

# Enhanced ionic conductivity of F<sup>-</sup>-assisted Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> solid electrolyte for solid-state sodium batteries

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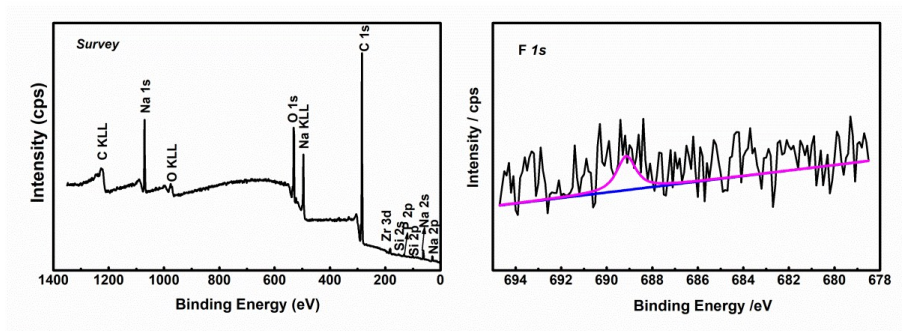


Fig.S1. XPS spectra of the interior of NZSPF0.7 pellets; (a) survey spectra, (b)  $F_{1s}$ .

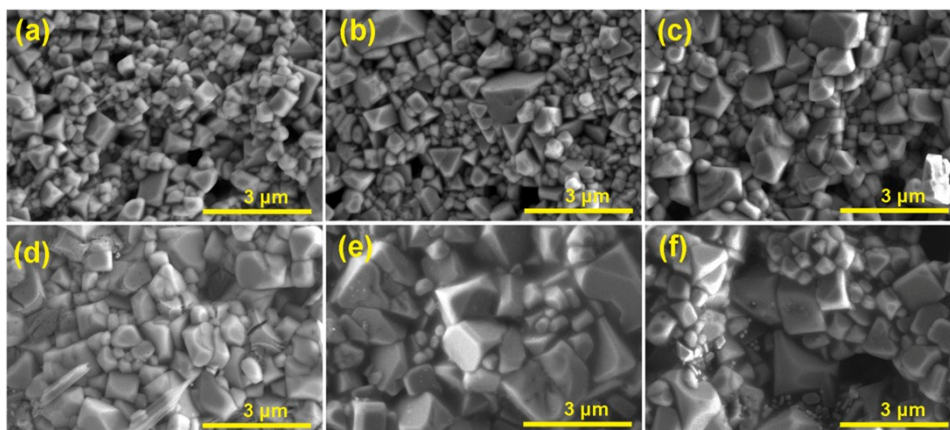


Fig.S2.SEM images of the surface of NZSPFx pellets. (a)  $x=0$ , (b)  $x=0.1$ , (c)  $x=0.3$ , (d)  $x=0.5$ , (e)  $x=0.7$  and (f)  $x=1.0$ .

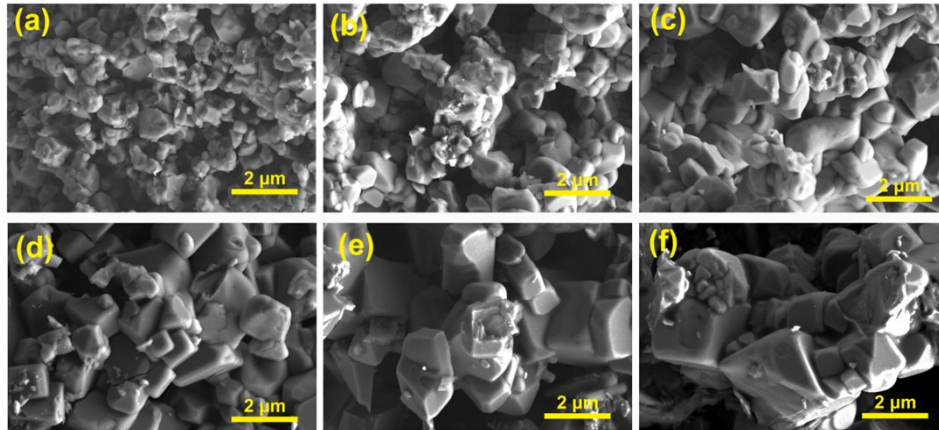


Fig.S3. SEM images of the powder of NZSPFx pellets. (a)  $x=0$ , (b)  $x=0.1$ , (c)  $x=0.3$ , (d)  $x=0.5$ , (e)  $x=0.7$  and (f)  $x=1.0$ .

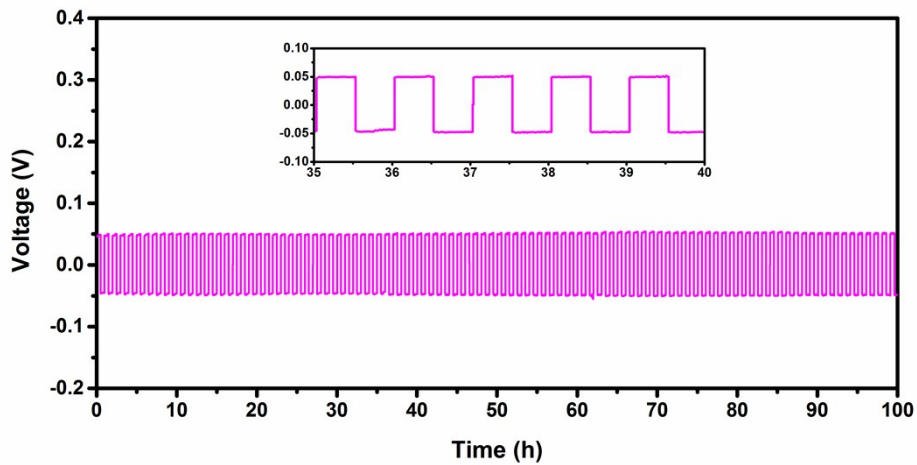


Fig.S4. Galvanostatic cycling of NZSPF0.7 at  $0.2 \text{ mA cm}^{-2}$  at room temperature using Na/NZSPF0.7/Na symmetrical cell (the inset shows the enlarged of partial galvanostatic cycling).

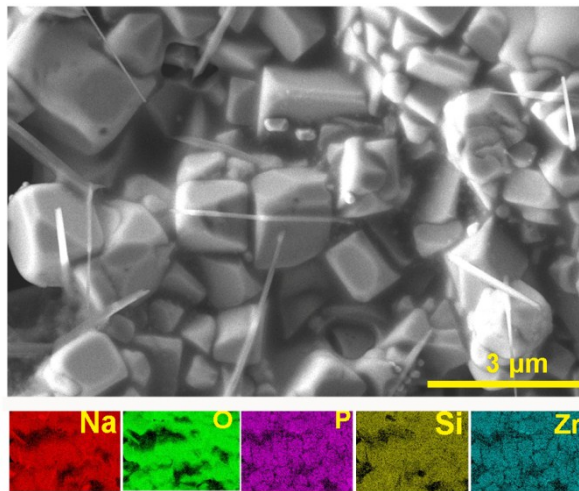


Fig. S5. SEM images of the surface of NZSPF0.7 solid electrolyte after cycling at 1C for 100 cycles.

Table S1

the composition of each samples (x=0, 0.1, 0.3, 0.5, 0.7, 1.0) calculated according to the refinement of the XRD patterns、 the stoichiometry analysis based on the XPS data as well as the EDS data are listed in Table S1 in the revised supporting information.

sample	Composition
x=0	$\text{Na}_{3.0061}\text{Zr}_{2.0016}\text{Si}_{2.0125}\text{P}_{0.9875}\text{O}_{12}$
x=0.1	$\text{Na}_{2.9950}\text{Zr}_2\text{Si}_{2.0054}\text{P}_{0.9946}\text{O}_{11.9896}\text{F}_{0.0104}$
x=0.3	$\text{Na}_{2.9865}\text{Zr}_{1.9986}\text{Si}_{2.0097}\text{P}_{0.9903}\text{O}_{11.9712}\text{F}_{0.0288}$
x=0.5	$\text{Na}_{2.9923}\text{Zr}_{1.9943}\text{Si}_{2.0109}\text{P}_{0.9891}\text{O}_{11.9586}\text{F}_{0.0414}$
x=0.7	$\text{Na}_{2.9781}\text{Zr}_{1.9954}\text{Si}_{2.0094}\text{P}_{0.9906}\text{O}_{11.9503}\text{F}_{0.0497}$
x=1.0	$\text{Na}_{2.9748}\text{Zr}_{1.9952}\text{Si}_{2.0086}\text{P}_{0.9914}\text{O}_{11.9470}\text{F}_{0.0530}$

Table S2

The features of P 2p spectra of NZSPF<sub>x</sub> (x=0 and 0.7) solid electrolytes.

Sample	Bonding energy (eV)	Peak area (CPS eV)
x=0	132.7	40699.15
x=0.7	133.1	39186.20