

Supporting Information for

**Stabilizing Polyether Electrolyte with 4 V metal oxide cathode by Nanoscale
Interfacial Coating**

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As the exploration of PEG electrolytes is to promote the thermal stability of batteries, we compare flammability of PEG electrolyte with their 1,2-dimethoxyethane (DME) counterpart. Shuhong Jiao et al. reported highly stable cycling of NMC electrode in DME by using concentrated salt (2 M LiTFSI + 2 M LiDFOB), during the preparation of this paper.¹ The reason behind is that the decomposition of salt helps forming a high-quality CEI to prevent the oxidation of this ether. However, DME is highly flammable even with highly concentrated salt inside (Figure S1). In contrast, PEG has much better thermal stability (Supplemental Note 2), and it is difficult to catch fire under mild ignition (Figure S1, supplemental video 1). In addition, such concentrated electrolyte approach does not result in steady cycling in PEG electrolyte, as shown in Figure S2.

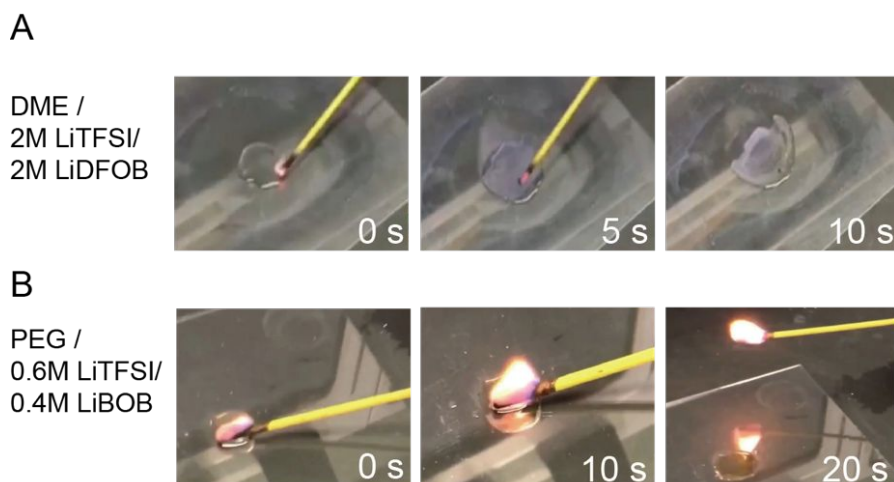


Figure S1. Flammability test. (A) 2M LiTFSI + 2M LiDFOB in DME and (B) our PEG-based electrolyte (0.6 M LiTFSI + 0.4 M LiBOB in PEG) at different times. DME electrolyte is easily ignited, while PEG one does not catch fire for 30 seconds. The whole video can be found as supplemental video 1.

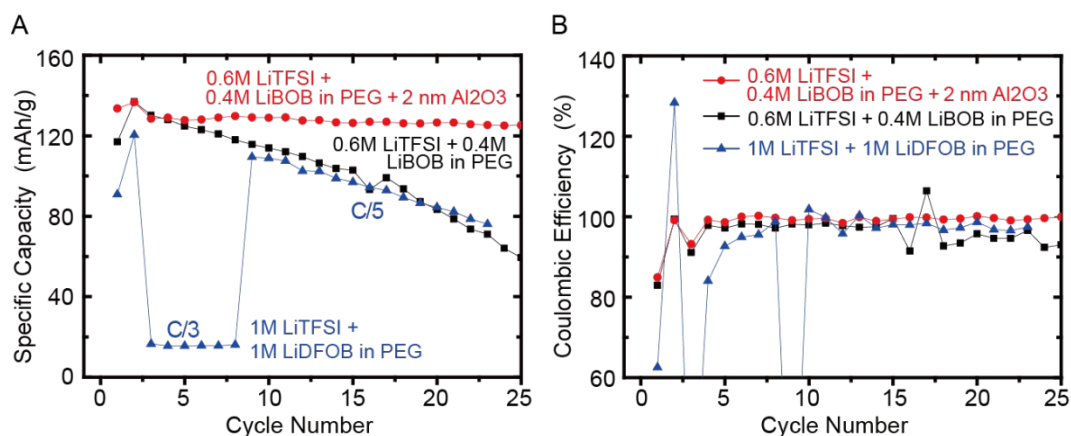


Figure S2. Effects of salt concentration. (a) Discharge capacity and (b) Coulombic efficiency vs. cycle number of concentrated 1 M LiTFSI + 1 M LiDFOB in PEG with bare NMC (blue), 0.6 M LiTFSI + 0.4 M LiBOB in PEG with bare NMC (black), and 0.6 M LiTFSI + 0.4 M LiBOB in PEG with 2 nm Al₂O₃-coated NMC (red). The data in red and black curves are the same as those in Figure 2. For 1 M LiTFSI + 1 M LiDFOB in PEG with bare NMC (blue), the cell is cycled at C/5 and C/10 for the 1st and 2nd cycle, respectively. The battery cannot be well cycled at C/3 due to reduced ionic conductivity, so the current was changed to C/5 at the 9th cycle. Therefore, due to the change of C rate, CE at the 3rd and 9th cycles are low, which are not included in (B). Bare NMC with 1 M LiTFSI + 1 M LiDFOB in PEG shows a similar cycling performance with bare NMC in 0.6 M LiTFSI + 0.4 M LiBOB in PEG, but it is much worse than 0.6 M LiTFSI + 0.4 M LiBOB in PEG with 2 nm Al₂O₃ coating. The average coulombic efficiency between cycle 10 and 23 is 98.03%, smaller than 99.44%, the CE with 2 nm Al₂O₃ coating in the same cycling range. This demonstrates the importance of surface coating to alter surface chemistry and improve stability against electrolyte oxidation.

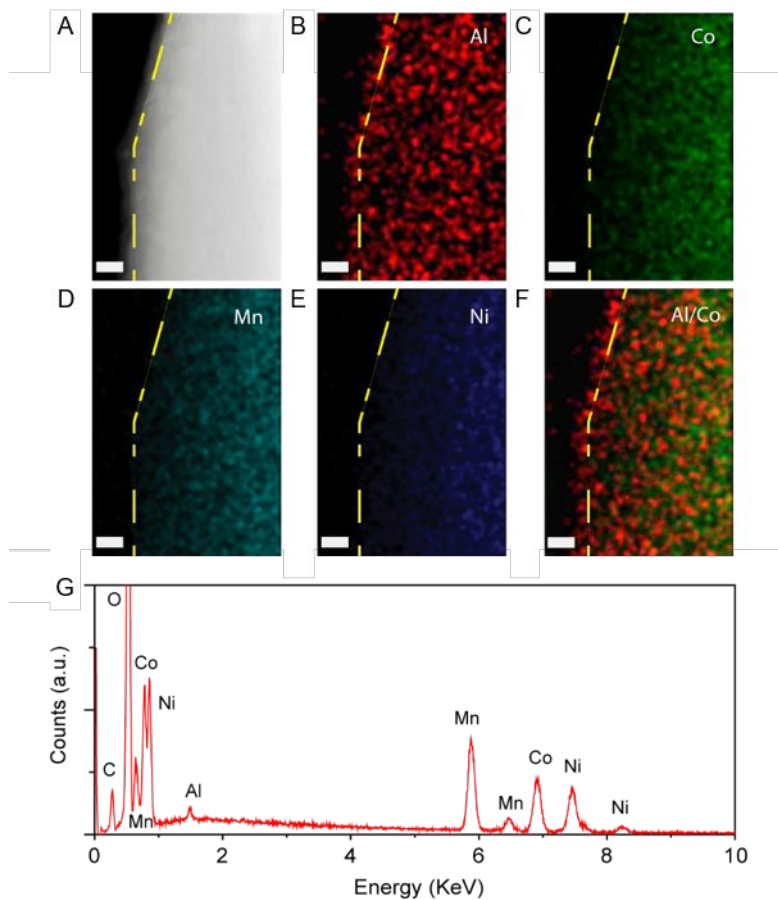


Figure S3. (A) HAADF image of an NMC electrode with 2 nm Al_2O_3 coating by atomic layer deposition (ALD). (B-E) EDS mapping of (B) Al, (C) Co, (D) Mn and (E) Ni. (F) Overlapping of Al and Co. Scale bars are 5 nm in all figures. (G) EDS spectrum in SEM for large area. Al peak is clear.

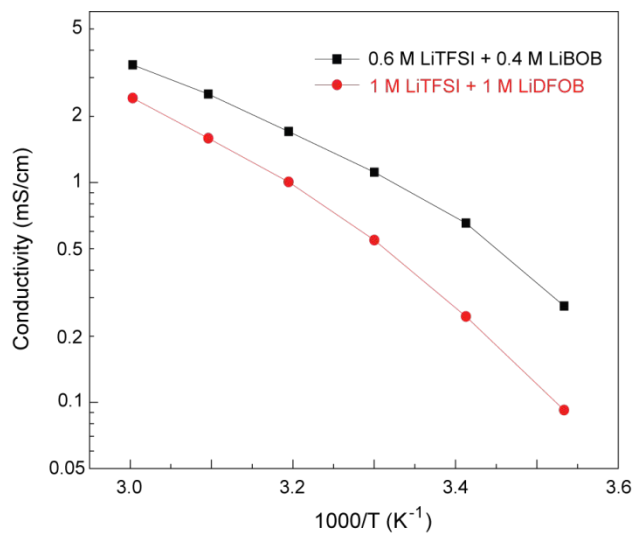


Figure S4. Conductivity of 0.6 M LiTFSI + 0.4 M LiBOB in poly(ethylene glycol) dimethyl ether ($M_w = 500$) and 1 M LiTFSI + 1 M LiDFOB in poly(ethylene glycol) dimethyl ether ($M_w = 500$) between 10 and 60 °C.

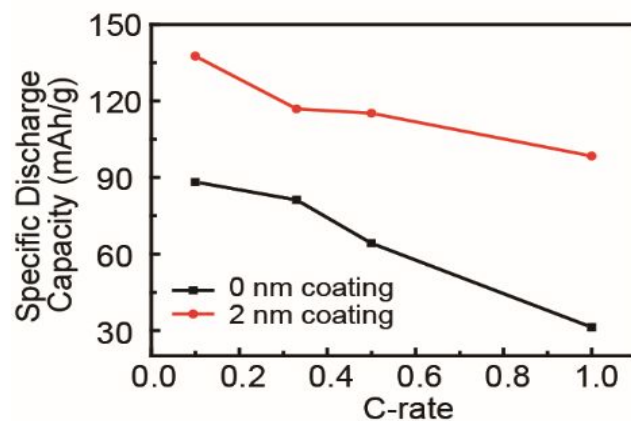


Figure S5. Specific discharge capacity vs. current rates for NMC electrode with 2 nm and without coating. The cells are cycled at $C/3$ between 4.2 and 2.7 V ($1\text{ C} = 150\text{ mA/g}$). A constant voltage step is added at the end of charging with a current cut-off of $C/20$.

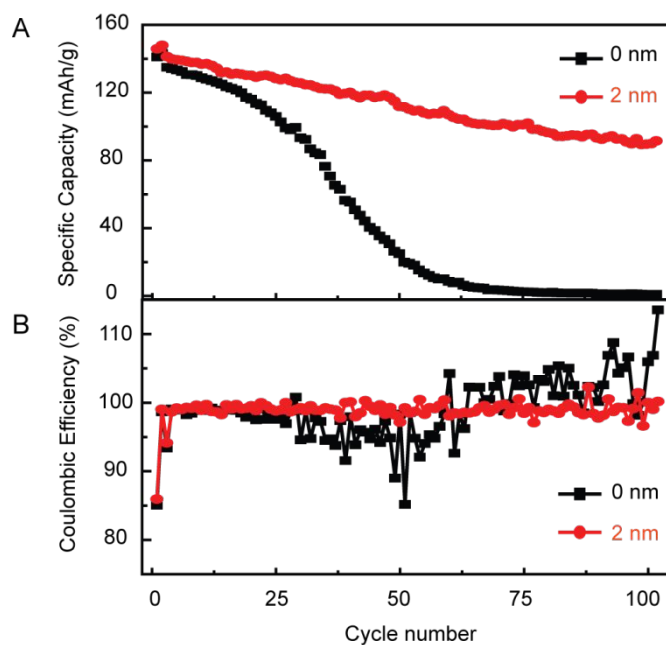


Figure S6. Electrochemical performance of Al_2O_3 -protected NMC electrodes cycled between 2.8 and 4.25 V vs. Li/Li^+ . (A) Cycling performance of NMC electrodes with 0 and 2 nm Al_2O_3 coatings. (B) Coulombic efficiency of NMC electrodes in (A). All cells are cycled at C/3 between 4.25 and 2.8 V (1 C = 150 mA/g). A constant voltage step is added at the end of charging with a current cut-off of C/20.

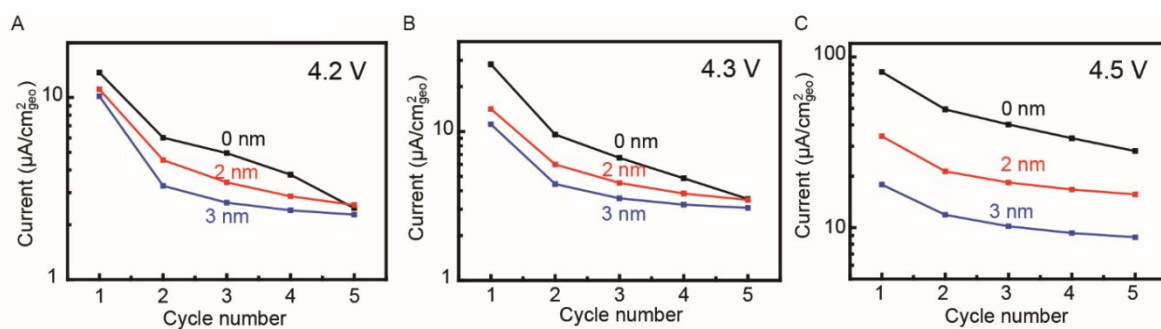


Figure S7. Electrochemical stability of PEG with NMC cathodes. (A-C) The anodic current densities for NMC electrodes with PEG electrolyte at (A) 4.2 V, (B) 4.3 V and (C) 4.5 V vs. Li/Li^+ . The scan rate is 1 mV/s. The background current due to double layer capacitance is subtracted based on the anodic current density at 3.4 V vs. Li/Li^+ in each cycle.

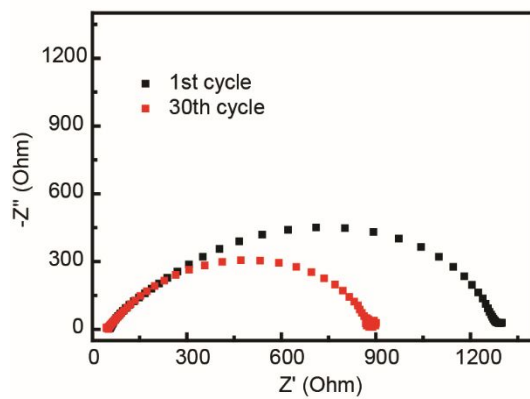


Figure S8. EIS measurement of Li | PEG | Li symmetric cell. The PEG electrolyte is 0.6 M LiTFSI and 0.4 M LiBOB in PEGDME with a molecular weight of 500.

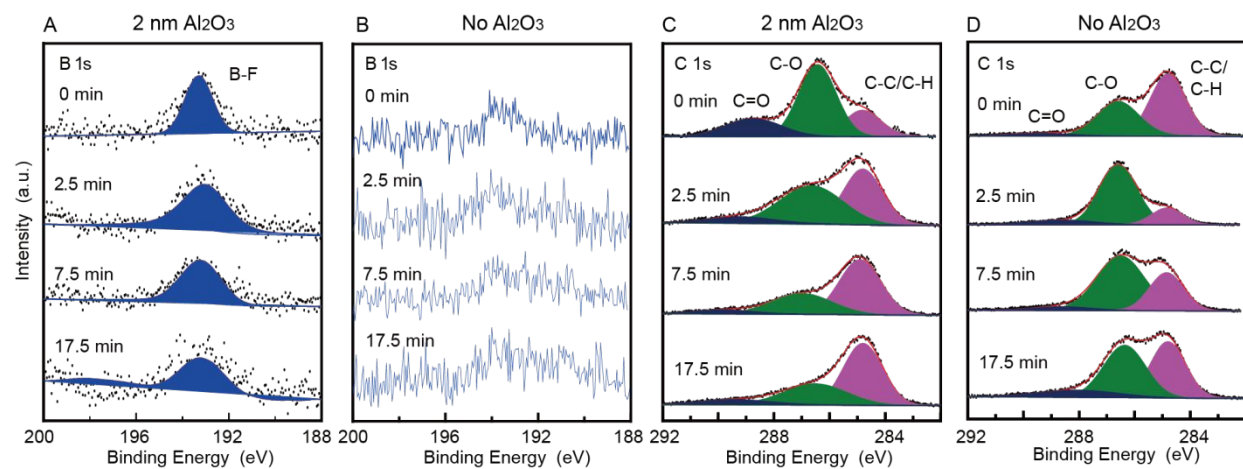


Figure S9. The XPS depth profile of NMC electrode after 50 cycles. (A and B) B-1s signal on NMC with 2 nm Al_2O_3 coating (A) and bare NMC (B). (C and D) C-1s signal on NMC with 2 nm Al_2O_3 coating (C) and bare NMC (D).

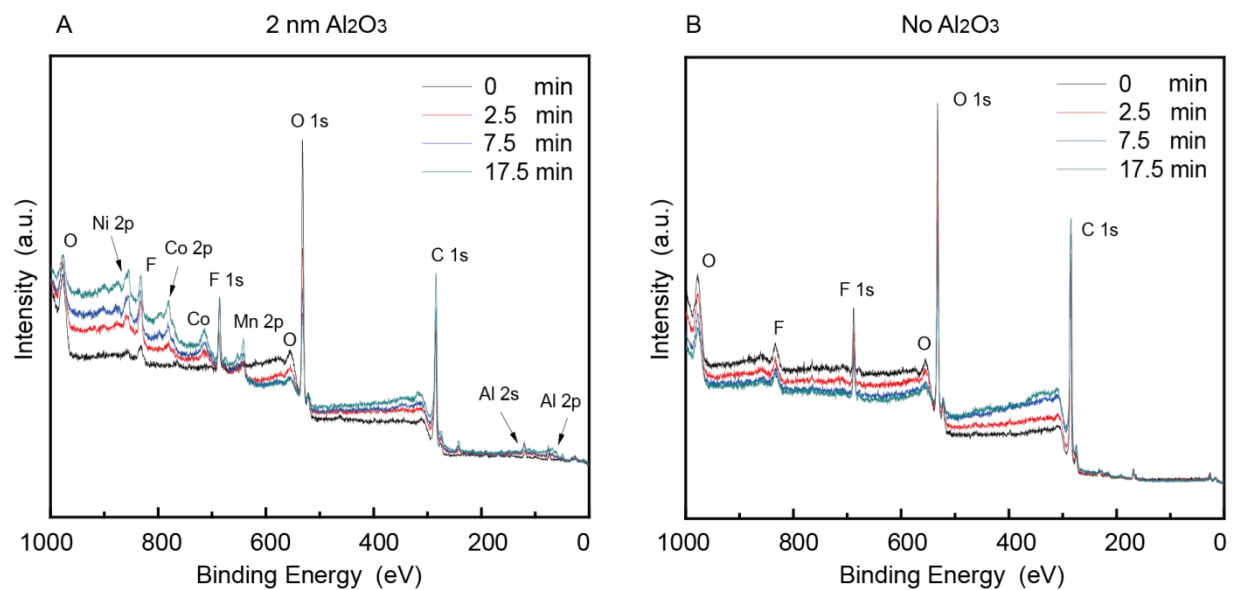


Figure S10. XPS surveys of NMC surface. (A) with 2 nm Al₂O₃ coating and (B) bare NMC. The peaks at 979 and 553 eV (in A and B) correspond to O Auger and O loss, respectively. The peak at 833 eV can be assigned to F Auger.

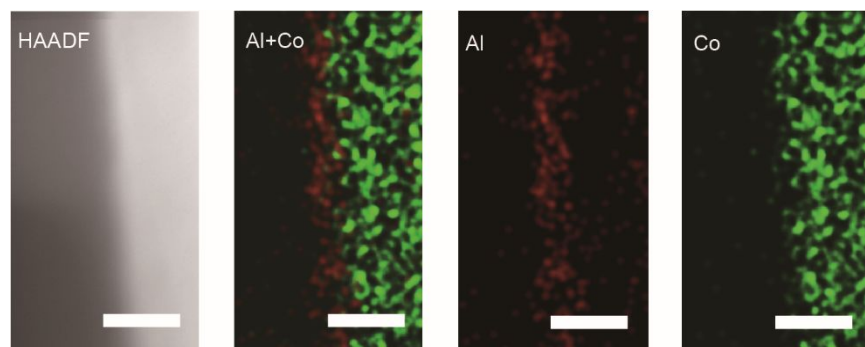


Figure S11. The HAADF image of an NMC electrode with 2 nm Al_2O_3 coating by ALD after cycling and EDS mapping of Al/Co overlapping, Al and Co. Scale bars are 5 nm.

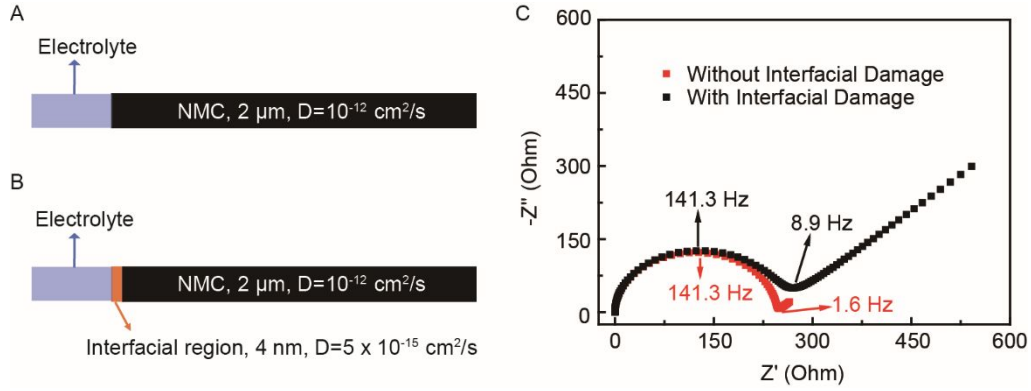


Figure S12. EIS simulation with COMSOL for the 1D case of lithium ions diffusion in bare NMC cathode. Schematic of the 1D structure of the NMC cathode without damage (A) and with damaged interfacial region (B) in COMSOL simulation. (C) COMSOL simulation of EIS for the two configurations with and without damaged NMC interfaces. The key simulation parameters are NMC length of 2 μm , interfacial region of 4 nm, NMC bulk diffusivity of $10^{-12} \text{ cm}^2/\text{s}$, interfacial diffusivity of $5 \times 10^{-15} \text{ cm}^2/\text{s}$, the double layer capacitance of 5 $\mu\text{F}/\text{cm}^2$, heterogeneous rate constant of $4.85 \times 10^{-8} \text{ cm/s}$, lithium ion bulk concentration of $2.5 \times 10^4 \text{ mol}/\text{m}^3$, and frequencies ranging from 10^6 Hz to 0.1 Hz, with the applied perturbation potential of 10 mV as in our experiments. In the two configurations, the interfacial layer means $\sim 10 \text{ nm}$ below the cathode NMC surface, to distinguish from the bulk of the cathode. When the low ionic diffusivity $10^{-12} \text{ cm}^2/\text{s}$ in NMC cathode is considered, the lower bound of frequency 0.1 Hz (10 s) corresponds to a 30 nm diffusion length based on the equation $\lambda = \sqrt{Dt}$, where D is the diffusivity and t is diffusion time, let alone that a potentially damaged NMC layer may have an even lower diffusivity. Therefore, the diffusion tail reflects $\sim 10\text{-}50 \text{ nm}$ below the surface, but not the majority of the bulk. The magnitude of first semicircle which results from the charge transfer resistance is also semi-quantitatively consistent with Figure 3B before and after cycling.

Supplemental Notes

Supplemental Note 1.

The background current due to double layer capacitance in Figure 3 is $\sim 1 \mu\text{A}/\text{cm}^2$ based on geometric footprint. As the scanning rate is $1 \text{ mV}/\text{s}$, the capacitance is $\sim 1 \text{ mF}/\text{cm}^2$. Since the double layer capacitance on porous carbon surface is $\sim 10 \mu\text{F}/\text{cm}^2$, the estimated true surface area is $\sim 100 \text{ cm}^2$, about 100 times of the geometric footprint.²

Supplemental Note 2.

The flash point of PEG with M_w of 500 can be found at

<https://www.sigmaaldrich.com/catalog/product/aldrich/445886?lang=en®ion=US>

Reference:

1. Jiao, S. et al. Stable cycling of high-voltage lithium metal batteries in ether electrolytes. *Nature Energy* **3**, 739-746 (2018).
2. Ji, H. et al. Capacitance of carbon-based electrical double-layer capacitors. *Nat Commun* **5**, 3317 (2014).