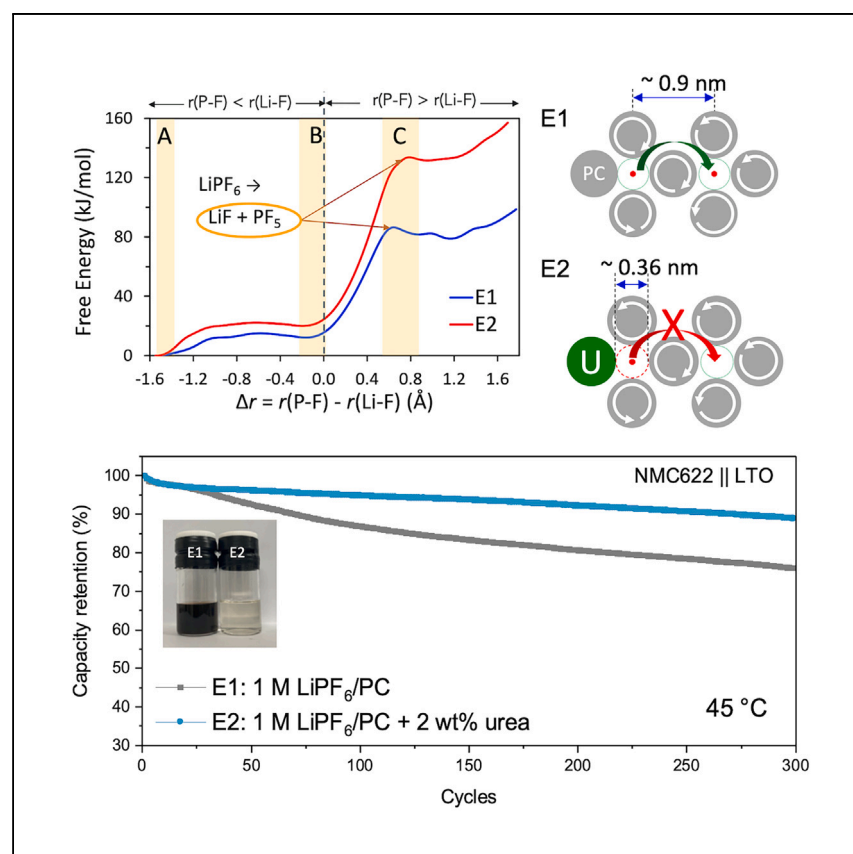


EX 1023

Article

Lithium-ion hopping weakens thermal stability of LiPF_6 carbonate electrolytes



Han and Lee et al. demonstrate lithium-ion hopping induced by the overall reorientation of carbonate molecules is responsible for thermal instability of LiPF_6 carbonate electrolytes. Thermally stabilized LiPF_6 carbonate electrolytes, via preserving the vehicular transport of lithium ions, can improve calendar and cycle life of lithium-ion batteries at elevated temperatures.

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Highlights

Carbonate solvents experience overall rotational motion at elevated temperatures

Overall rotation of carbonate solvents is responsible for lithium-ion hopping

Suppression of lithium-ion hopping improves stability of LiPF_6 carbonate electrolytes

Thermally stabilized electrolyte enhances calendar and cycle life of lithium-ion batteries

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Article

Lithium-ion hopping weakens thermal stability of LiPF₆ carbonate electrolytes

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SUMMARY

Lithium hexafluorophosphate (LiPF₆)-based carbonate electrolytes are widely used in commercial lithium-ion batteries (LIBs), but their thermal instability limits the cycle life and safety of LIBs at elevated temperatures. Few studies have yielded insight into the initial PF₆[−] decomposition reaction that promotes thermal instability of LiPF₆-based electrolytes. Here, we find that lithium-ion hopping assisted by the overall reorientational motion of propylene carbonate molecules facilitates PF₆[−] decomposition at elevated temperatures in 1 M LiPF₆/propylene carbonate electrolyte. Further, we demonstrate that urea additives, by preventing lithium-ion hopping, suppress the initial LiPF₆ decomposition reaction and enhance the thermal stability of the electrolyte. LIB cell tests with LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂||Li₄Ti₅O₁₂ show improved LIB performance at elevated temperatures with the thermally stabilized electrolyte. This study provides key insights into the design of thermally stable LiPF₆-based carbonate electrolytes for improving the cycle life, calendar life, and safety of LIBs in elevated-temperature applications.

INTRODUCTION

Lithium hexafluorophosphate, LiPF₆, is widely used as a primary lithium salt in carbonate electrolytes for commercial lithium-ion batteries (LIBs) because of its favorable overall performance compared to alternatives.¹ One area in which LiPF₆-based electrolytes do not perform favorably, however, is thermal stability; thermal instability of LIBs limits both cycle life and safety.^{1–3} Many attempts have been made to mitigate the thermal degradation from the electrolyte side reaction by coating or doping hetero-elements onto electrode materials.⁴ Further, because lithium loss (the main cause of battery degradation) is a result of electrolyte interaction with other components,^{3,5–9} alternative electrolytes have been considered for high-temperature LIBs.¹⁰ Many studies have investigated thermal decomposition phenomena in LiPF₆-based carbonate electrolytes, primarily focused on decomposition pathways,^{11–15} and they revealed that PF₅ (the product of the endothermic decomposition reaction LiPF₆ → LiF + PF₅) is responsible for the subsequent decomposition reactions.^{14,16} One attempt to mitigate decomposition used Lewis basic additives to form complexes with the Lewis acidic PF₅, trapping PF₅ to prevent subsequent reactions. Although this improved the thermal stability of the electrolyte, it did not diminish the loss of battery capacity at elevated temperatures due to the apparent reaction of the electrolyte to the electrodes.¹⁷ Then it seems that the best way to boost the thermal stability of LiPF₆-containing electrolyte and LIBs is the suppression of PF₅ generation. Little is known about why PF₆[−] decomposition occurs at elevated temperatures (≥ 80°C) in LiPF₆-based carbonate electrolytes.

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However, it is noteworthy that LiPF_6 hydrolysis and the following decomposition reactions are much slower in aqueous solutions than in organic carbonate solutions containing residual water because of the strong ability of water to facilitate salt dissociation.^{11,18} Based on the above observations, we hypothesize that LiPF_6 decomposition at elevated temperatures in carbonate solutions is due to changes in both the Li^+ solvation structure and the dynamic properties of the electrolyte components. It follows from this hypothesis that the thermal stability of LIBs could be improved by enhancing the thermal stability of the electrolyte via preventing LiPF_6 decomposition through stabilization of Li^+ solvation clusters by utilizing additives.¹⁹ To verify the above hypothesis, we added a small amount (2 wt %) of urea into the electrolyte, 1 M LiPF_6 dissolved in propylene carbonate (1 M LiPF_6/PC , the number ratio of $\text{Li}/\text{PC}/\text{urea} \approx 1.0/11.8/0.4$) due to its ability to affiliate lithium ion and carbonyl structure in common with carbonate solvents²⁰ and confirmed that this additive suppresses thermal decomposition of the electrolyte at 80°C (Figure S1). We investigated temperature-dependent rotational and translational dynamics and correlated lithium solvation structures and then lithium-ion transport mechanisms, in 1 M LiPF_6/PC with (E2) and without (E1) 2 wt % urea by using nuclear magnetic resonance (NMR) relaxation and pulsed-field gradient (PFG) NMR measurements in conjunction with *ab initio* molecular dynamics (AIMD) simulations combined with metadynamics calculations. In addition, to verify that E2 is practical in real applications, we tested cyclability and storage effects at elevated temperature (45°C) with $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2\|\text{Li}_4\text{Ti}_5\text{O}_{12}$ (NMC||LTO) cells.

Here, we demonstrate that lithium-ion hopping assisted by overall reorientational motion of PC solvent molecules is responsible for initializing decomposition of PF_6^- in carbonate-based electrolytes at elevated temperatures. Urea additives stabilized Li^+ solvation clusters and successfully suppressed lithium-ion hopping via their preferential interaction with lithium ions, thereby suppressing thermal decomposition of the electrolyte. Battery performance, in both cycle life and capacity after storage at elevated temperatures, was noticeably improved by using the more thermally stable urea-added electrolyte. Based on this insight, thermal stability of LIBs can be efficiently improved without additional modification of electrode materials by simply adding Li^+ holding agents to suppress Li^+ hopping at elevated temperatures. Our findings present new opportunities for long-term storage and high-temperature applications of conventional, well-developed, ambient-temperature LIB chemistry.

RESULTS AND DISCUSSION

Li^+ transport mechanism and solvent dynamics

To elucidate the Li^+ transport mechanism, temperature-dependent diffusion coefficients (D) and spin-lattice (T_1) relaxation times were measured. Temperature-dependent D of E1 and E2 (Figure S2) showed $D_{\text{Li}} < D_{\text{PF}_6} < D_{\text{PC}}$ for all measured temperatures, with little variation due to the presence of urea (Table S1). The fitting parameter $D_{0,\text{Li}}$ from the Vogel-Fulcher-Tammann (VFT) equation, $D = D_0 \cdot \exp(-B/(T-T_0))$, became the highest ($D_{0,\text{PF}_6} < D_{0,\text{PC}} < D_{0,\text{Li}}$) in E1 but the smallest ($D_{0,\text{Li}} < D_{0,\text{PF}_6} < D_{0,\text{PC}}$) in E2 due to strong coupling of urea toward Li^+ ^{20–22} that resulted in $D_{\text{urea}} \approx D_{\text{Li}}$ (Figure S2), suggesting that the long-range Li^+ transport mechanism in E1 is different at higher temperatures than the low-temperature vehicular transport mechanism,²³ and that the urea additive helps to maintain vehicular transport of Li^+ even in higher temperatures. For a detailed analysis of the Li^+ transport mechanism, we explored the rotational dynamics of Li^+ , PF_6^- , and PC across the samples E0 (pure PC), E1, and E2 from temperature-dependent ^7Li , ^{19}F , and ^1H T_1

(Figures 1A–1C). We found that the ^1H T_1 and ^{19}F T_1 behaviors did not vary significantly due to urea, while the ^7Li T_1 of E2 was strongly coupled with ^1H T_1 of urea, confirming the strong interaction of urea with Li^+ . From the measured T_1 and D , we calculated rotational correlation time, τ_c , and overall reorientational correlation time, τ_2 , which are correlated with the rotation of 1 and 2π radians, respectively (see experimental procedures). $\tau_{c,\text{PC}}$ (Figure 1D) and $\tau_{2,\text{PC}}$ (Figure 1E) noticeably increased due to the addition of LiPF_6 but did not change much due to urea, reflecting that urea additives minimally affect the PC solvent molecules. All τ_c s in E0, E1, and E2 but $\tau_{c,\text{Li}}$ and $\tau_{c,\text{urea}}$ in E2 abruptly jumped to the higher τ_c values at $T \approx 80^\circ\text{C}$ (Figure 1D) due to the presence of the high-temperature $T_{1,\text{min}}$ (Figures 1A–1C), while τ_2 gradually decreased without such discontinuities (Figure 1E). Using τ_c and τ_2 , the rotational flip angles, θ , for each electrolyte component were calculated (see experimental procedures) and plotted in Figure 1F. For PC and PF_6^- , θ values were gradually increased with the increase of temperature and abruptly jumped to greater than 360° at $\sim 80^\circ\text{C}$ (the data $\theta > 360^\circ$ are not shown in the plot), suggesting that the mode of rotational motion of PC and PF_6^- changed to overall reorientational motion at $\sim 80^\circ\text{C}$ from the low-temperature small-angle librational motion. Urea showed θ was larger than 360° at the temperature above $\sim 5^\circ\text{C}$ due to the faster $-\text{NH}_2$ group rotation. Similarly, the effective molecular radius, a_T (Figure 1G), was smaller than and similar to the actual size, $a = 0.27$ nm of PF_6^- ²⁴ and PC,²⁵ at the temperature below and above 80°C , respectively, confirming that the small-angle librational motion at the lower temperatures changed to the overall reorientational motion at $T \geq 80^\circ\text{C}$. For urea, $a_T \gg 0.05$ nm for $-\text{NH}_2$ with N–H distance ≈ 0.1 nm, suggesting that the $-\text{NH}_2$ groups of urea experience a faster localized overall reorientational motion. To verify the lithium-ion transport mechanism at elevated temperature, Li^+ jump distances, d_{Li} , were estimated as a function of temperature (Figure 1H). In E1 at temperatures higher than 80°C , as illustrated in Figure 1I, d_{Li} closes to ~ 0.9 nm, which corresponds to the distance between the two Li^+ solvation sites sharing one PC molecule in the $[\text{Li}(\text{PC})_4 \text{ or } 5]^+$ clusters^{23,26–28} with Li^+ –O distance of 0.178 nm,²⁹ suggesting that vehicular transport has ceased for Li^+ . Surprisingly, in E2, d_{Li} was reduced to ≤ 0.45 nm, clearly suggesting that urea additives maintain the vehicular transport of Li^+ at elevated temperatures. It is worth noting that with the increase of temperature, the slopes of ^1H $T_{1,\text{PC}}$ and $\tau_{c,\text{PC}}$ in E0 and E1 (Figure 1D) started to decrease at $\sim 40^\circ\text{C}$, probably due to the contribution of PC molecules experiencing overall reorientational motion, suggesting that the thermal decomposition reaction in E1 can be facilitated even at $T \approx 40^\circ\text{C}$. To clarify this, we measured temperature-dependent ^1H T_1 of the ternary mixture of ethylene carbonate/propylene carbonate/ethyl-methyl carbonate (EC/PC/EMC, 4:1:5 wt %) and observed a sharp $T_{1,\text{max}}$ at $\sim 40^\circ\text{C}$ (Figure S3), suggesting that $T \approx 40^\circ\text{C}$ is a critical point for thermal stability of LiPF_6 -based carbonate electrolytes and of real LIBs, which are fabricated with electrolytes composed of multiple types of carbonate solvents. Based on the above observations, as illustrated in Figure 1I, we concluded that (1) the first decomposition reaction, $\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5$, was accelerated at elevated temperatures due to the hopping motion of Li^+ assisted by the overall reorientational motion of PC, and (2) urea suppressed the activation of the first decomposition reaction by holding Li^+ inside the solvation cages.

Structural dynamics from AIMD simulations

To gain atomic-level understanding of the effects of temperature and urea addition on structural and dynamics properties correlated with thermal stability of the electrolytes, we performed AIMD simulations for E1 and E2 at 300 and 370 K. Using AIMD trajectories, radial distribution functions (RDFs) and their integrals between Li^+ and O of PC (O_{PC}), F of PF_6^- (F_{PF_6}), and O of urea (O_{u}) were calculated, which

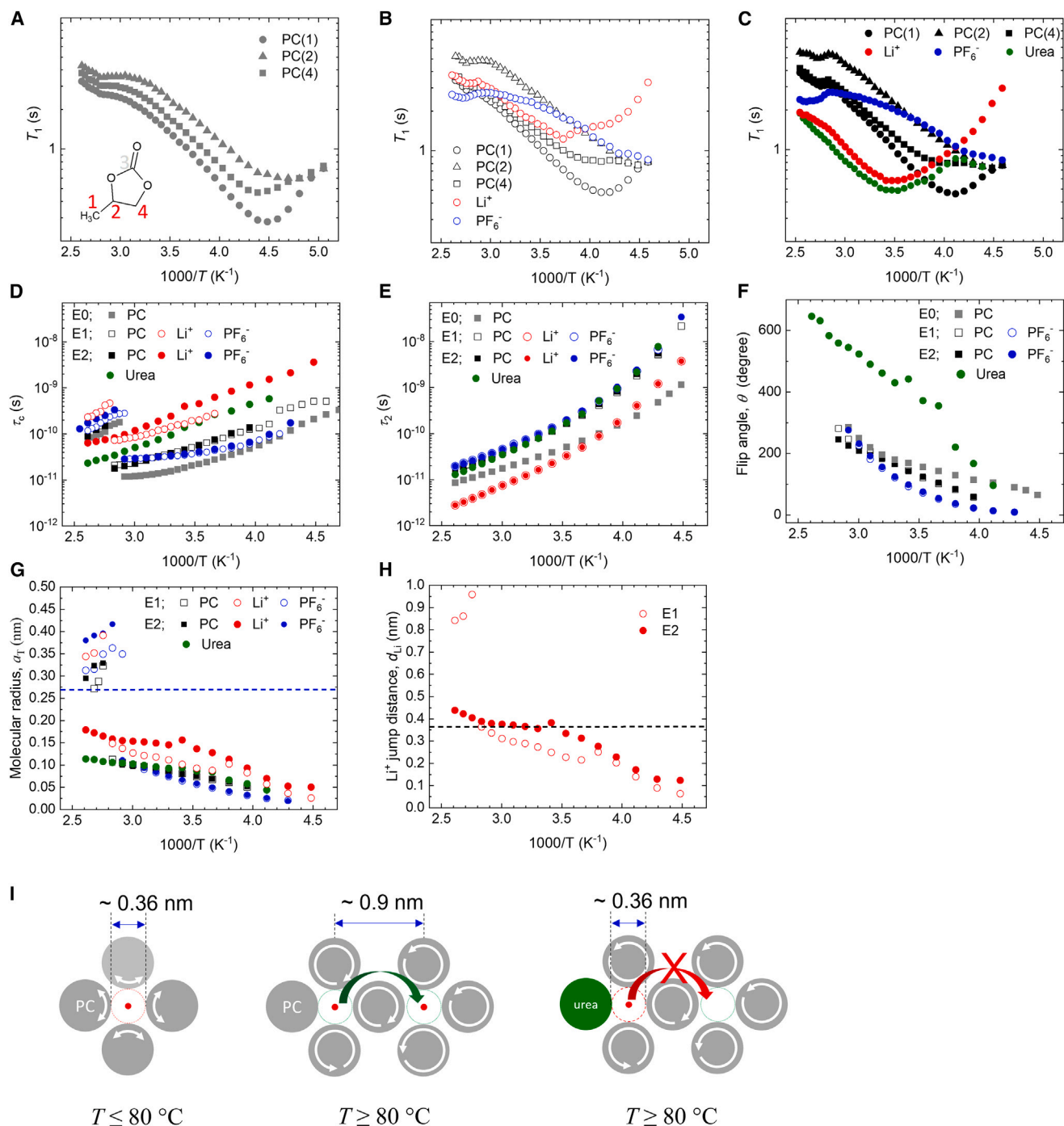


Figure 1. Li⁺ transport mechanism and electrolyte dynamics

Rotational dynamics of each electrolyte component and Li⁺ transport mechanism.

(A–E) Temperature-dependent ⁷Li, ¹⁹F, and ¹H T_1 for E0 (A), E1 (B), and E2 (C).

(D–H) Temperature-dependent τ_c (D), τ_2 (E), flip angle, θ , (F), apparent molecular radius, a_T , of Li⁺, PF₆⁻, PC, and urea (G), and Li⁺ jump distance, d_{Li} (H). Schematic of Li⁺ transport mechanism correlated with the rotational mode of PC with and without urea (I). See [experimental procedures](#) section for the details for the calculation of τ_c , τ_2 , a_T , and d_{Li} . In the inset of (A), the PC structure with numerals denotes ¹H resonance sites. In (B) and (C), the ¹⁹F and ⁷Li T_1 curves, especially in the temperatures lower than the low-temperature $T_{1,min}$, where the T_1 relaxation is less sensitive to the reorientational motion of molecules ($\omega_0\tau_c \gg 1$), were distracted due to the dipolar coupling between ¹⁹F-¹H and ⁷Li-¹H.²⁶ In (G), the horizontal line denotes the actual size, $a = 0.27$ nm, for PC and PF₆⁻. If the τ_c corresponds to small-angle reorientational motion, a_T will be smaller than a .³⁰ In (H), the horizontal line denotes the estimated diameter (= 0.36 nm) of the Li⁺ solvation cage in the [Li(PC)₄]⁺ cluster.²⁹

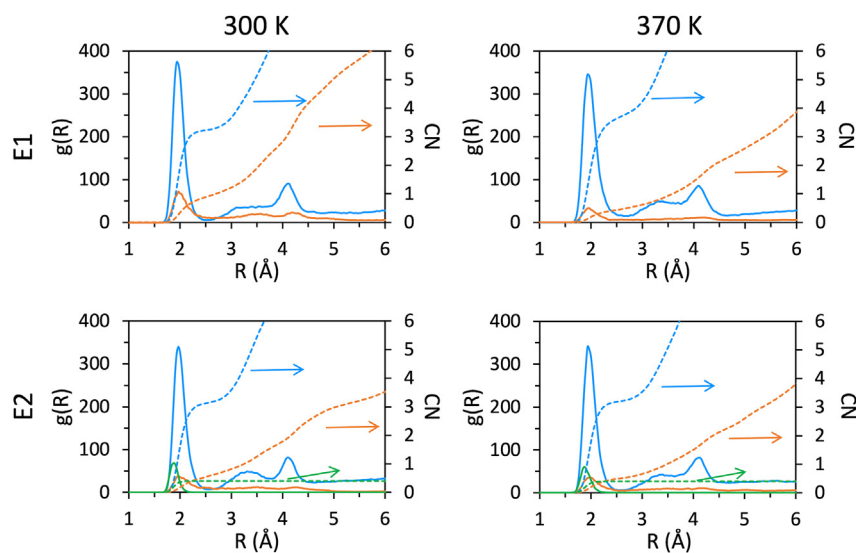


Figure 2. Structural analysis of electrolytes

Radial distribution functions $g(R)$ of Li^+ to O of PC (blue lines), F of PF_6^- (orange lines), and O of urea (green lines).

show the average distance and coordination number (CN) between two species, respectively. [Figure 2](#) shows that distances between Li and O_{PC} (blue line), and Li^+ and $\text{F}_{\text{PF}_6^-}$ (orange line) are nearly the same (1.93 Å), while in the presence of urea, $\text{Li}-\text{O}_{\text{U}}$ distance (green line) is 1.87 Å, shorter than $\text{Li}-\text{O}_{\text{PC}}$ and $\text{Li}-\text{F}_{\text{PF}_6^-}$. This indicates stronger interaction between Li^+ and urea compared with $\text{Li}^+-\text{PC}/\text{Li}^+-\text{PF}_6^-$ at both temperatures, which is consistent with the NMR result. Interestingly, unlike similar distances with increased temperatures and urea additive, CN of Li^+ to PF_6^- is decreased by about half at 370 K for urea additive. Although they give overall trends of structural properties, different interactions of each Li^+ with other molecules, especially with PF_6^- , may strongly impact the decomposition of PF_6^- ; the performance of LIBs is strongly influenced by chemical stability where interactions between ion-ion and ion-solvent have an important role.²⁷ Thus, we further analyzed (1) RDFs and CNs for each P with Li^+ ([Figure S4](#)), (2) CNs for each Li^+ with $\text{PC}/\text{PF}_6^-/\text{urea}$ molecules without ([Figure S5](#)) and with ([Figure S6](#)) urea, and (3) the structural details for Li^+ solvation clusters ([Figure S7](#)). The general trend observed from these analyses is that the urea additive mitigates the generation of free Li^+ /free anions (FI)/solvent-shared monomer and the structural deformation of PF_6^- anions, which is observed from the narrowing of the distribution of the calculated P–F distance probabilities ([Figure S8](#)), resulting in improved thermal stability of the electrolyte. Details for these structural analyses can be found in the [experimental procedures](#) and [supplementary information](#).

To test the dynamic properties of the electrolyte components, the root mean squared displacements (RMSD) were calculated. The results, presented in [Figure S9](#), show minimal thermal effect on the E2 in contrast to the E1. It is noteworthy that the RMSD of Li^+ at 370 K in E2 plateaued at ~0.3 nm from ~50 ps, while that of E1 reached ~0.5 nm at 70 ps, which exceeds the diameter of the Li^+ -solvation sheath (0.37 nm), suggesting that urea additives mitigate thermally activated molecular motion including Li^+ hopping and resulting in stabilizing the Li^+ -solvation structures. This finding is consistent with the NMR and structural AIMD analysis above.

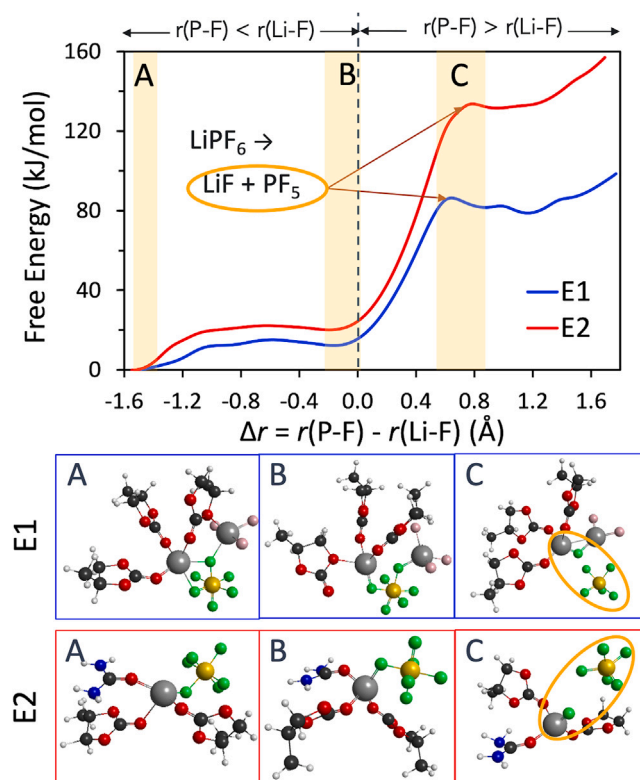


Figure 3. Li-PF₆ decomposition reaction from metadynamics simulations

(Top) Free energy of LiPF₆ decomposition forming LiF and PF₅. (Bottom) Structure of each minimum free energy showing as yellow bars labeled A, B, and C.

Li-PF₆ decomposition reaction from metadynamics simulations

As discussed above, the presence of urea hinders the first step of the Li-PF₆ decomposition reaction to form Li-F and PF₅ at elevated temperatures, which may be strongly impacted by structures. To corroborate this, we estimated reaction energy barriers of the first decomposition reaction at 370 K for CID1 (E1) and CUIM (E2) structures by conducting well-tempered metadynamics (MetaD) simulations.³¹ Figure 3 shows free energy as a function of distance difference (Δr) between $r(\text{P-F})$ and $r(\text{Li-F})$ where a positive value indicates that Li-F interaction is stronger than that of P-F, along with structures of the three energy minima for both E1 and E2. The structures of the two lower minima show that PF₆⁻ interacts with 2 Li⁺ in the E1 system, in contrast to the E2 system where it interacts with only 1 Li⁺. It can be clearly seen that the first decomposition of Li-PF₆ in the E2 system has a free energy barrier more than 1.5 times higher (134 kJ mol⁻¹) than the E1 system (86 kJ mol⁻¹). This difference clearly shows that the decomposition of Li-PF₆ in the presence of urea is both kinetically and thermodynamically unfavorable.

Lithium-ion battery cell test

To confirm the hypothesis that battery performance correlates with the thermal stability of the electrolyte, we conducted comprehensive electrochemical characterizations and gassing behavior analysis (Figure 4). These analyses were performed at an elevated temperature (45°C), which expedites the decomposition of LiPF₆. The full cell was fabricated using commercial LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) and Li₄Ti₅O₁₂ (LTO) as a cathode and anode electrode, respectively (see experimental procedures

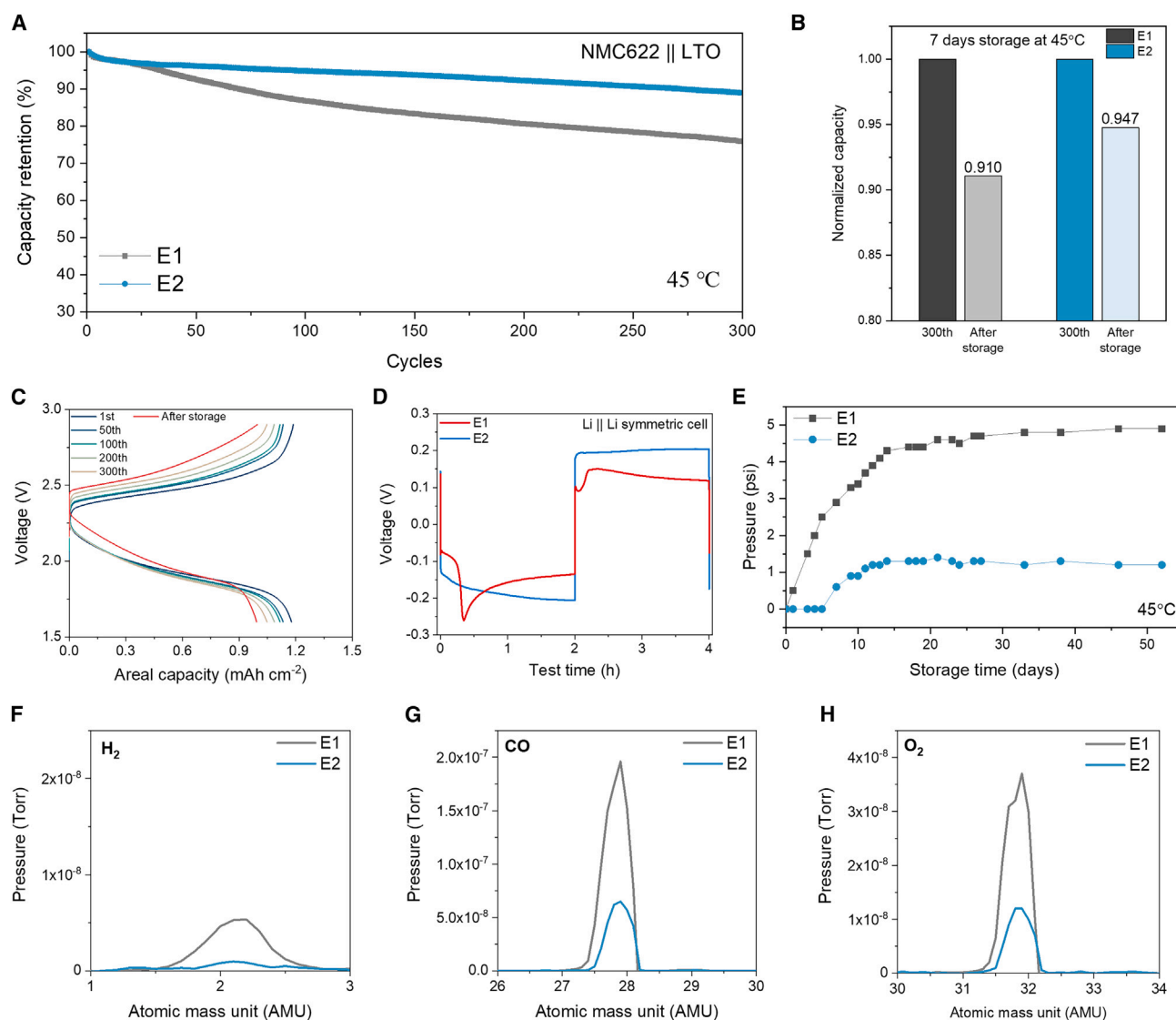


Figure 4. Lithium-ion battery (LIB) cell test

The full cell evaluation at elevated temperature.

(A) Full-cell cycling performance with each electrolyte at elevated temperature (45°C).

(B) Recovery capacity of each cell after 7 days cell aging at 45°C.

(C) Voltage profiles of full cell using E2 electrolyte at each cycle.

(D) Li||Li symmetric cell test for each electrolyte.

(E) Gassing behavior of each full cell assembled by a pressure measurement cell at fully charged state in 45°C for 52 days.

(F–H) Mass spectrometry of the collected gases (hydrogen in F, carbon monoxide in G, and oxygen in H) from the 52 days stored pressure measurement full cells at elevated temperature.

methods). According to the cycling test (Figure 4A), the cell fabricated with E2 (LIB-E2) provided a remarkable capacity retention (89.0%) over 300 cycles, while the cell fabricated with E1 (LIB-E1) has severe capacity degradation with gradual capacity decaying as observed from previously reported NMC||LTO cells.³² In order to evaluate the aging characteristic of each electrolyte, the cells fabricated with E1 and E2 were stored at an elevated temperature (45°C) for a period of 7 days following 300 cycles (Figure 4B). The LIB-E2 showed a better aging stability with a relatively smaller irreversible capacity loss of 5.3% compared with that of LIB-E1 (9.0%). The voltage

profiles of each cycle confirmed that LIB-E1 had capacity degradation with a relatively large voltage decay, while LIB-E2 provides relatively stable voltage profiles for 300 cycles, even after 7 days of the storage test (Figures 4C and S10). Furthermore, to clarify the interfacial stability of the E2, Li||Li symmetric cells were tested at the temperature of 45°C (Figure 4D). The symmetric cell using E1 electrolyte showed a rapidly increased overpotential with a sharp peak shape during the initial Li stripping process, which is a typical voltage profile of the cell with carbonate electrolytes due to non-uniform kinetics at the Li metal surface.^{33,34} In contrast, the symmetric cell using E2 electrolyte, in the initial Li stripping process, exhibited an arc-shaped voltage profile, which generally occurs due to a tortuous Li⁺ transport, suggesting the Li⁺ transport at the interface is slowed by urea additive that holding Li⁺ inside the solvation cage as depicted in Figure 1. These results indicate that the electrochemical stability of LIBs can substantially be improved at elevated temperatures by employing a thermally stabilized electrolyte.³⁵

To test the storability of LIBs, we conducted a long-term cell-aging test at 45°C from a fully charged state by monitoring the gassing behavior of LIBs using a pressure measurement cell configuration (Figure 4E). LIB-E1 exhibited a rapidly increased gas generation at an early stage of the aging, which stabilized around 4.5 psi after 14 days. In contrast, LIB-E2 showed a mitigated gassing behavior (1.2 psi) with a smooth increase and stabilization after 14 days of aging. For the details of the gassing behavior, mass spectrometry was performed with the collected gases from pressure measurement cells for both LIB-E1 and LIB-E2 (Figures 4F–4H), and the whole spectra of mass spectrometry are shown in Figure S11. The evolutions of H₂ (Figure 4F), CO (Figure 4G), and O₂ (Figure 4H) gases, which can be generated due to the electrolyte decomposition (H₂ and CO)^{36–38} and from a lattice of layered oxide cathode (O₂),^{39,40} was noticeably smaller in LIB-E2 compared with LIB-E1, implying the superior storability (i.e., calendar life) of LIB fabricated with E2. This observation strongly suggests that the calendar life of LIBs can effectively be extended by using a thermally stabilized electrolyte such as E2.

This study confirmed that high-temperature Li⁺ hopping, assisted by the overall re-orientational motion of solvent molecules, is responsible for the activation of the decomposition of LiPF₆ in a LiPF₆-based carbonate electrolyte at elevated temperatures. AIMD calculations showed that the strong interaction of urea can suppress thermally activated molecular motion, including Li⁺ hopping, resulting in higher structural stability of Li⁺ solvation clusters and PF₆[−] anions and a higher free energy barrier for the LiPF₆ decomposition reaction at elevated temperatures. Electrochemical characterization including long-term cell-aging test and gassing behavior analysis at 45°C performed with NMC||LTO cells showed a superior cycle and storage performance with the urea-added electrolyte. This work provides a new strategy: suppressing Li⁺ hopping at elevated temperature to design thermally stable LiPF₆-based carbonate electrolytes, enabling thermally stable LIBs with improved cycle and calendar life even at elevated temperatures.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Kee Sung Han (keesung.han@pnnl.gov).

Materials availability

This study did not generate new unique materials.

Data and code availability

The data presented in this work are available from the corresponding authors upon reasonable request. This study did not generate any code.

Sample preparation

Battery-grade 1 M LiPF₆ in PC solvent (Sigma-Aldrich) was used as E1 electrolyte, and 2 wt % of urea (99.0%–100.5%, Sigma-Aldrich) was added to prepare the urea-containing E2 electrolyte.

Diffusion and spin-lattice relaxation time measurements

Diffusion coefficient and T_1 relaxation measurements were performed on a 600-MHz (¹H NMR frequency at 14.1 T) NMR spectrometer (Agilent, USA) equipped with a 5-mm liquid NMR probe (Doty Scientific, USA) at the frequencies of 599.379, 563.937, and 232.940 MHz, respectively, for ¹H, ¹⁹F, and ⁷Li. Temperature-dependent diffusion coefficients of PC molecules, PF₆[−] anions, and Li⁺ cations for all samples in the temperature range of −50°C to 110°C were measured by ¹H, ¹⁹F, and ⁷Li PFG NMR using the stimulated echo sequence (Dbppste, VNMRJ, Agilent, USA) with the 90° pulse lengths of 11, 16, and 8.5 μs for ¹H, ¹⁹F, and ⁷Li, respectively. The PFG-echo profile obtained as a function of gradient strength (g) was fitted with the Stejskal-Tanner equation⁴¹:

$$S(g) = S(0)\exp\left[-D(\gamma\delta g)^2(\Delta - \delta/3)\right], \quad (\text{Equation 1})$$

where the echo intensities $S(g)$ and $S(0)$ are at a gradient strength of g and 0, respectively. D , γ , δ , and Δ are diffusion coefficient, gyromagnetic ratio for observing nucleus, $\gamma(^1\text{H}) = 2\pi \times 42.576$, $\gamma(^{19}\text{F}) = 2\pi \times 40.052$, and $\gamma(^7\text{Li}) = 2\pi \times 42.576$ rad·MHz·T^{−1}, gradient length, and diffusion delay, which is the duration between the two bipolar gradient pairs, respectively. For all diffusion measurements, δ and Δ were fixed at 2 ms and 50 ms, respectively. Temperature-dependent ¹H, ¹⁹F, and ⁷Li T_1 in the temperature range of −50°C to 110°C were obtained using the inversion recovery (180° – τ – 90° – acquire).

Usually, the diffusion coefficient is inversely proportional to viscosity of solution as predicted by the Stokes-Einstein equation: $D = k_B T / 6\pi\eta r_s$, where D is diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, η is viscosity, and r_s is the hydrodynamic radius of diffusing molecule. The diffusional behavior can be studied using the VFT equation, $D = D_0 \cdot \exp(-B/(T - T_0))$, where D_0 , B , and T_0 are adjustable parameters and the translational activation energy, E_a , that can be calculated using the Arrhenius equation, $D = D_0 \cdot \exp(-E_a/RT)$, where D_0 is the fitting parameter, R is the gas constant, and T is the absolute temperature.

For determination of rotational correlation times, τ_c

The rotational correlation times of each component, PC, PF₆[−], and Li⁺, of the electrolyte were estimated from temperature-dependent ¹H, ¹⁹F, and ⁷Li T_1 relaxation times using the Bloembergen-Purcell-Pound equation⁴²:

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right], \quad (\text{Equation 2})$$

where $\omega_0 = 2\pi\nu_0$ (rad·s^{−1}) with ν_0 is the observed frequency, and τ_c is the rotational correlation time. The $\nu_0(^1\text{H})$, $\nu_0(^{19}\text{F})$, and $\nu_0(^7\text{Li})$ are 599.379, 563.93, and 232.940 MHz, respectively. For ¹H and ¹⁹F T_1 relaxations, which occur mainly via the

dipole-dipole interactions between protons/fluorine in the same site, C in Equation 2 can be written as follows:

$$C_d = \frac{2}{5} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sum r_{ij}^{-6} I(I+1), \quad (\text{Equation 3})$$

where μ_0 is the vacuum permeability, γ is the gyromagnetic ratio of observing nucleus, such as $\gamma(^1\text{H}) = 2\pi \times 42.576 \text{ rad}\cdot\text{MHz}\cdot\text{T}^{-1}$ and $\gamma(^{19}\text{F}) = 2\pi \times 40.052 \text{ rad}\cdot\text{MHz}\cdot\text{T}^{-1}$, $\hbar$ is reduced Plank's constant, r_{ij} is the distance between protons/fluorine that is dipolar coupled to the proton/fluorine evaluated, and I is nuclear spin number of the proton/fluorine ($I = 1/2$). While ^7Li ($I = 3/2$) T_1 relaxation occurs mainly due to the quadrupolar interaction, C in Equation 2 can be correlated with the quadrupolar coupling constant, $\omega_q = 2\pi\nu_q$, as follows^{43,44}:

$$C_q = \frac{\omega_q^2}{50} \quad (\text{Equation 4})$$

Using the fact that $\omega_0\tau_c = 2\pi\nu_0\tau_c \approx 0.616$ at the T_1 minimum ($T_{1,\text{min}}$), unknown parameters $\sum r_{ij}^{-6}$ and ω_q in C_d and C_q , respectively, can experimentally be determined both for high- and low-temperature $T_{1,\text{min}}$. Then, it is possible to estimate the rotational correlation time for all measured T_1 values. At the $T_{1,\text{min}}$, the rotational correlation times, τ_c , for ^1H , ^{19}F , and ^7Li will be 1.63×10^{-10} (163 ps), 1.74×10^{-10} (174 ps), and 4.21×10^{-10} s (421 ps), respectively, in this study, under the external magnetic field intensity of 14.1 T.

For determination of overall isotropic reorientational correlation times, τ_2

We estimated overall isotropic reorientational correlation time, τ_2 , using the Stokes-Einstein-Debye relation as follows^{44,45}:

$$\tau_2 = \frac{V\eta}{k_B T}, \quad (\text{Equation 5})$$

where V is the volume of a molecule, η is the viscosity, k_B is the Boltzmann constant, and T is absolute temperature. In actual calculations, we used measured diffusion coefficients, D ($=k_B T/c\pi\eta a$), where a is the radius of diffusing molecule, and c is 6 in the stick boundary condition. Then Equation 5 could be written as follows^{44,45}:

$$\tau_2 = \frac{4a^2}{3cD} \quad (\text{Equation 6})$$

Here, the molecular radius $a = 0.27 \text{ nm}$ for both PF_6^- anion²⁴ and PC molecule,²⁵ and $a \approx 0.18 \text{ nm}$ for urea. The temperature-dependent flip angle of PC molecules was estimated using the τ_c and τ_2 obtained from the PC(4) site.

For determination of flip angles, θ

We calculated the flip angles, θ , of PC and PF_6^- in each solution as a function of temperature from the estimated rotational correlation time, τ_c , and overall isotropic reorientational correlation time, τ_2 , using the Stokes-Einstein-Debye relation as follows^{44,45}:

$$\theta = \frac{360\tau_c}{\tau_2} \quad (\text{Equation 7})$$

For estimation of apparent molecular radius, a_T

The apparent molecular radii, a_T , were estimated using the following relation⁴³:

$$a_T = \sqrt{\tau_c D} \quad (\text{Equation 8})$$

While, in Equation 8, D should be the rotational diffusion coefficient according to the Stokes-Einstein-Debye relationship, in this study, translation diffusion coefficients were used for the rough estimation of the molecular radius for the elucidation of

molecular motion. The estimated a_T will be smaller than the actual radius of the molecules if the molecule experiences a librational motion.

For estimation of lithium jump distance, d_{Li} , to obtain the information for the Li^+ cation translational mechanism, the jump distance, d , of a single Li^+ ion was estimated using the follow relation⁴³:

$$d_{Li} = \sqrt{6\tau_c D} \quad (\text{Equation 9})$$

AIMD simulations

To determine the local structure and their dynamics at a given temperature, model systems were generated consisting of PC and $LiPF_6$ in the absence and presence of urea following the experimental compositions of E1 and E2 samples with a 20-Å cubic box. Periodic density functional theory (DFT)-based AIMD simulations were carried out within the generalized gradient approximation with Perdew, Burke, and Ernzerhof exchange-correlation functionals⁴⁶ and Grimme's third-generation (DFT-D3)⁴⁷ for dispersion correction as implemented in the CP2K package.^{48,49} Goedecker-Teter-Hutter pseudopotentials are used for the core electrons,⁵⁰ while the valence wave functions are expanded in terms of double- ζ quality basis sets optimized for condensed systems to minimize linear dependencies and superposition errors. Electrostatic terms are calculated using an additional auxiliary plane-wave basis set with a 400-Ry cutoff. The Γ -point approximation is employed for the Brillouin zone integration because of the significant size of the supercell.

AIMD simulations are performed within the canonical NVT ensemble using a 0.5-fs time step and a Nosé-Hoover thermostat chain at 300 and 370 K. Each system was thermalized for at least 30 ps, and then well-equilibrated trajectories of >20 ps were collected to obtain reliable statistical properties.

Metadynamics simulations

We employed *ab initio* well-tempered metadynamics simulations³¹ implemented in the PLUMED2 code⁵¹ in combination with CP2K package. Gaussian hills with an initial height of 3.0 kJ mol⁻¹ and $\sigma = 0.15$ were deposited every 100 time steps with a bias factor of 50 along the collective variable (CV). For each simulation, we ran 50 ps after equilibration (~25 ps) with a 0.5-fs time step. For the CV, we considered the distance difference (Δr) between P-F and Li-F, i.e., $\Delta r = r(P-F) - r(Li-F)$ in the form of an anti-symmetric linear combination where Δr is limited from -6 to 6 Å. The error associated with this procedure is lower than 2 kJ mol⁻¹.

Electrochemical measurements

For the electrochemical measurements, it is well known that NMC622 and LTO electrode materials can provide an excellent cycling performance at room-temperature cell operation due to their good structural stability. For this reason, in this work, we fabricated a full cell using these electrode materials to focus solely on the electrolyte affecting the battery performance by minimizing the side reactions derived from the electrode material degradations. The cathode electrode was fabricated using commercial NCM622, the carbon black (Super P, TIMCAL), and polyvinylidene fluoride binder (PVdF, Kureha) with a mass ratio of 96:2:2 on the aluminum foil. Electrode porosity and mass loading level of the cathode were 30.0% and 10.0 mg cm⁻², respectively. For the anode, commercial LTO, Super P, and PVdF were mixed with a mass ratio of 94:3:3 on the aluminum foil. Electrode density and mass loading level of the anode were 35.0% and 10.0 mg cm⁻², respectively. The negative/positive capacity ratio (N/P ratio) was fixed at 1.1 for all tests. Each electrode was punched into

15 mm diameter for the coin-type full cell fabrication with 1.0 mAh of cell capacity. The coin-type full cells were assembled in the Ar-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm) with E1 and E2 electrolyte. The electrochemical tests were evaluated in a voltage range between 2.9 and 1.6 V at a 0.2 C-rate at the first cycle and 0.5 C-rate for the rest of the cycles. All electrochemical evaluations were performed by a battery tester (Arbin). The aging test was conducted by storing each cell in an isothermal chamber (45°C) at a fully discharged state for 7 days.

For the Li||Li symmetric cell evaluation, the coin-type cell was fabricated in the Ar-filled glovebox with Li chip (16 mm diameter, 250 mm thick, MSE supplies) as both the reference and counter electrode. The Li||Li symmetric cells were evaluated at 0.5 mA cm^{-2} for 2 h of Li plating/stripping process.

Storage test with gassing behavior analysis

The cell for storage test was fabricated using a commercial pressure measurement cell (MTI) with the same cathode and anode electrode. The pressure measurement cells were assembled in the Ar-filled glovebox ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm) with E1 and E2 electrolyte, respectively. These pressure cells were performed in the first cycle with 0.1 C-rate and fully charged at 2.9 V with 0.1 C-rate at room temperature. Then, the fully charged pressure cells were placed in an isothermal chamber (45°C) over 50 days. We manually recorded the gas pressure of each cell. To analyze the composition of gas generated for the cell storage, mass spectroscopy (RGA 200, Stanford Research System) for gas analysis was conducted after 52 days of cell aging.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2023.101768>.

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AUTHOR CONTRIBUTIONS

Conceptualization, K.S.H.; investigation, K.S.H., M.-S.L., N.K., D.C., S.C., J.R., G.P., R.R., and E.C.T.; writing – original draft, K.S.H., M.-S.L., and N.K.; writing – review & editing,

K.S.H., M.-S.L., D.C., and N.K.; funding acquisition, K.S.H., M.-S.L., and D.C.; supervision, K.S.H.

DECLARATION OF INTERESTS

The authors declare no conflict of interest.

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Supplemental information

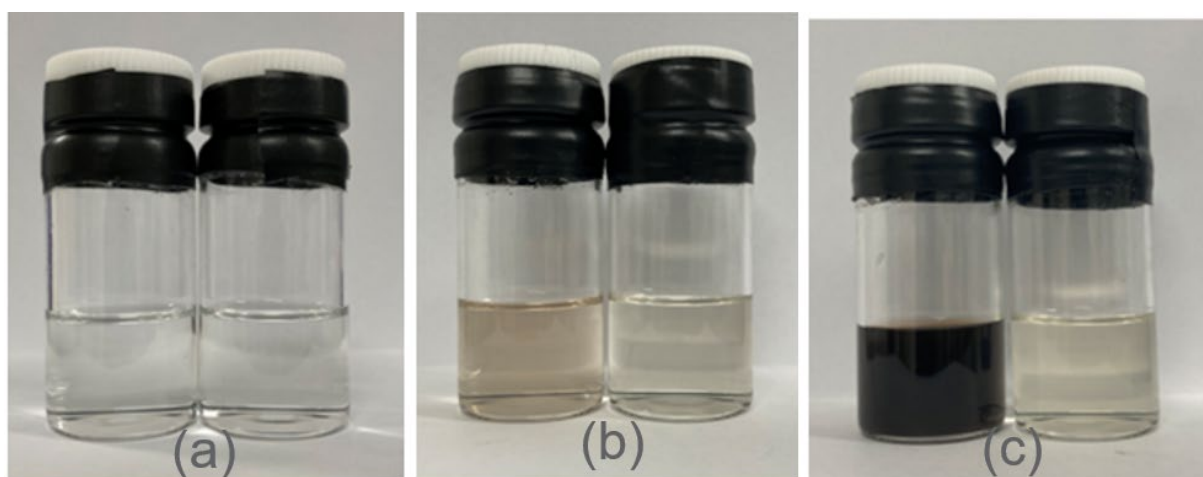
**Lithium-ion hopping weakens thermal stability
of LiPF₆ carbonate electrolytes**

Kee Sung Han, Mal-Soon Lee, Namhyung Kim, Daiwon Choi, Sujong Chae, Jaegeon Ryu, GiovanniMaria Piccini, Roger Rousseau, and Edwin C. Thomsen

Table S1. Diffusion behaviors of electrolytes.

Fitting parameters for the Vogel-Fulcher-Tammann (VFT) equation: $D = D_0 \exp(-B/(T-T_0))$ and the activation energies (E_a) calculated from the Arrhenius plot with the D above 30 °C.

Sample	Component	D_0 (m ² /s)	B (K ⁻¹)	T_0 (K)	R^2	E_a (kJ/mol)
E0	PC	2.96×10^{-8}	700	130	0.99952	15.5 ± 0.1
E1	PC	1.75×10^{-8}	650	159	0.99952	19.2 ± 0.3
	PF ₆ ⁻	1.48×10^{-8}	650	159	0.99944	19.3 ± 0.3
	Li ⁺	2.04×10^{-8}	898	140	0.99959	21.4 ± 0.2
E2	PC	2.75×10^{-8}	811	139	0.99994	19.5 ± 0.2
	PF ₆ ⁻	1.98×10^{-8}	754	145	0.99993	19.3 ± 0.3
	Li ⁺	1.93×10^{-8}	894	138	0.99998	21.1 ± 0.3
	urea	3.87×10^{-8}	1122	118	0.99987	21.9 ± 0.2

**Figure S1. Test of electrolyte stability at elevated temperature (80°C).**

For 0 h (a), 24 h (b), and 48 h. The E1 (left) and E2 (right) that stored (c). The pictures clearly show the suppression of electrolyte decomposition due to the presence of urea.

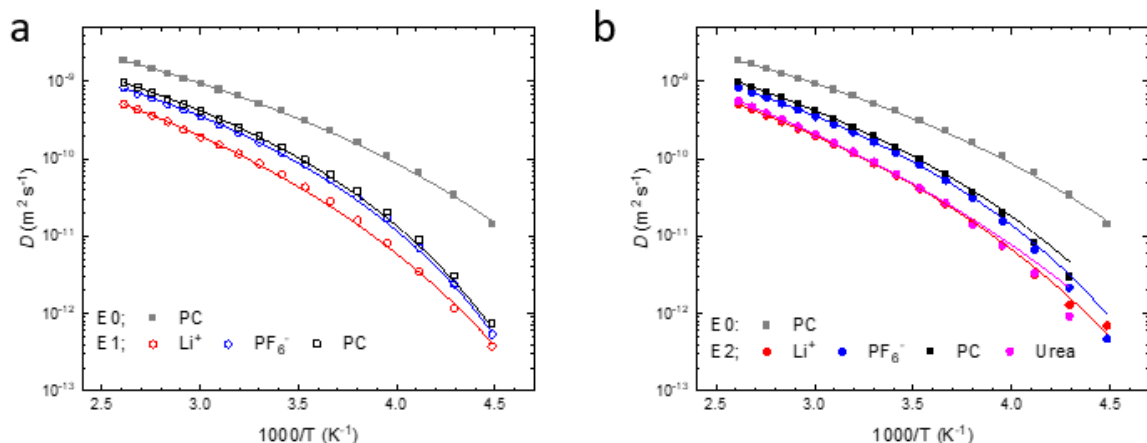


Figure S2. Temperature dependent diffusion coefficients.

Diffusional motion of each electrolyte component. a,b, Temperature-dependent diffusion coefficients of each component in E1 (a) and E2 (b). The lines are fits using the Vogel-Fulcher-Tammann equation: $D = D_0 \exp(-B/(T-T_0))$. The fitting parameters and activation energies, E_a , calculated from the Arrhenius plot: $D = D_0 \exp(-E_a/RT)$ using the D values above 30°C are summarized in Supplementary Table 1.

Temperature-dependent diffusion coefficients, D_s , of Li^+ , PF_6^- , PC, and urea denoted as D_{Li} , D_{PF_6} , D_{PC} , and D_{urea} respectively, for pure PC (E0), E1, and E2 were measured by PFG-NMR. In E1, D_{PC} decreased noticeably from D_{PC} observed in E0 due to increased viscosity (see experimental procedures). It showed, in all measured temperatures, D_{Li} is smallest and followed by D_{PF_6} and D_{PC} in both E1 and E2. In E2, urea negligibly influenced to D_{Li} , D_{PC} and D_{PF_6} while $D_{\text{urea}} \approx D_{\text{Li}}$, suggesting that urea coupled strongly to Li^+ with a minimal effect to other components. The fitting with the Vogel-Fulcher-Tammann (VFT) equation and translational activation energy, E_a , (see Table S1) calculated with the D values above 30°C using the Arrhenius equation (see experimental procedures) confirmed that the diffusional motion of electrolyte components varied slightly due to the presence of urea. The VFT parameters for both E1 and E2 showed that D_{PF_6} and D_{PC} have the similar temperature dependencies while $D_{0,\text{PC}}$ is slightly higher than D_{0,PF_6} . However, the behaviors of D_{Li} were completely different between E1 and E2. Surprisingly, in E1, $D_{0,\text{Li}} (= 2.04 \times 10^{-8} \text{ m}^2\text{s}^{-1})$ is larger than $D_{0,\text{PC}} (= 1.75 \times 10^{-8} \text{ m}^2/\text{s})$ and $D_{0,\text{PF}_6} (= 1.48 \times 10^{-8} \text{ m}^2/\text{s})$; $D_{0,\text{Li}} > D_{0,\text{PC}} > D_{0,\text{PF}_6}$, however, in E2, $D_{0,\text{Li}}$ became

smaller than $D_{0,PC}$ and $D_{0,PF6}$ ($D_{0,Li} < D_{0,PF6} < D_{0,PC}$).

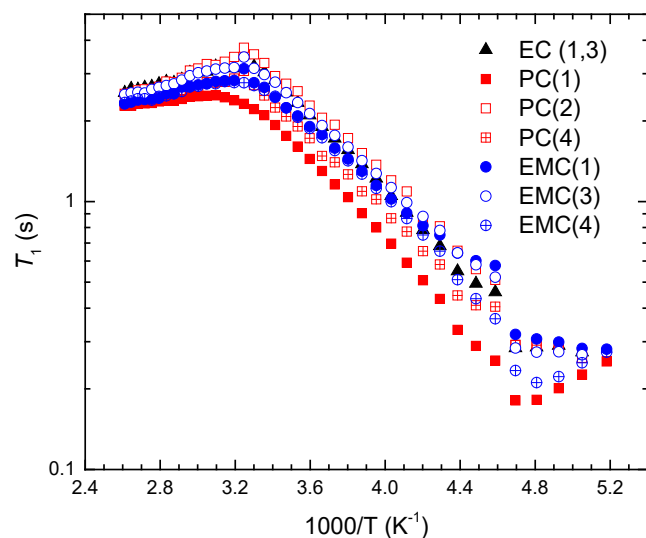


Figure S3. Temperature-dependent ^1H T_1 for the ternary mixture of EC/PC/EMC (4:1:5 wt.%).

The temperature dependencies are almost the same for all proton sites and the T_1 maxima appeared at $\sim 40^\circ\text{C}$. The discontinuities at $T \approx -55^\circ\text{C}$ are due to the melting of EMC¹.

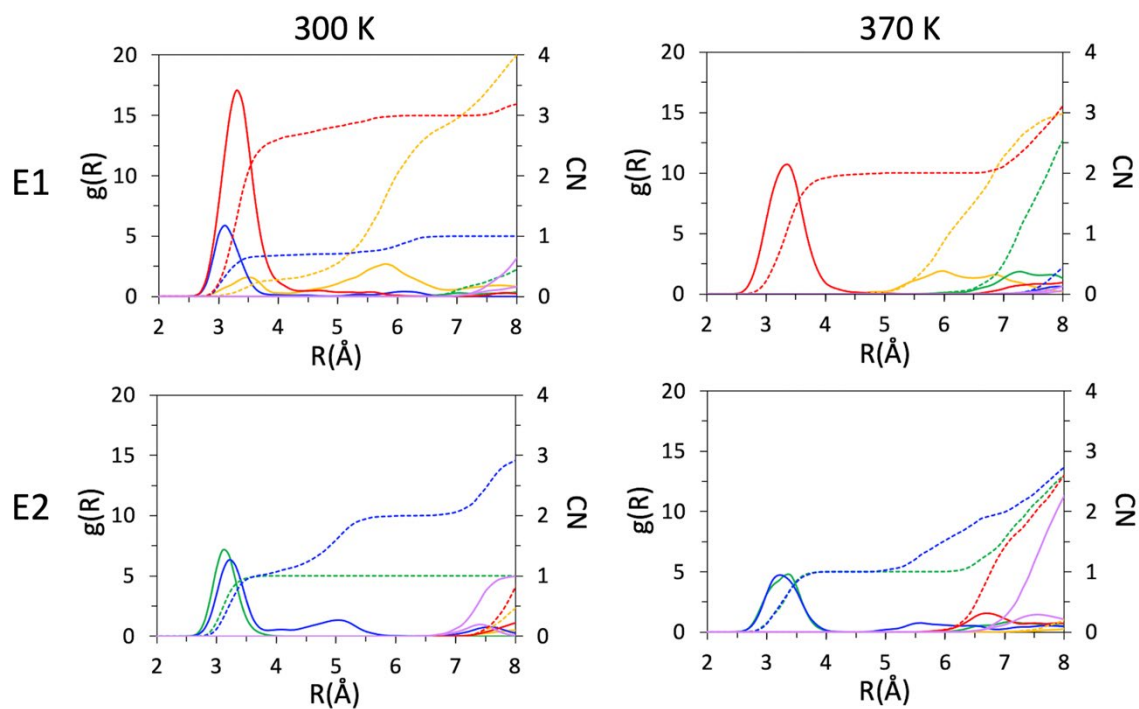


Figure S4. Structural properties of the electrolytes.

Radial distribution function, $g(R)$, and coordination number (CN) between P of PF_6^- and Li for each P of PF_6^- anion. $g(R)$ and CN of Li^+ ion to O of PC (blue lines), F of PF_6^- (orange lines), and O of urea (green lines). Solid lines show $g(R)$ and dashed lines show CN.

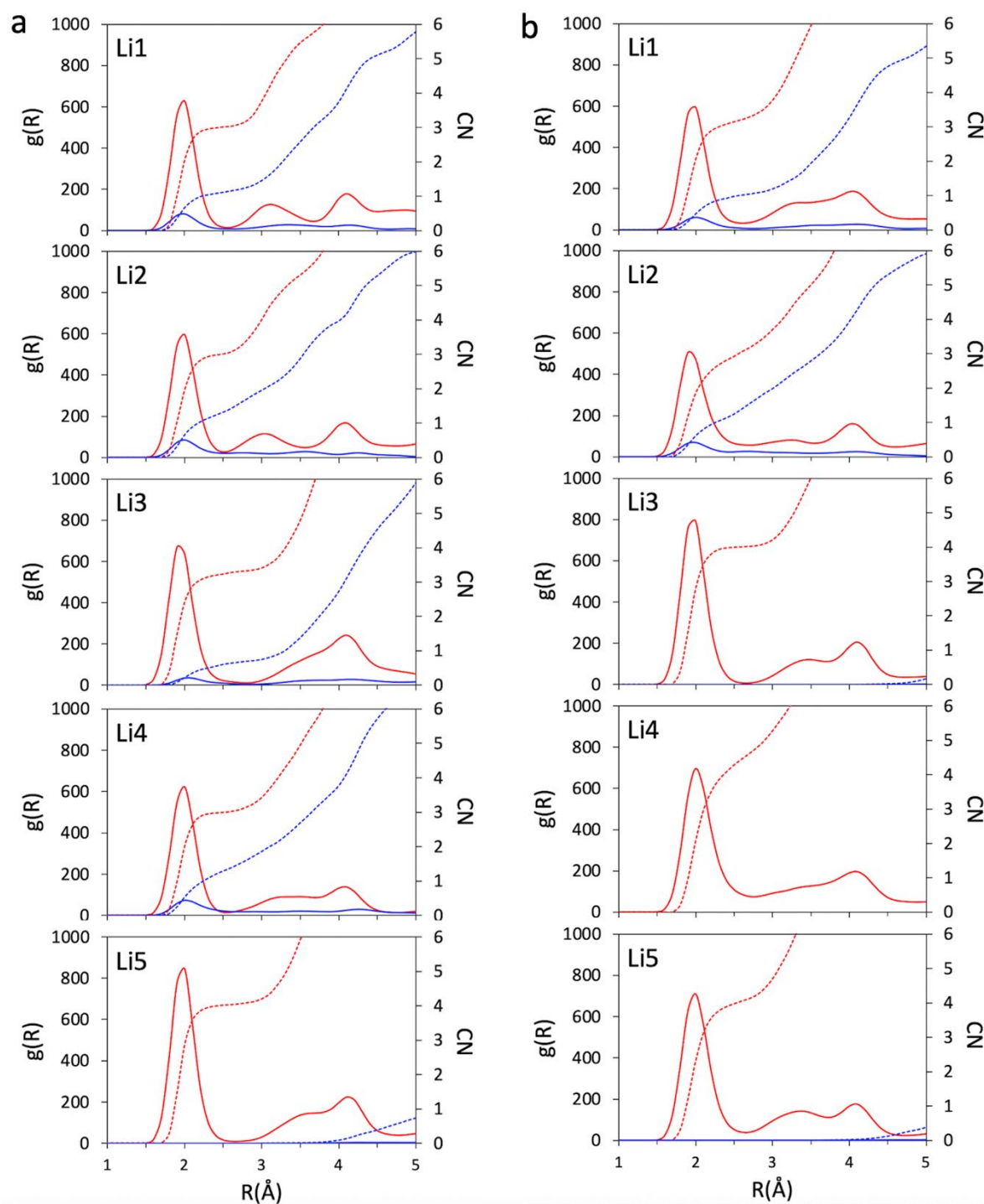


Figure S5. Lithium solvation structure in E1.

Radial distribution functions $g(R)$ and their integrals of each Li^+ at (a) 300 and (b) 370 K in the absence of urea (E1). Solid and dotted lines represent $g(R)$ and integral of $g(R)$, respectively. Color codes: red – Li-O of PC, blue – Li-F of PF_6^- . The plots show 4 Li^+ cations bind with PF_6^- at 300 K, while only 2 Li^+ ions bound to PF_6^- at 370 K.

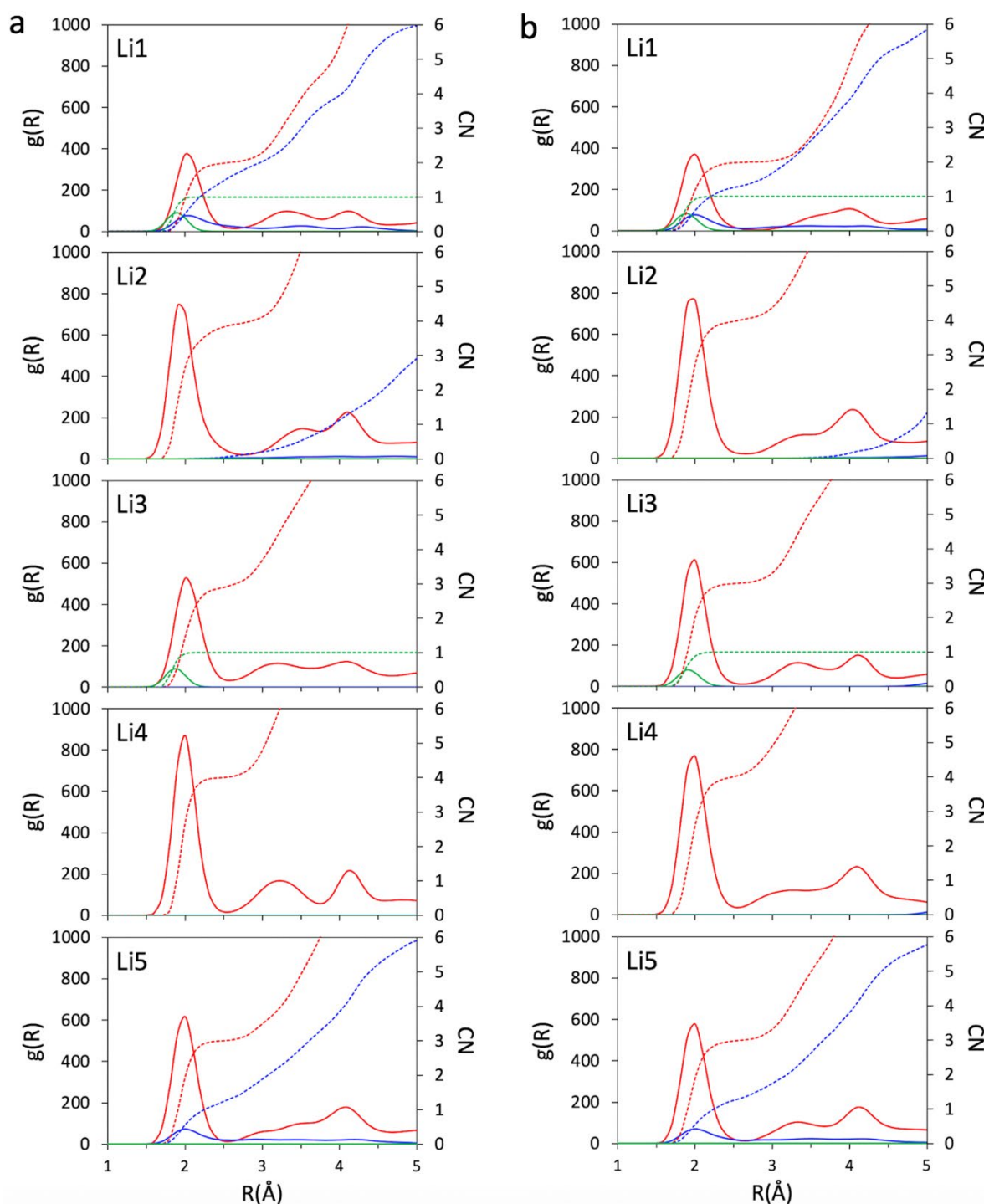


Figure S6. Lithium solvation structure in E2.

Radial distribution functions $g(R)$ and their integrals of each Li^+ at (a) 300 and (b) 370 K in the presence of urea, (E2). Solid and dotted lines represent $g(R)$ and the integral of $g(R)$, respectively. Color codes: red – Li-O of PC, blue – Li-F of PF_6^- , and green – Li-O of urea. At both temperatures one Li forms bonding with 2 PC, 1 PF_6^- and 1 urea while one Li interact with 3 PC and 1 urea in addition to Li interacting with 3 PC/1 PF_6^- and 2 Li interacting with 4 PC.

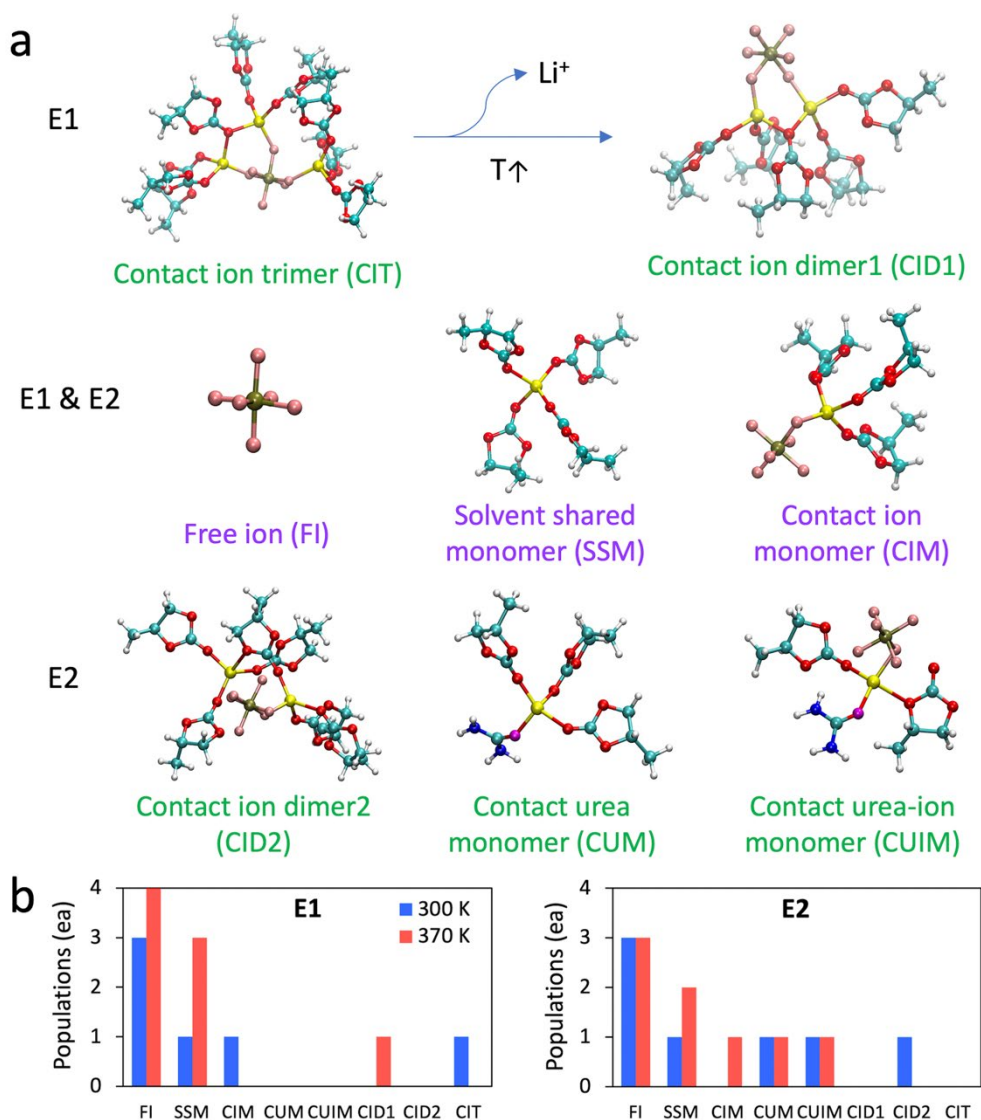


Figure S7. Structural analysis of E1 and E2 at 300 and 370 K from AIMD data.

(a) E1 shows structures observed only in E1, E2 shows structures observed only in E2, and E1&E2 shows commonly observed structures and (b) their populations.

Figures S7(a) and S7(b) show the detailed structural information for Li^+ solvation clusters and their populations, respectively. In the absence of urea *i.e.* E1, there are three different structures: one contact ion trimer (CIT) formed with three Li^+ ions connected via PC and PF_6^- , one solvent shared monomer (SSM)— $Li(PC)_4$, and one contact ion monomer (CIM)— $Li(PC_3)PF_6$ at 300 K. At 370 K, one of Li^+ in CIT moves away becoming a Li^+ dimer where PF_6^- interact with both Li^+ ions (contact ion dimer1, CID1). We also observed 3 SSM. For E2 having 2 urea molecules in the system, it observed one contact ion dimer2 (CID2), one SSM, one contact urea monomer (CUM), and one contact urea-ion monomer (CUIM) at 300 K. At the high temperature (370 K), the presence of urea engenders Li^+ ions being monomers (2 SSM, 1 CIM, 1 CUM, and 1 CUIM).

We also observe 3-4 PF_6^- free ions weakly interacting with other surrounded molecules in all systems studied. The high populations of free ions and SSM have also been observed in a previous study of LiPF_6 and LiBF_4 in PC solvent by Hwang et al.² Interestingly, lithium forms Li^+ trimer complex (CIT) at low temperature in the absence of urea, while Li^+ dimer complex is formed with increased temperature (CID1) or urea addition (CUIM). Furthermore, we observe only Li^+ monomers at elevated temperature in the presence of urea.

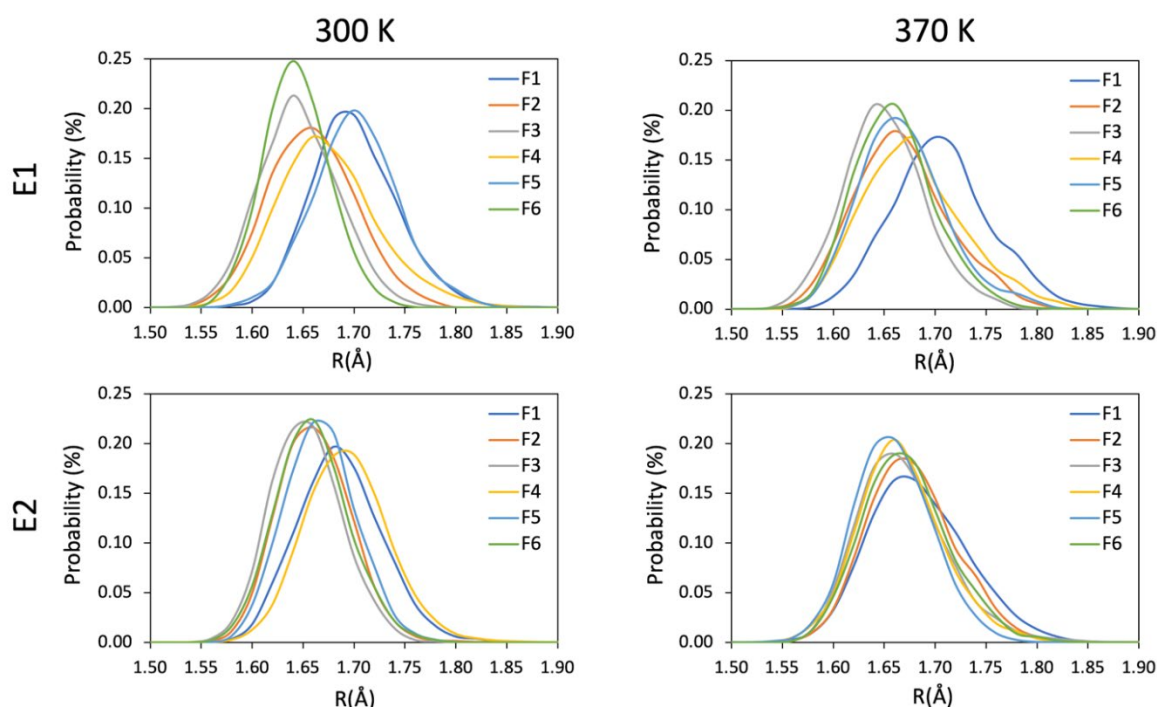


Figure S8. Calculated probability of P-F distances from AIMD trajectories.

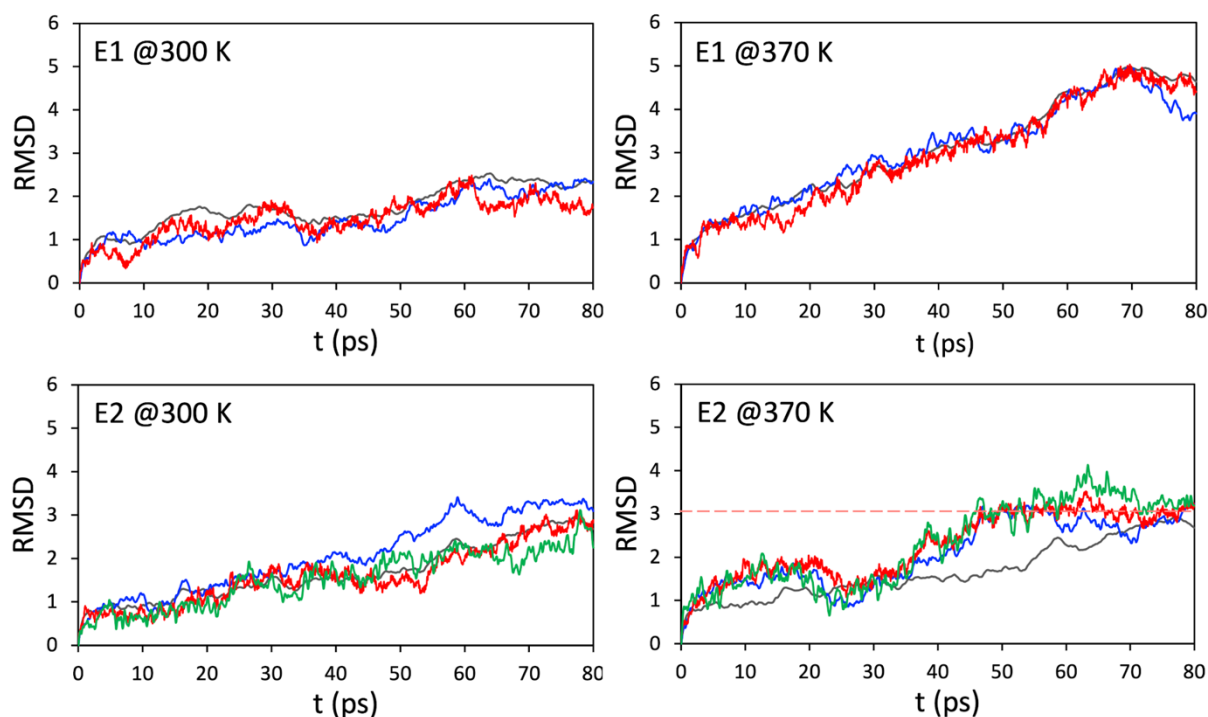


Figure S9. Simulation of translational mobility of electrolyte components.

Calculated root mean square displacement (RMSD, Å). Color code: PC – grey, PF_6^- – blue, Li^+ – red, Urea – green. Pink dashed lines in E1 @370 K and E2 @370 K show the plateau of RMSD.

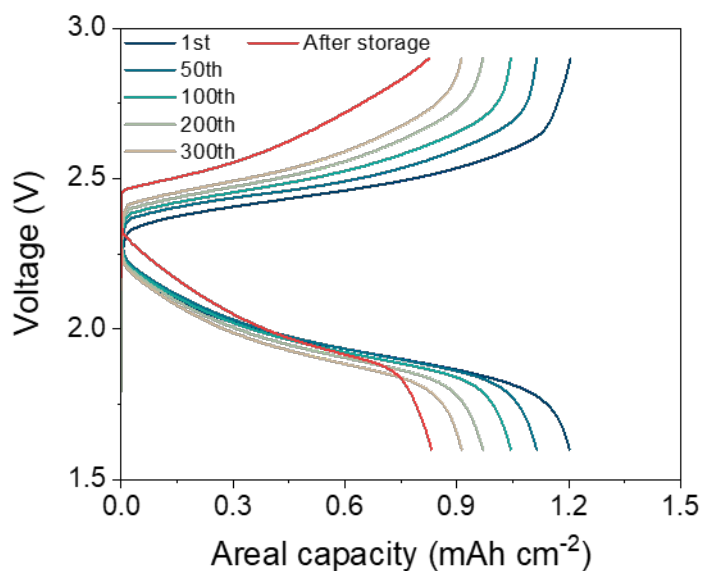


Figure S10. Evolution of voltage profile.

Voltage profiles of NMC||LTO full cell using E1 electrolyte at each cycle.

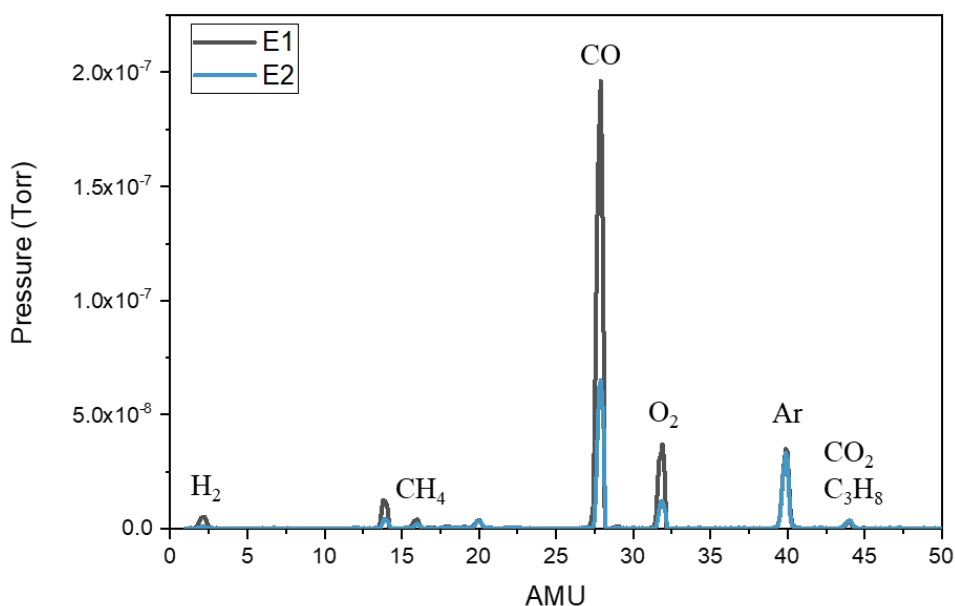


Figure S11. Comparison of gas evolution between E1 and E2.

Mass spectrometry of the collected gases from pressure measurement cells using each electrolyte. H_2 , CH_4 , CO , CO_2 , and C_3H_8 are common gases, which can be generated by electrolyte side reaction and catalytic decomposition of LTO at the elevated temperature. These gases generations are related to mainly electrolyte decomposition with consuming Li ions. Ar gas is included in the cell during cell assembly in Ar-filled glovebox.

References

1. Li, Q., Jiao, S., Luo, L., Ding, M.S., Zheng, J., Cartmell, S.S., Wang, C.-M., Xu, K., Zhang, J.-G., and Xu, W. (2017). Wide-Temperature Electrolytes for Lithium-Ion Batteries. *ACS Applied Materials & Interfaces* 9, 18826-18835. 10.1021/acsami.7b04099.
2. Hwang, S., Kim, D.-H., Shin, J.H., Jang, J.E., Ahn, K.H., Lee, C., and Lee, H. (2018). Ionic conduction and solution structure in $LiPF_6$ and $LiBF_4$ propylene carbonate electrolytes. *J. Phys. Chem. C* 122, 19438-19446. 10.1021/acs.jpcc.8b06035.