Tailored nonwoven supported non-flammable quasi-solid electrolyte enables an ultra-stable sodium metal battery

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Experimental:

All chemicals and materials, such as poly(vinylidene fluoride-hexafluoropropylene) P(VdF-HFP), (Mw \sim 455,000 g/mole, Sigma-Aldrich), acetate (Alfa), methyl propionate, trimethyl phosphate, sodium hexafluorophosphate and lithium hexafluorophosphate (Sigma-Aldrich) are used without further purification.

Electrolyte Preparation

Quasi-solid-state electrolytes are developed by following a simple solution cast procedure. First, by continuously stirring P(VDF-HFP) in acetone using a magnetic stirrer and heating at 60°C, 15 wt% P(VDF-HFP)/acetone was prepared. After P(VDF-HFP) was completely dissolved, the viscous solution was poured onto a nonwoven (NW) sheet (Oripol Industries, INDIA) and kept in a vacuum oven at 70 °C for 24 h to form a nonwoven textile-supported solid polymer mat (NW-SPM). The flexible dried mat is soaked/swallowed to form a gel within a particular liquid electrolyte to prepare a nonwoven-supported quasi-solid polymer electrolyte (NW-QSSE). The prepared compositions are the following.

NW-SPM: A nonwoven fabric with a 15% w/w coating of PVDF-HFP polymers. The fabric is rolled to reduce the thickness of 112 \mu m.

NaQSSE\textsubscript{X}: NW-SPM in 1M NaPF\textsubscript{6} in (PC: TMP: FEC (w/w)) \times [X=A,B,C; A: 85/10/5; B: 85/7/8; C:85/5/10].

A. Sample Characterization

A Bruker diffractometer (USA) with Cu K\alpha radiation (\lambda = 1.5\AA) was used to record The X-ray diffraction (XRD) patterns of the developed electrolytes. The thermal stability of the QSSE was investigated by TGA (PerkinElmer, Pyris Diamant, SDT 1606, USA) at a scanning rate of 10°C/ min from RT to 650°C in an inert atmosphere (nitrogen). The DSC was carried out with a heating rate of 10 °C/ min to measure melting temperature and melting enthalpies. The surface morphology of the as-prepared films was determined by field emission scanning electron microscopy (FESEM) (MERLIN, Germany). A PHI 5000 Versa Probe II system with monochromatic Al K\alpha (1486.6 eV) radiation at 100 W power was used for X-ray photoelectron spectroscopy (XPS). For binding energy calibration, the C 1s (284.8 eV) spectrum was fixed as the baseline spectrum.

B. Electrochemical characterization

An LCR meter (biological instrument) was used for the conductivity experiment. Electrolyte films were held between a pair of stainless-steel blocking electrodes (diameter ~ 16 mm) for electrical measurements.

A cell as Na|| NaQSSE\textsubscript{C} ||SS was constructed to measure cyclic voltammetry, where SS ~ stainless steel Na ~ sodium metal. Cells (CR2032 type button cells) were fabricated in an Ar-filled glove box (model Mbraun, Labstar) where O\textsubscript{2}
and H₂O were kept at <0.5 ppm. Electrochemical voltage stability was measured using the LSV technique at a scan rate of 5 mV/s. A VMP3 (Bio-Logic) electrochemical analyzer was used. The transfer number (T_{Na+}) of the QSSE is measured using a symmetrical Na||NaQSSE_{C}||Na cell. The electrolytes are sandwiched between two 14 mm diameter Na metal electrodes. The Na metal acts as the counter and working electrode. The Na-ion transfer number was measured using electrochemical impedance spectroscopy and chronoamperometry with an external DC potential step of V = 20 mV in an electrochemical analyzer (Bio-Logic, model VMP3). All the electrochemical experiments were carried out at room temperature.

To prepare the cathode, carbon-coated Na₃V₂(PO₄)₃, acetylene black, and sodium carboxymethyl cellulose (NaCMC) as an aqueous-based binder were mixed in a weight ratio of 70:20:10 in deionized water. A tabletop coating machine was then used to cast the smooth slurry onto an aluminum foil sheet (0.20 mm). These electrodes, as prepared, were dried in a vacuum oven at a temperature of 80 °C for 24 hours to get a loading of 1-1.5 mg/cm² (0.117-0.175 mAh/cm²) of NVP. A cycle tester (Arbin BT200; accuracy up to 0.02% for low power and 0.05% for high power applications) was used to charge/discharge Na||NVP cells at different current densities.

![Fig. S1: Optical image of as developed NaQSSE_{C} electrolyte.](image)

![Fig. S2: Flammability test of the as-developed NaQSSE_{C} electrolyte.](image)
Table S1: Z fit parameters of Nyquist plot of Na||NaQSSEc||NVP cell before and after cycling.

Equivalent circuit:

\[ R_B + \frac{Q_{SEI}}{R_{SEI}} + \frac{Q_{CT}}{R_{CT}} + W_{d1} \]

=== Z fit Analysis before cycling ===

Results:

\[ R_B = 26.59 \text{ Ohm} \]
\[ Q_{SEI} = 48.65 \times 10^{-9} \text{ F.s}^{(a - 1)} \]
\[ R_{SEI} = 651.50 \text{ Ohm} \]
\[ Q_{CT} = 3.43 \times 10^{-6} \text{ F.s}^{(a - 1)} \]
\[ R_{CT} = 1100.87 \text{ Ohm} \]
\[ W_{d1} = 15.44 \text{ Ohm} \]

=== Z fit Analysis after cycling ===

Results:

\[ R_B = 17.54 \text{ Ohm} \]
\[ Q_{SEI} = 52.60 \times 10^{-9} \text{ F.s}^{(a - 1)} \]
\[ R_{SEI} = 918.23 \text{ Ohm} \]
\[ Q_{CT} = 15.16 \times 10^{-6} \text{ F.s}^{(a - 1)} \]
\[ R_{CT} = 1120.96 \text{ Ohm} \]
\[ W_{d1} = 22.77 \text{ Ohm} \]