

TITLE

A soft-solid co-crystalline electrolyte for lithium-ion batteries

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ABSTRACT

Alternative solid-electrolytes are the next key step in advancing lithium batteries with better thermal and chemical stability. A soft-solid electrolyte (Adpn)₂LiPF₆ (Adpn = adiponitrile) is synthesized and characterized, which exhibits high thermal and electrochemical stability and good ionic conductivity, overcoming several limitations of conventional organic and ceramic materials. The surface of the electrolyte possesses a liquid nano-layer of Adpn that links grains for a facile ionic conduction without high pressure/temperature treatments. Further, the material can quickly self-heal if fractured and provides liquid-like conduction paths via the grain boundaries. A significantly high ion conductivity ($\sim 10^{-4}$ S/cm) and lithium-ion transference number (0.54) are obtained due to weak interactions between “hard” (charge-dense) Li⁺ ions and “soft” (electronically polarizable) -C≡N group of Adpn. Molecular simulations predict that Li⁺ ions migrate at the co-crystal grain boundaries with a (preferentially) lower E_a and within the interstitial regions between the co-crystals with higher E_a , where the bulk conductivity comprises a smaller but extant contribution. These cocrystals establish a special concept of crystal design to increase the thermal stability of LiPF₆ by separating ions in Adpn solvent matrix, and also exhibit a unique mechanism of ion-conduction via low-resistance grain-boundaries, which is contrasting to ceramics or gel-electrolytes.

MAIN TEXT

Replacement of volatile liquid electrolytes to improve safety in lithium metal or lithium-ion batteries (LIBs) has generated interest in the development of solid electrolytes. These have included polymers, polymer gels with nonvolatile liquids, and a wide range of inorganic materials¹ such as oxide and sulfide-based lithium (LICC) or sodium ion-conducting ceramics.² While LICCs can have good ionic conductivities (σ) and lithium-ion transference numbers (t_{Li^+} , the fraction of charge carried by Li^+), there are still problems associated with poor interfacial contact between the electrolyte and the electrodes. We have been investigating a new class of solid electrolytes: salt-organic co-crystals (also referred to as solvates) of lithium and sodium salts with weakly ligating molecular organic compounds. Similar to lithium-ion-conducting ceramics, these new “soft” co-crystals also have channels for ion migration but are not necessarily single-ion conductors. Unlike the rigid anionic lattices of ceramic electrolytes, the channels in the “soft” co-crystals consist of weakly Lewis basic donor groups of organic molecules, and in some examples, there are no $\text{Li} \cdots \text{anion}$ contacts³. Previously reported solvates of lithium salts with polyethylene oxide (PEO)^{4,5} or glymes⁶ can have ionic conductivities higher than their respective molten phases⁵, but are still very low (10^{-7} S/cm for PEO solvates^{5–7} and 10^{-6} S/cm for glyme solvates⁸) due to the tight chelation of the “hard” (non-polarizable) Li^+ ions with the “hard” ether oxygen donors. Nitriles and other triple bonded systems are known to be electronically soft due to polarizability, characterizable by the hardness factor.⁹ Previous work in other¹⁰ and our groups has focused on co-crystals of lithium (or sodium) salts with a coordinating ligand that has “soft” (polarizable), weakly electron-donating atoms, e.g. dimethyl formamide (DMF) with LiCl ¹¹ or NaClO_4 ^{12–14}, isoquinoline with LiCl ¹⁵, or adiponitrile (Adpn) with NaClO_4 ¹⁶, where the weaker binding promotes higher conductivity. Unlike inorganic ceramics where grain boundaries must be sintered

and can be resistive, the grain boundaries in soft-solid cocrystals are fluid, permitting easy reformation upon cracking and can be melted and are thus melt-castable at moderate temperatures.^{12,16}

In the current work, soft co-crystals formed with LiPF_6 salt and Adpn solvent: $(\text{Adpn})_2\text{LiPF}_6$ are investigated experimentally and theoretically. The components of these co-crystals, LiPF_6 and Adpn, have compatibility with high voltage cathodes (Adpn) and are used (LiPF_6) in most commercial LIBs despite poor thermal stability in pure or solvated form. Polar nitrile ($-\text{C}\equiv\text{N}$) groups, with high dipole moments and dielectric constants of ~ 30 , can solvate lithium ions more weakly than the ether oxygens of polyethylene oxide (PEO) or glymes, and have been incorporated as functional groups in liquids, plasticizers, plastic crystals (particularly succinonitrile (SN)^{17,18}), gels (e.g., polyacrylonitrile (PAN)^{19,20}), PAN polymer-in-salt^{21,22} and solid electrolytes used for LIB applications²³. These materials often have high anodic oxidation potentials ($> 4.5 \text{ V vs. Li}^+/\text{Li}$) and are thus resistant to electrochemical oxidation²⁴ and therefore have the potential to be used with high voltage cathodes²⁵, e.g., $\text{Li}[\text{Mn, Ni, Co}]\text{O}_2$ (NMC). Adpn has also been shown to enable the use of high voltage cathodes when added in small amounts (1%) to other electrolyte solutions, by film formation²⁶ or strong coordination between the Ni^{4+} on Ni-rich cathode surfaces and the nitrile groups²⁷. Although nitriles suffer from poor reductive stability²⁴ they can be used with lower-energy anodes such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO, $1.55 \text{ V vs Li}^+/\text{Li}$)^{18,28} or with graphitic anodes by addition of SEI forming co-solvents²⁹. More recently, it was shown that low concentrations of Adpn (1%) in mixed electrolytes formed stable SEIs on Li^0 metal²⁷. Of importance for the current work, the reductive stability of acetonitrile (AN) was improved in concentrated ($> 4 \text{ M}$) salt solutions, since all of the acetonitrile molecules were passivated by coordination to Li^+ ions³⁰.

The cocrystalline (Adpn)₂LiPF₆ has an effective molarity of 4.5 M and it exhibits desirable physical properties, including melt- and press-castability, self-healing, high conductivity for an organic solid electrolyte ($\sim 10^{-4}$ S·cm⁻¹), and a wide electrochemical stability window (5 V), stable cycling (> 50 cycles at C/20, C/10, C/5 rates) with capacities of 140 mAh·g⁻¹ to 100 mAh·g⁻¹ and > 99% Coulombic efficiencies using Li⁰/(Adpn)₂LiPF₆/LiFePO₄ half-cells and ~ 96% Coulombic efficiency with LTO/(Adpn)₂LiPF₆/NMC622. Further, our atomistic simulation models demonstrate an unforeseen mechanism of ion-conduction in these soft-solids where grain-boundaries are the most vital contributor to the net ionic conductivity, followed by the Li⁺ defects, which facilitate ion-conduction in the bulk co-crystal.

Structural and thermal characterization

The parent compound (Adpn)₂LiPF₆ is prepared by heating commercially available LiPF₆ in excess adiponitrile, in which it is sparingly soluble at room temperature²⁹. After complete dissolution at 165°C, cooling of the solution yields crystalline (Adpn)₂LiPF₆, whose stoichiometry is confirmed by XRD analysis of single crystals (**Fig. 1a,b**). The experimentally obtained powder XRD patterns of these crystals agree with those obtained theoretically from single crystal data, and for post-electrochemical and melt-recrystallized samples (**Fig. 1c,d,e,f**). The structure exhibits linear parallel Li⁺ ion channels (**Fig. 1b**), with a shortest distance of 6.23 Å between two successive Li⁺ ions in the *b*-crystallographic direction. Each Li⁺ ion is coordinated to four cyano groups, and does not interact with any PF₆⁻ anions. An important consequence of the isolation of the PF₆⁻ anion from the Lewis acidic Li⁺ is the improvement of the thermal stability of the salt; the thermogravimetric analysis (TGA) data (**Extended Data Fig. 1**) show that the stability of LiPF₆ increases from decomposition temperatures of 100 °C for pure LiPF₆ to 200 °C for co-crystalline (Adpn)₂LiPF₆,

such that the stability of the co-crystal is limited by the boiling point of Adpn (Adpn $T_m = 1\text{ }^{\circ}\text{C}$, $T_b = 295\text{ }^{\circ}\text{C}$). This is most likely due to the segregation of ions into separate channels preventing the formation of the usual decomposition product LiF. For comparison, the thermal stability of the molecular crystal of $\text{SN}_2\text{LiFSI}^{10}$ (SN = succinonitrile) was limited to $130\text{ }^{\circ}\text{C}$ (SN $T_m = 57\text{ }^{\circ}\text{C}$ and $T_b = 266\text{ }^{\circ}\text{C}$; LiFSI $T_m = 142\text{ }^{\circ}\text{C}$; $T_2 = 233\text{ }^{\circ}\text{C}$ for dry salts³¹). The behavior of co-crystals in TGA was simulated from MD simulations using model *V* (*vacuum*), which predicts that Adpn molecules form a liquid-like layer on the co-crystalline surface at room-temperature (**Extended Data Fig. 2a**) and evaporate as the cocrystals degrade at high temperature ($T > 400\text{ K}$) (**Extended Data Fig. 2b – d**). This experimental structure was used to benchmark the periodic model *P* used in MD simulation, provided in **Supplementary Fig. S1** and **S2**.

Differential scanning calorimetry (DSC) data (**Fig. 2a**) show that the co-crystals of $(\text{Adpn})_2\text{LiPF}_6$ reversibly melt at $182\text{ }^{\circ}\text{C}$, and recrystallize after slight supercooling to $\sim 150^{\circ}\text{C}$. The same crystalline phase is recovered after recrystallization based on PXRD (Figure S1b), demonstrating that the material does not decompose upon melting. For comparison, the SN_2LiFSI molecular crystal melts at $T_m = 59.5\text{ }^{\circ}\text{C}^{10}$. In the case of $(\text{Adpn})_2\text{LiPF}_6$, the presence of a small amount of free (i.e., at least one $\text{-C}\equiv\text{N}$ not coordinated to Li^+) Adpn in the cocrystal was observed by DSC (**Fig. 2a**) and Raman spectroscopy (**Fig. 2b**). The assignment of “free” and coordinated $\text{C}\equiv\text{N}$ peaks was validated using the DFT calculations for a geometry shown in **Fig. 2c** and theoretical vibrational spectra in **Fig. 2d** (and in **Supplementary Table S1**).

A liquid-like surface layer was observed in all SEM images of $(\text{Adpn})_2\text{LiPF}_6$ both before (in pressed and unpressed polycrystalline crystals (**Fig. 2e**, **Extended Data Fig. 3**), and after cycling (**Extended Data Fig. 4, 5**). Liquid Adpn juices out of the crystals on application of pressure in the

events like cell manufacturing (**Supplementary Fig. S3**), which is a preceded behavior.¹³ With the application of pressure, individual grains fracture into smaller pieces and fuse to one another. In the large 100 μm single crystals a mosaic structure of smaller, $< 1 \mu\text{m}$ crystalline domains (**Extended Data Fig. 3f**) could be observed.

Fluid grain boundaries:

EDX spectra (**Fig. 2f,g**) support the existence of fluid grain boundaries. Relative X-ray fluorescence peaks for carbon and nitrogen atoms of the Adpn are weaker compared with the fluorine and phosphorus atom peaks of the LiPF_6 in the grain boundary region than in the grains, suggesting that under the vacuum of the SEM, Adpn is evaporated, leaving behind LiPF_6 salt. Such surface liquid phases are well known and are due to a decrease in lattice energy for molecules near the surface of crystals, and most famously illustrated by the surface liquid water layer in ice.³² This nanoliquid surface behavior is a general characteristic of this class of electrolytes^{11–13,16,33} and is supported by the MD simulations performed on the model V (**Extended Data Fig. 2**).

The structure of the intergranular interface was modeled using model V_{8g} with eight nano-sized grains (1 grain supercell = $5 \times 5 \times 5$ unit cells) in a box of $30 \times 30 \times 30 \text{ nm}^3$ (**Fig. 3a**, details provided in Supplementary Information). The simulations show that within a span of a few nanoseconds, the grains interact at the surface and form a more mobile interfacial layer (**Fig. 3b, Supplementary Video 1**). The formation of this interfacial layer does not depend on the orientation of the grains or the size of the box, *viz.* does not require lattice matching. Since “excess” Adpn solvent molecules are trapped/confined between the grains during synthesis which form part of the grain-boundaries, a model $V_{2g,sol}$ was constructed, where “excess” Adpn molecules solvate two grains of $\text{Adpn}_2\text{LiPF}_6$. The model $V_{2g,sol}$ shows initial inter-phase contact between the two grains (**Fig.**

3c), where several Li^+ and PF_6^- ions from the crystal dissolve in the free Adpn solvent molecules (**Fig. 3d**) to facilitate a better grain boundary conduction (discussed in the mechanism of ion transport subsection) in contrast to ceramic organics, whose grains must be sintered to prevent insulating inter-grain gaps.

Electrochemical testing:

The electrochemical impedance spectroscopy (EIS) data (**Fig. 4a**) for a pressed pellet of $(\text{Adpn})_2\text{LiPF}_6$ in the temperature range between -10°C and 80°C (below its degradation temperature), show a RT conductivity of $\sigma \rightarrow 10^{-4} \text{ S cm}^{-1}$ (using a constant phase-element resistor (CPE)/constant phase-element (CPE) circuit shown in **Extended Data Fig. 6a**), with an Arrhenius activation energy $E_a = 37.2 \text{ kJ mol}^{-1}$. The variation of the DC current as a function of time (**Extended Data Fig. 6b**), in a $\text{Li(s)}/(\text{Adpn})_2\text{LiPF}_6/\text{Li(s)}$ cell, including the correction for the interfacial resistance before polarization (R_0) and at steady-state (R_s):

$$t_{\text{Li}^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_0 R_s)}$$

gave $t_{\text{Li}^+} = 0.54$. Unlike inorganic ceramics with a stationary anion lattice and mobile Li^+ sublattice ($t_{\text{Li}^+} \rightarrow 1$), here both the anions and cations are mobile, but with a better t_{Li^+} than in typical commercial liquid electrolytes.³⁴

The oxidative current begins to increase only at 5V (**Fig. 4b**), confirming the excellent oxidative stability of Adpn^{29,35}. While Li metal is thermodynamically unstable with most organic solvents,^{30,36} Adpn (with or without LiPF_6) remains colorless for weeks to months with an inserted piece of Li^0 metal (**Supplementary Fig. S4**).

Reversible Li^0 stripping/plating is observed for $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ (**Fig. 4b**). This is an improvement for the 4.5M $(\text{Adpn})_2\text{LiPF}_6$ over dilute AN/LiTFSI ($<3\text{M}$) where Li stripping is not observed.³⁰ During repeated lithium stripping, the oxidation peak at $\sim 0.5\text{ V}$ (vs Li^+/Li) superimposes onto itself, while during lithium plating, the reduction peak at $\sim -0.5\text{ V}$ decreases from the 1st through the 3rd cycles and then remains stable. This suggests that a stable, ionically conductive SEI layer is being formed during the first three cycles. Interfacial resistance (**Fig. 4c**) in a $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ cell stabilized at about 900Ω after 3 days. Li plating in the same cell (**Fig. 4d**) was stable for 20-25 days at low current densities ($J = 0.01\text{ mA/cm}^2$) but failed at higher current densities.

Excellent cycling data was obtained for the $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{LiFePO}_4$ half cells at C/20, C/10, and C/5 rates ($\sim 140\text{ mAh}^{-1}/\text{g}$) with little capacity fade (**Extended Data Fig. 6e,f**) between 2.7 and 4 V. The C/10 data ran for > 70 cycles before capacity fade (**Fig. 4e**). In previous studies with liquid Adpn/1 M salts, only 20 cycles could be obtained with efficiencies of $\sim 97\%$.³⁷ Thus, the highly concentrated $(\text{Adpn})_2\text{LiPF}_6$ improves compatibility with the Li^0 metal. A full cell with LTO/ $(\text{Adpn})_2\text{LiPF}_6/\text{NMC622}$ was also investigated to assess the potential for these electrolytes to be used with high voltage cathodes. The C-rate performance of LTO/ $(\text{Adpn})_2\text{LiPF}_6/\text{NMC622}$ cells (**Fig. 4f**) and the cycling performance at C/10 (**Extended Data Fig. 6g**) between 2V and 4.2V vs Li/Li^+ shows that the accessible capacity decreased with C-rate, as expected, but recovered when returned to the original C-rates. For cells cycled at C/10, the capacity faded up to 50 % over 100 cycles, but without a catastrophic failure (see **Extended Data Fig. 6g**). Further, the Coulombic efficiency was steady at $\sim 99.6\%$ for the whole 100 cycles. Comparison of the Li^0/Li^0 , $\text{Li}^0/\text{LiFePO}_4$, LTO/NMC622 and NMC622/NMC622 cells suggests that both the anodes and cathodes contribute to capacity fade, with comparable impedances for both anodes and cathodes.

Post-mortem analysis:

Interfacial resistance (**Fig. 4c**) in the $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ cell stabilized at about 900Ω after 3 days. Lithium plating in the same cell (**Fig. 4d**) was stable for 20-25 days at low current densities ($J = 0.01 \text{ mA/cm}^2$) but failed at higher current densities. Post-mortem analysis showed that the Li surface was black. SEM images (**Extended Data Fig. 4**) indicate that the SEI was rough (not flat) with a thickness $< 5 \mu\text{m}$ after ~ 30 days, suggesting a compact but mossy SEI layer, with no obvious dendritic growth. EDX analysis (**Extended Data Fig. 5**) of the surface showed residual $(\text{Adpn})_2\text{LiPF}_6$ crystals that adhered to the SEI layer, based upon their morphology and dominant signals for C, N, F and P atoms but no signal for O atom. At the SEI layer itself, the major peaks were O (from Li_2O) and C (from Adpn), with very little P and F (from PF_6^-). While further investigation is required, these peaks suggest the formation of lithium oxides and carbonates. The formation of compounds containing C (such as carbonates), and the scarcity of F, P, agree with predications from electronic structure calculations (**Extended Data Fig. 7**) that the Adpn reduction could cause solvent degradation leading to SEI layer formation at the Li^0 anode. However, the degradation stops after 3 cycles based on cyclic voltammetry (**Fig. 4b**), giving a stable, protective SEI.

Mechanism of ion transport:

Since the $\text{Adpn}_2\text{LiPF}_6$ electrolyte has a fluid surface region and contains Adpn solvent between the co-crystalline grains, possibly as a nano-confined liquid, the net ion conduction can have at least these two contributions – at the grain-boundaries (σ_{gb}) of the cocrystals and inside the cocrystal (σ_{bulk}) where vacancies form. Hence the net ionic conductivity σ_{eff} can be expressed as:

$$\sigma_{eff} = \sigma_{0,eff} e^{\frac{-E_a}{RT}} = \sigma_{bulk} + \sigma_{gb} \quad (1)$$

where

$$\sigma_{bulk} = \sigma_{0,bulk} e^{\frac{-E_{a(bulk)}}{RT}} \quad (2)$$

and

$$\sigma_{gb} = \sigma_{0,gb} e^{\frac{-E_{a(gb)}}{RT}} \quad (3)$$

In order to address these two important contributions, we calculated the MSD for 1000 Li^+ ions in the $V_{2g,sol}$ model, where two grains of $(\text{Adpn})_2\text{LiPF}_6$ are simulated in the presence of excess molecules of Adpn (details provided in Supplementary Information). **Fig. 5a-c** show the position overlapped trajectory maps for Li^+ ions in the last 5 ns of the production run with every frame recorded at 5 ps at 300, 325 and 350 K. The calculated MSDs vs. time plots for individual Li^+ ions (green thin lines) and their average (red thick line) at 300, 325 and 350 K are shown in **Fig. 5d-f**. The MSD vs. time plots for individual Li^+ ions show two major groups with low and high MSDs and some ions in between, at 300 K (**Fig. 5d**). The ions falling in these groups belong respectively to the bulk (ordered, less mobile, and thus sub-diffusive) and the surface (solvated, highly mobile, and thus linearly diffusive) part of the crystals. At 325 K, more ions solvate with excess Adpn molecules to become linearly diffusive (**Fig. 5e**) and less ions remain in the bulk-ordered structure (also visible in **Fig. 5b**). At 350 K, the individual MSDs which had been spread over a wide range on the y-axis at lower temperature become narrow (**Fig. 5f**), as all the Li^+ ions are now surface-solvated and thus exhibit linear diffusion.

The calculated diffusion coefficients (D_{Li^+}) from $V_{2g,sol}$ and 1.7 M solution models derived from linear regime of MSD plots (**Extended Data Fig. 8**) are provided in the **Table S2**, and are fitted to the Arrhenius equation (**Fig. 6a**). The calculated E_a from $V_{2g,sol}$ model considers all the Li^+ ions present in both the bulk and surface region, hence it should be comparable to $E_{a,exp}$ from impedance measurements (37 kJ·mol⁻¹). The calculated E_a from 1.7 M solution corresponds to a rough model of grain-boundary solvated Li^+ ions and considers all the Li^+ ions present in a nano-confined environment of Adpn, and is thus comparable to $E_{a,gb}$. The calculated E_a barrier from the $V_{2g,sol}$ model (comparable to $E_{a,exp}$) is 44 kJ·mol⁻¹ which is slightly higher than the experimental $E_{a,exp}$ (37 kJ·mol⁻¹). The $E_{a,gb}$ is 27 kJ·mol⁻¹, which suggests that most of the conduction occurs via grain boundaries.

Plane-wave DFT calculations were performed to calculate $E_{a,bulk}$ using Nudged Elastic Band (NEB) method. The array of Li^+ ions in the b crystallographic direction ($d_{Li---Li} = 6.3 \text{ \AA}$) serves as the minimum energy path (MEP) for Li^+ ion conduction in the bulk due to sterically unblocked channel with no interstitial PF_6 anions, in contrast to the paths in the a - and c - directions. The climbing image-NEB calculations suggest that a Li^+ ion migrates from an occupancy site to the nearby vacancy site via an intermediate (relative energy = 67 kJ/mol) with two transition state structures at either side of the intermediate ($E_a = 72 \text{ kJ/mol}$) (**Fig. 6b, Supplementary Video 2**). The calculated E_a barriers from various experimental and theoretical methods ($E_{a,exp} = 37$, $E_{a,MD} = 44$, $E_{a,bulk,DFT} = 72$, $E_{a,gb,MD} = 27$, all in kJ·mol⁻¹) suggest that the most feasible path for Li^+ conduction is diffusion via grain boundaries. Ion dynamics from model P , analysis of jump events and other mechanistic paths and corresponding structures are provided in **Supplementary Fig. S5 – S11**.

There are significant differences in the structures and mechanisms of ion conduction between the traditional solid electrolytes and the soft-solid electrolytes. In contrast to inorganic conductors, the soft-solid crystals of $(\text{Adpn})_2\text{LiPF}_6$ have an interstitial solvent mediated migration of Li^+ ions, which we demonstrate is a fluid surface layer on the co-crystals and possibly a supersaturated $\text{LiPF}_6/\text{Adpn}$ solution between the co-crystals, facilitating low resistance ion-conduction at the grain boundaries. Future efforts will explore the incorporation of deliberate defecting strategies with an optimal solvent and anion that increases the number of vacancy or interstitial sites (e.g., by isovalent or aliovalent doping, or introduction of defects by chain ends), to improve the ionic conductivity in these electrolytes.

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AUTHOR CONTRIBUTIONS STATEMENT

P. P. assisted with optimization of synthetic protocol, electrochemical data collection and interpretation and led computational efforts on MD simulations and DFT calculations. B. F. discovered and optimized the synthesis of the electrolyte, obtained electrochemical and physical data and assisted in interpretation, constructed and tested lithium-metal electrochemical cells. J. A. collected and interpreted Raman data and constructed and tested LTO|NMC full cells. L. S. prepared samples and performed pressing experiments shown in Figure S3. S. C. prepared cathode composite, assisted with cell assembly and with electrochemical data interpretation. P. R. C. designed electrochemical experimental testing, devised experimental strategy, and assisted with data interpretation. D. D. Obtained SEM, EDS data and assisted with interpretation. A. V.

supervised computational efforts. S. L. W. supervised electrochemistry and characterization efforts. M. J. Z. supervised synthetic and X-ray characterization efforts. P. P., A. V., S. L. W., and M. J. Z wrote and edited the manuscript.

COMPETING INTERESTS STATEMENT

The authors declare no competing interests.

FIGURE LEGENDS/CAPTIONS

Figure 1 | Crystal structure of soft-solid co-crystalline (Adpn)₂LiPF₆ electrolyte. (a) Representation of the basic structural unit of (Adpn)₂LiPF₆ showing tetracoordinated Li⁺ ions with four Adpn molecules, each shared with a second symmetry equivalent Li atom, and where PF₆⁻ anions occupy the available interstitial pocket in the crystal structure; (b) Packing diagram of (Adpn)₂LiPF₆ showing the channels of Li⁺ ions in the low-affinity matrix in the crystal structure. Gray- C; Yellow- Li; Blue- N; Red- P; and Orange- F. (c) Experimental Powder XRD spectra for Adpn, LiPF₆ and (Adpn)₂LiPF₆ cocrystals. Theoretical spectra for (Adpn)₂LiPF₆ is calculated using the single crystal structure in Mercury software. (d) PXRD spectra for (Adpn)₂LiPF₆, before and after conductivity measurements, before and after melt/recrystallization, an overdried sample and theoretical pattern generated from single crystal data. (e) PXRD spectra for (Adpn)₂LiPF₆ that was synthesized in the glass fiber separator, pressed pellet and theoretical pattern generated from single crystal data. PXRD data before and after conductivity measurements, and whether pressed or prepared in a glass fiber mesh exhibit no change in the structure due to conductivity measurements or preparation method. (f) A zoomed in view to the powder XRD patterns of Adpn and (Adpn)₂LiPF₆ (after conductivity measurements) showing that there are no peaks of *free* Adpn at 11, 14 or 17° in cocrystals after conductivity measurement.

Figure 2 | Thermal, structural, and spectroscopic evidence of free solvent molecules at the grain-boundaries of the crystals. (a) DSC data of (Adpn)₂LiPF₆, and Adpn showing melt and crystallization peaks for both; melting of this surface Adpn (with or without dissolved LiPF₆) occurs at approximately the same temperature as for neat Adpn, while crystallization occurs at

slightly lower temperatures than neat Adpn, suggesting confinement effects might modulate the heat of fusion; **(b)** Raman spectra in the $-C\equiv N$ region from experiment; **(c)** model used for DFT calculations; **(d)** Raman spectra from DFT calculations, where dots are the calculated frequencies and the solid lines are interpolated Gaussian curves obtained by using 1.8 cm^{-1} peak half-width at half height; and SEM image of pure polycrystalline $(\text{Adpn})_2\text{LiPF}_6$ powder (pressed neat sample) showing liquid inter-grain binding; **(f)** EDX of bulk grain; and **(g)** EDX of grain boundary regions.

Figure 3 | Simulation of vacuum model V_{8g} and solvated grains model $V_{2g,sol}$ of $(\text{Adpn})_2\text{LiPF}_6$.

(a) Initial condition of model V_{8g} , (total 160000 atoms) only the four grains in the front are visible, the other four grains are behind, **(b)** model V_{8g} , after a simulation time of 10 ns, under NVT ensemble, **(c)** model $V_{2g,sol}$ (140576 atoms) – where two grains of $\text{Adpn}_2\text{LiPF}_6$ are solvated with 6286 molecules of Adpn to model grain boundaries, after initial equilibration of 5 ns, **(d)** model $V_{2g,sol}$ after 15 ns production run.

Figure 4 | Electrochemical data on $(\text{Adpn})_2\text{LiPF}_6$. **(a)** Variable temperature conductivity data of a pressed neat pellet of $\text{SS}/(\text{Adpn})_2\text{LiPF}_6/\text{SS}$; model CPE circuit diagram is provided in **Extended Data Fig. 6a**; **(b)** cyclic voltammetry (CV) and linear sweep voltammetry (LSV) of $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{SS}$, with $(\text{Adpn})_2\text{LiPF}_6$ synthesized in glass fiber; **(c)** Interfacial resistance as a function of time in $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ cells using $(\text{Adpn})_2\text{LiPF}_6$ in glass fiber separator at room temperature, taken before cycling; **(d)** Li plating, in $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ cell for 2 h charge/discharge cycles at $J = 0.01\text{ mA/cm}^2$ for 120 cycles, $J = 0.05\text{ mA/cm}^2$ for 60 cycles and $J = 0.1\text{ mA/cm}^2$ for 60 cycles with a zoomed-in version provided in **Extended Data Fig. 6c,d**; **(e)** Discharge capacity and Coulombic efficiency as a function of cycle number in $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{LiFePO}_4$ cell at C/10 rate at $25\text{ }^\circ\text{C}$; inset shows the voltage vs. charge capacity for cycle # 1, 10, 50 and 56; and **(f)** Capacity and Coulombic efficiency of $\text{LTandADN})_2\text{LiPF}_6/\text{NMC622}$ cells at $25\text{ }^\circ\text{C}$ as a function of C-rate, with no conditioning cycles. Capacity and Coulombic efficiency at C/10 rate as a function of cycle number, 2h charge/2h discharge with two cycles of preconditioning at C/40 rate is provided in **Extended Data Fig. 6e**; theoretical capacity 160 mAh/g for NMC-622 and 161 mAh/g for LTO, according to manufacturers.

Figure 5 | Trajectory maps for 1000 Li^+ ions simulated as model $V_{2g,sol}$ where the position of each Li^+ ion is recorded every 5 ps and overlapped for 5 ns of production run to visualize

movement of Li⁺ ions. at (a) 300 K, (b) 325 K and (c) 350 K. **MSD vs. time plot for Li⁺ ions in model $V_{2g,sol}$:** at (d) 300 K, (e) 325 K and (f) 350 K, the distribution of MSDs is for each individual Li⁺ ion is shown as green colored thin lines. Dotted-black line shows the slope of 1. The averaged MSD for all Li⁺ ions is shown as a dashed red line. The average MSDs vs. time plots for Li⁺, PF₆⁻, and Adpn are provided in **Extended Data Fig. 8**.

Figure 6 | Activation energy barriers and mechanism of ion conduction in bulk cocrystals.

(a) Arrhenius plot for diffusion coefficients of Li⁺ ions from $V_{2g,sol}$ model and 1.7 M solution. The E_a barriers from a linear fit are provided with the legends. **(b)** Minimum energy path (MEP) for Li⁺ ion migration in the bulk, in *b*- crystallographic direction, as observed from a 1x2x1 supercell of (Adpn)₂LiPF₆: The geometries of initial, final and intermediate structures are shown above. The location for migrating Li⁺ ion can be seen in the highlighted spot. A dynamic visualization of the Li⁺ ion migration is presented in **Supplementary Video 2**.

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METHODS

Lithium metal, LiPF₆ salt, Adpn, and diethyl ether (Et₂O) were purchased from Sigma-Aldrich. Et₂O was distilled using sodium benzophenone ketyl as a water/oxygen scavenger. Single-crystal and powder X-ray diffraction data were obtained on a Bruker KAPPA Apex II DUO with sealed-tube Mo K α and Cu K α sources, a TRIUMPH monochromator for the molybdenum tube, and an Oxford Cryostream low temperature device. Thermal degradation analysis of (Adpn)₂LiPF₆ crystals was carried out on a Thermogravimetric Analysis (TGA) TA Instruments Hi-Res TGA 2950 at a ramp rate of 10 °C min⁻¹ with a flow of ultra-pure N₂ gas. A Differential Scanning

Calorimeter (DSC) TA Instruments 2920 was used to analyze the melt and crystallization temperatures of the $(\text{Adpn})_2\text{LiPF}_6$, with the sample in hermetically sealed Tzero aluminum pans. Samples were scanned from $-120\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ at a scan rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, under ultra-pure N_2 purge. The second cycle of the adiponitrile matrix and $(\text{Adpn})_2\text{LiPF}_6$ powder was reported out of the two measured cycles. Scanning electron microscope (SEM) data were acquired on a FEI Quanta 450FEG SEM) with energy-dispersive X-ray spectroscopy (EDS) capability (Oxford Aztec Energy Advanced EDS System). Raman spectra were recorded in the $100\text{--}3000\text{ cm}^{-1}$ region at room temperature using a Horiba LabRAM HR Evolution Raman spectrometer, with a resolution of 1.8 cm^{-1} , an excitation wavelength of 532 nm , 60 mW power, and a grating groove density of 600 gr/mm . Samples were measured with 8 acquisitions, and 2 to 8 seconds each, depending on peak intensity. Microscope photos of the pressed crystals were obtained using a Teslong NTE430 microscope inspection camera.

For the conductivity measurements, polycrystalline $(\text{Adpn})_2\text{LiPF}_6$ powder incorporated into glass fiber separator (which gave consistent separator thickness and prevented shorting). Alternatively, the separator could be prepared by pressing at 800 psi in a hydraulic crimper in an argon purged glove box. The conductivity measurements were performed in a homemade electrochemical cell placed in a N_2 purged, temperature-controlled gas chromatography (GC) oven. Temperature-dependent bulk impedance data was measured by AC electrochemical impedance spectroscopy (EIS) using a Gamry Interface 1000 potentiostat/galvanostat/ZRA in the frequency range $0.1\text{--}1\text{ MHz}$ in a temperature range between $80\text{ }^{\circ}\text{C}$ and $-10\text{ }^{\circ}\text{C}$ with increments of $10\text{ }^{\circ}\text{C}$. The cell was thermally equilibrated for 30 minutes at each temperature before the bulk impedance was measured during both the cooling and heating cycles.

Synthesis:

LiPF_6 (151 mg, 1.0 mmols) was dissolved in excess adiponitrile (Adpn) (4.5 ml, 4.0 mmol) by heating the mixture to $165\text{ }^{\circ}\text{C}$ under an argon atmosphere until it dissolved. The LiPF_6 was not soluble in Adpn at RT. Upon cooling, crystalline material started to form at about $115\text{ }^{\circ}\text{C}$ and was complete at room temperature (RT). A single crystal was removed from the precipitate for X-ray structure determination, and the remaining solid was rinsed five times with excess Et_2O and dried under vacuum for ~ 20 minutes to remove the residual amount of Adpn and Et_2O , after which the

dry, co-crystal solid was isolated; no visible liquid adiponitrile/solvent, was apparent by inspection. Water is rigorously excluded from all samples as we use a glove box with argon atmosphere where water levels are < 9 ppm at worst. The sample was incorporated concomitantly during the synthesis into Whatman glass microfiber filters (GF), grade GF/A (Sigma-Aldrich) 0.26 mm thickness. The co-crystal in the glass fiber filter was used as the separator between the electrodes to control the size and the amount of the electrolyte in the electrochemical experiments.

For all other electrochemical measurements (Li^+ ion transference numbers, plating and stripping, cyclic voltammetry, linear sweep voltammetry, and full cell cycling) the $(\text{Adpn})_2\text{LiPF}_6$ was incorporated in the glass filters (during the synthesis). Before use, the lithium metal was polished using Teflon blocks. For the plating and stripping experiments at room temperature with the $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{Li}^0$ cell, current densities of $0.01\text{mA}/\text{cm}^2$ for 1 to 120 cycles, $0.05\text{mA}/\text{cm}^2$ for 121 to 180 cycles, and $0.1\text{mA}/\text{cm}^2$ for 181 to 240 cycles were used. Li^+ ion transference numbers were obtained by the method of combined ac and dc measurements^{1,2}. The cathode was prepared from LiFePO_4 /carbon black/PVDF binder (8/1/1 by weight) using N-methyl-2-pyrrolidone (NMP) to form a slurry that was doctor-bladed onto battery-grade aluminum foil to form $1.9\text{--}2.2\text{ mg}/\text{cm}^2$ electrodes. The electrodes were dried in a vacuum oven overnight at 120°C . The dried electrodes were calendared with a Durston flat agile F130 mm rolling mill mechanical presser.

MD simulations:

Force field parameters for bonded and Lennard Jones (vdW) interactions for Adpn were taken from the OPLS all-atom force field³. The partial charges on all atoms of Adpn were calculated from the MP2//aug-cc-PVDZ optimized structure using the CHELPG method⁴. Since the Li^+ ion is present in tetra coordination with Adpn, the partial charge on Li^+ was calculated using the optimized structure with a long range and dispersion corrected ωB97xD functional with 6-311++G(d,p)_{optimization/aug-cc-PVDZ charge calculation} basis set. This calculation suggested a partial charge of 0.845 e^- unit on the Li^+ ions. The charge value on the Li^+ ion (0.845e) was used as the scaling factor to rescale the partial charges on PF_6^- ions (obtained from MP2//aug-cc-PVDZ calculations, separately). To compute theoretical Raman spectra for Adpn and $(\text{Adpn})_2\text{LiPF}_6$, vibrational frequencies were calculated using PBE/6-311++G(d,p) for the structures optimized using the same functional/basis set. All the gas phase quantum chemistry calculations were carried

out using the GAUSSIAN 9.0 software package⁵. Detailed protocol for force-field development is provided in **Supplementary Information**.

A supercell of 5x5x5 unit cells (20,000 atoms) of (Adpn)₂LiPF₆ was constructed in a cuboid with the dimensions of 55.35 x 64.75 x 63.25 Å³. This model was used for simulations under periodic boundary conditions to represent the bulk phase, and hence, is designated as model *P*. However, since the surface atoms have a large contribution towards the conduction and decomposition of these co-crystalline electrolytes, a different model *V* was used to understand the structure, dynamics and thermal behavior at the surface. Model *V* was constructed by placing a 5x5x5 supercell in a cube of 200 Å/side. GROMACS 5.0.7 software⁶ was used for simulations and analysis along with VMD 1.9.3 software⁷ for visualization of trajectories. The supercell models were energy minimized using standard protocols and algorithms implemented in the code. All the simulations for model *P* were carried out using *NpT* ensemble conditions, while for model *V*, canonical ensemble conditions were used. Details of temperature and pressure couplings and other MD parameters can be found in another work on a similar co-crystalline electrolyte material⁸.

Plane-wave periodic DFT calculations:

To examine the mechanism of conduction at the atomic level with precise energetics, PW-DFT calculations were performed using the QUANTUM ESPRESSO 6.1 software package⁹. A projector-augmented-wave-basis set (Kresse-Joubert)¹⁰ was used with PBE pseudopotentials¹¹ with a cut-off of 60 Ry and 360 Ry for kinetic energy and electron density, respectively. A unit cell of (Adpn)₂LiPF₆ cocrystals (from single-crystal XRD data) was relaxed in a fixed volume box and later in a variable cell manner to energy minimize the crystal structure. A threshold of 10⁻⁷ Ry was used for electronic optimization and 10⁻³ Ry/Bohr for force minimization. **Table S3** shows a comparison of unit cell parameters obtained from single-crystal XRD data and variable cell relaxation DFT calculations. To investigate the path of Li⁺ ion conduction in the cocrystal, 1x1x2, 3x1x1 and 2x1x2 supercells were created and optimized using the above discussed protocols. Due to the large system size of these supercells, all the calculations were performed with a Γ -only 1x1x1 k-mesh. For every supercell, a pair of Li⁺ ion-defected configurations was used as an initial and final image for Nudged Elastic Band (NEB) calculations to interpolate the minimum energy path (MEP). Several sets of images were used to obtain the MEP, with a threshold of 0.1 eV/Bohr

used for every individual image. Further, the MEP was refined using the climbing image (CI)-NEB method¹² with a more precise threshold of 0.01 eV/Bohr for every image along the path.

DATA AVAILABILITY

Additional details of simulation and DFT, and crystallographic tables are provided in the Supplementary Information files. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 1986269. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

METHODS-ONLY REFERENCES

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EXTENDED DATA FIGURE CAPTIONS

Extended Data Figure 1 | TGA data of (Adpn)₂LiPF₆, LiPF₆ and Adpn. LiF remains at 800 °C for LiPF₆ and (Adpn)₂LiPF₆. For Sample 1, a typical TGA pan (open) with N₂ purge was used. For Sample 2, a punch-holed Tzero aluminum pan (used in DSC) was used to avoid excessive removal of Adpn from crystals due to N₂ purge. The sample 2 shows a T_d at 200 °C, higher than the T_m = 180 °C from DSC (**Fig. 2a**).

Extended Data Figure 2 | Snapshots of (Adpn)₂LiPF₆ cocrystals after an equilibration of 10 ns (every temperature) using model V, at **(a)** 300 K, **(b)** 400 K and **(c)** 500 K. Li---N(Adpn) coordinated networks are shown as yellow tetrahedrons and PF₆⁻ anions are shown as red octahedrons. Adpn solvent is shown as line representations. **(d)** Non-bonded interaction energy vs. temperature during the simulated heating of (Adpn)₂LiPF₆ cocrystals in model V. The liquid-like surface-layer is shown in a cyan ring in **(c)**.

Extended Data Figure 3 | SEM SE images of (Adpn)₆LiPF₆ at different magnifications taken at RT. **(a, b, c)** pressed pallets; **(d, e)** pressed pallets quenched in liquid N₂; **(f)** pressed pellet that has been quenched in liquid N₂ so that some grain boundaries broken; **(g, h, i)** powders, fusion between the grains can be observed by comparison between powders and powders pressed to make pellets; even in powder, there can be connection between the grains **(i)**; in the pressed pellet the large grains contain smaller crystallites and there are needle-like structures between the grains; **(j, k, l)** samples synthesized in glass fiber.

Extended Data Figure 4 | SEM SE images of (Adpn)₆LiPF₆ after cycling. Post-mortem (30 days to failure) SEM images after Li plating/stripping of Li⁰/(Adpn)₂LiPF₆/Li⁰ showing places where the (Adpn)₂LiPF₆ cocrystal still adhered to the Li⁰, and the SEI layer at three magnifications **(a-c)**; **(d)** edge of Li⁰ metal showing thin SEI layer.

Extended Data Figure 5 | SEM EDX spectra of (Adpn)₆LiPF₆ post-mortem. **(a)** and **(b)** are EDX spectra taken at positions 2 and 4, respectively, in **Extended Data Fig. 4a**, which show places where the (Adpn)₂LiPF₆ cocrystal still adhered to the Li⁰, as indicated by strong C, F, N and P signals; **(c) – (g)** are EDX spectra taken at positions 5, 6, 7, 8 and 9 in **Extended Data Fig. 4b-c**, which show SEI layer dominated by strong O and C signals; **(h)** Atom % for EDX spectra.

Extended Data Figure 6 | Additional electrochemistry data. **(a)** Representative constant phase-element (CPE) circuit; **(b)** Li⁺ ion transference number (t_{Li⁺}) measured after stabilization of the

impedance; $t_{\text{Li}}^+ = 0.54$; a zoomed-in view of **Fig. 4d**, Li plating, 2 h charge/discharge cycles at (c) $J = 0.05 \text{ mA/cm}^2$ for 60 cycles, (d) $J = 0.1 \text{ mA/cm}^2$ for 60 cycles; (e) Discharge capacity as a function of C rate for a $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{LiFePO}_4$ half-cell #1 at RT, 2 h charge/2h discharge cycles. The cell did not recover after C/2; (f) Discharge capacity as a function of C rate for a $\text{Li}^0/(\text{Adpn})_2\text{LiPF}_6/\text{LiFePO}_4$ half-cell #2 at 10°C , 2 h charge/2h discharge cycles. The cell recovered after 1C. At high charge/discharge rates (1C), the capacity drops to zero since at 10°C the grain boundary region is close to the freezing point of the “free” Adpn in the $(\text{Adpn})_2\text{LiPF}_6$ cocrystals, possibly preventing growth of Li dendrites through the grain boundaries; (g) Capacity and Coulombic efficiency of LTO/ $(\text{ADN})_2\text{LiPF}_6/\text{NMC622}$ cells at 25°C at C/10 rate as a function of cycle number, 2h charge/2h discharge where two cycles of preconditioning at C/40 rate were performed; (h) Impedance spectra before and after the full cell cycling at RT, two semicircles represent interfacial resistance at the Li anode and LiFePO_4 cathode. Impedance increases after the cycling; (i) Impedance spectra (Nyquist plots) over time for NMC-622/ $(\text{Adpn})_2\text{LiPF}_6$ -glass fiber/NMC-622 (1 MHz – 0.01 Hz), a zoomed in view is shown inset.

Extended Data Figure 7 | Electronic structure interpretation of redox stability of cocrystals.

(a) Density of states (DOS) for $(\text{Adpn})_2\text{LiPF}_6$. Solid lines show p -orbital densities for optimized structure of $(\text{Adpn})_2\text{LiPF}_6 : [\text{Adpn}_2\text{LiPF}_6]_{\text{opt}}$. Dotted lines show the effect of one electron addition; after addition of the electron, the structure was optimized and then this ‘excess’ electron was removed to calculate DOS from SCF (without optimizing the structure): $[\{(\text{Adpn}_2\text{LiPF}_6)^{-1}_{\text{opt}}\} - e^-]_{\text{scf}}$; Differential Electron density map ($\rho_e[\text{Adpn}_2\text{LiPF}_6]_{\text{opt}} - \rho_e[\{(\text{Adpn}_2\text{LiPF}_6)^{-1}_{\text{opt}}\} - e^-]_{\text{scf}}$) showing the effect of addition of an electron to a unit cell of $(\text{Adpn})_2\text{LiPF}_6$ - (b) in the plane perpendicular to c -crystallographic direction and (c) in the plane perpendicular to b -crystallographic direction. Close to $\text{Li}^+ \cdots \text{CN}$: blue lobes are larger compared to red, suggesting greater change in the electron density close to $\text{C}\equiv\text{N}$ compared to $\text{P}-\text{F}$, on the addition of electron.

Extended Data Figure 8 | Average mean squared displacement of constituent Li^+ ions, PF_6^- ions and Adpn molecules in model $V_{2g,\text{sol}}$. (a) 300 K, (b) 325 K, and (c) 350 K. The calculated diffusion coefficients are provided in Supplementary Table S2.