

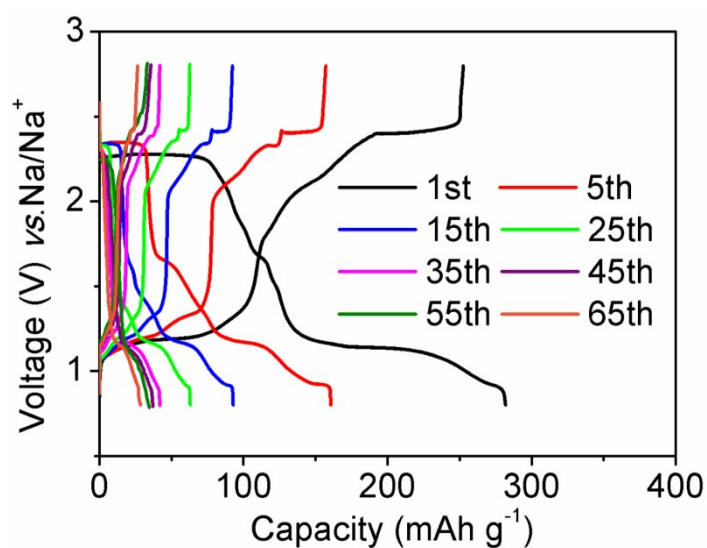
Supporting Information for:

## Free-standing protective films for enhancing the cyclability of organic batteries

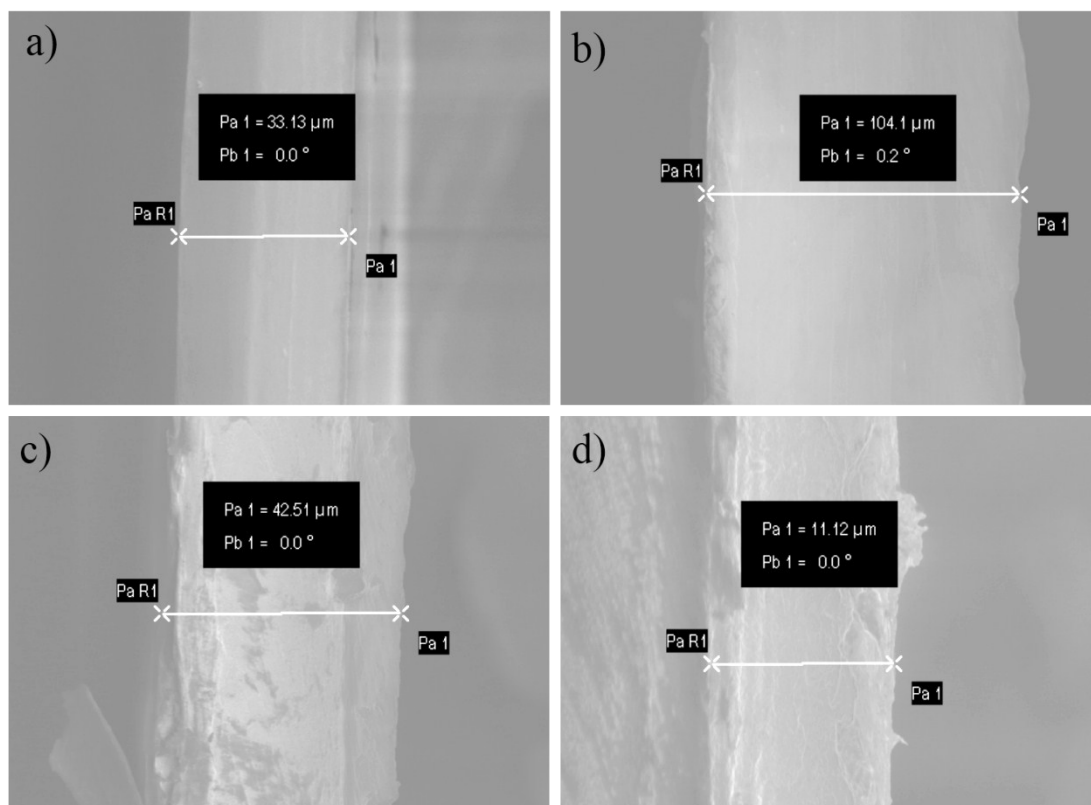
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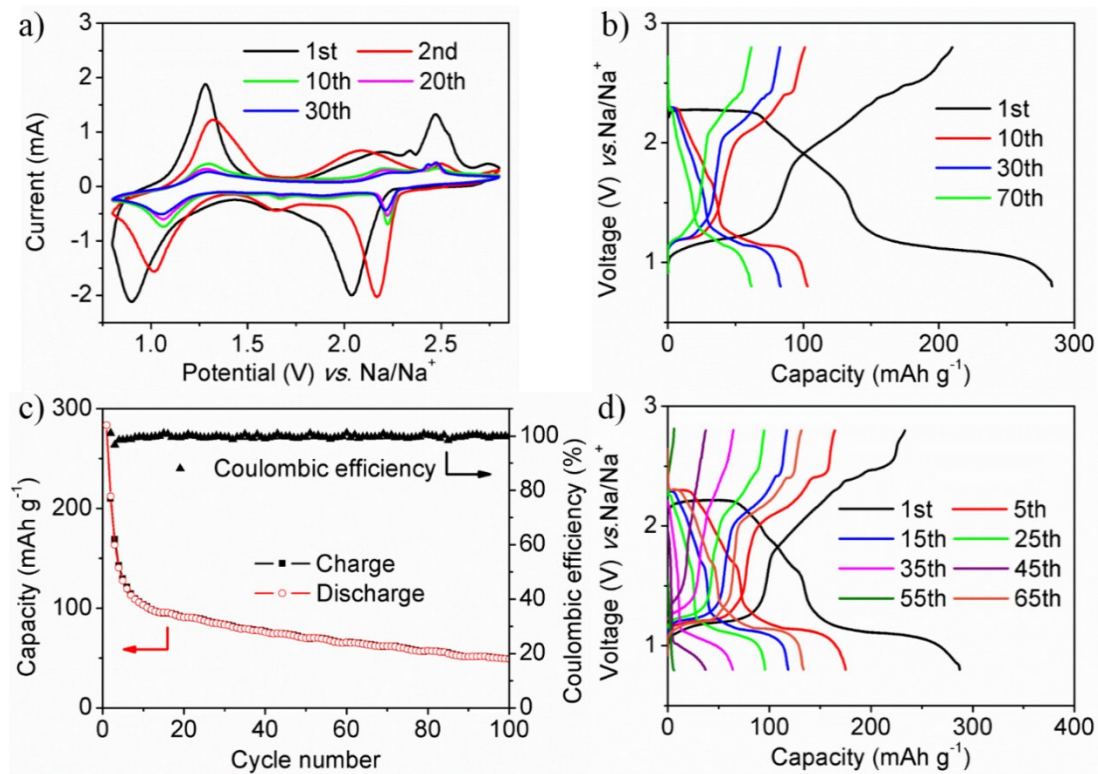
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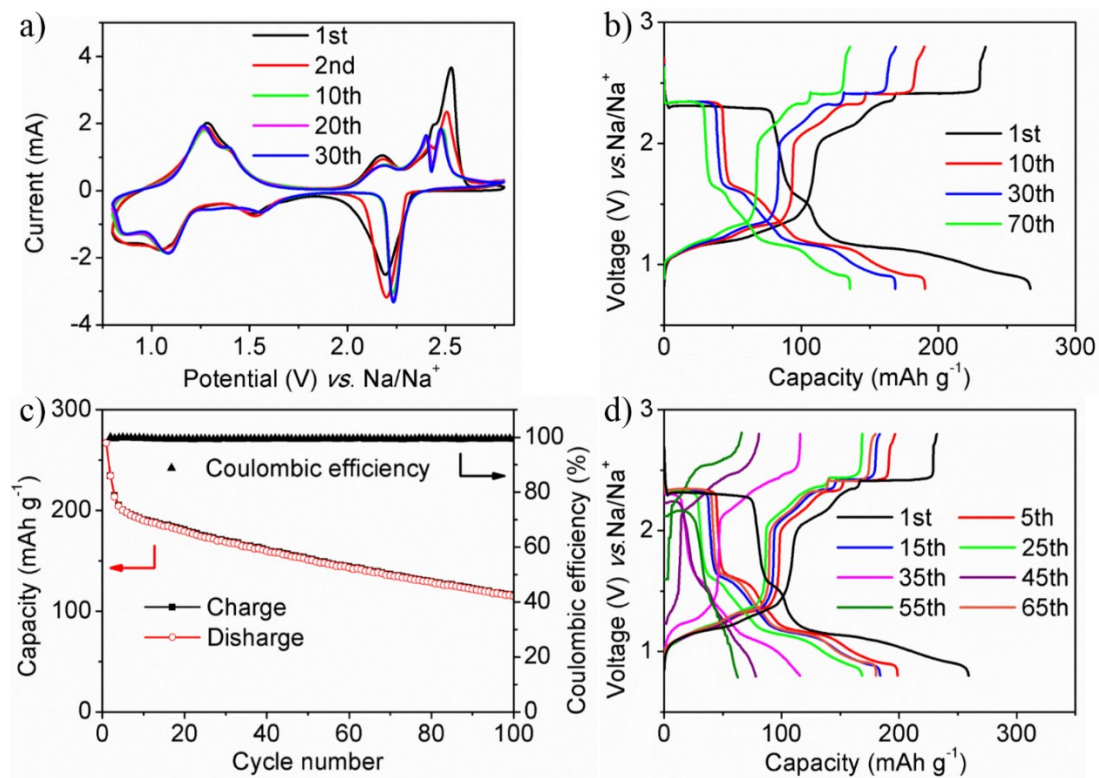
**Fig. S1** Voltage profiles of PT electrodes (without protective films) for rate performance (1<sup>st</sup>, 5<sup>th</sup> and 65<sup>th</sup> cycles: 50 mA g<sup>-1</sup>, 15<sup>th</sup> cycle: 100 mA g<sup>-1</sup>, 25<sup>th</sup> cycle: 200 mA g<sup>-1</sup>, 35<sup>th</sup> cycle: 500 mA g<sup>-1</sup>, 45<sup>th</sup> cycle: 1000 mA g<sup>-1</sup>, 55<sup>th</sup> cycle: 2000 mA g<sup>-1</sup>).



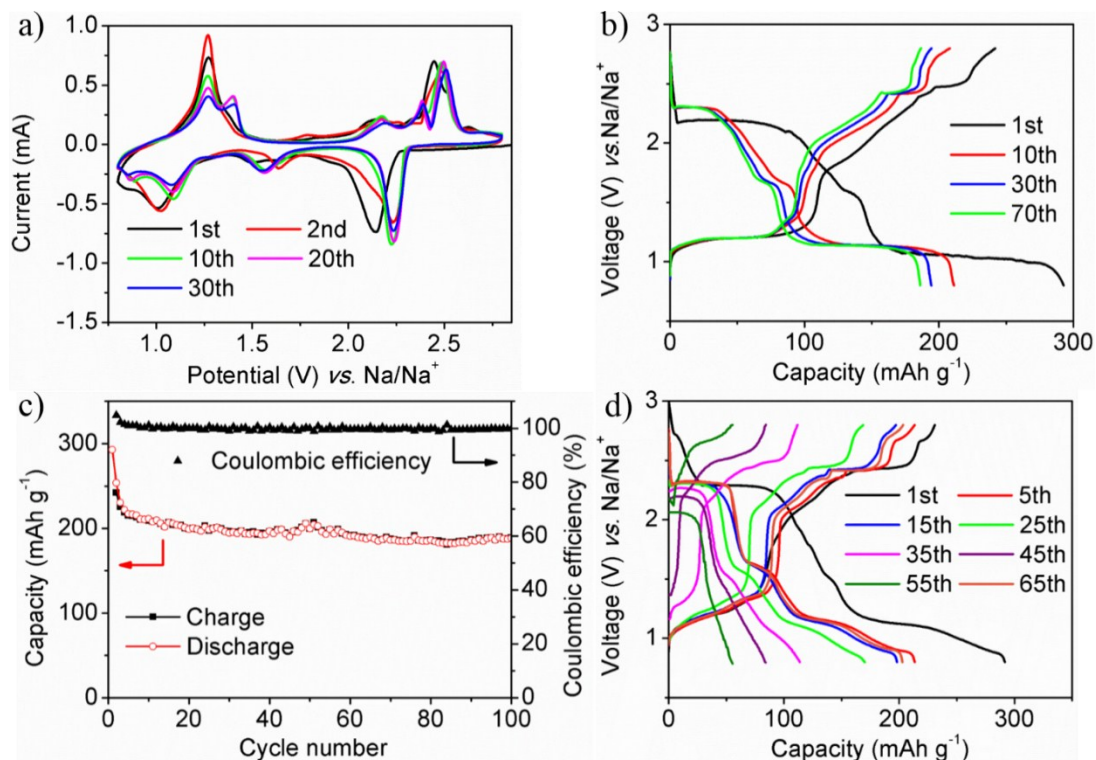
**Fig. S2** The SEM images of cross section of the free-standing protective films. a) PEO, b) PPF19, c) PPF37 and d) PPF55.



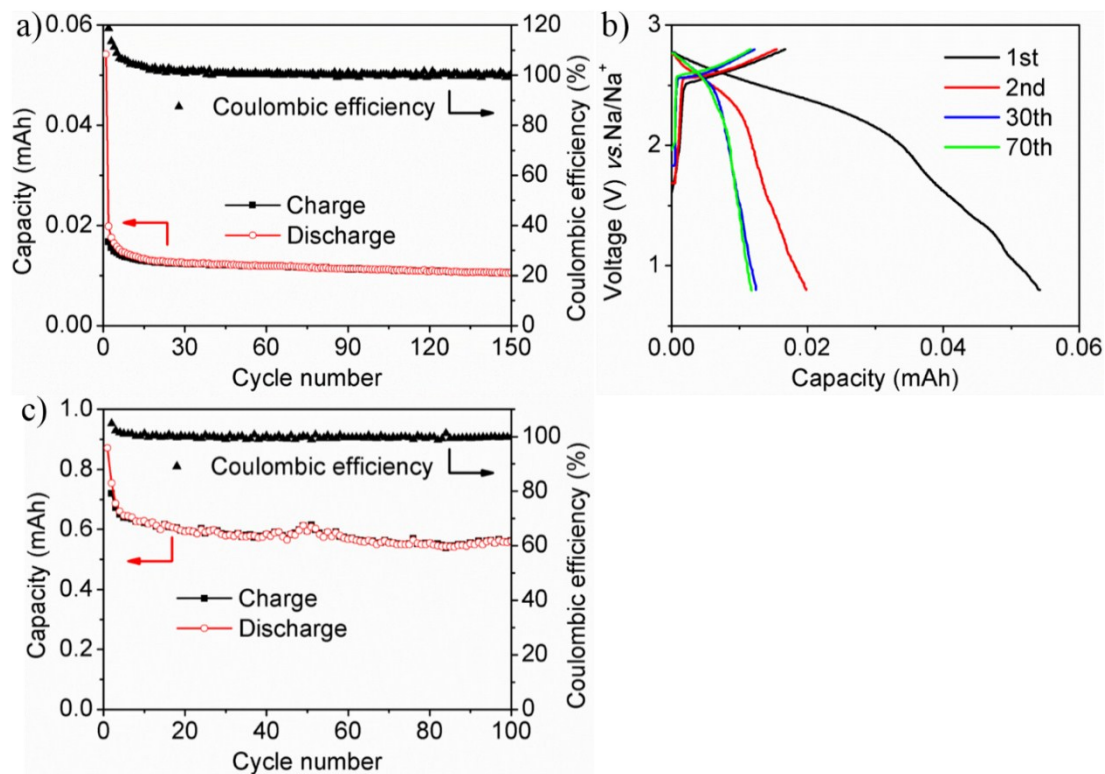
**Fig. S3** Electrochemical performances of PT electrodes assembled with PEO. a) CV curves of PT electrodes at the scan rate of  $0.5 \text{ mV s}^{-1}$ . b) Voltage profiles at the rate of  $50 \text{ mA g}^{-1}$  (the 1<sup>st</sup>, 10<sup>th</sup>, 30<sup>th</sup> and 70<sup>th</sup> cycles as representatives). c) Cycling performance at the rate of  $50 \text{ mA g}^{-1}$ . d) Voltage profiles for rate performance (1<sup>st</sup>, 5<sup>th</sup> and 65<sup>th</sup> cycles:  $50 \text{ mA g}^{-1}$ , 15<sup>th</sup> cycle:  $100 \text{ mA g}^{-1}$ , 25<sup>th</sup> cycle:  $200 \text{ mA g}^{-1}$ , 35<sup>th</sup> cycle:  $500 \text{ mA g}^{-1}$ , 45<sup>th</sup> cycle:  $1000 \text{ mA g}^{-1}$ , 55<sup>th</sup> cycle:  $2000 \text{ mA g}^{-1}$ ).



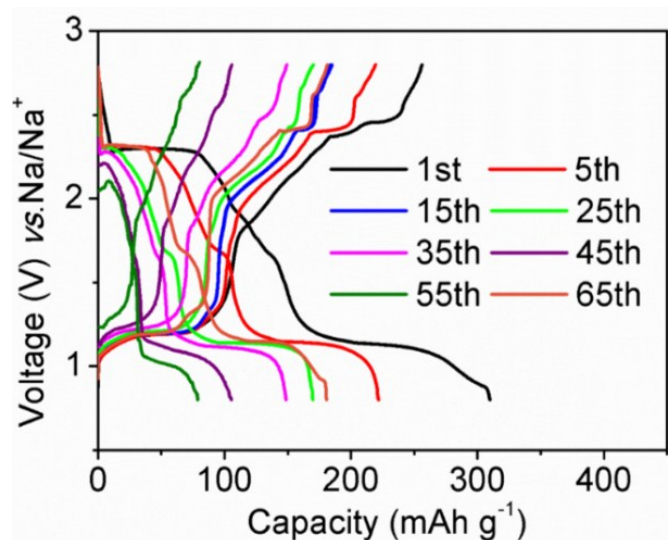
**Fig. S4** Electrochemical performances of PT electrodes assembled with PPF19 films. a) CV curves of PT electrodes at the scan rate of  $0.5 \text{ mV s}^{-1}$ . b) Voltage profiles at the rate of  $50 \text{ mA g}^{-1}$  (the 1<sup>st</sup>, 10<sup>th</sup>, 30<sup>th</sup> and 70<sup>th</sup> cycles as representatives). c) Cycling performance at the rate of  $50 \text{ mA g}^{-1}$ . d) Voltage profiles for rate performance (1<sup>st</sup>, 5<sup>th</sup> and 65<sup>th</sup> cycles:  $50 \text{ mA g}^{-1}$ , 15<sup>th</sup> cycle:  $100 \text{ mA g}^{-1}$ , 25<sup>th</sup> cycle:  $200 \text{ mA g}^{-1}$ , 35<sup>th</sup> cycle:  $500 \text{ mA g}^{-1}$ , 45<sup>th</sup> cycle:  $1000 \text{ mA g}^{-1}$ , 55<sup>th</sup> cycle:  $2000 \text{ mA g}^{-1}$ ).



**Fig. S5** Electrochemical performances of PT electrodes assembled with PPF37 films. a) CV curves of PT electrodes at the scan rate of  $0.5 \text{ mV s}^{-1}$ . b) Voltage profiles at the rate of  $50 \text{ mA g}^{-1}$  (the 1<sup>st</sup>, 10<sup>th</sup>, 30<sup>th</sup> and 70<sup>th</sup> cycles as representatives). c) Cycling performance at the rate of  $50 \text{ mA g}^{-1}$ . d) Voltage profiles for rate performance (1<sup>st</sup>, 5<sup>th</sup> and 65<sup>th</sup> cycles:  $50 \text{ mA g}^{-1}$ , 15<sup>th</sup> cycle:  $100 \text{ mA g}^{-1}$ , 25<sup>th</sup> cycle:  $200 \text{ mA g}^{-1}$ , 35<sup>th</sup> cycle:  $500 \text{ mA g}^{-1}$ , 45<sup>th</sup> cycle:  $1000 \text{ mA g}^{-1}$ , 55<sup>th</sup> cycle:  $2000 \text{ mA g}^{-1}$ ).



**Fig. S6** a) Cycling performance of PPF37 film (assembled without PT cathodes, only current collector was assembled in the cells) at a current of 150  $\mu\text{A}$  from 0.8 V to 2.8 V. The current density is similar to the current density used for PT experiments. b) Voltage profiles of PPF37 film at the current of 150  $\mu\text{A}$  (the 1<sup>st</sup>, 2<sup>nd</sup>, 30<sup>th</sup> and 70<sup>th</sup> cycles as representative). c) Cycling performance of PPF37 film (assembled with PT) at the rate of 50  $\text{mA g}^{-1}$  from 0.8 V to 2.8 V ( $\sim 150 \mu\text{A}$ , the quality of PT in each electrode is about 3 mg). The capacity contribution from the PPF thin films ( $< 2\%$ ) is negligible in the cells.



**Fig. S7** Voltage profiles of PT electrodes (assembled with PPF55 films) for rate performance (1<sup>st</sup>, 5<sup>th</sup> and 65<sup>th</sup> cycles: 50 mA g<sup>-1</sup>, 15<sup>th</sup> cycle: 100 mA g<sup>-1</sup>, 25<sup>th</sup> cycle: 200 mA g<sup>-1</sup>, 35<sup>th</sup> cycle: 500 mA g<sup>-1</sup>, 45<sup>th</sup> cycle: 1000 mA g<sup>-1</sup>, 55<sup>th</sup> cycle: 2000 mA g<sup>-1</sup>).