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

Supporting Information for

A Flexible Dual Solid-State Electrolyte Supercapacitor with Suppressed Self-Discharge and Enhanced Stability

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Calculations

Areal capacitance value (C_A, in mF/cm^2) was calculated from GCD curves based on Equation S1:

$$C_A = \frac{I\,\Delta t}{S\Delta V} \qquad (1)$$

Where I represents the discharge current, ΔV refers to the potential change within the discharge time Δt, and S is the working area.

Volumetric capacitance value (C_v, in F/cm^3) was calculated from GCD curves based on Equation S2:

$$C_v = \frac{I\,\Delta t}{V\Delta V} \qquad (2)$$

Where I is the discharge current, ΔV refers to the potential change within the discharge time Δt, and V is the whole volume of the device including the two electrode, the electrolyte and separator (0.09 cm^3 for DSES).

Energy density and power density were calculated using the following equations (Equation S3-S4)：

$$E = \frac{C \times (\Delta V)^2}{2} \qquad (3)$$

$$P = \frac{E}{\Delta t} \qquad (4)$$

Where C is the capacitance of the device, ΔV refers to the potential change, Δt is discharge time.

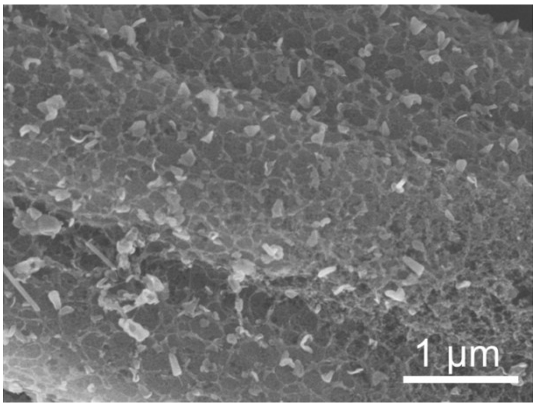

Fig. S1 SEM image of TCC.

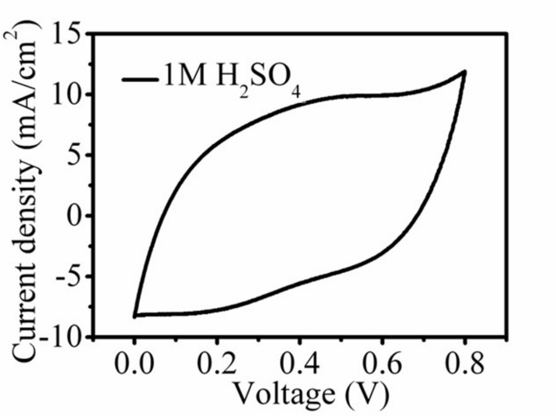

Fig. S2 CV of TCC electrode in 1 M H_2SO_4 at 5 mV/s.

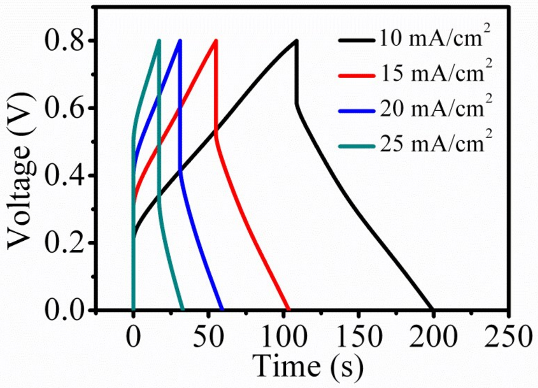

Fig. S3 GCD curves of TCC electrode in 1 M H_2SO_4 solution.

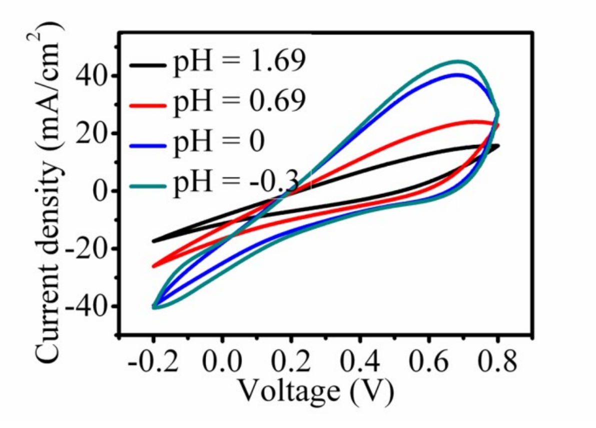

Fig. S4 CVs of TCC electrode at different pH.

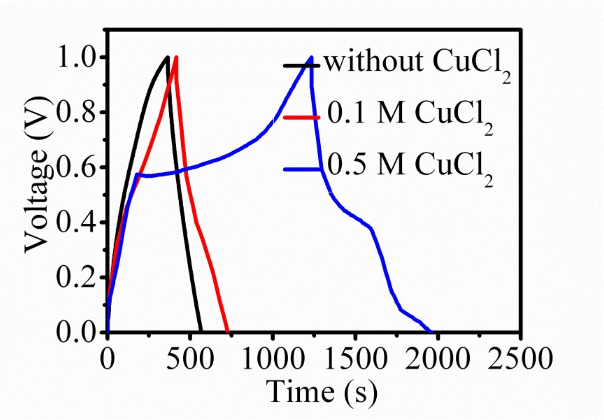

Fig. S5 GCD curves for SSES with 0 M 0.1 M, and 0.5 M CuCl$_2$ at 4 mA/cm^2.

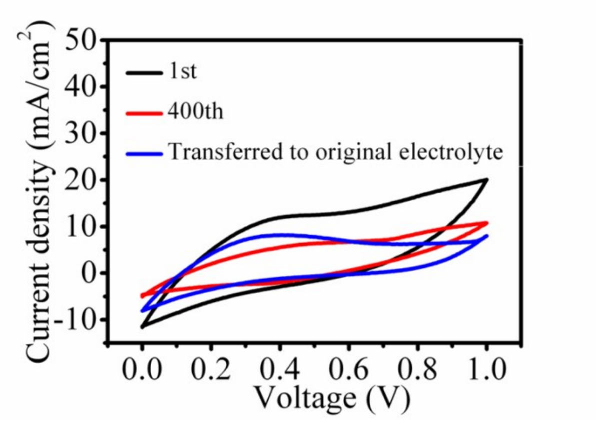

Fig. S6 CVs for TCC in two-electrode liquid redox 0.2 M CuCl$_2$/H$_2$SO$_4$ electrolyte at the first cycle (black), the 400th cycle (red) and after 400 cycles transferred to the original electrolyte.

Reaction Processes of Negative Electrode

The XRD results show that Cu, CuCl, Cu_2O and $Cu_4Cl(OH)_3$ are deposited on the surface of the negative electrode. This indicates the existence of an irreversible process during reduction process and the reduzate contain a complex mix of metallic copper and copper oxide as the fact that low concentrations of oxygen exist in electrolyte. According to the previous report[1], Cu^{2+} may involve the following two-step reduction mechanism in our system (Equation S5- Equation S6):

$$Cu^{2+} + e^- \longrightarrow Cu^+ \tag{5}$$

$$2Cu^+ + H_2O + e^- \longrightarrow Cu_2O_{aq} + H^+ \tag{6}$$

Therefore, stable Cu^+ and Cu_2O precipitation form. Then the oxidation/dissolution of Cu_2O_{aq} occurs on the reverse scan. The processes are shown as follows (Equation S7- Equation S9):

$$Cu_2O_{aq} \longrightarrow Cu^0 + CuO_{aq} \tag{7}$$

$$Cu_2O_{aq} \longrightarrow CuO_{aq} + e^- \tag{8}$$

$$CuO_{aq} + 2H^+ \longrightarrow Cu^{2+} + H_2O \tag{9}$$

Table S1 The values of R_s, R_{ct} and W_o are collected based on the Nyquist specrta.

Devices	R_s	R_{ct}	W_o
Aqueous electrolyte	2.11	0.30	0.56
Solid-state electrolyte	3.32	2.30	2.51

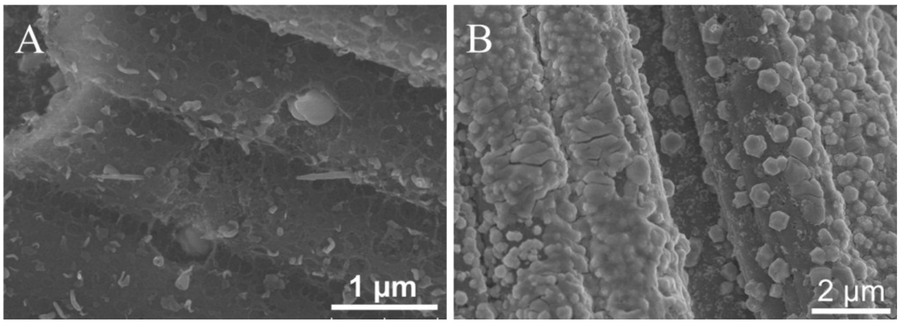

Fig. S7 SEM images for the positive and negative electrode tested after cycling in 0.2 M $CuCl_2/H_2SO_4$ solution. SEM images of (A) positive and (B) negative electrode materials after 400 CV cycles.

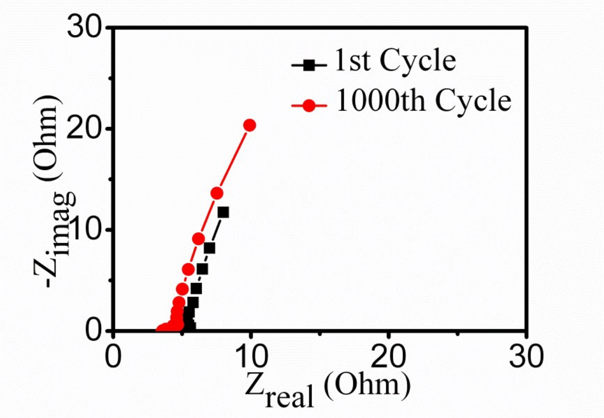

Fig. S8 Nyquist plots recorded after the 1st and 1000th cycles.

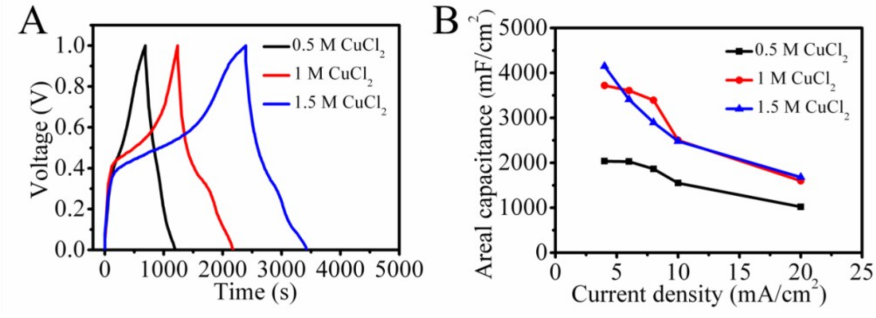

Fig. S9 (A) GCD curves for DSES at various loading of $CuCl_2$ at 4 mA/cm^2. (B) Specific capacitance at different current densities of DSES at various loading of $CuCl_2$.

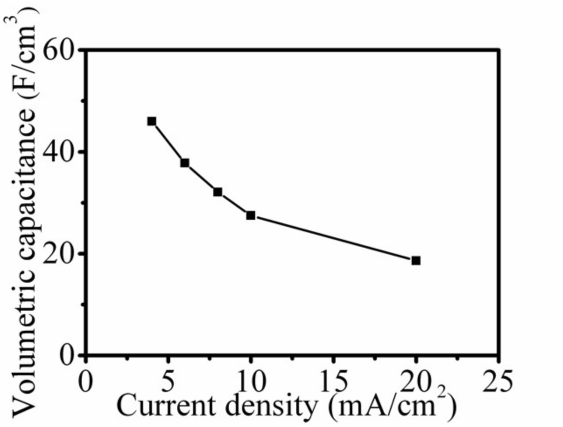

Fig. S10 Volumetric capacitances at different current densities of DSES in 1.5 M $CuCl_2$.

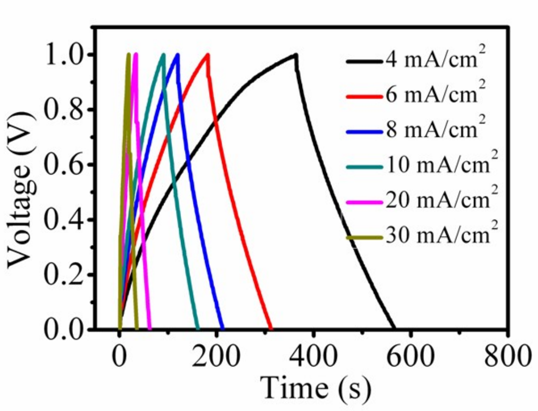

Fig. S11 GCD curves for solid-state SC in the absence of $CuCl_2$ at various current densities.

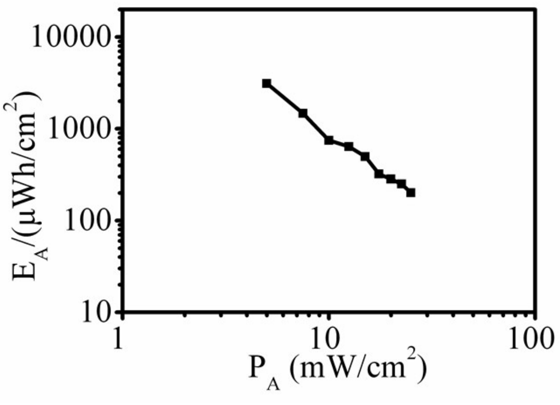

Fig. S12 Ragone plot of aqueous device with 0.3 M $CuCl_2$/1 M H_2SO_4 as electrolyte.

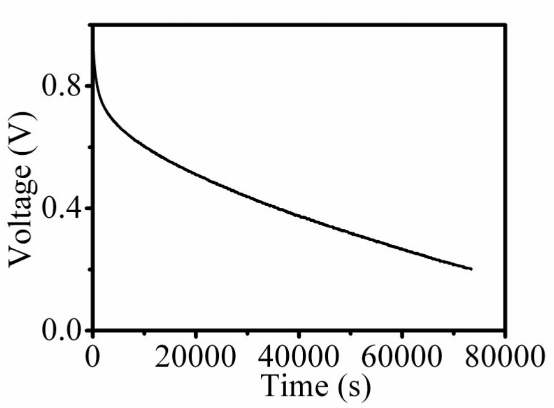

Fig. S13 Self-discharge profiles plotted as self-discharge time of DSES with 1.5 M $CuCl_2/H_2SO_4/PVA$ as solid-state electrolyte.

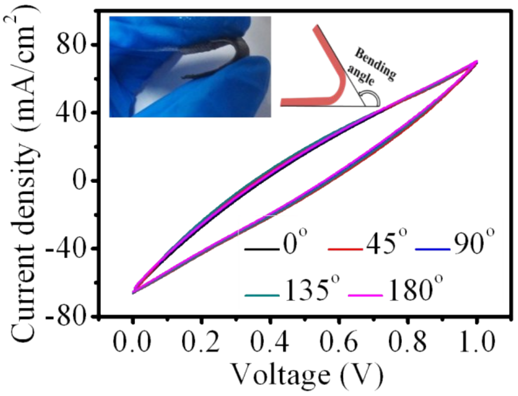

Fig. S14 CV curves at 100 mV/s under different bending angles, with the inset of digital photo of the flexible DSES.

References

1 J.-J. Velasco-Vélez, K. Skorupska, E. Frei, Y.-C. Huang, C.-L. Dong, B.-J. Su, C.-J. Hsu, H.-Y. Chou, J.-M. Chen, P. Strasser, R. Schlögl, A. Knop-Gericke and C.-H. Chuang, *J. Phys. Chem. B*, 2018, **122**, 780-787.