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Dual Aliovalent Ions doped NASICON Ceramic Filler embedded in PEO-NaTFSI Polymer Matrix for High-Performance Solid state Sodium-ion Battery

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S.1 Experimental Procedures

Ceramic electrolyte synthesis: The compound $Na_{(3+x)}Zr_{(2-x)}Mg_xSc_xSi_2PO_{12}$ with x = 0, 0.05, 0.10 and, 0.20 was synthesized by the conventional solid state synthesis process using sodium carbonate (Na_2CO_3, Alfa Aesar, purity > 99.5 %), zirconium oxide (ZrO_2, Sigma Aldrich, purity > 99 %), scandium oxide (Sc_2O_3, Sigma Aldrich, purity > 99.9 %), magnesium acetate ($C_4H_{14}MgO_8$, Sigma Aldrich, purity > 99 %), silicon oxide (SiO_2, Strem chemicals, purity > 98 %) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$, Alfa Aesar, purity > 98 %). First, the stoichiometric amount of precursors were weighed and mixed using mortar pestle for 2h and then heated for decarburization and denitrification at 500 °C for 12h. The mixture was further ground and mixed using ball mill for 12 h and calcined at 750 °C. Since the phase formation temperature of NZSP is slightly higher (>900 °C), the samples have to be heat treated above this temperature. To avoid the Na loss in ceramics during phase formation, the powder samples were uniaxially pressed with 300 MPa pressure in 1 mm thickness using a die of 10 mm diameter. The NZSP pellets were first sintered in the temperature range, 900-1150 °C to confirm the structure and subsequently all samples were further heated in 1100 - 1160 °C range. For composite fabrication, the ceramic pellets were ball milled for 4 h to obtain nearly uniform particle size.

Composite electrolyte fabrication: Initially, high molecular weight (≥ 600,000) PEO was dissolved in the Acetonitrile solvent and stirred till 12 h at 50 °C. The NaTFSI salt was then added and mixed for 6 h to obtain homogeneous salt dispersion followed by incorporation of NZSP-0.1MS ceramic filler. The stirring continued till 12 h for achieving uniform, ceramic particle distribution in the polymer-salt complex matrix. The mixed solution of polymer-salt and ceramic was cast on a Teflon sheet and dried at 40 °C for 48 h in vacuum. The dried polymer-ceramic composite film was punched in 16 mm dia and kept in the Ar-filled glovebox to avoid moisture attack. The obtained film thickness of the composite electrolyte was controlled to ~ 250 μm and the weight fraction of ceramic filler and polymer matrix was maintained at 50:50.

Positive and negative electrodes preparation: (i)The $Na_3V_2(PO_4)_3$ powder (with 5 % in-situ carbon), Super P (Carbon additive) were mixed using mortar pestle for 30 min. and then stirred on magnetic stirrer with the binder solution {Polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidone (NMP)} for 3 h. The weight ratio of NVP: Super P: PVDF was taken as 85:5:10. The obtained slurry was cast

on an Al foil using doctor blade and the coated positive electrode was dried at 90 °C for 12 h in a vacuum oven. The dried electrode was punched and heated at 90 ºC for 3 h in glove box ante-chamber to remove any residual moisture before use.

(a) (ii) Composite electrodes viz., Catholytes and Anolytes utilized in the present investigation for solid-state cell comprised of NVP Powder, composite electrolyte (PVDF-NaTFSI polymer electrolyte and NZSP-0.1MS ceramic electrolyte) and additive carbon. The weight ratio of NVP:NZSP-0.1MS:PVDF-NaTFI:(SuperP+Acetylene black) was taken as 45:35:10:10. To fabricate Catholyte/Anolyte, Polymer-salt complex electrolyte/binder solution was first prepared by addition of PVDF and NaTFSI salt in NMP and stirred for 12 h. The additive carbon (Super P: Acetylene Black in the ratio 70:30) was added in the binder solution and stirred using Kinki mixer for 20 min. Acetylene Black content was chosen based on several trials to ensure proper electronic wiring. Further, the NVP powder was mixed in the binder-carbon mixture in the Kinki mixer for the next 20 min.. Finally, the NZSP-0.1MS ceramic particle was introduced and further mixed for 20 min.. The thick composite electrode slurry was cast on an Al foil using doctor blade and the coated cathode sheet was dried at 90 °C for 12 h in a vacuum oven.

(b) Characterization:

The X-ray diffraction measurement was performed on sintered ceramic samples using Bruker Advance D8 with Cu-Kα radiation to confirm the crystal structure and phase transformation. The experimental density of the sintered pellets was calculated using Archimedes' method. The scanning electron micrographs in secondary electron and back scattered modes were collected through JEOL-JSM 7000 F electron microscopy. Elemental analysis was performed by EDX mapping and inductively coupled plasma optical emission spectrometry (ICP-OES) with Optima 5300 DV system (PerkinElmer, USA). To measure the ionic conductivity and impedance response, silver paste was coated on opposite surfaces of the sintered electrolytes and heated at 600 °C for 5 min to form non-ohmic contacts. A Novocontrol impedance analyzer (Alfa A high performance frequency analyzer) was used in the temperature range of RT to 90 °C to record the impedance response under an applied AC bias.

(c) Cell fabrication and testing

The all-solid state Na-ion cells were assembled in Swagelok cell and coin cell using ceramic electrolytes (NZSP and NZSP-MS based) and composite electrolytes, respectively, in an Ar- filled glove box (MBraun, Germany) in different configurations Na||NZSP-0||SS, Na||NZMSSP-0.1||SS, Na||NZSP-0||Na and Na|| NZMSSP-0.1||Na symmetric cells, NVP (cathode)|| NZMSSP-0.1||Na half-cell, and NVP (cathode)|| NZMSSP-0.1||NVP (anode) full cell where NZSP-0, NZMSSP-0.1, SS and NVP stands for undoped and doped ceramic electrolyte, stainless steel and sodium vanadium phosphate, respectively. Also, a tiny drop (< 3 μl) of liquid electrolyte (1.0 M of $NaBF_4$ in TEG) was introduced in between the NVP and ceramic electrolyte to provide facile sodium transport pathway in electrode and increase wettability. The active material loading in positive and negative electrodes were in the range of ~ 1-2

mg cm^{-2} and 3-4 mg cm^{-2}, respectively. The transference number and cyclic stability of the symmetric cells were performed using a computer controlled VMP3 (Biologic, France). The galvanostatic charging/discharging measurement on NVP|| NZMSSP-0.1||Na was carried out by BT-2000 battery testing station (Arbin Instruments, USA) in the voltage range of 2.3 to 4.2 V. To fabricate the NVP (cathode) ||NZMSSP-0.1||NVP (anode) symmetric full cell, the active material loading in negative electrode was maintained 2 times higher than the positive electrode according to the following reactions.

At positive electrode: $Na_3V^{3+}{}_2(PO_4)_3 \rightarrow Na_1V^{4+}{}_2(PO_4)_3 + 2Na^+ + 2e^-$ **(1)**

At negative electrode: $2Na_3V^{3+}{}_2(PO_4)_3 + 2Na^+ + 2e^- \rightarrow 2Na_4V^{2+}{}_2(PO_4)_3$ **(2)**

The charging-discharging profile and rate performance of the symmetric full cells were tested in the voltage range of 1.0 to 2.0 V.

Table S.1 *Phase fraction and lattice parameters obtained via Rietveld refinement of XRD data for pure and 10 %MS doped NZSP*

For pure NZSP			
Phases/ Properties	**Monoclinic**	**Rhombohedral**	**ZrO_2**
Phase fraction (%)	86	12.98	0.8
Lattice Parameters	*a = 15.64538 (40) Å* *b = 9.049857 (27) Å* *c = 9.220823 (21) Å* *β= 123.7439°*	*a = 9.29590 (12) Å* *c = 22.19998 (35) Å*	*a = 5.15013 (18) Å* *b = 5.29196 (12) Å* *c = 5.23268 (19) Å* *β= 80.9212°*
For 10 % MS doped NZSP			
Phases/ Properties	**Monoclinic**	**Rhombohedral**	**ZrO_2**
Phase fraction (%)	73.13	23.92	2.94
Lattice Parameters	*a = 15.67112 (66) Å* *b = 9.066555 (37) Å* *c = 9.208783 (23) Å* *β= 123.9223°*	*a = 9.126217 (15) Å* *c = 23.31891 (54) Å*	*a = 5.15719 (69) Å* *b = 5.19951 (19) Å* *c = 5.33304 (19) Å* *β= 80.8159°*

Table S.2 *The ionic conductivity calculated for PEO-NaTFSI/NZSP-0.1MS composite electrolyte at different temperatures.*

Temperature (°C)	Ionic Conductivity (S/m)
30	7.96×10^{-5}
35	9.09×10^{-5}
40	1.27×10^{-4}
45	3.53×10^{-4}
50	5.30×10^{-4}
55	9.03×10^{-4}
60	3.18×10^{-3}

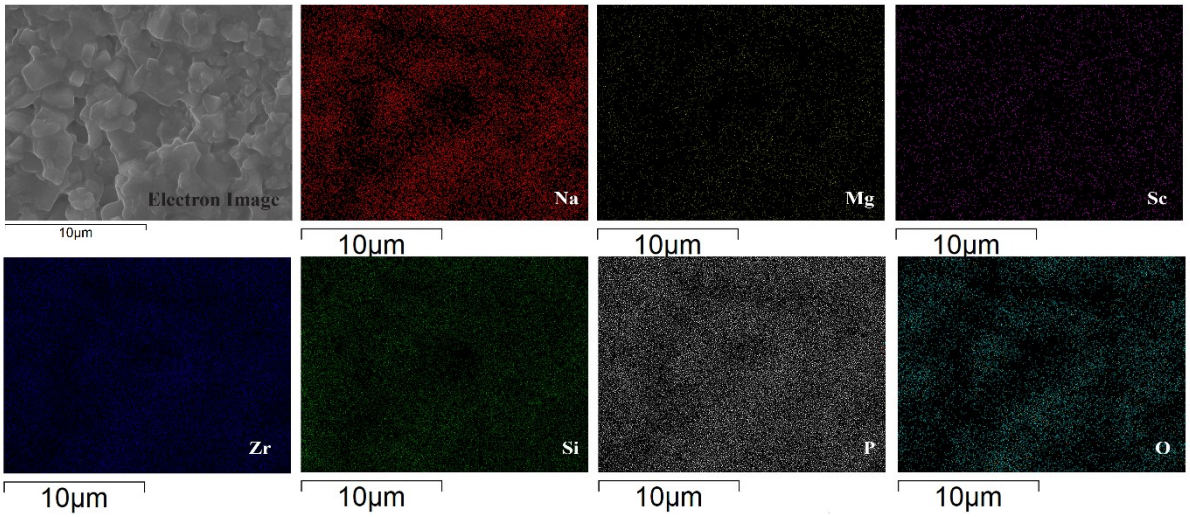

Figure S1. *EDX elemental mapping of various elements in NZSP-0.1 MS ceramic sample.*

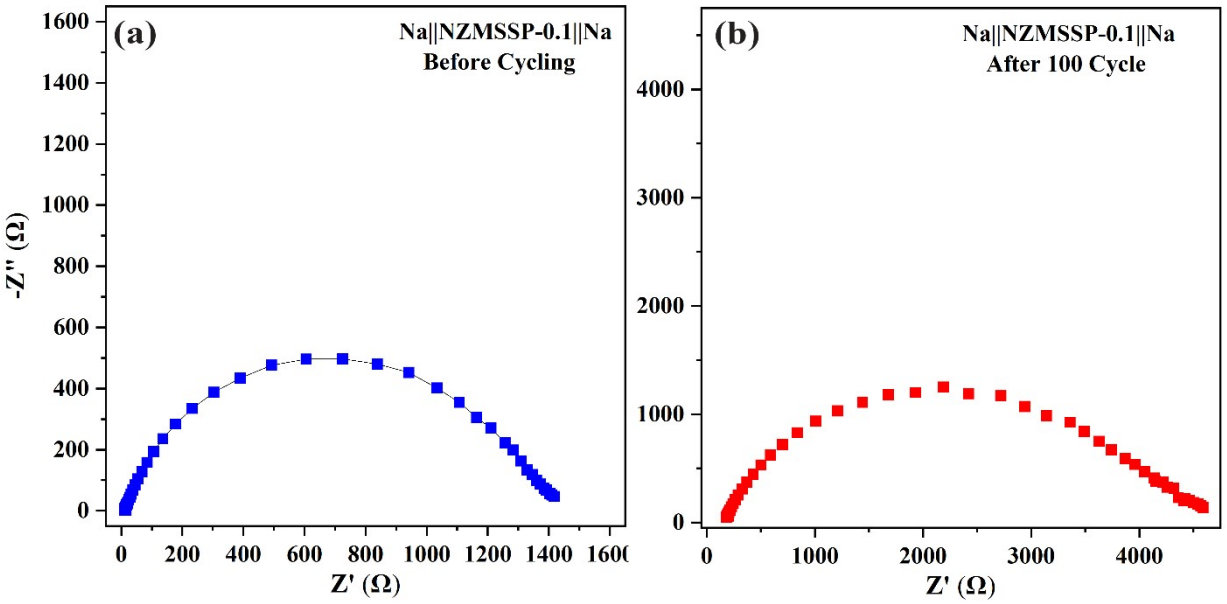

Figure S2. *Impedance spectrum of Na||NZSP-0.1MS||Na symmetric cell before and after cyclic testing*

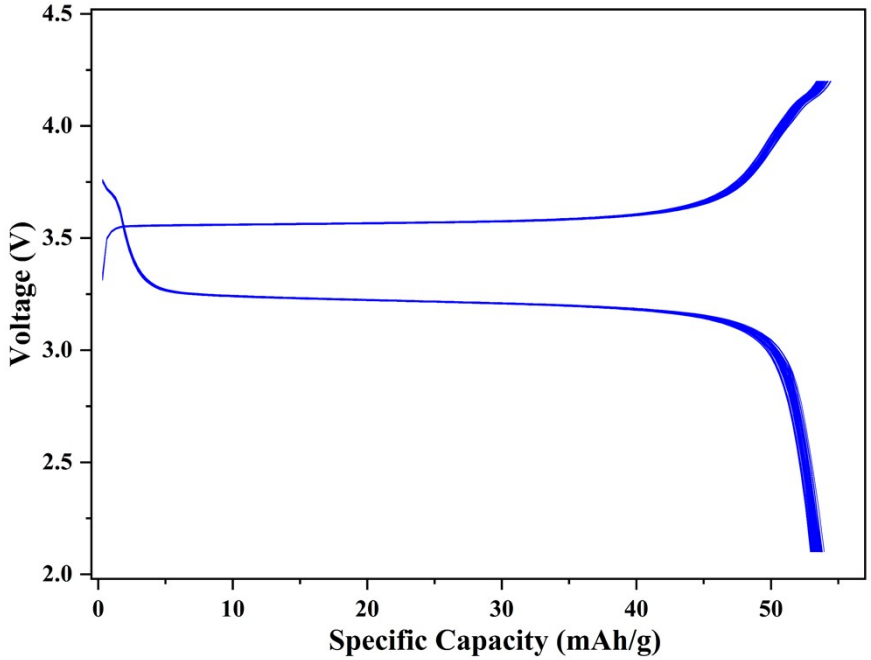

Figure S3. *Room temperature charge-discharge profile at 0.1C rate for Na||NZSP-pure|| NVP cell for 50 cycles*