Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

Genipin-crosslinked chitosan hydrogel as a quasi-solid-state electrolyte for sustainable electrochemical capacitors

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Chemicals

Medium-molecular-weight chitosan (CS) powder from crab shells was purchased from Sigma-Aldrich (Burlington, USA) and dried before use (105 °C for 72 h). Its degree of deacetylation was 83 ± 3 %, and its viscosity was 3.6 cP in a 2 wt % solution of 1 % acetic acid (25 °C). Acetic acid (≥ 99.5 %) and anhydrous lithium sulfate (Li_2SO_4) (≥ 98.5 %) were also provided by Sigma-Aldrich (Burlington, USA) and used as received. Genipin (GEN) powder (≥ 98.0 %) and glutaraldehyde (GA) aqueous solution (25 wt %) purchased from Sigma-Aldrich (Burlington, USA) were used for crosslinking. Redistilled water was used to prepare all aqueous solutions.

Characterization techniques

Attenuated total reflectance Fourier transform infrared spectroscopy. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed to qualitatively characterize the CS/GEN membrane. The presence of characteristic for crosslinked chitosan functional groups in obtained materials was analyzed using a Vertex 70 Series FTIR spectrometer (Bruker, Billerica, USA). All spectra were recorded using a wave number range of 4000 – 500 cm^{-1} (resolution of 1 cm^{-1}). Before examination, the samples were dried to a constant mass at 37 °C.

Scanning Electron Microscopy. The surface morphology and cross-section of the CS/GEN membrane were analyzed using scanning electron microscopy (SEM) images captured with a scanning electron microscope (S-3400N, Hitachi, Tokyo, Japan). Prior to scanning, the samples were sputter-coated with graphite before examination.

Atomic Force Microscopy. The topography and nanomechanical properties of the dry CS/GEN membrane were determined using atomic force microscopy (AFM). The three-dimensional images of the sample surface were recorded with an NX10 microscope (Park Systems, Suwon, Korea). The examined surface area was 20×20 μm, scanned with 512 lines

per image and an NCM mode scan speed set at approximately 0.3–0.4 Hz. The dry membranes' nanomechanical properties (adhesion force, energy dissipation, and Young's modulus) were examined in PINPOINT™ mode. All measurements were performed at 23 °C, and the resulting data were analyzed using the open-source Gwyddion software and XEI (Park Systems, Suwon, Korea) AFM analysis programs.

Contact Angle Measurements. The wettability and surface free energy (SFE) of the CS/GEN membrane in a dry state were evaluated by static contact angle measurements, with ethylene glycol and diiodomethane as the polar and dispersion components, respectively. Measurements were made using a sessile drop technique at 25 °C with a DSA10 0E drop shape analyzer (KRÜSS, Hamburg, Germany). The surface free energy was calculated using the Owens-Wendt-Rabel-Kaelble model.

Contact angle measurements and the surface free energy analysis

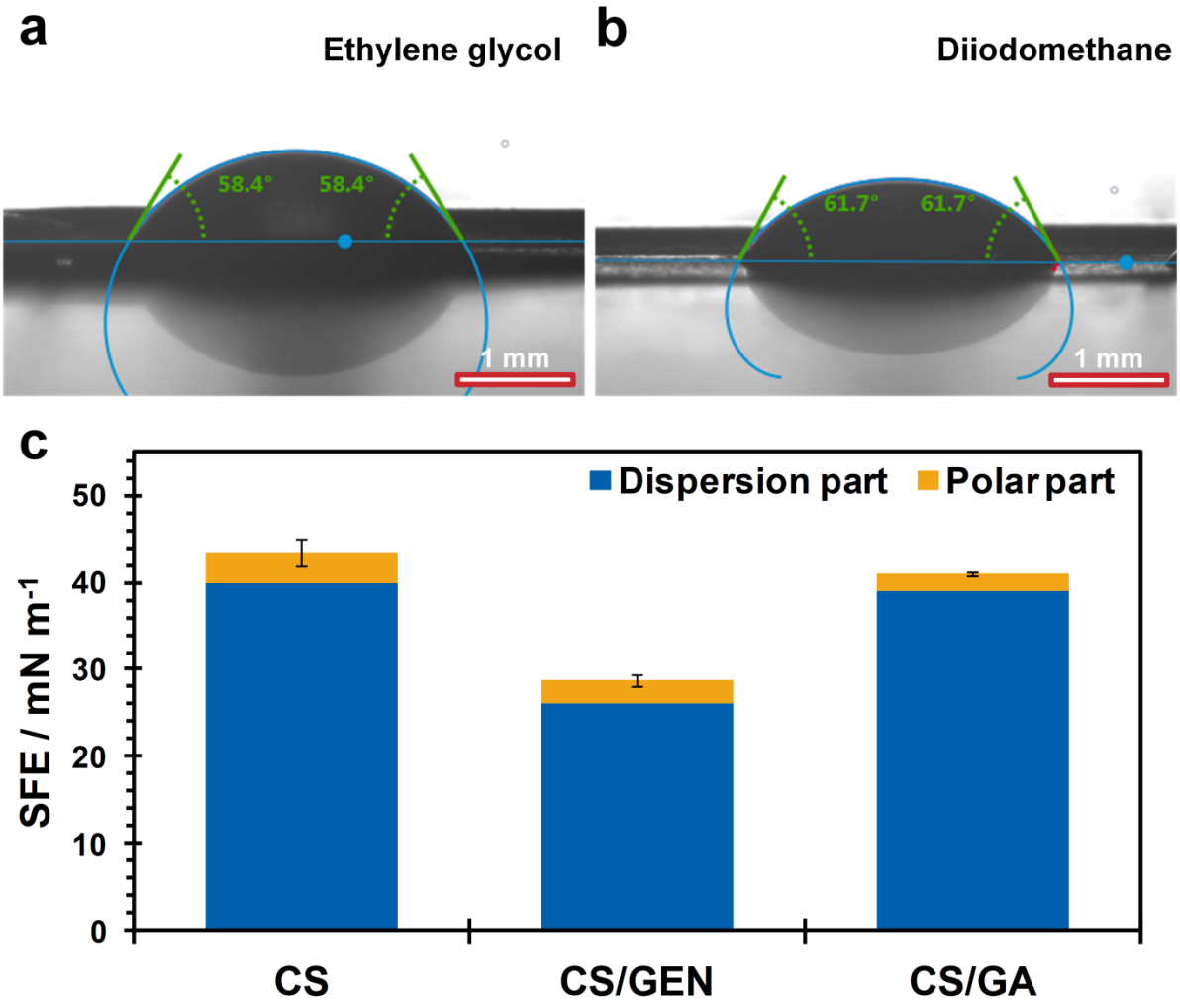

Fig. S1 Estimated equilibrium contact angles for CS/GEN membrane with (a) ethylene glycol and (b) diiodomethane as a drop liquid. (c) Surface free energy (SFE) of the investigated chitosan-based membranes.

EDLC electrochemical performance

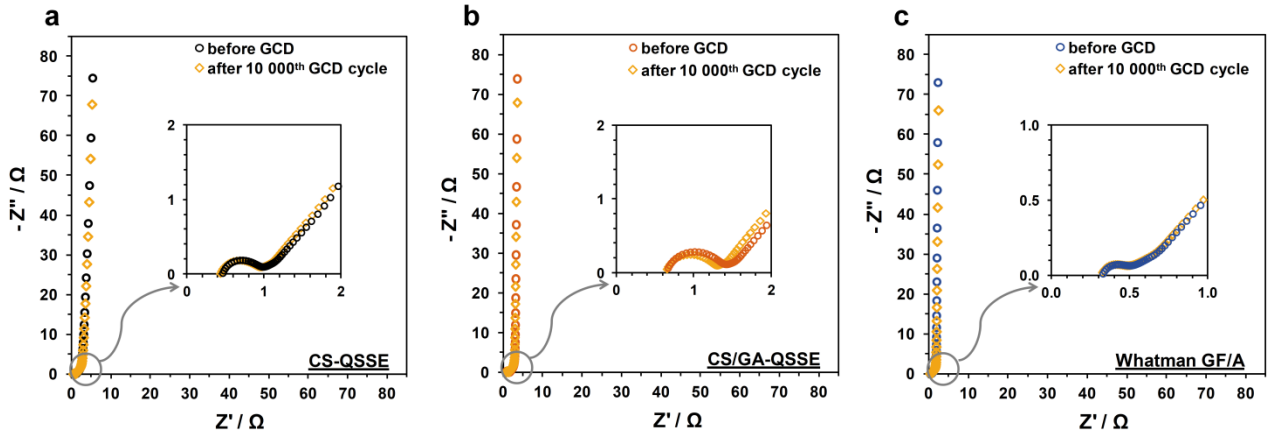

Fig. S2 AC impedance spectra for capacitors with: (a) CS-QSSE, (b) CS/GA-QSSE, and (c) Whatman GF/A glass fiber separator.

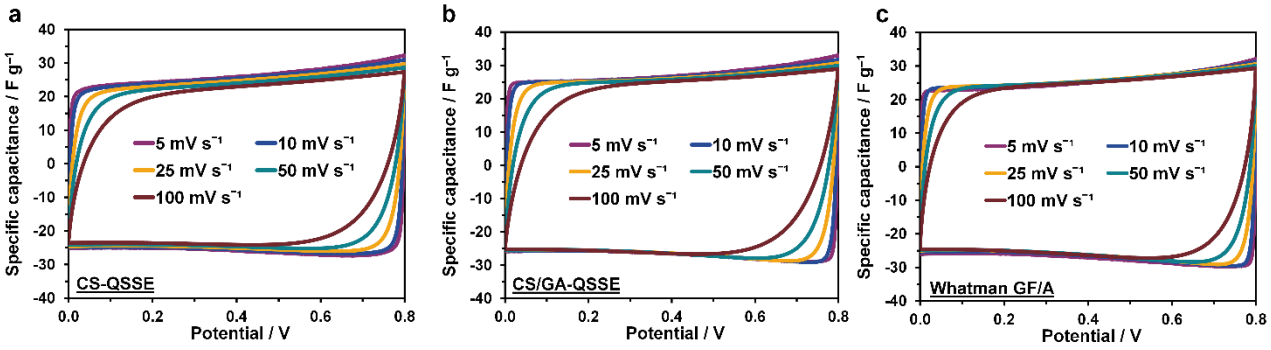

Fig. S3 CV curves (at sweep rate 5 – 100 mV s^{-1}) for EDLCs with (a) CS-QSSE, (b) CS/GA-QSSE, and (c) Whatman GF/A glass fiber separator.

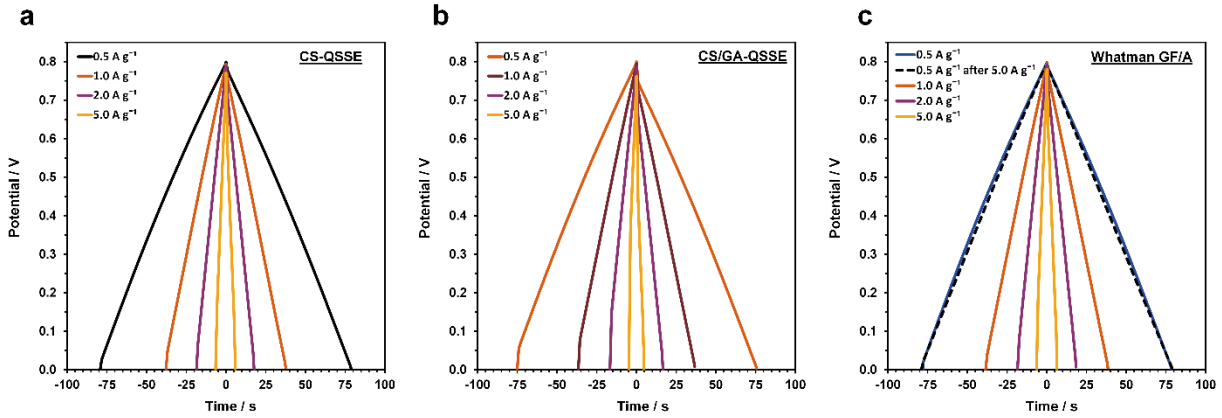

Fig. S4 Galvanostatic charge/discharge curves at the different current densities for EDLCs with (a) CS-QSSE, (b) CS/GA-QSSE, and (c) Whatman GF/A glass fiber separator.

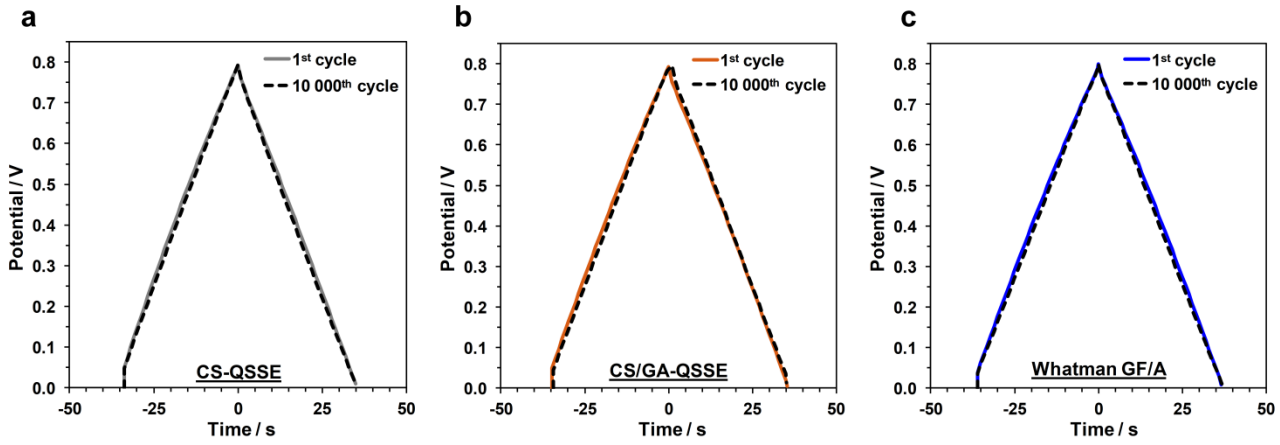

Fig. S5 Galvanostatic charge/discharge curves at the 1st and 10,000th cycle (at 1 A g^{-1}) for EDLCs with (a) CS-QSSE, (b) CS/GA-QSSE, and (c) Whatman GF/A glass fiber separator.

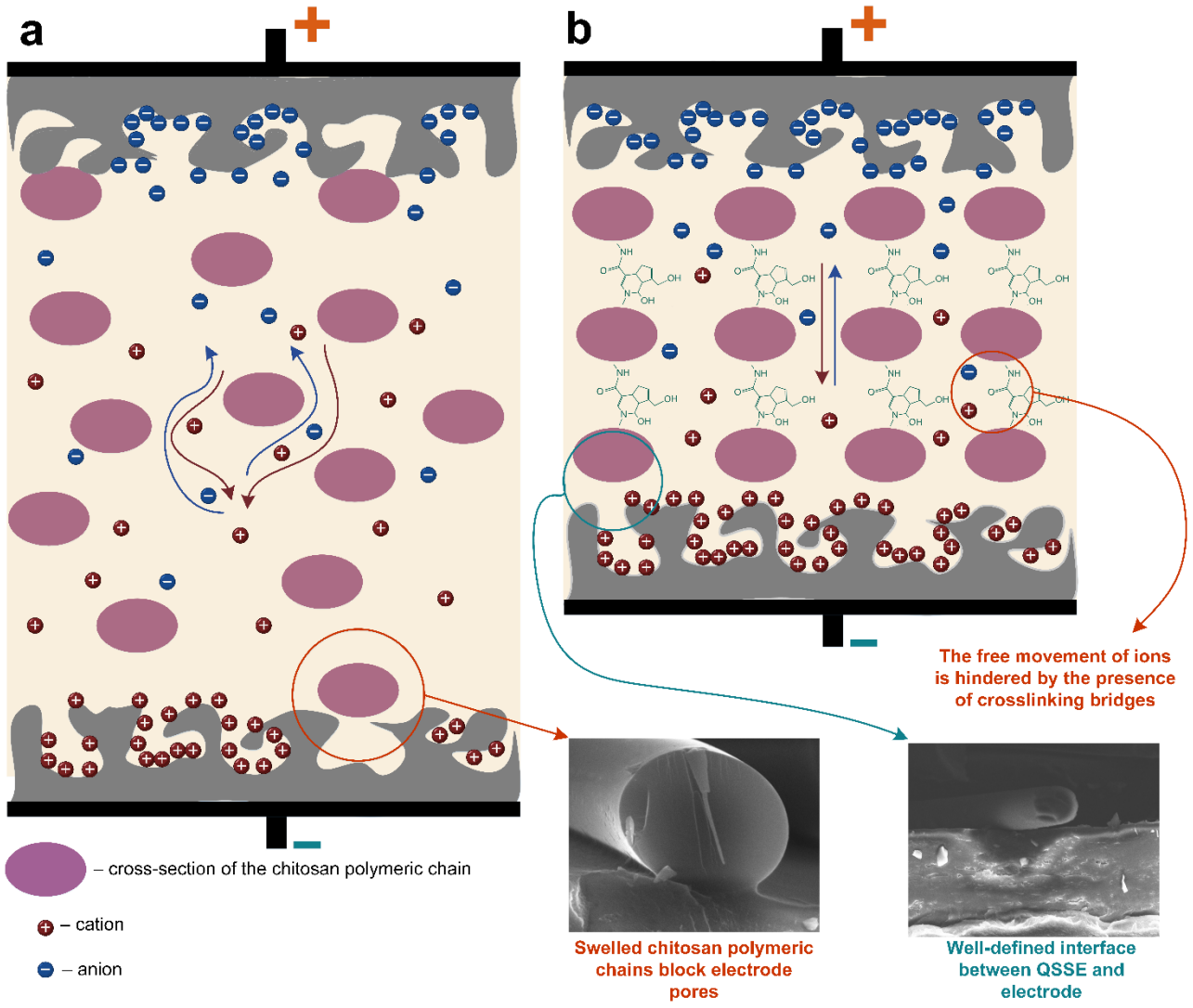

Fig. S6 Schematic representation of possible differences in charge storage phenomena within operational EDLCs: (a) chitosan-based QSSE without crosslinking and (b) chitosan-based QSSE crosslinked with genipin.

EDLC power and energy characteristics calculation methods

The EDLC energy density (E_D) was calculated as follow:

$$E_D = \frac{0.5 \times C_{EDLC,GD} \times \Delta U^2}{3.6} [Wh\ kg^{-1}] \quad \text{(S1)}$$

Where $\mathbf{C_{EDLC,GD}}$ is the specific capacitance [F g^{-1}] for entire device calculated from the galvanostatic discharge curves and $\Delta\mathbf{U}$ is the potential window [V] (here 0.8 V).

The EDLC power density (P_D) was calculated as follow:

$$P_D = \frac{3600 \times E_D}{\Delta t} [W\ kg^{-1}] \quad \text{(S2)}$$

Where $\mathbf{E_D}$ is the energy density [Wh kg^{-1}] and $\Delta\mathbf{t}$ is the discharge time [s].