Supporting Information

Chemically exfoliated boron nitride nanosheets induced robust interfacial layers for stable solid state Li metal batteries

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1. Experimental Section

1.1 Materials.

h-BN was purchased from Momentive Performance Materials Inc. . Poly(ethylene oxide) (PEO) was purchased from Sigma-Aldrich. Lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI) was purchased from Tokyo Chemical Industry. Acetonitrile was purchased from Sinopharm Chemical Reagent Co., Ltd. All chemical regents were used as received without further purification.

1.2 Preparation of BNNSs and monolayered MoS_2 via chemical exfoliation

2 g of h-BN flakes, 40 g of ZrO_2 balls (5 mm in diameter) and 20 mL of 5M NaOH aqueous solution were mixed together inside a ZrO_2 grinding bowl using a planetary ball mill (Restsch PM 100) at a rotation speed of 200 rpm for 48 h at room temperature. The milled product was washed with deionized water (DIW) to neutral. The obtained h-BN-OH flakes were dried at 80 ^oC for 24 h. A mixture of 0.4 g of h-BN-OH flakes and 2 g of Li metal foil was set in a tantalum crucible and magnetically stirred at 300 ^oC for 2 h under Ar atmosphere in a glovebox. After cooling to the room temperature, the tantalum crucible was transferred out of the glovebox. Ethanol (Et-OH) and deionized water (DIW) were added into tantalum crucible to react with the Li infused h-BN-OH flakes. The obtained BN flakes were collected by vacuum filtration and then rinsed with DIW to neutral and then were dispersed in Et-OH with following sonication for 2 h. The dispersed BN solution was centrifuged at 5000 rpm for 10 minutes to remove the thick flakes and the supernatant was collected as BNNSs/Et-OH suspension.

A mixture of 0.1 g of MoS_2 and 0.5 g of Li metal foil was set in a tantalum crucible and magnetically stirred at 300 ^oC for 1 h under Ar atmosphere in a glovebox. After cooling to the room temperature, the tantalum crucible was transferred out of the glovebox. Ethanol (Et-OH) and deionized water (DIW) were added into tantalum crucible to react with the Li infused

MoS_2. The obtained MoS_2 flakes were collected by vacuum filtration and rinsed by deionized water to neutral pH value and then were dispersed in Et-OH with the following sonication for 2 h. The obtained MoS_2 suspension was centrifuged at 5000 rpm for 10 minutes to remove the thick flakes and the supernatant was collected as the monolayered MoS_2/Et-OH suspension.

1.3 Preparation of PEO electrolyte

A mixture of PEO (2 g) and LiTFSI (0.725 g) was dissolved in acetonitrile and stirred for 24 h at room temperature. The molar ratio of ethylene oxide groups to Li ions was set as 18:1. The obtained slurry was poured into a Teflon mold after removing air bubbles by a treatment in a vacuum oven. The solvent was evaporated at room temperature and then dried in a vacuum oven at 60 ^{o}C for 48 h. The dried PEO electrolyte film was peeled off from the mold, cut with a puncher, and stored in the glovebox.

1.4 Fabrication of BNNSs coated PEO electrolyte

The as-prepared BNNSs was coated onto one side of a commercial polypropylene (PP) separator by the vacuum filtration of BNNSs/Et-OH suspension and dried at 60 ^{o}C for 6 h. The BNNSs coated PP separator was cut with a puncher and stored in the glovebox. BNNSs coating was transferred onto the surface of PEO electrolyte through hot-pressing at 60 ^{o}C for 1 h. After cooling to room temperature, the PP separator was peeled off to yield the BNNSs-coated PEO electrolyte. The mass loading of BNNSs on the PEO electrolyte was determined by the mass coating of BNNSs on the separator. The obtained BNNSs-coated PEO electrolyte was stored in the glovebox for the following characterizations.

1.5 Ionic conductivity measurements

The polymer electrolyte was sandwiched between two stainless steel electrodes and housed in a 2032 coin cell. The ionic conductivity of the polymer electrolyte was measured by electrochemical impedance spectroscopy from 1 MHz to 100 mHz with an alternating current amplitude of 10 mV for various temperatures from 30 ^{o}C to 100 ^{o}C on the VMP3 multichannel electrochemical station (Bio Logic Science Instruments, France). The value of ionic conductivity (σ) was calculated based on the thickness of BNNSs-coated electrolyte (L), the diameter of stainless electrodes (A) and the resistance of EIS (R).

$$\sigma = \frac{L}{RA}$$

1.6 Electrochemical tests

Li/polymer electrolyte/Li symmetrical cells were fabricated in an argon-filled glove box. The interface stability of the BNNSs-coated electrolyte against a Li metal electrode was examined by a galvanostatic cycling process. The Li/Li symmetric cells were tested at 60 ^{o}C by repeating one hour charge, 10 minutes rest and one hour discharge at a current density of 0.3 mA cm^{-2}. For the Li/polymer electrolyte/LFP cell, a slurry of $LiFePO_4$, carbon black (Super-P), PEO, LiTFSI (65:15:15:5 by weight) and acetonitrile (15 mL) was made using a planetary ball mill (Restsch PM 100) at a rotation speed of 300 rpm for 4 h at room temperature. The slurry was cast on a carbon-coated aluminum foil and dried at 60 ^{o}C under vacuum for 12 h. The active material loading on electrode ranged from 2 to 2.5 mg cm^{-2}. 2032 type coin cells were assembled in an argon-filled glovebox with Li foil as the anode and the BNNSs-coated PEO electrolyte as the solid electrolyte. The cells were cycled at various charge-discharge rates between 2.5-3.8 V on a Land 2001A battery testing system at 60 ^{o}C.

1.7 Characterizations

The SEM was performed on a JEOL-JSM-6700 scanning electron microscope at an acceleration voltage of 5 kV. The cross-section of BNNSs-coated PEO electrolyte was cut by an ion beam cutter (Leica-EMTIC3X) at -80 ^oC. The TEM images were acquired on a Hitachi HT-7700 transmission electron microscope with an accelerating voltage of 120 kV. High-resolution TEM (HRTEM) imaging was carried out on a JEOL ARM200F transmission electron microscope operated at 200 kV. In order to avoid distraction from the amorphous support film, the specimen used for HRTEM observation was prepared using a Cu grid coated with holey carbon film. Atomic force microscopy (AFM) measurements were achieved on a Veeco DI Nano-scope MultiMode V system in the tapping mode by depositing a drop of an aqueous dispersion of BNNSs onto freshly cleaved mica substrates. Rectangular specimens (25 mm×3 mm×0.12 mm) were used for the dynamic mechanical experiments. The dynamic mechanical thermal analyzer (DMA 850) was used for the evaluation of the dynamic moduli. The temperature range over which properties was measured range from 30 to 100 ^oC at a heating rate of 5 K/min. The tests were carried out at frequencies 1 Hz and at a oscillation strain of 0.05%.

2. **Figures**

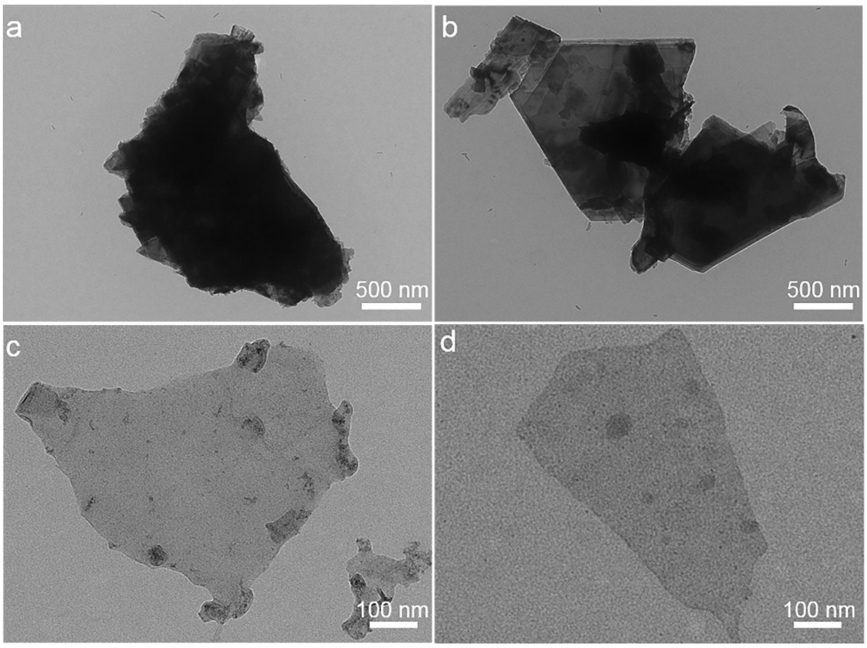

Figure S1. TEM image of pristine MoS2 and chemically exfoliated monolayer MoS2. (a, b) pristine MoS2. (c, d) monolayer MoS2

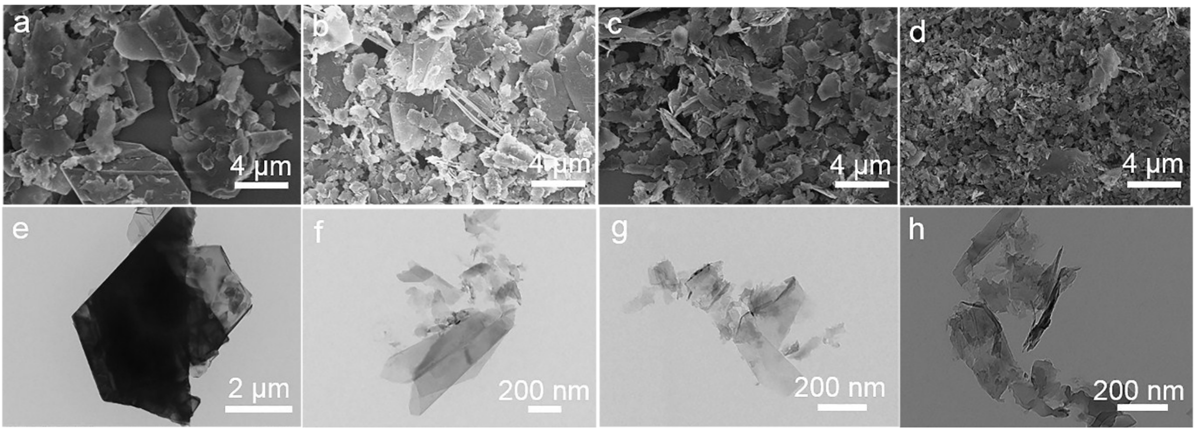

Figure S2. Microstructural characterizations of the unexfoliated h-BN flakes and the obtained BNNSs at different Li infusion reaction time. (a-d) SEM images of unexfoliated h-BN flakes for reaction time of 0 h, 1 h, 2 h, and 12 h, respectively. (e-h) TEM images of pristine h-BN flake and BNNSs for reaction time of 0 h, 1 h, 2 h, and 12 h, respectively.

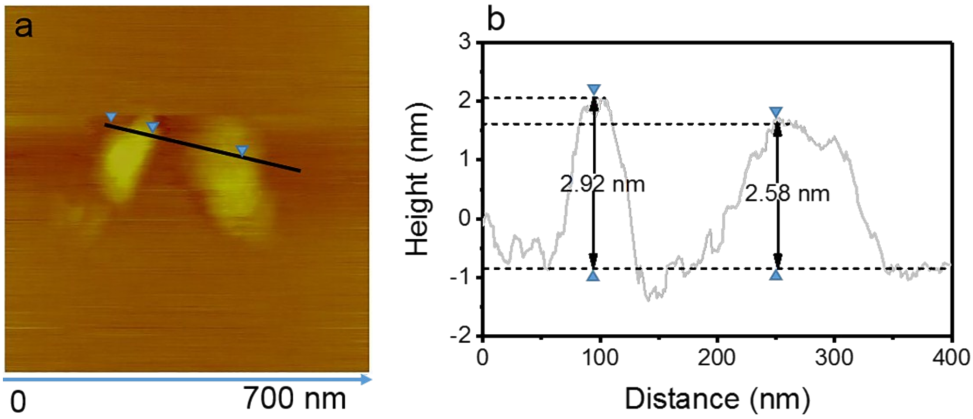

Figure S3. (a, b) AFM image and corresponding height line-scan profile of BNNSs.

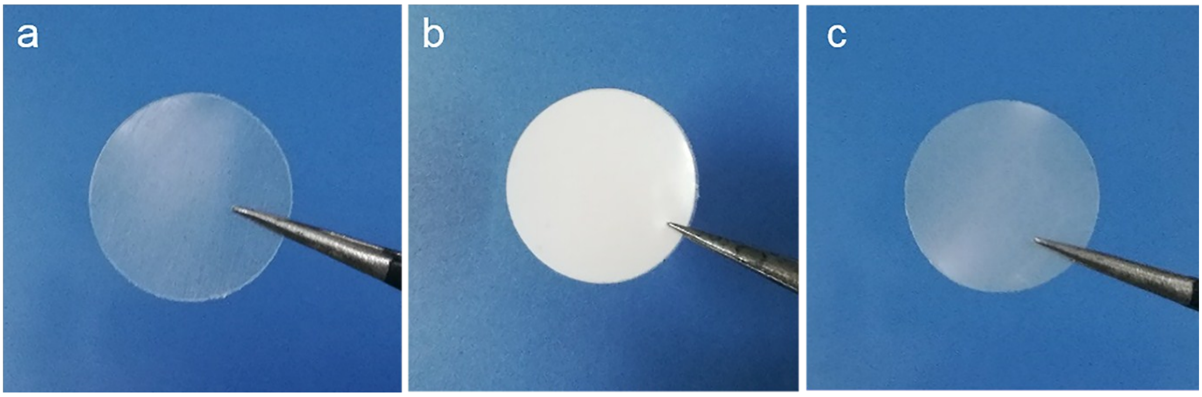

Figure S4. Photos of the solid electrolytes. (a) Pristine PEO electrolyte. (b) the PP/BNNSs-PEO-BNNSs/PP sandwiched layer. (c) BNNSs-coated PEO electrolyte.

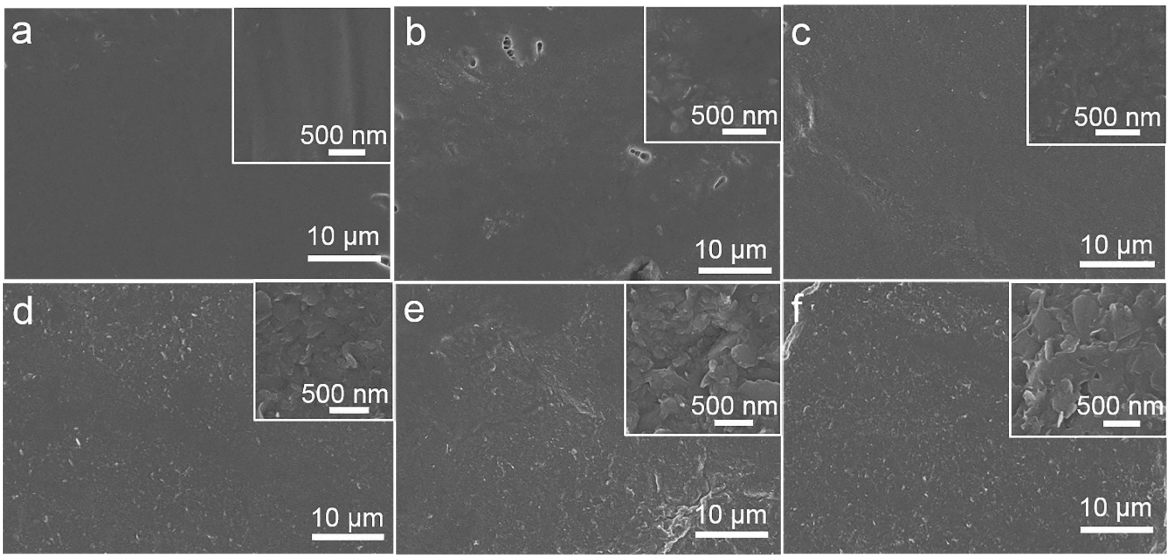

Figure S5. SEM images for the surface of PEO electrolyte and with different mass loading of BNNSs-coatings. (a) Pristine PEO electrolyte. (b, c, d, e, and, f) 0.005, 0.01, 0.02, 0.036 and 0.05 mg/cm^2 of BNNSs-coated electrolyte.

As shown in Figure S5, the surface was completely coated by BNNSs until the mass loading increase to 0.02 mg/cm^2.

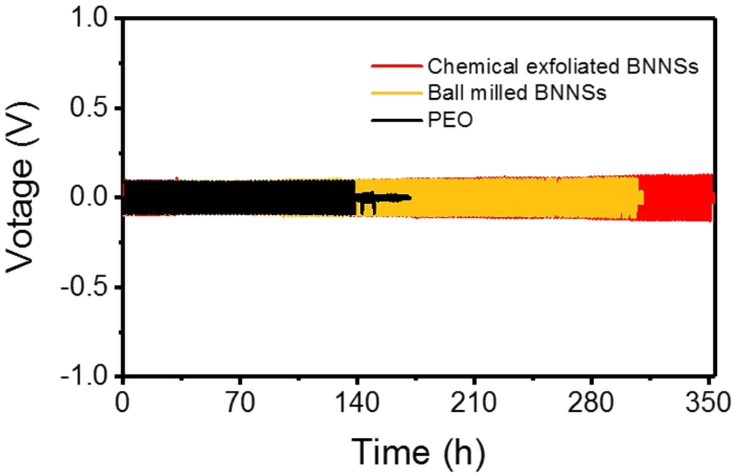

Figure S6. Galvanostatic cycling curves of Li/Li symmetrical cells based on 0.02 mg/cm^2 BNNSs-coated PEO electrolyte at a current density of 0.3 mA cm^{-2} and 60 ^{o}C. The BNNSs were obtained from chemically exfoliated or ball milled method.

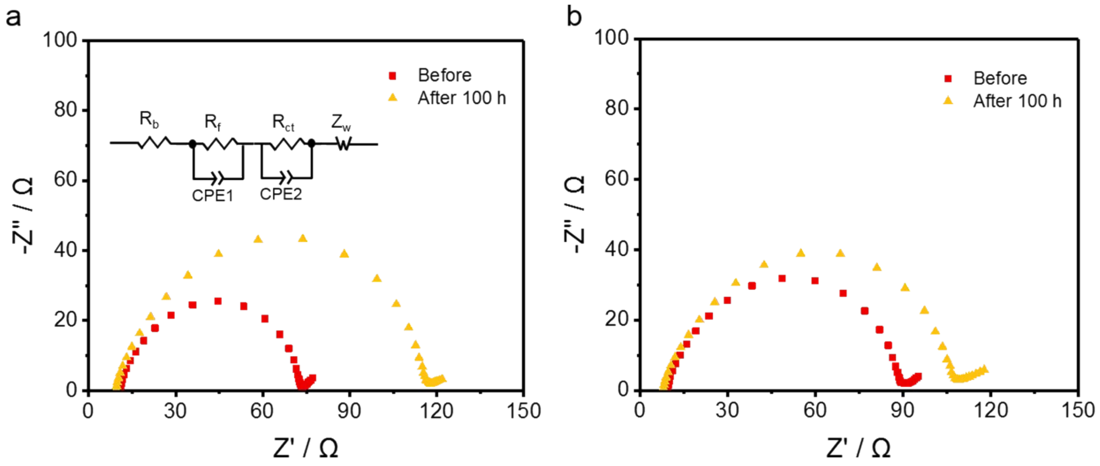

Figure S7. EIS profiles of the Li/PEO/Li cell and Li/BNNSs-coated PEO/Li cell before and after 100 h cycling. (a) Li/PEO/Li cell. (c) Li/BNNSs-coated PEO/Li cell. The inset is the simulating equivalent circuit (Figure S5a). In the Nyquist plots, the impedance spectra of the cells are comprised of one semicircle and one inclined line, corresponding to the interfacial impedance (R_f and R_{ct}) and the Warburg impedance (Z_w), respectively. At high frequency, the intercept of the spectra with the real axis decreases with the increase of cycling time, reflecting the decreased bulk impedance (R_b) of the electrolyte. The semicircle of the Nyquist plots at the high and middle-frequency regions exhibits the increase of interfacial impedance between PEO electrolyte and lithium metal during cycling.

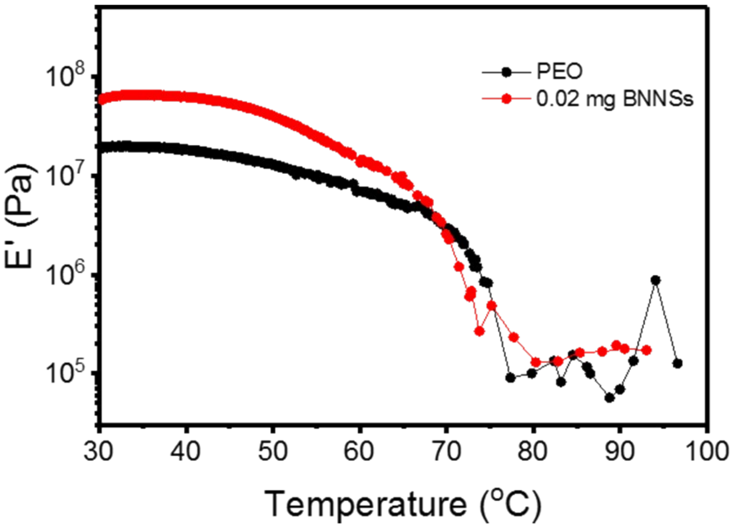

Figure S8. Storage modulus-temperature curves of the PEO and 0.02mg/cm^2 BNNSs-coated PEO electrolyte.The storage modulus-temperature curves were obtained from the DMA test. This curves intuitively exhibited the change of stiffness in PEO and 0.02mg/cm^2 BNNSs-coated PEO electrolyte with the elevated temperature. The improved stiffness of the BNNSs-coated PEO electrolyte can be attributed to the BNNSs coating layer. The mechanical stability of BNNSs-coated PEO electrolyte was better than PEO electrolyte at 60 ^{o}C.

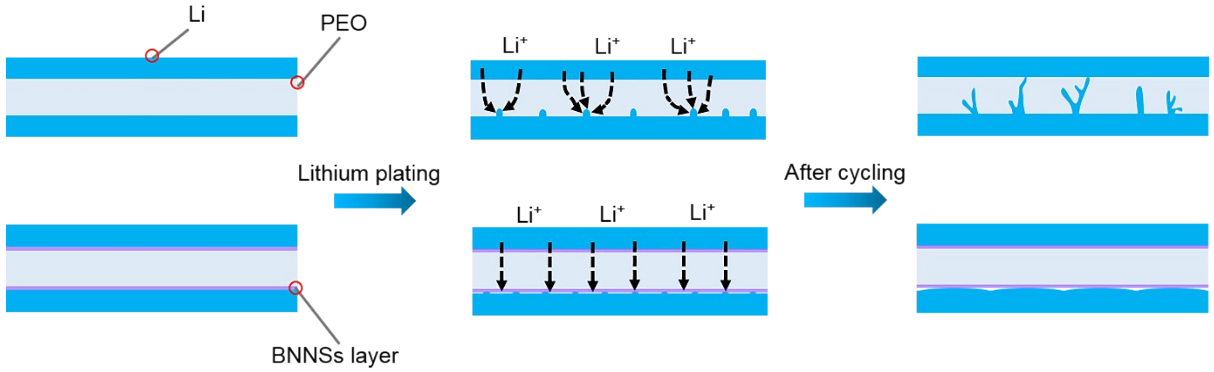

Figure S9. The mechanism schematics of BNNSs coating offering a stable interface for a uniform plating/stripping of Li in comparison to the growth of Li dendrites under pristine PEO electrolyte.

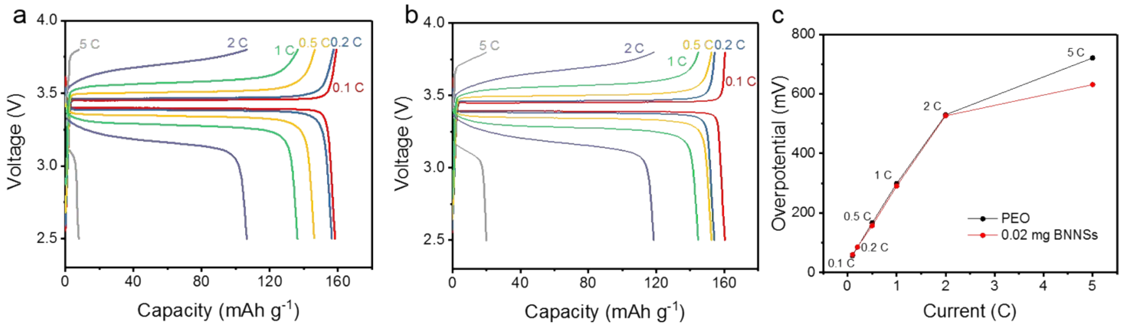

Figure S10. Charge and discharge voltage profiles of Li/$LiFePO_4$ cells with PEO and BNNSs-coated PEO electrolyte at different rates. (a) Li/PEO/LFP cell. (b) Li/BNNSs-coated PEO/LFP cell. (c) The plot of overpotential under different C-rates.