

A Unique Case of the “Goldilocks Rule” in Solid-State Electrolytes: Two Are Good, Four Are Too Many

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Abstract

We report the syntheses of two new series of methacrylate monomers with different backbones: ureidopyrimidinone (PU) and boron-substituted urea pyrimidine (U), which enhance both the mechanical and electrochemical properties of the solid-state electrolyte (SSE) while improving the cycle life of lithium iron phosphate (LiFePO₄,

LFP) cathodes. The PU backbone is characterized by four hydrogen bonds, while the U backbone bears only two. Importantly, our research reveals that two hydrogen bonds (H bonds) in these monomers are optimal; in contrast, four are excessive. The exceptional mechanical properties and processability of the SSE with the U series additives, resulting from the optimal H bonds, were unexpectedly achieved. This leads to the establishment of a “Goldilocks rule” for additive design. The key strategies include: 1) reducing hydrogen-bonding (H-bonding) sites by changing pyrimidinone to pyrimidine, and 2) shifting from intermolecular to intramolecular H-bonding and π - π bonding. This reduction in H-bonding also offers significant advantages in processability. The advancement can be extended to electrode fabrication, making the manufacturing of all-solid-state batteries more practical and efficient.

Keywords:

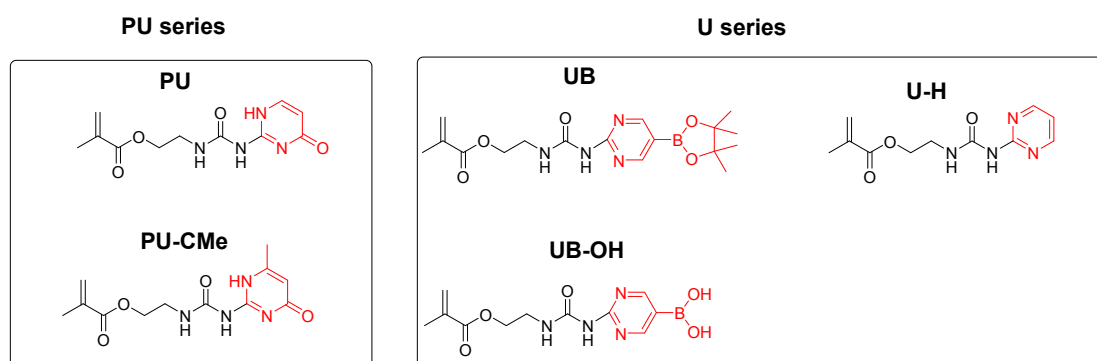
Solid-state electrolyte, polymer electrolyte, hydrogen bonding, mechanical strength, additive, π - π stacking, scale up

1. Introduction

The ever-increasing need for energy is creating more demand for higher, safer, and faster energy storage systems. Today the lithium-ion batteries (LIBs) technology is still the prevalent form of energy storage in the transportation sector for electric vehicles due to its high energy and power density, stability and cyclability. However, issues within LIBs arise from the scarcity of transition metal sources, the inherent safety concern with low reduction potential of lithium metal, and the usage of flammable liquid organic electrolyte. Solid-state batteries (SSB) are considered a safer alternative

to the current anode-free LIBs. Two key points of making solid-state batteries (SSB) a real competitor are the suppression of transition metal cross-talk between the anode and cathode,² and achieving the almost unity transference number in many of the single ion conducting solid state electrolytes.³ The state-of-art All-Solid-State Battery (ASSB) touts a specific capacity of 900 Wh L⁻¹, a coulombic efficiency of 99.8%, and a cycling life of > 1000 cycles.⁴ However, entering this new realm of batteries requires changes in both science and technology innovation to address arising challenges in fundamental materials sciences such as cathodes, interfaces, anodes, and SSEs, as well as scale-up commercialization capability. To list a few challenges current SSB technology is facing: high impedance resulting from two rigid interfaces (SSE and electrodes), voids that may form during charge and discharge cycles resulting from contraction and expansion of the electrodes, and the limited amount of SSE materials showing both high ionic conductivity and low impedance.^{1,5,6} Successful introduction of SSE at a commercial scale requires improvements in energy density, cyclability, and safety, along with capability to address issues like high impedance and low power density. Previous studies have demonstrated that incorporating electro spun lanthanum zirconate fibers incorporated into poly(propylene carbonate)-based solid electrolytes significantly enhances room-temperature ionic conductivity, interfacial compatibility, and cycling performance in solid-state lithium batteries using NMC.⁷ The interface consideration from the anode side has also been tested using a graphite-coating enabling high-voltage performance and long cycling stability by forming a protective LiC₆ interlayer that suppresses dendrite growth.⁸

H-bonding polymers, classified as one of the self-healing polymers, are well known for their dynamic H-bonding (i.e. rubber elasticity⁹) and their applications in improving a materials mechanical and electronic properties. The first introduction of self-healing polymers in energy storage began in the early 2010s when urea-modified polymers, initially developed for electronic skin,¹⁰ were utilized in silicon anode batteries.¹¹ In this report we explore design options of H-bonding agents to improve the mechanical and electrochemical properties of the current lithium ion conducting polymer SSE systems.^{12,13} These new urea monomers, when used at a low concentration, can enable the SSE system and improve cycling performance at a C/2 rate in a lithium iron phosphate (LiFePO₄, LFP) battery. The structures of the monomers are shown in Scheme 1, and are classified as two series, PU series with a ureidopyrimidinone unit, and U series with a urea pyrimidine unit.



Scheme 1. Molecular structures of the series of ureidopyrimidinone monomers (the PU series with PU and PU-CMe) and the urea pyrimidine monomers (the U series with UB, U-H, UB-OH).

To achieve the desired chemical, physical, and electrochemical performance, three strategies are implemented for a new synthetic design based on previously reported research on the H-bonding properties of ureidopyrimidinone (denoted as PU-CMe here)¹⁴: 1) Changing the substitution on the heterocyclic ring. This change can be

found in the design of changing from PU-CMe to PU where a methyl group is replaced by a H atom, as well as the change from U-H to UB and UB-OH, where a hydrogen atom is substituted by a boron containing group. 2) Controlling the H-bonding number mainly through changing the pyrimidinone to a fully aromatic pyrimidine, as demonstrated in U series (Scheme 1). The U variants, which have the reduced H-bonding sites compared to the PU variants (PU and PU-CMe) with carbonyl group in pyrimidinone (C=O), are easier to process while maintaining their high mechanical strength. As elaborated in the subsequent text, the improved electrochemical stability is also manifested in U-H with a “Goldilocks rule” of H-bonding: two H bonds are optimal. Another advantage is the increased aromaticity of pyrimidine, as manifested in UB and UB-OH, both of which can take H-bonding and π - π stacking simultaneously, enabling stronger interactions than U-H. As will be discussed in the latter text, in the case of U-H, unlike UB and UB-OH, the configuration with π - π stacking exhibits a much weaker interaction and H-bonds are the dominant interaction. 3) Incorporation of a boronic acid pinacol ester structure¹⁵ in addition to the urea-pyrimidine backbone as seen in UB and UB-OH. Both boron-substituted compounds demonstrated improved processability compared to the PU series. Notably, UB-OH was identified as a spontaneous hydrolysis product of UB.

2. Results

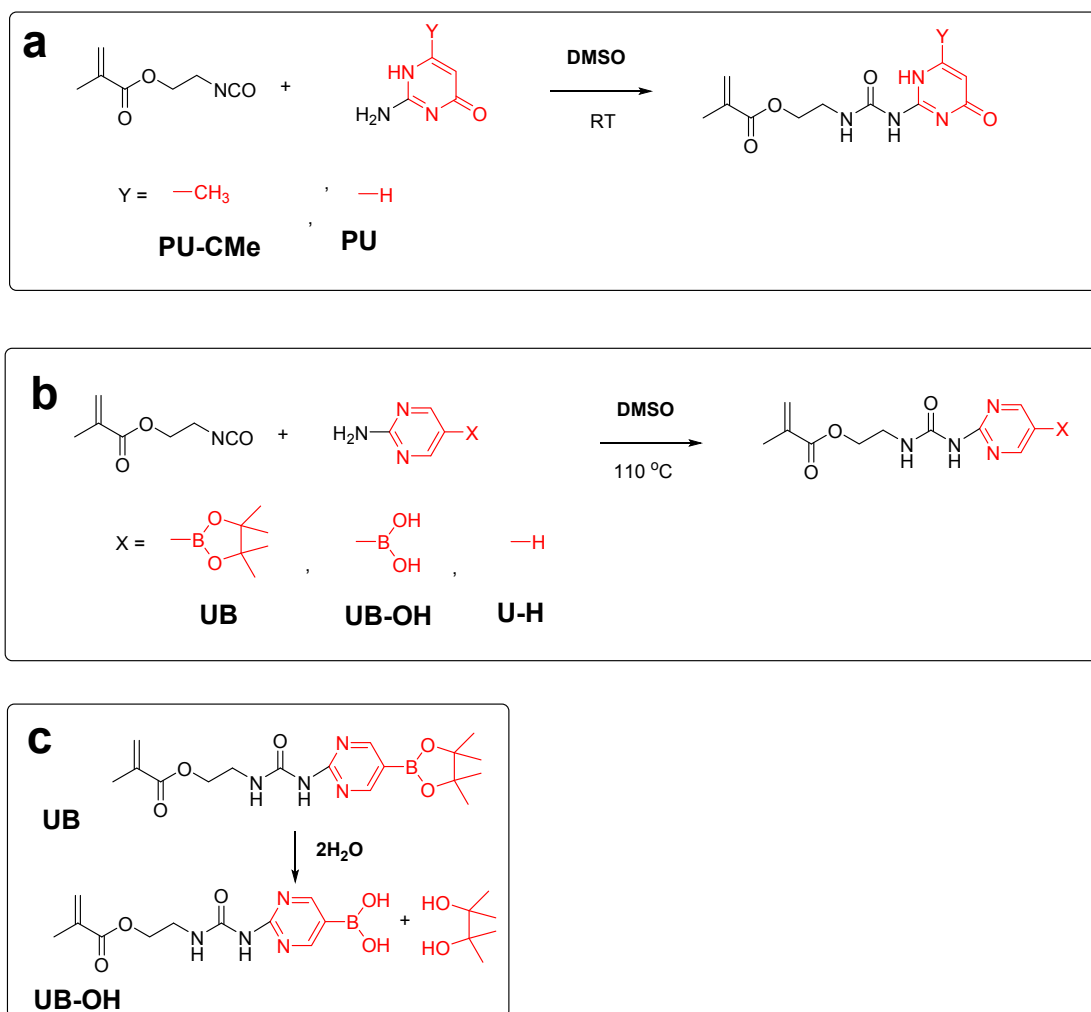
Our approach addresses potential challenges in scaling up and enhancing performance by utilizing an additive that strengthens the polymeric scaffold, thereby improving both mechanical strength and electrochemical performance. Incorporation of the U-series

additives yields exceptional mechanical robustness and electrochemical stability. Furthermore, the low required dosage of this H-bonding agent pave the way for broader adoption in SSBs for large-scale production.

2.1 Syntheses

2.1a Syntheses of the H-bonding crosslinkers

The syntheses of the PU series (Scheme 2a) are modified from the previous work¹⁴ and proceed at room temperature. The reaction is a classic urea synthesis through reaction with isocyanate, with the designed functional group (in red) on the primary amine. The syntheses of U series, however, changing the pyrimidinone to a fully aromatic pyrimidine and introducing the boron ester (Scheme 2b) require higher activation. As a result, new reactions require a higher temperature of 110°C overnight. These structural changes enable optimal H-bonding capabilities, which are essential for the application in scaled up manufacturing of SSE. All compounds were synthesized, purified, and characterized using ¹H NMR spectroscopy (Supplementary Information, Figures S4-8).



Scheme 2. (a) Synthetic procedure for the PU series from the literature.¹⁴ (b) Synthetic procedure using increased temperature for the U series with either boronic acid pinacol ester pyrimidinylurea (UB and UB-OH) or simply pyrimidine (U-H). (c) Spontaneous hydrolysis of UB to UB-OH.

During our efforts to scale up the UB compound, we observed the deprotection of pinacolyl boronate esters leading to spontaneous formation of a hydrolysis product, i.e., UB-OH, as illustrated in Scheme 2c. UB-OH also exhibits improved mechanical strength and processability, albeit slightly reduced compared to UB. While hydrolysis of UB was observed, this primarily occurred during the synthesis steps involving an aqueous workup. In the initial batches, UB was successfully synthesized; however, in subsequent batches that included aqueous workups, only the hydrolyzed product, UB-OH, was obtained. Specifically, water used during the precipitation step promoted the

hydrolysis of UB, resulting in the formation of a yellow, fluffier UB-OH compound.

In contrast, hydrolysis of UB is unlikely under the SSE preparation conditions, as all procedures are conducted either inside a glovebox or within a humidity-controlled dry room. Therefore, the hydrolysis pathway illustrated in Scheme 2c is relevant primarily to the synthetic process involving immersion in water, rather than to the SSE fabrication conditions.

2.1b Syntheses of the deep eutectic solvent (DES) and polymer crosslinking systems

DES refer to systems with lower melting points than their single components and have found their applications in energy storage, through mixing H-bonding donors and acceptors (ethylene glycol/choline chloride), or ion-dipole (LiTFSI/urea). They can be directly used as electrolytes^{16,17} or target the optimal solubility of transition metal oxides and solvents for recycling Co (hydrometallurgy).¹⁸ Previous work emphasizes using a DES system of mixing N-methylurea (NMU) or N-methylacetamide (NMA) with a sulfonyl imide salt.¹⁶ Given the low melting point (mp) of NMA (mp = 26-28 °C), it was initially tested as the DES system with LiTFSI and as part of the U system. However, a semi-solid gel formed, suggesting the development of a 3D network and an overly strong coordination system, which is due to the polarity of acetamide ($-C(=O)-NH-CH_3$) groups forming coordinated structures with the LiTFSI salts (Li^+ and $TFSI^-$) and 3D micro-domains.¹⁷

Consequently, the following text will primarily focus on the NMU/LiTFSI system with U series additives. The mps of NMU and LiTFSI are reported at 98 and 234 °C, respectively, yet upon mixing, a viscous liquid mixture system was obtained. A molar ratio of 2 was selected for NMU:LiTFSI for optimal viscosity and ionic conductivity.

Besides the DES system, the polymer system designed to enhance both mechanical and interfacial stability consists of a crosslinked framework incorporating poly(ethylene glycol) diacrylate (PEGDA, $M_n = 600$) with about 13 units of ethylene oxide (EO). The incorporation of EO chains facilitates the movement of Li^+ inside the SSE, together with addition of propylene carbonate (PC). As shown in Figure 1, the new SSE consists of the DES with crosslinked PEGDA, and a small amount of H-bonding agents. The scaffold-enabling additive of the U series demonstrates effectiveness at a concentration as low as 0.7 wt%. Despite the small changes implemented in the U series compared with that of the PU series in structure, the processability of the crosslinker increased dramatically. For instance, PU-CMe causes the system to turn into elastic gel with no processability. Removing the methyl group on PU-CMe produces PU (Scheme 1), however the processability still remains poor: when 0.7 wt% of PU is added, the mixture quickly transforms into an elastic gel, making it impossible to process into a film. Indeed, the processable additives-UB, UB-OH, and U-H-featuring a pinacolboranyl ($-B(O-C(CH_3)_2-C(CH_3)_2-O-)$ group, boric acid ($-B(OH)_2$), and 1,3-pyrimidine (the red moieties in Scheme 1), significantly enhanced the processability.

The DES functions as a bulk electrolyte, providing ion transport within the system. This solvent is relatively viscous and serves both as a medium for Li ion conduction and as a plasticizer. The interactions between the solvent and the polymer framework are much weaker than covalent bonding. The polymer network, formed by PEGDA and the U/PU series, is covalently crosslinked and therefore maintains structural integrity. In contrast, the hydrogen bonding and π - π stacking interactions are dynamic :they can

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4 form and break reversibly in response to volume changes of the electrolyte, contributing
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6 to rubber-like elasticity without being significantly affected by solvent choice.
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9 The SSE is formed by crosslinking PEGDA and U/PU within a plasticizer and Li-
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11 conducting medium. The plasticizer/LiTFSI/NMU component establishes a dynamic
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13 and fast Li-ion transport network. Both DES and PC exhibit high Li ion conductivity,
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15 and the formulation is optimized to achieve a balance between mechanical robustness
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17 and processability, allowing facile large-scale slot-die coating from solution.
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21 In general, LiTFSI/NMU (37-50 wt%), PEGDA (30-33 wt%), PC (15-26 wt%), and
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23 UB (0.7 w%) were mixed with different ratio and stirred for about 2 hours (or overnight).
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27 All H-bonding agents, specifically the U and PU series, are to be used exclusively at a
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29 concentration of 0.7 wt% relative to the total formulation. Then the initiator 2,2'-
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31 azobis(2-methylpropionitrile (AIBN) was added to the mixture and stirred for another
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33 hour until it dissolved to form a clear solution. If no PC is used, the solution cannot be
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35 stirred overnight, a semi-opaque solution with H-bonding is formed immediately. The
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37 concentration of 0.7 wt% was selected to maintain an overall H-bonding to PEGDA
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39 ratio of approximately 1:25. A higher concentration by increasing the H-bonding
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41 component ~ fivefold to 3.3 wt%; however, the performance decreased significantly,
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43 likely due to an increase in the glass transition temperature (T_g). This observation aligns
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45 with our “Goldilocks rule” — two hydrogen bonds appear to be optimal, and excessive
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47 H-bonding becomes detrimental. We did not investigate lower concentrations, as our
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49 goal was to maximize the observable effects and differences among the various H-
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51 bonding monomers.
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The introduction of H-bonding through molecular design induces chemical, physical, and electrochemical changes. However, due to the low concentration (0.7 wt%), these effects are difficult to observe spectroscopically. We investigated how hydrogen bonding influences electrolyte properties. As the chemical changes are expected to be very subtle, FTIR analysis did not reveal any obvious differences (Figure S13). In contrast, the physical effects are pronounced: the processability varies dramatically depending on the number of hydrogen-bonding sites. Systems with two H-bonding sites (e.g., UB and U-H) remain in solution and are readily processable, whereas those with four H-bonding sites (e.g., PU and PU-CMe) rapidly gel, making solution processing impossible.

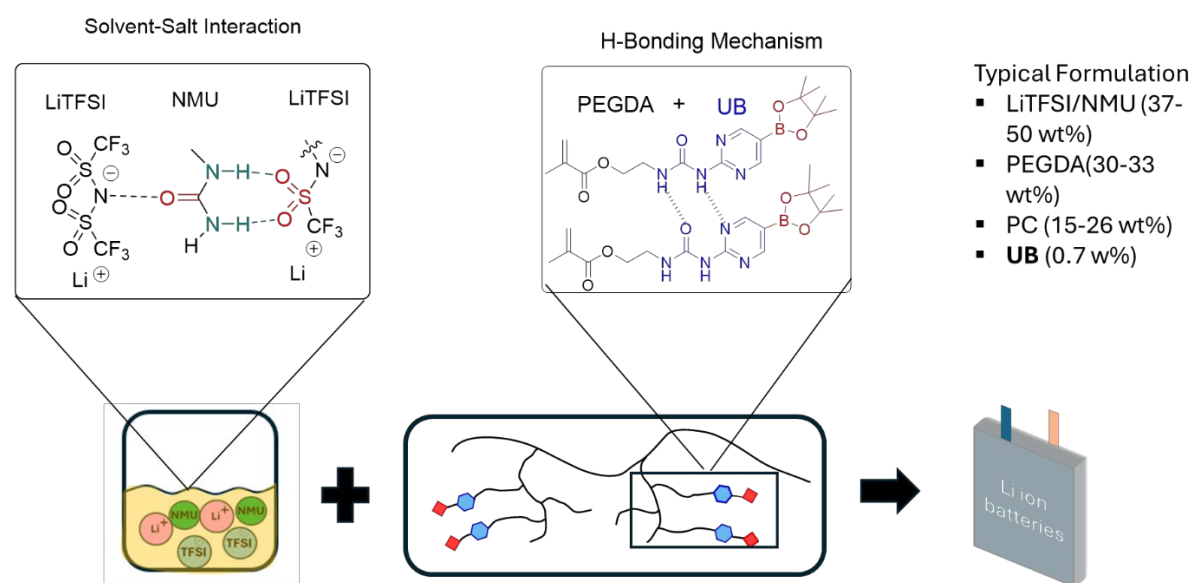


Figure 1. The electrolyte composition of SSE with lithium trifluoromethylsulfonyle imide (LiTFSI), NMU, and the PEGDA (polyethylene glycol diacrylate), and the additives (using UB as an example) that are capable of H-bonding. The H-bonding mechanism shows how UB can exceptionally improve both mechanical strength of the polymeric systems.

In our approach, solution processing is preferred, as it allows seamless transferability from existing wet-chemistry-based lithium-ion battery manufacturing technologies.¹⁹

This method is particularly advantageous because it is compatible with slot-die coating,

a technique that readily integrates into roll-to-roll (R2R) processing, enabling scalable and continuous production of SSE. In this process, the precursor solution, comprising monomers or oligomers for the polymer electrolyte, can be homogeneously mixed and dispersed with inorganic fillers such as oxides or sulfides to tailor ionic conductivity and mechanical strength. The resulting composite formulation is then applied via slot-die coating, ensuring uniform film thickness and high reproducibility.

Although rubbery, elastic polymers can, in principle, be cast directly into free-standing films or processed using other thin-film techniques (microcompounding using twin-screw extruder to blend polymers, additives, and fillers), these methods are less compatible with large-scale SSE manufacturing. Our design incorporating hydrogen-bonding monomers supports the goal of scalable, solution-processed SSE. H-bonding enhances mechanical integrity during film formation and curing, while the addition of viscoelastic components further improves strength and flexibility.²⁰ This combination enables solution processing followed by thermal or UV curing, providing a practical route toward robust and manufacturable SSEs.

2.2 Computational Chemistry Calculations

2.2a Computational methods

The computational chemistry calculations were executed by a two-step approach: first, geometry optimization was carried out using the semi-empirical PM7 method;²¹ then the geometry was further refined using Density Functional Theory (DFT) at the wB97XD/6-31g(d) level of theory.²² Both steps were carried out using the Gaussian 16 software package²³ in a gas phase. All the optimized structures were confirmed to be at the local minimum of potential energy surfaces by the absence of imaginary frequencies

from the vibrational frequency analysis. For monomer calculations, conformers of UB, U-H, PU-CMe, and UB-OH monomers (schematic of the structures are shown in Figure 2) were generated with two different dihedral angles of $O=C-N-H$ of the urea scaffold ($\phi_{O=C-N-H}$ at around 0° and 180°), where the N atom is coordinated with a heterocyclic functional group (PU is neglected due to its high similarity to PU-CMe). For dimer calculations (two interacting monomers), multiple initial alignments of selected monomers were manually generated and optimized at the PM7 level, and the low-energy conformers were further refined via DFT calculations. The potential energy differences between conformers as well as monomer-monomer interaction energies were reported in terms of Gibbs free energy (ΔG). Thermochemical corrections were computed assuming 25°C and 1 atm.

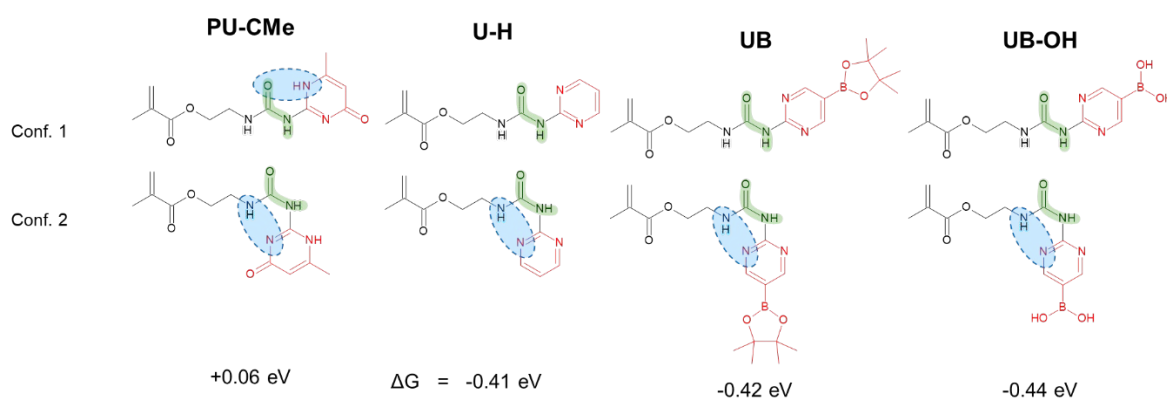


Figure 2. Molecular structures of two conformers (Conf.) of U-H, PU-CMe, UB, and UB-OH monomers, which are generated with two different dihedral angles of $O=C-N-H$ ($\phi_{O=C-N-H}$) of the urea scaffold (highlighted in green). Intramolecular H-bonds are highlighted by blue circles. The Gibbs free energy differences between two conformers ($\Delta G = G_{\text{Conf.2}} - G_{\text{Conf.1}}$) are reported.

2.2b Conformers of urea pyrimidine monomers

We examined two conformers (Conf. 1 and Conf. 2) of each monomer as shown in Figure 2. For U-H, UB, and UB-OH, Conf. 2 is significantly more stable than Conf. 1 by ~ 0.4 eV in ΔG , whereas the two conformers of PU-CMe are isoenergetic. This trend

in relative stability is attributed to the presence of the intramolecular H-bonding: U-H, UB, and UB-OH monomers exhibit intramolecular H-bonds only when $\phi_{O=C-N-H}$ is small (as in Conf. 2), whereas both conformers of PU-CMe possess such bondings (Figure 2). Based on these findings, we selected the H-bonding-featuring molecules for further investigation of their intermolecular interactions.

3. Discussion

3.1 Influence of chemical structure groups

The first change is implemented in the changes from the PU series to the U series, from the pyrimidinone to pyrimidine structure. While pyrimidinone exhibits tautomerism with switching between *enol* and *keto* forms, it does not have full aromaticity. Pyrimidine, as seen in the newly designed UB, UB-OH, and U-H, has full aromaticity and can enable π - π stacking, a weaker interaction. This reduced interaction allows easier processing, as the addition of PU-CMe, even at a mere 0.7 wt%, can cause the solution to gel. Replacing the methyl group on the pyrimidinone with a hydrogen atom (i.e., PU) reduced the gelling effect. However, this modification could not completely prevent gelling during the film-making process, making it impossible to cast into a film. Secondly, electrochemical and interfacially friendly moieties are incorporated. Structures such as fluoroborate and fluorophosphate are particularly of interest for high voltage lithium-ion batteries for their capabilities of forming benign interphases, which can help with lowering the interfacial resistance. In our case, the boron ester is mainly used as an interface modifier,²⁴ similar to the action of lithium bisoxalato borate (LiBOB) and lithium difluoro(oxalate) borate (LiDFOB). It is

noteworthy that the extensively used LiBOB and LiDFOB feature a 4-coordinated, negatively charged boron center, while the UB and UB-OH have a three-coordinated neutral one. The coordination difference between UB, LiBOB, and LiDFOB is not critical, as the effect of interface will be manifested through electrochemical decomposition of the additive and the consequent interface formation on cathodes and anodes. There are also reports on boron ester ($B(OR)_3$) species or networks leading to decreased anion mobility and higher transference number due to its Lewis acidity and interaction with the triflate anions.²⁵⁻²⁷ The enhanced electrochemical performance observed with the additives UB and UB-OH (Figure 6) indicates that the boron-derivative contributes to the improvements. Understanding the interface in SSE is challenging because it is intricately connected to the cathodes, electrolytes, and anodes, making it difficult to isolate. Our differential capacity data (dQ/dV , Figure S11) suggests that neither cell, nor without the additive, shows significant solid electrolyte interface (SEI) change in the first cycle. However, further testing shows performance improvements in the UB cells compared to that of the baseline. Our previous study²⁴ suggested a strong dependence of electrochemical properties on the mechanical and electrochemical interfacial properties.

3.2 Electrochemical and Mechanical Properties

Table 1. Variation in the ratio of NMU to PC, along with changes in U/PU content. ¹						
Name	LiTFSI	NMU	PC	NMU:PC	PEGDA ²	Additive amount
UB-1/4	33.2	6.65	26.4	1/4	33.1	0.7
UB-2/3	33.1	13.4	19.9	2/3	32.9	0.7

UB-1	33.3	16.6	16.5	1	32.9	0.7
UB-1-B	32.86	16.69	16.88	1	30.29	3.28
UB-3/2	32.7	19.9	13.4	3/2	32.7	0.7
UB-OH-1	33.3	16.6	16.5	1	32.9	0.7
U-H-1	33.1	16.6	16.4	1	32.9	0.7

¹ All chemical composition values reported here are given in weight percent (wt%)

² PEGDA refers to poly(ethylene glycol) diacrylate, M_n 600.

As shown in Table 1, the naming system refers to the SSE with specific formulations, and the SSE consisted of the DES system and a PC plasticizer to facilitate Li ion transport, as well as the additive to improve mechanical strength. 1) “A” denotes the baseline formulation, whereas the chemical acronym of specific H-bonding additive represents the SSE with specific additive is added; 2) the number indicates an SSE system with varying NMU to PC ratios; 3) The suffix “B” denotes that the additive amount exceeds the standard concentration of 0.7%. For instance, “A-1” denotes the baseline system that does not include any additive yet retains the same component and formulation with an NMU:PC ratio of 1.

3.2a Ionic conductivity

As illustrated in Figure 3, the ionic conductivity of UB-1, A1, and UB-3/2 are comparable, with UB-1 exhibiting slightly superior performance compared to A-1 and UB-3/2. The ionic conductivity ranks in the order of UB-2/3 > UB-1-B ≈ UB-3/2 ≈ UB-1 ≈ A-1 > UB-OH-1. Although UB-2/3 displays the highest ionic conductivity, it does not significantly outperform the other formulations, indicating that ionic conductivity alone is not the primary driver of enhanced performance.

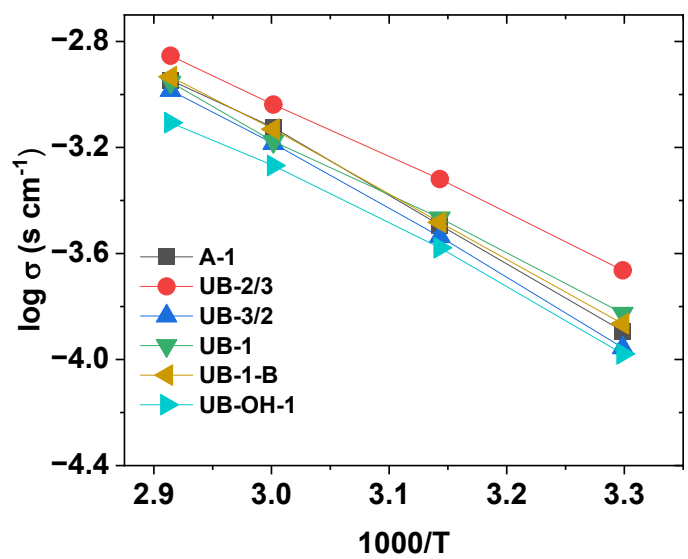


Figure 3. Ionic conductivity of the baseline A-1, and UB series with various ratios of NMU:PC, UB with extra additive concentration, and pure UB-OH.

3.2b Lithium plating/stripping and transference number

Lithium plating and stripping measurements can be used to evaluate the performance and compatibility of the SSE with Li metal. Li-dendrites are formed on a bare Li metal electrode in a thermodynamically favored manner: an unstable SEI layer on the Li anode also leads to the rapid loss and/or consumption of both active Li and electrolyte. In this work, the symmetric Li//SSE//Li cells were used to plate and strip Li at the constant current densities indicated in Figure 4a. The detailed voltage profiles with indicated current densities and cycle times are shown in Figure 4b. For the baseline A-1, the overpotential increases from 0.030 to 0.113, and later to 0.210 V along with the increase of current densities of 0.1, 0.4 and 0.8 mA/cm². When UB-1 was utilized, the overpotential increases were smaller, ranging from 0.019 to 0.081 V and reaching 0.165 V as the current increases. The improvement is attributed to enhanced mechanical strength, which effectively suppresses lithium dendrite formation.

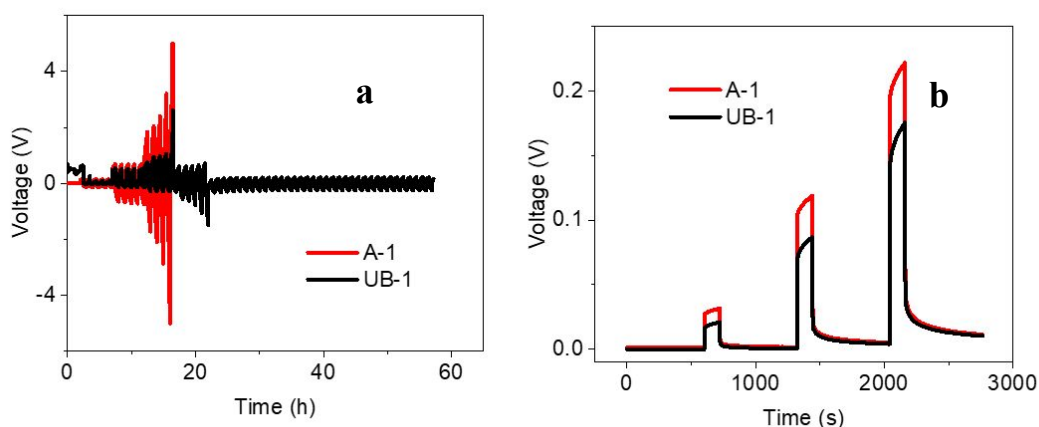


Figure 4. (a) Critical current density (CCD) determination of SSE with baseline A-1 and additive (UB-1) via DC polarization (0.1, 0.4 and 0.8 mA/cm²). (b) Voltage profile comparison of A-1 and UB-1 at 0.1, 0.4, and 0.8 mA/cm².

On the other hand, the transference number indicates that A-1 and UB-1 are within a similar range (Figure S9 and Equations S1-2), with UB-1 exhibiting slightly inferior transport properties compared to A-1. This suggests that factors beyond ionic conductivity may contribute to improved performance. As will be elaborated later, the improvement could originate from improved mechanical strength due to optimal H-bonding.

3.2c Optimization of electrolytes

As shown in Supplementary Information (Figures S1-3), three different preparation methods of the SSE would result in a slight difference in performance. For instance, utilizing Method 1 from Supplementary Information section 3.1 yields a film thickness of 60 μm (Figure 5a), whereas Method 2 results in a film thickness of 50 μm , which also demonstrates slightly better performance over 40 cycles. However, due to the scalability potential of method 1, all our samples have been prepared using Method 1, and the schematic illustration is shown in Figure 5a. Note that our study aims to

elucidate the role of H-bonding in enhancing SSE and the resulting cell performance. The observed performance differences at 50 cycles, particularly with optimized H-bonding agents, are sufficient to demonstrate their effect. Although long-term cycling was not conducted, it is expected that the presence of H-bonding agents would enable stable long-term cycling. Due to limitations in both bulk and interfacial properties of the SSE, mainly arising from the DES composed of LiTFSI and NMU, and from PEGDA containing ester groups, the cathode used in this study is lithium iron phosphate. While PC is included as a plasticizer, its widely recognized electrochemical stability ensures that it does not limit performance. However, the instability of NMU at high voltages makes it incompatible with high-voltage cathodes such as lithium nickel manganese cobalt oxide (NMC) and lithium cobalt oxide (LCO). (Figure S12).

By comparing the electrochemical performance of SSE with different formulations, we can draw the following conclusions:

1. Increasing amounts of NMU:PC ratio enhance performance, but only up to an optimal ratio of 1:1. As can be seen in Figure 5b, the amount of NMU varies from a ratio of NMU: PC from 0.67 to 1.5. An SSE with a low NMU:PC ratio of 0.25 was prepared but it showed no cycling performance. At 45 °C, UB-1 has the best performance, with an initial and final specific capacity of 141.8 and 123.95 mAh g⁻¹, respectively. The baseline A-1 exhibits rapid degradation, with significant performance loss observed after just 10 cycles. With varying amounts NMU:PC, the performance varies, following the order of UB-1>UB-3/2>UB-2/3. The optimal NMU:PC ratio is 1:1, and beyond this point, further increases can deteriorate electrochemical

performance.

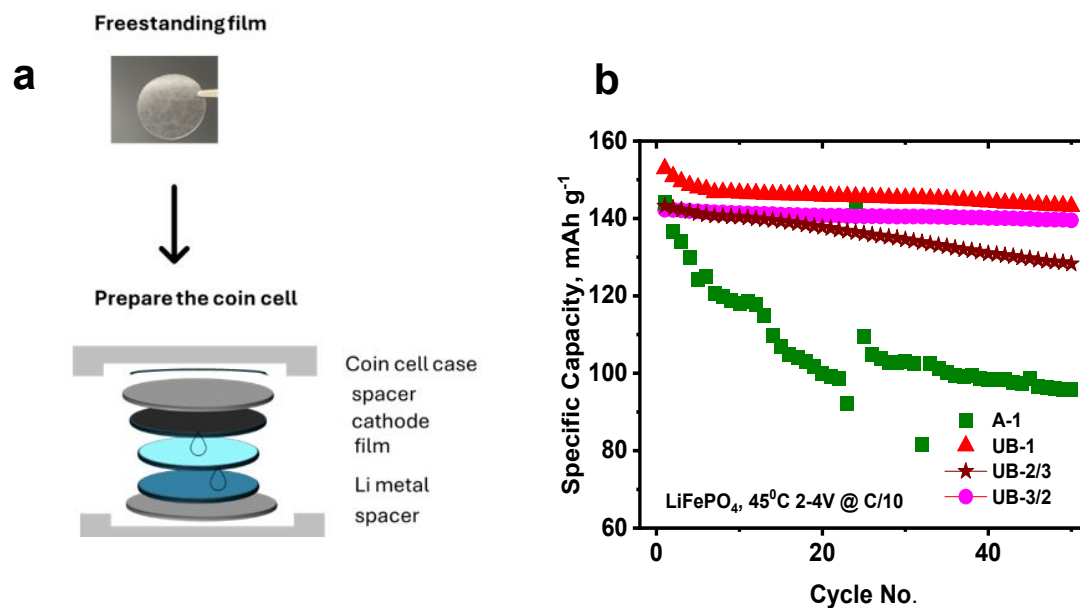


Figure 5. (a) Optical images of flexible SSE prepared by cutting with round shape cutter. (b) Specific capacity of the LFP//Li at 45 °C in the baseline A-1 and UB series with various PC:NMU amount, with a ratio of NMU: PC from 0.67 to 1.5.

2. Temperature plays a critical role on electrochemical performance, as demonstrated by comparing UB-1 and U-H-1. At 30 °C, cycling performance is maximized in UB-1, following the order: UB-1 > U-H-1, as shown in Figure 6a. However, increasing the temperature to 45 °C significantly enhances their performance, bringing it to an optimized level. Since most additives perform better at higher temperatures, a higher temperature (45 °C) was selected to test all the U series additives in the next section. Note the rate performance rate of A-1 is similar to that of UB-1. (Supplementary Information Figure S10), and the performance rank is changed as temperature increases to 45 °C (Figure 6b) to: U-H-1 > UB-1.

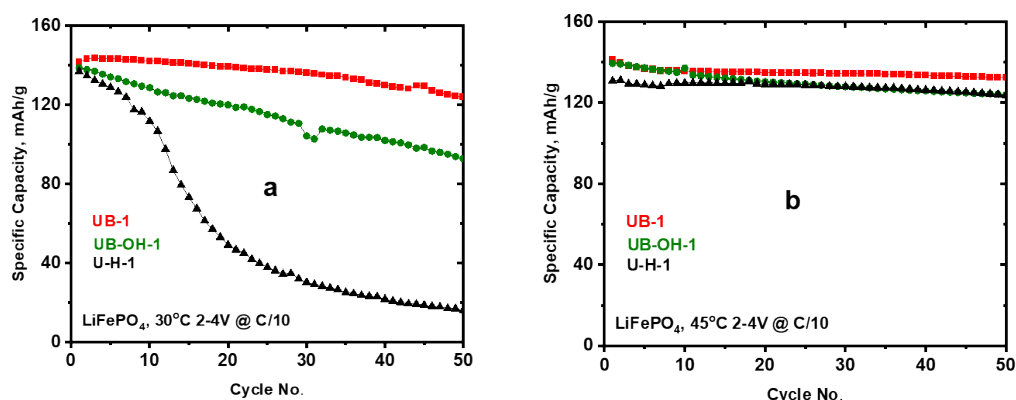


Figure 6. Specific capacity of the LFP//Li at (a) 30 °C and (b) at 45 °C in the baseline A-1 and UB-1.

3.2d Properties of SSE containing various U series additives

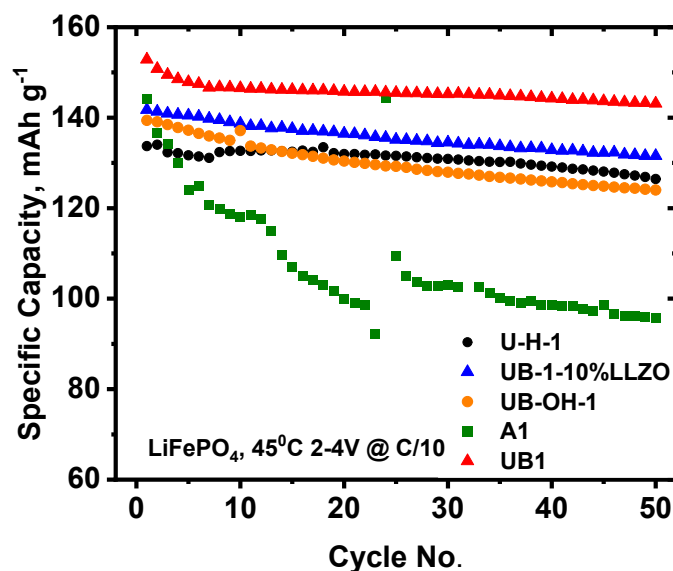


Figure 7. Cycling performance comparison LFP//Li using SSE with different additives at 45 °C.

As illustrated in Figure 7, the performance of the SSE with an LFP//Li coin cells with all the U series additives surpasses that of the baseline (A-1) at 45 °C. The moderately increased temperature enhances the performance of the batteries, offering a better visualization for comparison between the additives. When the additive is absent (as in A1), the initial capacity of LFP//Li cell comes at 144 mAh g⁻¹; however, the capacity dropped continuously and significantly to 95.7 mAh g⁻¹ over 50 cycles. With

the inclusion of any U series additive, a more stable cycling performance is achieved. Overall, UB-1 exhibits the best performance with a final specific capacity of 143.1 mAh g⁻¹. UB-OH-1 and U-H-1 exhibit similar performance, with a slightly higher final specific capacity of 126.5 mAh g⁻¹ for U-H-1, while UB-OH-1 demonstrates a slightly higher initial specific capacity.

3.2e Mechanical Properties

The interplay between mechanical strength, the resulting interface, and improved electrochemical performance has garnered significant interest in recent research.²⁸⁻³⁰ For instance, our previous research with LLZO demonstrated the critical role of interfacial and mechanical strength, highlighting the close tie between those two properties and electrochemical performance.²⁴ It is also reported that as a pure polymeric SSE example using poly(p-phenylene benzobisoxazole) nanofibers provides as a mechanically strong backbone for polyethylene oxide solid state electrolyte. Notably, the surface hardness of sample A-1 was measured at 224.2 kPa. When 0.7 wt% UB was added, the mechanical strength increases more than fourfold to 971.9 kPa (Figure 8). This substantial increase in mechanical strength underscores its pivotal role in improving electrochemical performance.

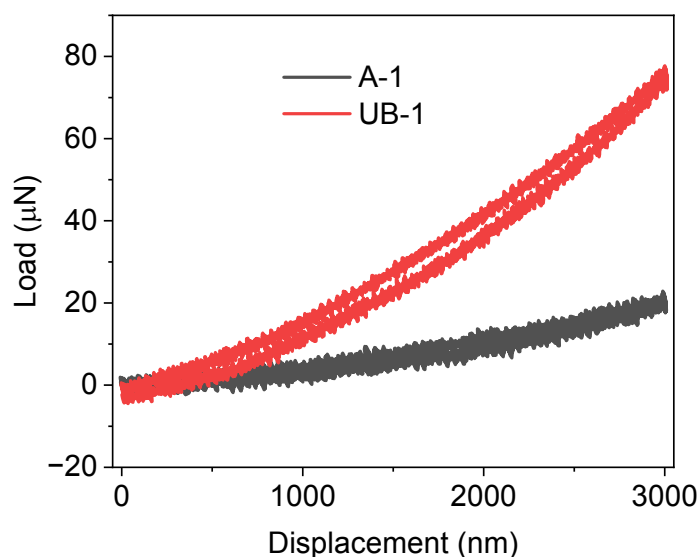


Figure 8. Nano-indentation process shows the maximum indentation load and vs. the depth at maximum load. UB-1 shows a 4-fold increase in strength than that of A-1.

Although the hardness of our SSE is not yet within the regime^{31,32} where dendrite growth can be completely suppressed by mechanical rigidity alone, (note the measurement is from nano-indentation and not Young's modulus in elasticity, but they are highly correlated), this observation also aligns with the understanding that H-bonding primarily imparts rubber-like elasticity rather than extreme stiffness. As will be discussed in the latter text, H-bonding and π - π stacking are the two dominant intermolecular interactions in our systems, and variations in the extent of H-bonding significantly influence both the physical state (e.g., gelation behavior) and mechanical strength of the material. However, the observed enhancement in electrochemical performance cannot be attributed solely to dendrite suppression by mechanical strength. Instead, it likely arises from improved interfacial contact and better supramolecular interactions within the polymer matrix.

3.3 Intermolecular Interactions

Since UB is a universally effective additive with consistently strong performance, and UB-OH is an unavoidable byproduct formed spontaneously during the synthesis of UB, specifically during the workup process involving H₂O, calculations and subsequent NMR characterizations primarily focus on UB and UB-OH. Computational utilizing computation chemistry show that intramolecular H-bonding plays a crucial role in the monomer configuration (Figure 2). Interestingly, both conformers of PU-CMe bear intramolecular H-bond and therefore are energetically equivalent, but they exhibit markedly different intermolecular interactions (Figure 9a). In the interaction of two Conf. 1 molecules, the oxygen atom of the urea scaffold in one monomer coordinates with two N-H groups of the other (Figure 9b, Conf.1), where the computed binding free energy is -0.96 eV. In U-H, the interaction between Conf. 1 and Conf. 2 features three independent H-bonds, resulting in stronger binding ($\Delta G = -1.34$ eV, Figure 9a, Conf. 1&2). Furthermore, when two Conf. 2 molecules interact, four H-bonds are formed, further enhancing the binding strength ($\Delta G = -1.73$ eV, Figure 9a, Conf. 2). Hence, PU-CMe preferentially adopts Conf. 2 upon interactions with a significantly high binding strength. The strong intermolecular interactions corroborate with the experimental observation that PU-CMe-added samples (0.7% solution mixture) exhibit gelation.

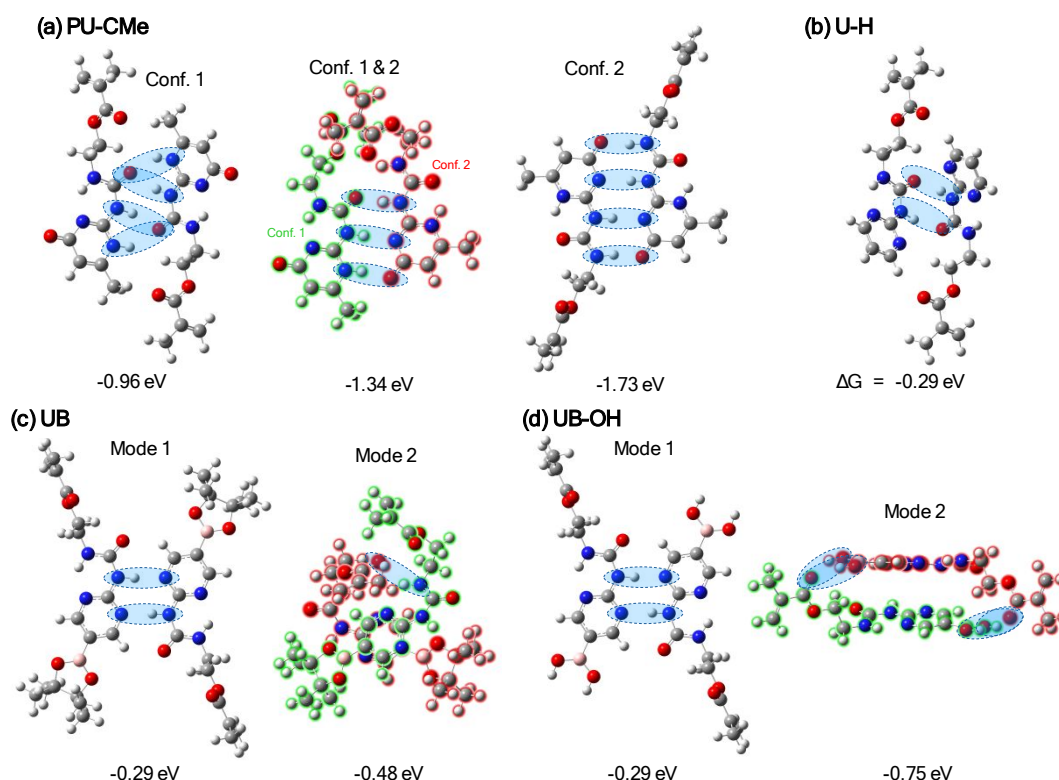


Figure 9. Molecular structures of two interacting monomers of a) PU-CMe, b) U-H, c) UB, and d) UB-OH, with corresponding interaction free energies

In comparison, the functionalization with a simple pyrimidine ring (i.e., U-H monomer) features only two intermolecular H-bonds and therefore relatively weak binding ($\Delta G = -0.29$ eV; Figure 9b). While the additional boron-functionalization on the para position of the pyrimidine ring (i.e., UB and UB-OH) does not increase the number of the H-bonds, it moderately improves intermolecular interactions by enabling π - π stacking (see mode 2 of Figure 9c, d). U-H monomers can also align to feature π - π stacking; however, in this configuration, they lose H-bonding, resulting in a weaker binding strength ($\Delta G = -0.14$ eV; structure not shown). Collectively, the computational chemistry calculations demonstrate that the functional groups in urea pyrimidine additives dictate the formation of intermolecular H-bonds and π - π interactions, thereby modulating the binding strengths as summarized in Figure 10.

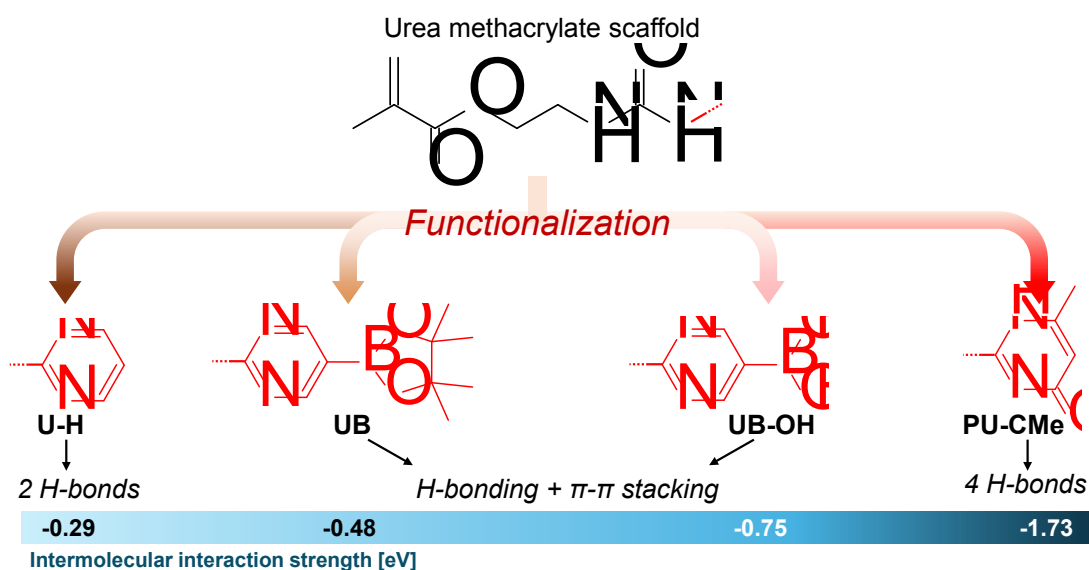


Figure 10. Summary of the role of the functionalization in their intermolecular interaction modes and corresponding interaction energies (ΔG) from DFT calculations.

From a mechanistic standpoint, H-bonding and π - π stacking are similar in function but distinct in nature; in other words, there is no trade-off between them, as they are not contradictory. Hydrogen bonds serve as molecular forces that construct supramolecular structures while preserving segmental mobility. H-bonding is also one of the strongest intermolecular interactions. In the U and PU series, even at concentrations below 1 wt%, it significantly enhances mechanical strength, as evidenced by the gelling of elastic balls, which renders solution processing followed by crosslinking into thin films impossible. In contrast, π - π stacking is weaker, approximately one-fifth the strength of hydrogen bonding, and depends on interactions between planar, delocalized π -electrons. In our system, the presence of $-\text{C}=\text{O}$, $-\text{NH}(\text{C}=\text{O})\text{NH}$, and pyrimidine units enables hydrogen bonding across all additives.

However, the presence of four hydrogen bonds introduces excessive rigidity, thereby eliminating solution processability. In contrast, π - π interactions are weaker but provide structural reinforcement without immobilizing the soft, ion-conducting phase.

Increasing either the strength/number of hydrogen bonds or the π - π content beyond the optimal range reduces free volume, which raises the transport barrier and decreases ionic conductivity even as the modulus increases. The optimum, therefore, represents a dual-network structure which supports both ion transport and with high mechanical robustness.

The effects of hydrogen bonding and π - π stacking on ionic conductivity are reflected in the ionic conductivity (Figure 3). Data on the PU series could not be collected due to their poor processability, which prevented formation of workable SSEs. The enhanced conductivity observed in the UB systems with varying compositions (e.g., UB-3/2, UB-1-B, UB-3/2, UB-1) indicates that a 0.7 wt% crosslinking agent facilitates ionic transport, by increasing the free-ion concentration, suppressing crystallinity, and connecting polar domains, thereby improving pathway continuity. Meanwhile, π - π stacking enhances conductivity by further reducing crystallinity.

Note that H-bonding enhances elastic recovery, particularly in low-molecular-weight polymers or systems with limited intrinsic elasticity. Although not required for classical rubber elasticity, reversible H-bonds act as transient physical cross-links (sacrificial bonds): they dissociate under strain to permit deformation and reform unloading to restore the network. Consequently, H-bonded polymers often exhibit increased elastomer-like behavior relative to non-H-bonded analogues, even when they are not conventional rubbers. While this supramolecular elasticity is unlikely to be the sole contributor to improved solid-state performance, experiments indicate that introducing reversible H-bonding, and the attendant internal elastomeric character, yields

significant performance gains.

DFT calculations show that among the H-bonding monomers of the U and PU series, PU-CMe exhibits the strongest intermolecular interaction at -1.73 eV, while U-H shows the weakest at -0.29 eV. The UB and UB-OH systems achieve an optimal balance of hydrogen bonding and π - π stacking, with interaction energies ranging from -0.48 to -0.75 eV. Due to its relative weakness, π - π stacking does not induce gelling, maintaining processability while still strengthening intermolecular interactions to achieve optimal mechanical performance.

Experimentally, the UB system exhibited the most significant improvement in cell performance (Figure 7), reflecting contributions from both enhanced mechanical properties and interfacial strengthening (Figure 6, Section 3.1). As demonstrated by the physical and processability changes observed upon adding only 0.7 wt% of PU and PU-CMe, where the solution gelled, the small number of H-bonding agents is sufficient to significantly alter the material properties. This is further supported by hardness and electrochemical tests, indicating that the inclusion of these H-bonding components is the primary factor driving the observed changes, which predominantly affect mechanical properties and interfacial behavior.

3.4 NMR

To investigate how modifications of the aforementioned intra- and intermolecular hydrogen-bonding network influenced transport in polymer membranes, diffusion behaviors of Li^+ and TFSI^- were measured using ^7Li and ^{19}F pulsed-field gradient (PFG) NMR at various diffusion times and temperatures. As shown in Figure 11a-c, the

diffusion coefficients of Li^+ ($D(\text{Li}^+)$) and TFSI^- ($D(\text{TFSI}^-)$) decrease significantly when the diffusion time (Δ) increases from 7 ms to 100 ms, then gradually reach a plateau as Δ increases further to 480 ms. This behavior suggests that ions experience restricted diffusion in all the free-standing films of the three solid state electrolytes of A-1, UB-1, and UB-OH-1.

The root-mean-square displacement, d_{rms} , can be estimated directly from the effective diffusion coefficient D_{eff} at Δ :

$$d_{rms} = \sqrt{\langle (r(\Delta) - r(0))^2 \rangle} = \sqrt{6D_{\text{eff}}\Delta}$$

When d_{rms} is plotted against Δ (Figure 11 d-e), it is clear that all membranes exhibit a confining environment with an effective domain size of 1.0 – 2.0 μm at all tested temperatures. This micrometer-scale confinement may be attributed to the crosslinked framework present in each membrane. As Δ increases, ions collide more frequently with the confinement boundaries and eventually diffuse beyond these domains into interconnected regions, which explains the increasing d_{rms} vs Δ and the plateauing of $D(\text{Li}^+)$ and $D(\text{TFSI}^-)$. Despite this micrometer-scale confinement, Li^+ and TFSI^- ultimately traverse the entire membrane at the plateau diffusion coefficients as $\Delta \rightarrow \infty$. Furthermore, after fitting temperature dependence of $D(\text{Li}^+, \Delta \rightarrow \infty)$ and $D(\text{TFSI}^-, \Delta \rightarrow \infty)$ to the Arrhenius equation: $D(\Delta \rightarrow \infty) = D_0 \exp(E_a/RT)$, the activation barrier E_a for Li^+ and TFSI^- diffusion are estimated to be 38 ± 1 and 45 ± 3 kJ/mol, respectively, for all three tested membranes.

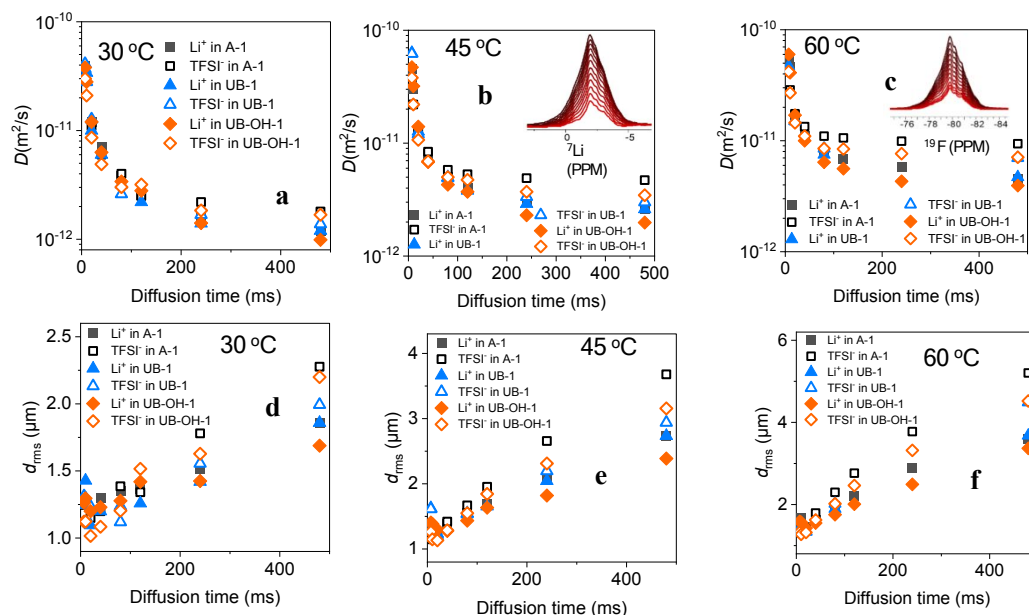


Figure 11. Restricted ion diffusion within the polymer membranes revealed by PFG-NMR. Measured diffusion coefficients (a-c) and estimated diffusion lengths (d-f) of Li⁺ and TFSI⁻ within the membranes as a function of diffusion time, at 30 °C (a and d), 45 °C (b and e), and 60 °C (c and f). The insets in (b) and (c) show examples of ⁷Li and ¹⁹F NMR spectra during PFG measurements.

When comparing the three polymers between 30 °C and 60 °C, we observe that $D(\text{TFSI}^-)$, $\Delta \rightarrow \infty$) decreases by ~5 – 30% from A-1 to UB-1 and UB-OH1. Meanwhile, $D(\text{Li}^+)$, $\Delta \rightarrow \infty$) in UB-OH-1 decreases by 10 – 20% relative to A-1, but in UB-1 it remains comparable to or slightly higher than that of A-1. Despite the remarkable improvements in the mechanical strength provided by UB-1 and UB-OH-1, the relatively minor reductions in ion diffusion – particularly the unaltered Li diffusion in UB-1 – suggest that the enhanced hydrogen-bonding network does not substantially impede ion transport, especially for Li⁺.

4. Conclusion

In conclusion, the development of boron-substituted urea pyridine (U) monomers has demonstrated significant advancements as SSE for LFP based lithium ion batteries. By optimizing H-bonding through the “Goldilocks Rule”, which identifies two

hydrogen bonds as optimal, the U series monomers enhance both mechanical and electrochemical properties of SSEs. More significantly, the reduction from four to two hydrogen bonds from the PU to U series results in improved processability and mechanical strength, addressing key challenges in scaling up solid-state battery technology. The incorporation of boronic acid pinacol ester structures further enhances interfacial stability, contributing to better cycle life and electrochemical performance. Combined computational and experimental results confirm that these structural modifications lead to a more robust H-bonding network without significantly impeding ion transport, particularly for lithium ions. This research marks a significant step toward the practical and scalable manufacturing of ASSB.

CRedit authorship contribution statement.

Bingning Wang: Data collection and analysis, Writing - review & editing. **Yan Qin:** Experiment design, Data collection and analysis, Writing - review & editing. **Ying Chen:** Data collection and analysis, Writing – original draft & editing **Sungil Hong:** Data collection and analysis, Writing – original draft & editing. **Lihong Gao:** Experiment design, Writing - review & editing. **Andrew Jansen:** Funding, Writing - review & editing. **Rajeev Surendran Assary:** Writing - review & editing. **Kin Lung See Tho:** Writing - review & editing. **Jiyu Cai:** Data collection and analysis, Writing - review & editing. **Zonghai Chen:** Writing - review & editing. **Yang Qin:** Writing - review & editing **Zhengcheng Zhang:** Funding, Writing - review & editing **Wenquan Lu:** Supervision, Writing - review & editing. **Chen Liao:** Experiment design, Supervision, Conceptualization, Funding, Writing - original draft, Writing - review &

editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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