Electronic Supplementary Material (ESI) for Energy Advances.

Supporting Information

PolarClean & Dimethyl Isosorbide: Green Matches in Formulating Cathode Slurry

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Experimental Section

Materials. $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC111), conductive carbon (Super P C45), PVDF (purity >99.5%, M_w ~600,000 g/mol) binder were purchased from MTI Corporation and stored at RT. NMC111 was calcined at 600 ºC for 2 h before cathode fabrication. Isosorbide dimethyl ether (DMI, Sigma-Aldrich, >99%), N-methyl-2-pyrrolidine (NMP, anhydrous, >99 %, Sigma-Aldrich), 1 M lithium hexafluorophosphate ($LiPF_6$) solution in ethyl carbonate (EC) and dimethyl carbonate (DMC) mixture (EC:DMC 1 : 1, v/v) (LP30, battery grade, Sigma-Aldrich), lithium metal (99.9%, Sigma-Aldrich) were commercially purchased, stored at ambient temperature in argon-filled glovebox and used without further purification. PolarClean was kindly supplied by Solvay USA Inc., New Jersey and used as received.

Slurry preparation and electrode fabrication. Electrode slurries were prepared by dry mixing, by hand, 0.4 g $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NMC111), and 0.05 g conductive carbon in a mortar and pestle. Next, 0.05 g of PVDF was dissolved in 2 mL NMP, DMI, or PolarClean at RT using a magnetic stirrer/sonication, with the resulting binder concentration of 2.5 wt/vol%. The dissolved PVDF was added into the dry mixture of NMC 111 and conductive carbon and mixed thoroughly for ~15-20 minutes until a smooth slurry is obtained (photographs of the resulting slurries are shown in **Fig. S1**). To examine the effect of solubility of PVDF on electrode cycling performance, another set of slurry was prepared by dissolving PVDF in DMI at elevated temperature (120 ºC) for 20 minutes before mixing. All these slurries were casted at RT onto 15 μm thick aluminum substrate with a custom-made wet film coating applicator (doctor blade). ~150 μm thick coatings (**Fig. S2**) were obtained after drying. A range of drying temperature (50 -120 ºC) and duration (1-4 days) were tested for the electrodes to examine the effect of drying on the internal structure of the electrode. The 150 µm thick electrodes have been found to crack during drying at higher temperature of 100-120 ºC (**Fig. S14**). Cracks were also developed when the electrodes were dried at a shorter time, for example air drying on a hot plate for 12 h, followed by 24 h of drying under vacuum. The optimized drying condition was selected as air drying of electrodes at 60 ˚C on a hot plate for a day, followed by 48 h of slow drying under vacuum at 60 ºC. Though DMI and PolarClean have higher boiling point and lower vapor pressure compared to NMP (**Table S1**), crack-free dry electrodes with no significant traces of solvent residue were found in each case after applying this optimized drying condition. Electrode composite film photographs and their internal structures are shown in **Fig. S7, Fig. S9, Fig. S10** and **Fig. S11**. No calendaring was performed on these films. Dried electrodes were punched into 12.7 mm diameter discs using a precision disc cutter and transferred into an argon-filled glovebox. It is worth mentioning that no film delamination from Al substrate was observed during the handling and punching of the electrodes. The lack of delamination verifies that (partially) dissolved PVDF in DMI or PolarClean at RT still allows the film to adhere to the Al current collector, and that higher temperatures for complete dissolution are not required to make a mechanically stable coating.

Table S1. Solvent properties.[1-3]

Solvent	Boiling Point (ºC)	Vapor Pressure (Pa @ 25ºC)
NMP	202	40
DMI	235	31
PolarClean	280	1

Characterization of the composite slurries and resulting electrode films. The rheological properties of the slurries were measured at 25 ºC using a TA Instruments Discover HR-2 Rheometer in a parallel plate geometry with a diameter of 40 mm. The gap between the two plates was set to 300 µm, and the soaking time was maintained for 45 s. The shear rate range was applied from 0.01

to 200 s^{-1}. Top-view surface morphologies, cross-sectional views and energy dispersive X-ray spectroscopy (EDS/EDX) analysis/mapping of the electrodes were acquired using Hitachi S3400N SEM. Samples were mounted on an aluminum stub using carbon adhesive and images were collected using an acceleration voltage of 15 keV. A secondary electron detector was used, and the working distance was maintained at 6-10 mm.

Battery fabrication and electrochemical testing. Li half cells were assembled in 2032 coin cells (MTI) using lithium metal as the counter electrodes with a Celgard 2325 separator. Coin cells were made using a crimper inside an Ar-filled glovebox each using 200 μL of LP30 electrolyte. Li/NMC111 half cells were cycled at C/10 (using the theoretical specific capacity of NMC of 275 mAh/g from 2.7 to 4.2 V vs Li^+/Li.

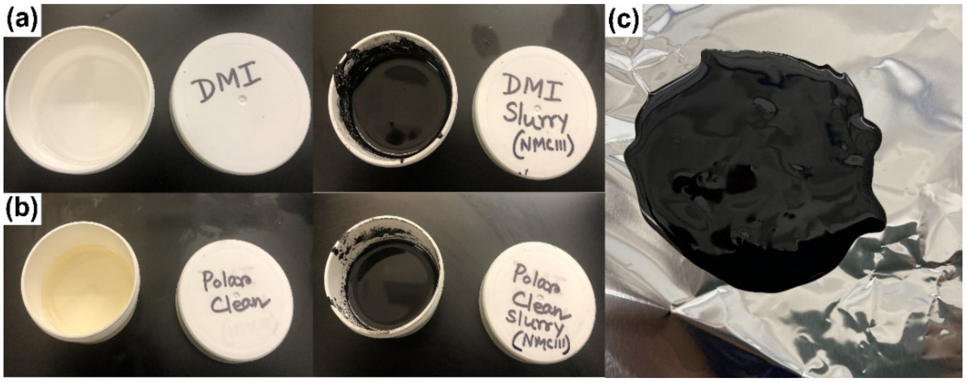

Fig. S1. Photographs of the solvent and slurry made at RT with NMC111, conductive carbon and PVDF binder in clear colorless DMI (a) and slightly yellowish clear solvent PolarClean (b), respectively. Resultant slurry (smooth texture) obtained from PolarClean was deposited on Aluminum substrate right before the coating starts, shown in (c).

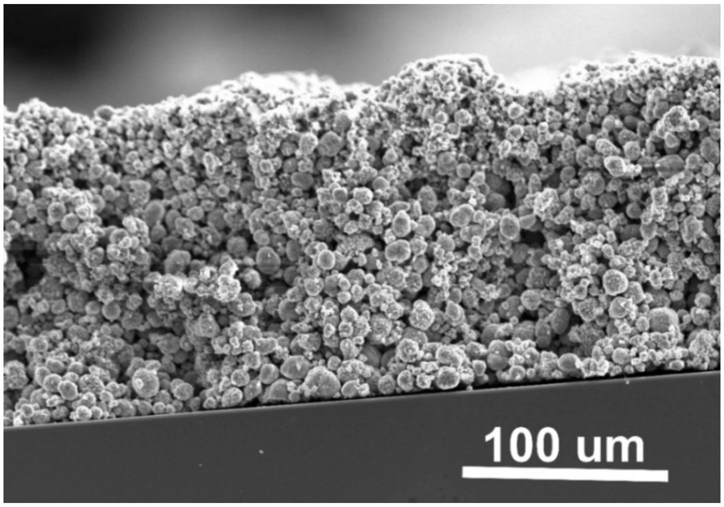

Fig. S2. SEM cross-section of 150 µm thick dried electrode composite film (NMC111, made with PolarClean) prepared via a custom-made wet film coating applicator (doctor blade), followed by air drying at 60 ˚C on a hot plate for a day, and 36-48 h of slow drying under vacuum at 60 ºC.

Solubility Tests of PVDF in N-methyl pyrrolidone (NMP), Dimethyl Isosorbide (DMI), and Polar Clean.

1, 3 and 10 wt% binder solutions were prepared by adding 0.01, 0.03 and 0.1 g PVDF in 1 mL NMP, DMI, and PolarClean. Solubility was first checked at room temperature (RT) with 5 minutes vortex. To improve the polymer dispersibility, the same solution was sonicated at RT for 5 minutes followed by heating at 60 ºC for an hour. Temperature was further increased to 120 ºC and dissolution was continued for overnight. Solubility tests for each concentration in specified solvents are presented in **Fig. S3-Fig. S6**.

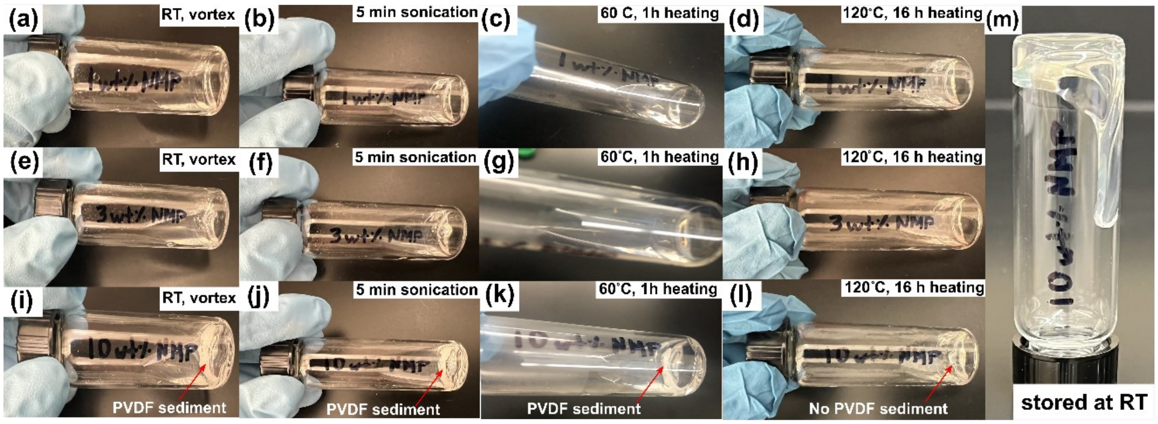

Fig. S3. PVDF solubility test in NMP: 1 wt% (a-b) and 3 wt% (e-f) solutions at room temperature (RT) result into forming clear solutions. However, 10 wt% polymer solution demonstrates PVDF residue while vertexing (i) and sonicated (j) at RT. Sedimentation remains unaltered even after 1 h heating at 60 ºC (k) which disappeared completely and resulted into clear solution after heating at 120 ºC for 16 h (l). Upon cooling the 10 wt% solution converted into gel, shown in (m).

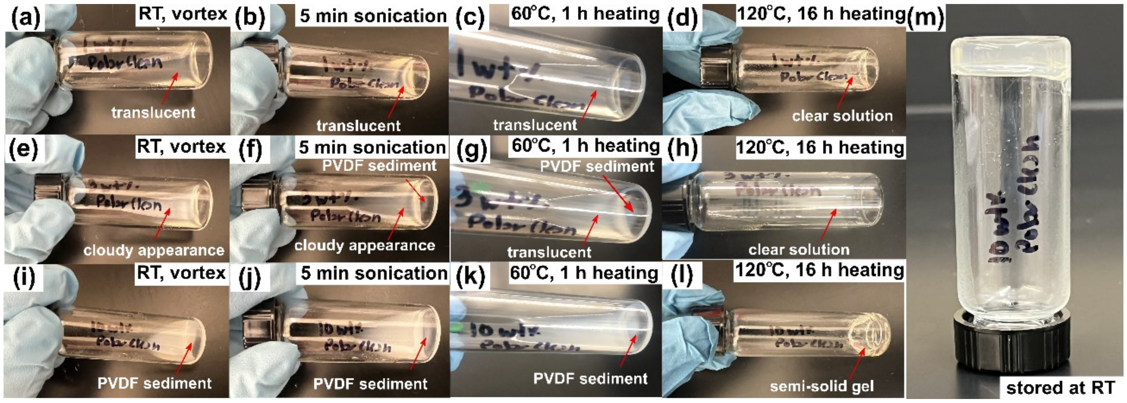

Fig. S4. PVDF solubility test in PolarClean: 1 (a) and 3 wt% (e) PVDF solutions in PolarClean at RT result into forming translucent and cloudy solutions, respectively, whereas the 10 wt% shows PVDF sediments at the bottom (i). Sonication and heating at 60 ºC improve the polymer dispersibility in 3 wt% solutions (f, g), though the sedimentation disappeared only after heating the solution at 120 ºC for 16 h (h). Sedimentation remains unchanged for 10 wt% PVDF solution even after 1 h heating at 60 ºC (k) which disappeared completely and turned into a semi-solid gel upon heating at 120 ºC (l). Upon cooling the gel remains same, shown in (m).

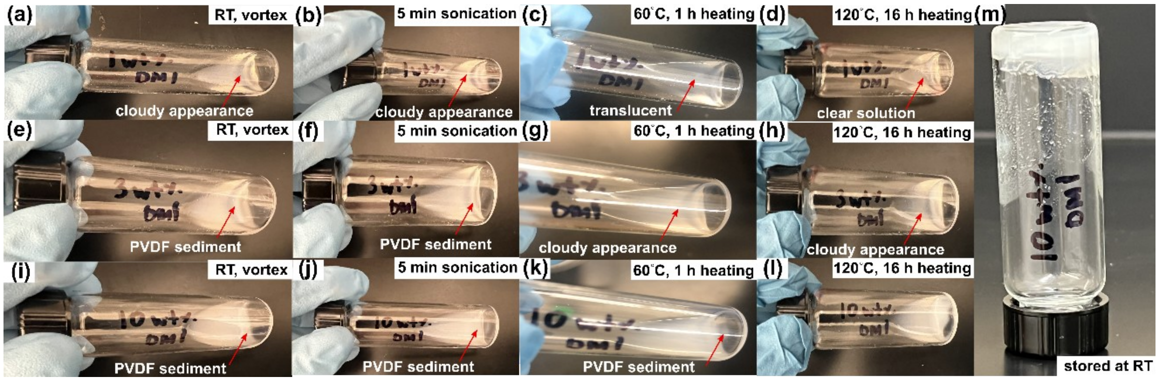

Fig. S5. PVDF solubility test in DMI: 1 wt% (a) PVDF in DMI at room temperature (RT) result into forming cloudy appearance which becomes clear while heated at 120 ºC (d). 3 wt% PVDF in DMI at RT results (e) into forming a solution with traces of PVDF sediment. Dispersibility increases with sonication (f), and results into translucent solution after heating at 120 ºC (h). 10 wt% solution shows PVDF sediments at the bottom (i-k) which slightly improved (l) while heated at 120 ºC and converts into gel upon cooling (m).

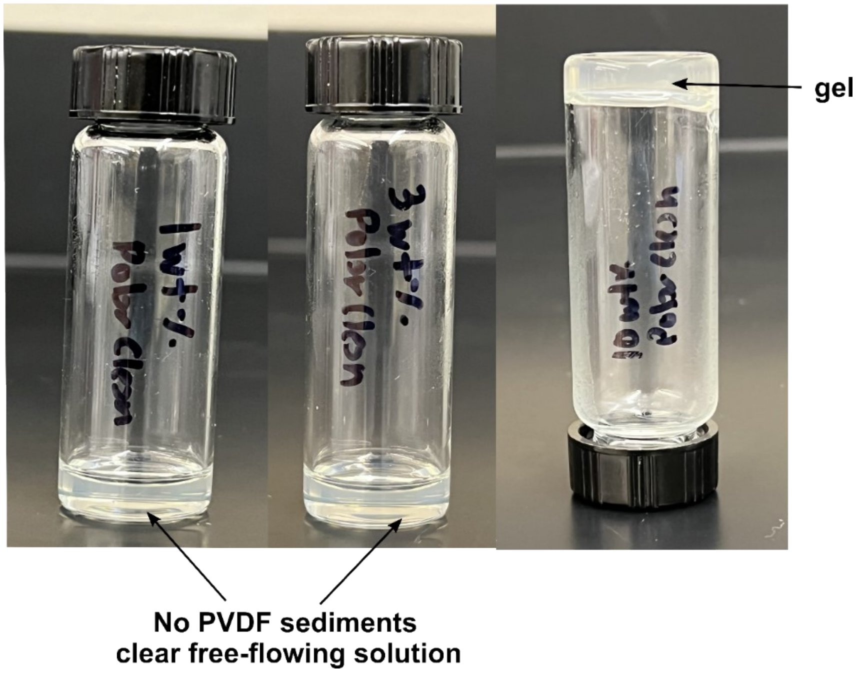

Fig. S6. PVDF remains solubilized in different concentrations in PolarClean after prolonged storage at RT.

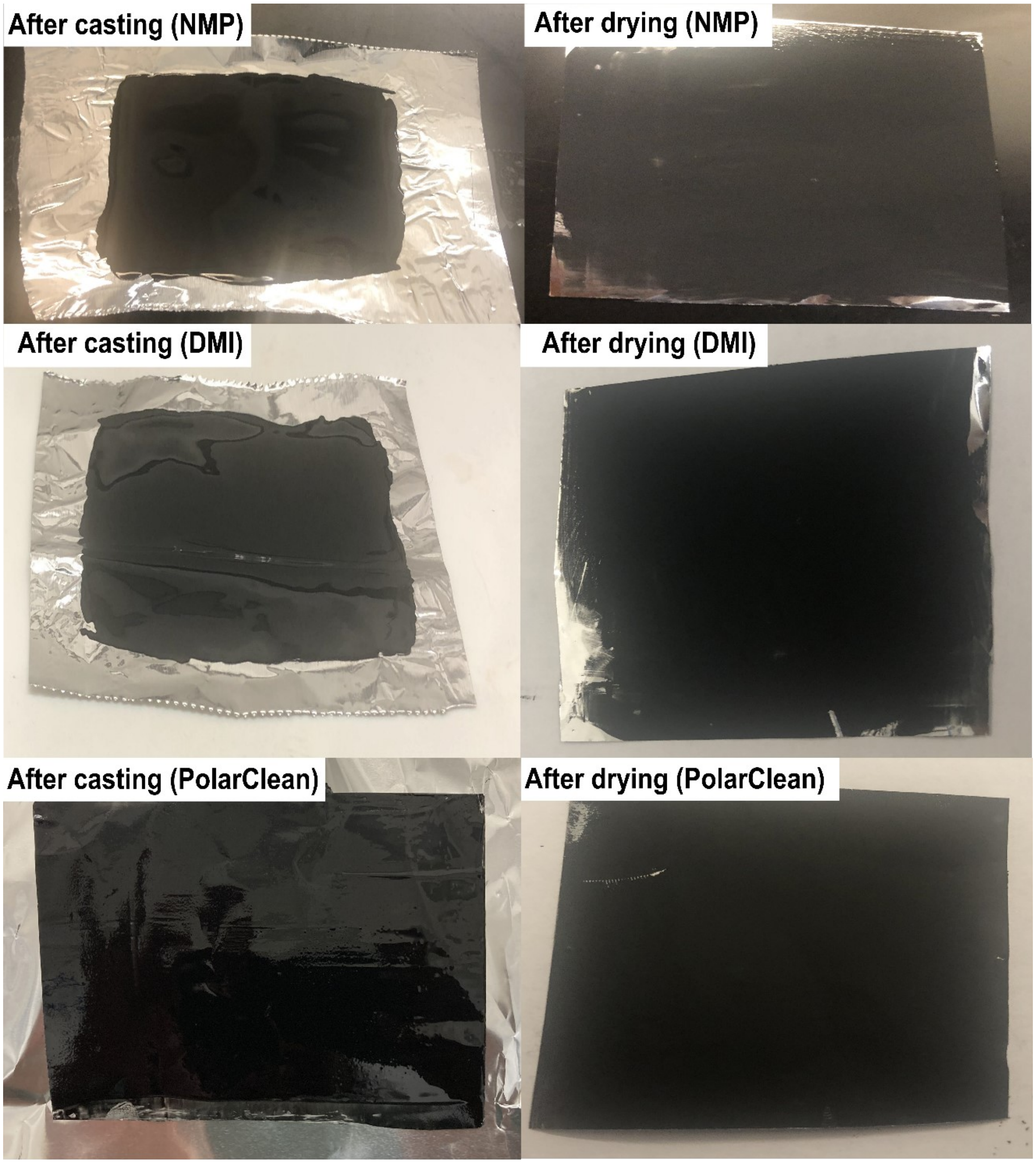

Fig. S7. Photographs of slurries, casted and dried from NMP (a), DMI (b) and PolarClean (c), respectively. Uniform and crack free coatings were found for all three cases. To remove solvent residue, electrodes were air dried at 60 ºC for a day, followed by drying at 60 ºC under vacuum for 2 days. It is worth to mention that no "peeling-off" of materials from Al substrate were noticed during the handling and punching of the electrodes. It suggests that PVDF dissolved in DMI, or PolarClean at RT sufficiently adheres to the Al current collector.

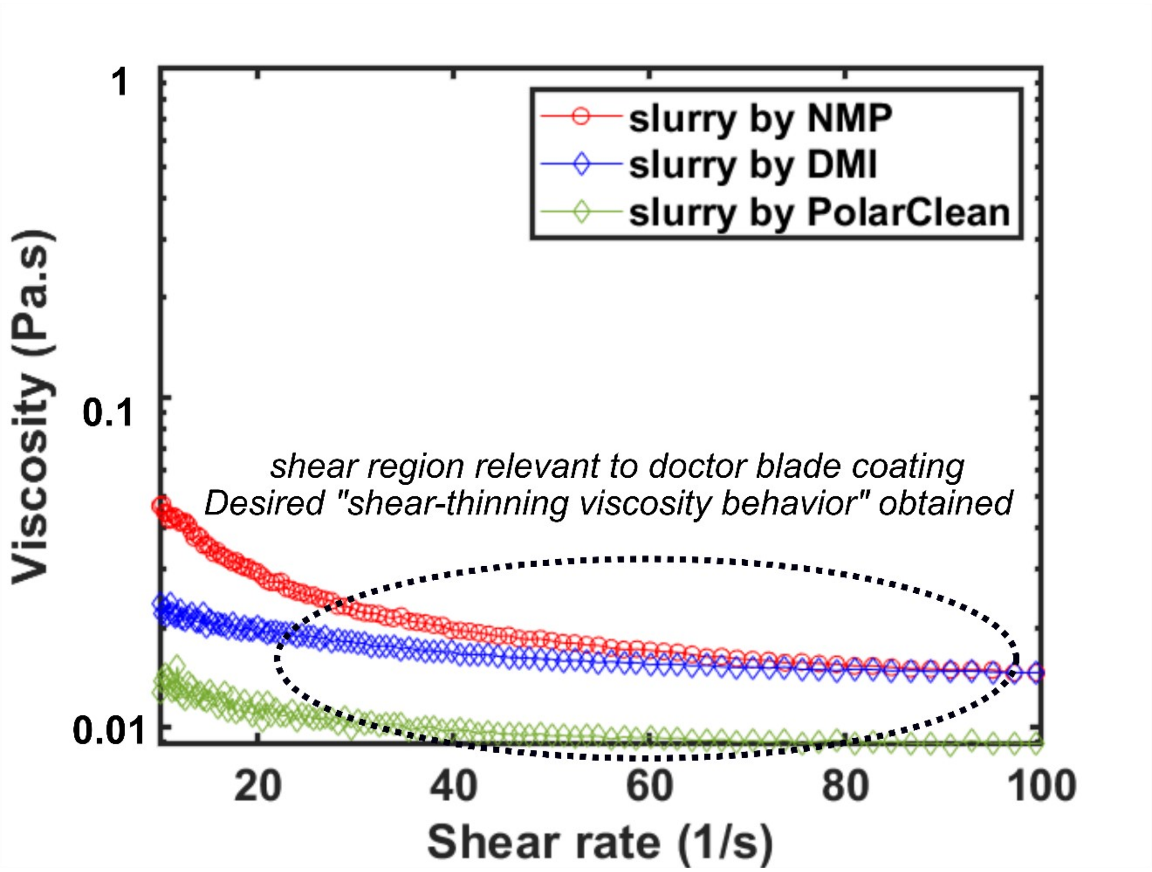

Fig. S8. Reduction of viscosities of NMC111 slurries with increasing shear stress is presented. Shear rate range of 10-100 is highlighted here as this is relevant for a doctor blade coating process.

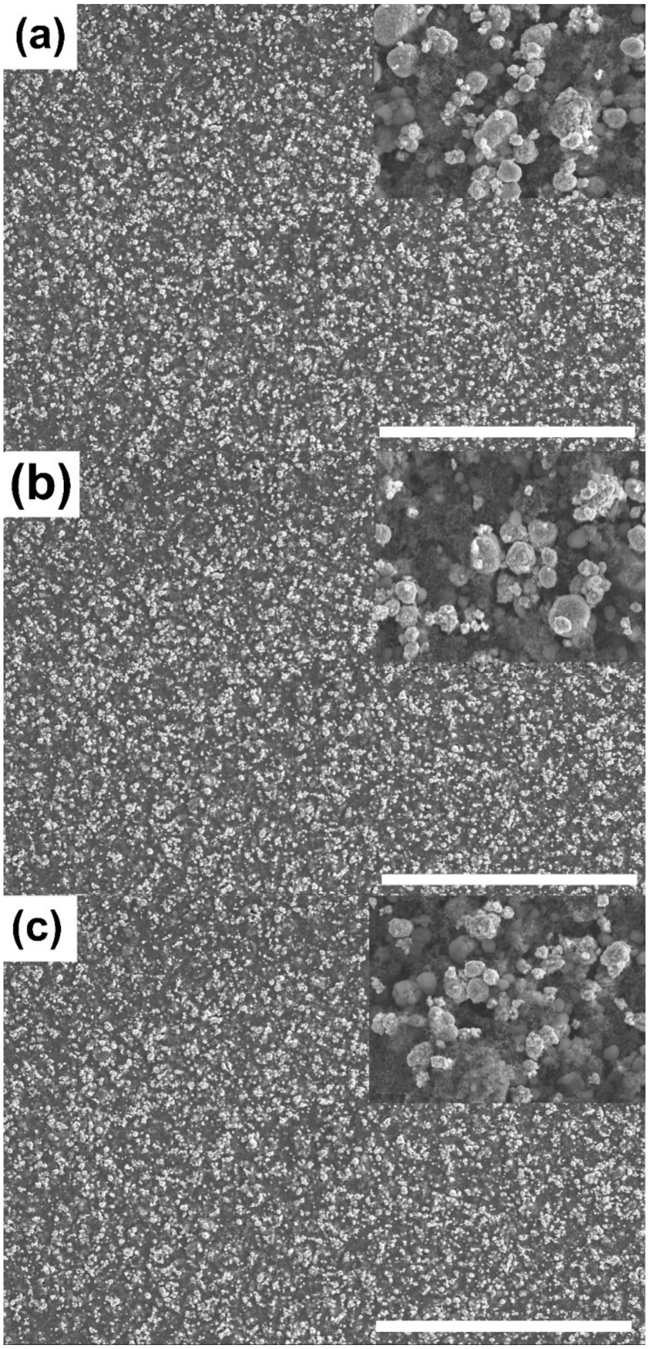

Fig. S9. Top-view SEM images of composite cathode films prepared using NMC111, PVDF and conductive carbon mixtures in NMP (a), DMI (b), and PolarClean (c) respectively. All dried electrodes demonstrate homogeneous, uniform, crack and defect free coating (expanded view inserted). The scale bars are set at 500 μm.

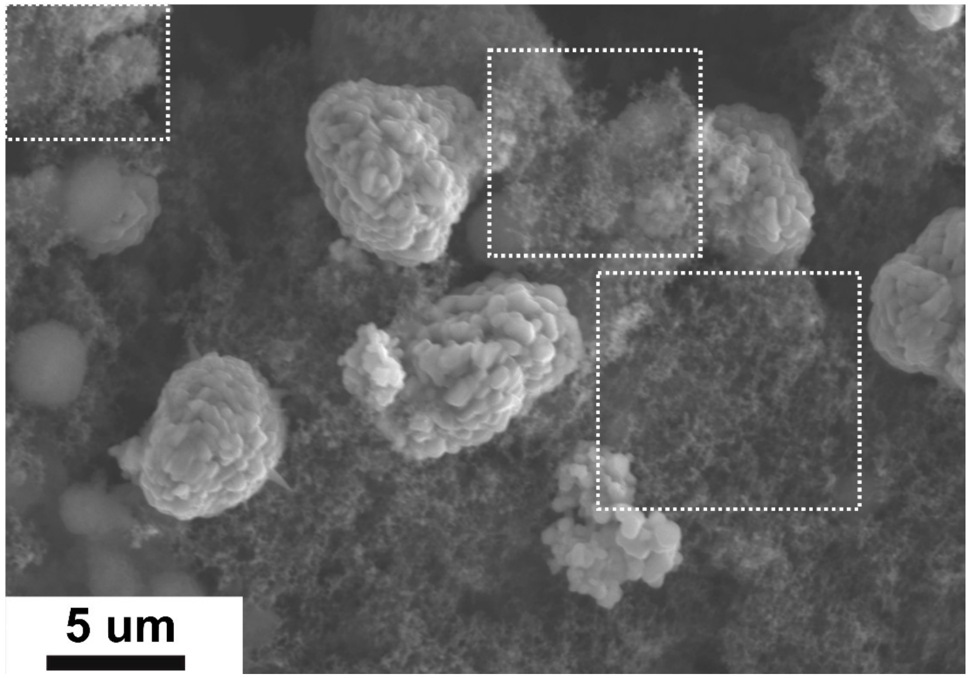

Fig. S10. A representative higher magnification top-view SEM image of electrodes prepared by PolarClean. This electrode demonstrates high degree of adsorption of the conductive carbon and PVDF binder on the surfaces of NMC111 (shown in square box).

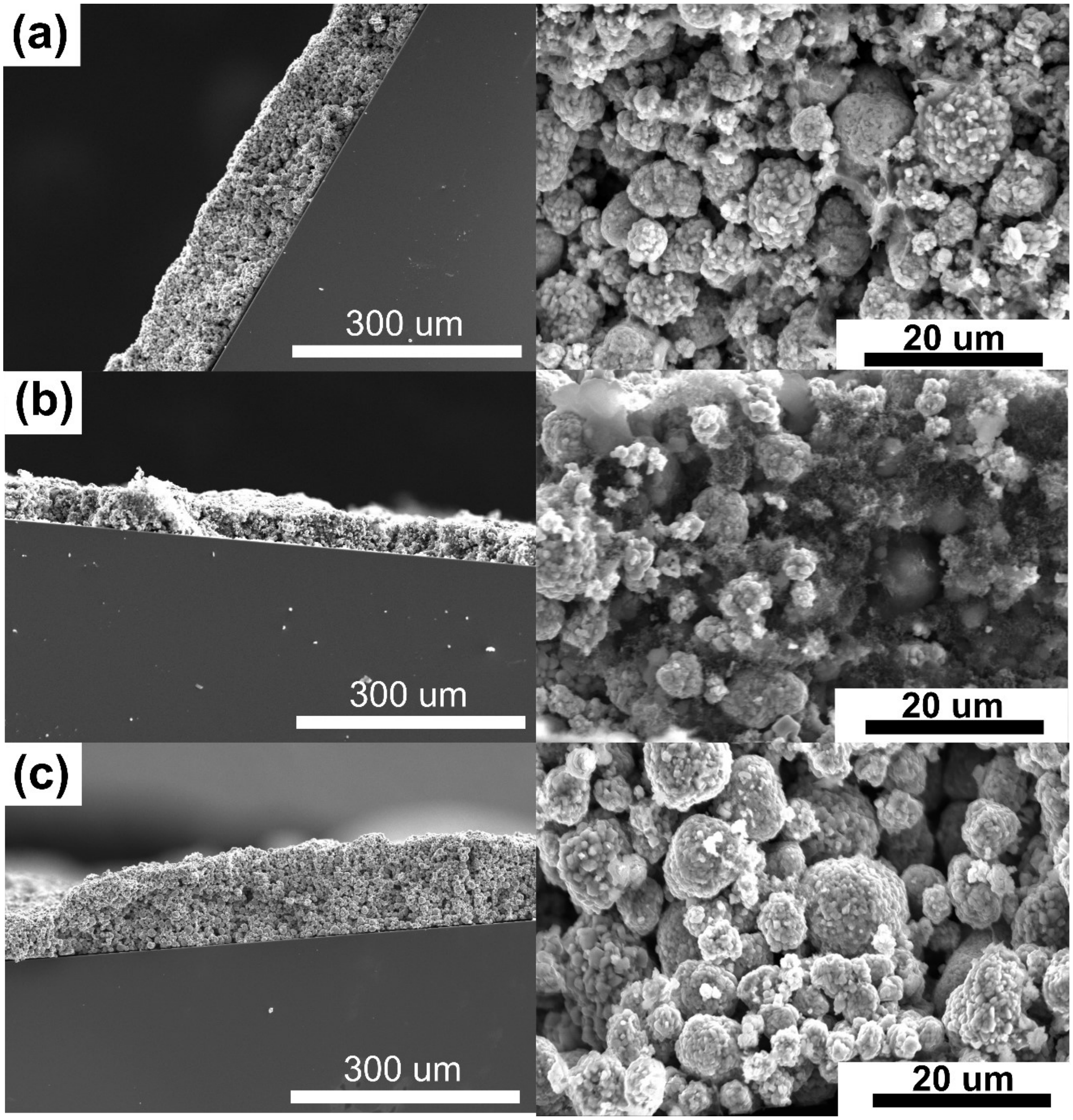

Fig. S11. Cross-sectional SEM images of dried electrodes prepared using NMP (a), DMI (b), and PolarClean (c), respectively.

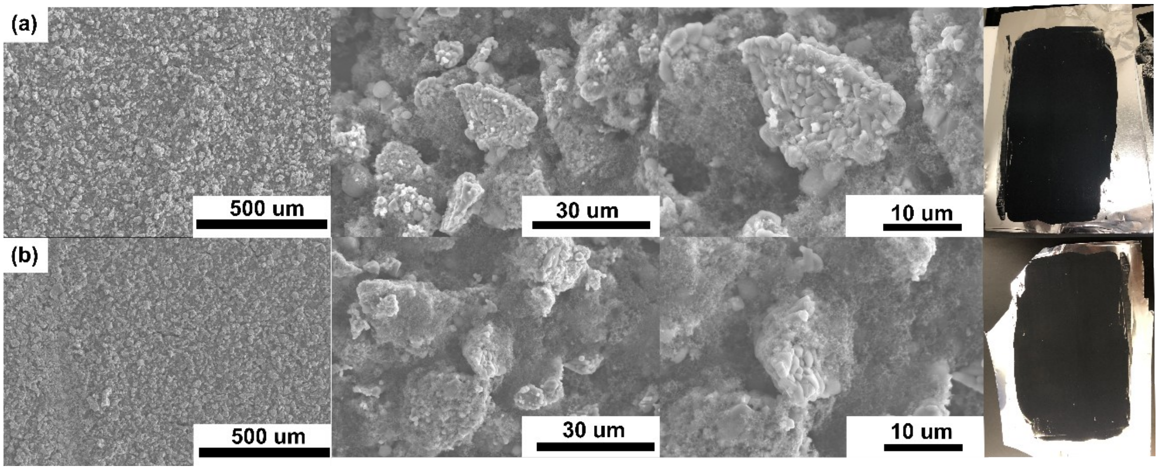

Fig. S12. Top-view SEM and photograph of electrode prepared using $LiMn_2O_4$, conductive carbon and PVDF binder in DMI (a) and PolarClean (b).

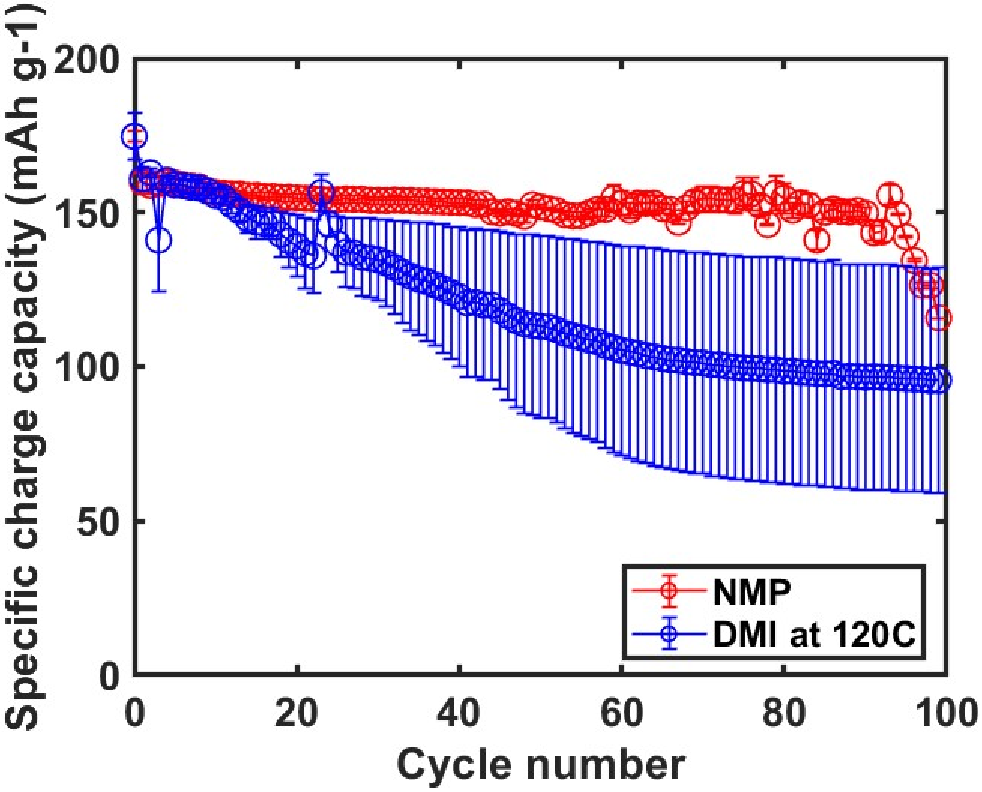

Fig. S13. Cycling performances of the electrodes made using the NMC111 slurry with dissolved PVDF in DMI at 120 ºC. Cycling performance was compared with the control cells made using NMP at RT. Error bars represent standard error of the mean (N=3 for both datasets).

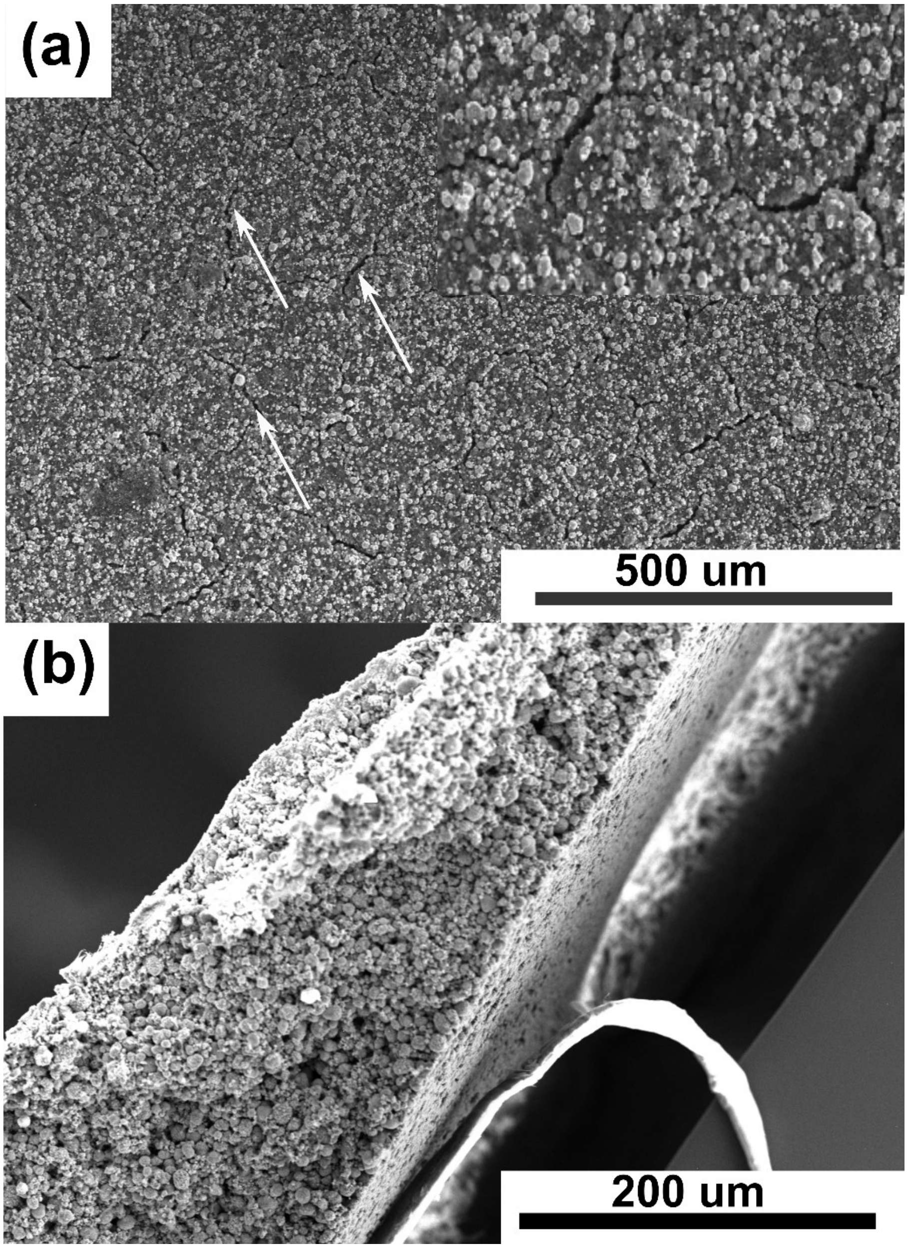

Fig. S14. Top-view (a) and cross-section (b) SEM of NMC111 electrodes made by PolarClean, dried at 120 °C in hot plate for 12 h and vacuum dried at 100 ºC for 24 h. Micrographs demonstrate cracks on the electrode surface (a) and delamination of coating from the substrate (b) during the quick heating process at higher temperature. High temperature and quick drying may cause weakening of PVDF adhesion and result into delamination.

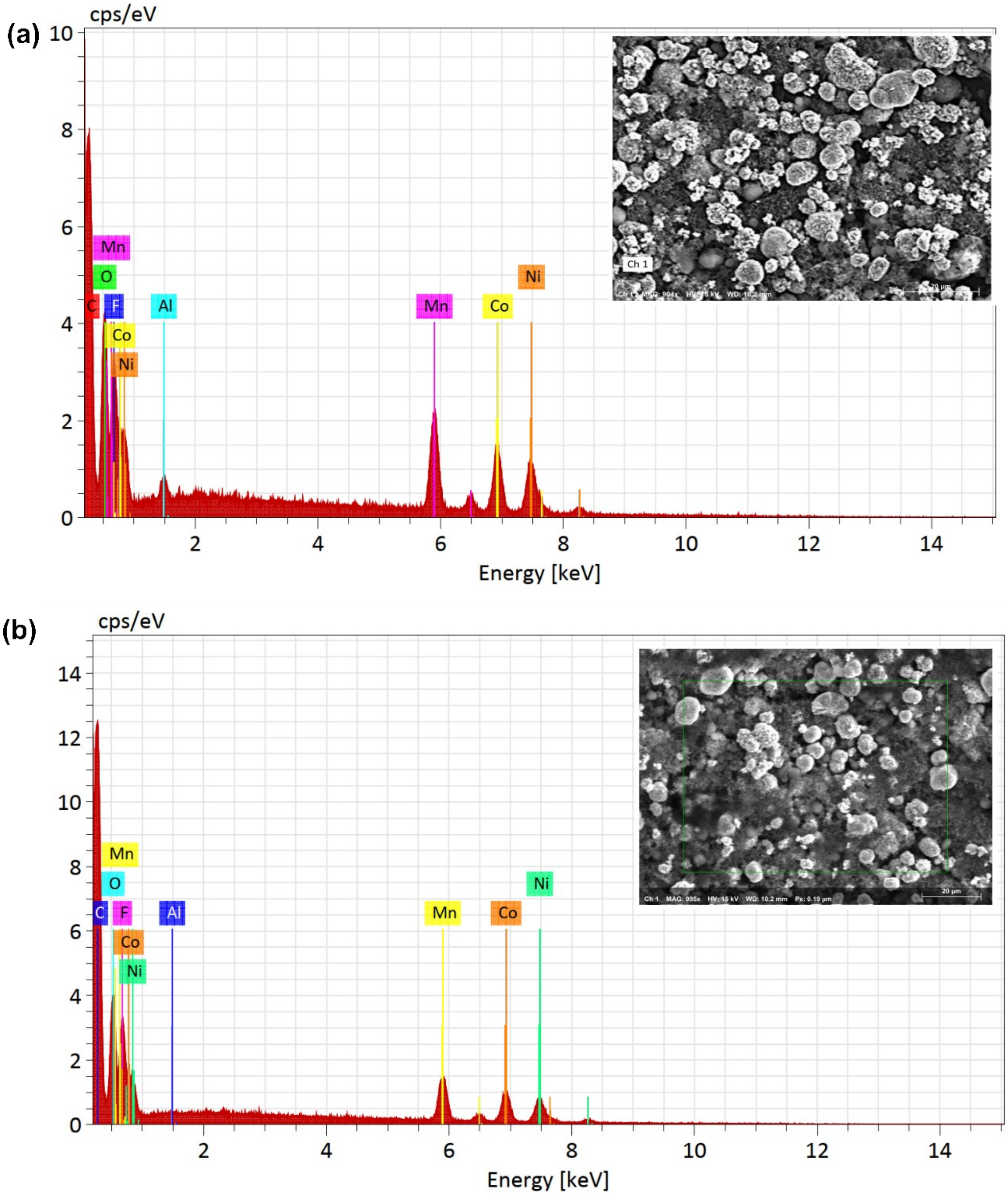

Fig. S15. EDS analysis of electrodes made by DMI (a) and PolarClean (b).

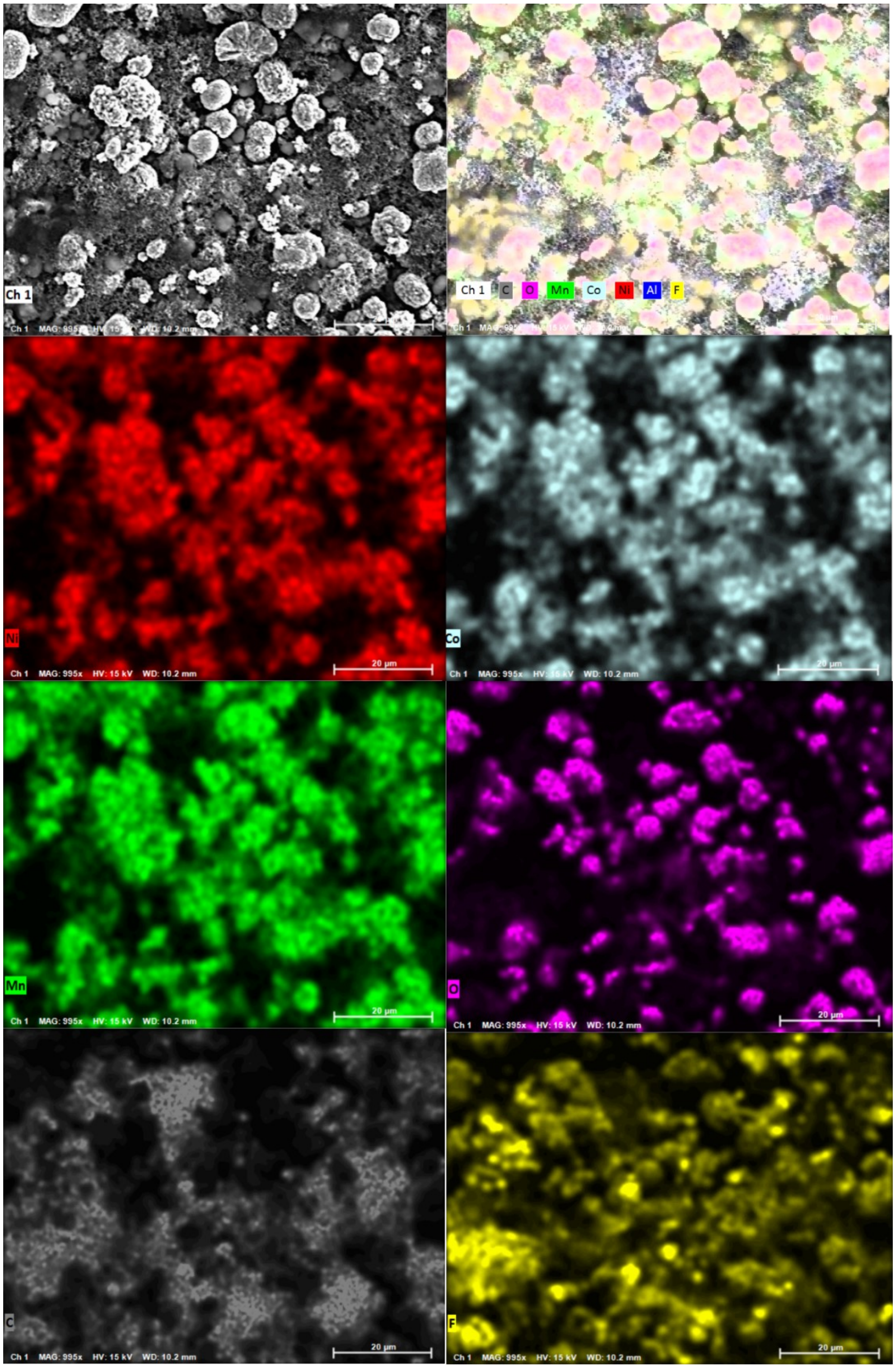

Fig. S16. EDS mapping of electrode made by PolarClean demonstrates the uniform dispersion of slurry components.

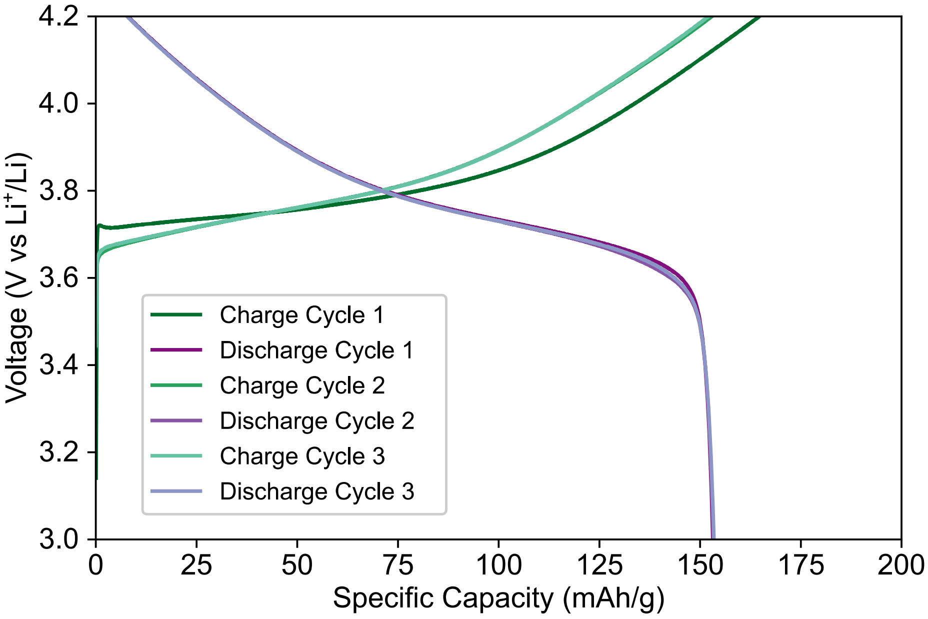

Fig. S17. Plot of voltage vs. specific capacity for the first three cycles of a Li|NMC111 cell using NMP as the slurry solvent.

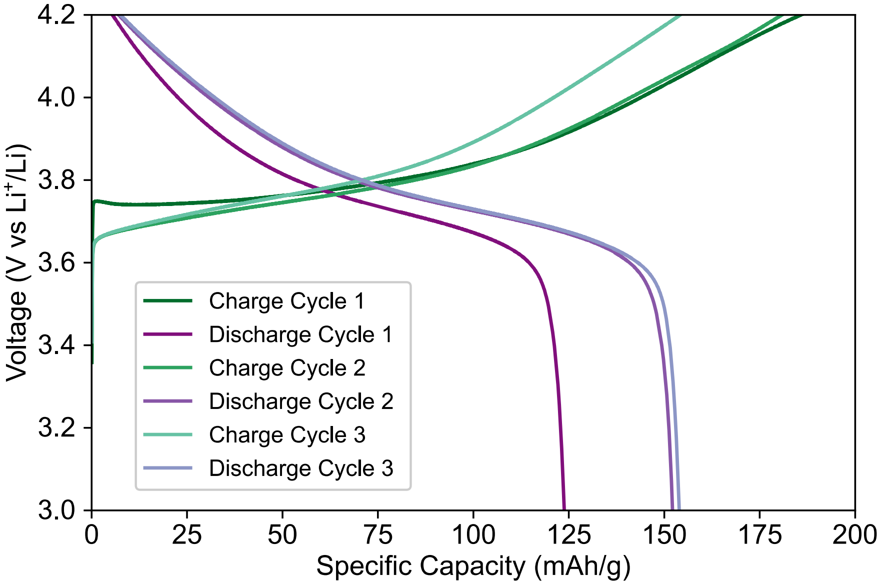

Fig. S18. Plot of voltage vs. specific capacity for the first three cycles of a Li|NMC111 cell using PolarClean as the slurry solvent.

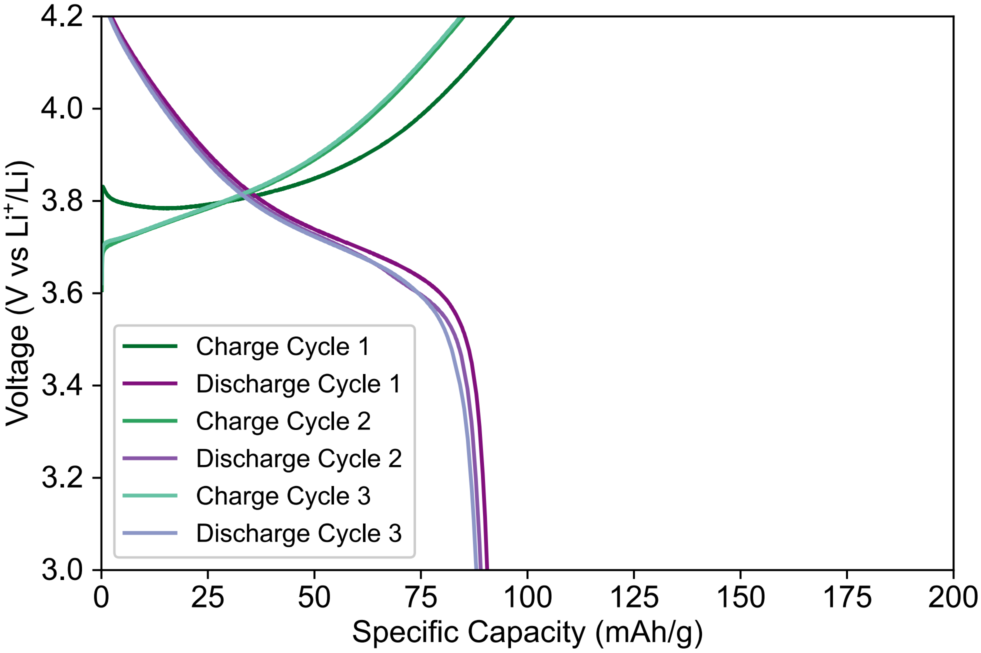

Fig. S19. Plot of voltage vs. specific capacity for the first three cycles of a Li|NMC111 cell using DMI as the slurry solvent.

Note: **Fig. 4** and discussion of irreversible capacities in the main text refer to average specific capacities over multiple cells (N=3 for NMP, N=2 for DMI and PolarClean), while **Fig. S17-S19** show representative voltage profiles for individual cells. Thus, there will be discrepancies between the average irreversible capacity reported in the main text and the capacities shown in **Fig. S17-S19.**

References:

1. https://www.solvay.com/sites/g/files/srpend221/files/tridion/documents/Polarclean.pdf (accessed July 27, 2022).
2. http://www.perflavory.com/episys/ps1252931.html. (accessed July 27, 2022).
3. http://www.ddbst.com/en/EED/PCP/HCP_C284.php (accessed July 27, 2022).