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Supporting Information

A multifunctional interlayer activated by lithiophilic electrospun Ag nanowires/polyvinylpyrrolidone nanofibers for efficient lithium storage

Zicheng Wang,[a] *Jianguo Song,*[a] *Yuan Tian* *[a] *and Cheng Wang* *[a]

[a]Institute for New Energy Materials and Low-Carbon Technologies, Tianjin Key Laboratory of Advanced Functional Porous Materials, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, China.

*Corresponding author:

Email: tianyuan@email.tjut.edu.cn (Y. Tian); cwang@tjut.edu.cn (C. Wang)

Experimental Section

Synthesis of Ag nanowires (AgNWs): In a typical synthesis procedure, 1.52 g polyvinylpyrrolidone (PVP, Mw=58 000) was firstly added to 103 mL ethylene glycol (EG, anhydrous, 99.8%) in a conical flask. The mixture was vigorously stirred at room temperature until completely dissolved in EG. Then 0.08 g sodium chloride (NaCl, AR, 99.5%) and 0.05 g potassium bromide (KBr, AR) were injected into the as-prepared transparent and uniform solution. The mixture was added into a 250 ml three-necked flask and heated up to 160 °C with stirring at 300 rpm under Ar atmosphere. Once the temperature in the bottle rose to 160℃, 10 ml of 0.85 g $AgNO_3$/EG solution was added the above-mentioned solution and started the reaction, the synthesis process lasted 3 hours and ensured sufficient conversion from $AgNO_3$ to AgNWs. After the reaction, the solution was cooled in ice water to room temperature, and the AgNWs was added to the acetone solution at a ratio of 1:5. The solid floss in the solution was removed and added to ethanol and dispersed in the centrifuge tube for 15 minutes at 3000 rpm, the collected solid product was dispersed in 2 ml ethyl alcohol for the next fabrication processes.

Synthesis of Ag nanoparticles (AgNPs): Uniform AgNPs can be synthesized by adjusting the molar ratio of PVP and $AgNO_3$. The mixture were centrifuged at 4500 rpm for 10 min, and the collected powder was washed with distilled alcohol several times. The optimal molar ratio of PVP:AgNO3= 8:1 is proved through a series of experiments.

Synthesis of Ag nanowires/polyvinylpyrrolidone (AgNWs/PVP) nanofibers: Firstly, 1g PVP (Mw=150 000) was dissolved in the mixed liquor of 2 mL N,N-dimethylformamide (DMF, AR) and 6 mL alcohol (EtOH) by stirring 2 h at room temperature. Then, 2 mL of 2.78 M AgNWs/EtOH was added into the above mixture under vigorous stirring for 5 h. The obtained

homogeneous electrospinning precursor were placed in a syringe with a feeding rate of 0.3 mL h^{-1} and a high voltage power supply of 24 kV. Finally, the collected Ag nanowires/polyvinylpyrrolidone nanofibers (denoted as AgNWs/PVP) were dried in a vacuum oven at 80 °C overnight. For comparison, PVP nanofibers was prepared under the same conditions without the presence of AgNWs. The same goes for AgNPs/PVP nanofibers.

Characterizations: The phase constituents were determined by X-ray diffraction (XRD, SmartLab 9KW). The morphology was examined using scanning electron microscope (SEM, Verios 460L) and transmission electron microscope (TEM, Talos F200 X).

Electrochemical Measurements: All the batteries using a CR2032 coin cell were assembled in the Ar-filled glove box. The polypropylene (PP) film (Ceglard 2500) was used as the separator and the electrolyte containing 1.0 M $LiPF_6$ dissolved in a mixture of diethyl carbonate, ethyl methyl carbonate and ethylene carbonate (1:1:1 v/v/v). Li-Cu half-cells were assembled using Cu foil as the counter electrode, lithium foil as the working electrode and PVP (AgNPs/PVP or AgNWs/PVP) as the interlayer between the Celgard 2500 separator and lithium foil. Notably, these interlayers covered on the top of the lithium foil was denoted as PVP-Li (AgNPs/PVP-Li or AgNWs/PVP-Li), respectively. For the Li||Li symmetric cells, two pieces of identical interlayer were need to separately insert the separator and lithium metal. The galvanostatic charge/discharge measurement and rate performance were conducted on the battery testing system (LAND C2001A) at different current densities and capacity to investigate the Li stripping/plating behavior. The electrochemical impedance spectroscopy (EIS) plots were carried out on the CHI 660D electrochemical working station with a frequency range from 0.01 to 10^5 Hz. The full lithium metal batteries were assembled by a configuration of commercial $LiFePO_4$ (LFP, PULEAD Technology Industry Co., Ltd.) cathode/separator/interlayer/lithium metal anode,

which was denoted as Li||PVP (AgNPs/PVP or AgNWs/PVP)||LFP. The LFP cathode was prepared in a mixed slurry of LFP, super P, and polyvinylidene fluoride (7:2:1 in weight ratio) in N-methyl-2-pyrrolidone and coated on the Al foil. Then, the above-mentioned cathode was cut into a wafer with a diameter of 12 mm and dried under vacuum at 60 °C. The thickness and areal mass loading of the LFP cathode were 33 μm and 1.86 mg cm^{-2}, respectively. All electrochemical measurements were performed in a LAND C2001A testing system between 2.0 V and 4.0 V.

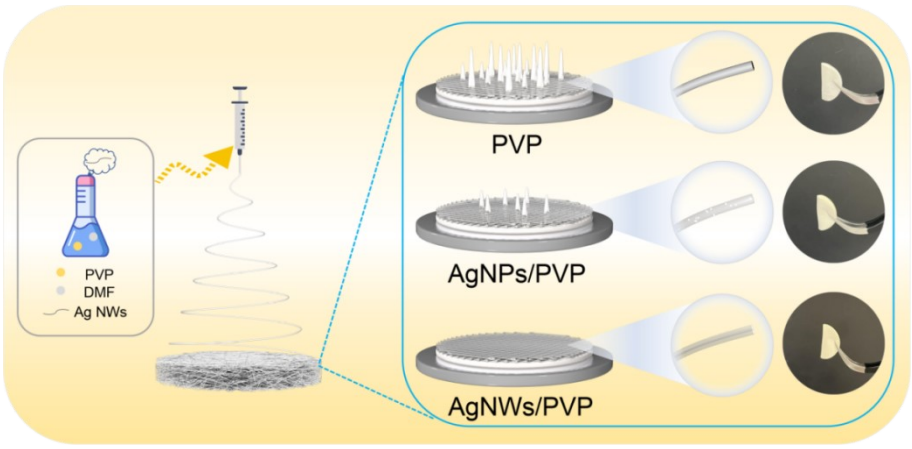

Fig. S1 Schematic illustration of the synthetic procedure for the PVP, AgNPs/PVP and AgNWs/PVP nanofibers.

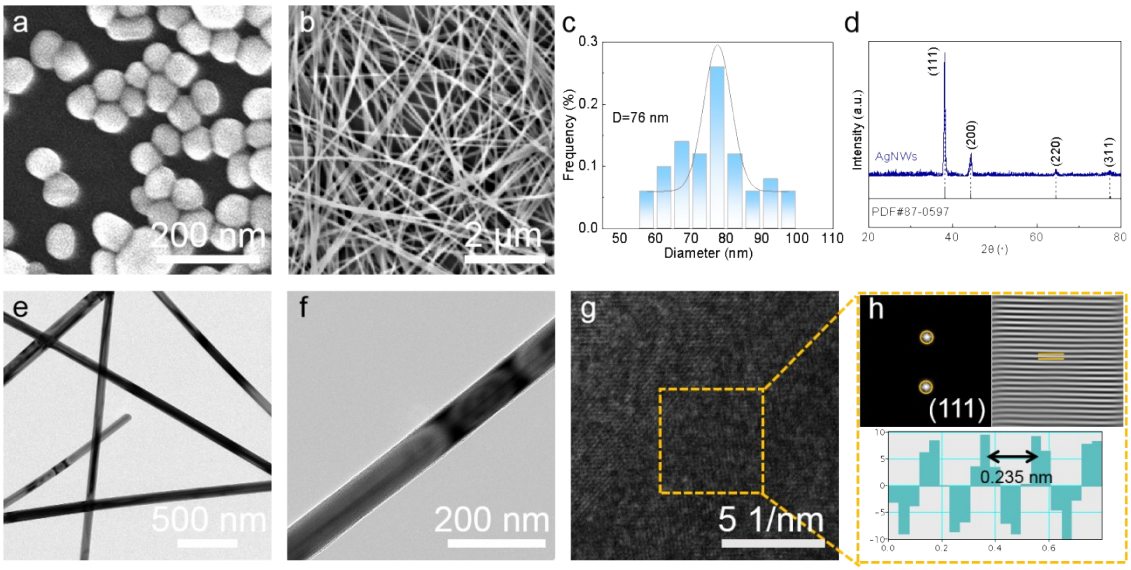

Fig. S2 SEM images of (a) AgNPs and (b) AgNWs; (c) statistical distribution of diameter from optical image of AgNWs; (d) XRD pattern of AgNWs; (e, f) TEM images in different magnifications, (g) HRTEM image, (h) FFT pattern, IFFT pattern and lattice spacing profile at selected area for AgNWs.

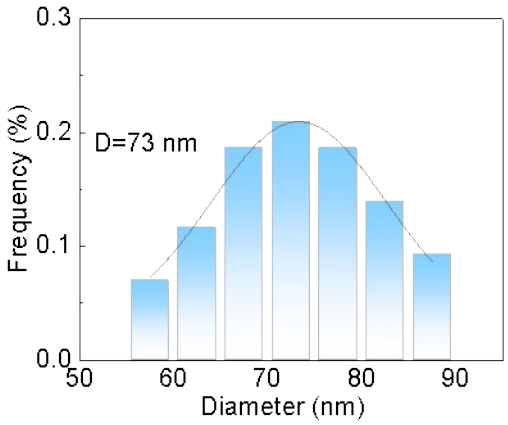

Fig. S3 Statistical distribution of diameter from optical image of AgNPs.

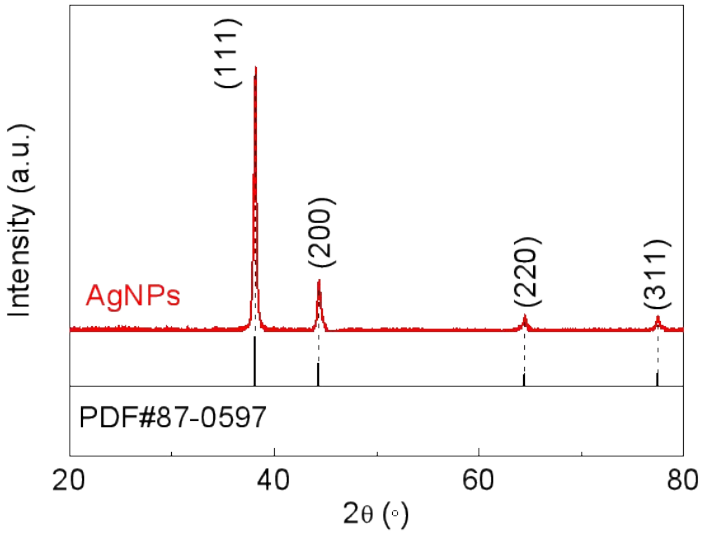

Fig. S4 XRD pattern of AgNPs.

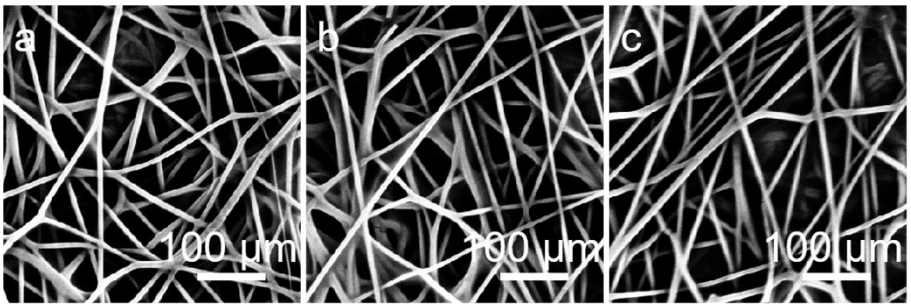

Fig. S5 SEM images of (a) PVP, (b) AgNPs/PVP, (c) AgNWs/PVP.

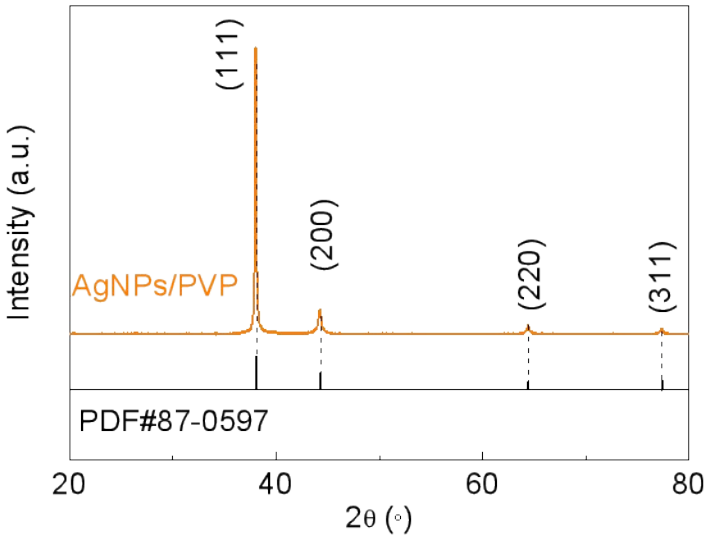

Fig. S6 XRD pattern of AgNPs/PVP.

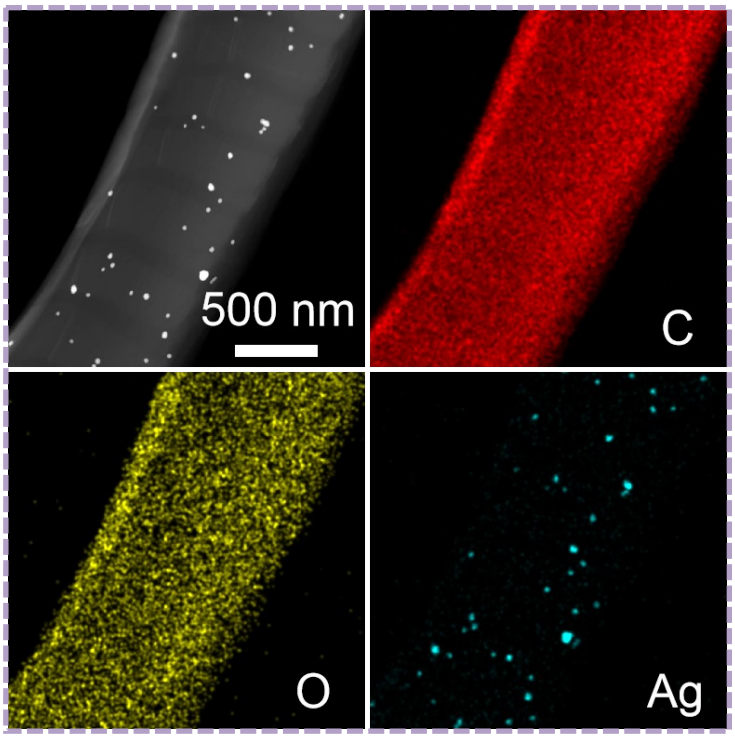

Fig. S7 Elemental mappings of AgNPs/PVP.

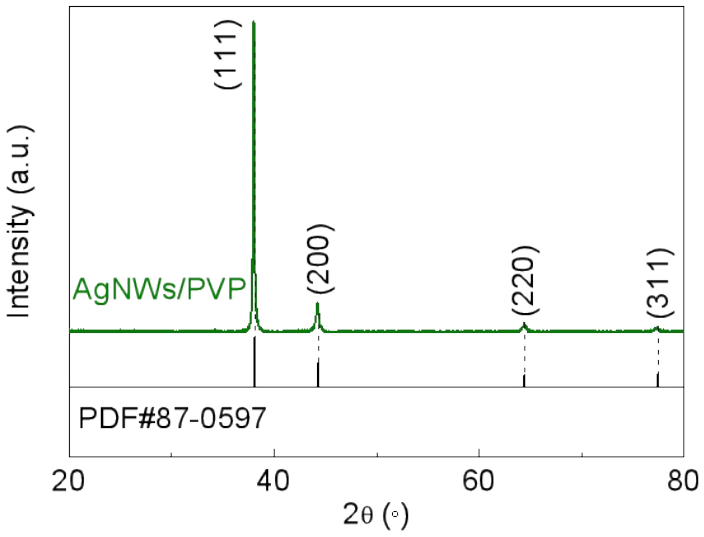

Fig. S8 XRD pattern of AgNWs/PVP.

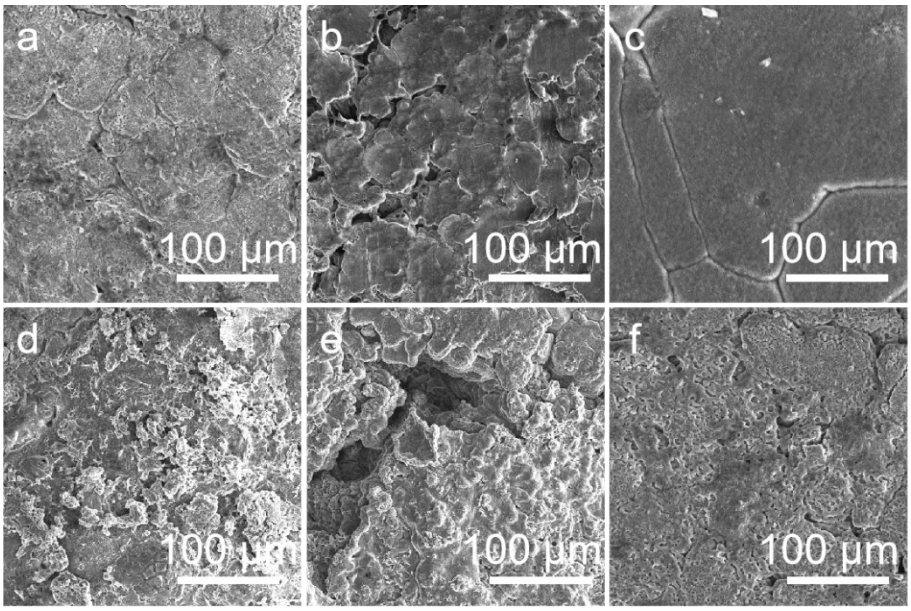

Fig. S9 SEM images of Li surfaces with (a) PVP, (b) AgNPs/PVP and (c) AgNWs/PVP interlayers after 50 cycles; the SEM images of Li surfaces with (d) PVP, (e) AgNPs/PVP and (f) AgNWs/PVP interlayers after 150 cycles.

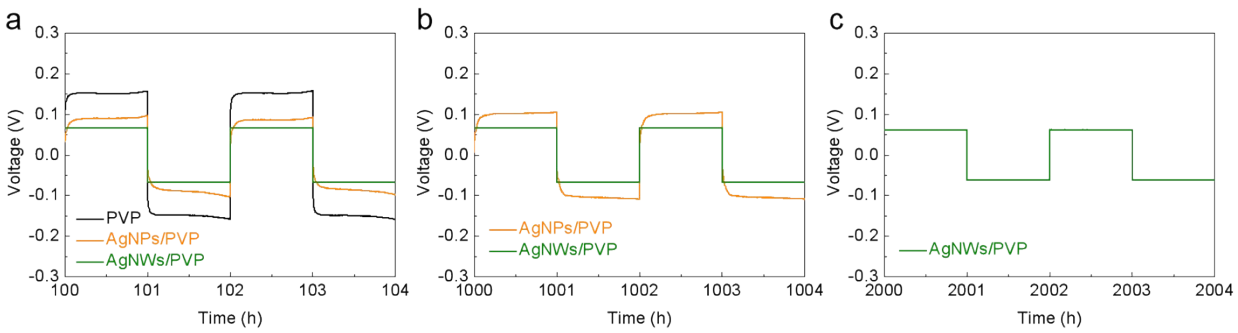

Fig. S10 Enlarged voltage profiles of the Li||Li symmetric cells with different modified interlayers at 1 mA cm^{-2} for 1 mAh cm^{-2} after (a) 100 h, (b) 1000 h and (c) 2000 h.

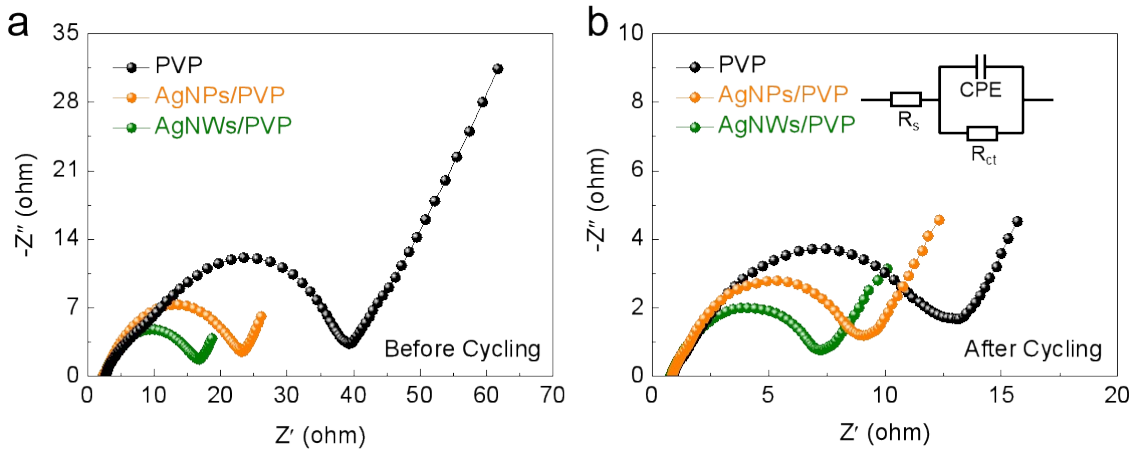

Fig. S11 EIS plots of Li||Li symmetric cells with different modified interlayers (a) before cycling and (b) after cycling (the inset shows the obtained equivalent circuit).

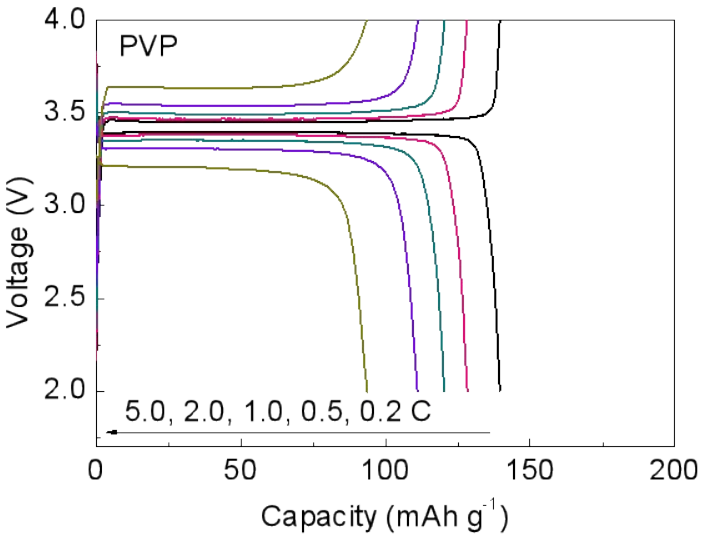

Fig. S12 The charge/discharge curves at different current densities of the Li||PVP||LFP full cell.

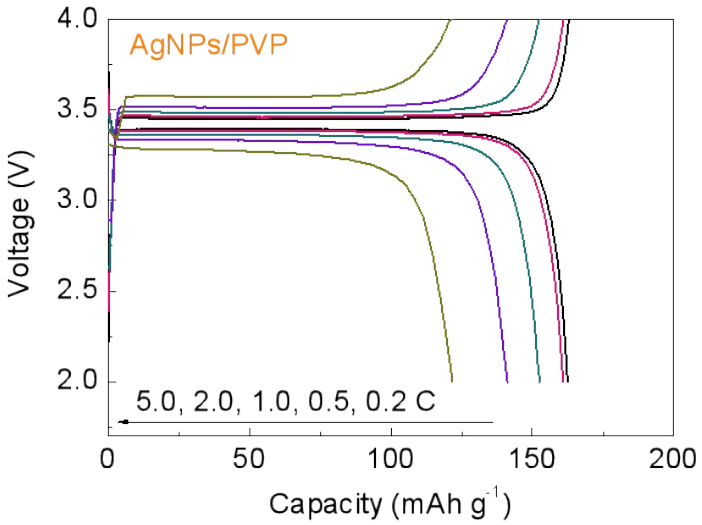

Fig. S13 The charge/discharge curves at different current densities of the Li||AgNPs/PVP||LFP full cell.

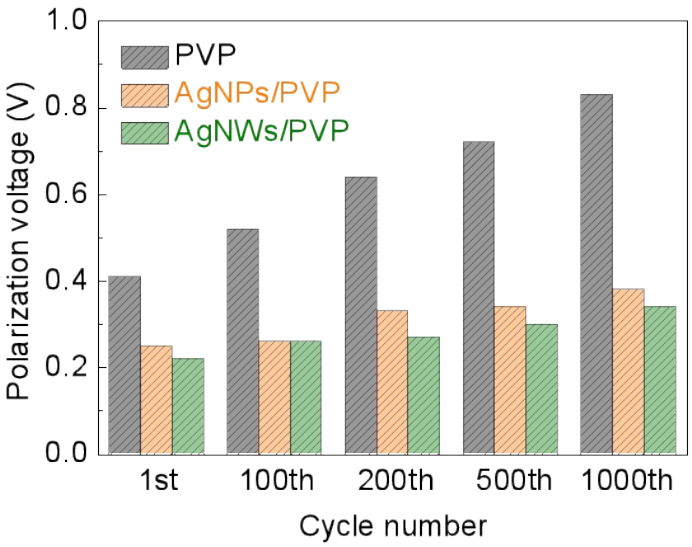

Fig. S14 Polarization voltage at different cycles of the Li||LFP full cells with PVP, AgNPs/PVP and AgNWs/PVP modified interlayers.