Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Tailored metallacarboranes as mediators for boosting the stability of carbon-based aqueous supercapacitors

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Electronic Supplementary Information

Experimental

Materials

A commercial activated carbon (YP50F, Kuraray Chemical, Japan, labelled as Y) has been used as the active phase of the electrodes employed in the electrochemical characterization and construction of the supercapacitors. Carbon electrodes have been prepared by physical mixing of Y carbon with acetylene black followed by the addition of a certain volume of a 0.6% wt. polytetrafluoroethylene (PTFE) solution (prepared from a 60% PTFE solution, Sigma-Aldrich) in a weight percent ratio of 90:5:5.

Na[COSANE],[1] Na[Cl_2-COSANE],[2] Na[Cl_6-COSANE][3] were prepared following reported procedures for the synthesis of their Cs salts, and later converted into the sodium salts[4],[5]. Na[Cl_4-COSANE] were synthesized as follow:

To a solution of 50 mg of Cs[COSANE] in 2 mL of acetonitrile in a 10 mL round bottomed flask was slowly added SO_2Cl_2 (1 mL) drop by drop. The mixture was stirred 40 minutes at room temperature. Then, volatiles were removed in the rotavapor and the resulting syrup was extracted with diethyl ether (15 mL) and 1 M aqueous HCl (15 mL) to remove all the impurities. The washing process was done two more times with 1 M aqueous HCl (2 x 15 mL) and then the organic layer was dried over $MgSO_4$. After filtration, the liquid was evaporated and dissolved in the minimum volume of water. An aqueous solution containing an excess of $[N(CH_3)_4]Cl$ was added, resulting in the formation of an orange precipitate. This $[N(CH_3)_4]$[Cl_4-COSANE] was filtered off and washed several times with water. The sodium salt of $[Cl_4\text{-COSANE}]^-$ species was obtained by means of cationic exchange resin.[5]

Characterization of Na[Cl_4-COSANE]: ATR-FTIR (cm^{-1}):ν 3576 (brd, O-H), 3053 (wk, C_c-H), 2586, 2545 (shp, B-H), 1615 (shp, H_2O). MALDI-TOF-MS: m/z calcd for $[Cl_4\text{-COSANE}]^-$: 461; m/z found (%): 427.13 $[Cl_3\text{-COSANE, 1.70\%}]^-$, 461.09 $[Cl_4\text{-COSANE, 84.31\%}]^-$ and 496.06 $[Cl_5\text{-COSANE, 13.99\%}]^-$. $^1H\{^{11}B\}$ NMR (300.13 MHz, CD_3OCD_3): δ 4.33 (br s, 4H, C_c-H), 3.47, 3.21, 3.13, 2.33, 2.24, 1.74, 1.31 (br s, 14H, B-H). ^{11}B NMR (96.29 MHz, CD_3OCD_3): δ = 13.16, 5.50, 2.33, 0.05, -1.97, -3.28, -5.30, -14.34, -16.67, -18.36, -19.48. $^{13}C\{^1H\}$ NMR (75.74 MHz, CD_3OCD_3): δ = 52.00 (C_c-H), 50.15 (C_c-H).

Physicochemical characterization of the activated carbon and their mixtures with Na[Cl_4-COSANE]

The textural properties of Y carbon with and without adsorbed Na[Cl_4-COSANE] were assessed by physical adsorption of N_2 at −196 °C, using an automatic adsorption system (Autosorb-6, Quantachrome). Prior to measurements, the samples were degassed at 150 °C for 8 h. Temperature programmed desorption (TPD) experiments were carried out in a DSC-TGA equipment (TA Instruments, SDT Q600) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3). The thermobalance was purged for 2 h under a helium flow rate of 100 ml min^{-1} and then heated up to 950 ºC (heating rate 20 ºC min^{-1}). X-ray powder diffraction patterns of Na[Cl_4-COSANE] and Y carbon before and after saturation with Na[Cl_4-COSANE] were measured in a Miniflex II Rigaku diffractometer using CuKα radiation ($\lambda = 1.5406$ Å) in a 2θ region between 3° and 100°. The X-ray generator was set to 30 kV at 15 mA.

Adsorption of Na[Cl_4-COSANE]

Solutions of Na[Cl_4-COSANE] were prepared with distilled water at different concentrations ranging from 10^{-4} to $2 \cdot 10^{-3}$ M. For the equilibrium tests, samples of 10 mL of the solution and 10.0 mg of dry activated carbon were put inside glass flasks and contacted in an orbital incubator (X, model Y) at 15.0, 25.0 ºC and 35.0 ºC and 200 rpm equivalent stirring rate for 36 hours. The adsorbate concentrations were determined by UV spectroscopy (λmax: 319nm, concentration at 1.0 absorbance: $3.1 \cdot 10^{-6}$ M detection limit: $5 \cdot 10^{-8}$ M) with an UV-Visible (JASCO, Model V-670) spectrophotometer. The adsorption capacities at equilibrium were determined by measuring the equilibrium concentration of Na[Cl_4-COSANE] on the solution after the adsorption experiments. The determination of the adsorption isotherm at 25 ºC allowed to adsorb different Na[Cl_4-COSANE] loadings on Y carbon electrodes employing 10^{-4} M solutions and a certain volume, which was selected for achieving intended loadings of 0.05, 0.15, 0.45 and 1.00 mmol g^{-1}. The resulting Na[Cl_4-COSANE]-loaded activated carbons and electrodes has been named Y-XXX, where XXX is a number between 000 (no Na[Cl_4-COSANE] loading) and 100 (1.00 mmol of Na[Cl_4-COSANE] per gram of activated carbon). In order to favour the wetting of the electrodes (which takes more time than in powdered activated carbon due to the presence of PTFE in their formulation), the Na[Cl_4-COSANE] loading experiments were preceded by a vacuum treatment (1 Torr, 1 hour) of the electrodes while submerged in the solution, followed by the adsorption procedure previously mentioned.

Electrochemical characterization

The electrochemical behavior of Y-000 and Y-100 electrodes (with a loading of active phase of ca. 7 mg/cm^2 and both of them attached to a titanium mesh) have been analyzed by cyclic voltammetry in Na_2SO_4 0.5 M using a conventional three electrode cell, using a coiled platinum wire as counter electrode and a Ag/AgCl/Cl- reference electrode inside a luggin capillary.

In the case of the construction of supercapacitors, carbon electrode sheets were manually spread using a glass bar over a clean and smooth glass surface and cut into a circular shape using two molds of 4 and 14 mm, achieving geometrical areas of 0.126 cm^2 (for Swagelok cells) or 1.54 cm^2 (in the case of coin cells) and electrode weights of ca. 1 and 10 mg (active material), respectively. Afterwards, the electrodes were loaded with different amounts of Na[Cl_4-COSANE] (from 0 to 0.45 mmol g^{-1}) as previously detailed and wetted in Na_2SO_4 0.5 M for 1 day at room temperature. The resulting electrodes have been placed over titanium collectors and inserted in a T-type Swagelok in configuration of three electrode cell for the electrochemical characterization. A wetted nylon membrane (pore size 450 nm) and a counter electrode consisting in a Y-000 with nearly twice the weight of the working electrode, and a Ag/AgCl/Cl$^-$ reference electrode have been employed. The electrochemical characterization consisted in the separate exploration of the positive and negative potential windows by means of cyclic voltammetry (CV), using the open circuit potential as the potential limit in order to avoid the exposition of each electrode to potentials that are would be outside its working range in the supercapacitor cell. Capacitance was assessed from the charge enclosed by the voltammograms. These measurements have been performed in a VSP potentiostat (Bio-logic).

2-electrode Swagelok symmetric cells from Y-000, Y-015 and Y-045 were constructed employing the same materials as negative and positive electrodes and submitted to durability tests of 5000 GCD cycles at 1 A g^{-1} using voltage loadings of U=2.0-2.2 V (SCTS, Arbin instruments). Asymmetric configuration was also studied at similar conditions. Capacitance measurements of the supercapacitors were carried out using galvanostatic charge-discharge (GCD) measurements at 1 A g^{-1}, the capacitance (F g^{-1}) being calculated from the expression $C_g=Q\,\Delta V^{-1}\,w^{-1}$, where Q is the total charge measured during the discharge step (C), ΔV is the voltage (V) and w is the weight of the active phase of the electrodes (g). Energy density (*E,* W h kg^{-1}) is calculated from the discharge step as follows:

$$E = \frac{\int_{0}^{Q} \Delta V \cdot dQ}{3.6 \cdot w}$$

Coin cells consisting in stainless steel cases, spring and collectors were also built for the most relevant materials and submitted to the same durability tests. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Autolab PGSTAT302N potentiostat equipped with a FRA2 module. The voltage was fixed at 0.05 V. A sinusoidal signal was applied with an amplitude of 10 mV r.m.s. The frequency interval was set between 10 kHz and 1 mHz (taking 70 points logarithmically distributed) apparent capacitance was calculated from the imaginary component of impedance, *Z"*, using the next equation:

$$C_g = \frac{1}{2 \cdot \pi \cdot f \cdot Z" \cdot w}$$

In it, *f* stands for the frequency (Hz). The electrodes were recovered after the durability test for post-mortem analyses. Asymmetric cells with optimized weight of electrodes were also constructed in both Swagelok and coin cells.

N_2 adsorption isotherms

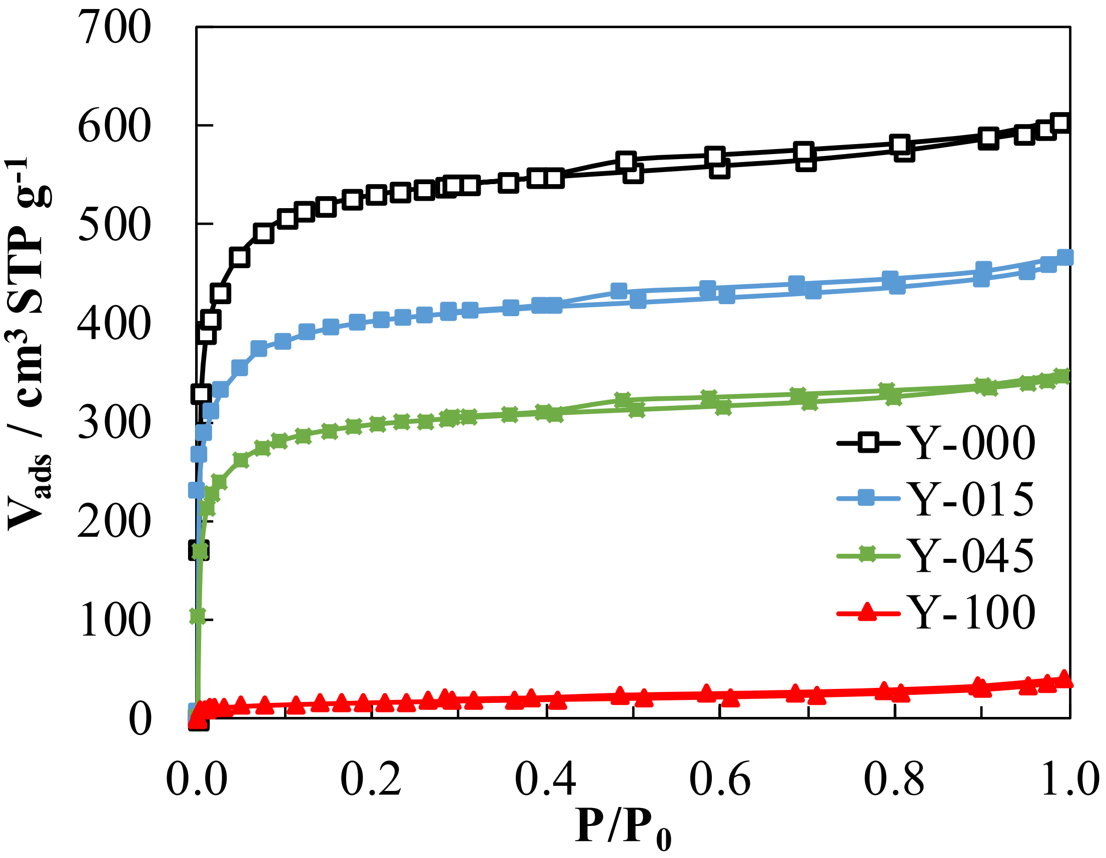

Figure. S1. N_2 adsorption isotherms of Y activated carbon loaded with different amount of Na[Cl_4-COSANE].

TPD profiles

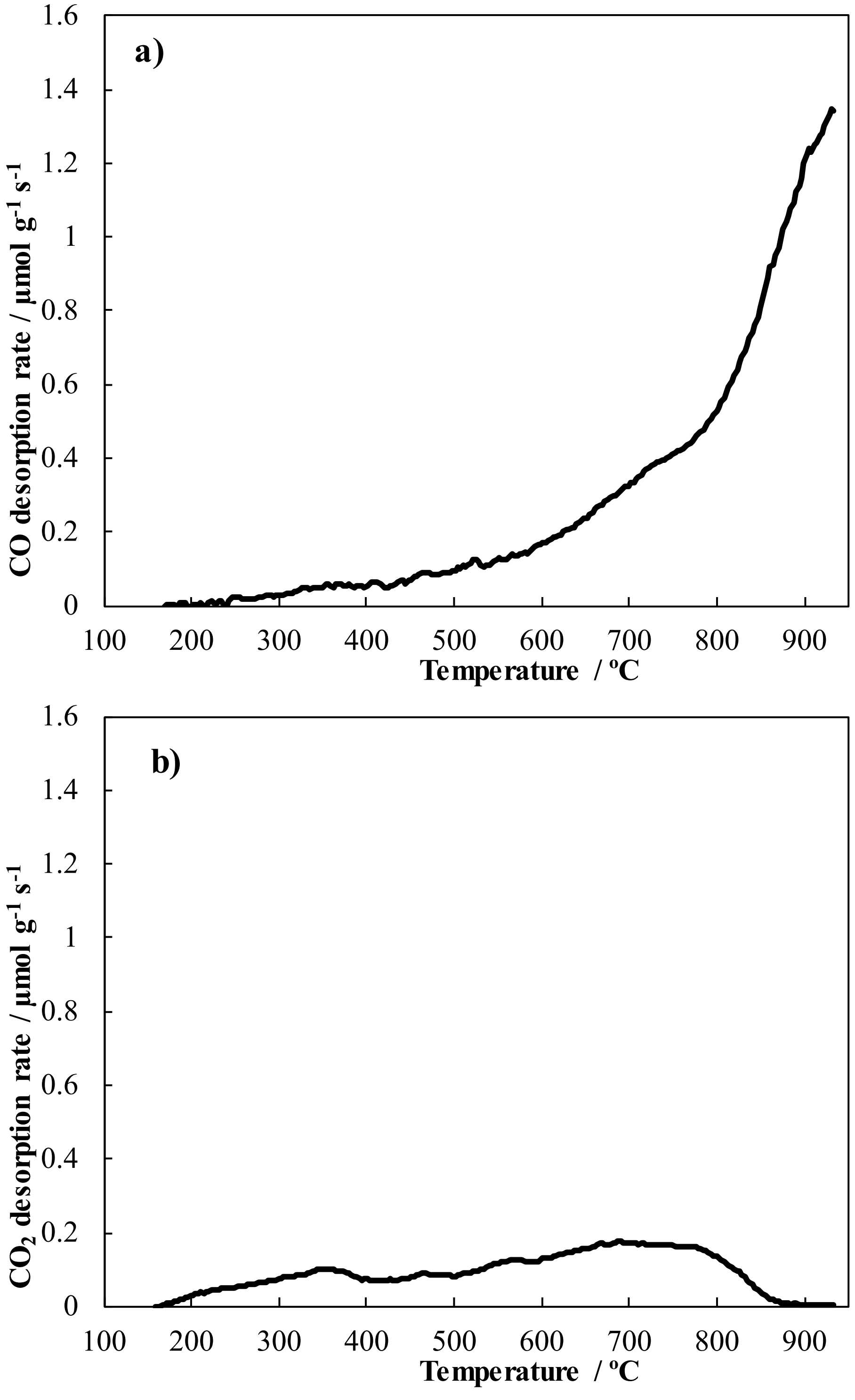

Figure S2. a) CO and b) CO_2 TPD profiles for Y-000 activated carbon.

Na[Cl_4-COSANE] adsorption isotherm in Y-000

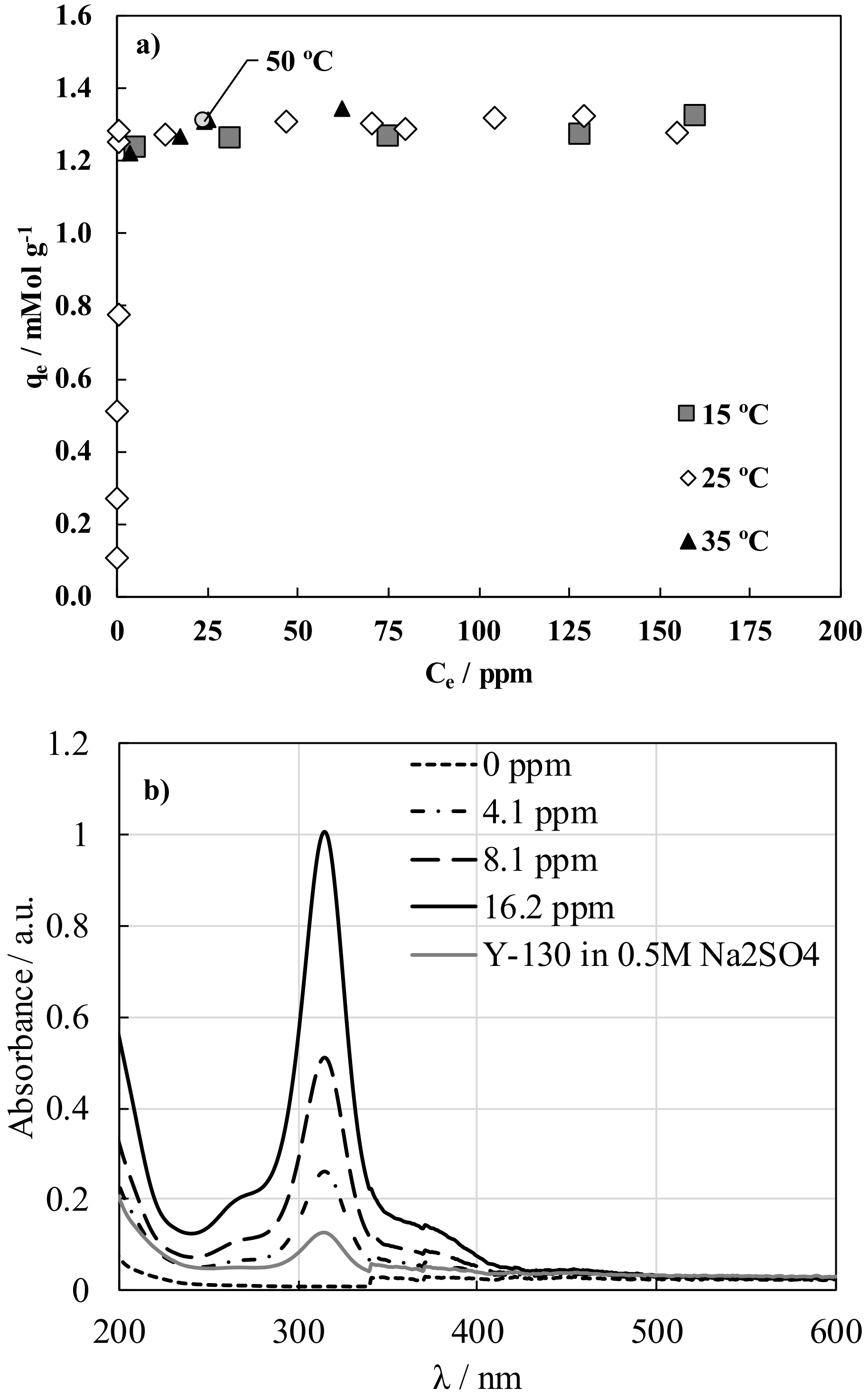

Figure S3. a) Na[Cl_4-COSANE] adsorption isotherms at different temperatures. b) UV-VIS spectra of Na[Cl_4-COSANE] solutions and solution recovered after the desorption experiment

Pore size distribution curves

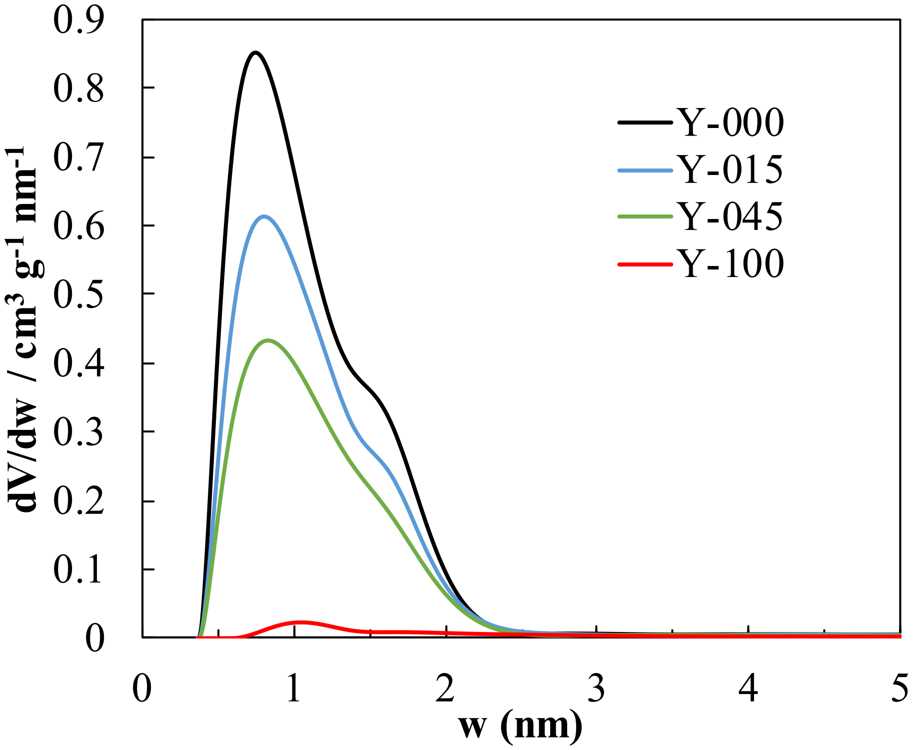

Figure S4. NLDFT Pore size distribution of activated carbons before and after being loaded with Na[Cl_4-COSANE].

X-Ray Diffraction profiles

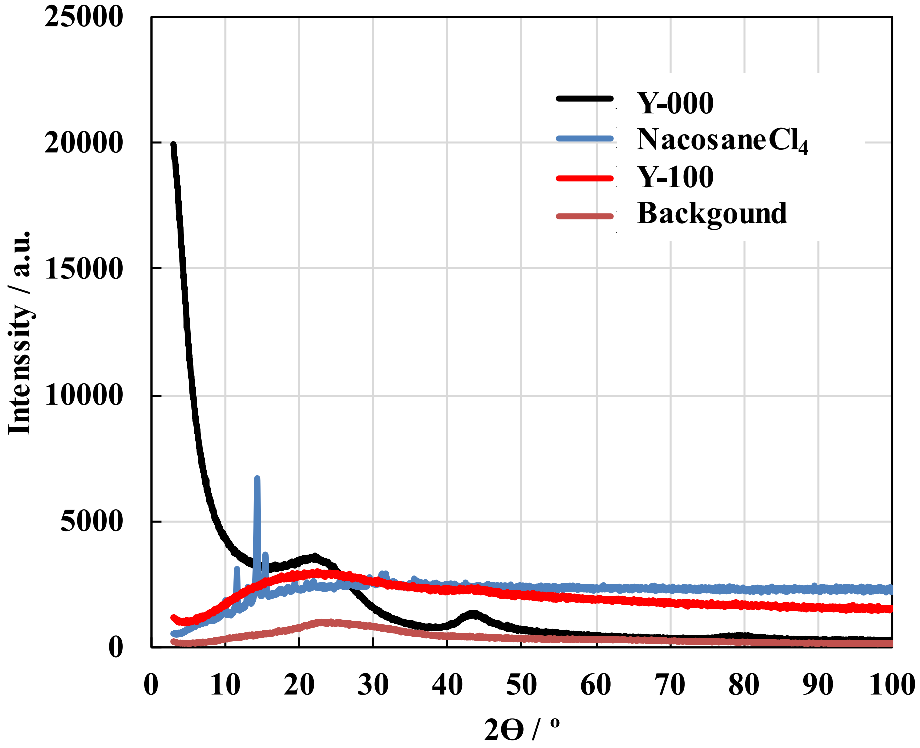

Figure S5. XRD profiles of Na[Cl$_4$-COSANE] and of activated carbon before and after being loaded with Na[Cl$_4$-COSANE].

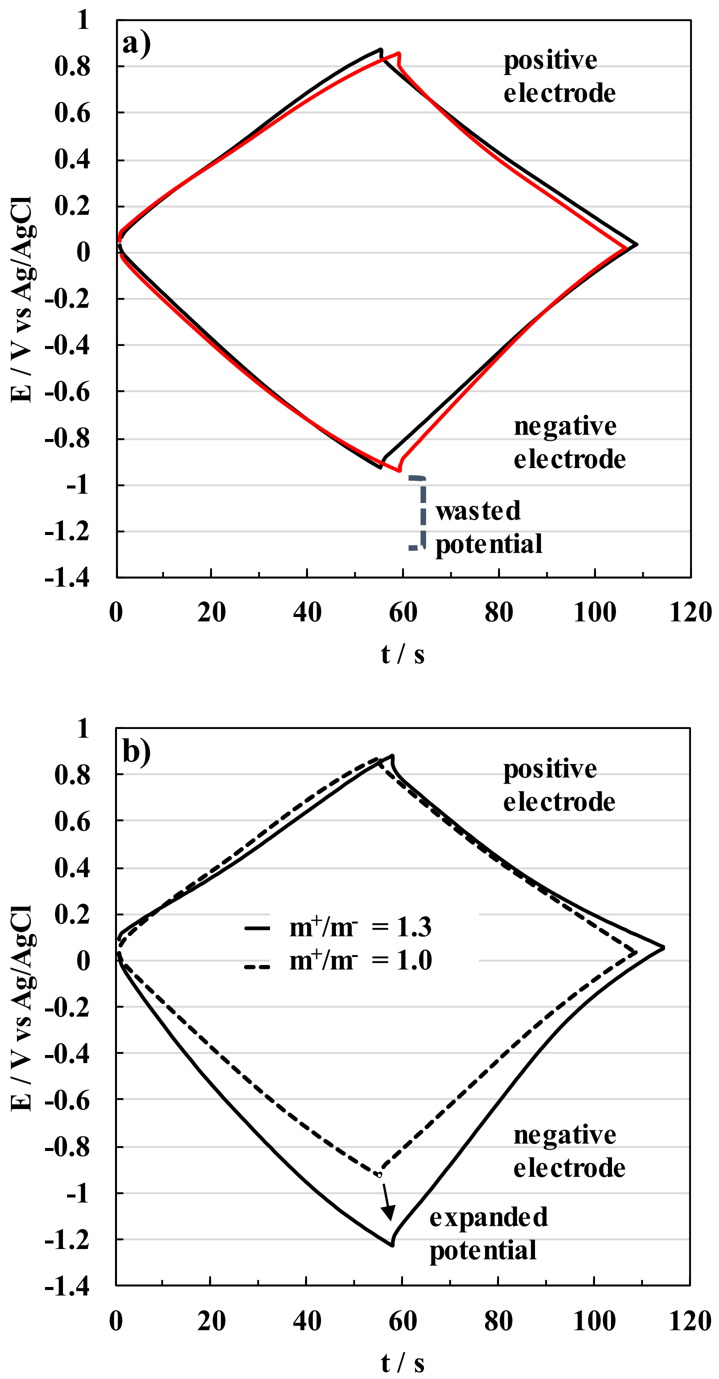

Figure S6. Electrode potentials vs time during a galvanostatic charge-discharge experiment (current density: 1 A g^{-1}) recorded using a T-type Swagelok cell. a) Y-000 (black line) and Y-015 (red line) at 1.8 V; b) Y-000 using two different mass ratios (m^+/m^-) for the positive and negative electrodes

Cyclic Voltammetry of optimized coin cells

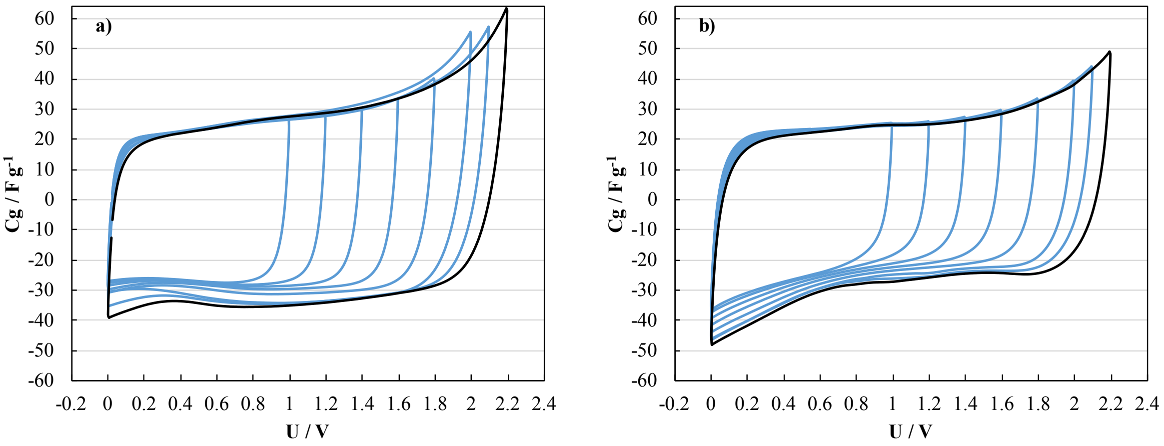

Figure S7. CV response of coin cells constructed with a) Y-000 and b) Y-015 electrodes with optimized mass ratios. Scan rate: 20 mV s^{-1}

Electrochemical Impedance Spectroscopy of optimized coin cells

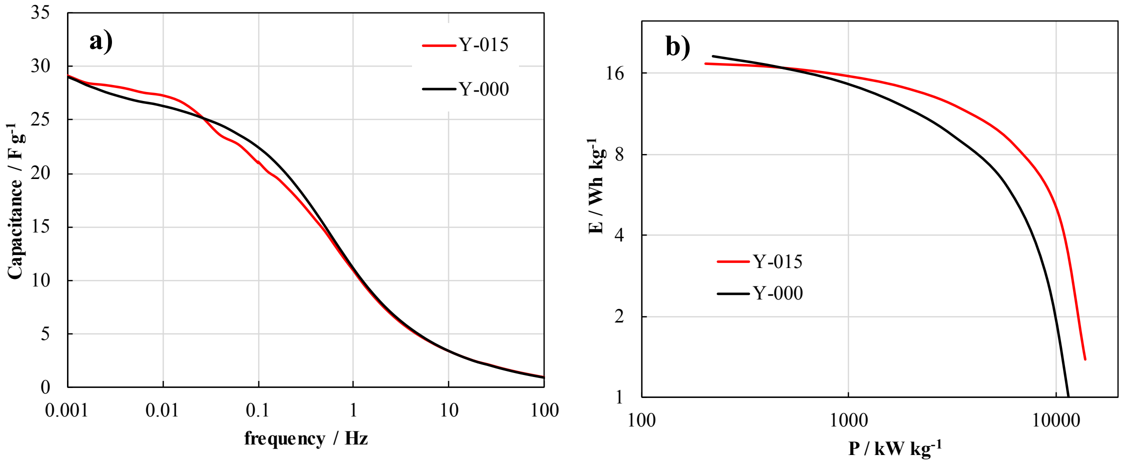

Figure S8. a) Gravimetric capacitance versus frequency for coin cells constructed from Y-000 and Y-015 electrodes with optimized mass ratios. b) Ragone plot at 2.2 V of Y-000 and Y-015 supercapacitors constructed with Swagelok cells with optimized mass ratios.

Coulombic efficiency during durability test

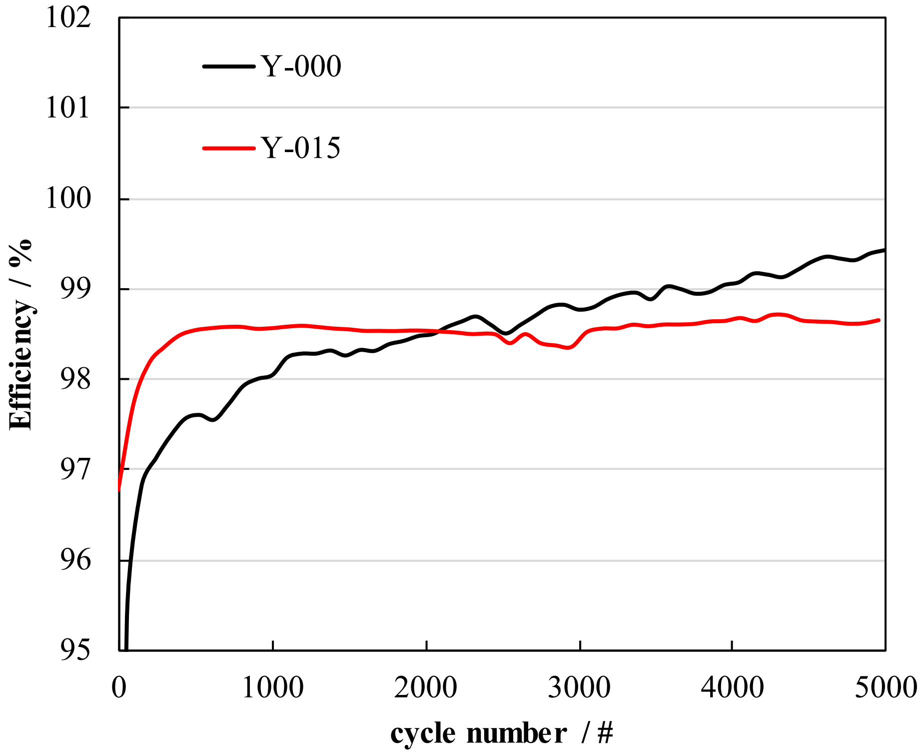

Figure S9. Evolution of efficiency (Q discharge divided by Q charge) during the durability test for Y-000 and Y-015 with optimized mass capacitors.

Cyclability test results of Y-015 and Y-000 supercapacitors at 2.0V

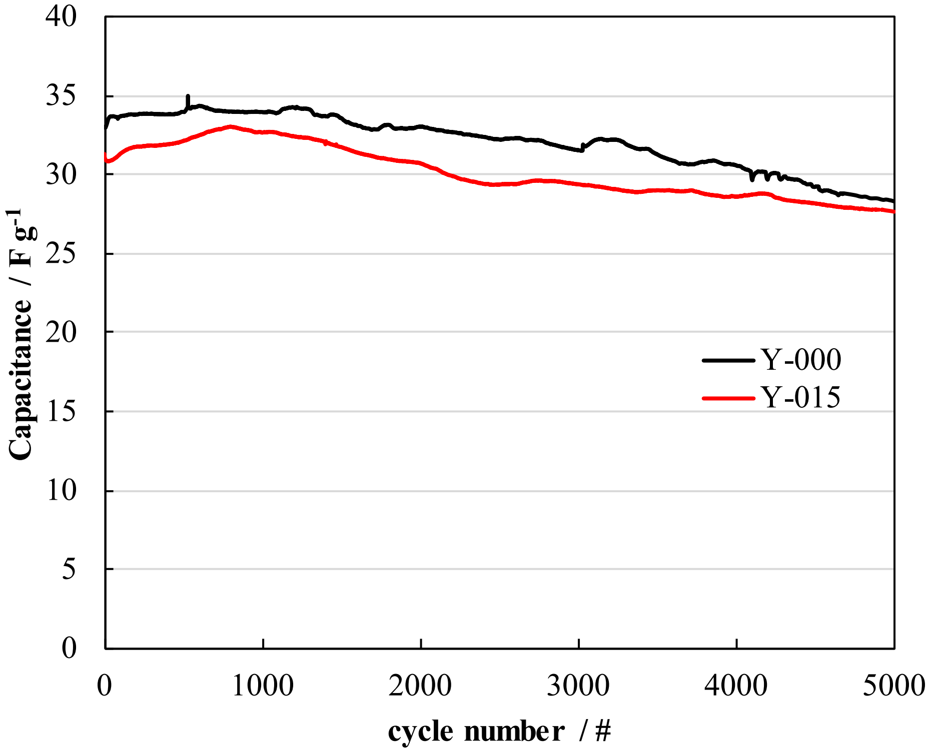

Figure S10. gravimetric capacitance evolution during a cyclability test (j = 1 A g^{-1}, ΔV = 2.0 V) of Y-000 and Y-015 asymmetric in mass supercapacitors

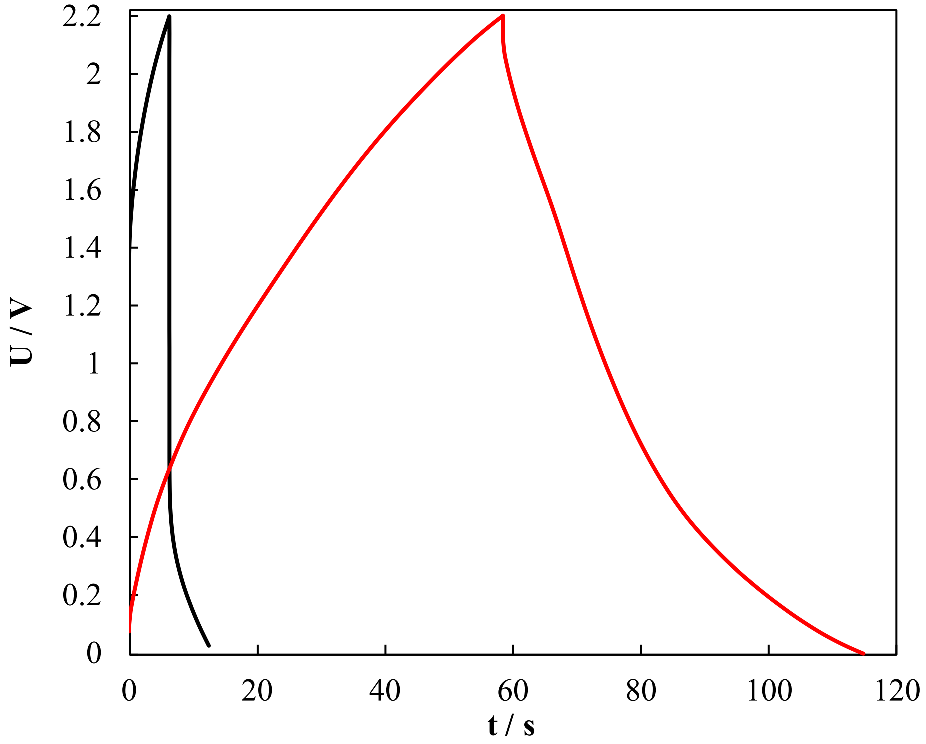

Figure S11. GCD profiles of Y-000 (black line) and Y-015 (red line) after completing the cyclability test and being submitted to 2h of floating test at 2.2V.

TPD analyses after the durability tests

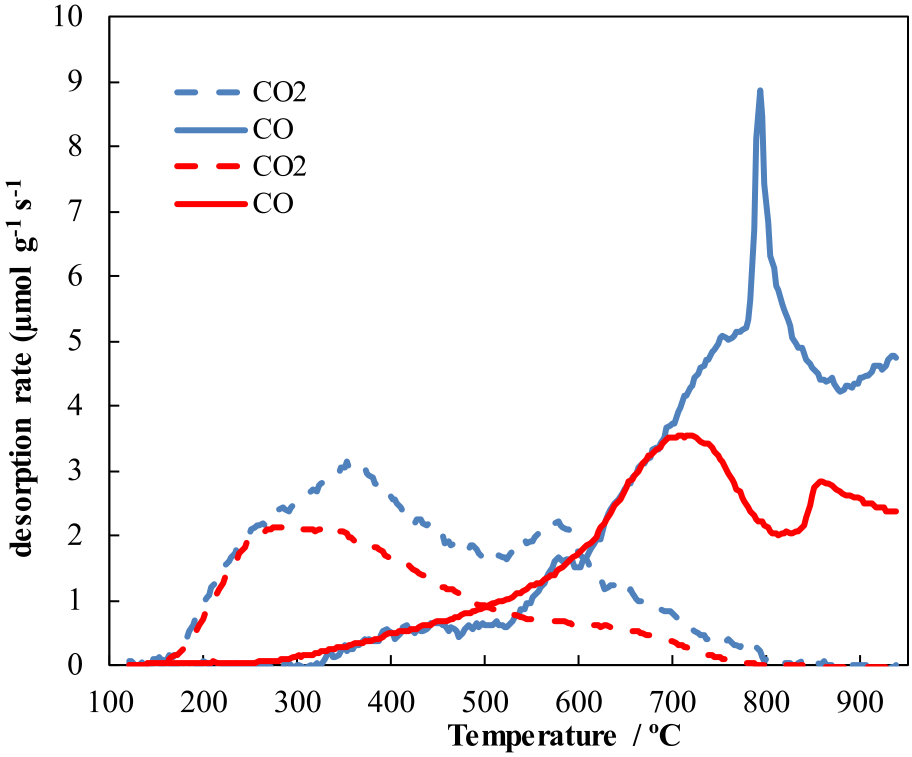

Figure S12. CO and CO_2 TPD profiles for Y-000 (blue lines) and Y-015 (red lines) positive electrodes after the durability test in symmetrical coin cell at 2.2 V.

Effect of Na[Cl4-COSANE] addition in the negative electrode

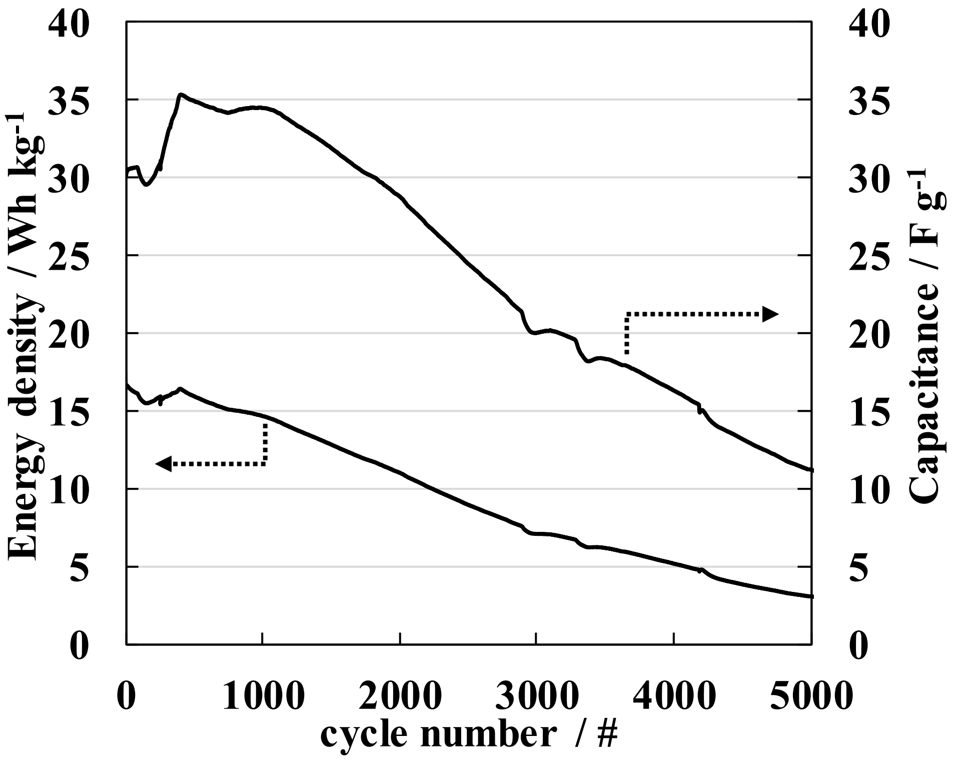

Figure S13. Energy density and gravimetric capacitance evolution during a cyclability test (j = 1 A g^{-1}, ΔV = 2.2 V) performed over a supercapacitor cell constructed using Y-000 as positive electrode and Y-015 as negative electrode

List of references

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