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Supporting Information

Journal name: RSC Advances

Title: Asymmetrically coated LAGP/PP/PVDF-HFP composite separator film and its effect on the improvement of NCM battery performance

Authors: Tian Liang,[a,b] Jianhua Cao,[a] Weihua Liang,[a] Quan Li,[b,c] Lei He[a,b] and Dayong Wu*[a]

Author affiliations:

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Science, 29 zhongguancun east road, Haidian District, Beijing 100190, P. R. China*

[b] *University of Chinese Academy of Science, Beijing 100049, P. R. China*

[c] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100190, P. R. China*

*Corresponding author: dayongwu@mail.ipc.ac.cn

Method

Preparation of Inorganic Ion Conductor, LAGP

Firstly, Li_2CO_3 (11.60 g), $Al(OH)_3$ (7.80 g), $NH_4H_2PO_4$ (69.00 g), GeO_2 (31.38 g), ethanol (35 mL) were thoroughly mixed by the planetary ball milling for 12 h. The ratio between balls and material was 1.1:1 (mass ratio). Then, the well-mixed sample was placed in an alumina crucible, and pre-sintered at 700 °C for 2 h in a tube furnace. After cooling to room temperature, the calcined product was subjected to mash grinding for 20 min (80 rpm), and treated in a tube furnace for 2 h at 900 °C. Finally, the agglomerated LAGP material was collected at room temperature.

The LAGP prepared above was sequentially treated with jaw crusher (30 Hz), mortar grinder (80 rpm, 20 min), and ball-milling. The weight ratio of grinding media to material was 2:1. The ball milling time was 3 h. The obtained powder was sieved with a 150 mesh vibrating sieve. The sieved powder was dried at 70°C for 12 h under vacuum.

Additives used in LAGP slurry

10.4 g of additives including 1.8 g of plasticizer dibutyl phthalate (DBP), 1.8 g of coupling agent γ-glycidoxypropyltrimethoxysilane (KH560), 5.4 g of dispersant BYK111 and 1.4 g of wetting agent BYK307 was added into 1408 g of LAGP slurry and dispersed thoroughly.

Additives used in PVDF-HFP Aqueous Slurry

94.5 g of additives including 9.0 g of aqueous anti-settling agent LAPONITE RD, 60.0 g of aqueous dispersant BYK-LPC 22136, 10.5 g of aqueous wetting agent

BYK-LPX 20990 and 15.0 g of aqueous defoamer BYK-1785 was added into 1458 g of PVDF-HFP slurry.

Ball milling treatment

The program was set as: forward for 5 min and reverse for 5 min at a speed of 200 rpm for 12 h. And an intermittent was set between every forward and reverse rotation for 3 min.

Measurement

The melting point of three separators was measured using a differential scanning calorimeter (DSC, Mettler with a heating rate of 10 °C min^{-1} from 50 °C to 250 °C), and the results are shown in Fig. S1. The thermal decomposition temperature (T_d) data was obtained using a thermogravimetric analyzer (Fig. S2) with a heating rate of 10 °C min^{-1} from 25 °C to 700 °C. The impedance of three types of separators was determined on an electrochemical workstation system (Fig. S3).

The grounded LAGP powder was pressed into pellet (thickness:1 mm, diameter: 13mm) under the pressure of 20 MPa. The soaked LAGP pellet with a mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, w/w/w) was sandwiched between two stainless-steel blocking electrodes to form the test cells. The ionic conductivity of the LAGP pellet was measured by electrochemical workstation system (Zennium 6, Germany) with an AC amplitude of 5 mV in the frequency range of 0.1 Hz -1 MHz. The Nyquist plot of LAGP pellet was shown in Fig. S4.

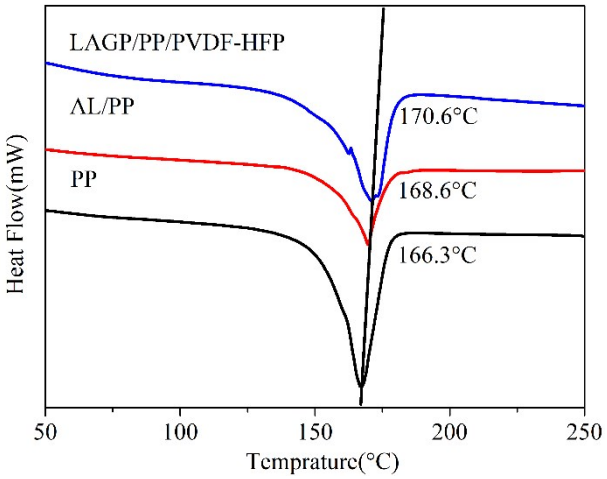

Fig. S1 DSC curves of PP, AL/PP, LAGP/PP/PVDF-HFP separator films.

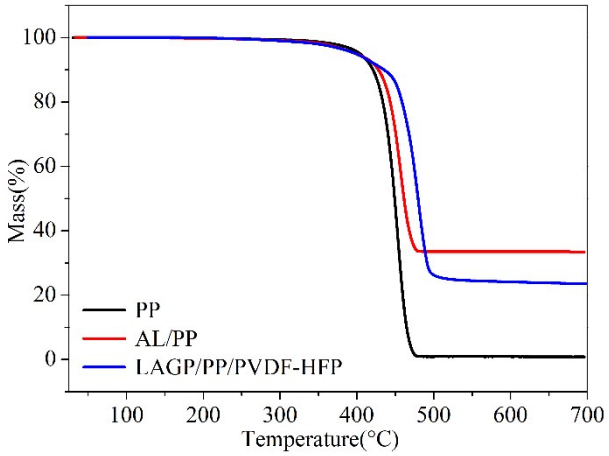

Fig. S2 TGA curves of PP, AL/PP, LAGP/PP/PVDF-HFP separator films.

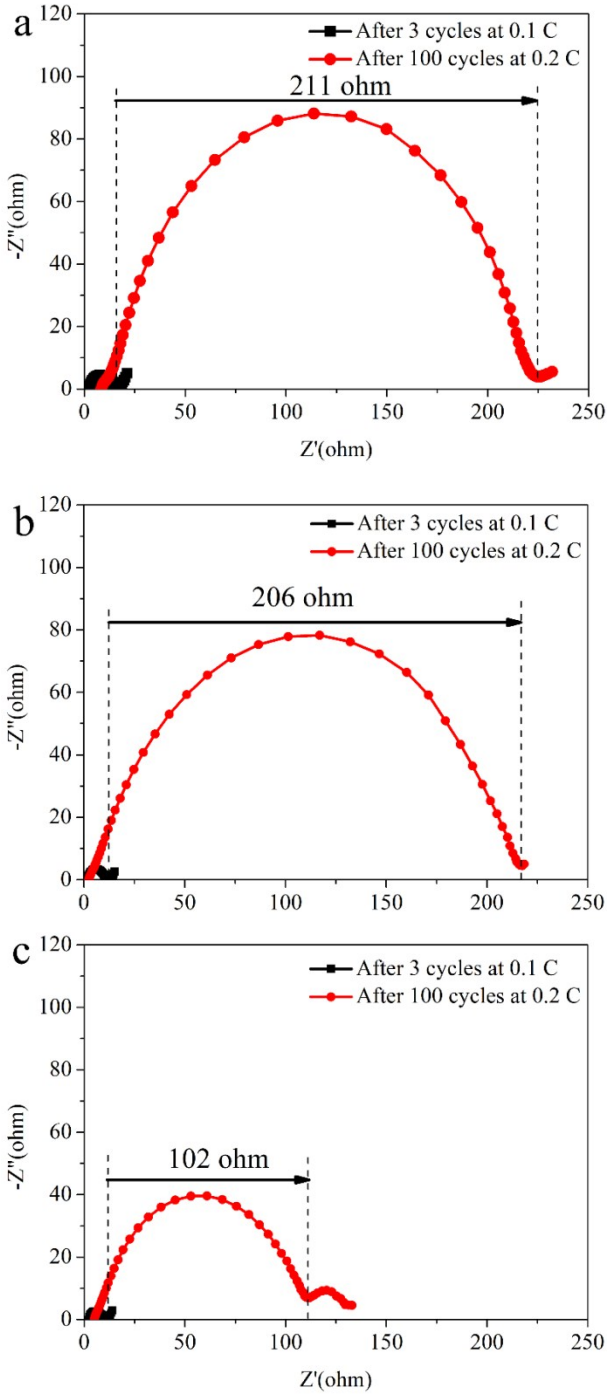

Fig. S3 Variations of the impedance spectra of NCM811|separator|Li half-cells before and after 100 cycles at 0.2 C a) PP, b) AL/PP, c) LAGP/PP/PVDF-HFP separator film.

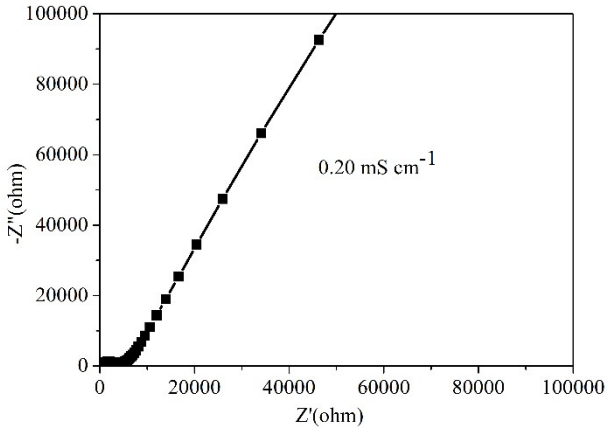

Fig. S4 Nyquist plot of LAGP pellet.

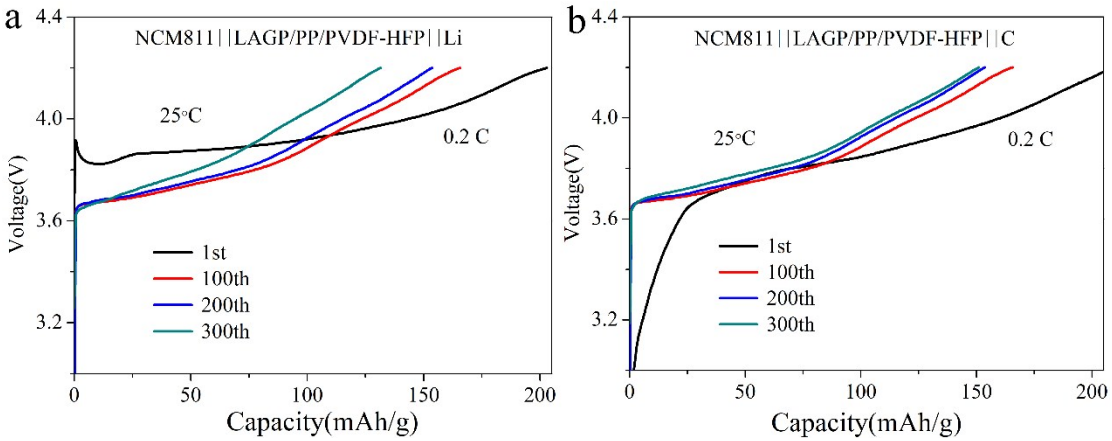

Fig. S5 Charge profiles of (a) NCM811||Li cell with LAGP/PP/PVDF-HFP separator film; (b) NCM811||C cell with LAGP/PP/PVDF-HFP separator film.