Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

A facile method for synthesis of sintering dense nano-grained $Na_3Zr_2Si_2PO_{12}$ Na^+-ion solid-state electrolyte

Experiment

Preparation of zirconia-silica precursor. The zirconia-silica precursor was prepared by following the modified classical Stöber approach.[1] In a typical procedure, 23 mL of deionized water, 37 mL of ethanol and 13 mL of $NH_3 \cdot H_2O$ were mixing to buffer solution. Then, 1.8 mL of zirconium butoxide (80 w/w in butanol, Aladdin) and 3.2 mL of tetraethoxysilane (TEOS) were first dissolved in 65 mL of ethanol and subsequently added dropwise into the buffer solution under vigorously stirring over 5 h. The precipitate was received after centrifugation and washed with deionized water and subsequently dried at 60 ^oC for 24 h. Last, the dried precipitate was heated at 900 ^oC for 3 h to collect the precursor zirconia-silica.

Preparation of $Na_3Zr_2Si_2PO_{12}$. To obtain the nano-grained $Na_3Zr_2Si_2PO_{12}$, stoichiometric amounts of salts of sodium and phosphate, and the zirconia-silica precursor were milled using zirconia jar for 4 h. Annealing the mixture at 900 ^oC for 12 h gave the NASICON-structured powder. Sintering the as-pressed powder at 1260 ^oC for 16 h yielded the dense nano-grained $Na_3Zr_2Si_2PO_{12}$. The micron-grained $Na_3Zr_2Si_2PO_{12}$ was also prepared through conventional solid-state reaction method. Stoichiometric amounts of salts of sodium and phosphate, zirconia, and silica were milled for 4 h, annealed at 900 ^oC for 12 h, and sintered at 1260 ^oC for 16 h.

Characterizations. The phase structures and morphologies were examined by X-ray diffraction (XRD, Bruker D2 PHASER, Cu-Kα), scanning electron microscope (SEM, Hitachi, Su8020), and transmission electron microscopy (TEM, JEM-2100F). The distribution of elements was analysed by energy dispersive X-ray spectroscopy (EDX,

HORIBA, EX250). The Na^+-ion conductivity was determined by electrochemical impedance spectroscopy (Autolab PGSTAT302N) with Ag ion-blocking electrodes, under amplitude voltage of 10 mV and frequency range of 10^6-10^{-1} Hz. Na $Na_3Zr_2Si_2PO_{12}$/Na symmetric cells were fabricated to measure the galvanostatic cycling with 1 h deposition and 1 h stripping at current density of 10 μA cm^{-2} and temperature of 25 ^oC.

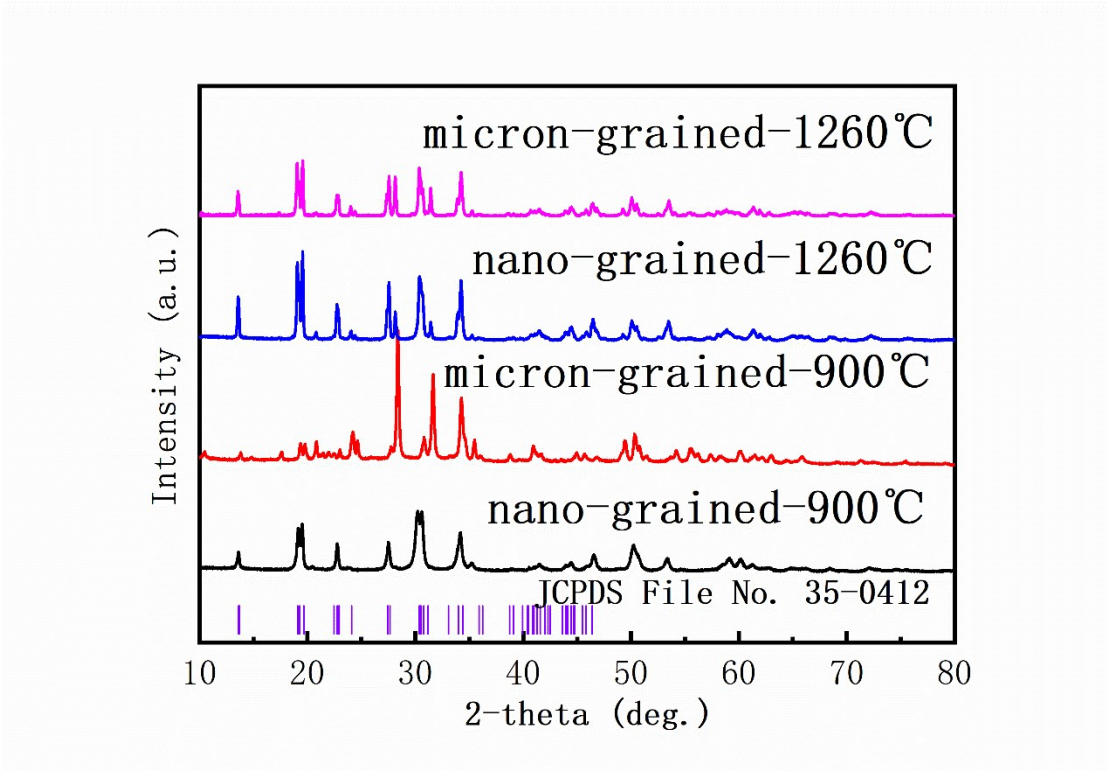

Figure S1. XRD patterns of the nano-grained and controlled micron-grained $Na_3Zr_2Si_2PO_{12}$ annealing at 900 °C and sintering at 1260 °C.

$Na_3Zr_2Si_2PO_{12}$ was prepared with the zirconia–silica binary oxides and salts of sodium and phosphate, annealing at 900 °C and sintering at 1260 °C. Shown in Figure S1 is XRD patterns of the as-prepared samples, revealing the phase comparison of the solid-state electrolyte synthesized by the pre-calcined zirconia–silica precursor method with the conventional solid-state method. Intriguingly, annealing the mixture at 900 °C through the pre-calcined zirconia-silica precursor method displays the desired NASICON structure of a monoclinic phase (space group *C*2/*c*, JCPDS File No. 35-0412), except for a slight Na_3PO_4 impurity. In comparison, processing the raw materials at the same temperature of 900 °C but through the conventional solid-state method presents a mainly monoclinic ZrO_2 phase (JCPDS File No. 37-1484) which is the same as that of the raw monoclinic zirconia, together with Na_3PO_4,

Na_4SiO_4, and NASICON phases, indicating that the raw monoclinic zirconia hardly reacts with the other components under these conditions. Sintering the samples at 1260 °C through both methods presents, unsurprisingly, the NASICON structure.

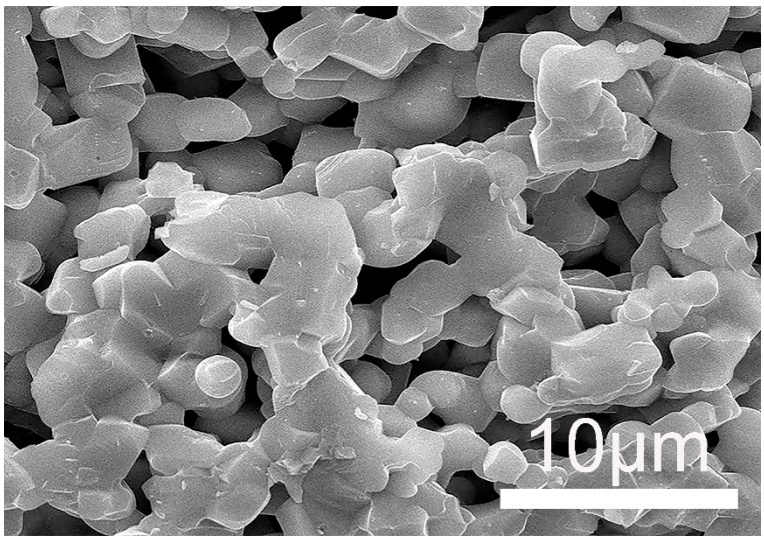

Figure S2. Top SEM view of controlled micron-grained $Na_3Zr_2Si_2PO_{12}$ sintering at 1260 °C.

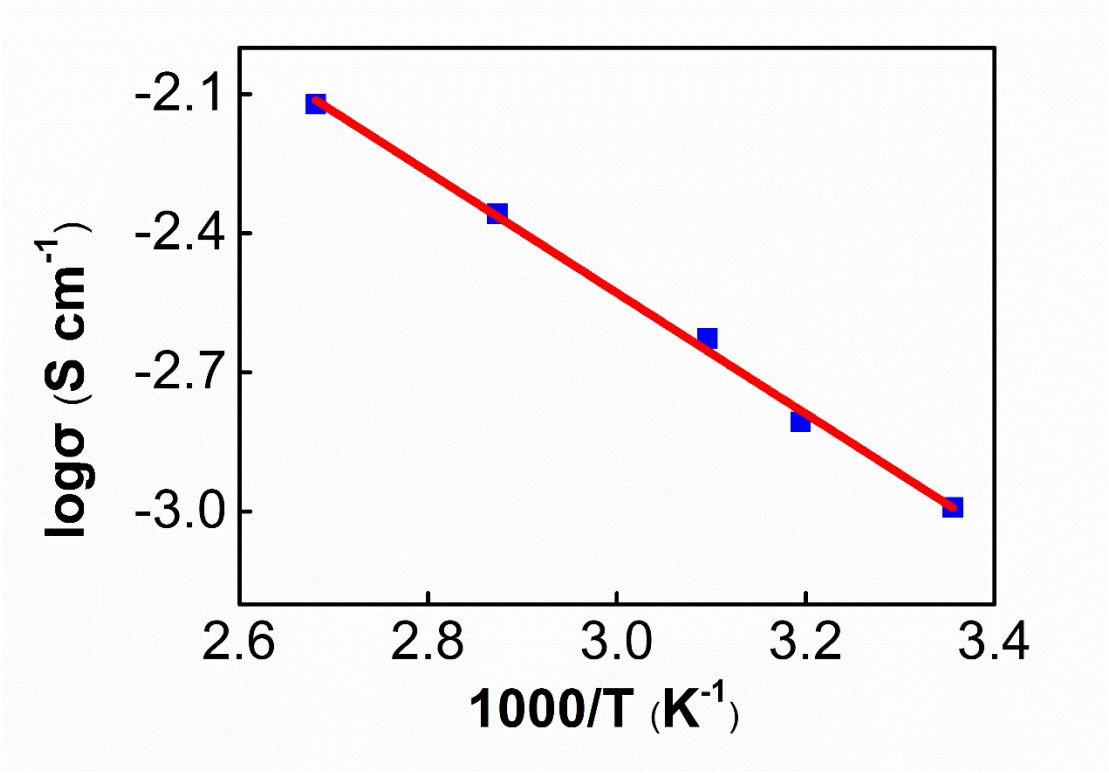

Figure S3. Arrhenius curve of the nano-grained $Na_3Zr_2Si_2PO_{12}$.

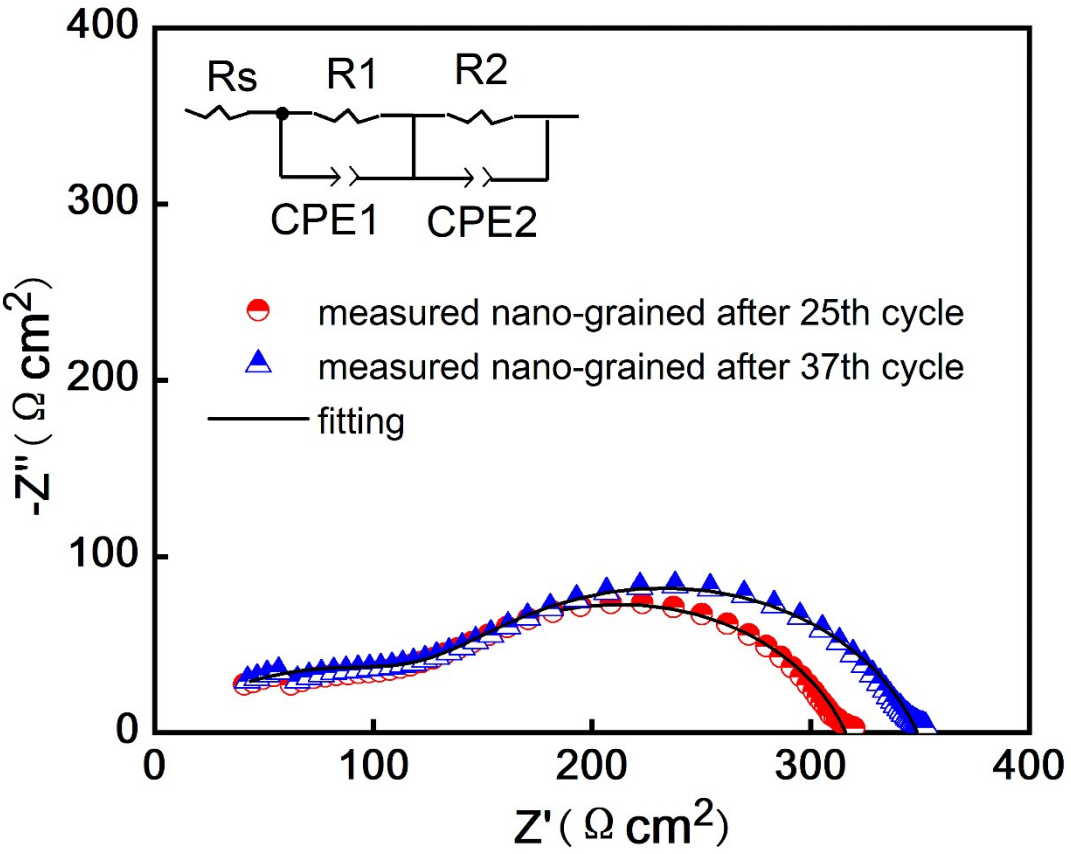

Figure S4. Nyquist plots of Na/nano-grained $Na_3Zr_2Si_2PO_{12}$/Na symmetrical cell for the 25th and 37th cycling. A (Rs)(R1CPE1)(R2CPE2) equivalent circuit (inset of Fig. 3d) is used to fit the impedance spectra, where Rs and R1 represent the grain and grain-boundary resistances of the electrolyte, and R2 represnets the interfacial resistances for Na and electrolyte, CPE represents a constant phase element.

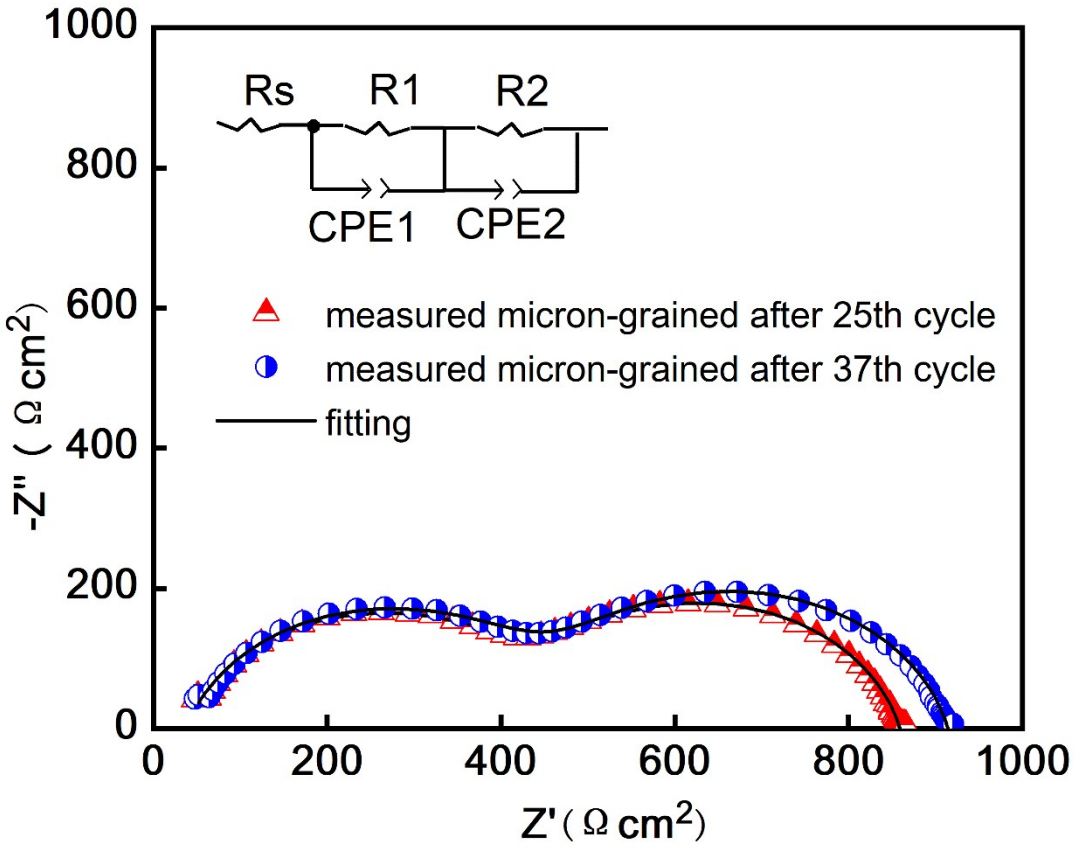

Figure S5. Nyquist plots of Na/micron-grained $Na_3Zr_2Si_2PO_{12}$/Na symmetrical cell for the 25th and 37th cycling.

Supporting Note

1 W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26,** 62.