

## Supporting Information

### **Ultrastable lithium-ion batteries prepared with introducing $\gamma$ -LiAlO<sub>2</sub> in gel polymer electrolyte for 50 °C working temperature**

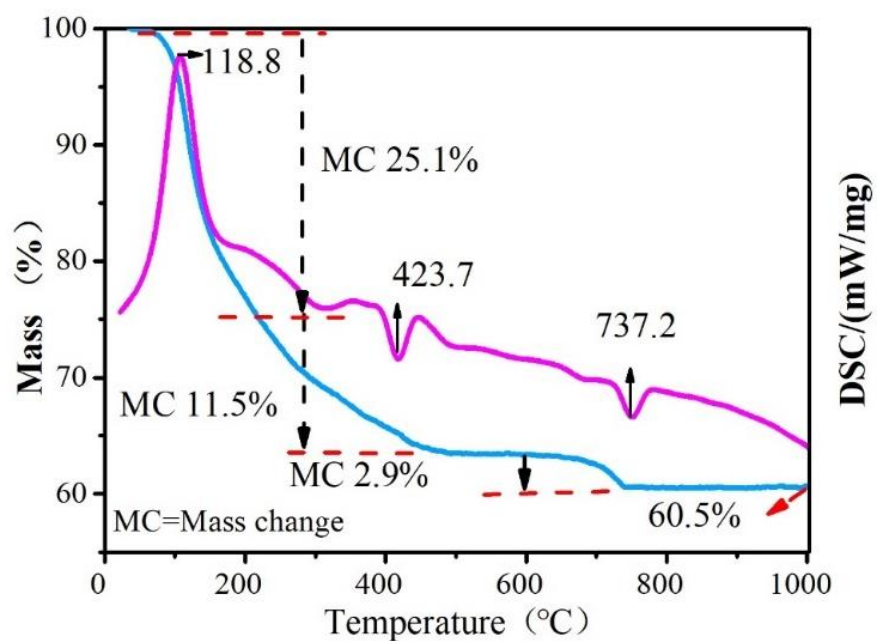
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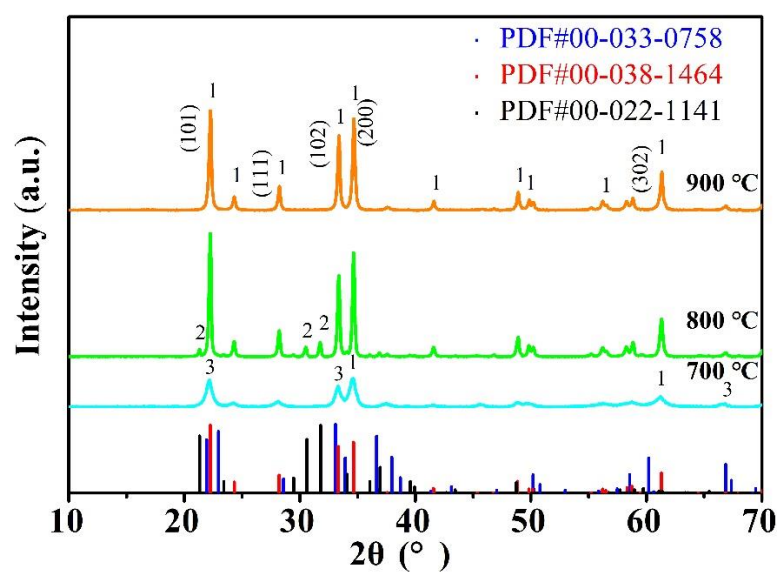
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**Figure S1.** TGA-DSC curves of precursor of LAO



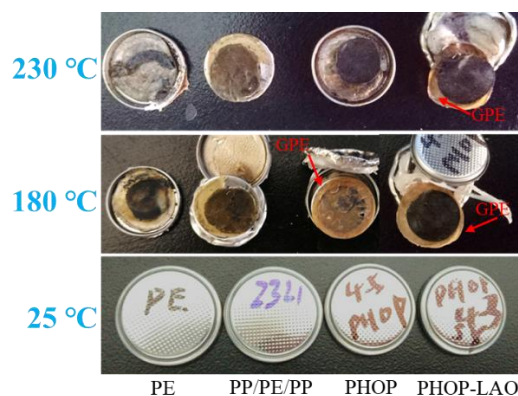
**Figure S2.** XRD patterns of LAOs (1:  $\gamma$ -LAO, 2:  $\text{Li}_2\text{CO}_3$  and 3:  $\beta$ -LAO)

**Table S1.** Phase and content in products at different calcination temperatures

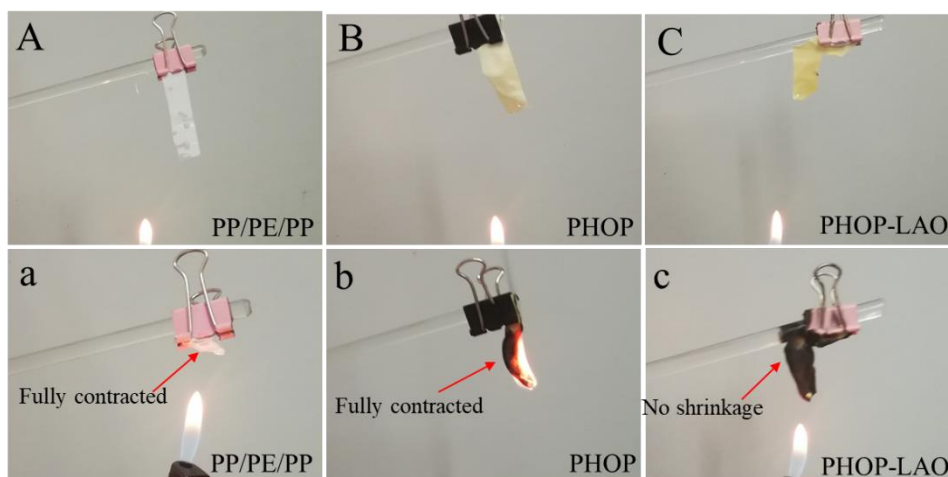
Temperature/ °C	Phase and its relative content/%			
	$\gamma$ -LAO	$\beta$ -LAO	$\text{Li}_2\text{CO}_3$	other
700	12.21	67.23		20.56
800	91.73	1.28	6.26	0.73
900	98.25			1.75

Figure S1 shows that there are three weight loss stages. The first stage occurring at 25.0-210.5 °C with a maximum peak at 118.8 °C (weight loss: 25.1 %) is attributed to the loss of moisture and pyrolysis of Tween 80 and Span 80. The second stage occurring at 210.5-465.1 °C (weight loss: 11.5 %) is due to the loss of crystal water of  $\text{LiOH}\cdot\text{H}_2\text{O}$  and the formation of  $\beta$ -LAO and  $\gamma$ -LAO, and the third stage occurring at 465.1-750.6 °C is due to the formation of a small amount of  $\text{Li}_2\text{CO}_3$  from the reaction of  $\text{CO}_2$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$ , and there is an exothermic peak at 737.2 °C from DSC corresponding to the conversion of the  $\gamma$ -LAO crystal.

Figure S2 shows that  $\gamma$ -LAO,  $\text{Li}_2\text{CO}_3$  and  $\beta$ -LAO phase formed when the calcination temperature is raised from 700 to 900 °C [1], which also indicate  $\gamma$ -LAO (PDF#00-038-1464) can be prepared as the reaction temperature at 900 °C. The diffraction peaks at 1, 2 and 3 correspond to the crystal faces of  $\gamma$ -LAO,  $\text{Li}_2\text{CO}_3$  and  $\beta$ -LAO, respectively, and all diffraction peaks match the standard peaks very well. The phase and content in products at different calcination temperatures are also listed in Table S1. As the temperature of calcinations is raised, the sample prepared at 900 °C has the highest relative content of  $\gamma$ -LAO (98.25 %).



**Figure S3.** Disassembled cell components after heat treatment at 180 and 230 °C for 1h.



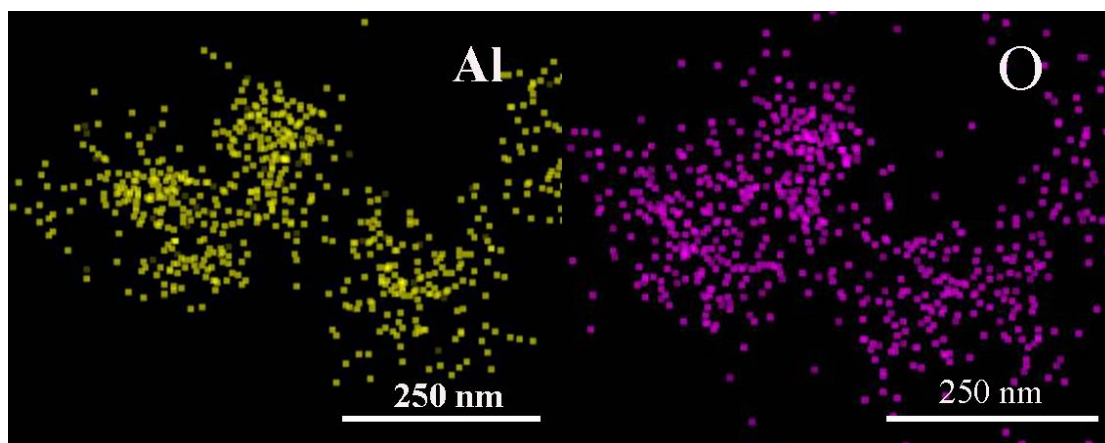
**Figure S4.** Flammability test of commercial separator and gel polymer electrolyte membranes (A, a) Celgard2325, (B, b) PHOP and (C, c) PHOP-LAO before and after pictures

The resistance and thermal stability of the PHOP-LAO and PHOP membranes were evaluated in tests using coin cells without additional separator. The cathode was  $\text{Li}_{1.04}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC111). The cells were fully charged to 4.2 V with a 0.1 C rate, and then heated to 180 °C and 230 °C for 1 h. The cell resistance results are summarized in Figure S3. The NCM and membranes can be clearly seen in the disassembled cell, and compared to other commercial separator, PHOP and PHOP-LAO

membranes remain the original size after being burned at a high temperature of 230 °C. The flame retardancy property of the Celgard2325 (PP/PE/PP), PHOP and PHOP-LAO membranes was evaluated in tests using combustion method. The strip samples were clipped onto the sample holder and subjected to flame for certain time. The samples immersed in 1:1:1 (by volume) mixed organic solvent of ethylene carbonate (EC) /dimethyl carbonate (DMC) /ethyl methyl carbonate (EMC) for 1 h prior to testing. All membranes were ignited in a ventilated box, and recorded the burning time. The flame retardancy of the PHOP and PHOP-LAO membranes was compared to commercial polyolefin separator (Celgard2325) using wet flame tests. The results before and after burning are shown in Figure S4. As the flame approaches, the Celgard2325 separator shrunk into a ball within a second, and PHOP and PHOP-LAO remained the dimensions until they were carbonized after three and five seconds.

**Table S2.** The detailed parameters of the GPEs obtained from TGA and DSC curves

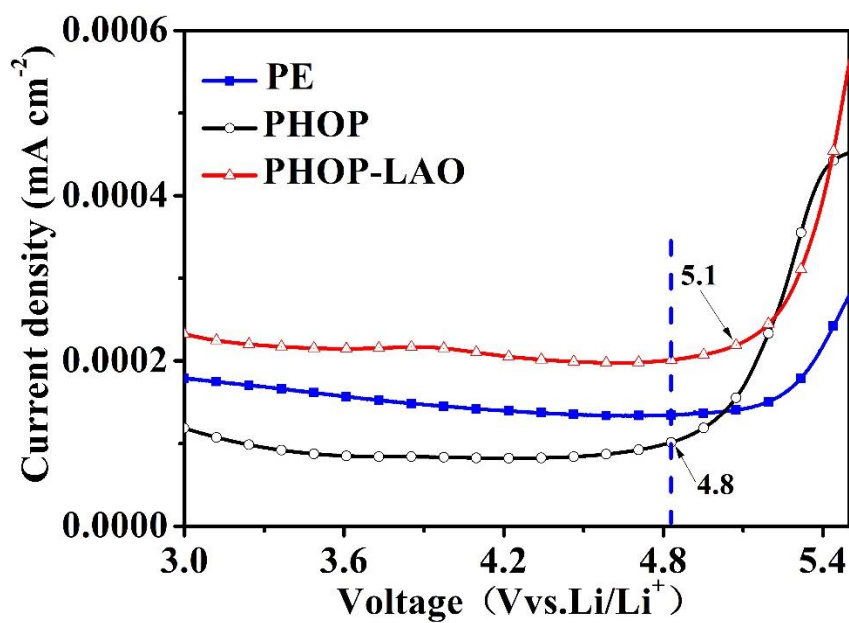
Sample	Temperature (°C)					MDR (% min <sup>-1</sup> )
	T <sub>onset</sub>	T <sub>rp</sub>	T <sub>50%</sub>	T <sub>melset</sub>	T <sub>mel</sub>	
PHOP	435.8	465.2	474.9	146.0	165.0	12.9
PHOP-LAO	454.2	472.7	482.0	153.0	169.0	2.4



**Figure S5.** O and Al elemental mapping images of  $\gamma$ -LAO

**Table. S3** Ion migration numbers of GPEs

GPE	$\Delta V$ (mV)	$I_0$ (mA)	$I_l$ (mA)	$R_0$ ( $\Omega$ )	$R_l$ ( $\Omega$ )	$n$
PHOP	10	0.08806	0.08157	101.4	104.9	0.65
PHOP-LAO	10	0.06848	0.06317	80.3	81.9	0.84



**Figure S6.** LSV curves with different GPEs

The electrochemical stability of the PHOP-LAO, PHOP GPEs and commercial PE separator are shown in Figure S6 by linear sweep voltammetry measurement. The

electrochemical window of those GPEs and PE separator are similar in the range from 3 to 6 V (vs Li/Li<sup>+</sup>), and the decomposition of the liquid electrolyte above at 4.8 V (vs Li/Li<sup>+</sup>) of the oxidation peak can be visible in high-voltage range. The decomposition voltage of PHOP-LAO is higher than that of PHOP due to the stable electrochemical properties  $\gamma$ -LAO [2, 3].

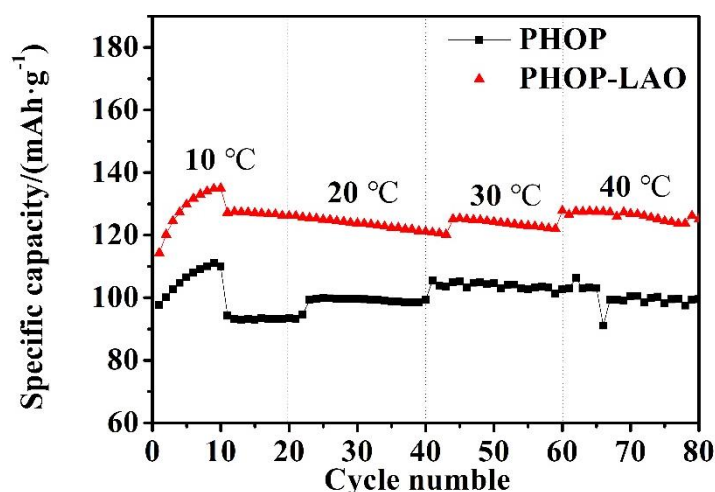


Figure S7. The cycling stability at 2 C of NCM (111)/PHOP or PHOP-LAO-liquid electrolyte/Li cells from 10-40 °C.

To investigate the influence of the temperature on electrochemical performance of PHOP and PHOP-LAO gel polymer electrolytes, the coin cells with NCM (111)/PHOP or PHOP-LAO-liquid electrolyte/Li are measured from 10 °C to 40 °C at 2 C as shown in Figure S7. The initial discharge capacity retention rate of PHOP-LAO is similar to the cell with PHOP gel polymer electrolyte due to the low temperature that need require a certain process for electrolyte wetting with gel polymer electrolyte. As the temperature rises, the tends of capacity with PHOP and PHOP-LAO are slightly rising. This is because temperature has a beneficial influence on lithium-ion conductivity and migration, which is consistent with most research conclusions [4, 5].

## REFERENCES

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