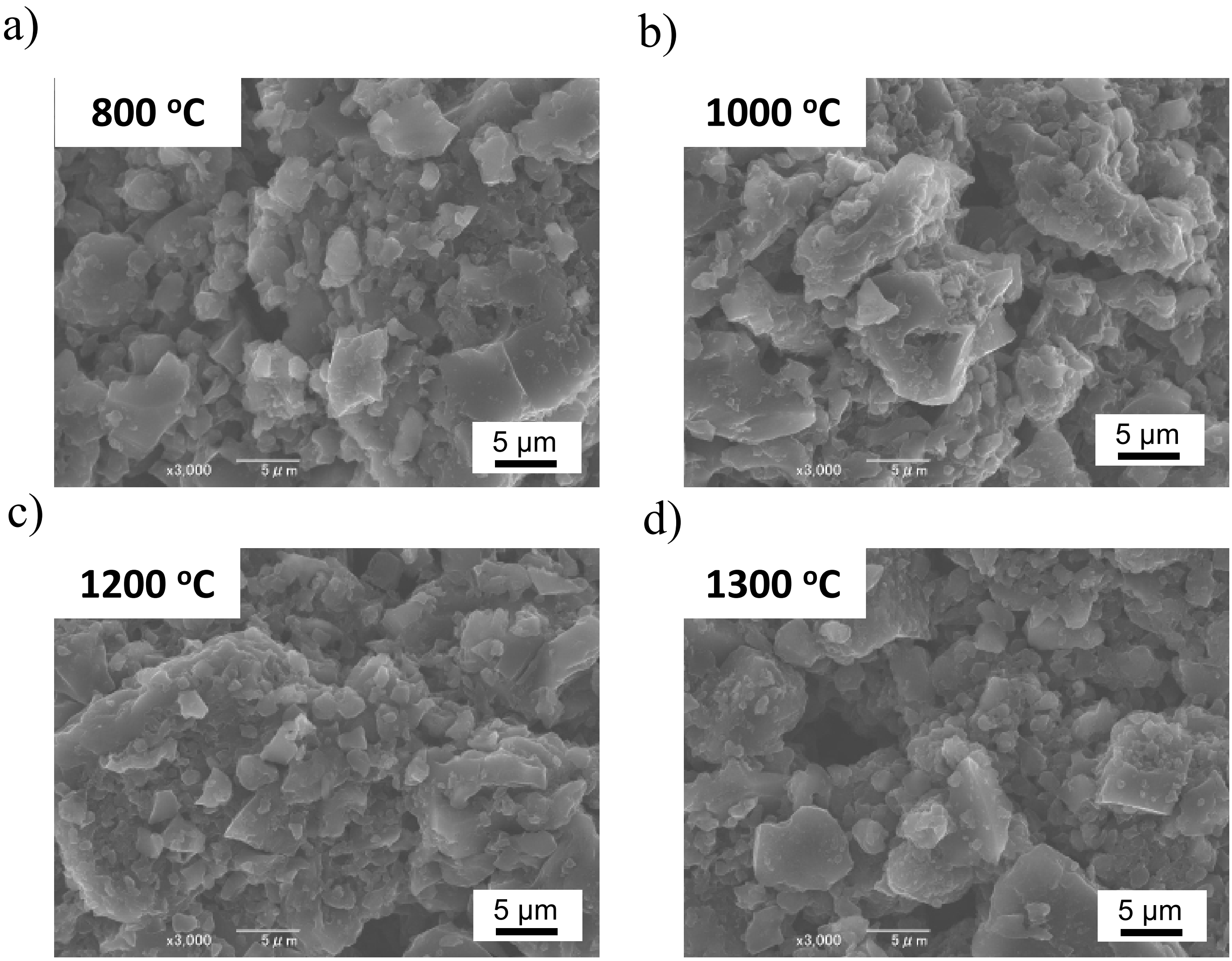

Figure S7: Electrode morphology observed by SEM of HCl-treated materials a) Argan-800W, b) Argan-1000W, c) Argan-1200W, and d) Argan-1300W.

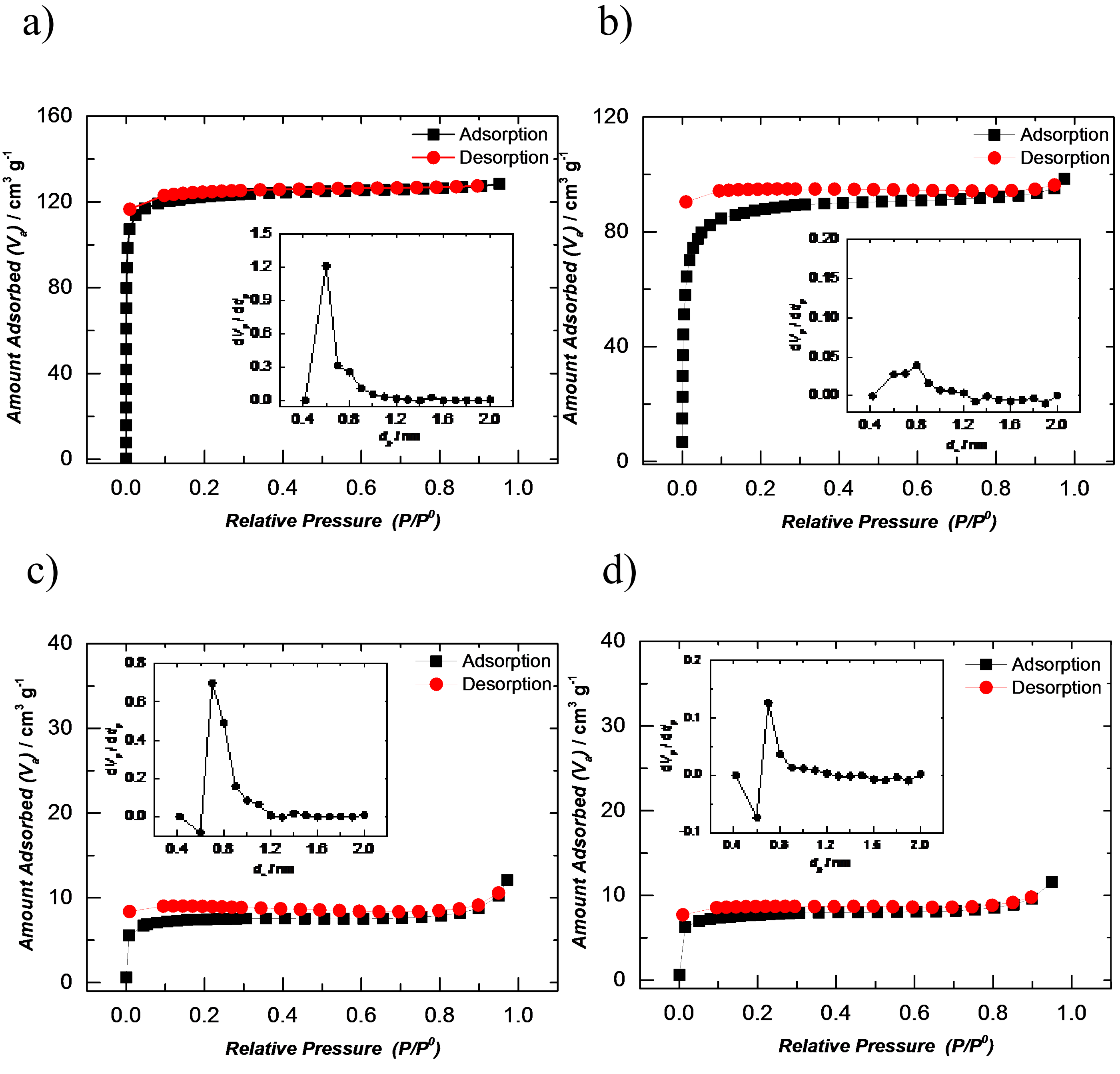

Figure S8: N$_2$ adsorption−desorption isothermal curve of HCl-treated materials a) argan-800W, b) argan-1000W, c) argan-1200W, and d) argan-1300W. The insert is corresponding pore size distribution.

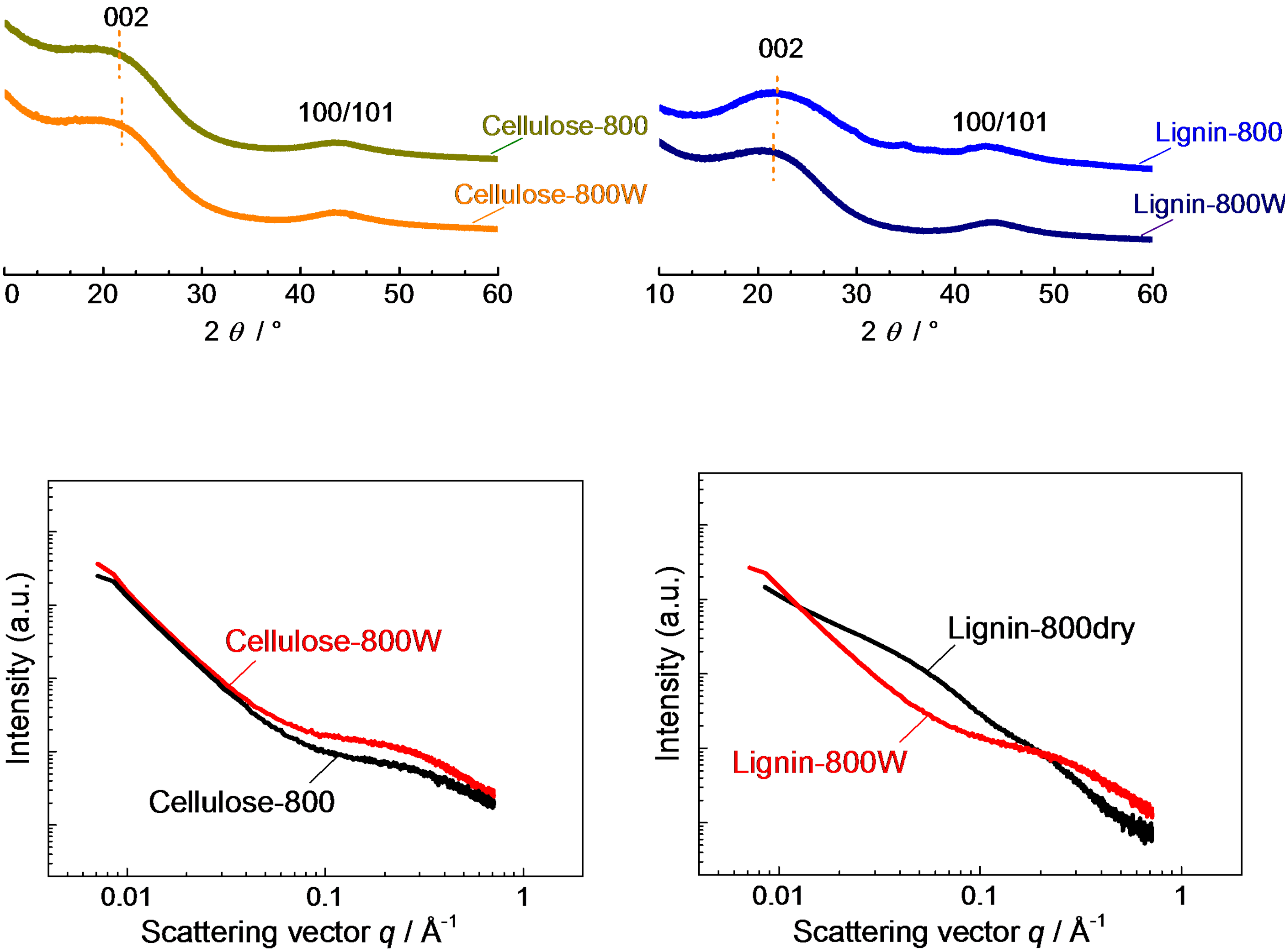

Figure S9: XRD (top) and SAXS (down) patterns of Cellulose-800, Lignin-800, Cellulose-800W, and Lignin-800W hard carbons.

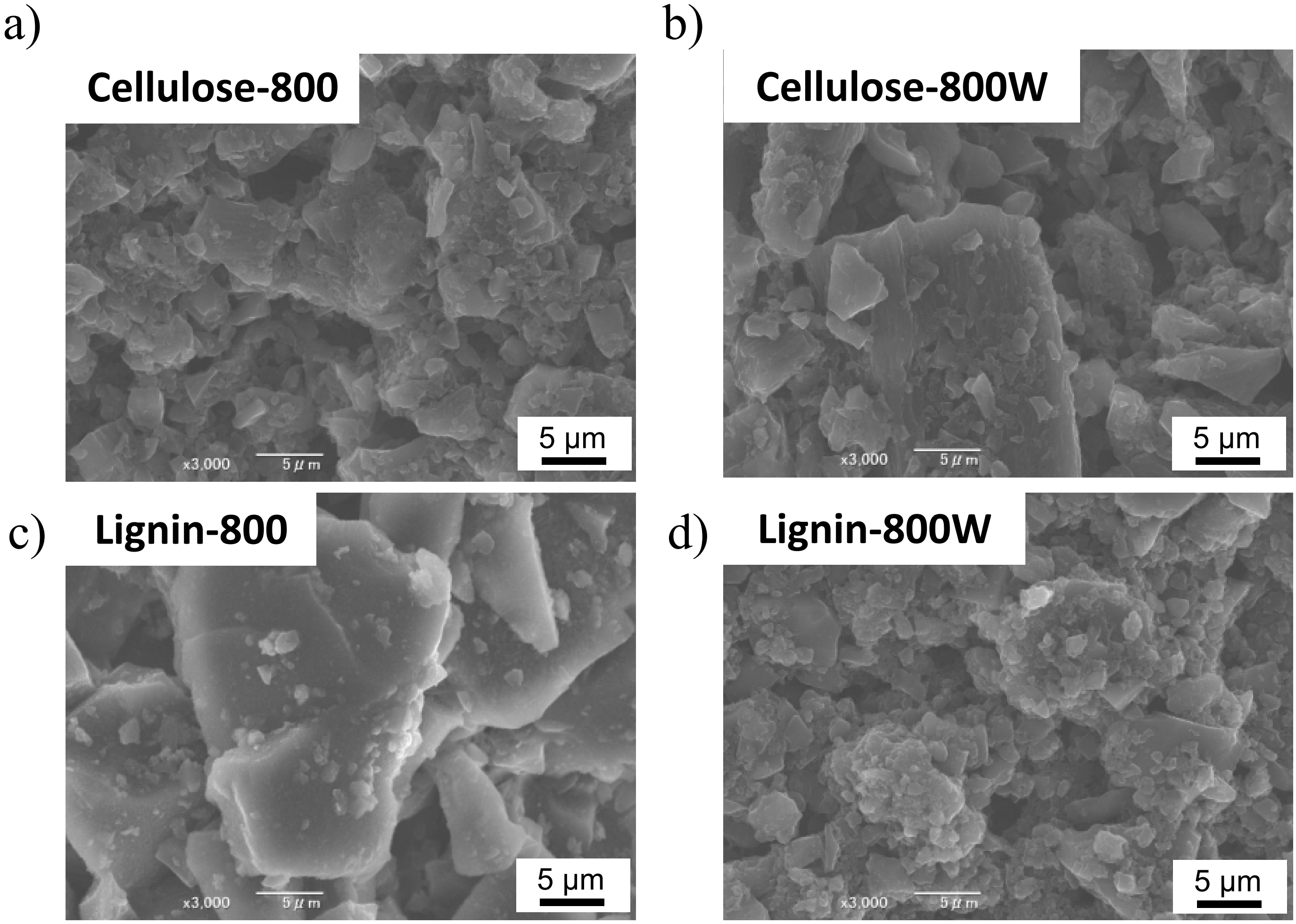

Figure S10: Electrode morphology observed by SEM of carbonized cellulose and lignin materials at 800 °C: a) cellulose-800, b) cellulose-800W, c) lignin-800, and d) lignin-800W.

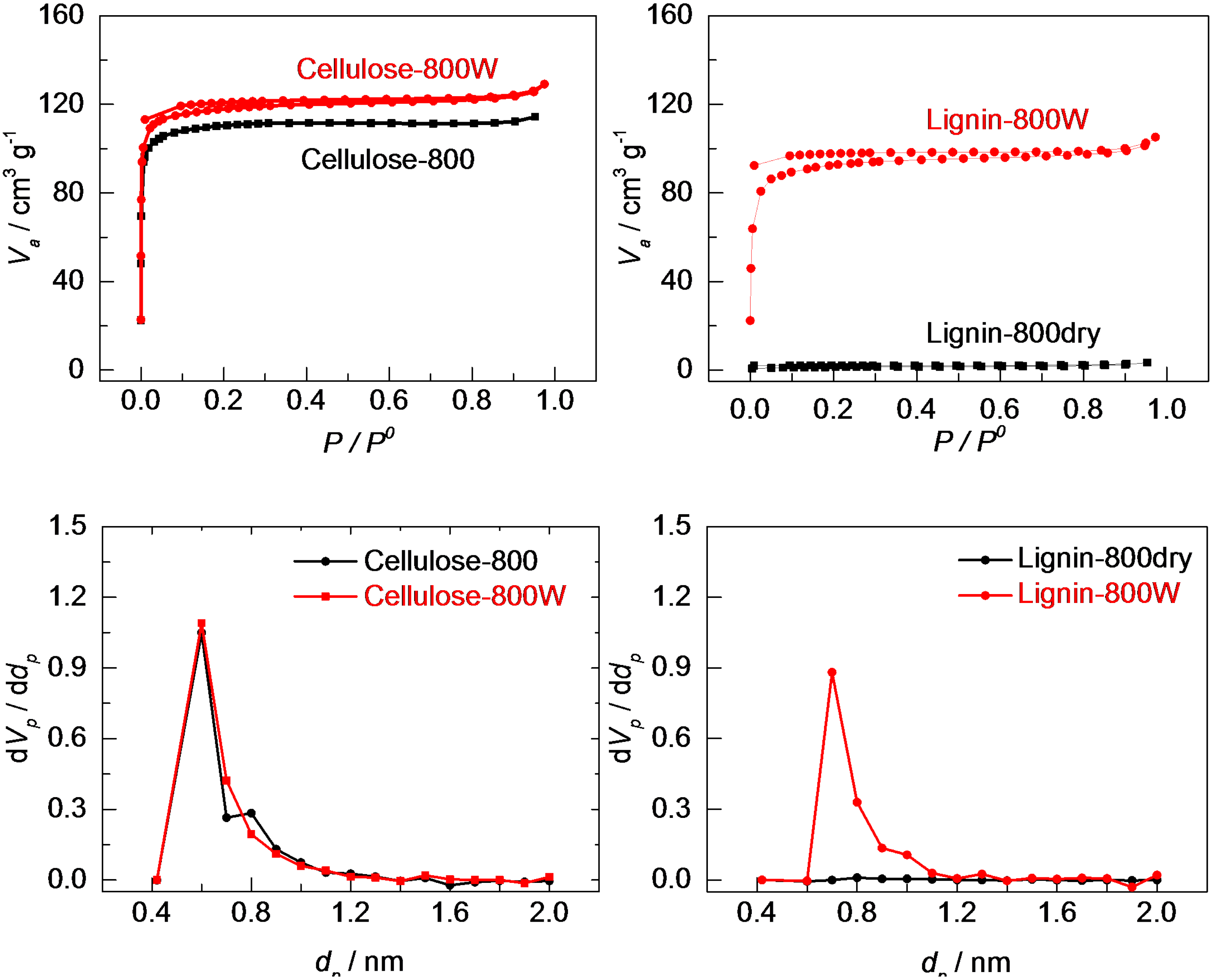

Figure S11: N_2 adsorption−desorption isothermal curve (top) and corresponding pore size distribution (down) of cellulose and lignin materials.

Table S1: Physical parameters for hard carbon samples synthesized by pyrolysis of Argan shell, cellulose and lignin at 800 °C .

Sample	d_{002} / Å	L_c / nm	Radius of micro-pores by SAXS / Å	Surface area / m^2 g^{-1}	Average pore diameter by BET / nm	Total pore volume / cm^3 g^{-1}
Argan-800	4.00	8.99	6.6	99	2.2	0.0540
Argan-800W	3.91	10.1	8.9	380	2.1	0.2000
Cellulose-800	4.09	9.3	6.3	425	1.66	0.1768
Cellulose-800W	4.05	4.05	7.1	352	2.3	0.2000
Lignin-800dry	3.91	8.8	14.6	4.4	4.7	0.0052
Lignin--800W	4.04	9.02	8.9	287	2.3	0.1600

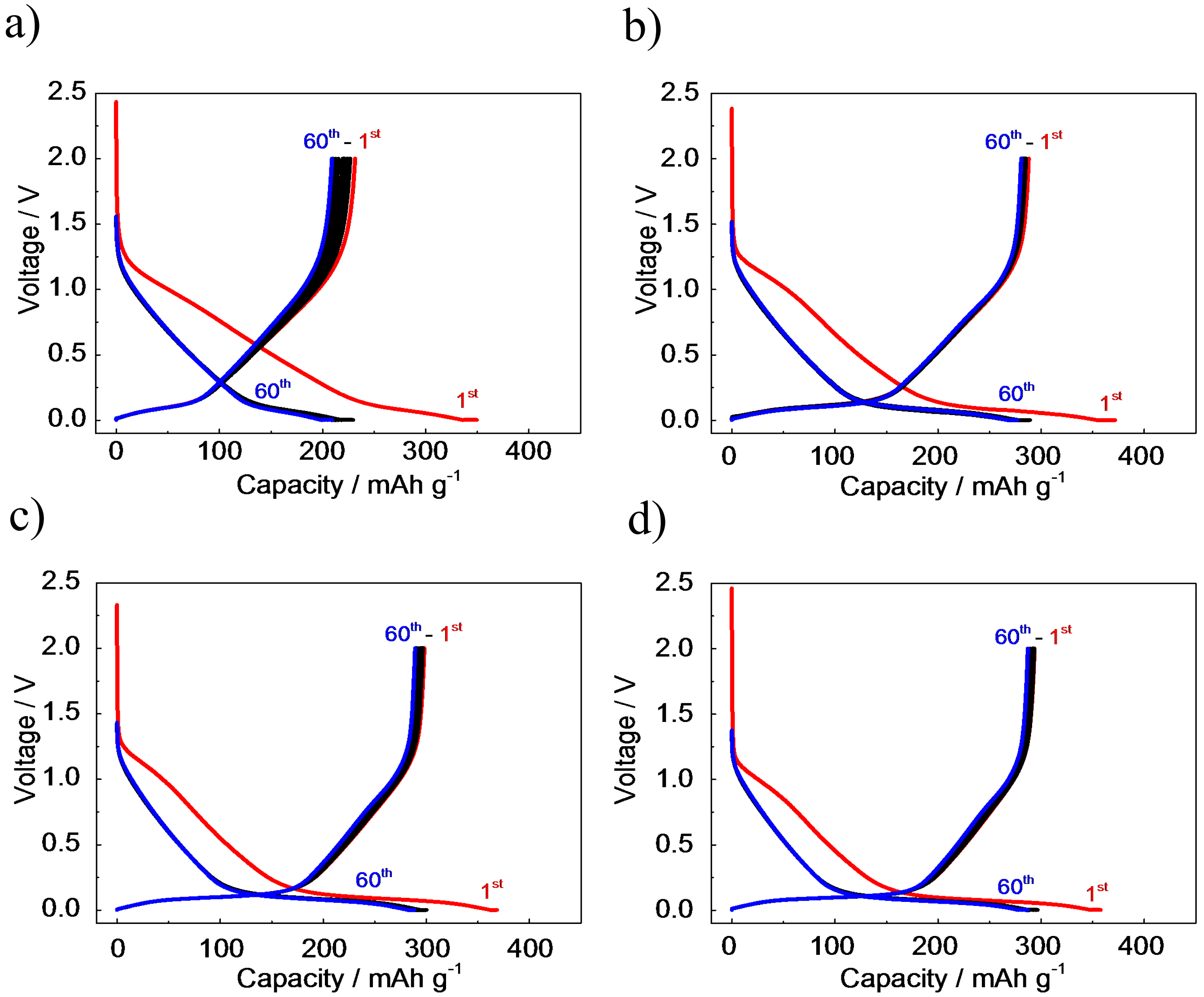

Figure S12: Charge/discharge curves of a) Argan-800, b) Argan-1000, c) Argan-1200, and d) Argan-1300 electrodes with PANa binder cycled between 2.0 and 0.0 V at a rate of 25 mA g^{-1} in 1.0 mol dm^{-3} NaPF$_6$ EC:DEC solution.

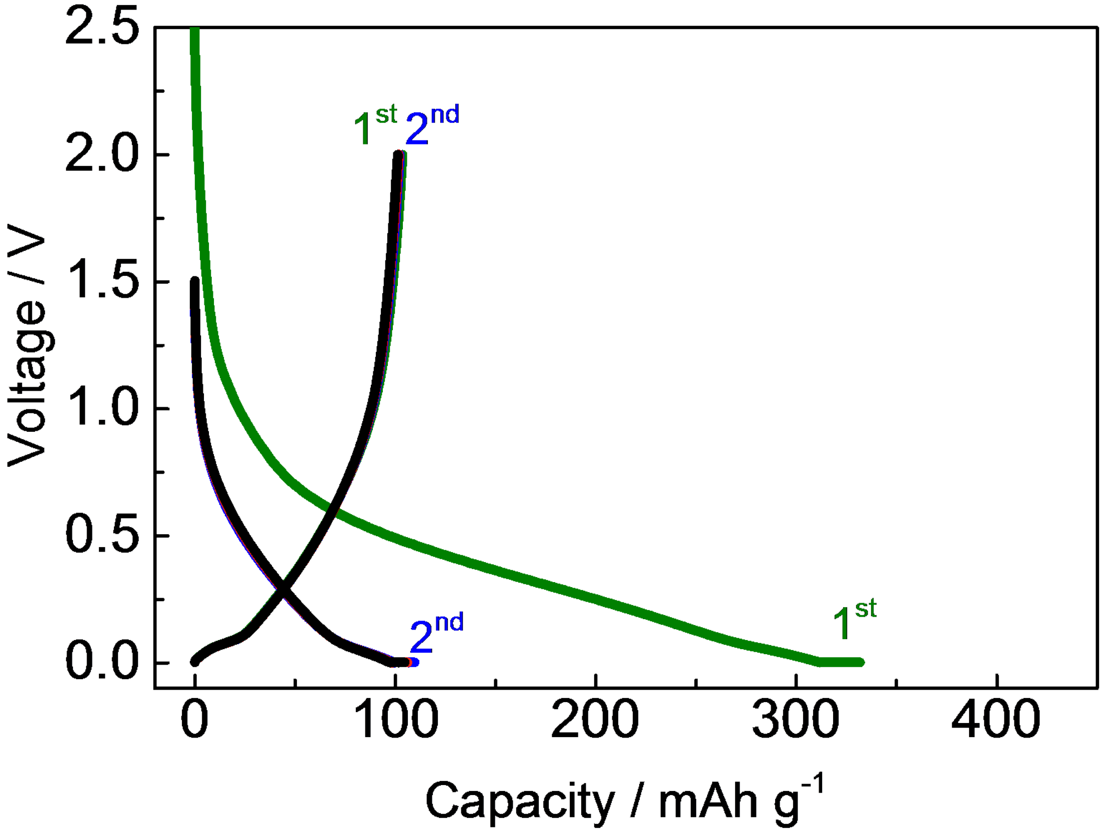

Figure S13: Charge/discharge profiles of Argan-1300W electrode pretreated by HCl without drying in vacuum at 110 °C, cycled between 2 and 0 V in PANa binder at a rate of 25 mA g^{-1} in 1.0 mol dm^{-3} $NaPF_6$/EC/DEC.

Table S2: Electrochemical performances of hard carbon electrodes synthesized by pyrolysis of argan shell, cellulose and lignin at 800 ^{O}C .

Sample	1st sodiation capacity / mAh g^{-1}	1st desodiation capacity / mAh g^{-1}	1st Coulombic efficiency / %
Argan-800	350	232	66.2
Argan-800W	372	286	76.9
Cellulose-800	357	197	55.2
Cellulose-800dry	344	267	77.6
Cellulose-800W	361	285	78.9
Lignin-800dry	247	158	64.0
Lignin--800W	378	285	75.4

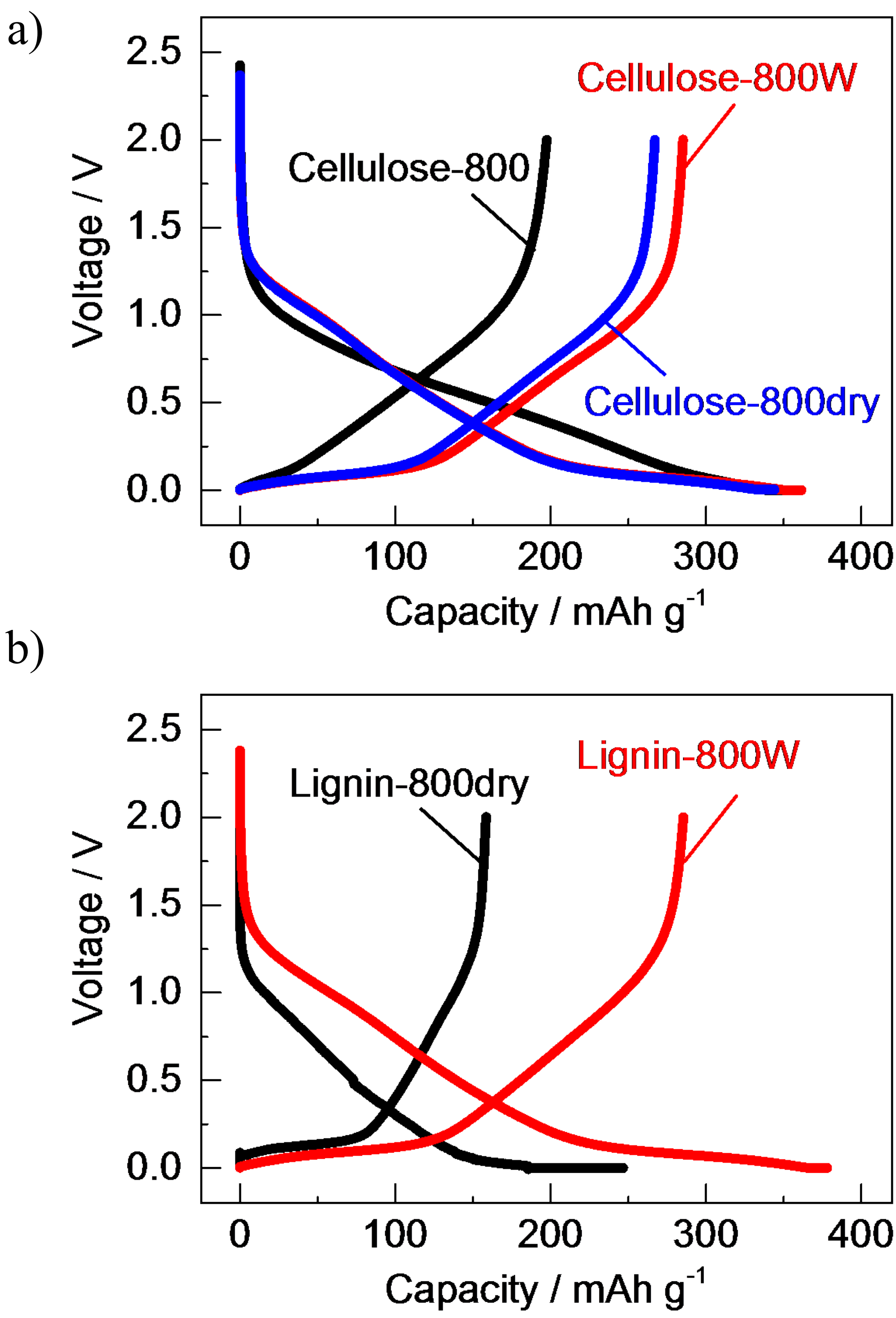

Figure S14: First charge/discharge profiles of a) Cellulose-800, Cellulose-800dry, and Cellulose-800W, b) Lingin-800, and Lignin-800W electrodes cycled between 2 and 0 V at a rate of 25 mA g^{-1} in 1.0 mol dm^{-3} $NaPF_6$ EC:DEC.

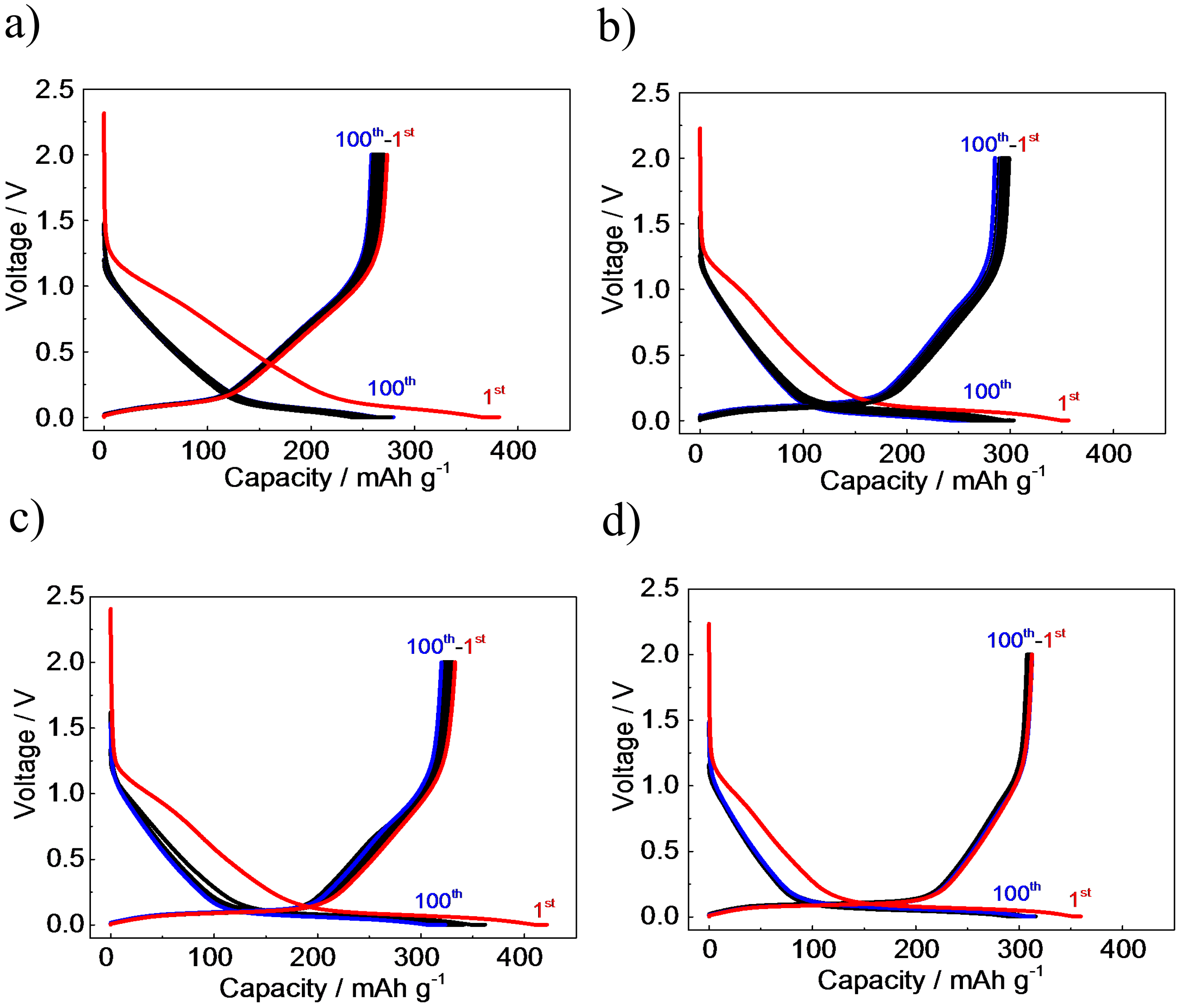

Figure S15: Charge/discharge curves of a) Argan-800W, b) Argan-1000W, c) Argan-1200W, and d) Argan-1300W electrodes with PANa binder cycled between 2.0 and 0.0 V at a rate of 25 mA g^{-1} in 1.0 mol dm^{-3} NaPF$_6$ EC:DEC solution.

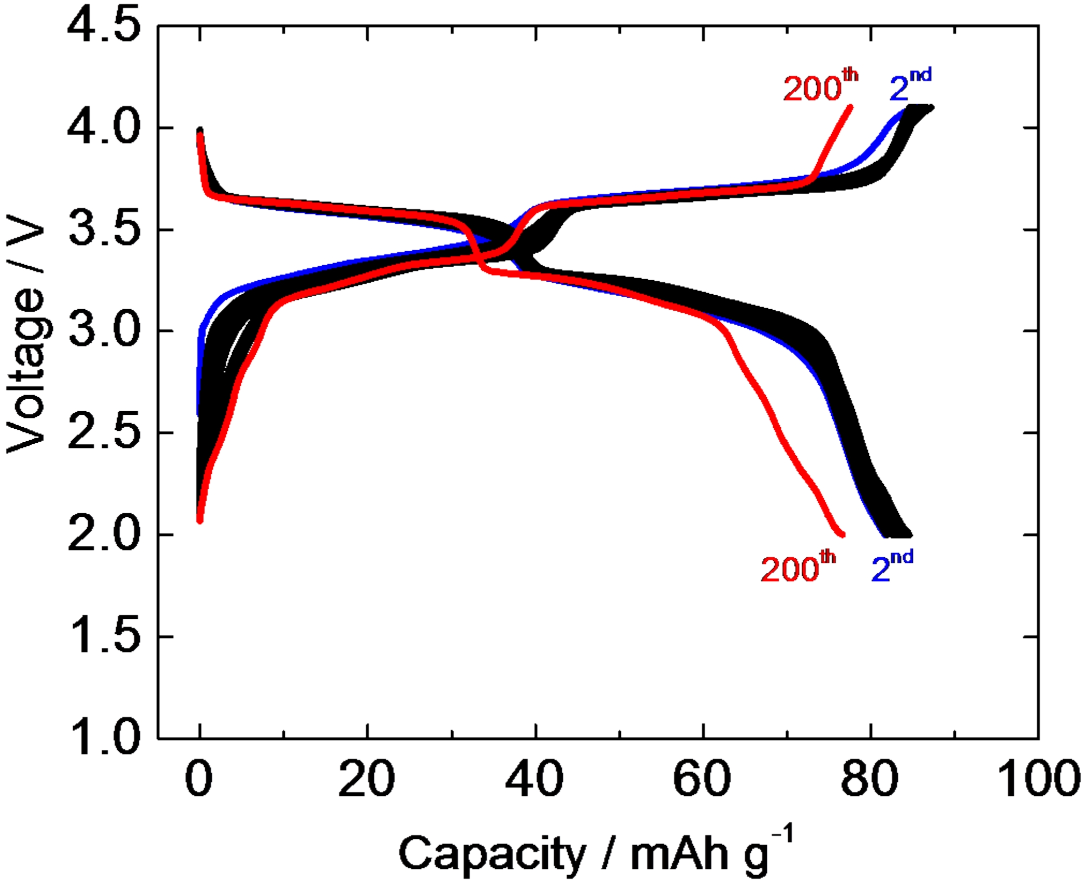

Figure S16: Galvanostatic charge/discharge curves of $Na/Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ in Na cell at 25 mA g^{-1} in 1.0 mol dm^{-3} $NaPF_6$/EC/DEC.