Electronic Supporting Information

## A 3D mixed ion-electron conducting framework for dendrite-free lithium metal anodes

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## **Experimental Section**

Synthesis of LLTO particles. The stoichiometric ratio of  $Li_2CO_3$ ,  $La_2O_3$  and  $TiO_2$  were mixed and wet ball-milled in ethyl alcohol using planetary ball mill at a speed of 300 rpm for 12 h. 20wt% excess of  $Li_2CO_3$  was added to compensate for the potential Li loss during sintering. Then the mixture was dried at 80°C for 24 h. Subsequently, the powder was calcined at 800°C for 8 h at a heating rate of 5°C min<sup>-1</sup> in a muffle furnace. At last, the product was cooled and then heated again at 1150°C to obtain the final LLTO particles.

**Preparation of LLTO@CNT MIEC anode.** The prepared LLTO powder (52.5 wt%), CNT slurry (5%), benzyl butyl phthalate (BBP, 6 wt%), Triethanolamine (TEA, 1 wt%) and 5  $\mu$ m cross-linked polymethyl methacrylate spheres (PMMA, 27.5%) were mixed in N-methyl-2-pyrrolidone (NMP), where PMMA spheres served as a porogen. Then the mixed slurry was coated on the Cu foil and dried at 80°C overnight. Later, the film wat cut into disks with a diameter of 12 mm, followed by heated at 450°C for 90 min in tube furnace under N<sub>2</sub> atmosphere to remove the porogen. The pure LLTO anode was prepared in the same way without the addition of CNT slurry. The typical thickness of the MIEC is ~45  $\mu$ m with a porosity of ~46%, which can accommodate Li metal with a high areal capacity of 4 mA h cm<sup>-2</sup>.

**Materials Characterizations.** The morphology of samples was observed by field-emission scanning electron microscopy (SEM, Phenom LE). The structures of the materials were characterized by X-ray diffraction system (Lab XRD-6000) with Cu K $\alpha$  radiation ( $\lambda$ =1.54 Å).

**Electrochemical Measurements.** The CR2032 half cells were assembled in argon-filled glove box with polyethylene (PE) as separator and Li foil as a counter electrode. The electrolyte was prepared by adding 0.84 g LiFSI and 0.087 LiODFB in 1 mL 1,2-dimethoxyethane (DME) and 2 mL ethoxy(pentafluoro)cyclotriphosphazene (PFPN) to get a PFPN diluted localized high concentration electrolyte (PFPN-DHCE). The amount of electrolyte was controlled as 30 µL for coin cells. The cycling performances were conducted on Neware battery testing system at 27°C. Electrochemical impedance spectrometry (EIS) was performed on Biologic electrochemical workstation with the frequency ranging from 20 kHz to 0.1 Hz. Cyclic voltammetry (CV) was carried out on the same workstation with a scan rate of 0.1 mV s<sup>-1</sup> and a voltage range of 0.01–2.50 V (vs. Li/Li<sup>+</sup>). The ionic and electronic conductivity of the anode were measured using a combination of AC and DC electrochemical methods with Li-ion blocking electrodes on Biologic electrochemical workstation. The total ionic and electronic conductivity was obtained by EIS using a 50 mV perturbation voltage at frequencies ranging from 100 mHz to 100 kHz. The electronic conductivity was measured by chronoamperometry test. Then the ionic conductivity could be derived from the difference between them. When performing lithium metal depositing tests, the half cells were first discharged to 0 V and then plated with a certain amount of lithium. For full cells, NCM622 cathode was prepared by mixing NCM622, carbon black and poly(vinylidene fluoride) with a mass ratio of 90:6:4 in Nmethyl-2-pyrrolidone (NMP). Then the slurry was coated on the Al foil, and dried in a vacuum oven at 80°C overnight. For the pre-depositon full cells, they were first cycled at 0.1 C for two cycles to form a stable SEI, and then cycled at a current density of 0.2 C charge/0.5 C discharge between 3-4.3 V in subsequent cycles. For anode-free full cell, it was cycled at 0.1 C between 2.75-4.2 V.



Fig. S1. Elemental analysis of as-prepared LLTO.



Fig. S2. (a) Cross-sectional SEM image of LLTO electrode without CNTs. (b) High-magnification SEM image of LLTO@CNT MIEC electrode.



Fig. S3 CV curves of pure LLTO anode.



**Fig. S4** AC impedance spectra of (a) LLTO@CNT anode and (b) LLTO anode before and after discharged to 0V. DC electrochemical measurement for (c) LLTO@CNT anode and (d) LLTO anode before and after lithiation. Comparison of the ionic and electronic conductivity of (e) LLTO@CNT anode and (f) LLTO anode before and after lithiation process.



Fig. S5 Surface morphologies of the Cu foil after depositing (a) 0.2 mAh cm<sup>-2</sup> and (b) 0.5 mAh cm<sup>-2</sup> of Li.



Fig. S6 Cross-sectional SEM image of (a) LLTO@CNT anode and (b) Cu foil after 10 cycles of Li plating/stripping.



**Fig. S7** Coulombic efficiency of Li metal on different anodes cycled at a current density of 2 mA cm<sup>-2</sup> with an areal capacity of 2 mA h cm<sup>-2</sup>.



**Fig. S8** Cycling performance profile of LLTO@CNT||NCM622 anode-free full cell at 0.1 C between 2.75-4.2 V.