ChemElectroChem

Supporting Information

Sustainable Modification of Chitosan Binder for Capacitive Electrodes Operating in Aqueous Electrolytes

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Supplementary information

Solubility test

To evaluate electrode stability in water we immersed an AC electrode with MA-modified binder in 10 mL of water. After a period of one month, the electrode was still well preserved, without presenting any cracks or material loss, as shown in Figure S1.

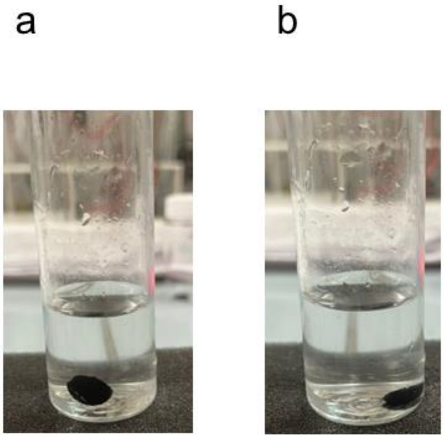

Figure S1. Solubility test: electrode with chitosan modified with maleic anhydride as binder (a) just immersed in water and (b) after one month of immersion in water.

SEM Images

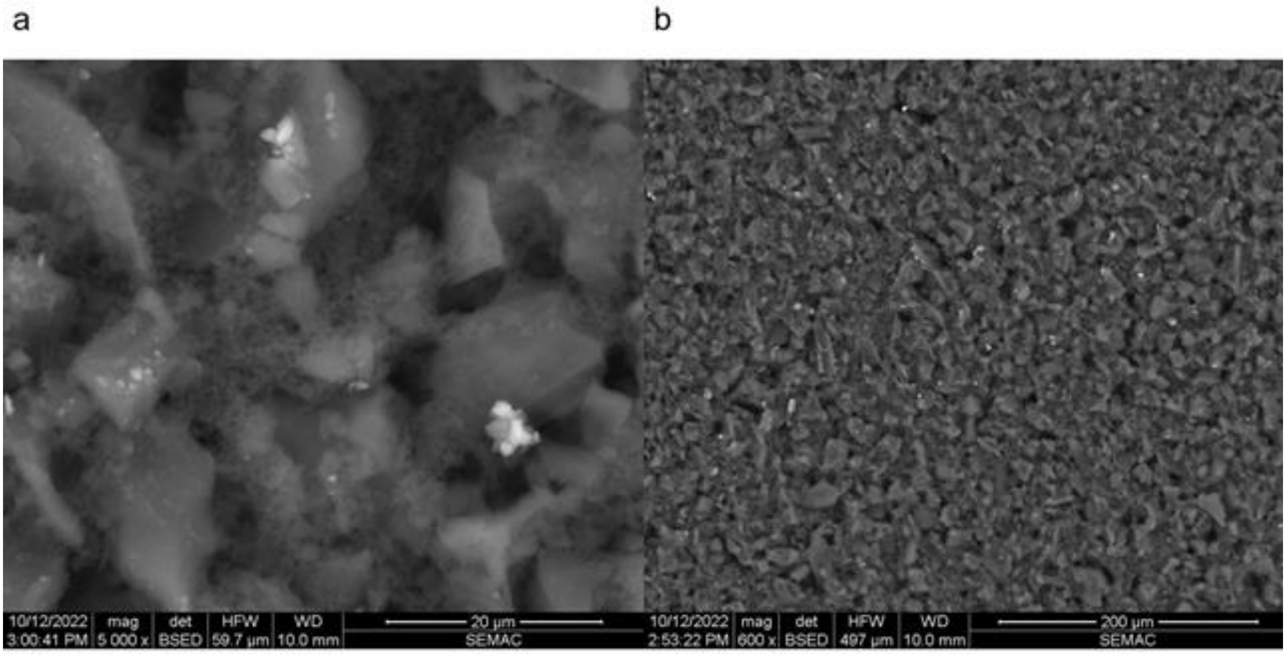

Figure S2. SEM images of pristine electrodes with MA-modified chitosan at different magnifications

Electrochemical Impedance Spectroscopy

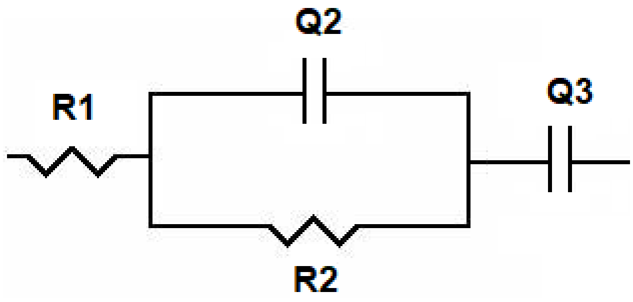

Figure S3. Equivalent circuit for the fitting of the Nyquist plots in Figure 7.

Table S1. Fitting parameters of the equivalent circuit components, and ESR values from EIS and from GCD, of AC electrodes in different electrolytes just after assembling (t_0) and after 50 cycles at 0.5 A g^{-1} (t_1)

	Na_2SO_4 1.5 M	Error (%)	KOH 6M	Error (%)
t_0				
R_1 (Ω)	0.64	4.5	0.32	8.4
R_2 (Ω)	3.8	2.1	7.2	4.1
Q_1 ($\Omega^{-1}\cdot s^{\alpha}$)	$1.1\cdot10^{-5}$	27.5	$2.1\cdot10^{-5}$	34.4
α	0.99	2.6	0.99	3.2
Q_2 ($\Omega^{-1}\cdot s^{\alpha}$)	0.18	4.9	0.10	10.6
α	0.96	3.3	0.82	8.2
ESR_{EIS} (Ω)	4.4	2.0	7.5	3.9
ESR_{GCD} (Ω)	4.5	2.6	7.6	3.8
t_1				
R_1 (Ω)	0.64	3.2	0.31	8.5
R_2 (Ω)	3.7	2.1	5.0	4.4
Q_1 ($\Omega^{-1}\cdot s^{\alpha}$)	$1.0\cdot10^{-5}$	28.8	$2.7\cdot10^{-5}$	38.9
α	0.99	2.6	0.99	3.7
Q_2 ($\Omega^{-1}\cdot s^{\alpha}$)	0.18	4.8	0.099	9.3
α	0.95	3.2	0.80	7.0
ESR_{EIS} (Ω)	4.2	2.1	5.3	2.7
ESR_{GCD} (Ω)	4.2	2.4	5.5	3.2

Conductivity measurements were performed by EIS at 48 kHz using a four poles conductivity probe (CDC861T, Radiometer Analytical) to determine conductivity of Na_2SO_4 1.5 M and KOH 6 M solutions.

Table S2 Measured ionic conductivity of different electrolytes at 30° C

	Na_2SO_4 1.5 M	KOH 6 M
Conductivity ($mS\cdot cm^{-1}$)	114.2	584.4

Figure S4 shows the Nyquist plot of AC electrodes with chitosan crosslinked with EDC (AC EDC). The tests were performed in symmetrical cell, in three electrode modes, in Na_2SO_4 1.5 M, recorded after cell assembly (t_0) and after 50 cycles at 0.5 A g^{-1} (t_1).

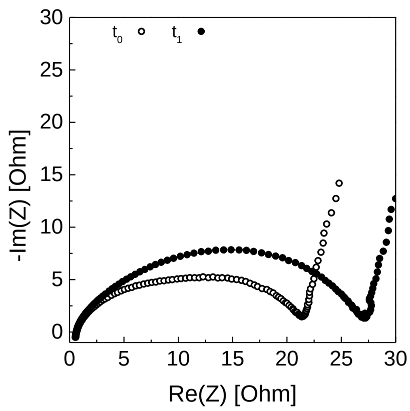

Figure S4. EIS spectra of AC EDC electrodes in Na_2SO_4 1.5 M recorded after cell assembly (t_0, plain circles) and after 50 cycles at 0.5 A g^{-1} (t_1, full circles)

Galvanostatic charge/discharge cycles.

The electrochemical behaviour of AC electrodes with EDC-modified chitosan was evaluated in Na_2SO_4 1.5 M, in three-electrode symmetrical cells with galvanostatic charge and discharge cycles at different current densities.

Initial capacitance values (Figure S5a) were around 75 F g^{-1} at the lowest current density. This value was nearly recovered after high-rate cycle for 200 cycles and maintained stable for over 500 cycles.

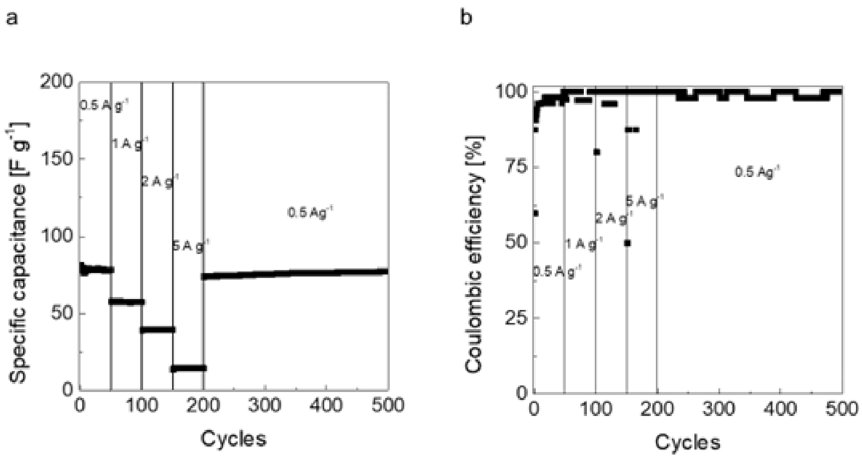

Figure S5. (a) Rate capability at different current densities of AC electrodes with EDC-modified chitosan binder in Na_2SO_4 1.5M and (b) coulombic efficiency values

Specific capacitance values were calculated by using Csp = i Δt/ ΔE m, where i is the applied constant current, Δt the time of discharge, ΔE is the difference between the initial and the final potential (measured vs. a reference electrode) in the discharge process and m is the mass of the active material contained in the electrode. ESR from galvanostatic discharge was evaluated by ½ ΔV/i, where half of the ohmic drop (ΔV) during the discharge process was divided by the current i.

Table S3. Capacitance values with relative errors at different specific currents of AC electrodes with MA- modified chitosan in Na_2SO_4 1.5 M (MA Na_2SO_4) and in KOH 6 M (MA KOH) compared with the AC electrode with PVdF binder in Na_2SO_4 1.5 M (PVdF Na_2SO_4).

	0.5 A g^{-1}	1 A g^{-1}	2 A g^{-1}	5 A g^{-1}
MA Na_2SO_4	141 ± 9	122 ± 4	95 ± 5	69 ± 3
MA KOH	106 ± 8	82 ± 5	59 ± 3	40 ± 2
PVdF Na_2SO_4	113 ± 4	94 ± 3	71 ± 4	29 ± 3

Electrode recycling

Immediately after immersion in the 1% vol. solution of acetic acid, the AC electrode with MA-modified chitosan as binder swelled. After sonication treatment, the electrode shattered into a powder suspension.

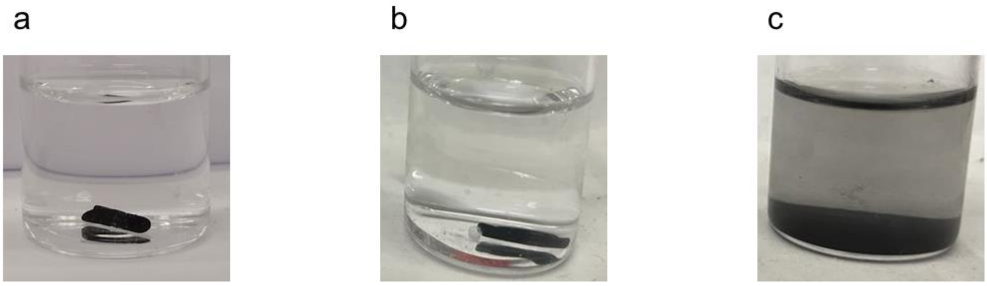

Figure S6. Different steps of recycling of AC electrodes with MA-modified chitosan binder: (a) immersion in 1% vol. solution of acetic acid, (b) after 16 hours and (C) after sonication.