## Ionically Conducting Inorganic Binders: A Paradigm Shift in Electrochemical Energy Storage

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## Experimental:

## **Commercial Material Sources:**

Sodium trimetaphosphate (product number (PN): T5508), sodium hexametaphosphate (PN:305553), sodium polyphosphate (PN:1.06529), sodium metasilicate (PN:307815), lithium dihydrogen phosphate (PN:442682), lithium polysilicate solution (PN:420719), sodium carboxymethyl cellulose (NaCMC) (PN: 21902), sodium polyacrylate (NaPAA)(PN:420344), sodium alginate (NaALG) (PN:180947), magnesium oxide (PN:243388), lithium hydroxide monohydrate (PN:62528), titanium (IV) oxide (PN:248576) were purchased from Sigma Aldrich. Sodium hydrogen pyrophosphate (PN:13439) from Alfa Aesar. PVDF from Kynar flex (PN:2801-00), Manganese (II) acetate tetrahydrate from Acros Organics, Sodium oxide (PN:11093), dopamine HCI (PN: A11136) were purchased from Alfa Aesar. 25%, ammonia solution (Product code: 1.05432) was purchased from Merck. Graphite from Timcal, IMERYS was used. 1 M LiTFSI in 1:1 v/v ethylene carbonate: dimethyl carbonate from Solvionic (product code: E03750) was used as the electrolyte for LIBs. For SSB, Na beta-alumina (SBA) discs of diameter 10 mm and thickness 0.5 mm were obtained from Ionotec Ltd, England.

### Synthesis:

Binders

Mixed binders: 1:1 wt.% of individual binders were taken, and the ball milled for 2 h at 200 rpm.

LiPO<sub>3</sub>: LiPO<sub>3</sub> was synthesized by heating LiH<sub>2</sub>PO<sub>4</sub> to  $300^{\circ}$ C for 6 hours to dehydrate it.

**Lithium polysilicate (Li<sub>2</sub>Si<sub>5</sub>O<sub>11</sub> -LPS):** 20 wt.% lithium polysilicate aqueous solution was used directly for the aqueous coatings. The solution was sedimented using a few drops of ethanol. The supernatant was decanted, sedimented, and then dried at 120 °C for 12 hours to get solid powder. The resulting powder was characterized and pressed into pellets for impedance measurements.

### **Electrode Materials**

**Hard carbon (HC):** Coconut-shell-derived charcoal powder was imported from Vietnam and ball-milled at 400 RPM for 4 h to reduce its grain size (silicon nitride milling medium was used). It was then heated at 600 °C for 12 h and then at 1200 °C for 4h under argon at a heating rate of 5 °C/minute. The product was used as such without any washing.

**P2-Na<sub>0.7</sub>Mn<sub>0.9</sub>Mg<sub>0.1</sub>O<sub>2</sub> (NMO):** Stoichiometric amounts of Na<sub>2</sub>CO<sub>3</sub>, MnO<sub>2</sub>, and MgO were ball milled for 2h at 500 rpm. The obtained powder was calcined at 900 °C for 12 h in air.

 $Na_3V_2(PO_4)_3$  (NVP): Stoichiometric amounts of  $V_2O_5$ ,  $Na_3P_3O_9$  (STMP), and 30 % carbon S65 as a reducing agent. The precursors were ball milled at 500 RPM for 6 h and then heated at 750 °C for 12 h in argon at the rate of 5 °C/min.

 $Li_4Ti_5O_{12}$  (LTO): Stoichiometric amounts of  $Li_2CO_3$  (with 3% excess Li) and  $TiO_2$  were hand-ground with mortar and pestle and heated at 700 °C for 12 h in an alumina crucible. After cooling, the resulting powder was reground with 10% excess Li and heated at 850 °C for 48 h to form LTO with a cubic spinel structure as verified by XRD analysis.

**LiMn<sub>2</sub>O<sub>4</sub> (LMO):** LMO was synthesized by co-precipitation followed by sintering. The precursors used were Mn (CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and LiOH.H<sub>2</sub>O. Firstly, Mn (CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O was dissolved in 250 ml of deionized (DI) water, and the solution was maintained at 60 °C under constant stirring for five minutes (solution A). Another solution was prepared by first dissolving LiOH.H<sub>2</sub>O in 50 ml of DI water at room temperature under constant stirring, followed by the addition of 10 ml of 25% ammonia solution and stirred further for five minutes (solution B). Solution B was added dropwise to solution A which was under constant stirring resulting in a brownish solution that was heated at 90 °C to obtain a brownish precipitate. The stirring was continued during the evaporation process. The precipitate was extracted from the beaker, ground with mortar and pestle, and heated at 400 °C for 12 h in an alumina crucible. Following this step, the powder obtained was reground and calcined at 820 °C for 12 h to form LiMn<sub>2</sub>O<sub>4</sub> with a cubic spinel structure as verified by XRD analysis.

## **Electrode fabrication**

Hard carbon was studied as an anode for both SIBs and LIBs. For SIBs, we studied HC anode with all three phosphate-based Na-ion conductors (SHMP, STMP, SPP) & one silicate-based Na-ion conductor (SMS). Additionally, sodium hydrogen pyrophosphate (NHPYO) was also studied for SIB. For LIBs, we studied HC anode with two phosphate-based Li-ion conductors (LHPO & LPO) & one silicate-based Li<sup>+</sup> conductor (LPS). We also studied SHMP as a binder for LIB due to its excellent performance and binding properties found in SIBs. HC: PVDF cell was also studied for both SIBs and LIBs for reference. We also studied graphite anode for LIBs with LHPO, LPO LPS, and SHMP binders and compared their performance with PVDF. We also evaluated the performance of phosphate (SHMP, STMP, SPP) and silicate (SMS) binders with NMO and

NVP cathode materials for SIBs. For LIBs, LPO and SHMP binders were tested with LMO and LTO active materials. For comparison, we also evaluated all these four active materials with a PVDF binder.

Active material, conducting carbon (if needed), and binders were taken in desired ratios and ground well with mortar and pestle for about 20 minutes. This dry mixing was followed by mixing and dropwise addition of distilled water to form a uniform and thick slurry. This slurry was coated on pre-cleaned steel current collectors of area 1.13 cm<sup>2</sup> with mass loading of  $\sim$  2-3 mg. The hard carbon and graphite electrodes were dried at 60 °C for 4 h followed by 120 °C for 12 h. For LPO, coatings were made with HC/graphite & LHPO in the desired ratio and then dried at 60 °C, 120 °C, and then 320 °C sequentially for 4 hours each. Heating at 320 °C, dehydrates LHPO, and it gets converted to LPO. Graphite & SHMP did not show good compatibility. 5% of dopamine HCl was added along with SHMP using Tris buffer as the solvent medium and coated on a steel current *collector*. The electrodes were dried at 320 °C to remove dopamine to avoid irreversible capacity loss. All the aqueous coatings were done under ambient conditions at room temperature. The NMO and LMO electrodes were dried at 80 °C for 12 h followed by 300 °C for 4 h. The NVP electrodes were dried at 80 °C for 12 h followed by 200 °C for 4 h.

Fabrication for electrodes in PVDF/NMP system was done in an argon-filled glove box ( $O_2/H_2O$ : <0.1/0.1 ppm). A uniform solution of PVDF in NMP was made by stirring. This was added directly to the active material & carbon (if needed) mixture and ground well-using mortar and pestle to form a thick slurry. The slurry was coated on a steel current collector of the same size and dried at 80 °C for 12 h and 120 °C for 4 h under an argon atmosphere.

#### **Electrochemical measurements:**

Electrochemical studies were performed in Swagelok-type cells. The cells were fabricated in an argonfilled glove box. For SIB, sodium metal was pressed on a steel current collector and used as a counter & reference electrode. A borosilicate glass fiber sheet (GF/C) soaked in the electrolyte was used as a separator. 1.0M NaClO<sub>4</sub> in propylene carbonate (PC)/fluoroethylene carbonate (FEC) (98+2 v/v%) was used as the electrolyte. Anhydrous PC and FEC were dried under molecular sieves before use. For, LIB lithium metal was pressed on the steel current collector, and 1 M LiTFSI 1:1 v/v in ethylene carbonate: dimethyl carbonate was used as the electrolyte. The cells were cycled in an Arbin battery unit maintained at a constant temperature of 25 °C. Different anode half cells were sequentially discharged and charged in different potential windows: - HC/SIB: 0-2.2 V, HC/LIB: 0-3 V, G/LIB: 0-3 V, LTO/LIB: 1-2.5 V. Similarly, different cathode half cells were first charged and then discharged: NMO/SIB: 4.5-1.5 V, NVP/SIB: 3.8-2.5 V, LMO/LIB: 4.3- 3.1 V.

#### **Electrochemical impedance spectroscopy (EIS):**

lonic conductivities were calculated from EIS spectra of pellets of 7 mm diameter and thickness of ~ 1 mm. 50 nm thick Au film was sputtered on each side of the pellet as ion blocking electrodes. The EIS was measured using Zahner/IM6 device from 200-60 °C (top-down) under an argon atmosphere. The measurements were carried out between 100 mHz –1 MHz range with an amplitude of 20 mV. The data were fitted using RelaxIs3 software by applying an equivalent circuit.

#### Materials characterization:

X-ray diffraction (XRD) analysis of the materials was measured by STOE STADI-P instrument with Cu-Kα or Mo-Kα source in transmission mode. Morphological investigations were done by Zeiss, Crossbeam 340, high resolution scanning electron microscope. Thermogravimetric analysis (TGA) & Differential scanning calorimetry (DSC) measurements were carried out in the TA Discovery instrument in an alumina crucible

and aluminum crucibles under an  $N_2$  atmosphere with a heating rate of 10°Cmin<sup>-1</sup>. Fourier-transform infrared spectra (FT-IR) were measured under ambient conditions by PerkinElmer Spectrum Two FT-IR spectrometer.

**Binder characterization:** Pristine sodium phosphate binders were heated at different temperatures (200 °C, 300 °C & 600 °C). XRD and FTIR patterns of these samples were measured to study the effect of temperature on binders (Fig. S3). In another experiment, these binders were dissolved in water, dried, and then heated to different temperatures. XRD and FTIR of these samples were recorded to test their hydrolysis (Fig. S4). To ascertain the possibility of reaction between binder and electrode material, NMO: STMP: C (8:1:1) and NMO: SHMP: C (8:1:1) based thick aqueous slurry were taken and heated at 100 °C, 300 °C & 600 °C. Both XRD and FTIR were recorded for the heated samples (Fig. S6). Until 600 °C, no binder peak was observed, confirming the strong interactions between NMO and binders. The binders are not separated out even by heating at high temperatures (600 °C). The digital photograph in figure S3 shows that after heating at 600 °C, an electrode with PVDF binder is burned out while one with STMP is still intact. Ionic conductivities of all the binders and their mixtures were measured using EIS (Fig. 1f & S4-S8). Their activation energy was calculated from the Arrhenius plot. Table S1 summarizes ionic conductivities and activation energies of different binders and their mixtures.



Figure S1: a) TGA of commercial Na-CMC, NA-alginate & Na-PAA. b) DSC of discharged graphite electrodes with PVDF, SHMP, and LHPO binders. Graphite: binder (9:1) electrodes were discharged to 0 V. The cells were disassembled in the glove box, electrodes were washed with DMC, and then dried at 80°C. The powder was scratched and sealed in the crucible for DSC measurements.



Figure S2: Arrhenius plots of dried (200°C) & air exposed (25°C) samples: a) Na-CMC, c) Na-PAA & e) Naalginate.



**Figure S3: Characterization of directly heated binders**: XRD (Fig. a, c, e, g) & FTIR (Fig. b, d, f, h) patterns of directly heated pristine sodium phosphate binders at 200 °C, 300 °C and 600 °C.



**Figure S4: Characterization of water dissolved binders:** XRD (Fig. a, c, e, g) & FTIR (Fig. b, d, f, h) patterns of water dissolved sodium phosphate binders heated at 100 °C, 300 °C & 600 °C. The binders were dissolved in water in equal concentrations by stirring under the same conditions and then heated at different temperatures.



Figure S5: FTIR of phosphate binders: a) pristine b) heated at 100 °C.



**Figure S6: Characterization of IB-based slurry:** XRD (Fig. a, c) & FTIR (Fig. b, d) of the slurry of NMO: binder: C (8:1:1) heated at 100 °C, 300 °C & 600 °C. XRD patterns of NMO: SHMP/STMP: carbon (8:1:1) electrodes do not show any peak which corresponds to binders until 600 °C. The strong interactions between NMO and binder might have inhibited the crystallization of these binders. The evolution of new unidentified peaks at 600 °C manifests solid-state reactions between the electrode material and phosphate binders. The digital photographs of the NMO electrode with PVDF and STMP binders is shown after heating at 600 °C for 2 hours. The PVDF electrode is burned off due to the low thermal stability & melting point (177 °C) of the PVDF binder as compared to STMP. STMP is stable in this temperature range, and hence the electrode is intact. **Mixed Binders:** 



**Figure S7: Characterization of mixed binders**: a) EIS spectra of mixed binders at 200 °C. b) Arrhenius plot of mixed binders from 200 °C-60 °C. c) FESEM image of HC: (STMP-SPP) (9:1) at 100  $\mu$ m, 10  $\mu$ m and 1  $\mu$ m. b) FESEM image of NMO: (STMP-SPP):C (8:1:1) at 100  $\mu$ m, 10  $\mu$ m, and 1  $\mu$ m. Among the mixed binders, SHMP-STMP shows the least impedance of ~ 80 K $\Omega$ , and SMS-SPP shows the highest impedance of ~ 620 K $\Omega$  at 200 °C. SMS-SPP shows the least AE of 0.69 eV among mixed binders. Details on IC and AE are summarized in table S1.

#### Sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub> – SMS):

The below figure shows the crystal structures of sodium metasilicate.  $Na_2SiO_3$  crystallizes in an orthorhombic system (Pmcn). The structure is a build-up of an isolated  $SiO_4$  tetrahedron connected threedimensionally (3D) through  $NaO_4$  tetrahedra.  $NaO_4$  tetrahedra are connected through a common edge along the c-axis. The distance between the two Na1 atoms is 3.914Å along the c-axis. Interestingly these  $Na1O_5$  polyhedra are populated along the a-axis as well. However, there is no direct connection between Na1 atoms along the a-axis. The distance between the two Na1 atoms along the a-axis is 3.5Å. The  $Na_2O_5$ polyhedra are also running along the a-axis, and they are connected through common corner-sharing oxygen atoms. The distance between Na2 atoms is 3.417 Å. The  $Na_2O_5$  polyhedra are diagonally arranged with respect to  $Na1O_5$ . The distance between Na1 and Na2 atoms is 3.576 Å. Though  $Na1O_5$  polyhedra are not connected directly along the a-axis, they are connected diagonally to  $Na_2O_5$  through a common edge, and this results in a jig-jag pathway for Na<sup>+</sup> diffusion along the a-axis. This unusual inter and intra connection of Na<sub>1</sub>O<sub>5</sub> and Na<sub>2</sub>O<sub>5</sub> polyhedra is leading to 3D paths for Na<sup>+</sup> diffusion in the structure. The 3D diffusion paths for Na<sup>+</sup> diffusion are vital for binder applications as the transport of ions will be more efficient and eliminate any orientation issues.



**Figure S8: Characterization of sodium metasilicate (SMS) binder**: a) XRD b) FT-IR patterns of pristine SMS and heated samples at 100 °C, 300 °C, 600 °C, and 1000 °C; c) EIS spectra of SMS1000 at 200 °C; d) Arrhenius plot of SMS1000 between 200 °C-60 °C; e) TGA curve showing thermal stability of SMS1000 between 40 °C to 1000 °C; f) FESEM images of HC: SMS (9:1) anode & NMO:SMS: C (8:1:1) cathode. SMS was heated at 1000 °C for 4 hours (SMS1000). This was used for IC measurements so as not to overestimate IC due to H<sup>+</sup> conduction.



Lithium hydrogen phosphate ( $LiH_2PO_4 - LHPO$ ) and Lithium phosphate ( $LiPO_3 - LPO$ ):

**Figure S9: Characterization of lithium phosphate (LHPO & LPO) binders.** a) XRD of LHPO (LiH<sub>2</sub>PO<sub>4</sub> - commercial) and LPO (LiPO<sub>3</sub>) synthesized after heating LHPO at 400 °C. b) FTIR of LHPO and LPO. c) Impedance of LPO binder at 200 °C & LHPO binder at 200 °C (inset). d) Arrhenius plot of LHPO and LPO measured between 200°C and 60 °C. e) TGA of LHPO from 40 °C to 1000 °C. The XRD patterns of LHPO and LPO are indexed to their pure forms. Impedance of LHPO and LPO at 200 °C are 1.7 x 10<sup>4</sup>  $\Omega$  and 8.1 x 10<sup>5</sup>  $\Omega$ . The  $E_a$  of LHPO and LPO are 0.72 eV & 0.73 eV respectively. The ionic conductivities of LHPO and LPO at 200 °C are found to be 2 x 10<sup>-5</sup> S/cm & 4 x 10<sup>-7</sup> S/cm respectively. The wt.% of water in LHPO (LiPO<sub>3</sub>-H<sub>2</sub>O) corresponds to 17.3 % which dehydrates upon heating and 82.65 wt.% of material is retained exhibiting an excellent thermal stability of LPO until 1000 °C.



**Figure S10:** Characterization of Lithium polysilicate binder: a) XRD. b) FTIR. c) EIS at 160 °C. d) Arrhenius plot from 160 °C – 60 °C. e) TGA f) FESEM of graphite: LPS (9:1) & LMO: LPS:C (8:1:1) pristine electrodes. LPS powder used above was derived from 20 wt. % solution of LPS and dried at 120 °C as mentioned in synthesis section. XRD shows that LPS is amorphous. The impedance spectrum shows the impedance of 1.98x10<sup>8</sup>  $\Omega$  at 160 °C. The ionic conductivity at 160 °C is 1 x 10<sup>-7</sup> S/cm. TGA shows the 10% wt. loss until 200 °C and 13.6% wt. loss until 1000 °C.



**Figure S11: Characterization of sodium hydrogen pyrophosphate (Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>-NHPYO).** a) XRD, b) TGA, c) EIS at 300 °C, d) Arrhenius plot from 300 °C – 60 °C, e) First 5 cycles of HC:NHPYO (9:1) at 10 mA/g, f) Cycling performance of HC:NHPYO (9:1) at 10 mA/g. NHPYO has a crystalline structure. Until 200 °C, there is no weight loss. Until 1000 °C, it shows a weight loss of 9.5 %. The impedance at 300 °C is ~54 K $\Omega$  and the corresponding conductivity is 6.3x10<sup>-6</sup> S/cm. The reversible capacity of HC:NHPYO (9:1) at 10 mA/g is 178 mAh/g with a capacity retention of 82%.

Binder E <sub>a</sub> (eV)		Conductivity (S/cm) @ 60 °C	Conductivity(S/cm) @ 200 °C	
SHMP	0.89	6.5 x 10 <sup>-10</sup>	5.3 x 10 <sup>-6</sup>	
STMP-c	0.66	6.1 x 10 <sup>-11</sup>	1.2 x 10 <sup>-7</sup>	
STMP-a	0.94	4.7 x 10 <sup>-10</sup>	5.0 x 10 <sup>-6</sup>	
SPP	0.87	4.2 x 10 <sup>-10</sup>	2.4 x 10 <sup>-6</sup>	
NHPYO	0.60	8.5 x 10 <sup>-10</sup>	2.9 x 10 <sup>-7</sup>	
SMS	0.52	5.3 x 10 <sup>-10</sup>	1.5 x 10 <sup>-7</sup>	
LHPO	0.72	1.6 x 10 <sup>-8</sup>	2.0 x 10 <sup>-5</sup>	
LPO	0.73	3.7 x 10 <sup>-10</sup>	4.0 x 10 <sup>-7</sup>	
LPS	0.76	2.9 x 10 <sup>-10</sup>	*1.0 x 10 <sup>-7</sup>	
SHMP-STMP	0.85	6.2 x 10 <sup>-10</sup>	4.1 x 10 <sup>-6</sup>	
STMP-SPP	0.89	1.7 x 10 <sup>-10</sup>	1.1 x 10 <sup>-6</sup>	
SHMP-SPP	0.85	3.5 x 10 <sup>-10</sup>	1.8 x 10 <sup>-6</sup>	
SMS-SPP	0.69	5.8 x 10 <sup>-10</sup>	5.1 x 10 <sup>-6</sup>	
NaCMC	-	#1.1 x 10 <sup>-10</sup>	1.4 x 10 <sup>-8</sup>	
NaPAA	-	8.7 x 10 <sup>-10</sup>	2.5 x 10 <sup>-6</sup>	
NaALG	-	1.1 x 10 <sup>-10</sup>	1.3 x 10 <sup>-7</sup>	

**Table S1:** Ionic conductivities of pure ICIB and their 1:1 mixtures at 60 °C and 200 °C, STMP was crystalline as received (STMP-c), therefore, it was ball milled at 600 RPM for 4 hours to make it amorphous (STMP-a). \*Measured at 160 °C, #measured at 100°C.



**Figure S12:** *Digital images of ICIB (SHMP) binder. a) normal b) magnified*. SHMP was dissolved in distilled water by stirring. The uniform solution was cast in to a Petri dish and dried at 80 °C overnight. The sample sticks strongly to the glass substrate.



Figure S13: XRD patterns of different electrode materials. a) NVP, b) NMO, c) LTO, & d) LMO.



Figure S14: FESEM images of different electrode materials. a) NVP, b) NMO, c) LMO, & d) LTO

#### Sodium ion battery (SIB):

Anode half cells (HC) and cathode half cells (NMO & NVP) were studied with sodium phosphate and sodium silicate binders in 5% and 10% composition for SIB. Fig. S15-S20 show first five cycles & rate capabilities of these electrode materials with different binders. Fig. S21 shows the high temperature cycling performance for NMO-SHMP and NVP-STMP cathodes. Their performance is also compared with PVDF based cells. The reversible capacities and capacity retention of different electrode materials with different binders is summarized in table S2 and S3 respectively. Fig. S22 shows large area fabrication with SHMP binder and electrochemical performance of HC and NMO electrode materials on Cu and Al foils respectively.



*Figure S15: First 5 cycles of hard carbon with different binders in the ratio 9:1 a*) *SHMP, b*) *STMP, c*) *SPP, d*) *SMS, e*) *PVDF* & *f*) *STMP-SPP (MB)* 



*Figure S16: a) First 5 cycles of HC:SHMP:C (8:1:1). b) First 5 cycles of HC:PVDF:C (8:1:1). c) rate test for HC: binder: C (8:1:1)* To impart high-rate capability, conductivity is an important factor, hence conducting carbon (S65) was added to test at 60 mA/g for longer cycles.



**Figure S17: First 5 cycles of hard carbon with different binders in ratio 95:5** a) SHMP, b) STMP, c) SPP, d) SMS, e) PVDF & f) Cyclic performance. In the cyclic performance, it can be seen that the reversible capacities for SHMP, STMP, SPP, SMS, PVDF binders are 243 mAh/g, 158 mAh/g, 234 mAh/g, 196 mAh/g and 261 mAh/g respectively. They show capacity retention of ~99%, 95%, 90%, 94%, 63% for SHMP, STMP, SPP, SMS and PVDF respectively after 60 cycles. The first 30 cycles for SHMP and PVDF seem to overlap but at higher rates SHMP outperforms PVDF due its excellent adhesive property and IC.



*Figure S18: First 5 cycles of NMO, carbon and different binders in ratio 8:1:1 a*) *SHMP, b*) *STMP, c*) *SPP, d*) *SMS, e*) *STMP-SPP & f*) *PVDF*.



*Figure S19: First 5 cycles of NMO: binder: C (85:5:5), a) SHMP; b) STMP; c) SPP; d) Rate tests of NMO: binder: C (85:5:5).* 



**Figure S20: First 5 cycles of NVP, carbon and different binders in ratio 8:1:1** a) SHMP, b) STMP, c) SPP, d) SMS, e) STMP: SPP & f) PVDF



**Figure S21: High temperature cycling performance** a) NMO: SHMP:C (8:1:1), b) NVP:STMP:C (8:1:1) compared with PVDF binder. The best performing binders for NMO and NVP cathodes were studied at 40 °C.

Binder	Reversible capacity (mAh/g)			
	HC: binder (9:1)	NMO: binder: C	NVP: binder: C	
	@10 mA/g	(8:1:1), @C/10	(8:1:1), @C/10	
STMP: SPP (1:1)	340	136	105	
SHMP	306	137	111	
STMP	283	152	114	
SPP	262	126	95	
SMS	276	142	97	
NHPYO	178	-	-	
PVDF	243	159	102	

# Table S2: Showing reversible capacities for SIB with different binders

 Table S3: Shows capacity retention with different systems in SIB

Binder	Capacity retention (%)				
	HC: binder (9:1)	HC: binder (95:5)	NMO: binder: C	NMO: binder: C (85:5:10)	NVP: binder: C (8:1:1)
	(after 70 cycles)	(after 60 cycles)	(8:1:1) (after 150 cycles)	(after 120 cycles)	(after 150 cycles)
STMP: SPP	82	-	69	-	96
SHMP	83	99	87	62	96
STMP	-	95	61	57	94
SPP	-	90	66	72	97
SMS	-	94	74	-	95
NHPYO	82 (30 cycles)	-	-	-	-
PVDF	60	63	59	-	95



**Figure S22:** Large area fabrication and corresponding electrochemical performance. a) First five cycles of HC: SHMP: D-HCl (85:10:5) on Cu foil at 10 mA/g. b) First five cycles of HC: SHMP: C (80:10:10) on carbon coated on Al foil at C/10. To show large area fabrication, hard carbon: SHMP: dopamine HCl were taken in the ratio 85:10:5 & dry mixed for at least 15 minutes and then tris buffer (10mM, pH 8.5) was used as a solvent to formulate a uniform slurry. This slurry was coated on the copper foil using a doctor blade. The buffer triggers self-polymerization of dopamine on the surface of hard carbon<sup>1</sup>. This allows a better adhesion with the copper foil. The coating was allowed to dry at room temperature for few hours and then at 120 °C for 12 hours. The coating was flexed and rolled to test its mechanical strength as show in inset of figure a). Similarly, for cathode, uniform aqueous slurry of NMO: SHMP:C (8:1:1) was directly coated on carbon coated aluminum foil without any modifications. The coatings on Al foil were robust enough to be flexed and rolled as shown in the inset of figure b). The circular electrodes of diameter 12 mm were punched and fabricated in Swagelok cells with Na metal as the CE and 1.0 M NaClO<sub>4</sub> in PC/FEC (98+2 v/v %) as the electrolyte to test their electrochemical performance.

**Lithium-ion battery**: Anode half cells (HC, graphite & LTO) were made with lithium phosphate and lithium silicate-based binders for LIBs. Similarly, cathode half cells for LMO were also studied. Fig. S23, shows first five cycles of LMO & LTO electrodes with different binders. Fig. S24 shows electrochemical performance of different electrode materials with LPS binder. The electrochemical performance of four different electrode materials with different binders is summarized in table S4 & S5.



**Figure S23:** First 5 cycles of LMO and LTO electrodes with different binders a) LMO: SHMP:C (8:1:1) b) LTO: SHMP:C (8:1:1) c) LMO: LPO: C (8:1:1) d) LTO: LPO:C (8:1:1) e) LMO: PVDF:C (8:1:1) f) LTO: PVDF: C (8:1:1).



**Figure S24: Electrochemical performance of HC, graphite, LMO and LTO electrodes with LPS** binder a) First 5 cycles of hard carbon with LPS binder b) Rate capability of hard carbon with LPS and PVDF binder. c) First 5 cycles of graphite with LPS binder d) Rate capability of graphite with LPS and PVDF binder. e) First 5 cycles of LMO cathode with LPS binder f) Rate capability of LMO cathode with LPS and PVDF binder. g) First 5 cycles of LTO anode with LPS binder h) Rate capability of LTO anode with LPS and PVDF binder. In case of LMO and LTO, 5% PDA was mixed to the slurry. Those electrodes were dried at 80°C for overnight and 320 °C for 4 h.

Binder	Reversible capacity (mAh/g)				
	Graphite: binder (9:1), @C/10	HC: binder (9:1), @10	LMO: binder: C (8:1:1), @C/10	LTO: binder: C (8:1:1), @C/10	
		mA/g			
LHPO	403	301	-	-	
LPO	382	259	105	147	
LPS	292	214	79	120	
PVDF	368	264	124	179	
SHMP	390	215	110	154	

**Table S4**: Showing reversible capacities for LIB with different binders.

Table S5: Showing capacity retention with different binders in LIB

Binder	Capacity retention (%)				
	Graphite: binder (9:1) (after	HC: binder	LMO: binder: C	LTO: binder: C (8:1:1),	
	60 cycles)	(9:1)	(8:1:1)	(after 50 cycles)	
		(after 70	(after 45 cycles)		
		cycles)			
LHPO	84.8	85.4	-	-	
LPO	91	69	61	94	
LPS	91	89	68	87	
PVDF	~100	65	76	94	
SHMP	95	87	69	97	

**Solid state battery**: SSB using PVDF, IB was fabricated. SHMP and mixed binder (MB) i.e. 1:1 mixture of STMP-SPP was used to cycle SSB. MB shows the 1<sup>st</sup> discharge capacity of 11 mAh/g at C/60 which fades out in subsequent cycles at RT. SHMP showed decent capacity retention at 80 °C and is described in the manuscript. Its capacity fading is ascribed to the rise in impedance with cycling (Fig. S25) Capacity with PVDF binder is nil at RT. At 80 °C, it was no better than 2.1 mAh/g. Similar studies were also performed with organic binders (Fig. S26). Table, S6 describes the performance of SSB. The performance of IB outperforms with that of PVDF for pure SSB.



*Figure S25: Impedance spectra of NMO: SHMP:C/SBA/Na at 80 °C after 10 cycles & 25 cycles.* Impedance is ~ 198 K $\Omega$  after 10 cycles and 3.8 K $\Omega$  after 25 cycles.



**Figure S26:** a) Impedance spectra of NMO: CMC:C/SBA/Na at RT, 80 °C and with LE (inset) b) Impedance spectra of NMO: PAA:C/SBA/Na at RT 80 °C. c) First five cycles of NMO:CMC:C/SBA/Na with a drop of LE at RT d) Cyclic performance of SSB: NMO: binder: C (8:1:1)SBA/Na) with NaCMC at RT, NaCMC with LE at RT and NaPAA at 80 °C.

**Table S6**: Showing impedance and electrochemical performance of SSB: Na/SBA/NMO-binder-C(8:1.1) at C/60. # is not a pure SSB. \*Performance of NMO:PVDF:C (8:1:1)/Na with liquid electrolyte at C/10 taken from figure 2(e).

Binder/ Temperature	Impedance	1 <sup>st</sup> & 2 <sup>nd</sup> discharge capacity (mAh/g)	Capacity after
			(n <sup>th</sup> cycle)
PVDF/RT	~ 400 KΩ	0.014, 0.011 @C/60	0.00 (30)
PVDF/80 °C	-	2.18, 2.14 @C/60	1.75 (30)
<pre>#PVDF/RT/drop of LE</pre>	234 Ω	145, 133 @C/10	113 (10)
MB (STMP-SPP)/RT	-	11, 0.90 @C/60	0.13 (30)
SHMP/RT	80.5 KΩ	-	-
SHMP/80 °C	6.8 ΚΩ	99, 84	<b>68</b> (10)
PVDF/LE based battery*	-	177, 159 @C/10	140 (10)
Na-CMC/RT	1.8 MΩ	0.15 mAh/g @C/60	

Na-CMC/80 °C	137 ΚΩ	Does not work	
Na-CMC/RT with LE	6.9 KΩ	30, 29 @C/10	
Na-PAA/RT	350 KΩ	Does not work	
Na-PAA/80 °C	120 ΚΩ	0.11 mAh/g @C/60	

#### Morphological investigations:

Detailed morphological and elemental analysis was carried for different binders for both pristine (noncycled) and cycled electrodes. Cycled electrodes were measured after washing in DMC and drying at 80 °C. The results from FESEM and elemental analysis (Fig. S27- S45) show that all the binders are well distributed over the coating. Fig. S28 shows high magnification (1  $\mu$ m) FESEM and EDX of HC:SHMP (9:1) electrode, where it can be seen that binder has a good interaction with the active material and does not look to be separated out. The binder distribution is uniform and active material has not degraded after cycling. In some images, glass fibers from separators can be seen for post cycling samples. Post cycling samples show Cl which must be from the electrolyte. Results with PVDF binder have also been shown. Overall, the results give an idea of binder distribution in pristine and cycled electrodes. The ICIBs are robust enough to handle electrochemical cycling without pulverizing or degrading the material. This is also in agreement with capacity retention values.



*Figure S27: FESEM, EDX spectra and mapping of Hard carbon: SHMP (9:1) pristine electrode.* 



**Figure S28:** FESEM, EDX spectra and mapping of hard carbon: SHMP (9:1) pristine electrode at high magnification (1  $\mu$ m scale). The binder components (Na, P & O) are uniformly distributed over hard carbon even on micro level.)



Figure S29: FESEM, EDX spectra & mapping of hard carbon: SHMP (9:1) cycled electrode.



*Figure S30:* FESEM, EDX spectra & mapping of HC: SMS pristine electrode.



*Figure S31*: FESEM, EDX spectra & mapping of hard carbon: SMS (9:1) cycled electrode.



**Figure S32:** FESEM of cycled electrodes; a) HC: STMP (9:1) at 20 μm b) HC: STMP (9:1) at 2 μm c) HC: SPP (9:1) at 2 μm d) HC: SPP (9:1) at 2 μm



*Figure S33:* FESEM, EDX spectra & mapping of hard carbon: LPO (9:1) pristine electrode.



**Figure S34:** FESEM images of pristine electrodes a) hard carbon: (STMP- SPP) (9:1) at 100  $\mu$ m, b) hard carbon: (STMP- SPP) (9:1) at 1  $\mu$ m. c) Graphite: LPO (9:1) at 100  $\mu$ m d) Graphite: LPO (9:1) at 1  $\mu$ m



*Figure S35:* FESEM, EDX spectra & mapping of graphite: LPS cycled.



Figure S36: FESEM, EDX spectra & mapping of HC: PVDF (9:1) pristine electrode.



*Figure S37:* FESEM, EDX spectra & mapping of HC: PVDF (9:1) cycled electrode.



*Figure S38:* FESEM, EDX spectrum & elemental mapping of NMO: SHMP: C (8:1:1) pristine electrode. EDX spectrum and mapping corresponds to (a).



*Figure S39:* FESEM, EDX spectrum & elemental mapping of NMO: SHMP: C (8:1:1) cycled electrode. EDX spectrum and mapping corresponds to (a).



*Figure S40:* FESEM & EDX spectrum of: a-c) NMO: SMS: C (8:1:1) pristine electrode. d- f) NMO: SMS: C (8:1:1) cycled electrode.



*Figure S41:* FESEM & EDX spectrum of: a-c) NVP: SHMP: C (8:1:1) pristine electrode. d- f) NVP: SHMP: C (8:1:1) cycled electrode.



*Figure S42:* FESEM & EDX spectrum of: a-c) NVP: STMP: C (8:1:1) pristine electrode. d- f) NVP: STMP: C (8:1:1) cycled electrode.



**Figure S43:** FESEM & EDX spectrum of: a-c) LMO: LPO: C (8:1:1) pristine electrode. d- f) LMO: LPO: C (8:1:1) cycled electrode, g-i) SEM of LMO: LPS: C (8:1:1) pristine electrode and its EDX spectrum



*Figure S44:* FESEM images and EDX spectrum of NMO: PVDF:C (8:1:1) pristine electrode. EDX spectrum and mapping corresponding to (a)



*Figure S45:* FESEM images and EDX spectrum of NMO: PVDF:C (8:1:1) cycled electrode. EDX spectrum and mapping corresponding to (b).



Figure S46: Architecture and picture of the Swagelok cell used for electrochemical studies



**Figure. S47** XP spectra of hard carbon. C-C: Aliphatic chain of adventitious carbon; C-O:C-O-C environment of adventitious carbon; C=O: CO<sub>2</sub> environment of adventitious carbon



**Figure. S48** a) XRD and b) FT-IR patterns of LTO and modified-LTO (M-LTO). M-LTO was prepared by dispersing LTO in 1M HNO<sub>3</sub> for 4h, followed by overnight drying at 80 °C.

#### **References:**

1. Lee, H., Dellatore, S. M., Miller, W. M. & Messersmith, P. B. Mussel-Inspired Surface Chemistry for Multifunctional Coatings. *Science* **318**, (2007).