Supporting Information

Flexible Light-weight Lithium-ion Conducting Inorganic-organic Composite Electrolyte Membrane

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Experimental procedures and characterization

The final recipe of the hybrid inorganic-organic membrane consists of NASICON-type LAGP as the fast-ion conducting ceramic filler (synthesis method can be found elsewhere)[18,41] within a polymer blend consisting of the plasticizer benzyl n-butyl phthalate ($C_{19}H_{20}O_4$, 98% Alfa Aesar), a polyvinyl butyral resin (($C_8H_{14}O_2$)n, Butvar B98, Sigma Aldrich), lithium tetrafluoroborate ($LiBF_4$, 98% Sigma Aldrich) as the dopant salt and polyvinylidene fluoride binder (PVdF, Alfa Aesar). Amongst all the available options for the use as binder, polyvinyl butyral stands out by the combination of a high binding efficiency for ceramics and its high stability in both acidic and basic aqueous solutions. Hence it was chosen as one of the main components in the recipe. Benzyl butyl phthalate is employed as plasticizer to enhance the flexibility. The optimised composition of the membrane includes 81 wt% LAGP, 3 wt% benzyl butyl phthalate, 4 wt% polyvinyl butyral resin, 4 wt% LiBF4 and 8 wt% PVDF. N-methyl-2-pyrrolidinone (NMP) is used as solvent and the (≈ 3.5 ml for 1 g of LAGP ceramic). Preparation of the above-mentioned exemplary recipe involves mixing of the components in a glass beaker at 70 ºC using a magnetic stirrer (300 rpm rotation speed). After 6 hours of stirring, the mixture was tape cast onto an aluminum foil and left to dry at 80 ºC over night.

Structural characterization of the samples was carried out using a X-ray powder diffractometer (Bruker D8) with Cu Kα radiation (λ=1.5406 Å). XRD patterns were collected in the 2θ range 10–90° with a nominal scan rate of 160 s/step and a step size of 0.02°. Generalized Structure Analysis System (GSAS) software along with the graphical user interface, EXPGUI, is applied to refine the X-ray patterns. The microscopic structure of the samples was examined using scanning electron microscopy (SEM, Zeiss Supra 40 VP). AC impedance measurements were performed using an impedance spectrometer (Solartron SI1260, Schlumberger) in the frequency range of 0.1 Hz to 5 MHz inside a Swagelok cell (X2 Labwares Pte Ltd). As a measure of chemical stability, hybrid membranes were immersed in catholyte solutions with varying pH values and the effect of immersion time on the structure of the crystalline component, ionic conductivity and the surface topography were examined. Cyclic performance studies of Li-air cells using the hybrid membrane to protect the Li from direct contact with the catholyte were performed using a potentiostat/galvanostat (Arbin BT2000 equipped with MITS pro software).