

Supporting Information

Surface Engineering of a LiMn_2O_4 Electrode Using Nanoscale Polymer Thin Films via Chemical Vapor Deposition Polymerization

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S1. Initiated Chemical Vapor Deposition

Table S1. Summary of iCVD polymerization experimental parameters

Parameter	Values
Substrate temperature (°C)	25
Filament temperature (°C)	230
Reactor pressure (Torr)	0.5
Initiator flow rate (sccm)	2.0
Monomer flow rate (sccm)	1.3
Argon flow rate (sccm)	8.5
* P_m/P_{sat}	0.14

* P_m is the partial pressure of monomer inside chamber, P_{sat} is the saturation pressure of monomer at the substrate temperature. P_m/P_{sat} can be viewed as a direct measure of monomer surface concentration on the substrate.¹

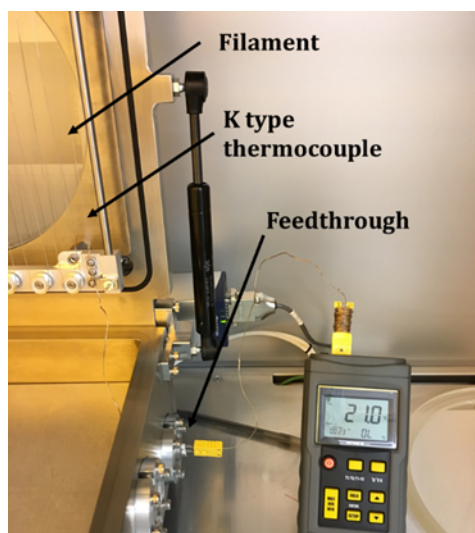


Figure S1. Home-built temperature measurement device for the nichrome filaments. A K-type thermocouple is attached on one of the filament wire, and it is connected to a thermometer through a feedthrough.

Table S2. Filament temperatures at different voltages.

Voltage (V)	18	20	22	24
Current (A)	0.76	0.82	0.89	0.97
Temperature (°C)	181.0	197.6	213.0	228.2

S2. TEM Sample preparation

Copper grids (300 mesh) coated with ~ 50 Å thick amorphous carbon film were purchased from Ted Pella. 2 mg LiMn_2O_4 powder (MTI cooperation) was dispersed into 5 mL isopropanol (IPA, Sigma-Aldrich) followed by ultrasonic treatment for 10 min. TEM samples were prepared by placing two drops of the isopropanol solution on the surface of a grid. LiMn_2O_4 particles were left on the grid after the IPA solution was evaporated. Then, iCVD and oCVD polymerization was conducted and ultra-thin PDVB and PEDOT films were grown on the TEM grid.

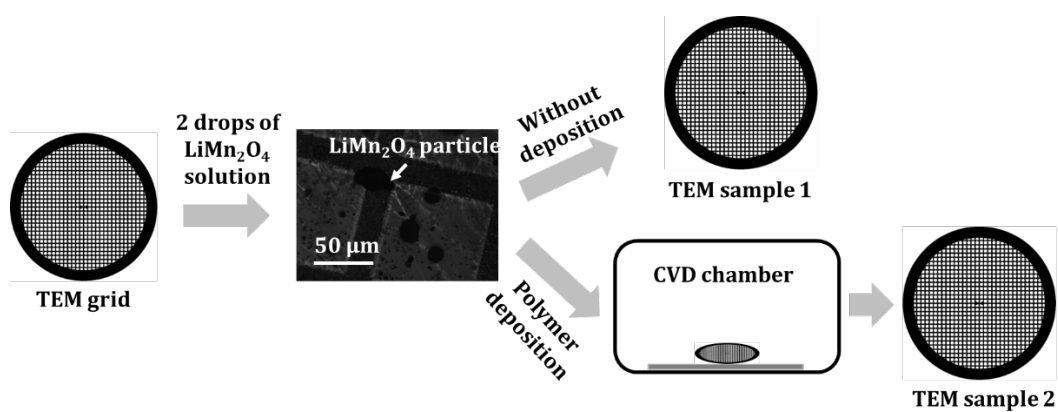


Figure S2. TEM samples preparation steps.

S3. Temperature calibration for coin cells

A thermistor from U.S. SENSOR corp. was attached on a coin cell that was then put into the Thermo Scientific furnace. After the temperature was stabilized for around 5 hours, the resistance of the thermistor was read using a multimeter. The actual temperature of the coin cell was then derived from the measured resistance and the calibration curve of the thermistor, as shown in Fig. S2 (c). It need to be noted that the actual coin cell temperature was 50°C when the furnace was set to 55°C.

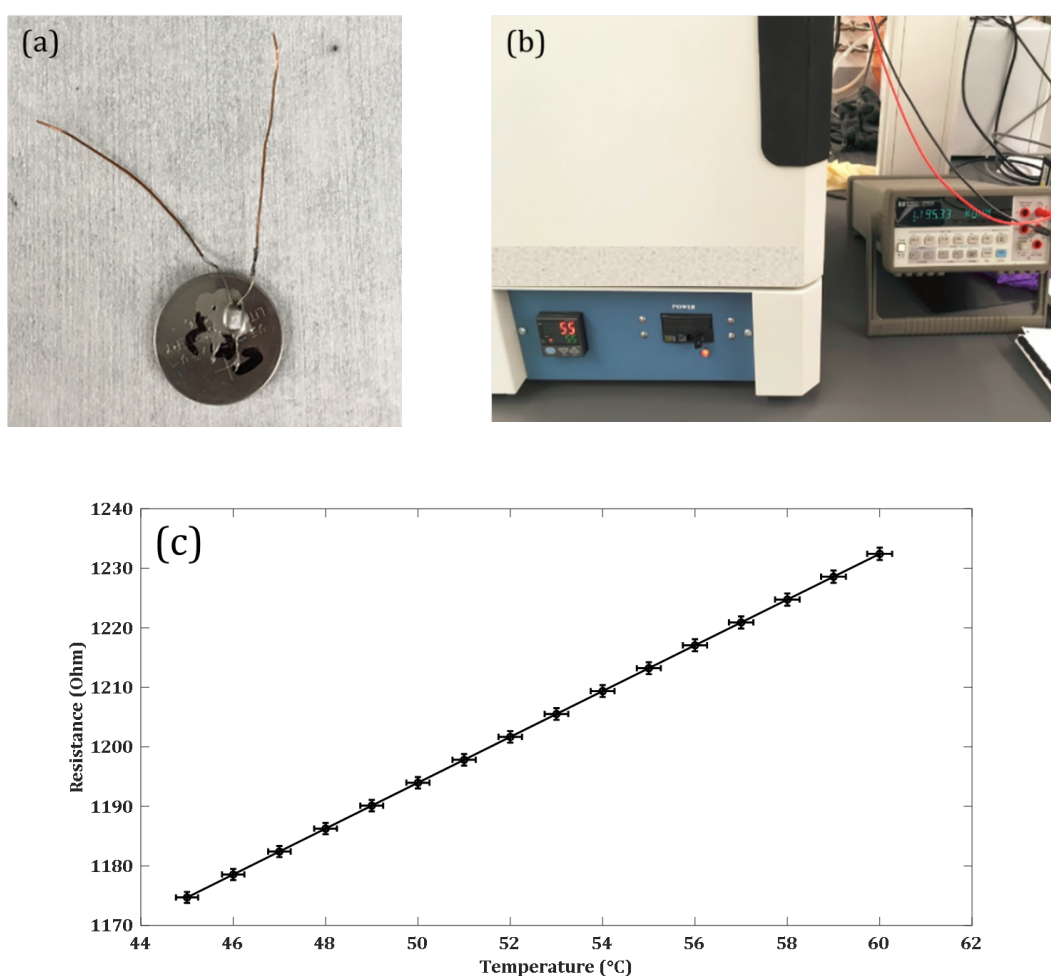


Figure S3. Calibration of actual temperature of a coin cell in the Thermo Scientific furnace. (a) A thermistor is attached onto the surface of a coin cell that will be put into the furnace, (b) experiment setup for the calibration process, and (c) calibration curve of the thermistor.

S4. Fourier Transform Infrared Spectroscopy

FTIR and Raman spectroscopy were applied to identify the successful polymerization of PDVB and PEDOT thin films. The two techniques provide a structural fingerprint by which molecules can be identified. The main difference between the two techniques lies in the nature of the molecular transitions.² For an IR detectable transition, the molecule must undergo dipole moment change during vibration. In contrast, a transition to be Raman active must be a change in the polarizability of the molecule during the vibration because the Raman utilizes inelastic scattering of light.

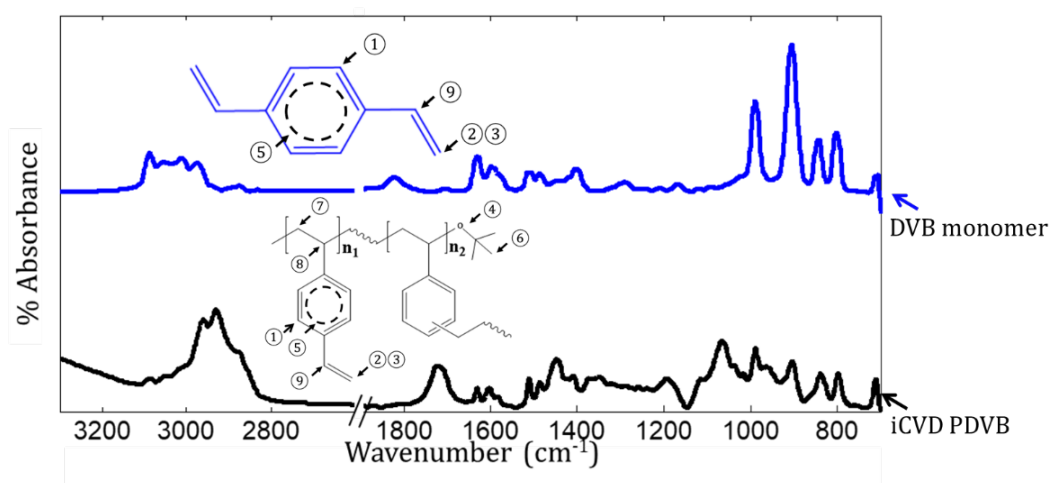


Figure S4. FTIR spectra of the DVB monomer and iCVD PDVB. The structures of DVB and PDVB are depicted, and functional groups that yield peaks are labelled. The relationship between these functional groups and peak positions can be found in Table S3.

Table S3. The relationship between different functional groups and their corresponding wavenumber in FTIR spectra. The label in the last column represents the position of each functional group in DVB monomer and PDVB polymer, as shown in Figure S4.

Wavenumber		
(cm ⁻¹)	Functional group	Label
600-900	Aromatic sp ² C-H bend	①
903	vinyl group -CH ₂ out-of-plan vibration	②
1000	Alkene sp ² C-H bend	③
1000-1150	C-O alkoxy	④
1400-1700	Aromatic C=C stretch	⑤
2870	sp ³ CH ₃ stretching	⑥
2930	sp ³ CH ₂ stretching	⑦
2960	sp ³ CH stretching	⑧
3000-3100	sp ² CH stretch	⑨

S5. Film Thickness Measurement

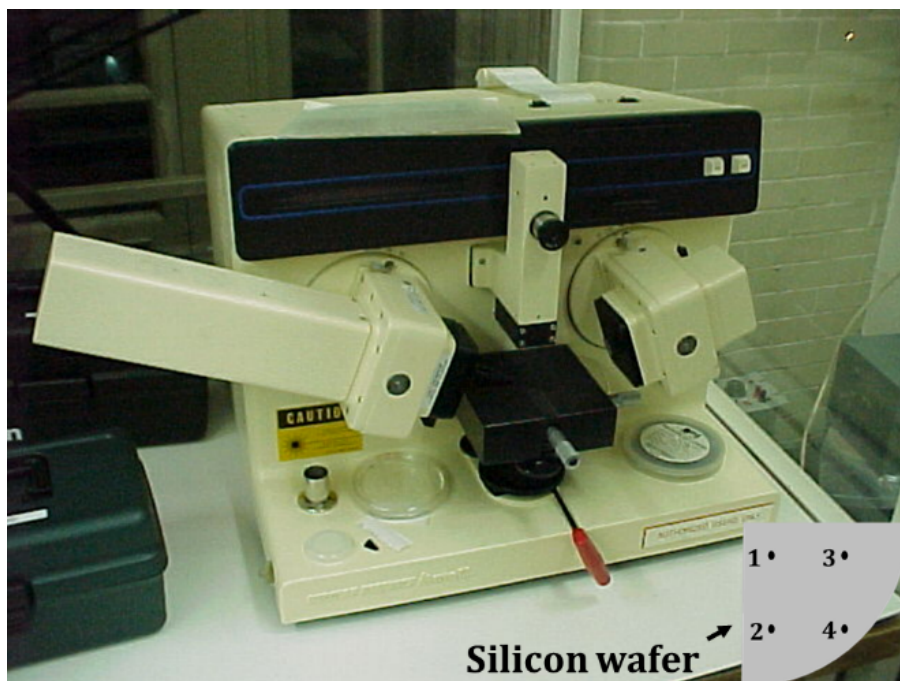


Figure S5. The ellipsometer used for nanoscale thickness measurements. A beam of He-Ne laser is circularly polarized by a compensator and then incident on to the surface of sample at 70° . The relative phase and amplitude change of s and p polarized light are analyzed to calculate the film thickness and refractive index. This device is capable of measuring film thickness varying from several tens of nm to 10 micrometers accurate to 1 nm. The inserted picture in the right bottom zone shows the points where thickness measurements were made on the silicon wafer.

Table S4. Thickness and refractive index of the PDVB polymer thin film at different measurement points using ellipsometry.

Point	Thickness (nm)	Refractive Index
1	22.6	1.6
2	23.7	1.6
3	22.6	1.6
4	23.9	1.5

The thickness of the oCVD PEDOT films were measured using a KLA Tencor P-15 profilometer. The film deposited on a flat substrate was used for this measurement. The film was scratched in multiple places to expose the underlying substrate such that the film thickness can be measured. For this, a soft tip tweezer was used to avoid placing scratches in the substrate itself. The thickness was measured at multiple locations across the sample and then averaged.

S6. Electrochemical Stability of PDVB Films

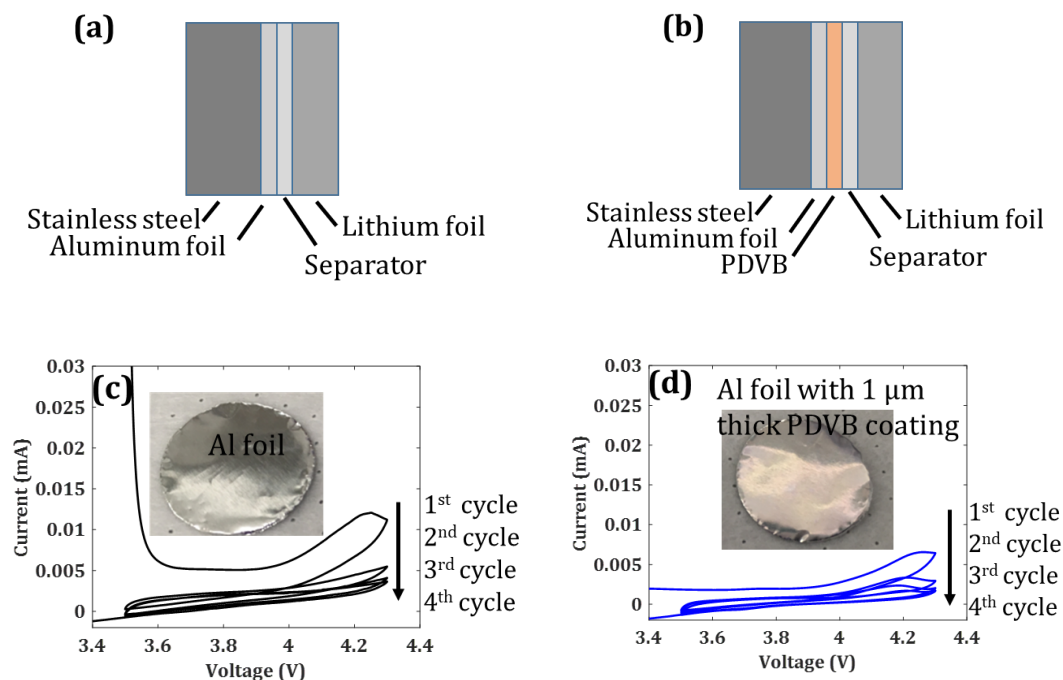


Figure S6. Electrochemical stability test of PDVB thin films in voltage range of 3.5 – 4.3 V. (a), (b) Experiment setup of two types of coin cells with and without PDVB coating on the surface of Al foil, (c), (d) cyclic voltammetry test (CV) results of the two types of coin cells. The inserted pictures show the Al foil with and without PDVB coating that used in the coin cells for CV testing. Compared with (c), (d) shows no new peaks between 3.5 - 4.3 V, indicating the PDVB is electrochemical stable within this voltage range. The peak at 4.2 V in (d) is lower than that in (c), suggesting that the PDVB coating inhibits side reactions of electrolyte during the CV test.

S7. Electrochemical Impedance Spectroscopy

Table S5. Simulation results from impedance spectroscopy data using a three-order RC equivalent circuit model.

	R_0 (Ohm)	R_{SEI} (Ohm)	R_{ct1} (Ohm)	R_{ct2} (Ohm)
Pristine	2.8	26.0	26.4	35.9
PDVB coated	3.1	5.1	32.7	62.1
PEDOT coated	3.0	9.1	14.9	22.5

S8. Cell performance after cycling tests

Figure S7 (a) compares discharge curves of three coin cells after the cycling test. The PEDOT coated coin cell have more capacity remaining and smaller overpotential compared to pristine one, while PDVB coated cell shows the opposite trend. Figure S7 (b) displays incremental capacity analysis (ICA) of the three discharge curves in (a)³. The peak at ca. 4.15 V in (b) corresponds to the discharge plateau at that position in (a). The peak position reflects cell resistance and the area under a peak suggests the amount of active material. Compared to the pristine cell, the peak position shifts to a higher voltage in the PEDOT coated LiMn_2O_4 coin cell, while it shifts to a lower voltage in the PDVB coated one. The main contribution of resistance increase is from SEI growth. Therefore, PEDOT inhibits SEI growth during the cycling test. Besides, the PEDOT coated cell has larger area under the peak, indicating more LiMn_2O_4 active material remains after the cycling test.

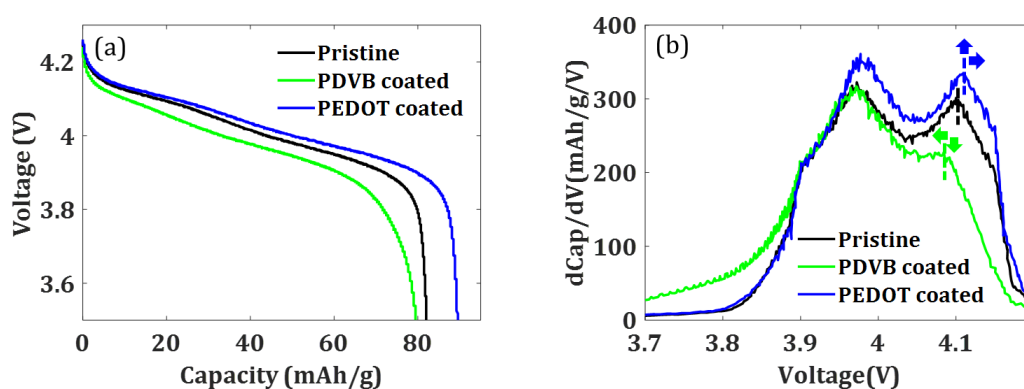


Figure S7. Performance comparison of the three types of cells after the cycling test. (a) Discharge curves of these cells at C/3, (b) incremental capacity analysis of the discharge curves in (a).

S9. The Effect of FeCl_3 on Cell Performance

Fig. S8 compares the effect of PEDOT coating on the performance of coin cells with and without methanol rinsing for PEDOT coated LiMn_2O_4 electrode after the oCVD experiment. The results suggest that the rate performance of LiMn_2O_4 reduced without the rinsing step (perhaps due to FeCl_3 impurity), compared with the samples with rinsing. However, the rinsing step seemed to have little effect on cell cycling performance. Therefore, rinsing PEDOT coated electrode with methanol is necessary to get the best performance of LiMn_2O_4 .

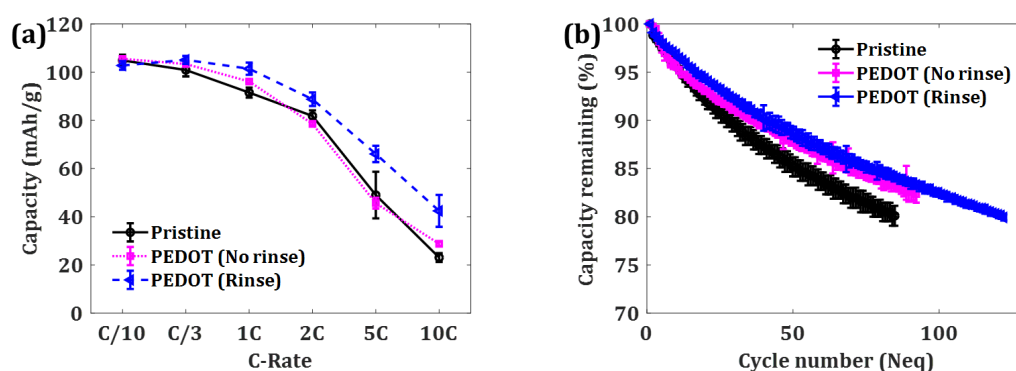


Figure S8. The effect of FeCl_3 on the (a) rate performance and (b) cycling performance of LiMn_2O_4 electrodes. Samples were rinsed in methanol for 5 mins to remove residual monomer and FeCl_3 oxidant in the “Rinse” group.

S10. The Effect of PDVB Film Thickness on Cell Performance

It needs to be noted that we applied C/3 as the charging rate and 1C as the discharge rate here during these tests. The setting introduced more serious calendar aging because nearly double time was needed to finish one cycle compared to the setting that charging and discharging a cell at both 1C. Therefore, the capacity of a cell decreased faster with respect to cycling number compared to a cell that was cycled at 1C rate, as mentioned before. This explains why the cells here can only be cycled around 60 times before its capacity decreased to 80% of its initial capacity.

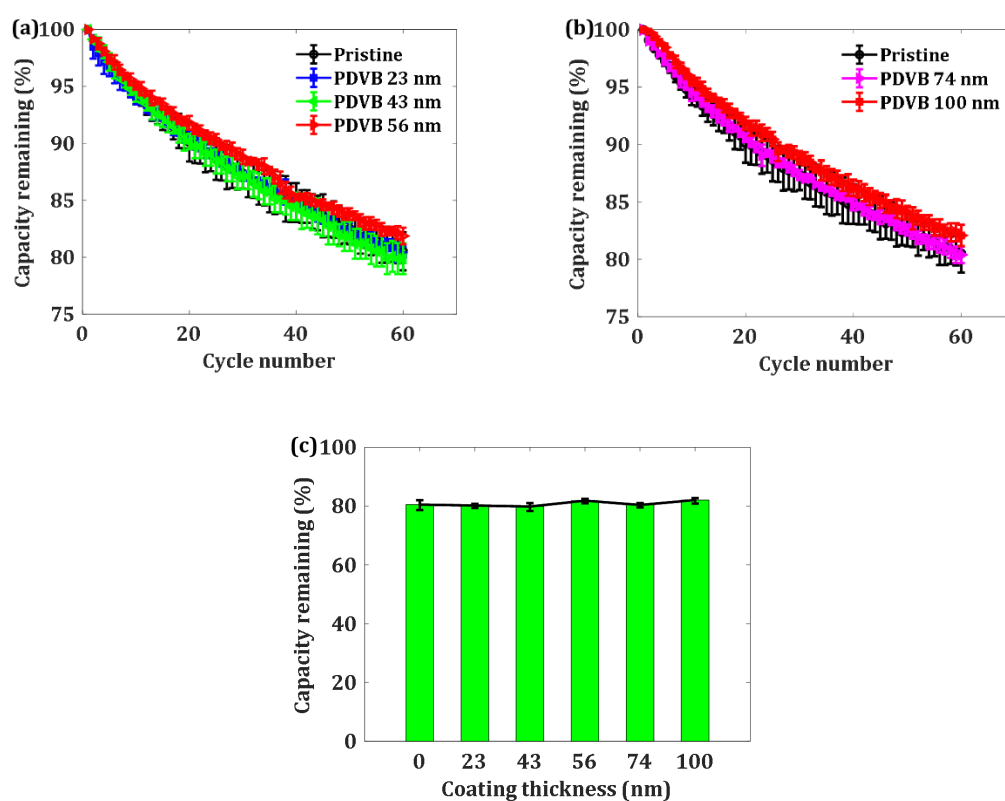


Figure S9. Cycling results of coin cells with different thicknesses of PDVB coating on LiMn₂O₄ electrodes at 50 °C. (a) and (b) capacity remaining with respect to cycle number, (c) capacity remaining after 60 times of cycling. Cells were charged at C/3 and discharged at 1C within voltage range of 3.5 – 4.3 V.

S11. X-Ray Photoelectron Spectroscopy

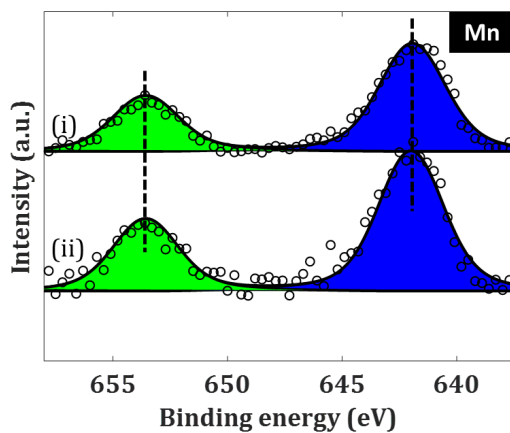


Figure S10. Comparison of Mn 2p binding energy of in (i) pristine LiMn₂O₄ sample and (ii) LiMn₂O₄ with PDVB coating. No obvious shift of binding energies can be found for the Mn 2p after PDVB coating.

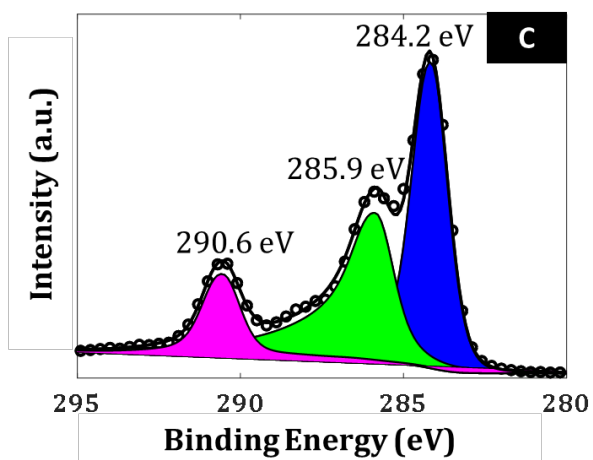


Figure S11. Binding energy of C 1s in pristine LiMn₂O₄ sample. The peak at 284.2 eV is from graphite (C-C), the peak at 285.9 eV is from Li₂CO₃ (C-O), and the peak at 290.6 eV is from Polyvinylidene fluoride (PVDF) binder (CF₂).

S12. Preliminary cycling result of LiCoO₂ electrode with polymer thin film coatings

LiCoO₂ electrodes were coated by PEDOT and PDVB thin films using the aforementioned CVD polymerization techniques. Three coin cells were made for each case using with/without polymer coated LiCoO₂ as cathode and lithium metal as anode. These cells were cycled within voltage range of 3.0 – 4.5 V at C/2 rate using constant current for both charging and discharging.

The following figure shows PEDOT coating largely extends cycling life of LiCoO₂ during the high voltage cycling, while PDVB has little effect on cell cycling performance.

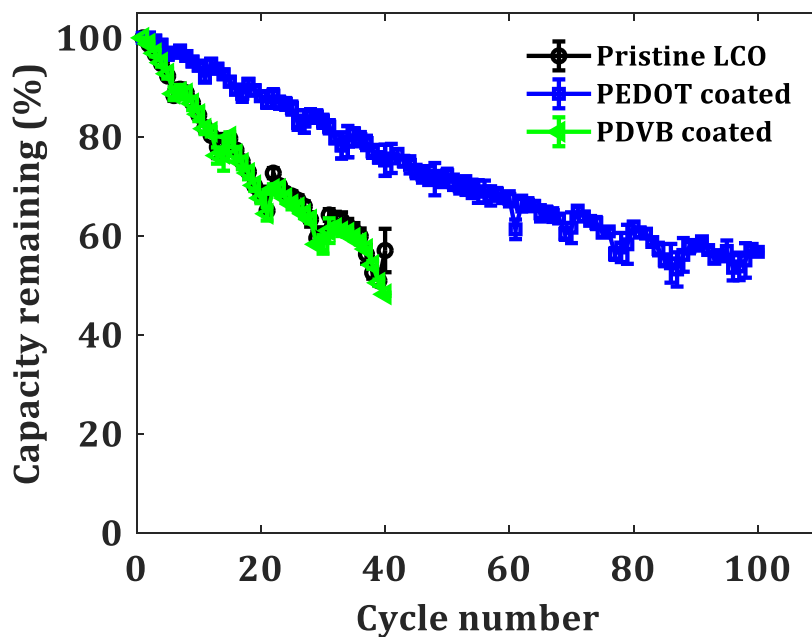


Figure S12. Capacity remaining during high voltage cycling of three types of LiCoO₂ coin cells. PEDOT coating largely improves cell cycling performance, while PDVB coating has little effect.

References:

- (1) Petruczuk, C. D.; Yang, R.; Gleason, K. K. Controllable cross-linking of vapor-deposited polymer thin films and impact on material properties. *Macromolecules* **2013**, *46*, 1832-1840.
- (2) Wiercigroch, E.; Szafraniec, E.; Czamara, K.; Pacia, M. Z.; Majzner, K.; Kochan, K.; Kaczor, A.; Baranska, M.; Malek, K. Raman and infrared spectroscopy of carbohydrates: A review. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2017**, *185*, 317-335.
- (3) Dubarry, M.; Truchot, C.; Liaw, B. Y.; Gering, K.; Sazhin, S.; Jamison, D.; Michelbacher, C. Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part II. Degradation mechanism under 2C cycle aging. *Journal of Power Sources* **2011**, *196*, 10336-10343.