Electronic Supplementary Information for

A rational configuration for ultralong lifespan all-solid-state organic sodium-metal batteries

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Contents

1. Computational details

DFT calculations

Calculations of vertical electron affinities (VEA) was carried out by Multiwfn 3.8 programs [1]. The definition of VEA was:

$VEA_i = E(N+i-1) - E(N+i)$

where N was the electrons of the compound (molecule) studied and the i was the i^{th} VEA, respectively. $E(N+i-1)$ and $E(N+i)$ denoted the total energy of the compound (molecule) with $N+i-1$ electrons and that of the compound (molecule) with $N+i$ electrons, respectively. The calculations of lowest unoccupied molecular orbital (LUMO) energies of FEC and FEC-Na^+ complexes were performed on the Gaussian 16 software at the B3LYP/6-311++G(d,p) level of theory [2]. The LUMO and HOMO plots were obtained by visual Molecular Dynamics V1.9.3 and Multiwfn 3.8 programs [1].

2. Experimental Section

Preparation of pristine and pretreated Na metal

The Na tablets (Aladdin, AR) were cut with a knife and cured into circles (14 mm in diameter) to get the pristine Na anodes. To obtain the pretreated Na anodes, Na tablets were soaked for different times (30 s, 1 min, and 3 min) in the saturated solution of $NaClO_4$/FEC and wiped completely by filter paper. All operation steps were performed in an Ar-filled glove box (H_2O and O_2 levels < 0.1 ppm).

Preparation of Pillar[5]quinone (P5Q) cathode

The synthesis of P5Q was referred to the previous literature [4].

P5Q powder was prepared by adding active material (P5Q), conductive carbon (Ketjen black), and binding agent (polyvinylidene fluoride, PVDF) to the organic solution (N-methyl-2-pyrrolidone, NMP) in a mass ratio of 3:6:1. Then P5Q powder was coated on Al foil and dried under vacuum at 80 °C for 10 h. The Al foil was cured into circles in diameter of 12 mm. The neat loading on the Al foil was 1.7 mg cm^{-2}, where the amount of P5Q was 0.5 mg cm^{-2}.

Preparation of $NaClO_4$/succinonitrile plastic crystal electrolytes ($NaClO_4$/SN PCEs)

The $NaClO_4$/SN PCEs consisting of SN (Aladdin, AR 99.0%) and $NaClO_4$ (Tianjin Guangfu Fine Chemical Research Institute, AR) was prepared as follows. Accurately weigh a certain quality of SN into a small pre-washed vial, and then add an appropriate amount of $NaClO_4$ according to a certain ratio. The mixture was stirred at 50 ℃ for 10 min until SN was completely dissolved. After cooling, the $NaClO_4$/SN PCEs was obtained. In addition, due to the poor mechanical properties of the electrolyte, we chose quantitative filter paper (ϕ = 16 mm) as the skeleton to prepare the paper-supported film.

Characterization and electrochemical measurements

The surface morphology of Na metal was characterized by scanning electron microscope (SEM, SUPRA 55) and the composition change of electrolytes after Na tablets soaked-in was investigated by infrared spectroscopy (IR). Liner sweep voltammetry (LSV) curves of $NaClO_4$/SN PCEs were obtained in the potential between 1.2 and 5.3 V at a scan rate 1.0 mV s^{-1} on CHI660 electrochemical workstation, employing stainless steel as inert working electrode and the pretreated Na electrode as the counter electrode and reference electrode. The cyclic voltammetry curve (CV) of 5mol% $NaClO_4$/SN PCE was performed at 0.2 mV s^{-1} within the voltage of -0.5-1.2 V. The thermal characteristics of $NaClO_4$/SN PCEs were measured by differential scanning calorimetry (DSC) with a heating-rate of 5 °C min^{-1} from -60 °C to 60 °C under the protection of N_2. The thermal stability of $NaClO_4$/SN PCEs were tested by thermogravimetric analysis (TGA) with a heating-rate of 10 ℃ min^{-1} from room temperature to 800 ℃ under the protection of Ar. The Na^+ ion transference number (t_{Na+}) of the 5mol% $NaClO_4$/SN PCE was determined by a combined DC polarization and AC impedance method and calculated according to the equation:

$$t_{Na+} = I_s(\Delta V - I_0R_0) / I_0(\Delta V - I_sR_s)$$

I_0 and I_s were the initial and steady state currents. ΔV was the polarization voltage applied on the Na/Na symmetrical batteries. R_0 and R_s were the initial and steady state impedance values. Na||Na symmetrical batteries equipped with pristine/pretreated Na anodes and 5 mol% $NaClO_4$/SN PCE were prepared and applied to investigate the Na plating/stripping behavior. Electrochemical impedance spectroscopy (EIS) tests were carried out in the frequency range of 0.01-100k Hz with

the ac voltage amplitude of ± 5 mV. The all-solid-state organic sodium-metal batteries (OSMBs) were tested by using CR2032 coin-type batteries with pretreated Na metal anode, P5Q cathode and 5 mol% $NaClO_4$/SN PCE. CV curves of the P5Q||Na batteries were performed on a potential range of 1.3-3.9 V at a scan rate of 0.2 mV s^{-1}. All electrochemical tests were carried out at room temperature.

3. The optimized structure and theoretically calculated value of FEC

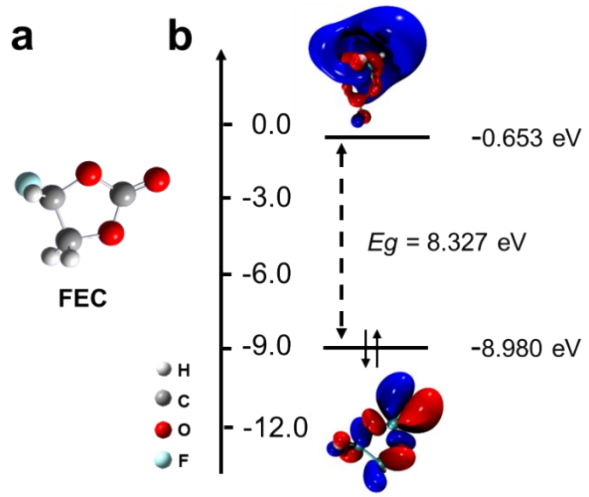

Fig. S1. (a) The optimized structure and (b) theoretically calculated value of FEC.

4. Optimization of immersion time between Na tablets and the saturated solution of $NaClO_4$/FEC.

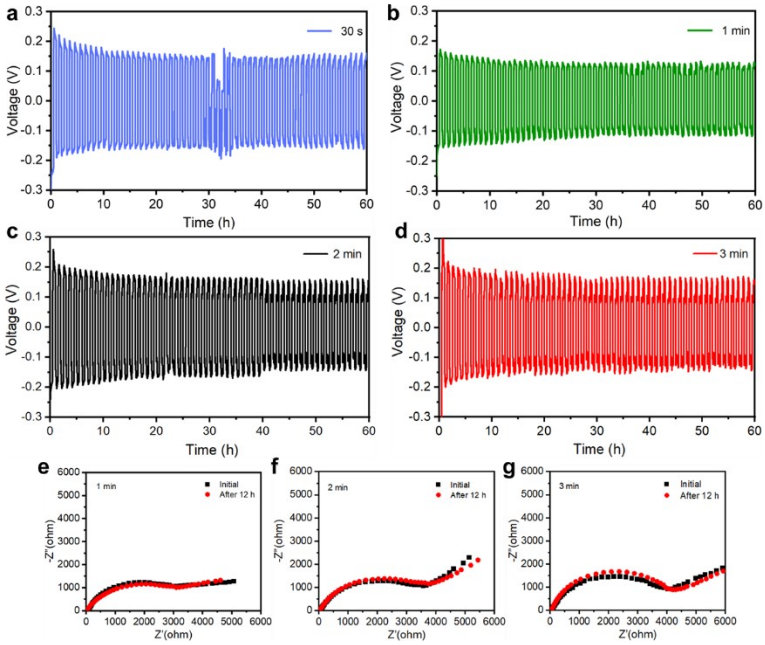

Fig. S2. Optimization of immersion time. Voltage profiles of symmetric batteries of pretreated Na tablets with different treatment times: (a) 30 s, (b) 1 min, (c) 2 min and (d) 3 min. Impedance tests of the symmetric batteries with different pretreated Na anodes: (e) 1 min, (f) 2 min and (g) 3 min.

5. Comparison of recent literature reports on the electrochemical performance of different SN-based PCEs.

Table S1. Comparison of recent literature reports on the electrochemical performance of different SN-based PCEs.

Electrolyte	Electrochemical window (V)	Ionic conductivity (mS cm^{-1})	Note & Ref
5 mol% $NaClO_4$/SN PCE	5.0	0.79	This work
5 mol% $NaClO_4$ /SN/PVDF-HFP	4.86	0.51	[5]
(1 M $NaClO_4$/SN)-20 wt% B-HEMA	5.0	0.36	[6]

PVDF-HFP: poly (vinylidene fluoride-co-hexafluoropropylene); B-HEMA: boron-containing cross-linker

6. Cyclic voltammetry curve of 5mol% $NaClO_4$/SN PCE.

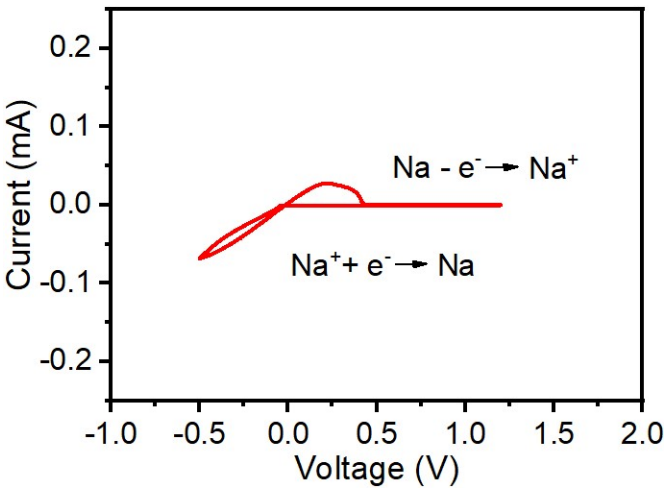

Fig. S3. Cyclic voltammetry curve of 5mol% $NaClO_4$/SN PCE

7. Na^+ transference number of 5mol% $NaClO_4$/SN PCE.

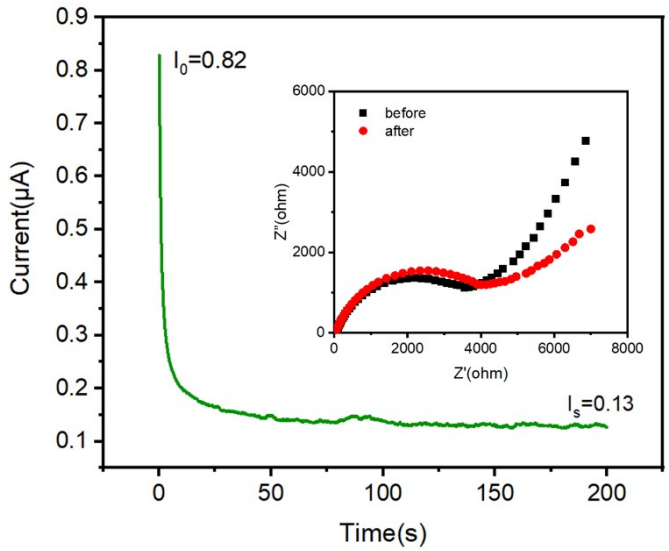

Fig. S4. Na^+ transference number of 5mol% $NaClO_4$/SN PCE

8. SEM images of different Na tablets after soaked in 5 mol% $NaClO_4$/SN PCE for 60 h at RT.

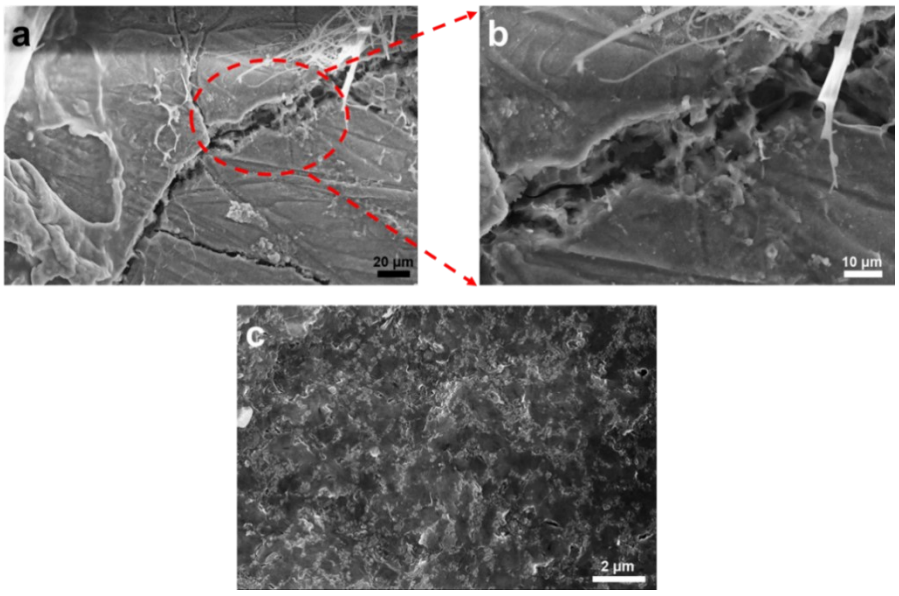

Fig. S5. SEM images of different Na tablets after soaked in 5 mol% $NaClO_4$/SN PCE for 60 h at RT: (a, b) pristine Na and (c) pretreated Na.

9. Voltage profile of the symmetrical battery of pretreated Na electrodes at a current density of 0.3 mA cm^{-2} in 5 mol% $NaClO_4$/SN PCE.

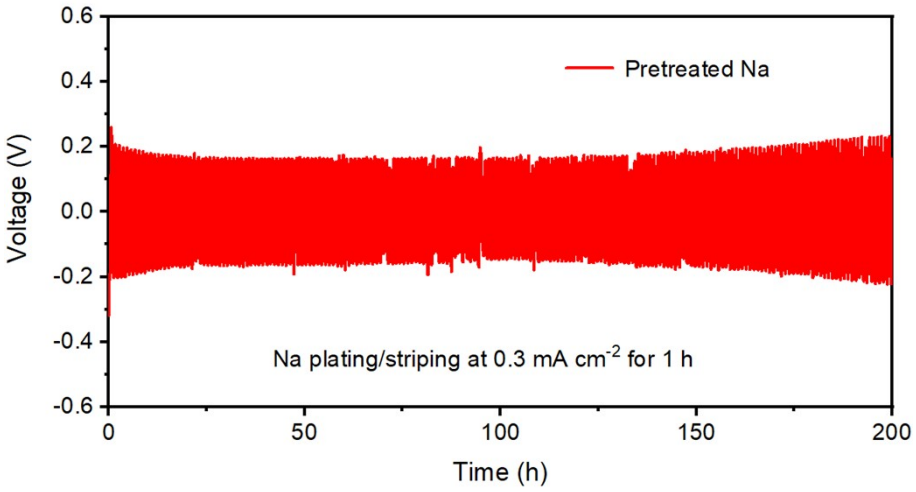

Fig. S6. Voltage profile of the symmetrical battery of pretreated Na electrodes at a current density of 0.3 mA cm^{-2} in 5 mol% $NaClO_4$/SN PCE.

10. The structure and discharge-charge mechanism of P5Q.

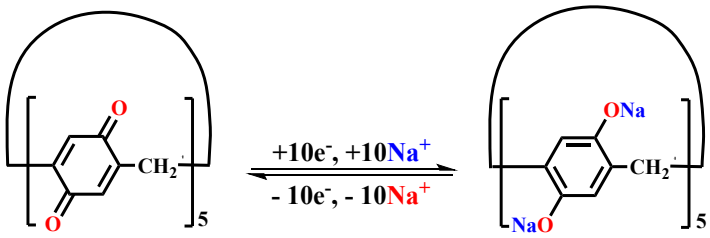

Fig. S7. The structure and discharge-charge mechanism of P5Q.

11. The optical photograph of the paper-supported $NaClO_4$/SN PCE.

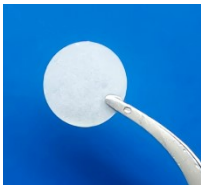

Fig. S8. The optical photograph of the paper-supported $NaClO_4$/SN PCE.

12. Visualization dissolution experiment of P5Q in different electrolytes.

Fig. S9. Visualization dissolution experiment of P5Q in 5 mol% $NaClO_4$/SN PCE and $NaClO_4$/EC+DMC electrolytes.

13. The charge-discharge curves of P5Q in 5 mol% $NaClO_4$/SN PCE at various current rates.

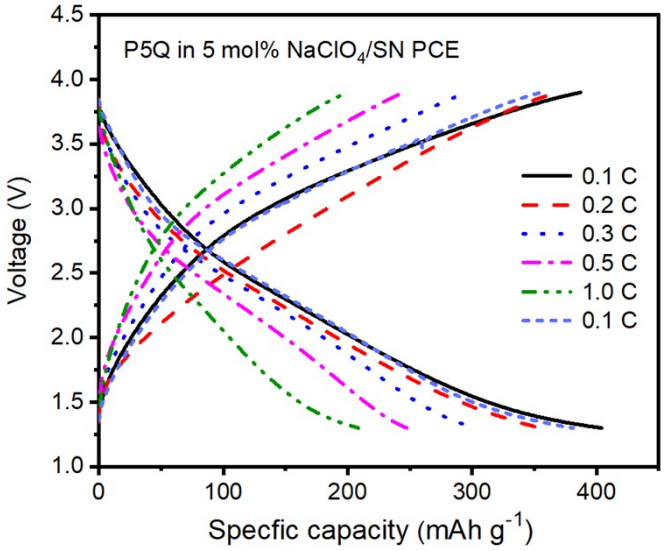

Fig. S10. The charge-discharge curves of P5Q in 5 mol% $NaClO_4$/SN PCE at various current rates.

14. References

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4. Y. Lu, Y.C. Cai, Q. Zhang, L.J. Liu, Z.Q. Niu, J. Chen, A compatible anode/succinonitrile-based electrolyte interface in all-solid-state Na-CO2 batteries, *Chem. Sci.*, **10** (2019) 4306-4312.
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