## **Supporting information**

**Figure S1:** Morphology of the  $Na_7V_3(P_2O_7)_4$ -based hybrid foam. (a) Lowresolution TEM image, (b) TEM image partially enlarged from a, (c) HRTEM image of polyanion crystal. The well-resolved lattice fringe indicates the single-crystal nature of polyanion crystals.



**Figure S2:** Morphology of the (a, b)  $Na_7V_4(P_2O_7)_4(PO_4)$ - and (c, d)  $Na_7V_3(P_2O_7)_4$ -based reference samples. Both reference samples have large microscale particles in solid nature.



**Figure S3:** XRD patterns of the (a)  $Na_7V_4(P_2O_7)_4(PO_4)$ - and (b)  $Na_7V_3(P_2O_7)_4$ -based reference samples. All the diffraction peaks of the  $Na_7V_4(P_2O_7)_4(PO_4)$ -based reference sample can be indexed to the tetragonal phase with space group of *P*-42<sub>1</sub>*c*, and those of the  $Na_7V_3(P_2O_7)_4$ -based reference sample can be indexed to the monoclinic structure with *C*2/*c* space group. The absence of impurity phases indicates the high purity of all the reference samples.



**Table S1** Atomic ratios of the (a)  $Na_7V_4(P_2O_7)_4(PO_4)$ - and (b)  $Na_7V_3(P_2O_7)_4$ based hybrid foams and reference samples.

Element ratio of Na: V: P	Na <sub>7</sub> V <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>4</sub> (PO <sub>4</sub> )	Element ratio of Na: V: P	$Na_7V_3(P_2O_7)_4$
Hybrid foam	6.987:4:9.041	Hybrid foam	6.991:3:8.031
Reference sample	7.021:4:9.032	Reference sample	6.997:3:8.026
Designed value	7:4:9	Designed value	7:3:8