

Supplementary Information:

Fabrication of Ultra-thin, Flexible, Dendrite-free, Robust and Nanostructured Solid Electrolyte Membrane for Solid State Li-batteries

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Fabrication of 0.1Mn-doped Li₇La₃Zr₂O₁₂ (LLZO) Nanofibers by the Electrospinning Technique.:

The electrospinning technique produced the nanostructured Mn-doped LLZO nanofiber. Herein, all the precursors were used without any preheat treatment or purification. Two different colloidal solutions were initially prepared for material precursors and the polymeric network. In material solution, lithium nitrate (LiNO₃, ≥ 98.5%), manganese(II) nitrate hydrate (Mn(NO₃)₂·xH₂O, ≥ 98.0%), lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, ≥ 99.0%) and zirconium oxynitrate hydrate (ZrN₂O₇·XH₂O, ≥ 99.0%) was dissolved into 2.5 mL DI water, in molar stoichiometric ratio 6.9:0.1:3:1.9 respectively, (where 10% excess Li were used to compensate loss during calcination). After that, the solution was stirred for 6 h until a transparent solution was achieved. On the other hand, for the polymeric solution, polyvinylpyrrolidone (PVP, (C₆H₉NO)_n, Mw ~ 1,300,000), having the equal weight of all metal precursors was dissolved in ethanol (C₂H₅OH, ≥ 99.0%) to make 10% concentration of polymer solution. Subsequently, both the solutions were mixed together by pouring the material solution into the polymeric one with continuous stirring. After getting a transparent solution, 200 μL acetic acid (CH₃COOH, ≥ 99%) was further added into the solution and again stirred for 2 h. Here, the acetic acid served as catalysts that accelerate the reaction rate and as a coordination substitution, delaying the hydrolysis process. Finally, this transparent and viscous solution was transferred into a 3 mL hypodermic syringe equipped with a stainless-steel needle (23-gauge) for electrospinning.

For the electrospinning, the working voltage of 10-12 kV and the distance between the needle tip and the collector were kept at 10-12 cm. The feeding rate of the polymeric solution was

set at 0.3-0.5 mL/h. After getting the sufficient yield, the as-spun nanofiber was peeled off from the collector as a free-standing, flexible non-oven mat. Further, it was dried in a vacuum oven at 80 °C and then calcined in an alumina combustion boat in the air at 750 °C for 3 h with a heating rate of 1 °C /min (Nabertherm Tube Furnace, Germany) to remove all the organic components. Finally, the Mn-LLZO nanofiber was achieved and stored in a vacuum desiccator for further characterization.

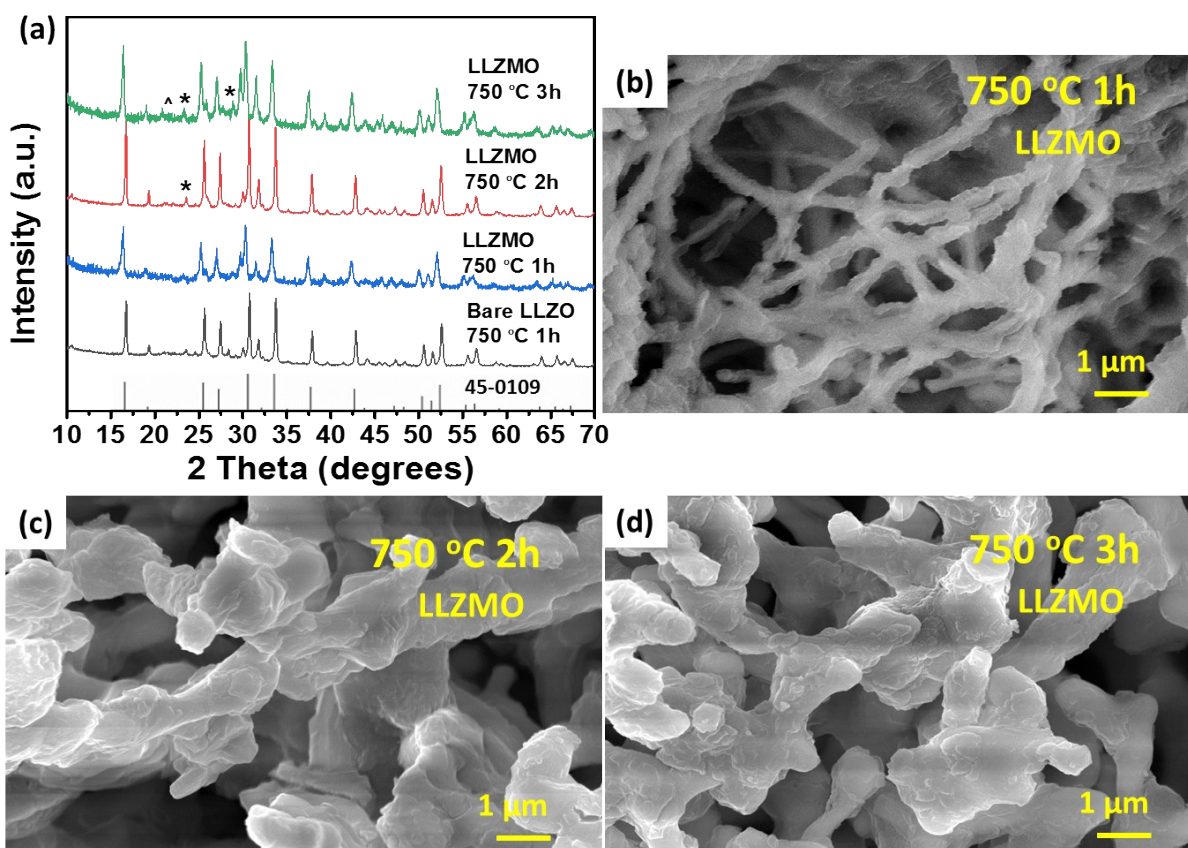


Figure S1. (a) Powder XRD patterns of bare LLZO and LLZMO nano-fibers synthesized at 750 °C for 1h, 2h and 3h, FE-SEM image of (b-d) LLZMO nanofibers synthesized at 750 °C for 1h, 2h, and 3h respectively. All the heat treatments are conducted with a heating rate 1 °C /min. The impurity phases of Li-La phase and Li_2CO_3 have been displayed by * and ^, respectively.

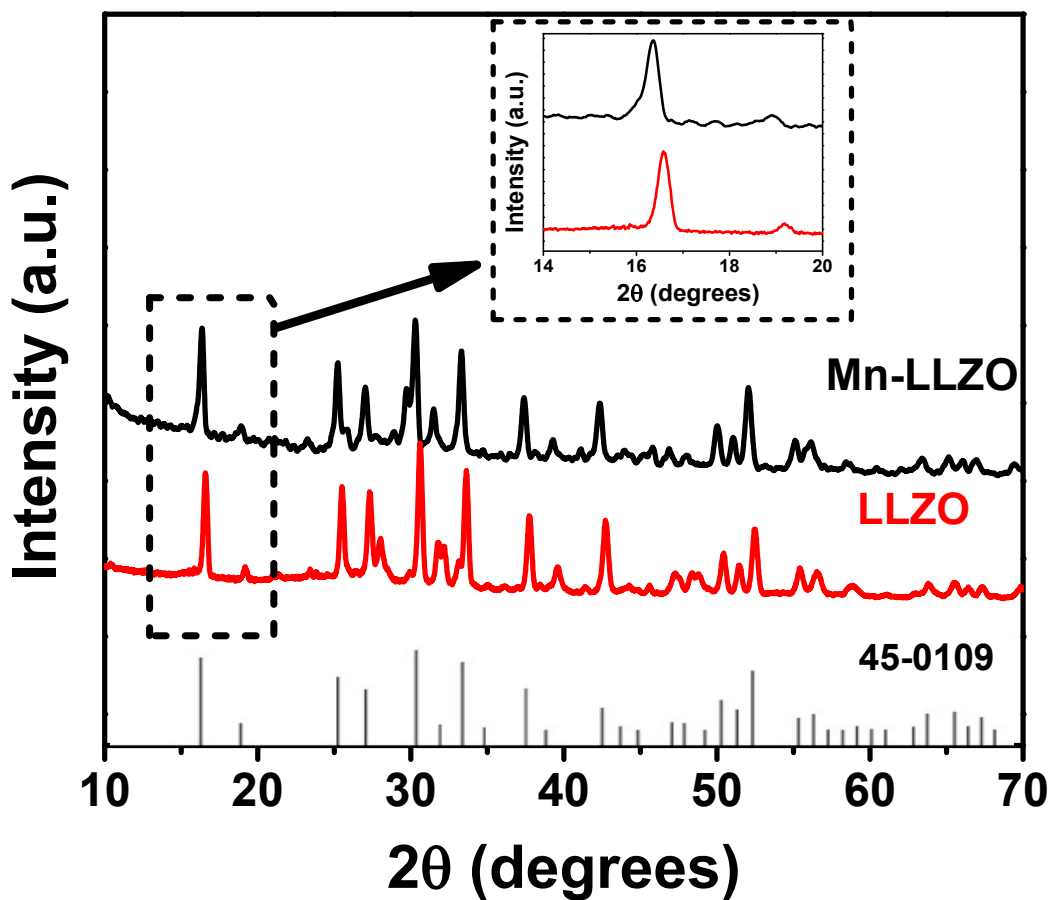


Figure S2. Powder XRD patterns of bare LLZO and LLZMO nano-fibers synthesized at 750 °C for 1h with a heating rate 1 °C /min. The shifting of the peak can be seen in the inset diagram.

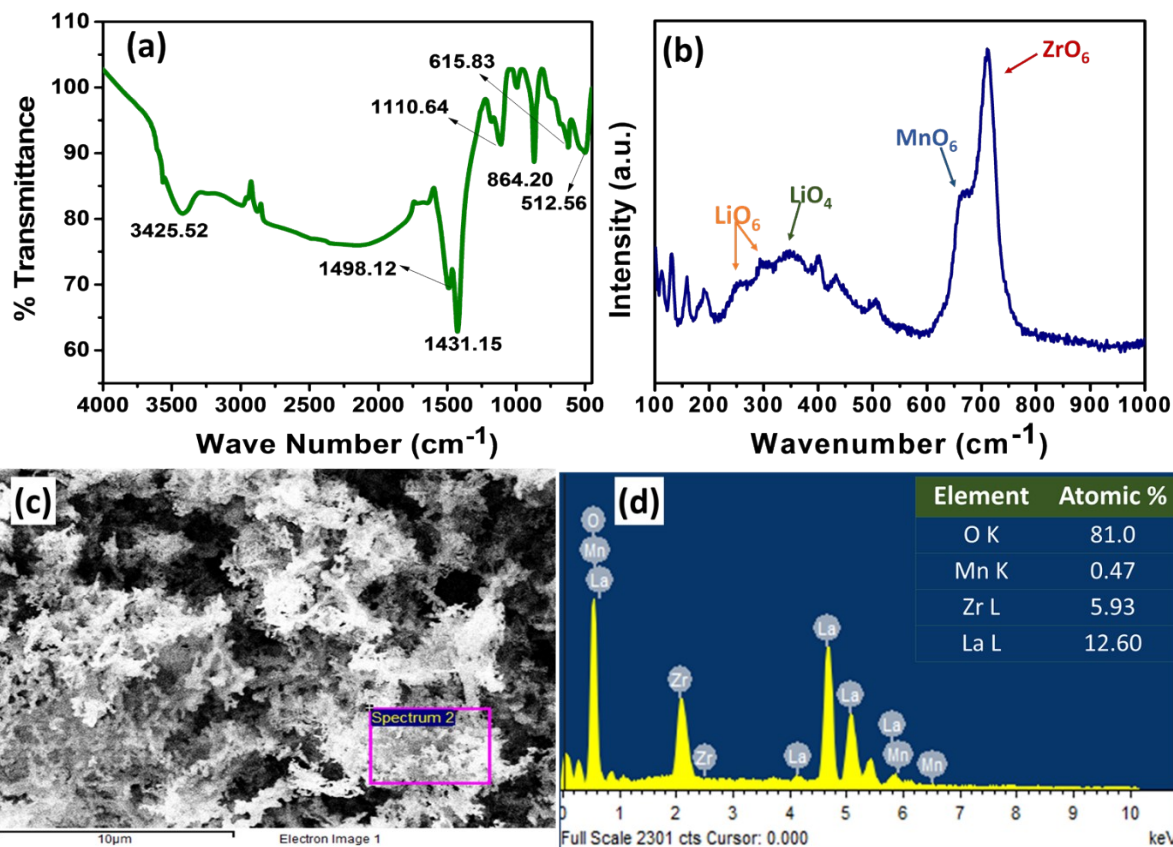


Figure S3. The elemental analysis of LLZMO by (a) FTIR spectrum, (b) Raman spectrum, and (c, d) EDX spectra of the sintered LLZMO nanofiber (750 °C, 1h).

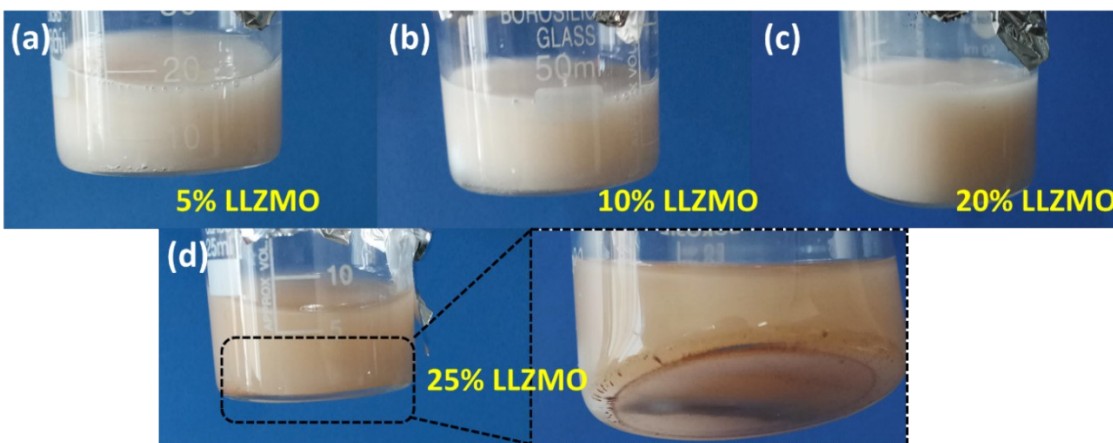


Figure S4. Snapshot of the prepared polymeric solution for electrospinning, having different LLZMO content.

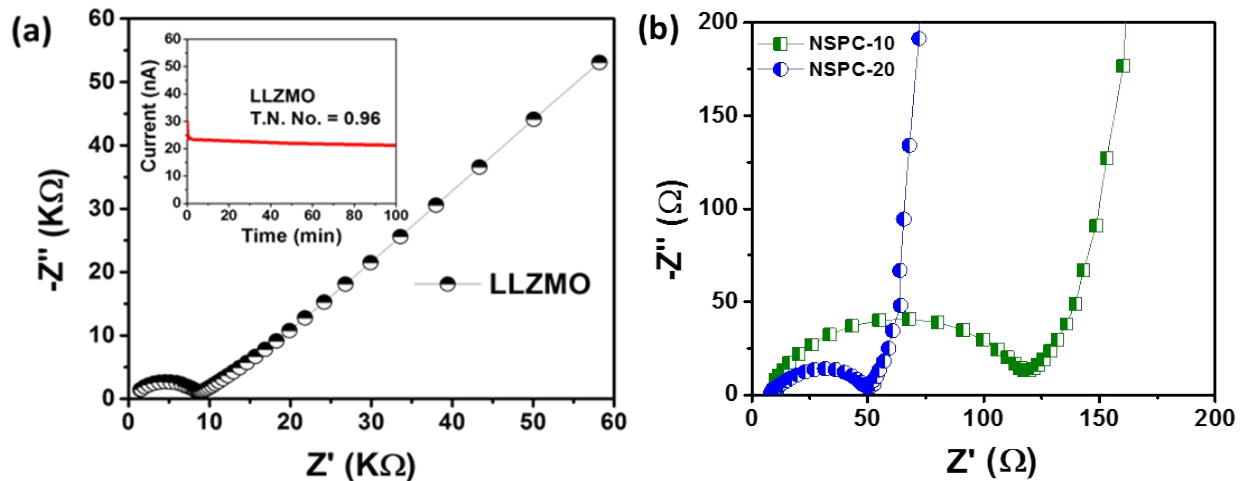


Figure S5. EIS spectra of (a) LLZMO pallet, transference number analysis is shown in inset and (b) for fresh NMC/Li cell using NSPC-10 and NSPC-20.

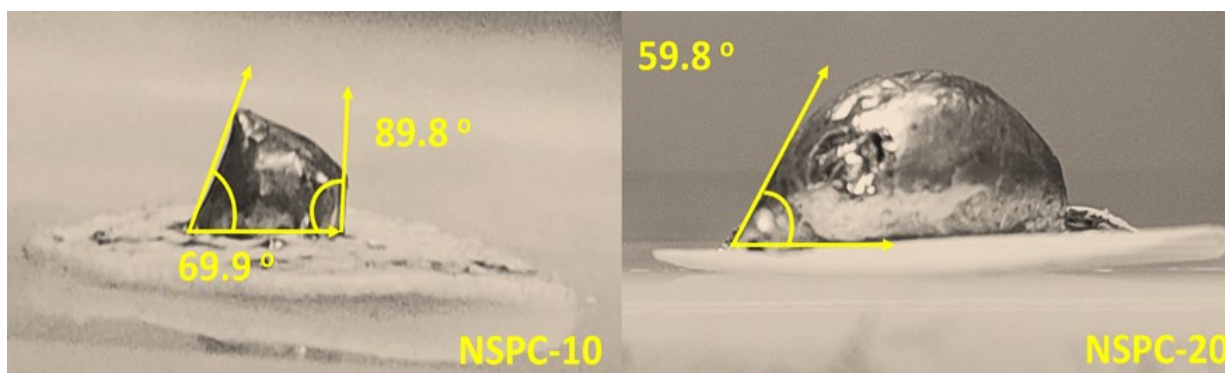


Figure S6. The snapshot of the contact angle of molten Li on the surface of NSPC-10 and NSPC-20 membrane, where higher surface wettability against the Li metal can be seen in the NSPC-20 membrane.

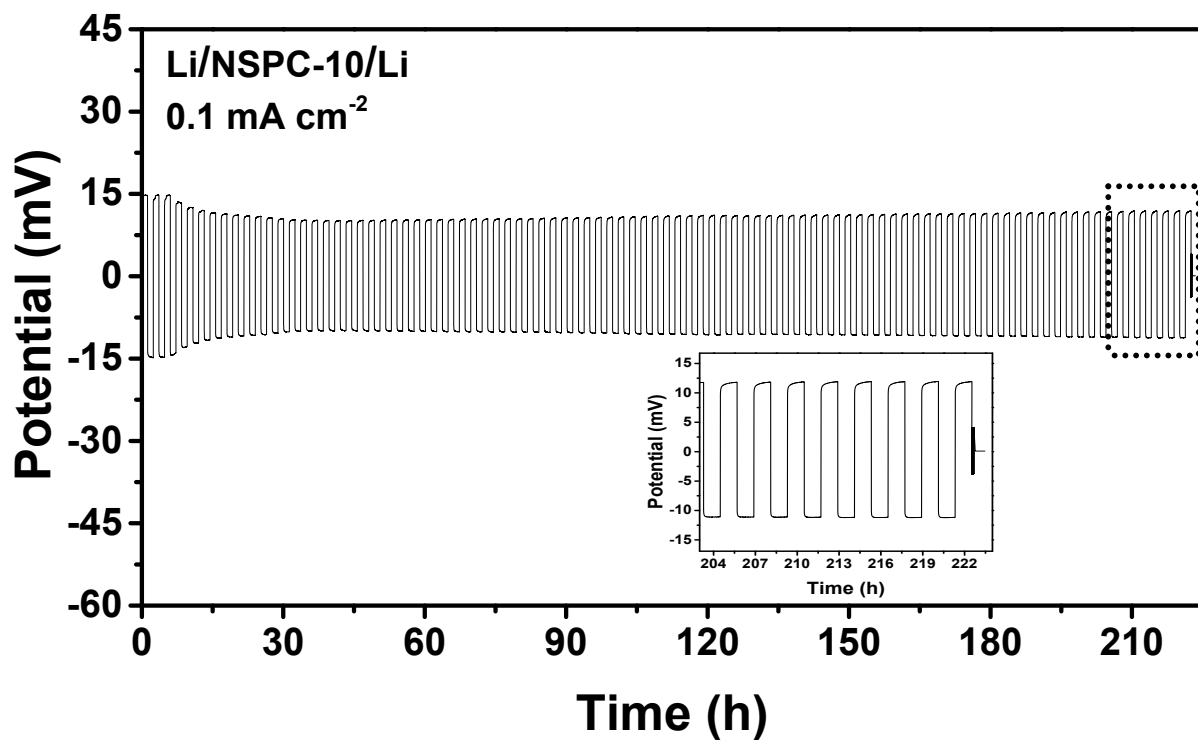


Figure S7. Galvanostatic cycling of Li/NSPC-10/Li cell with a current density of 0.1 mA cm⁻² for 225 h cycling. After 220 h of cycling, short-circuiting of the battery is observed.

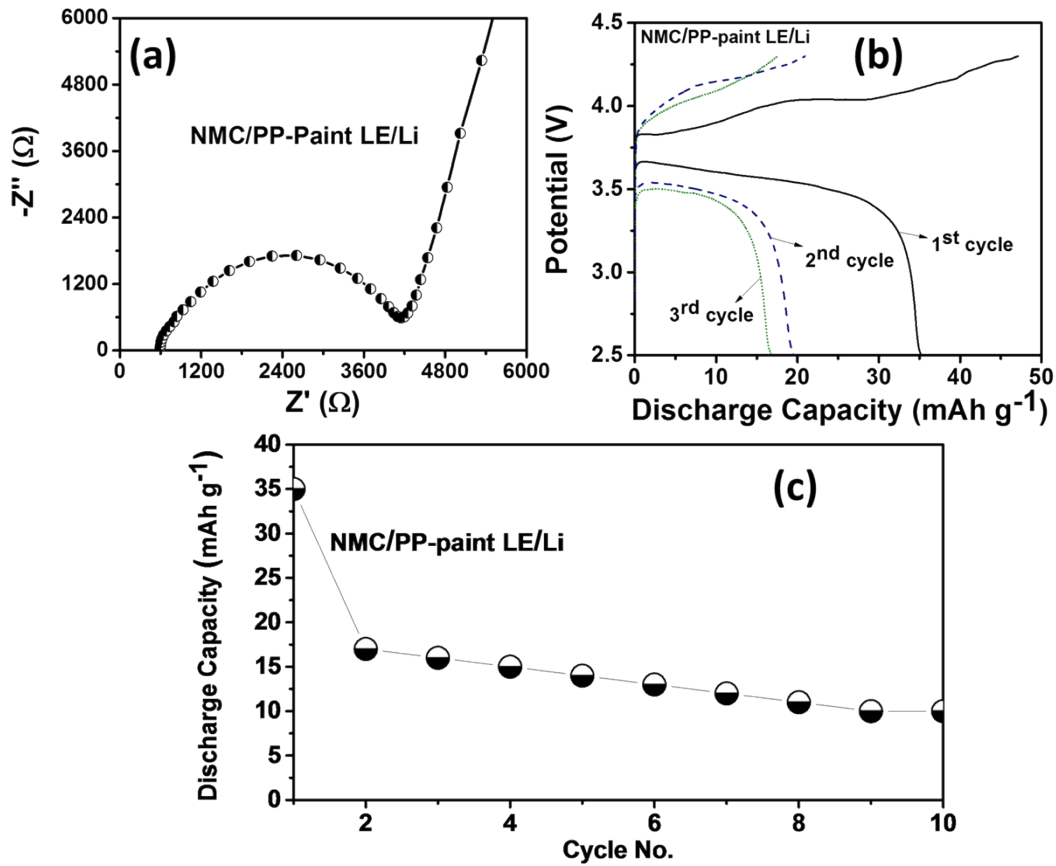


Figure S8. EIS spectra before cycling and (b,c) Galvanostatic charge discharge and cyclability data of liquid electrolyte painted polypropylene based NMC/Li (NMC/PP-paint LE/Li) cell.

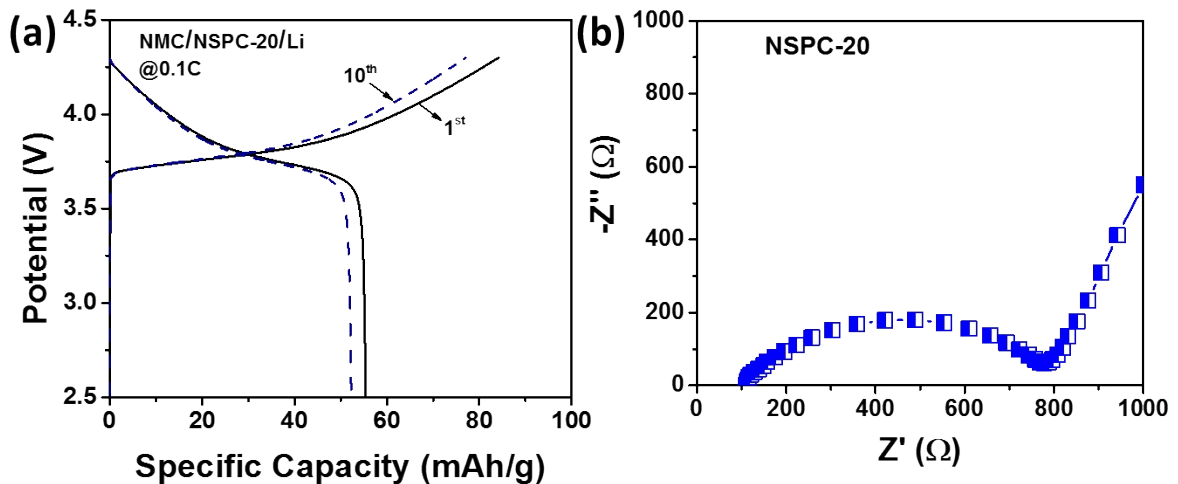


Figure S9. (a) Galvanostatic charge-discharge profile for 1st and 10th cycle and (b) EIS after 1st charge of the NMC/Li cell with intrinsic NSPC-20 membrane. The large impedance of the cell leads to poor electrochemical performance.

Conductivity Calculations:

The conductivity for all the membrane was used using,

$$\sigma = \frac{1}{R} \times \frac{t}{A}$$

t is the thickness, A is area and R is associated resistance of the membrane used in the EIS measurement.

Table S1: Calculation parameter and outcomes of conductivity analysis

	Polypropylene	NSPC-5	NSPC-10	NSPC-20
Thickness (μm)	25	31	32	30
Electrode Area (cm^2)	0.5	0.5	0.5	0.5
Resistance	3800	602	138	56
Conductivity (mS cm^{-1})	0.001	0.01	0.05	0.11

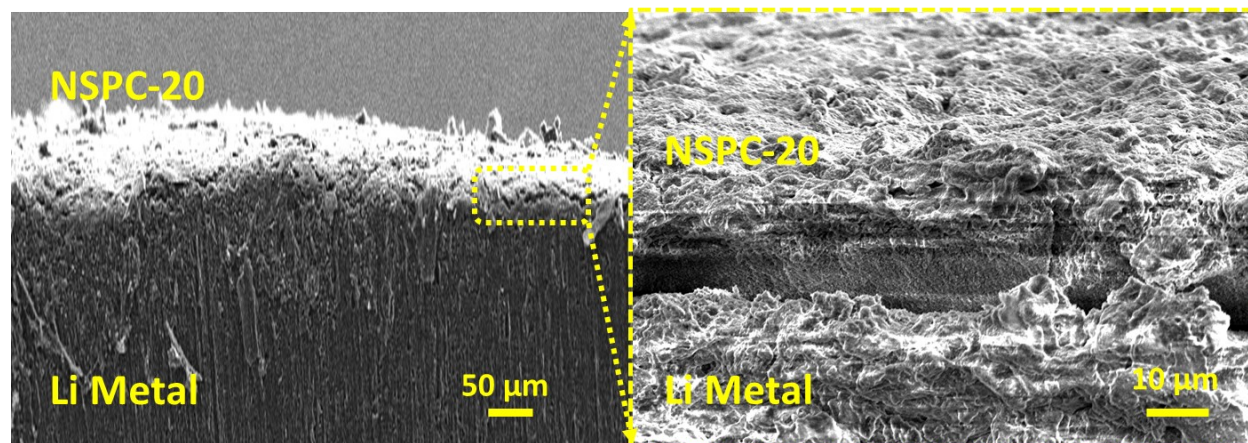


Figure S10. FESEM image of NSPC-20 after stripping plating cycling (0.8 mA cm^{-2}). The high-resolution image can clearly see a large interfacial gap, which attributes to very high interfacial resistance.

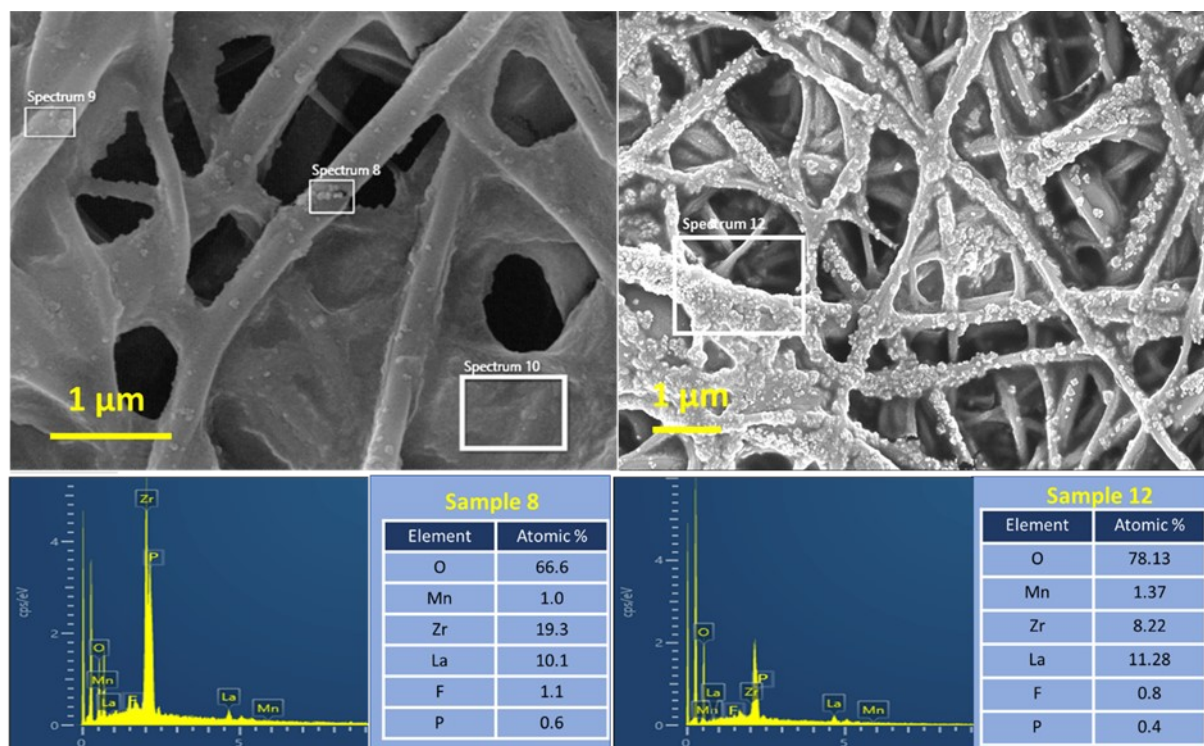


Figure S11. EDAX spectra and associated elemental mapping of NSPC-20 before and after stripping plating cycling (0.1 mA cm^{-2} , 100 h).