

Figure S1. TGA curves of example 3.

The comparative analysis of Example 3, Control Example 2, and Control Example 3 demonstrates that the glycerol-to-PVA ratio is a critical parameter decisively governing the electrolyte's overall functionality by determining the essential compromise between mechanical integrity and electrochemical performance. Mechanically, glycerol acts as a plasticizer; however, when its proportion is excessively high, as in Control Example 3 (Figure S2), it disrupts the cohesive hydrogen-bonding network of the PVA matrix, resulting in a fluid-like consistency that lacks the structural integrity required for a freestanding membrane. This indicates a clear upper limit for the plasticizer to maintain a solid matrix. Electrochemically, the optimal ratio in Example 3 leads to significantly enhanced performance compared to Control Example 2, as evidenced by  $R_s$  and  $R_{ct}$  (Table 2). The reduced  $R_s$  signifies improved bulk proton conductivity, attributable to glycerol's dual role in providing hydroxyl groups for proton hopping and increasing polymer chain mobility to facilitate ion transport. Simultaneously, the lower  $R_{ct}$  indicates more favorable kinetics at the electrode-electrolyte interface, likely due to improved interfacial contact enabled by the optimized membrane morphology. Therefore, the glycerol-to-PVA ratio must be carefully balanced: sufficient PVA is necessary to form a robust structural scaffold, while an optimal amount of glycerol is required to maximize ionic conduction and interfacial properties without causing structural collapse.

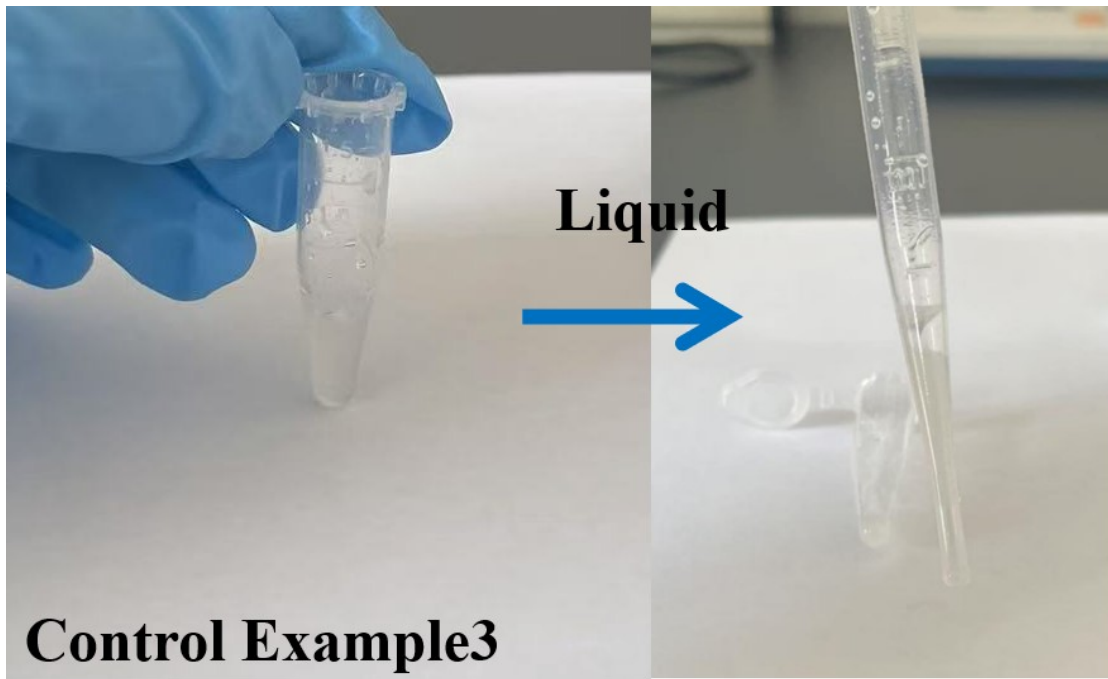


Figure S2. Optical image of control example 3.

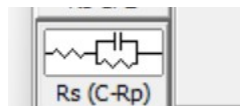


Figure S3. the equivalent circuit fit plot.

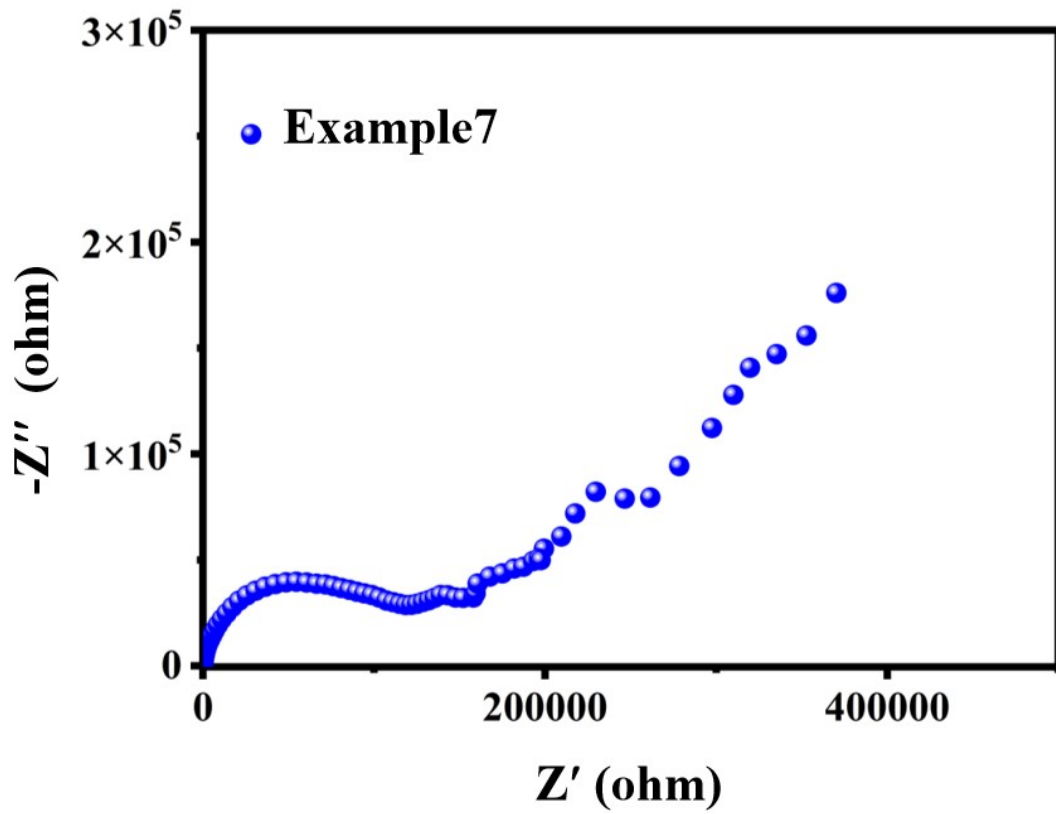


Figure S4. The EIS spectra of example 7.

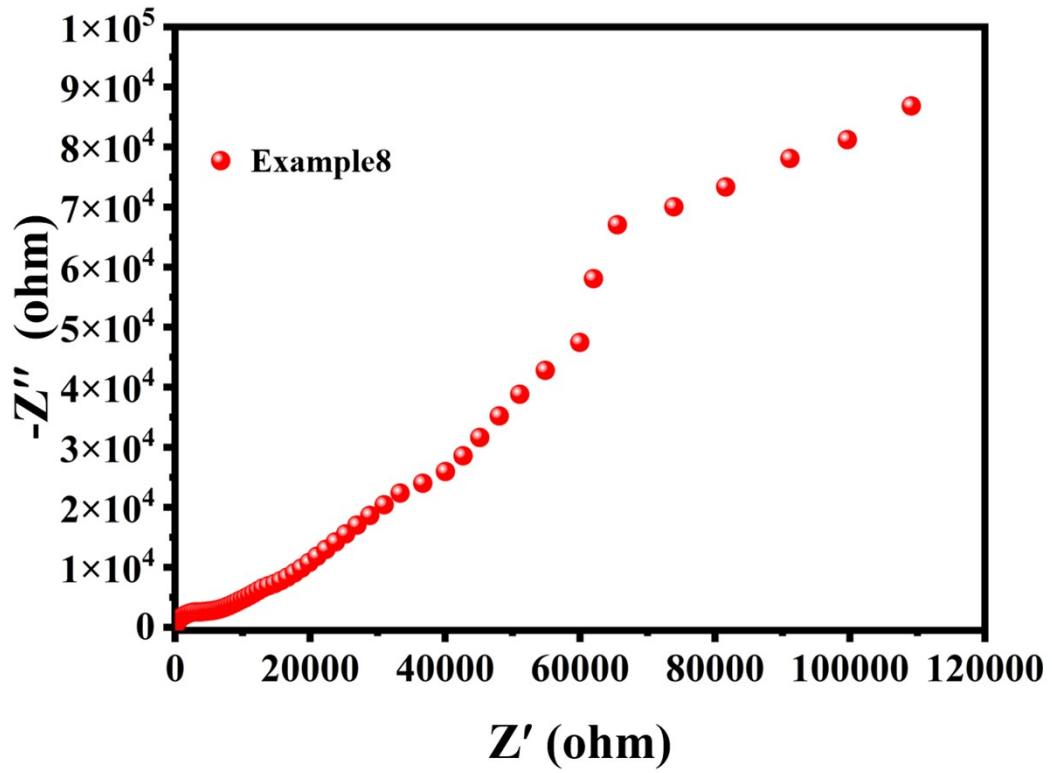


Figure S5. The EIS spectra of example 8.

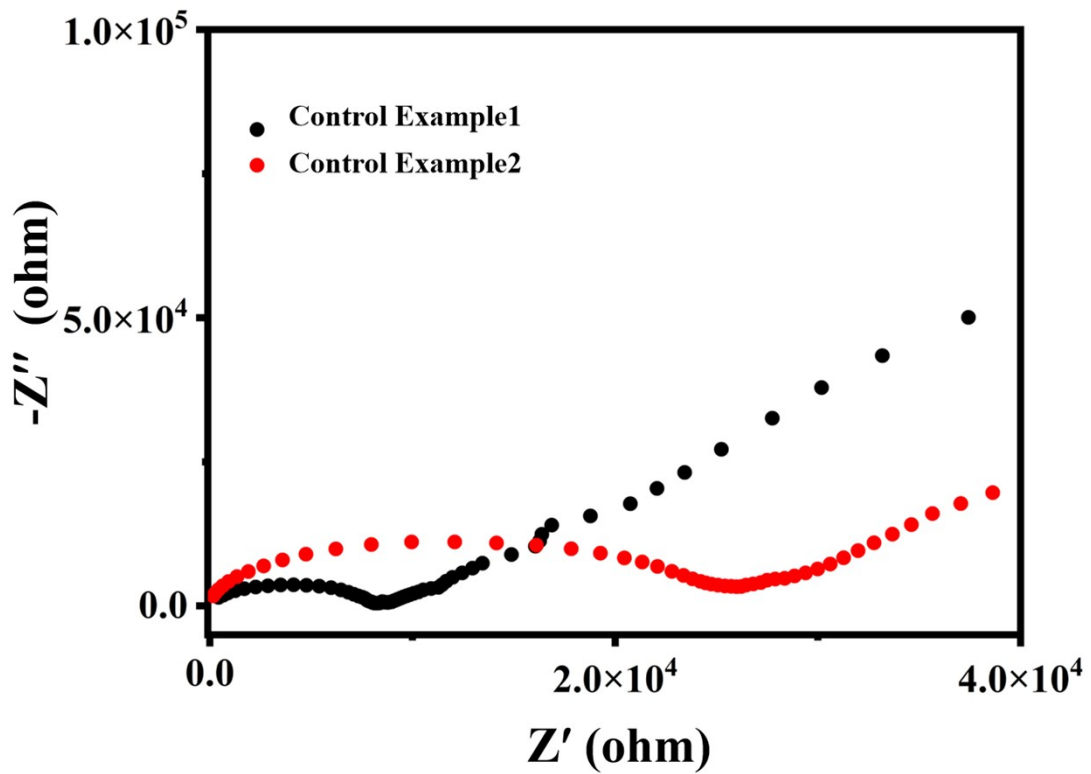


Figure S6. The EIS spectra of Control Example 1 and Control Example 2.

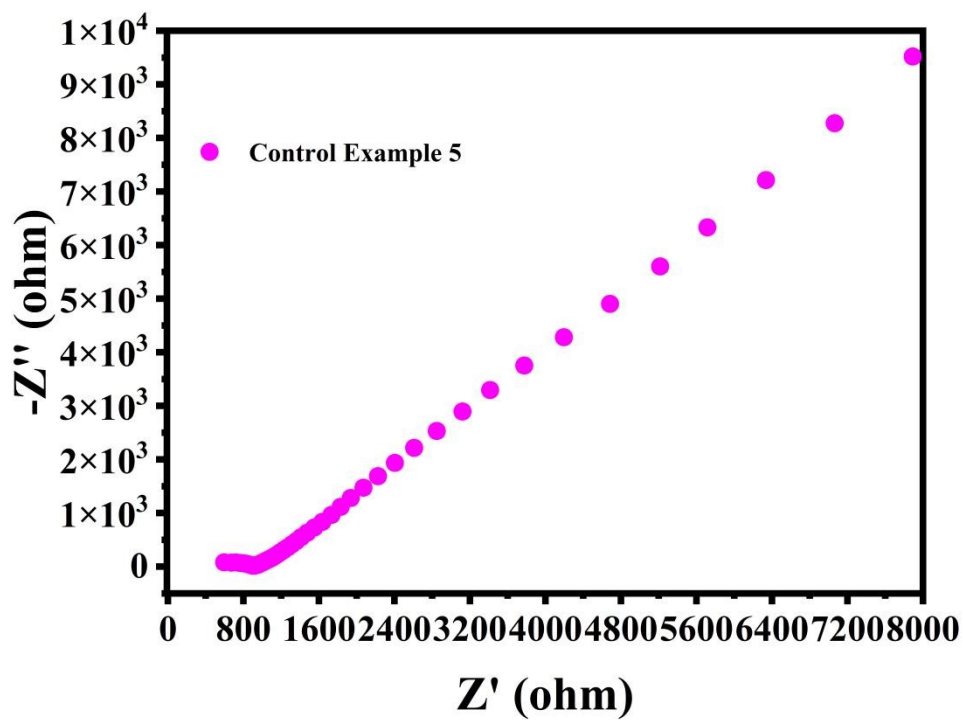


Figure S7. The EIS spectra of Control Example 5.

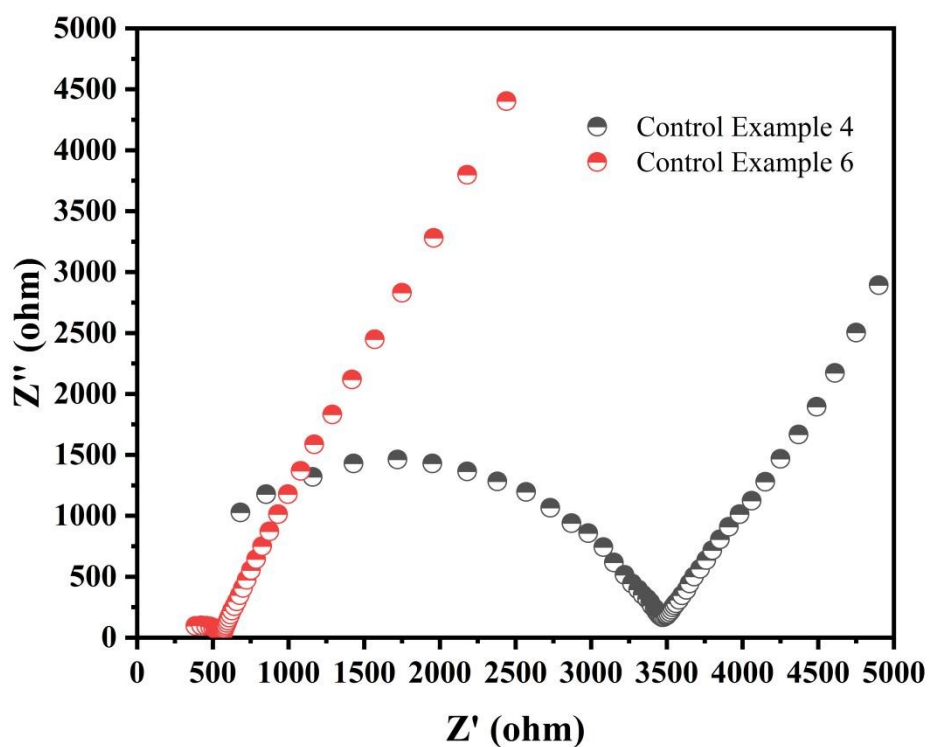


Figure S8. The EIS spectra of Control Example 4 and Control Example 6.

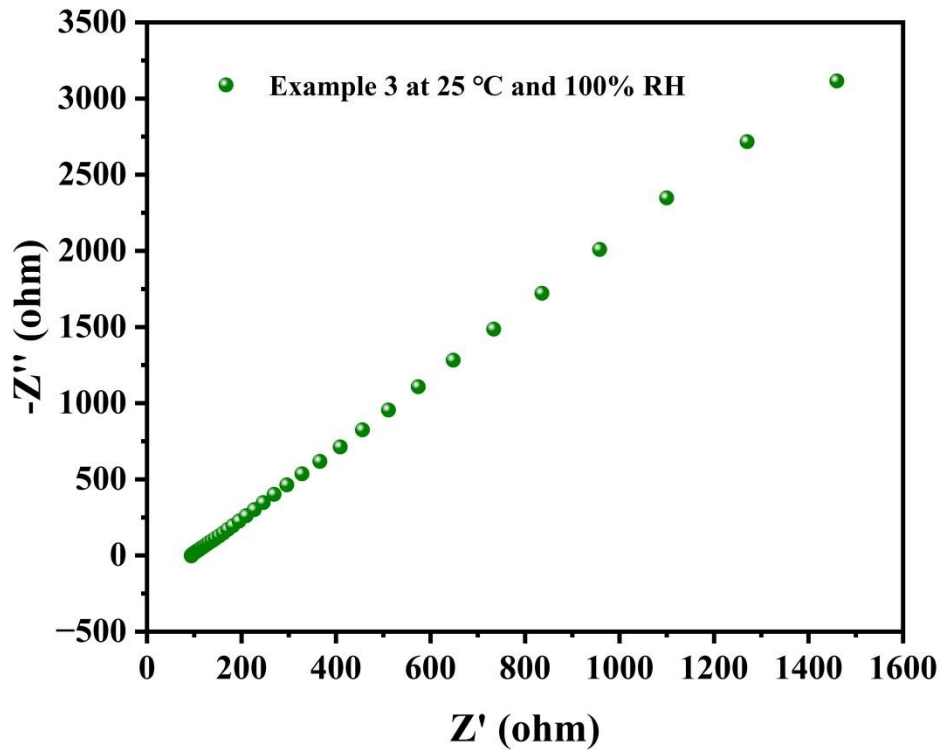


Figure S9. The EIS spectra of example 3 at 25 °C and 100% RH.

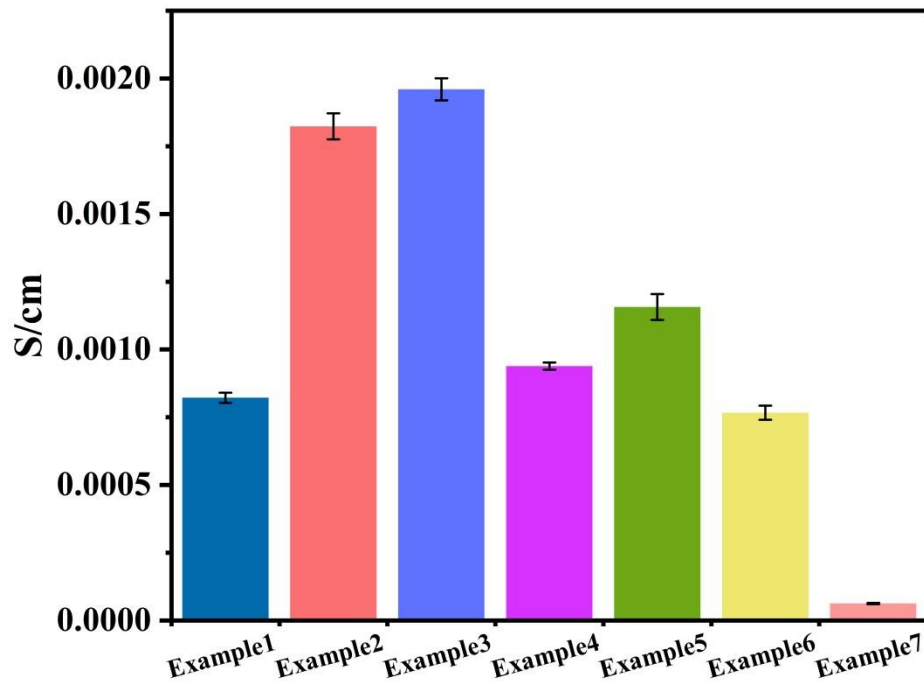


Figure S10. Bar chart of proton conductivity for different samples at 30 °C and 45% RH.

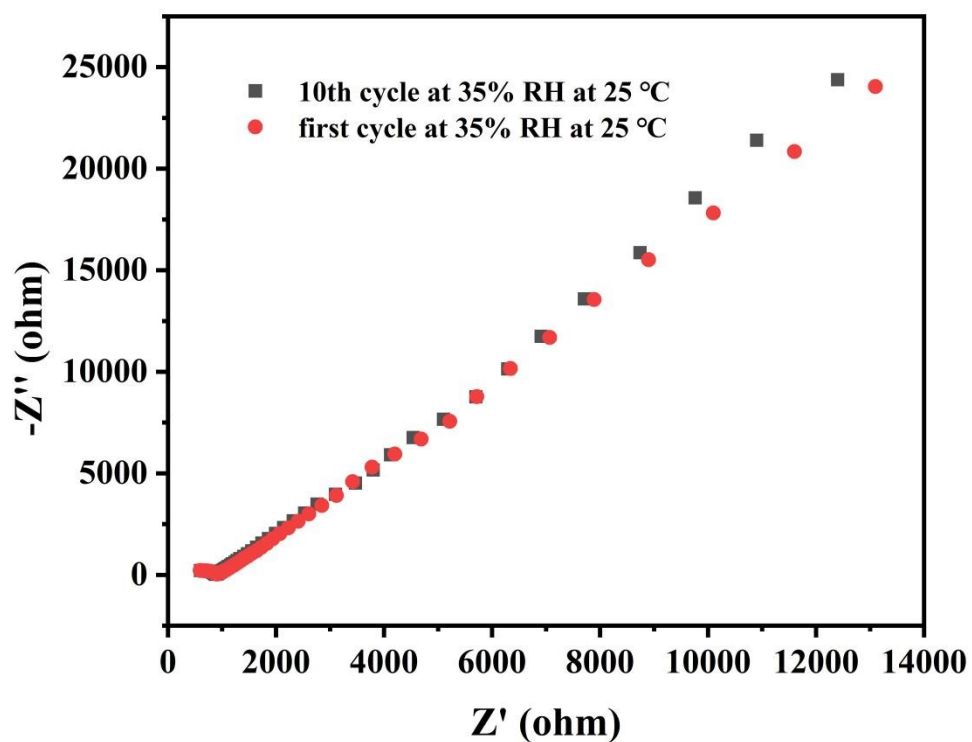


Figure S11. The EIS spectra of example 3 at 25 °C and 35% RH.

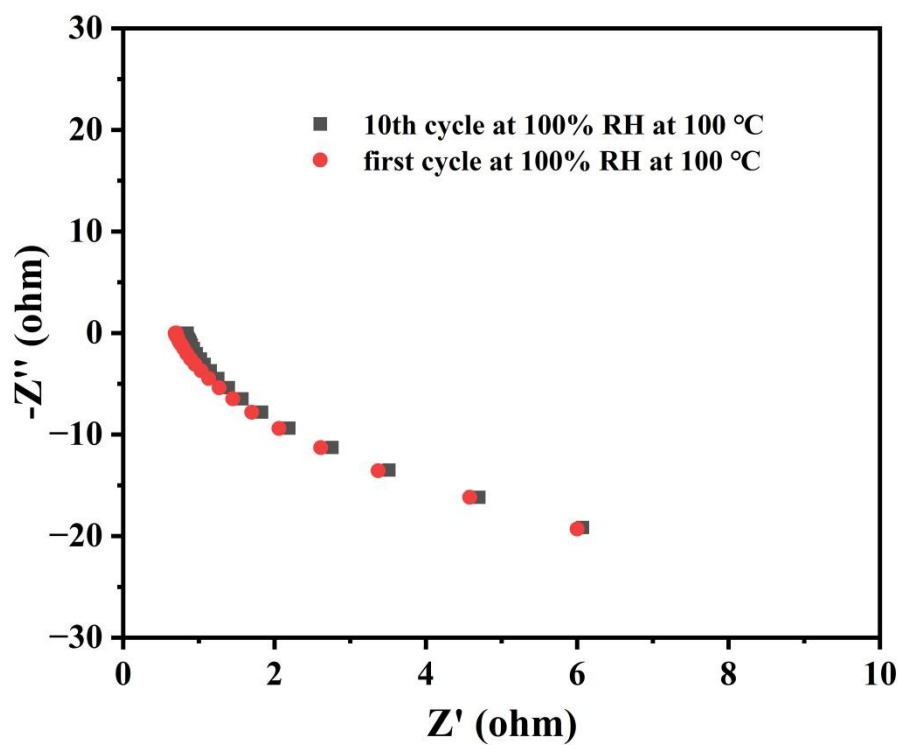


Figure S12. The EIS spectra of example 3 at 100 °C and 100% RH.

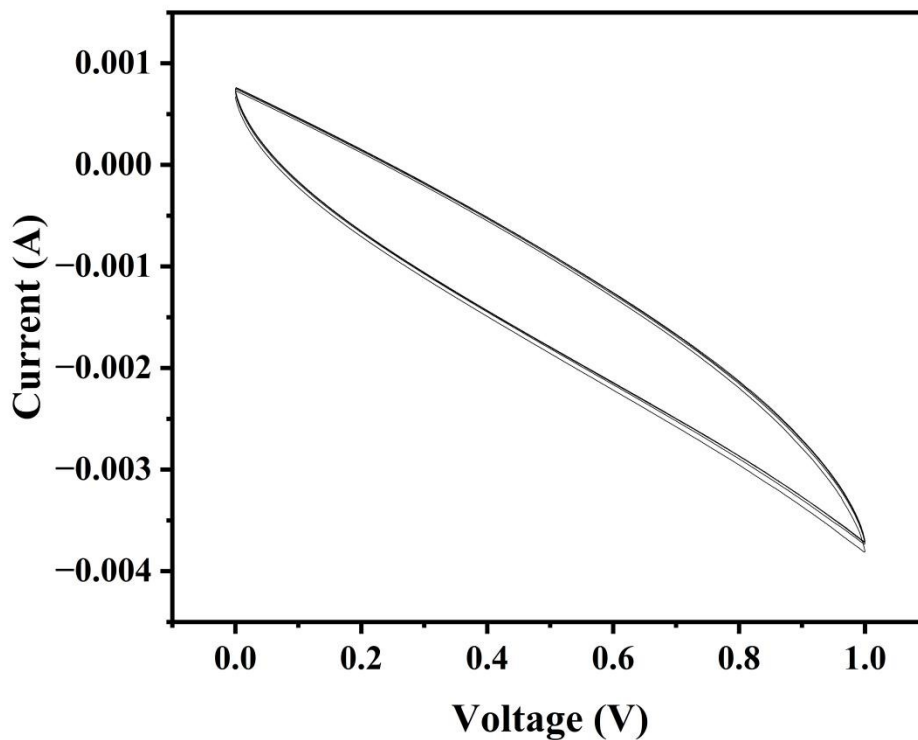


Figure S13. The cyclic voltammetry (CV) curves for the assembled symmetric supercapacitor.

Table S1 Conductivity ( $\sigma'$ ) values extracted by the RBM model.

Temperature (°C)	$\sigma'$ (S/cm)
-60	$2.31 \times 10^{-11}$
-50	$3.76 \times 10^{-10}$
-40	$4.47 \times 10^{-9}$
-30	$3.41 \times 10^{-8}$
-20	$1.89 \times 10^{-7}$
-10	$7.85 \times 10^{-7}$
0	$2.80 \times 10^{-6}$
10	$8.52 \times 10^{-6}$

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20	$2.30 \times 10^{-5}$
30	$5.17 \times 10^{-5}$
40	$1.14 \times 10^{-4}$
50	$2.25 \times 10^{-4}$
60	$4.45 \times 10^{-4}$
70	$7.88 \times 10^{-4}$
80	$1.18 \times 10^{-3}$
90	$1.57 \times 10^{-3}$
100	$1.85 \times 10^{-3}$
110	$2.03 \times 10^{-3}$

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