

Electronic Supplementary Information

Experimental details

Preparation of UIO-66 nanoparticles: UIO-66 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_8\text{H}_4\text{O}_4)_6$) was prepared based on the procedures of the previously reported literature.¹⁹ First, 3.00 g of terephthalic acid, 1.26 g of zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), 50 mL acetic acid and 240 mL of N,N-dimethylformamide (DMF) were added in a 500 mL glass reactor and stirred at room temperature for 2 h, which was then heated at 90 °C for 24 h in an oven. About 20 nm UIO-66 nanoparticle was collected by centrifuging, washed with N,N-dimethylformamide, methanol and deionized water, and activated by heating at 150 °C in dynamic vacuum for 5 h. In addition, about 200 nm UIO-66 nanoparticle was given by modulating the acetic acid concentration to two times without changing the other reaction conditions and the final processes. The two activated UIO-66 nanoparticles of different sizes were stored in an Ar glove-box (O_2 , H_2O < 0.1 ppm) for further use.

SLE preparation: 50 mg of UIO-66 (about 20 nm) was mixed into 450 mg of UIO-66 (about 200nm) to obtain a hybrid UIO-66 nanoparticles. 0.574 g of bis(trifluoromethane)sulfonimide lithium (LiTFSI, Shanghai Aladdin Bio-Chem Technology Co., Ltd, China)) was dissolved in 4.225 g of N-butyl-N-methylpyrrolidinium bis(trifluoromethyl sulfonyl)imide ([BMP][TFSI], Lanzhou Greenchem ILs (OR Centre for Greenchemistry and Catalysis), LICP, CAS, China) to obtain Li-IL. Different amount of Li-IL was mixed into the hybrid UIO-66 nanoparticles, ground into homogeneous mixtures and heated at 150 °C in the vacuum for 5 h to obtain white

powdery SLE particles. The SLE powders were then pressed into pellets with diameter of 12 mm under 8 t force.

Cathode preparation: 500 mg of two different types of electroactive substance (Commercial LFP, Shenzhen Dynanonic Co., Ltd, China; LiCoO₂, Tianjin B&M Science and Technology Joint-Stock Co., Ltd, China) were respectively mixed into the mixture of 500 mg of Li-IL@UIO-66 SLE and 200 mg of acetylene black by milling into homogeneous mixtures as the solid-state composite cathode in Ar glove-box.

Electrochemical tests: In an Ar-filled glovebox, 55mg Li-IL@UIO-66 was pressed into a pellet with diameter of 12 mm under 8 t force and assembled into CR2025 coin cells for electrochemical tests. The lithium ion transference number (t_{Li^+}) was confirmed via the method of steady state current proposed by Bruce and Vincent with 10 mV of constant polarization potential at room temperature and calculated by the calculations of the following equation:

$$t_{Li^+} = \frac{I_s R_f (\Delta V - I_0 R_0)}{I_0 R_i (\Delta V - I_s R_s)}$$

(Wherein ΔV , I and R is respectively replaced with the applied direct current potential, the current and the interface resistance, and 0 and s respectively represent the initial and the steady states.)

14 mg composite cathode material was pressed into an 8 mm pellet under 5 t force, resulting in active material loadings varying from 10 to 15 mg cm⁻². The part of cathode piece was then added to mould with 65 mg SLE particles dispersed on its top homogeneously, which were then pressed into a 12mm bilayer pellet under 8 t force. Solid-state batteries were assembled and tested in CR2025 coin cells using Li foil as anode and the bilayer pellet as cathode and electrolyte.

Characterization methods: Powder X-ray diffraction (XRD) data were recorded by a Bruker D8

Advance diffractometer using Cu K α , $\lambda=1.541$ Å, with 2θ from 3 to 60°. The scanning electron microscopy (SEM) morphology and energy dispersive spectrometer (EDS) mapping were investigated using ZEISS Supra 55 scanning electron microscopy with an Oxford AZtec energy dispersive spectrometer. Thermo gravimetric analysis (TGA) was carried out in a N₂ atmosphere at a scan speed of 10 °C min⁻¹ on a Mettler Toledo TGA/DSC STAR system. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250XL instrument in a scan step of 0.1 eV. N₂ adsorption/desorption isothermal was recorded on a Micromeritics ASAP 2020 HD88 tool. The cyclic voltammetry (CV, 0.2 mV s⁻¹), linear sweep voltammetry (LSV, 0.2 mV s⁻¹) and electrochemical impedance spectroscopy (EIS, 1–10⁶ Hz) data were collected with a CHI600E electrochemical workstation. The Li plating/stripping cycles and battery cycling performance were obtained with a LAND battery cycler.

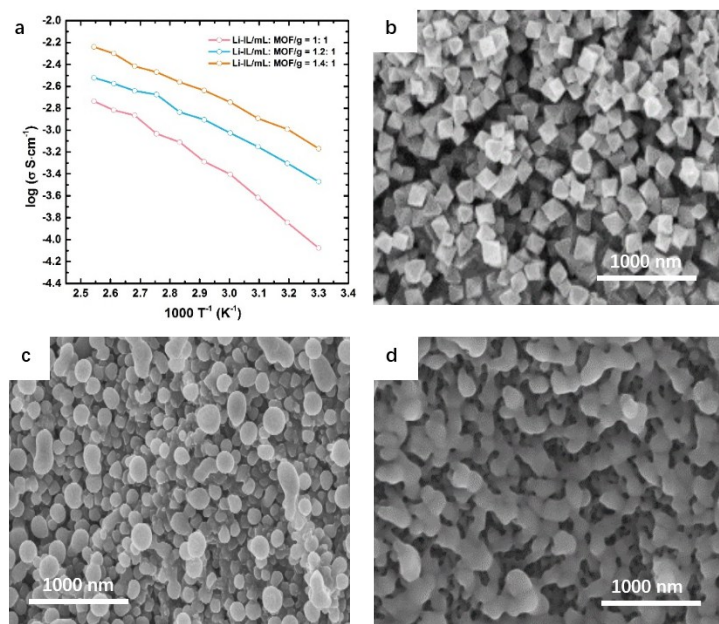


Figure S1. a) Arrhenius plots for the ionic conductivity of SLEs with different Li-IL loading amount. SEM images of b) pristine hybrid UIO-66, c) Li-IL@hybrid UIO-66 (ratio, 1.2 mL: 1.0 g) and d) Li-IL@hybrid UIO-66 (ratio, 1.4 mL: 1.0 g) mixtures before being pressed into pellets.

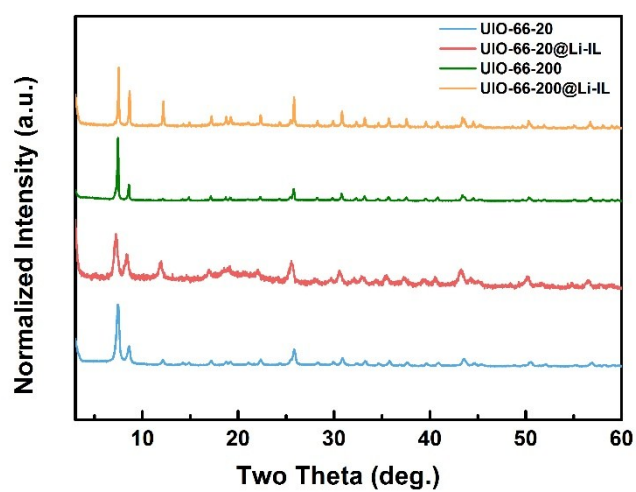


Figure S2. XRD patterns of the synthesized UIO-66 (about 20 and 200 nm) host.

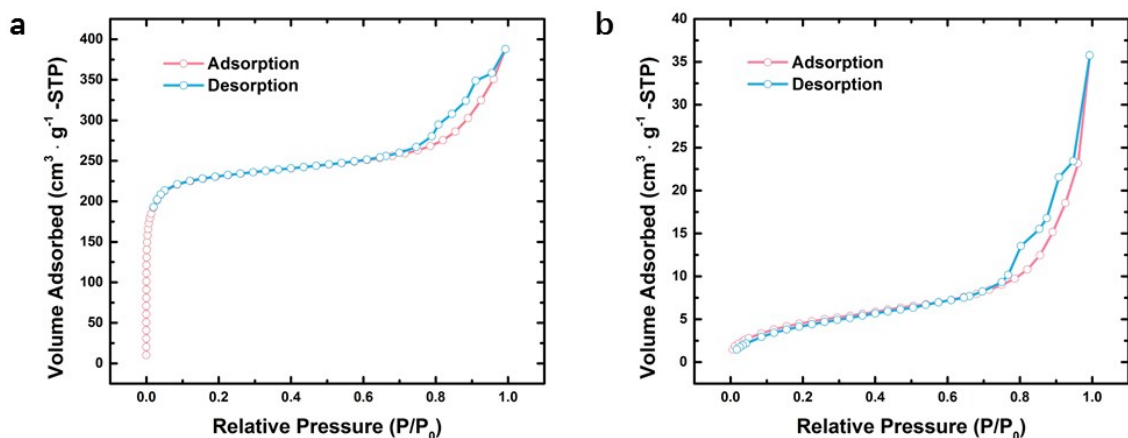
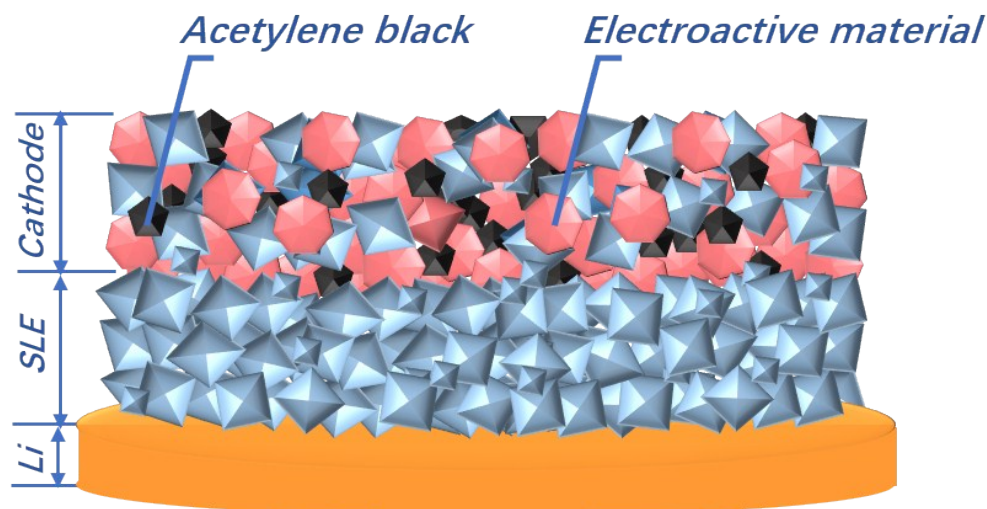


Figure. S3. N2 adsorption/desorption isothermal of a) pristine UIO-66 and b) Li-IL@hybrid UIO-



66.

Scheme S1. Schematic illustration of cell configuration.

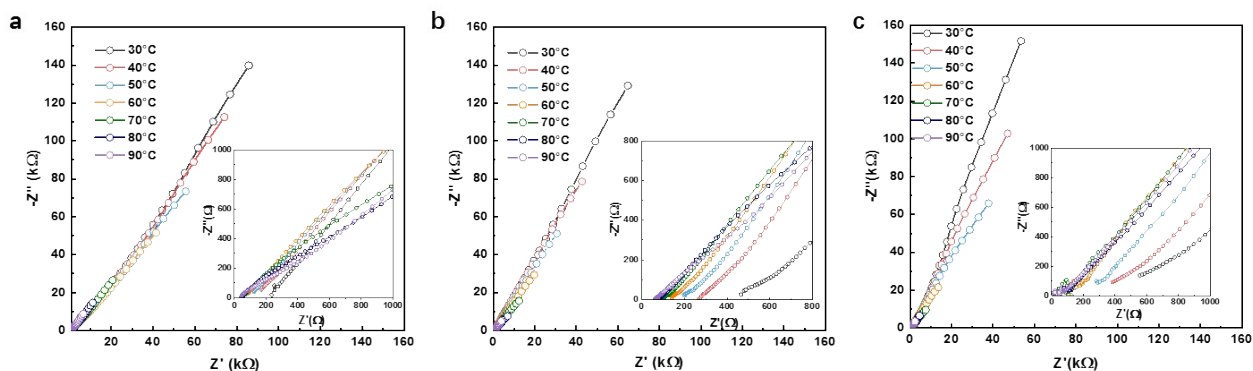


Figure S4. EIS of a) SLE-H, b) SLE-L and c) SLE-S (Li-IL@UIO-66 = 1.2 mL: 1.0 g) at temperatures from 30 to 90 °C the inset shows magnified high-frequency region). d) Arrhenius plots for the ionic conductivity of Li-IL@UIO-66 with different UIO-66 sizes.

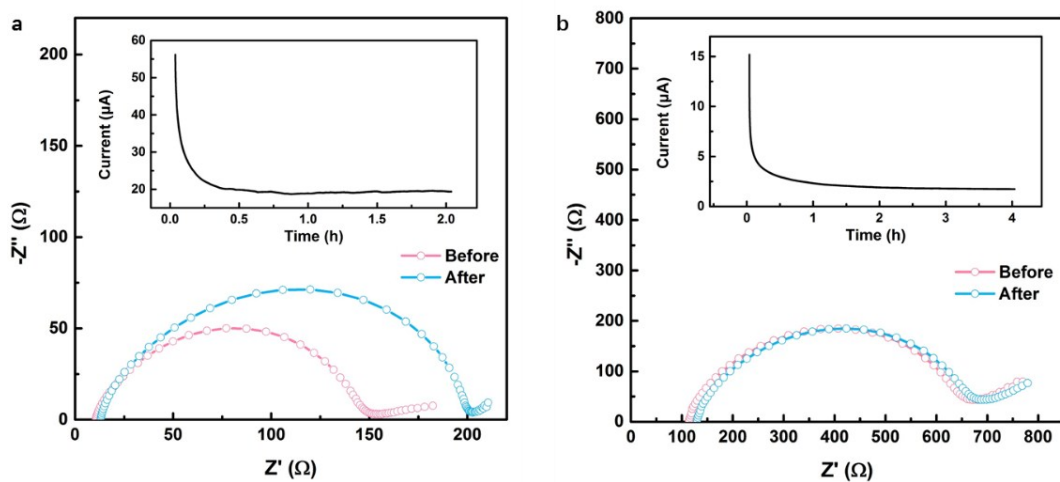


Figure S5. EIS of Li symmetric cells using a) Pristine Li-IL and b) SLE-H as electrolytes before and after polarization under room temperature. The insets show the variation of current with time during polarization at an applied voltage of 10 mV at room temperature.

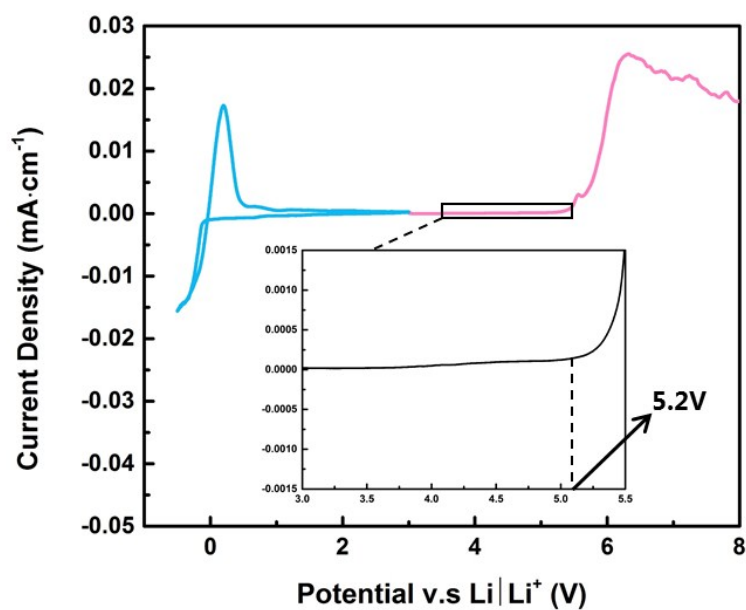


Figure S6. CV (-0.5–3V) and LSV (3–8V) profiles of Li|Li-IL|SS asymmetric cell at room temperature at a scan speed of 0.2 mV s⁻¹.

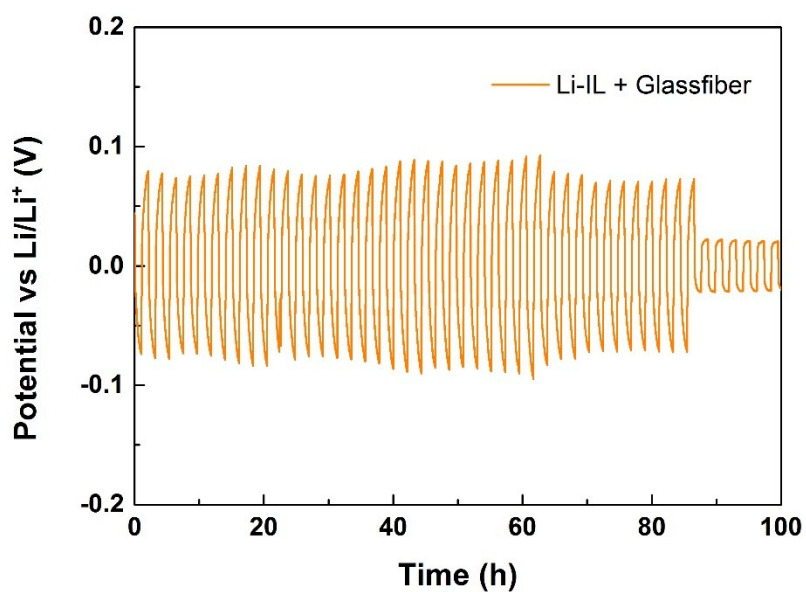


Figure S7. Li plating-stripping performance of $\text{Li}|\text{Li-IL+glassfiber}|\text{Li}$ symmetric cell under a current density of 0.1 mA cm^{-2} .

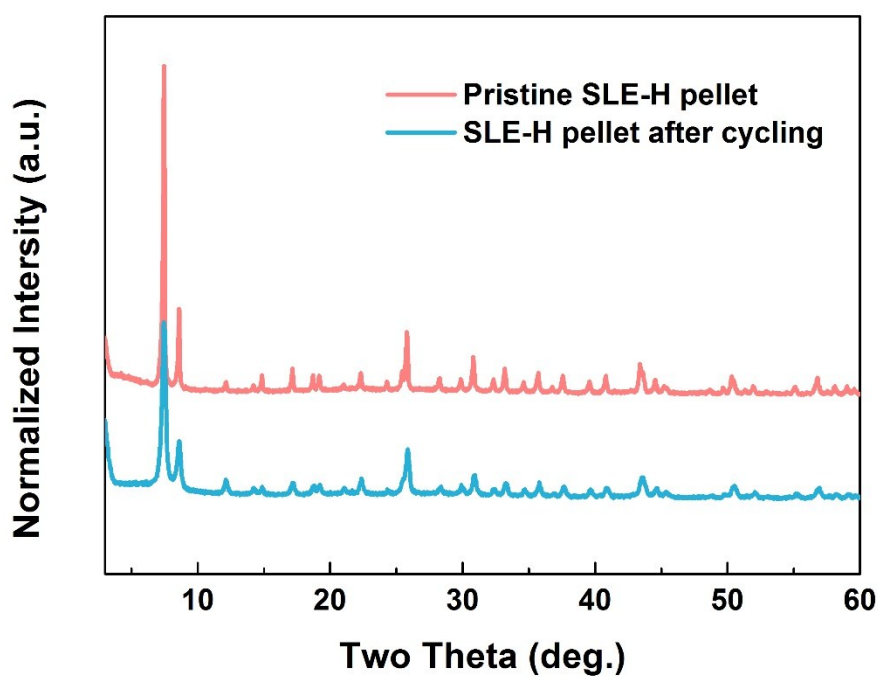


Figure S8. XRD patterns of SLE-H pellet before and after cycling in a Li-Li symmetric cell.

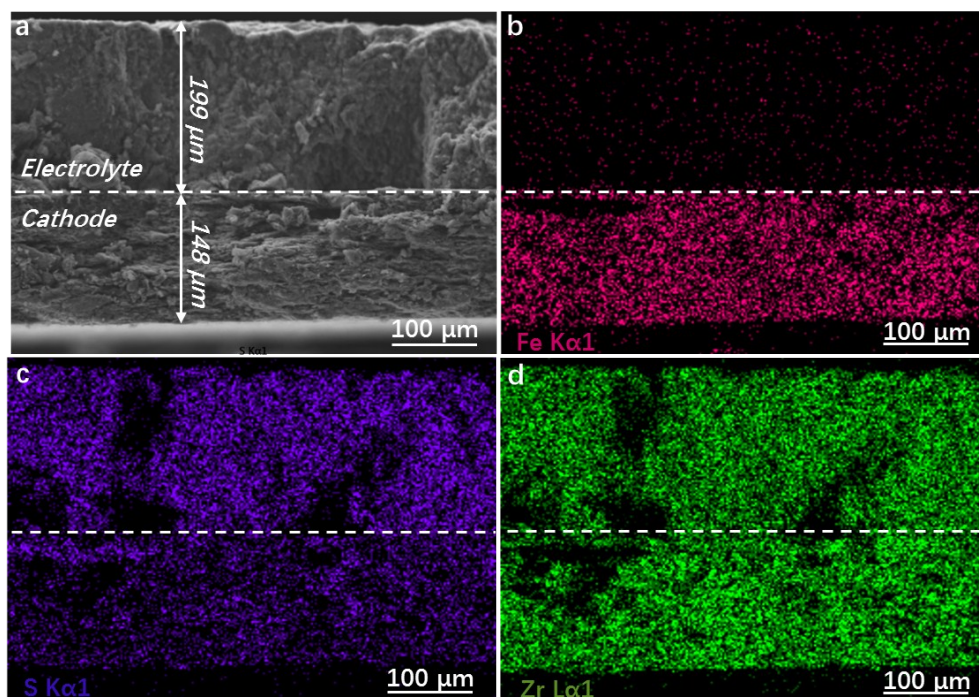


Figure S9. a) SEM morphology for the cross section view of bilayer membrane of LFP cathode and SLE with b, c, d) corresponding EDS elements mappings.

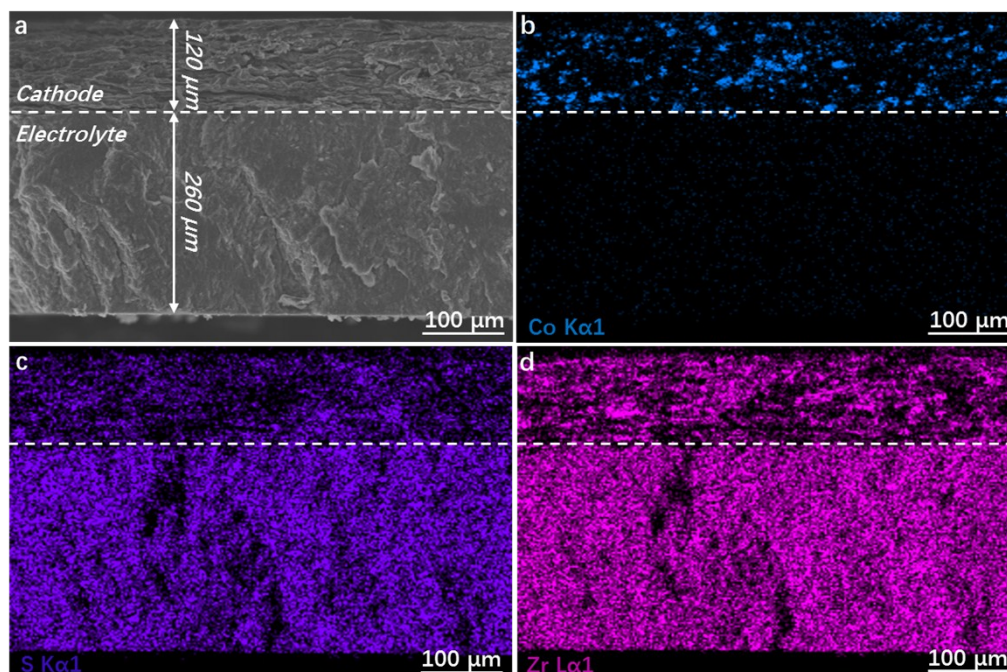


Figure S10. a) SEM morphology for the cross section view of bilayer membrane of LCO cathode and SLE with b, c, d) corresponding EDS elements mappings.