Supporting information.



Figure S1. The TGA curves of the P(SSPSILi-alt-MA) single-ion conductor and PVDF-HFP membrane.



Figure S2. The stress-strain the curve of the commercial PP separator.



Figure S3. The impedance plots at the different temperature for the bisulfonyl imide based SPEs in the different articles.



Figure S4. The Nyquist plot of the commercial PP separator (1M LiPF_6 in EC/PC) at the room temperature.



Figure S5. Time-dependence curves of DC polarization for the cells with (a) 50 wt%, (b) 33 wt%, (c) 20 wt%, (d) 10 wt% and (e) 5 wt% P(SSPSILi-alt-MA) SPE membrane sandwiched between two lithium electrodes. Inserts are electrochemical

impedance spectroscopies of the corresponding cells before and after polarization.



Figure S6. I-V diagram obtained from the linear-sweep voltammetry of 20 wt% P(SSPSILi-alt-MA) SPE membrane in the Li metal cell at a scan rate of 10 mV s⁻¹ at room temperature.



Figure S7. Thermal shrinkage (a) at 25 °C(b) at 50 °C (c) at 110 °C (d) at 150 °C of the SPE membrane(swollen with EC/PC)and commercial separator with conventional organic electrolyte (1M LiPF₆ in EC/PC).



Figure S8. The polarization tests of the Li symmetric cells with the 20 wt% SPE membrane and the commercial PP separator at the current density of 1mA cm⁻².



Figure S9. The EIS plots of LTO and LFP half-cells with the 20 wt% SPE membrane.



Figure S10. Electrochemical performances of Li metal batteries. First galvanostatic charge-discharge voltage profiles of the (a) LTO and (b) LFP half-cells with the 20 wt% SPE membrane at 0.2 C. Cycling performances at 0.2 C of the (c) LTO and (d) LFP half-cells with the 20 wt% SPE membrane and commercial separator for 100 cycles. Rate performances of the (e) LTO and (f) LFP half-cells with the 20 wt% SPE membrane and commercial separator. Performances of the (g) LTO and (g) LFP half-

cells with the 20 wt% SPE membrane and commercial separator at a high rate of 2 C for 200 cycles.

The LiTi₄O₅ (LTO) half-cell and LiFePO₄ (LFP) half-cell with the 20 wt% SPE membrane was measured as the construction of "Li | SPE membrane (EC/ PC) | LTO (or LFP)". The first galvanostatic charge-discharge voltage profile of the two half-cells at room temperature was displayed with the characteristic evolution of the battery voltage as a function of its discharge capacity (Figure S8). In the above charge-discharge voltage profile, two typical platforms around 1.52-1.57 V are observed, which are corresponding to the reported two phase coexistence reaction for the LTO electrode. The cell operating at room temperature was capable of delivering a discharge capacity of 159 mAh g⁻¹ at 0.2 C, gaining 91% of the theoretical capacity of the LTO cell. Similarly, two platforms of 3.34-3.53 V coincident with two phase coexistence reaction for the LFP electrode were seen in the charge-discharge voltage profile of the LFP cell and the cell exhibits a capacity of 161 mAh g⁻¹ at 0.2 C, gaining 95% of the theoretical capacity.

The cycling stability of the two half-cells with the SPE membrane investigated by prolonged cycling of galvanostatic charge-discharge at the 0.2C rate, with the commercial separator as the comparison (Figure 8a,b). In half-cells with the commercial separator, the electrolyte of 1 M LiPF₆ in EC/PC was utilized. Both two half-cells with the SPE membrane performed the excellent cyclability with coulombic efficiencies maintaining close to 100% for 100 cycles and the capacity retentions keep stable during the cycling at the room temperature, which can be comparable to the

ones with commercial separator.

The performances of the LTO and LFP cells at different charge-discharge rates ranging from 0.2 to 10 C were measured at room temperature. As shown in the Figure 8c, the capacity retentions of the LTO cell with the SPE membrane operating at 0.5 C, 1C, 2 C, 5C and 10 C are 141.1, 129.8, 119.3, 96.1 and 67.8 mAh g⁻¹, respectively, which are higher than those of the cell with commercial separator (136.1, 120.5, 112.2, 79.5 and 28.5 mAh g⁻¹, respectively). Compared to the commercial separator, the LTO cell with the SPE membrane shows an obviously better rate performance. For LFP cells, the one assembled with the SPE membrane shows the capacity retentions reaching 118.3, 102.9, 85.3 and 73.3 mAh g⁻¹ at 1 C, 2 C, 5 C and 10 C, respectively (Figure 8d). The LFP cell with the commercial separator exhibits the relatively inferior rate performance (98.1, 83.9, 64.3 and 53.7 mAh g⁻¹ under the corresponding rates). For the two half-cells with the SPE membrane, the excellent rate performance is attributed to the high ion conductivity of the SPE membrane. It is noted that the two assembled cells with the SPE membrane are still able to respectively retain the specific capacity of 153.6 mAh g⁻¹ and 162.6 mAh g⁻¹ when the charge-discharge rate returned to 0.2 C, suggesting the good electrochemical stability of the two cell systems. To further evaluated the electrochemical performance of the SPE membrane at the high C rate, the assembled LTO and LFP half-cells were charge-discharged continuously for 200 cycles at 2 C. The two cells with the SPE membrane both show the steady specific capacities with no obvious decay, while the ones equipped with commercial separator display obviously decayed specific capacities after dozens of cycles (Figure 8c,d). Better rate performances and electrochemical stability of the cells with the SPE membrane demonstrate that the prepared SPE membrane is applicable for use in lithium-ion batteries at room temperature.