## **Electronic Supplementary information (EIS) for**

## Exploration of calcium-organic framework as an anode material for

## sodium-ion batteries

Yan Zhang <sup>a,b</sup>, Yubin Niu <sup>a,b</sup>, Min-Qiang Wang<sup>a,b</sup>, Jingang Yang<sup>a,c</sup>, Shiyu Lu <sup>a,b</sup>, Jin Han <sup>a,b</sup>, Shu-Juan Bao <sup>a,b</sup>, Maowen Xu<sup>a,b\*</sup>

- a. Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, P.R. China.
- b. Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energies, Chongqing 400715, P.R. China.
- c. Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China.

E-mail: xumaowen@swu.edu.cn



Fig.S1 The PXRD patterns and crystal structure of Ca<sub>2</sub>BTEC • 6H<sub>2</sub>O



**Fig.S2** TGA curves of  $Ca_2BTEC$ . **Pristine**: The  $Ca_2BTEC$  sample as synthesized; **As prepared**: The  $Ca_2BTEC$  sample prepared according to the similar procedure of electrode fabrication (first

dispersed in water and then dried at  $120^{\circ}$ C in vacuum). The **As prepared** sample shows no obvious mass loss before  $200^{\circ}$ C and two curves are almost overlapped indicating the hydrated compound can not form during electrode fabrication procedure.



**Fig.S4** Structural stability of Ca<sub>2</sub>BTEC electrodes upon repeated discharge/charge processes. The XRD patterns of pristine electrodes and in the discharged state after 50 cycles (at a current density of 50mA/g) indicate good structural stability during repeated discharge/charge processes. This means the repeated insertion and exertion of Na<sup>+</sup> do not significantly affect the structure of Ca<sub>2</sub>BTEC.



**Fig.S5** The optical photographs of Na<sub>4</sub>BTEC and Ca<sub>2</sub>BTEC before and after electrolytes injection. After electrolytes injection and shaking, Na<sub>4</sub>BTEC was dissolved and formed an almost transparent solution while Ca<sub>2</sub>BTEC was not dissolved and form a white turbid liquid. The results can prove the lower solubility of Ca<sub>2</sub>BTEC in electrolytes than Na<sub>4</sub>BTEC.



**Fig.S6** Molecular formula of Na<sub>4</sub>BTEC and Ca<sub>2</sub>BTEC.Due to the smaller molecular weight than Na<sub>4</sub>BTEC, Ca<sub>2</sub>BTEC owns a larger theoretical specific capacity.



Fig.S7 The cyclic performance of Ca<sub>2</sub>BTEC • 6H<sub>2</sub>O



Fig.S8 The cyclic performance of Na<sub>4</sub>BTEC



**Fig.S9** The cyclic performance of Super P at a current density of 40 mA g<sup>-1</sup>. The first discharge and charge capacity of super P carbon are 206.5 and 103.1 mA h g<sup>-1</sup>, resulting in an initial Columbic efficiency of only 49.93%. After 35 cycles, the discharge and charge capacity fade to 84 and 82 mA h g<sup>-1</sup>. In consideration of that the super P content in Ca<sub>2</sub>BTEC electrodes is 30% by weight, so the capacity contribution of super P carbon during initial and 35<sup>th</sup> cycle is only 61.95 (206.5×30%) and 25.2 (84×30%) mA h g<sup>-1</sup>.