High-Performance Polymer Ion Conductors Enabled by Decoupled Fast Ions in Molecular Channels

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High-Performance Polymer Ion Conductors Enabled by Decoupled Fast Ions in Molecular Channels

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Abstract:

While solid-state batteries are tantalizing for achieving improved safety and higher energy density, solid ion conductors currently available fail to satisfy the rigorous requirements for battery electrolytes and electrodes. Inorganic ion conductors allow fast ion transport, but their rigid and brittle nature prevents good interfacial contact and impedes device integration and stability. Conversely, flexible polymeric ion conductors provide better interfacial compatibility and mechanical tolerance, but suffer from inferior ionic conductivity ($< 10^{-5} \text{ S cm}^{-1}$ at room temperature) due to the coupling of ion transport with the polymer chain motion¹⁻³. In this work, we report a general design strategy for achieving one-dimensional (1D), high-performance polymer solid-state ion conductors through molecular channel engineering, which we demonstrate via Cu^{2+} -coordination of cellulose nanofibrils. The cellulose nanofibrils by themselves are not ionic conductive; however, by opening the molecular channels between the cellulose chains through Cu^{2+} coordination we are able to achieve a Li-ion conductivity as high as $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature—a record among all known polymer ion conductors. This improved conductivity is enabled by a unique Li^+ hopping mechanism that is decoupled from the polymer segmental motion. Also benefitted from such decoupling, the cellulose-based ion conductor demonstrates multiple advantages, including a high transference number (0.78 vs. 0.2–0.5 in other polymers²), low activation energy (0.19 eV), and a wide electrochemical stability window (4.5 V) that accommodate both Li metal anode and high-voltage cathodes. Furthermore, we demonstrate this 1D ion conductor not only as a thin, high-conductivity solid-state electrolyte but also as an effective ion-conducting additive for the solid cathode, providing continuous ion transport pathways with a low percolation threshold, which allowed us to utilize the thickest LiFePO_4 solid-state cathode ever reported for high energy density. This approach has been validated with other

49 polymers and cations (e.g., Na⁺ and Zn²⁺) with record-high conductivities, offering a universal
50 strategy for fast single-ion transport in polymer matrices, with significance that could go far
51 beyond safe, high-performance solid-state batteries.

52 **Keywords:** Nanocellulose, Ion coordination, Polymer electrolyte, Super ion conductor, Solid-state
53 batteries

54 **One Sentence Summary:** A four-decade-long challenge of low ionic conductivity in polymer
55 electrolytes is overcome by engineering fast ion-conduction channels between polymer chains.

Introduction

Solid-state batteries are attractive for next-generation energy-storage systems with high energy density and safety, but the realization of these promises depends largely on the development of superior ion conductors as the solid-state electrolyte as well as additives for ion-insulating cathode materials. Recent advances in inorganic solid electrolytes based on ceramic materials have achieved fast ion transport, but their rigidity and brittleness present new challenges for battery integration and stability. Solid polymer electrolytes (SPEs) are a promising alternative due to their mechanical flexibility and facile processability compared with inorganic solid-state electrolytes⁴⁻⁶. However, Li ion (Li^+) transport in SPEs, which are typically ether-based represented by poly(ethylene oxide) (PEO)^{3,7}, is highly coupled with the segmental relaxation of the polymer chains, resulting in limited ionic conductivity (σ) (generally $<10^{-5} \text{ S cm}^{-1}$ at room temperature²) and low Li^+ transference numbers (0.2–0.5 in most SPEs)^{8,9}.

Recent studies have generally focused on improving the ionic conductivity of SPEs by increasing the mobile Li^+ concentration (n) or mobility (μ), given that $\sigma = en\mu$ (e : elementary charge). However, the concentration of mobile Li^+ is limited by the low solubility of salts in polymers^{10,11}. To improve the Li^+ mobility, a common practice is to increase the temperature of SPEs, even above their melting point (e.g., $\sim 60^\circ\text{C}$ for PEO), to promote the polymer segmental motion for faster ion movement. But increasing the temperature deteriorates the mechanical strength of the SPE and compromises the safety of the battery. Other efforts to improve the Li^+ conductivity and transference number include modifying the polymer matrix with crosslinked polymers¹²⁻¹⁴, block copolymers¹⁵, single-ion-conducting polymers¹⁶, and the addition of inorganic fillers^{7,17,18}. Despite these approaches, the tradeoff between the ion conduction, transference number, and mechanical strength in SPEs has persisted for over four decades, with the room-

temperature ionic conductivity barely approaching a ceiling value of 10^{-4} S cm⁻¹, mainly because the Li⁺ movement has remained coupled to the polymer segmental motion. Additionally, SPEs feature poor ionic percolation when used as additives to improve the ionic conductivity in cathode materials, requiring a threshold content of ~25 wt% SPE^{19,20}, which further reduces the energy density of the battery. Clearly, the conventional SPE structure and Li⁺ transport mechanism must be drastically transformed in order to meet future energy storage needs.

In this work, we explore a new SPE design strategy based on expanding the inter-molecular polymer structure and decoupling the Li⁺ transport from the polymer segmental relaxation to produce polymer ion conductors with record-high ionic conductivity. We first demonstrate this approach using cellulose nanofibrils (CNFs). CNFs are abundantly available from various biomass sources (e.g., wood, bamboo, grass, etc.) and feature an aligned, one-dimensional (1D) hierarchical structure rich in oxygen-containing polar functional groups (e.g., hydroxyl) in the form of repeating anhydroglucose units (AGUs) that make up the cellulose molecular chains (Fig. 1a)²¹⁻²³. Such polar functionalities could solvate Li⁺ and aid in its fast movement. Through Cu²⁺-coordination of the CNFs (Cu-CNF) via a scalable solvent exchange process, we show the spacing between the polymer chains can be expanded into molecular channels that enable rapid Li⁺ transport (Fig. 1a). In such 1D conduction passages, the abundant oxygen-containing functional groups of cellulose, along with bound water, assist in the Li⁺ movement in a manner independent of the polymeric segmental relaxation. As a result, the Li⁺-intercalated Cu-CNF (Li-Cu-CNF) ion conductor features a high ionic conductivity of 1.5×10^{-3} S cm⁻¹ (10–1000-times that of other SPEs) and a high transference number of 0.78 at room temperature (Fig. 1b). Furthermore, the amorphous Li-Cu-CNF ion conductor demonstrates extremely low activation energy of 0.19 eV, compared to ~1 eV for PEO³ and ~0.6 eV for PEO-inorganic composites⁷, allowing utilization at

102 room temperature as well as a wide electrochemical stability window (0–4.5 V vs. Li^+/Li), on top
103 of the material's fundamental low cost, scalability, and flexibility (Fig. 1c). In addition to serving
104 as a thin and dense solid-state electrolyte film, the 1D structure of Li-Cu-CNF also makes it an
105 effective ion-conducting additive for composite solid-state electrodes where low ionic
106 conductivity has been a key hurdle. Indeed, the effective ionic percolation of Li-Cu-CNF allowed
107 us to fabricate the thickest LiFePO_4 solid-state cathode ever reported, suggesting the material's
108 potential as an additive for increasing battery energy density. This design principle based on facile
109 coordination chemistry and expansion of the polymer molecular channels to provide fast diffusion
110 pathways for uncoupled Li^+ can be applied to other polymers and cations, enabling the
111 development of highly conductive solid-state ion conductors that may go far beyond high-energy-
112 density and safe all-solid-state batteries.

Fig. 1 | The structure and performance of the Li-Cu-CNF solid-state ion conductor. a,
Schematic illustration of the hierarchical structure of CNFs, which are derived from wood
cellulose fibers and are composed of elementary fibrils, each of which is comprised of individual

cellulose molecular chains. Cu-ion coordination with the hydroxyl groups of cellulose opens the spacing between molecular chains, creating cellulose molecular channels in the CNFs that serve as Li^+ conducting pathways in the resulting Li-Cu-CNF ion conductor. The scanning electron microscopy (SEM) image shows the morphology of the CNFs, which are naturally aligned in the cellulose fibers. **b**, A plot of the transference number and ionic conductivity of Li-Cu-CNF and other SPEs^{13,14,17,24}. **c**, A digital photo of a 1-meter long Li-Cu-CNF roll.

We fabricated the solid-state Li-Cu-CNF ion conductor using a simple ion-coordination and solvent-exchange process. The CNFs, obtained by oxidization of commercial wood pulp, were first immersed in Cu^{2+} -saturated alkaline solution (20% NaOH), where gradual Cu-ion coordination with the cellulose molecular chains occurs, forming a blue-colored Cu-CNF-NaOH complex material filled with NaOH solution (Fig. 2a). After washing the NaOH from Cu-CNF-NaOH with water, displacing the water with dimethylformamide (DMF), and finally evaporating the DMF under vacuum, we obtained the solid-state Cu-CNF material. Li^+ was then intercalated into the Cu-CNF by soaking in LiPF_6 electrolyte and subsequently evaporating the solvent, producing the polymeric Li-Cu-CNF ion conductor (Fig. 2a).

We applied fiber X-ray diffraction (XRD, Fig. 2b-e and Extended Data Fig. 1a-d) and X-ray absorption spectroscopy (XAS, Extended Data Fig. 1e-h) to track the structural evolution during the fabrication process. Additionally, we constructed the material structures by molecular dynamics (MD) simulations (details in Methods and Extended Data Fig. 2) based on the fiber XRD results. The pristine CNFs featured a typical monoclinic diffraction pattern of cellulose I_β , with diffraction peaks at (110), (200), etc. (Fig. 2b), showing a cellulose molecular spacing (d_{200}) of 0.39 nm²⁵. The corresponding simulation of the crystalline CNF (Fig. 2c) suggests the material cannot accommodate the intercalation of Li^+ between the inter-molecular spacing due to the

140 closely packed cellulose chains. In contrast, the Cu-CNF-NaOH obtained from the Cu^{2+} -saturated
141 alkaline solution featured a hexagonal crystal structure, with threefold symmetry along the
142 cellulose chain direction (Fig. 2d), consistent with the crystal structure of alkaline-cellulose-Cu
143 reported in the literature²⁶. In the simulated structure of the Cu-CNF-NaOH (Fig. 2e), each
144 cellulose chain has three neighboring chains with an inter-chain distance of 0.87 nm, which are
145 bridged by Cu^{2+} via four coordinated Cu-O bonds, opening the close molecular packing of the
146 CNFs. We note the spaces between the less densely packed cellulose chains of Cu-CNF-NaOH
147 are filled with NaOH aqueous solution. After NaOH removal and water displacement by DMF,
148 the crystalline Cu-CNF-NaOH becomes amorphous Cu-CNF (Fig. 2f, 2g). Such amorphous
149 structure has a much lower cellulose packing density (4.7 AGU/nm^3 , Fig. 2g) than the pristine
150 CNF material (6.1 AGU/nm^3 , Fig. 2c), with the molecular channels open for Li^+ intercalation. The
151 final Li-Cu-CNF structure with Li^+ intercalated maintains the amorphous state (Fig. 2h) with a low
152 packing density (4.4 AGU/nm^3 , Fig. 2i). These XRD and simulations results are also consistent
153 with the XAS data (Extended Data Fig. 1e–h), which confirm that in the amorphous Cu-CNF and
154 Li-Cu-CNF materials the Cu^{2+} ions are bonded with O atoms, with an average bonding distance of
155 $1.97 \text{ \AA}$.

156 Interestingly, thermogravimetric analysis (TGA, Extended Data Fig. 3a) shows the pristine
157 CNF and Li-Cu-CNF contain the same amount of water ($\sim 6 \text{ wt\%}$), which is bound to the cellulose
158 molecules through multiple hydrogen bonding according to the Fourier-transform infrared spectra
159 (FTIR, Extended Data Fig. 3b, 3c). Quasi-elastic neutron scattering (QENS, Extended Data Fig.
160 3d, 3e) experiments also confirm the absence of free water or solvent in the Li-Cu-CNF. We also
161 note the solid 1D Li-Cu-CNF material features high tensile stress of 29.2 MPa , among the strongest
162 SPEs (Extended Data Fig. 3f), possibly due to its amorphous nature.

Fig. 2 | Structural evolution during the synthesis of Li-Cu-CNF. **a**, Digital images showing the fabrication process of Li-Cu-CNF, during which the CNF starting material was immersed in Cu²⁺ alkaline solution to produce Cu-CNF-NaOH. The aqueous solution in Cu-CNF-NaOH was then displaced with DMF to obtain Cu-CNF, and finally exchanged with LiPF₆ organic electrolyte for Li⁺ intercalation and then dried to form Li-Cu-CNF. The fiber XRD patterns (middle row) and simulated structures (bottom row) of **b** and **c**, the pristine CNFs showing cellulose I_β structure; **d** and **e**, Cu-CNF-NaOH, with coordinated cellulose chains packed in a hexagonal unit cell consistent with the literature²⁶; **f** and **g**, Cu-CNF, in a largely amorphous state; and **h** and **i**, Li-Cu-CNF, which features an amorphous structure (with some weak diffraction signals of cellulose II²⁵). The white arrows in the fiber XRD patterns indicate the fiber direction. Different cellulose chains in the simulated structures are denoted by different colors.

The amorphous Li-Cu-CNF material, featuring 1D cellulose molecular chains opened by Cu²⁺ coordination, serves as an excellent Li⁺ conductor. At 25 °C, Li-Cu-CNF has a high Li⁺ conductivity of $1.5 \times 10^{-3} \text{ S cm}^{-1}$ along the cellulose molecular chain direction (measured by galvanostatic cycling and electrochemical impedance spectroscopy (EIS), Extended Data Fig. 4a-d), which is higher by orders of magnitude compared to that of all known SPEs, including PEO-inorganic composites⁷, crosslinked polymers^{12,13}, single-ion-conducting polymers^{15,16}, and high Li concentration electrolytes²⁴ (Fig. 3a). Such high ionic conductivity along with the observed high mechanical strength (Extended Data Fig. 3f) strongly suggests the ion transport is completely decoupled from the polymer segmental relaxation. Additionally, the temperature dependence of the ionic conduction in Li-Cu-CNF follows an Arrhenius-like behavior (i.e., linear conductivity vs. $1/T$) (Fig. 3a), which typically reflects an ion hopping mechanism through crystalline or ordered matrices, and is distinctly different from the so-called Vogel-Tammann-Fulcher-like behavior observed for ion transport in other amorphous materials, such as SPEs, gel polymer electrolytes (GPEs), and liquid electrolytes^{1,27}. According to the Arrhenius equation, the activation energy of Li-Cu-CNF is 0.19 eV, which is much lower compared with PEO (~1 eV)³ and PEO-inorganic composite electrolytes (~0.6 eV)⁷. In addition, the Li-Cu-CNF shows a high Li⁺ transference number of 0.78 (measured by the Bruce-Vincent method²⁸, Extended Data Fig. 4e, 4f), which is much higher than that of other SPEs (0.2–0.5, Fig. 1b), except single-Li-ion conducting polymers^{15,16} (close to 1.0, although achieved at the impractical expense of the ionic conductivity at room temperature). As a control experiment, we synthesized Li-CNF using the same procedure shown in Fig. 2a but in absence of Cu-ion coordination, and found it displayed a Li⁺ conductivity of just $7 \times 10^{-7} \text{ S cm}^{-1}$ at 25 °C (Fig. 3a) and a low transference number of 0.35 (Extended Data Fig. 4g–i), confirming the indispensable role of Cu²⁺ in promoting Li⁺-transport.

We also note the Cu^{2+} coordinated in Li-Cu-CNF contribute negligible ionic conductivity (5×10^{-7} S cm^{-1} , Extended Data Fig. 4j, 4k) but are critical for maintaining the open cellulose molecular spacing necessary for the high Li^+ conductivity.

Fig. 3b compares the ionic conductivity of Li-Cu-CNF with other types of solid-state electrolytes. Li-Cu-CNF offers a similar ionic conductivity ($\sim 10^{-3}$ S cm^{-1}) as oxide-based electrolytes (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)) but at much lower Li concentration (1.2 mol L^{-1} in Li-Cu-CNF vs. 41.3 mol L^{-1} in LLZO²⁹), which is preferential for lower cost. Such Li concentration is similar to PEO ($\sim 1.1 \text{ mol L}^{-1}$)²⁹, but Li-Cu-CNF features a ~ 500 -times higher Li^+ diffusion coefficient ($D_{\text{Li}} = 6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, as measured by pulse field gradient NMR) and over two-times the cation transference number. Thus, we attribute the high ionic conductivity of Li-Cu-CNF entirely to the high-mobility of the Li^+ in the material due to the opening of the cellulose molecular channels.

The Li^+ in the Li-Cu-CNF molecular channels can form multiple Li-O coordination bonds that are critical for the Li^+ migration, as we demonstrate via NMR and simulations. We used solid-state ^6Li NMR to probe the local environment of Li^+ (Extended Data Fig. 5a-d), which revealed the Li^+ -mobility in the Li-Cu-CNF molecular channels derives from multiple Li-O coordination bonds. In Li-Cu-CNF, the Li^+ are mainly bonded to the rich oxygen-containing functional groups of cellulose, including hydroxyl (ROH), carboxyl (COO), alkoxy (RO), and ether (EO) moieties, as well as bound water and some residual LiPF_6 (schematically shown in Fig. 3c). Chemically, the molar ratio of Cu:Li:AGU is approximately 1:6:18 based on the inductively coupled plasma (ICP) analysis of the contents of Li^+ (1.3 wt%) and Cu^+ (1.9 wt%) in the Li-Cu-CNF, which indicates the number of oxygen atoms is ~ 20 -times the number of Li^+ . Compared with Li-CNF, the Li-Cu-CNF material shows a drastically increased number of Li^+ coordinated with oxygen atoms

(RO $\cdots$ Li, COO $\cdots$ Li, and ROH/H₂O $\cdots$ Li) (Fig. 3d), further suggesting the Li⁺ is intercalated in the opened molecular channels of Li-Cu-CNF where more Li-O coordination can occur. To further investigate the Li⁺ transport pathways, we performed ⁶Li tracer-exchange NMR, which is a combination of ⁶Li isotope replacement of ⁷Li and high-resolution solid-state ⁶Li NMR (Extended Data Fig. 5e-g)³⁰. We electrochemically cycled the Li-Cu-CNF electrolyte (natural abundance: 92.4 % ⁷Li and 7.6 % ⁶Li) between two ⁶Li-rich metal electrodes, during which the ⁶Li⁺ from the electrodes partially replaced ⁷Li⁺ in the ion diffusion pathway of the electrolyte. After the ⁶Li tracer exchange, the number of ⁶Li⁺ coordinated with COO⁻, RO⁻, and ROH/H₂O in Li-Cu-CNF increased by 15-, 20-, and 25-times, respectively, compared to Li-Cu-CNF prior to cycling (Fig. 3e), suggesting that the Li⁺ coordinated with these oxygen-containing functional groups are not “dead Li⁺”, but remain active to diffusion and migration.

MD simulations further revealed that in Li-Cu-CNF each Li⁺ is coordinated with 4.5 oxygen atoms on average, a number much larger than that in Li-CNF (3.0) (Fig. 3f). The relatively low coordination number in the closely packed Li-CNF is due to the spatially forbidden of Li⁺ to access these oxygens within the cellulose channels. Hence the Li⁺ can only absorb on the external surface of the CNFs (Extended Data Fig. 6), whereas in Li-Cu-CNF, intercalated Li⁺ are fully coordinated by the rich oxygen groups in the open cellulose channels (Fig. 2i). DFT calculations (Extended Data Fig. 2a and 2b) demonstrate the importance of coordination number for Li⁺-mobility: if Li⁺ is coordinated with just 1 or 2 anionic oxygen species, the Li-O binding energy (2.9–5.5 eV) is prohibitively high for Li-O dissociation; whereas the Li⁺ migration energy barrier can be significantly reduced (~0.3 eV) if a 5-oxygen-coordinated Li⁺ moves in inorganic materials, because this Li⁺ can dissociate from just 1–2 bonded oxygen atoms while still coordinating with other nearby oxygen groups³⁴. The simulated activation energy barrier for Li-Cu-CNF is 0.31 eV,

which is as low as that in inorganic materials (~ 0.3 eV)³⁴, suggesting the Li^+ transport in Li-Cu-CNF is likely following the similar mechanism in inorganic ion conductors. Therefore, these abundant oxygen atoms in the open molecular channels effectively stabilize the Li^+ during its partial dissociation for transport.

We employed MD simulations to further understand the Li^+ transport mechanism in Li-Cu-CNF. A fast-moving Li^+ travels across the AGUs along or between the cellulose molecular chains with a displacement of 18.8 Å in 5.0 ns, while the cellulose backbone moves little (Fig. 3g). The counter-anions (COO^- and RO^-) in the cellulose backbone move much less than the Li^+ , as indicated by their small mean square displacements (MSD, Extended Data Fig. 7a), resulting in a high transference number (0.80 by simulation, close to the experimental value 0.78). The MSD plots for additional Li^+ (Extended Data Fig. 7b) further indicate Li^+ hopping between COO^- and RO^- sites in Li-Cu-CNF, instead of moving with its local solvation cage formed by the polymer chain segment. This represents a typical “structural diffusion” behavior, i.e., the Li^+ moves independent from its local solvation environment³¹. Due to the abundance of COO^- and RO^- groups in Li-Cu-CNF, the average distance between these functionalities provides a Li^+ hopping distance of ~ 3.0 Å (Extended Data Fig. 7c), which is close to the hopping distance in fast inorganic ion conductors, such as $\text{Li}_{1.33}\text{Ti}_{1.67}\text{Al}_{0.33}(\text{PO}_4)_3$, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, and LLZO ³². Thus, the rich oxygen groups in Li-Cu-CNF (COO^- , RO^- , etc.) are likely to form a continuous hopping pathway that enables high Li^+ mobility independent of the polymer chain motion.

MD simulations also reveal the critical importance of H_2O molecules for the fast Li^+ movement. We found the fast-moving Li^+ in the system are coordinated with more water molecules (1.6), as compared with the slower moving Li^+ (0.7), despite the fact that all of them have almost the same total Li-O coordination number (~ 4.5) (Fig. 3h). This difference strongly suggests that

the fast-moving H₂O molecules, as indicated by the large MSD (Extended Data Fig. 7d) and high diffusion coefficient ($D_{\text{H}} = 9.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ vs. $D_{\text{Li}} = 6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ by NMR), effectively assist the Li⁺ transport, possibly by knocking the Li⁺ out of the coordination sites (i.e., the COO⁻, RO⁻, EO, and ROH groups of cellulose) for fast Li⁺ diffusion. Indeed, we see a dramatic increase in the Li⁺ displacement and diffusivity for Li-Cu-CNF featuring bound water molecules compared to Li-Cu-CNF without water and Li-CNF (Fig. 3i). Thus, the unprecedentedly high ionic conductivity in Li-Cu-CNF can be attributed to the decoupled Li⁺ hopping mechanism, which is jointly enabled by the open cellulose molecular channels, local environment rich in Li-O coordination, and the assistance of bound water molecules.

Upon closer examination of the bound water molecules in Li-Cu-CNF, we found that they do not exist as a condensed liquid phase, which contains electrochemically active species like H⁺, H₃O⁺, and OH⁻, but instead are isolated neutral H₂O molecules bound with the cellulose framework (Extended Data Fig. 7e). Such isolated water molecules would differ from bulk water molecules chemically and electrochemically. For example, they do not readily gain or lose electrons and are thus electrochemically stable³³. We confirmed the electrochemical stability by DFT calculations (Extended Data Fig. 8), which predict the Li-Cu-CNF with bound water molecules has a wide electrochemical stability window that is comparable to ethylene carbonate, a typical electrolyte solvent used in commercial lithium-ion batteries. Additionally, the linear sweep voltammogram shows the Li-Cu-CNF features a wide electrochemical stability window of 0–4.5 V vs. Li⁺/Li (Fig. 3j), which would allow for the reversible operation of the Li metal anode and high-voltage cathodes needed for high-energy-density solid-state batteries.

Fig. 3 | Li⁺ conductivity and transport mechanism in Li-Cu-CNF. **a**, The temperature-dependent conductivity of Li-Cu-CNF and Li-CNF (without Cu²⁺ coordination) and linear fitting according to the Arrhenius equation, the slope of which indicates the activation energy. The temperature-dependent conductivity plots (i–ix) of typical SPEs are included for comparison (i¹², ii–iv⁷, v¹⁵, vi¹³, vii²⁴, viii¹⁶, ix³). **b**, Comparison of the Li⁺ diffusion coefficient and Li⁺

294 concentration of Li-Cu-CNF with other solid-state electrolytes (PEO and LLZO). **c**, Schematic of
 295 the chemical environment of Li^+ in the Li-Cu-CNF system with different types of oxygen atoms.
 296 The C, H, O, Cu, and Li atoms are denoted by grey, white, red, blue, and purple spheres,
 297 respectively. The hydrogen atoms that are bonded with carbon are not shown for clarity. **d**, Relative
 298 ^6Li number in different Li chemical environments in Li-CNF and Li-Cu-CNF, derived from NMR
 299 (Extended Data Fig. 5) by normalizing the mass-specific ^6Li number in Li-Cu-CNF to 100%. **e**,
 300 Relative ^6Li number for different Li chemical environments in the Li-Cu-CNF before and after
 301 $^6\text{Li} \rightarrow ^7\text{Li}$ tracer exchange. **f**, The average Li-O coordination numbers from MD simulations for Li-
 302 CNF and Li-Cu-CNF. **g**, Structural snapshots from MD simulations of a fast-moving Li^+
 303 transporting in Li-Cu-CNF for 5 ns. **h**, The coordination numbers of Li^+ coordinating with all
 304 available oxygen atoms (Li-O, including the oxygen atoms in cellulose and bound water
 305 molecules) and just water molecules (Li-H₂O) in Li-Cu-CNF for the 6 fastest and 6 slowest Li^+
 306 ions in the Li-Cu-CNF model. **i**, MSD plots for the Li-Cu-CNF systems with/without water
 307 molecules and the Li-CNF system with water molecules on the surface of the CNFs. **j**,
 308 Electrochemical stability window of the Li-Cu-CNF measured by linear sweep voltammogram
 309 from 0 V to 5.5 V (vs. Li^+/Li) at 0.1 mV s^{-1} .

The 1D, nanoscale Li-Cu-CNF ion conductor can be applied as both an independent solid-state electrolyte when densely packaged into a freestanding film and an effective ion-conducting additive for constructing continuous Li^+ transport networks in electrodes, which is particularly important for high energy density cathode materials that feature intrinsically low ionic conductivity, such as LiFePO_4 and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$. Both functions (electrolyte and additive) are crucial for building high-performance all-solid-state batteries (Fig. 4a). We first demonstrated the Li-Cu-CNF can be assembled and pressed into a thin ($\sim 50\text{ }\mu\text{m}$) yet dense film with three-dimensionally, randomly distributed nanofibrils (Fig. 4b and Extended Data Fig. 9a, 9b) to form a solid-state film electrolyte with low resistance (Extended Data Fig. 9c). The Li-Cu-CNF film electrolyte shows a through-plane ionic conductivity of $3.4 \times 10^{-4}\text{ S cm}^{-1}$ at room temperature (Extended Data Fig. 9d), still much higher than other SPEs reported in the literature^{3,7,12,13,15,16,19,24}. Additionally, the dense and highly conductive Li-Cu-CNF film electrolyte enables stable Li cycling performance at 0.5 mA cm^{-2} for 400 h in a Li metal symmetric cell without dendrite-induced short-circuiting (Extended Data Fig. 9e).

The individual Li-Cu-CNF fibrils were also applied as an effective ion-conducting additive for battery electrodes. To overcome low ionic conductivity, a general approach in fabricating solid-state electrodes has involved blending the material with flammable liquid electrolytes or using a significant amount of polymer electrolyte (e.g., 25–30 wt% PEO/LiTFSI^{19,20}) due to the poor ionic percolation of bulk polymers, which inevitably drives down the energy density of the battery. As an alternative, Li-Cu-CNF has the following advantages as an ion-conducting additive, including: (1) the high aspect ratio (~ 200) of the CNFs, which should enable a low percolation threshold³⁴; (2) compatibility with the traditional slurry-casting method for scalable electrode manufacturing; and (3) the ability to serve as both an ionic conductor and polymer binder for fabricating thick

electrodes with good mechanical integrity. As a proof-of-concept, we selected LiFePO₄ as a cathode material to demonstrate the incorporation of Li-Cu-CNF as a 1D additive to form an ion percolation network within the solid-state cathode (Fig. 4c). The resulting cathode featured a percolation threshold of 15 vol% (Fig. 4d), which corresponds to < 5 wt% of the Li-Cu-CNF additive in the composite. Moreover, the use of the Li-Cu-CNF ion-conducting additive is compatible with the traditional slurry-casting method for electrode preparation (Fig. 4e and Extended Data Fig. 10a), which allows large-scale, roll-to-roll manufacturing of all-solid-state batteries.

We also demonstrated the effective Li⁺ transport enabled by Li-Cu-CNF in an all-solid-state full battery featuring both the Li-Cu-CNF film electrolyte and a thick (120 μm, 10–11 mg cm⁻² LiFePO₄) solid-state LiFePO₄ cathode composite containing the Li-Cu-CNF additive (Fig. 4f). The LiFePO₄ solid-state cathode demonstrated in this work is 3–5-times thicker than other LiFePO₄ solid-state cathodes reported in the literature^{13,19,20,35}. However, due to the excellent ionic percolation made possible by the nanocellulose-based Li-Cu-CNF ion-conducting additive (9 wt% in the cathode), the impedance of such a thick cathode limited by ion transport was only 390 Ω cm², ~45 times lower compared to the control LiFePO₄ cathode made using the Li-CNF additive (17680 Ω cm²) (Extended Data Fig. 10b, 10c). With Li-Cu-CNF, the all-solid-state LiFePO₄ battery featured a high initial discharge capacity of 137 mA h g⁻¹ and a relatively low overpotential of 0.17 V (Fig. 4g). In contrast, the cathode made using the Li-CNF control showed an initial capacity of 110 mA h g⁻¹, which declined rapidly to almost 0 within 5 cycles, as well as demonstrating a high overpotential of 0.8 V (Fig. 4g). The cycling stability of the all-solid-state LiFePO₄ battery was also significantly improved by using the Li-Cu-CNF electrolyte and ion-conducting additive, successfully reaching 100 cycles at 0.2 C (1 C = 170 mA g⁻¹) at room

temperature (Fig. 4h). Additionally, the flexibility of the Li-Cu-CNF electrolyte and LiFePO₄ composite cathode allowed us to fabricate an all-solid-state battery that remained operational when folded (inset in Fig. 4h and Extended Data Fig. 10d). A rechargeable LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC) high-voltage cathode was also made to further demonstrate the capability of Li-Cu-CNF as a film electrolyte and ion-conducting additive in an all-solid-state battery, which showed lower interfacial resistance, reduced overpotential, and increased capacity (180 mA h g⁻¹ initial discharge capacity) (Extended Data Fig. 10e, 10f), demonstrating the stability of the Li-Cu-CNF at high voltage and its compatibility with high-energy-density all-solid-state batteries.

Fig. 4 | Demonstration of all-solid-state batteries using the Li-Cu-CNF ion conductor. **a**, Schematic of an all-solid-state full battery consisting of a Li metal anode, the Li-Cu-CNF film SPE, and the solid-state cathode (black spheres) featuring the Li-Cu-CNF as an ion-conducting additive (green fibers). **b**, Top-view and side-view SEM images of the dense electrolyte made of the 1D Li-Cu-CNF. **c**, SEM image of the LiFePO_4 cathode with the Li-Cu-CNF ion-conducting additive (false color: grey, LiFePO_4 ; green, Li-Cu-CNF). **d**, The ionic conductivity of LiFePO_4

371 cathodes made with different amounts of Li-Cu-CNF to achieve ion percolation. **e**, Photo of the
372 cathode slurry consisting of LiFePO₄ and Cu-CNF additive for casting the electrode and
373 subsequent Li⁺ intercalation. **f**, Cross-sectional SEM images of a 120 μm thick LiFePO₄ cathode
374 made using Li-Cu-CNF and carbon nanotube additives. **g**, Galvanostatic charge/discharge voltage
375 profiles of the thick LiFePO₄ solid-state cathodes made by filtration-pressing with Li-Cu-CNF or
376 Li-CNF additive and Li-Cu-CNF electrolyte. The arrows indicate the overpotentials at half
377 capacity. **h**, The cycle performance (0.2 C) of an all-solid-state LiFePO₄ cell made using Li-Cu-
378 CNF ion-conducting additive in the cathode, the Li-Cu-CNF film electrolyte, and Li metal anode.
379 Inset: digital photo of the folded all-solid-state battery based on the LiFePO₄ cathode and Li-Cu-
380 CNF as both the solid-state electrolyte and ion-conducting additive. **i**, Comparing the performance
381 of the Li-Cu-CNF electrolyte with SPEs and GPEs reported in the literature. **j**, Digital photos of
382 M-Cu-polymer electrolytes (analogue to Li-Cu-CNF), where M = Li, Na, or Zn, and the polymers
383 include chitosan, carboxymethyl cellulose (CMC), alginate acid, and xanthan gum (XG).

Conclusions

As a 1D solid-state ion conductor, Li-Cu-CNF demonstrates a record-high ionic conductivity ($1.5 \times 10^{-3} \text{ S cm}^{-1}$) and high transference number (0.78) at room temperature, which was made possible by decoupling the Li^+ transport from the local solvation environment. The Li^+ transport follows a rapid ion hopping mechanism via the polar functional groups and bound water molecules available in the cellulose molecular channels that have been opened by simple Cu^{2+} coordination chemistry. The Li-Cu-CNF ion conductor provides exceptional safety, stability, scalability, facile-processability, and good mechanical strength for high-energy-density batteries, which are significant advantages over conventional polymer electrolytes (solid or gel), as shown in Fig. 4i. This 1D ion conductor can also function as an ionic building block to form solid-state ionic conducting networks, providing a unique opportunity to enable thick cathodes and achieve high-energy-density all-solid-state batteries. The success of this new design strategy creates a new class of polymer ion conductors that enable fast conduction by various cations (e.g., H^+ , Na^+ , and Zn^{2+}) with high room-temperature ionic conductivities that have been impossible from traditional polymer electrolytes. For example, we investigated this same approach for the synthesis of ion conductors made of chitosan, alginate acid, carboxymethyl cellulose (CMC), and xanthan gum (XG) (Fig. 4j), all of which showed record-high room-temperature ionic conductivities ($\sigma_{\text{Li}} = 3 \times 10^{-4} \text{ S cm}^{-1}$ for Li-Cu-chitosan, $\sigma_{\text{Na}} = 2 \times 10^{-4} \text{ S cm}^{-1}$ for Na-Cu-alginate, and $\sigma_{\text{Zn}} = 9 \times 10^{-4} \text{ S cm}^{-1}$ for Zn-Cu-XG/CNF). This novel design approach provides both material and conceptual breakthroughs for the development of many other high-performance solid-state ion conductors that could have a broad impact beyond just safe solid-state batteries, examples of which could include electrochemical synaptic devices, solid-state sensors, or redox-controlled information processing and storage.

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Methods

Fabrication process

The Li-Cu-CNF was fabricated by the following three steps: (1) CNFs, which were produced by (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO) oxidation of pulp (International Paper)³⁶, were immersed in Cu^{2+} -saturated alkaline solution (20% NaOH) for 1–2 weeks. The CNFs gradually turned blue (indicating Cu^{2+} coordination with the CNFs), with the product referred to as Cu-CNF-NaOH. (2) The free water in the Cu-CNF-NaOH was then replaced by DMF solvent exchange, which was then evaporated to produce the Cu-CNF. (3) After soaking the Cu-CNF in a Li salt solution (1 M LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate, 1/1 volumetric ratio) in an argon-filled glovebox and evaporating the solvent in vacuum, the Li-Cu-CNF solid-state ion conductor was obtained. For the Li-CNF control sample, the CNFs were treated using the same steps except the material was immersed in the NaOH solution without Cu^{2+} in Step 1.

For different uses of the Li-Cu-CNF, the materials or synthesis process described above were slightly changed. To obtain the Li-Cu-CNF with aligned orientation for measuring the intrinsic conductivity, mechanical strength, and fiber XRD along the fibril direction, basswood was cut along the longitudinal direction (i.e., the growth direction of the tree), delignified, pressed, and directly used as the cellulose source without further TEMPO-treatment in Step 1. To fabricate the Li-Cu-CNF thin-film electrolyte, the Cu-CNF-NaOH obtained in Step 1 (derived from TEMPO-oxidized CNFs, as described previously) was vacuum filtrated and pressed into a film and further processed in Steps 2 and 3. To mix the Li-Cu-CNF with the LiFePO_4 (BTR New Material Group Co.) or NMC (ANL) cathode materials, the Cu-CNF-NaOH obtained in Step 1 was washed and mixed with the cathode material and carbon nanotubes (CNT, XFNANO) (typical mass ratio of

cathode material: CNT:Cu-CNF = 8:1:1) in water solution and then either filtrated as a free-standing cathode or cast on Al foil with the addition of 9 wt% sodium alginate binder, followed by the same treatment in Steps 2 and 3.

The Li-Cu-CNF system was extended to other M-Cu-polymer systems via slightly modified synthesis methods. In this work, aqueous solutions of chitosan, sodium alginate, and sodium CMC (all from Sigma Aldrich) were cast-dried and pressed into thin films. The XG (TCI) was mixed with the TEMPO-oxidized CNF material (XG/CNF, mass ratio 1:1) in solution, filtrated, and also pressed into a thin film. The polymer films were coordinated with Cu^{2+} to form Cu-polymer via a similar method in Step 1. The Cu-chitosan was further similarly treated with Steps 2 and 3 for Li^+ intercalation. The Cu-CMC was soaked in a Na^+ ion electrolyte (3 M NaClO_4 in DMF) for intercalating Na^+ and forming Na-Cu-CMC. The Cu-alginate was treated with a Na^+ ion electrolyte (4 M NaClO_4 aqueous solution) to form Na-Cu-alginate for Na^+ conduction. The Cu-XG/CNF was treated with a Zn^{2+} ion electrolyte (2 M ZnSO_4 aqueous solution) to form Zn-Cu-XG/CNF for Zn^{2+} conduction. All samples were dried in vacuum before electrochemical testing.

The solid-state batteries were assembled in an argon-filled glovebox. The Li symmetric cells were assembled by sandwiching the Li-Cu-CNF electrolyte between two Li metals. The solid-state full cells were made with a Li metal anode, Li-Cu-CNF electrolyte, and a LiFePO_4 cathode or NMC cathode containing Li-Cu-CNF additive (9 wt%). To measure the ion percolation behavior of Li-Cu-CNF in the cathode, the LiFePO_4 cathode was fabricated with the same method using different ratios of Li-Cu-CNF (Li-CNF was used as the “zero” Li-Cu-CNF control) and without CNTs. The all-solid-state flexible cell was assembled using a thin Li metal anode, Li-Cu-CNF electrolyte, and LiFePO_4 cathode with Li-Cu-CNF additive in a paper pouch.

Characterization

A Hitachi SU-70 field emission SEM coupled with an energy-dispersive X-ray spectroscopy system was employed for SEM and elemental analysis. FTIR was conducted on a Nexus 670 made by Thermo Electron with a "Smart Endurance" Attenuated Total Reflectance accessory. The fiber XRD measurements were conducted on a Xenocs Xeuss SAXS/WAXS system with a Cu K α ($\lambda = 1.5418\text{\AA}$) source and Detris Pilatus 300k detector. A home-made sample holder was used to bring samples close to the detector. The content of Li and Cu in Li-Cu-CNF was analyzed by dissolving the sample in nitric acid, the metal concentration of which was measured using a multi-collector ICP mass spectrometer (Thermo-Finnigan Element 2). The stress-strain measurement of the Li-Cu-CNF (along the cellulose fiber direction) was performed with a Tinius Olsen H5KT testing machine.

XAS measurements were performed at the 8-ID Beamline of the National Synchrotron Light Source II at Brookhaven National Laboratory (BNL). X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) data were collected at the Cu K-edge in transmission mode. The samples were placed between two Kapton tapes, which allow for high transmissivity for X-ray measurements. The spectra of the standards were obtained from Cu foil (provided by BNL), commercial copper (I) oxide (Cu₂O) powder, and copper (II) oxide (CuO) powder (Sigma Aldrich). XAS data were analyzed using the IFEFFIT package, which included ATHENA and ARTEMIS³⁷.

For isotope tracing, the tracer exchange (⁶Li $\rightarrow$ ⁷Li) was driven by electrochemical cycling using ⁶Li-enriched metal (95 atom%, Sigma-Aldrich) as electrode foils. The Li-Cu-CNF (or Li-CNF as a control) electrolyte was assembled between two ⁶Li foils to form a symmetric cell (⁶Li | Li-Cu-CNF | ⁶Li). The cell was galvanically polarized for 50 cycles with a current density of 32 $\mu\text{A cm}^{-2}$

and the current switched the direction every 30 min. After cycling, the electrolyte was removed from the cell for ^6Li NMR measurements. ^6Li magic-angle-spinning NMR experiments were performed on a Bruker Avance III-500 spectrometer with a ^6Li Larmor frequency of 73.6 MHz. Samples were packed in 2.5 mm rotors and spun at a speed of 25 kHz. A single pulse was employed to acquire the ^6Li NMR spectra with a 90° pulse length of $2.5\ \mu\text{s}$ and a recycle delay of 10 s. ^6Li NMR chemical shifts were referenced to solid LiCl at $-1.1\ \text{ppm}$.

^7Li and ^1H pulsed-field gradient NMR measurements were performed on 300 MHz and 400 MHz NMR spectrometers on a double resonance probe equipped with a maximum gradient of $1200\ \text{G cm}^{-1}$ and $50\ \text{G cm}^{-1}$, respectively. Double-stimulated echo or spin-echo pulse sequences were used to measure the diffusion coefficients. The signal was accumulated by using a minimum of 64 up to a maximum of 1536 transients with 2 s recycling delay. The gradient strength was varied from 2–50 G/cm or 2–700 G/cm over 16 increments. The diffusion time (Δ) and the diffusion pulse length (δ) were in the range of 50–400 ms and 2–9 ms, respectively. The diffusion coefficients (D) were calculated using the Stejskal-Tanner equation,

$$\frac{I}{I_0} = \exp \left[-(G\gamma\delta)^2 \left(\Delta - \frac{\delta}{3} \right) D \right]$$

in which γ is the gyromagnetic ratio and G is the gradient strength.

Electrochemical test

The electrochemical tests (EIS, DC polarization, and linear sweep voltammogram) were done on a Biologic electrochemical working station. The EIS spectra were measured in a frequency range of 1 MHz–1 Hz with a voltage amplitude of 20 mV. Electrochemical stripping and plating for Li symmetric cells and galvanostatic cycling tests for solid-state cells were conducted on a LAND electrochemical testing system with galvanostatic conditions.

DFT calculations

DFT calculations were performed using the Gaussian 16 code (Revision AVX2)³⁸. The hybrid PBE0 functional³⁹ and the basis set 6-311+G** were used for geometry optimizations, energy calculations, and frequency calculations. The D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ)⁴⁰ was adopted to correct for the weak interactions.

Molecular dynamics simulations

The crystalline Cu-CNF-NaOH was built using the Materials Studio (MS, version 7.0)⁴¹ Visualizer with experimental input for the lattice constant and crystal symmetry²⁶. The Forcite module in MS was used to conduct classical molecular dynamics (MD) simulations. The COMPASS II forcefield⁴², which is extended for polymer systems, was adopted to account for both the bonded and non-bonded interactions. The force field type and charges listed in Extended Data Fig. 2a result in Li-O interactions for different functional groups comparing well with DFT calculations (Extended Data Fig. 2b). Since the Cu²⁺ did not diffuse in experiments, an additional Harmonic potential with a force constant of 25,000 kcal mol⁻¹ Å⁻² was applied to the Cu-O bond term to keep the Cu-O distances at the values obtained from DFT calculations (Extended Data Fig. 2c). The Nosé method⁴³ was used for constant temperature dynamics and the Berendsen method⁴⁴ was used for NPT (constant particle number, pressure, and temperature) dynamics. The Ewald summation method was used to calculate the Coulombic interactions with an accuracy of 0.001 kcal/mol and a cutoff distance of 12.5 Å. A total simulation time of 5.0 ns with a timestep of 1.0 fs was applied to typical production MD runs.

Computational model for the Li-Cu-CNF system and the procedure for the MD simulations

We started by building the atomic structure of the crystalline Cu-CNF-NaOH based on the experimental inputs on the lattice parameters and crystal symmetry. The 2×2 supercell of the Cu-

CNF backbone structure (Extended Data Fig. 2d) was assigned with lattice parameters of $a = b = 15.0 \text{ \AA}$ with a hexagonal symmetry, which agrees with the experimental measurements. Every two nearby cellulose chains were connected by one Cu atom through the hydroxyl O atoms in the simulation cell. A long cell was built with $c = 90.0 \text{ \AA}$. In our MD simulations, the 2×2 supercell was used to avoid the interactions between periodic images. An appropriate number of H_2O molecules were added by the Amorphous Cell module in MS (Extended Data Fig. 2e). Our simulated cell contains 144 AGUs, 1600 water molecules, and 12 Cu atoms. 24 CH_2OH groups were replaced by COOH groups. Room temperature (298 K) and a pressure of 1 bar were kept constant during NPT dynamics for 1.0 ns to obtain the density at this stage. Next, we removed most water molecules to model the drying process with only 144 H_2O molecules left in the system. The Li^+ intercalation was achieved by replacing the 24 -COOH groups with 24 -COOLi groups and the 24 - CH_2O groups with 24 - CH_2OLi groups, as shown in Extended Data Fig. 2g. There were 48 Li^+ ions in the modeling system, and the Li:AGU ratio was set to 1:3, which is the value estimated by the ICP experiment. Then NPT dynamics simulations were performed to obtain the equilibrated amorphous Li-Cu-CNF (Extended Data Fig. 2g). A high temperature of 600 K was used to accelerate the dynamics; compared with room temperature simulations no mechanism change was observed. Finally, production runs for 5.0 ns were performed at 600 K under NVT (constant particle number, volume, and temperature) ensemble to investigate the Li transport mechanism. The Li-Cu-CNF without any H_2O molecules was also simulated for comparison.

XANES calculations

The Cu K-edge theoretical XANES calculations for the $\text{Cu}-(\text{AGU})_2$ system (Extended Data Fig. 2c) were conducted in the framework of the real-space full multiple scattering scheme with the muffin-tin approximation for the potential as implemented in the FDMNES code⁴⁵.

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Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions

L. Hu conceived the SPE concept and supervised the project. C. Yang, W. Xie, and S. He designed the experiments and conducted the material synthesis, characterization, and electrochemical tests. Y. Qi and Q. Wu carried out the density functional theory and molecular dynamics simulations. X. Zhang and R. Briber contributed to the structural analysis. J. Zheng, Y.-Y. Hu, M. Garaga, and

696 S. Greenbaum conducted the NMR analysis and determination of the ion diffusion coefficient. Y.
697 Mao and M. Tyagi performed the XANE characterization. B.H. Ko and F. Jiao contributed to the
698 XAS analysis. J. Dai drew the schematic of the battery. L. Hu, C. Yang, Y. Qi, Q. Wu, A. Brozena,
699 A. Isogai, and K. Xu collectively wrote the paper. All authors commented on the final manuscript.

700 **Competing interests**

701 The authors declare no competing interest.

702 **Additional information**

703 **Supplementary information** is available for this paper.

704 **Correspondence and requests for materials** should be addressed to L.H. and Y.Q.

705 **Reprints and permissions information** is available at <http://www.nature.com/reprints>.

Extended Data Fig. 1 | Structural characterization during the synthesis of Li-Cu-CNF. **a–d**, The fiber XRD patterns of the CNFs after the following treatment steps: **a**, Cu-CNF-NaOH obtained from Cu^{2+} -saturated NaOH aqueous solution. The peaks are indexed based on the literature²⁶. The (003) reflection is observed with a spacing of 0.51 nm while the (001) and (002) reflections are absent, indicating the Cu-CNF-NaOH features a threefold symmetric structure along the cellulose molecular chain direction. **b**, The Cu-CNF washed with water to remove NaOH, demonstrating an amorphous structure. **c**, Cu-CNF after removing water by DMF exchange and evaporating DMF. The fiber XRD pattern shows a mostly amorphous structure with a small angle peak at ~ 2 nm corresponding to cellulose II²⁵, possibly due to a small number of cellulose chains without coordinated Cu forming cellulose II after NaOH is removed. A high q peak at ~ 0.4 nm in the equatorial direction indicates the average molecular chain-to-chain distance of cellulose II. The green arrow in the meridian direction shows a peak corresponding to 0.47 nm in real space. The yellow arrows are pointing to peaks indicating the repeating unit of the Cu-CNF is ~ 1 nm along the cellulose chain. Both 0.47 nm and 1 nm repeating distances are absent in all known cellulose structures and therefore we attribute them to the unique structure of the Cu-CNF. **d**, The Li-Cu-CNF after intercalating Li^+ in Cu-CNF and evaporating the solvent. The amorphous cellulose structure is maintained with some weak diffraction peaks of cellulose

II. The yellow and green arrows indicate the same peaks as in **c**. **e–h**, XAS analysis of the Cu-CNF and Li-Cu-CNF samples: the Cu K-edge X-ray absorption near edge structure (XANES) spectra of **e**, Cu-CNF, Li-Cu-CNF, and a CuO standard, as well as **f**, Cu₂O and Cu standard samples. **g–h**, The Fourier-transformed Cu K-edge extended X-ray absorption fine structure (EXAFS) spectra of **g**, Cu-CNF and **h**, Li-Cu-CNF.

Comparing the XANES spectra of the Cu-CNF and Li-Cu-CNF samples with the Cu, Cu₂O, and CuO standards, the Cu-CNF and Li-Cu-CNF show similar yet broadened pre-edge peaks as CuO at 8986 eV (1s → 3d transition). The characteristic Cu(I) peak (Cu₂O) at ~8981 eV and the Cu metal peaks are not observed in the Cu-CNF and Li-Cu-CNF samples. Thus, the Cu²⁺ is coordinated in the CNF (with or without Li) in a +2 chemical valence state. By fitting the Cu K-edge EXAFS spectra of Cu-CNF and Li-Cu-CNF, we obtained the structural parameters for the first coordination shell of the Cu atoms. In Cu-CNF, the Cu²⁺ is bonded with O atoms, with an average bonding distance of 1.97 Å. The Cu-O bonding distance is longer than that in CuO (1.91 Å)⁴⁶ and consistent with Cu-organic complexes reported in the literature⁴⁷, indicating that the Cu²⁺ is coordinated with the O in the AGUs of the cellulose molecules. The calculated XANES spectrum of the Li-Cu-CNF material (the green dashed line in Extended Data Fig. 1e) is in good agreement with the experimentally measured system, showing that the theoretical model for the Cu-O complex structure described in Extended Data Fig. 2c is reasonable.

The structural parameter values for the first coordination shell of the Cu atom, obtained from the EXAFS.

	CN _{Cu-O}	$R_{\text{Cu-O}}$ (Å)	$\sigma^2_{\text{Cu-O}}$ (10 ⁻³ Å ²)	ΔE_0 (eV), Cu K-edge
Cu-CNF	2.1(3)	1.96(1)	2.1(1.8)	2.8(1.5)
Li-Cu-CNF	2.1(3)	1.97(2)	3.7 (2.4)	5.7(1.8)

CN: coordination number, R : bond distance, σ^2 : mean-square disorder, and ΔE_0 : energy shift. The single-digit numbers in the parentheses for CN and R are the last digit errors and the numbers in parentheses for σ^2 and ΔE_0 are full errors.

Extended Data Fig. 2 | DFT calculations and MD simulations of the Li-Cu-CNF structure. **a**, The assigned COMPASS II force field types and atomic charges in typical cellulose units for MD simulations. **b**, The optimized atomic structures of the representative systems of Li-Cu-CNF used to evaluate interactions between Li⁺ and different oxygen-containing functional groups and water molecules, and corresponding

energy-distance relationships for different Li^+ bonding environments given by molecular mechanics calculations using COMPASS II FF and by DFT calculations. The difference between the total system energy at $r = 10.0 \text{ \AA}$ and minimum energy is taken as the Li^+ dissociation energy. The Li^+ is strongly bonded with both anionic COO^- and RO^- groups with dissociation energies of $> 5.0 \text{ eV}$. The dissociation energy of the Li^+ is $\sim 3.0 \text{ eV}$ for ROH and EO groups and 1.5 eV for H_2O molecules. The strong interactions between the Li^+ and 1 or 2 oxygen species in cellulose suggest slow Li^+ movements in the absence of multiple Li-O coordination. In the H_2O molecule, the O atom has an atom type of *o2** and charge of $-0.82 e$, while the H atom has an atom type of *h1o* and a charge of $+0.41 e$ for force field calculations. **c**, To simulate Cu^{2+} coordination in cellulose, we optimized the atomic structure of two AGUs connected by one Cu^{2+} ($\text{Cu}(\text{AGU})_2$ system) to serve as a structural building block. Two H atoms are deprotonated by the Cu. The average optimized Cu-O bond length ($1.96 \text{ \AA}$) is close to that observed in the experiment ($1.97 \text{ \AA}$), and the calculated XANES of the $\text{Cu}(\text{AGU})_2$ system is also in good agreement with the experimental measurement (Extended Data Fig. 1e), showing that our computational model for the structure of the Cu-O complex is reasonable. Atom types and atomic charges in force field calculations are given for Cu and its connected O atoms, which are categorized as ROH for statistics (Fig. 3c in the main text). **d**, Top view of a 2×2 supercell of the periodic Cu-coordinated CNF structure as a starting structure for the simulation, built with the most reasonable model that we proposed based on the fiber XRD pattern (Fig. 2d). Every two nearby cellulose chains are connected by one Cu atom through the hydroxyl oxygen atoms. The unit cell is denoted by dashed blue lines. **e**, Top and side views of the Cu-CNF-NaOH. **f**, Top and side views of the Cu-CNF obtained by removing NaOH aqueous solution from Cu-CNF-NaOH and then equilibrating the system with NPT dynamics simulations. In Cu-CNF, we reserved 144 H_2O molecules to keep an $\text{H}_2\text{O}:\text{AGU}$ ratio of 1:1. **g**, Schematic of the computational approach used to obtain the atomic structure of the final amorphous Li-Cu-CNF model (top and side views).

Extended Data Fig. 3 | Bound water and mechanical property analysis of Li-Cu-CNF. **a**, Thermogravimetric analysis (TGA) curves of the CNF starting material and Li-Cu-CNF. **b**, FTIR of the pristine CNFs and solid-state Li-Cu-CNF electrolyte. Both the pristine CNFs and Li-Cu-CNF show a broad -OH stretching peak at ~3300 cm⁻¹. **c**, The -OH stretching peak of Li-Cu-CNF deconvoluted into three bands at 3464, 3235, and 2886 cm⁻¹, which can be assigned to bound water molecules in different hydrogen-bonding states^{48,49}. **d**, The atomic mean-square displacement change in CNF and Li-Cu-CNF as a function of temperature measured by QENS. The Cu-CNF sample after DMF solvent exchange with some residual DMF (Cu-CNF-DMF) is also shown for comparison. **e**, The elastic neutron scattering intensity versus the temperature of free water (60 μL H₂O on Cu foil) upon cooling, obtained from the literature⁵⁰. **f**, The stress-strain curve of Li-Cu-CNF along the CNF fiber direction.

The TGA curves of CNF and Li-Cu-CNF both display 6% weight loss at 100 °C (highlighted in blue in Extended Data Fig. 3a), indicating they contain the same amount of bound water. We characterized the bound water by FTIR and QENS. The FTIR spectra of the CNFs and Li-Cu-CNF electrolyte (Extended Data

Fig. 3b) do not show a peak at 3629 cm^{-1} that would be attributed to “free water” not participating in hydrogen-bonding interactions with the cellulose, nor do the samples feature a peak at 3535 cm^{-1} due to weakly hydrogen-bonded water^{48,49}. Compared with the -OH stretching peak of free water at 3629 cm^{-1} , the -OH stretching bands of Li-Cu-CNF shift to much lower wavenumbers (3464 , 3235 , and 2886 cm^{-1} , Extended Data Fig. 3c), which indicates stronger water-cellulose interactions through multiple hydrogen bonding. In addition, we attribute the weak peak at 1640 cm^{-1} to -OH bending of bound water in the cellulose,⁵¹ further suggesting that water is bound in the CNFs and Li-Cu-CNF electrolyte.

The QENS spectra (Extended Data Fig. 3d) show that the Cu-CNF with a small amount of residual DMF solvent (Cu-CNF-DMF) features a drastic decrease of the displacement near 195 K , slightly below the freezing point of DMF (212 K). This characteristic change due to DMF is not seen in Li-Cu-CNF, indicating the Li-Cu-CNF is DMF-free. Meanwhile, the elastic scan of free water when cooling shows an abrupt intensity increase near 266 K (Extended Data Fig. 3e). In contrast, no sharp change near 266 K is observed in the CNF or Li-Cu-CNF samples (Extended Data Fig. 3d), indicating there is no free water in the Li-Cu-CNF electrolyte.

The amorphous Li-Cu-CNF material without free water or DMF solvent displays good mechanical properties as a solid-state electrolyte. A high tensile stress of 29.2 MPa is achieved in Li-Cu-CNF (Extended Data Fig. 3f), which is stronger than most reported SPEs⁵²⁻⁵⁶.

Extended Data Fig. 4 | The ionic conductivities and transference numbers of Li-Cu-CNF and Li-CNF.

a, Voltage profile of the galvanostatic Li plating and stripping between two ends of the Li-Cu-CNF with aligned cellulose fibers (length: 1 cm) at 0.01 mA. **b**, EIS Nyquist plots of aligned Li-Cu-CNF materials of different lengths, ranging from 1 cm to 3 cm, for measuring the intrinsic conductivity of Li-Cu-CNF along the cellulose molecular chain direction. **c**, The resistance corresponding to the high-frequency semi-circle in **b** of the aligned Li-Cu-CNF with different lengths. **d**, EIS Nyquist plots of the aligned Li-Cu-CNF with a length of 3 cm and cross-sectional area of 0.03 cm² at different temperatures, ranging from 10 °C to 60 °C. **e**, DC polarization curve and **f**, EIS Nyquist plots before and after polarization of the Li|Li-Cu-CNF|Li cell. **g**, DC polarization curve and **h**, EIS Nyquist plots before and after polarization of the Li|Li-CNF|Li cell. **i**, Table showing the parameters measured by DC polarization and EIS for calculating the Li⁺ transference number. **j**, **k**, The conductivity of the Cu²⁺ in the Li-Cu-CNF electrolyte measured by **j**, DC polarization and **k**, AC (EIS) methods in a Cu | Cu-CNF | Cu cell.

814 We first confirmed the Li^+ transport along the direction of the Li-Cu-CNF ion conductor by the
 815 galvanostatic Li plating/stripping cycling (Extended Data Fig. 4a) between two ends of the aligned Li-Cu-
 816 CNF membrane (length: 1 cm) at room temperature. To distinguish the resistances of the electrolyte and Li-
 817 electrolyte interface, we measured the EIS of the same Li-Cu-CNF membrane at different lengths (Extended
 818 Data Fig. 4b). The EIS spectra of the Li-Cu-CNF ion conductor shows two semi-circles, which are attributed
 819 to the electrolyte and interface resistance. The semi-circle at the high-frequency region increases linearly as
 820 we increase the electrolyte length from 1 cm to 3 cm (Extended Data Fig. 4c). Thus, the high-frequency
 821 semi-circle is attributed to the resistance of the Li-Cu-CNF electrolyte. The calculated Li^+ conductivity of
 822 Li-Cu-CNF at different temperatures (Extended Data Fig. 4d) is plotted in Fig. 3a, following the Arrhenius-
 823 type relationship.

824 The Li^+ transference numbers (t_{Li}) in Li-Cu-CNF and Li-CNF (without Cu coordination) were measured
 825 based on the Bruce-Vincent method²⁸. The DC polarization measurements were conducted with a potential
 826 of $\Delta V = 10$ mV in the Li | Li-Cu-CNF | Li and Li | Li-CNF | Li cells until the current reached a steady state,
 827 and the corresponding EIS measurements were collected before and after the DC polarization (Extended
 828 Data Fig. 4e-h). t_{Li} was calculated according to $t_{\text{Li}} = \frac{I_{\text{ss}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{ss}} R_{\text{ss}})}$, where ΔV is the applied potential, I_0 is the
 829 initial current, R_0 is the initial resistance, I_{ss} is the steady-state current, and R_{ss} is the steady-state resistance.
 830 The measured results of these parameters are listed in Extended Data Fig. 4i.

831 We measured the Cu-ion conductivity in a Cu | Cu-CNF | Cu cell to enable only Cu^{2+} transport, which
 832 was $1 \times 10^{-8} \text{ S cm}^{-1}$ using the DC method (Extended Data Fig. 4j) and $5 \times 10^{-7} \text{ S cm}^{-1}$ as measured by the
 833 AC technique (Extended Data Fig. 4k), much lower than the Li^+ conductivity in Li-Cu-CNF. Therefore, the
 834 ionic conductivity of Li-Cu-CNF is contributed by the material's Li^+ rather than Cu^{2+} .

Extended Data Fig. 5 | NMR analysis of the Li coordination environment and diffusion pathway. a, b, The ^6Li NMR spectra and simulations of **a**, Li-Cu-CNF and **b**, Li-CNF. **c, d**, The ^6Li NMR spectra of **c**, CH $_3$ COOLi $\cdot$ 2H $_2$ O and **d**, LiPF $_6$ as references for the COO $\cdots$ Li and LiPF $_6$ peak assignments in Li-Cu-CNF. **e, f**, The ^6Li NMR spectra and simulations of **e**, Li-Cu-CNF and **f**, Li-CNF after $^6\text{Li} \rightarrow ^7\text{Li}$ tracer exchange, which was performed by cycling Li-Cu-CNF or Li-CNF electrolyte (natural abundance: 92.4% ^7Li and 7.6% ^6Li) between two ^6Li -enriched metal electrodes (i.e., symmetric ^6Li | Li-Cu-CNF | ^6Li cells). **g**, Table showing the amount of Li $^+$ in different chemical environments in Li-Cu-CNF and Li-CNF before and after $^6\text{Li} \rightarrow ^7\text{Li}$ tracer exchange, derived from the relative spectral areal integral of the ^6Li resonances in the NMR spectra shown in **a**, **b**, **e**, and **f**.

845

846 **Extended Data Fig. 6 | Simulated structure of Li-CNF by MD.** The Li-CNF system consists of 16
 847 cellulose chains surrounded by Li^+ and water molecules. Different chains are denoted by different colors.
 848 Li^+ ions are indicated by purple spheres and water molecules are presented as stick models. The size of the
 849 Li-CNF system is given roughly. The simulations show that without the participation of Cu^{2+} , the Li^+ and
 850 water molecules only adsorb on the surface of the cellulose structures. This structure leads to the low MSD
 851 of the Li^+ in Li-CNF, as shown in Fig 3i.

Extended Data Fig. 7 | Numerical analyses of molecular dynamics simulations. **a**, MSD plots for Li⁺, COO⁻ and RO⁻ groups, and Cu²⁺ in the model (Fig. 2i and Extended Data Fig. 2g), which features an H₂O:AGU ratio of 1:1 (obtained from TGA curves, as shown in Extended Data Fig. 3a). The average MSD plots show that Li⁺ move fast while COO⁻ and RO⁻ groups and Cu²⁺ in the Li-Cu-CNF backbone move much slower. **b**, Displacement plots of six Li⁺ in the simulation that have displacements of > 15.0 Å, and the index of COO/RO atoms that are bonded to the six Li⁺ (Li-O distance < 2.5 Å). **c**, Radial distribution functions (RDF) for Li-Li and COO-RO pairs in Li-Cu-CNF with an H₂O:AGU ratio of 1:1. The locations of the first peak of the Li-Li pair and the second peak of the COO-RO pair indicate the hopping distance

(~3.0 Å) between the residence sites. The first peak of the COO-RO pair indicates the distance between the two O atoms within the same COO group. **d**, MSD plot of water molecules for the Li-Cu-CNF system, which shows that the water molecules move much faster than Li⁺ (as presented in **a**) and thus can kick Li⁺ out of the residence sites. **e**, Radial distribution function and coordination number plots for the H₂O-H₂O pairs of the bound water in Li-Cu-CNF.

The diffusion coefficients of Li⁺, COO⁻, and RO⁻ were computed according to $D = \frac{\text{MSD}}{6\Delta t}$, where the linear diffusion region of the MSD plot (Extended Data Fig. 7a) was used³² and Δt was the time interval. The calculated diffusion coefficients in the simulated Li-Cu-CNF for the Li⁺, COO⁻, and RO⁻ were $D_{\text{Li}^+} = 2.03 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $D_{\text{COO}^-} = 0.49 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and $D_{\text{RO}^-} = 0.56 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively, at 600 K. The transference number was calculated to be 0.80 based on its definition $t_{\text{Li}^+} = D_{\text{Li}^+} / (D_{\text{Li}^+} + D_{\text{anion}})$, where D_{anion} is the average diffusion coefficient for the COO⁻ and RO⁻ anions. The calculated transference number is in good agreement with the experimental value of 0.78. The Li⁺ conductivities at temperatures of 500 K, 600 K, and 700 K were calculated based on $\sigma = \frac{ne^2D}{kT}$, where n is the volume concentration of Li⁺, e is the electron charge, k is the Boltzmann constant, and T is the absolute temperature. Then, the ionic conductivities were fitted with the Arrhenius equation $\sigma = Ae^{\frac{-E_a}{kT}}$, where A is a pre-exponential factor (constant), k is the Boltzmann constant, and E_a is the activation energy. The calculated activation energy in Li-Cu-CNF was 0.31 eV, slightly larger than the experimental value (0.19 eV), likely due to overestimation of the Li-O interactions by the force field.

Our computational modeling system of Li-Cu-CNF (as shown in Fig. 2i and Extended Data Fig. 2g) contains a total of 3420 atoms, among which there are 48 Li atoms and 888 O atoms. Each atom is labeled with a number between 1 and 3420. For example, the Li⁺ labeled with the number 682 is denoted as Li-682. Six Li⁺ ions (Li-682, Li-1928, Li-2178, Li-2697, Li-2908, and Li-2912) have displacements of > 15.0 Å,

883 and their MSD plots are given in Extended Data Fig. 7b. All the MSD plots show an abrupt increase at
884 certain moments, indicating the hopping of the Li^+ . The COO and RO atoms that are bonded with the selected
885 Li^+ are shown in Extended Data Fig. 7b as well. The simulation results indicate that Li^+ diffuses via hopping
886 between COO and RO groups instead of continuous movement coupled with chain segment motion.

887 The COO/RO atoms are residence sites for Li^+ , and the RDF plot for the COO/RO pairs is given in
888 Extended Data Fig. 7c. The first peak at 2.2 Å represents the distance between the two oxygen atoms in one
889 COO group, while the second peak at ~3.0 Å gives the average distance between oxygen atoms in
890 neighboring COO/RO groups, which is indicative of the hopping distance. The RDF plot for the Li-Li pair
891 shows that the average Li-Li distance is ~3.3 Å, close to the hopping distance.

892 The single coordination sphere in RDF and low coordination number (< 2) in Extended Data Fig. 7e
893 indicate the H_2O molecules are isolated (gas-like) and do not form a liquid phase. The typical narrow
894 electrochemical window of bulk water (< 1.5 V) is due to the presence of H^+ (H_3O^+) and OH^- , as the H^+ and
895 H_3O^+ species are easily reduced, while OH^- can be easily oxidized. In contrast, the isolated neutral H_2O
896 molecules in Li-Cu-CNF do not easily gain or lose electrons and are thus electrochemically stable³³.

897

898

Extended Data Fig. 8 | Computations of the redox potentials. (Top) Reduction and oxidation potentials (vs. Li^+/Li) obtained from DFT calculations for (bottom) different structures representative of the cellulose and Li-Cu-CNF systems, including (1) glucose, (2) AGU dimer, (3) AGU-COOLi, (4) and (5) two isomers of $(\text{AGU})_2\text{-COOLi}$, (6) AGU- CH_2Oli , (7) and (8) two isomers of $(\text{AGU})_2\text{-CH}_2\text{Oli}$, (9) Cu- $(\text{AGU})_2$, (10) H_2O dimer, and (11) $(\text{AGU})_2\text{-(H}_2\text{O)}_2$. The C, H, O, Li, and Cu atoms are represented by grey, white, red, purple, and blue spheres, respectively. The experimental oxidation potential for the Li-Cu-CNF system (black) and the redox potentials for ethylene carbonate (EC, red and blue) are denoted with dashed lines for reference. The water molecules are depicted with stick models. The redox potentials vs. Li^+/Li were calculated as $E_{\text{re}} = -\frac{G_A - G_N}{F} - 1.4$ and $E_{\text{ox}} = \frac{G_C - G_N}{F} - 1.4$, respectively. Here G_N , G_A , and G_C denote the Gibbs free energies for the optimized neutral species and corresponding anion and cation species, respectively. F is the Faraday constant. The temperature was set at 298 K.

The calculation results show that almost all the representative structures have low reduction potentials and high oxidation potentials. One exception is that the Cu- $(\text{AGU})_2$ system could be reduced (with a reduction potential of 2.18 V vs. Li^+/Li). Since the Cu^{2+} has a low concentration and are mainly coordinated inside the Li-Cu-CNF, the reduction of the Cu-O complex is likely to be passivated by a solid electrolyte interphase layer when contacting anode materials (e.g., a Li metal anode).

915

916 **Extended Data Fig. 9 | Li-Cu-CNF film electrolyte and its electrochemical performance. a,** Top view

917 SEM image of the Li-Cu-CNF film electrolyte. **b,** Digital photos (top and back) of a permeability test of the

918 Li-Cu-CNF film electrolyte to demonstrate the film's denseness. The electrolyte prevents liquid dye added

919 to the top of the film from permeating to the back (from the back, only a dark shadow of the dye on top is
920 seen through the translucent film). **c**, EIS Nyquist plot of the Li-Cu-CNF film electrolyte at different
921 temperatures and **d**, the corresponding Arrhenius plot. The Li-Cu-CNF film electrolyte shows an overall
922 ionic conductivity of $3.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. **e**, The Li plating/stripping cycling performance
923 of the Li-Cu-CNF film electrolyte at 0.5 mA cm^{-2} , with 1 h for each plating/stripping half cycle, for a total
924 of 400 h at room temperature.

925

926 **Extended Data Fig. 10 | Battery demonstration with Li-Cu-CNF as a film electrolyte and ion-**
 927 **conducting additive. a**, The fabrication steps for incorporating the cathode material (LiFePO₄ here) with
 928 the Li-Cu-CNF ion-conducting additive via the traditional slurry-casting method. The Cu-CNF solution is

929 first mixed with the cathode material, a carbon additive (carbon nanotubes), and sodium alginate binder in
930 an aqueous solution to obtain the cathode slurry. The slurry is then cast on aluminum foil by a doctor blade
931 and vacuum dried at 35 °C. The cathode electrodes are then soaked in Li⁺ electrolyte for Li⁺ intercalation of
932 the Cu-CNF, followed by vacuum drying to obtain solid electrodes containing the Li-Cu-CNF additive. **b**,
933 **c**, EIS of the solid-state batteries using thick LiFePO₄ cathodes (~120 μm) made by filtration-pressing with
934 the addition of **b**, Li-Cu-CNF and **c**, Li-CNF. **d**, A pouch all-solid-state battery made using a Li anode, the
935 Li-Cu-CNF film SPE, and a LiFePO₄ solid-state cathode containing the Li-Cu-CNF ion-conducting additive,
936 which shows good flexibility while still powering an LED light. **e**, EIS of solid-state batteries made using
937 the Li-Cu-CNF film electrolyte and the NMC cathodes (9 mg cm⁻²) with and without the addition of Li-Cu-
938 CNF. **f**, Charge/discharge voltage profiles of the solid-state NMC cathode with and without the addition of
939 Li-Cu-CNF at 0.02 C (1 C = 200 mA g⁻¹).

Figures

Figure 1

The structure and performance of the Li-Cu-CNF solid-state ion conductor. a, Schematic illustration of the hierarchical structure of CNFs, which are derived from wood cellulose fibers and are composed of elementary fibrils, each of which is comprised of individual cellulose molecular chains. Cu-ion

coordination with the hydroxyl groups of cellulose opens the spacing between molecular chains, creating cellulose molecular channels in the CNFs that serve as Li⁺ conducting pathways in the resulting Li-Cu-CNF ion conductor. The scanning electron microscopy (SEM) image shows the morphology of the CNFs, which are naturally aligned in the cellulose fibers. b, A plot of the transference number and ionic conductivity of Li-Cu-CNF and other SPEs^{13,14,17,24}. c, A digital photo of a 1-meter long Li-Cu-CNF roll.

Figure 2

Structural evolution during the synthesis of Li-Cu-CNF. a, Digital images showing the fabrication process of Li-Cu-CNF, during which the CNF starting material was immersed in Cu²⁺ alkaline solution to produce Cu-CNF-NaOH. The aqueous solution in Cu-CNF-NaOH was then displaced with DMF to obtain Cu-CNF, and finally exchanged with LiPF₆ organic electrolyte for Li⁺ intercalation and then dried to form Li-Cu-CNF. The fiber XRD patterns (middle row) and simulated structures (bottom row) of b and c, the pristine CNFs showing cellulose β structure; d and e, Cu-CNF-NaOH, with coordinated cellulose chains packed in a hexagonal unit cell consistent with the literature²⁶; f and g, Cu-CNF, in a largely amorphous state; and h and i, Li-Cu-CNF, which features an amorphous structure (with some weak diffraction signals of cellulose II²⁵). The white arrows in the fiber XRD patterns indicate the fiber direction. Different cellulose chains in the simulated structures are denoted by different colors.

Figure 3

Li⁺ conductivity and transport mechanism in Li-Cu-CNF. a, The temperature dependent conductivity of Li-Cu-CNF and Li-CNF (without Cu²⁺ coordination) and linear fitting according to the Arrhenius equation, the slope of which indicates the activation energy. The temperature-dependent conductivity plots (i–ix) of typical SPEs are included for comparison (i12, ii–iv7, v15, vi13, vii24, viii16, ix3). b, Comparison of the Li⁺ diffusion coefficient and Li⁺ concentration of Li-Cu-CNF with other solid-state electrolytes (PEO and

LLZO). c, Schematic of the chemical environment of Li⁺ in the Li-Cu-CNF system with different types of oxygen atoms. The C, H, O, Cu, and Li atoms are denoted by grey, white, red, blue, and purple spheres, respectively. The hydrogen atoms that are bonded with carbon are not shown for clarity. d, Relative ⁶Li number in different Li chemical environments in Li-CNF and Li-Cu-CNF, derived from NMR (Extended Data Fig. 5) by normalizing the mass-specific ⁶Li number in Li-Cu-CNF to 100%. e, Relative ⁶Li number for different Li chemical environments in the Li-Cu-CNF before and after ⁶Li↔⁷Li tracer exchange. f, The average Li-O coordination numbers from MD simulations for Li- CNF and Li-Cu-CNF. g, Structural snapshots from MD simulations of a fast-moving Li⁺ transporting in Li-Cu-CNF for 5 ns. h, The coordination numbers of Li⁺ coordinating with all available oxygen atoms (Li-O, including the oxygen atoms in cellulose and bound water molecules) and just water molecules (Li-H₂O) in Li-Cu-CNF for the 6 fastest and 6 slowest Li⁺ ions in the Li-Cu-CNF model. i, MSD plots for the Li-Cu-CNF systems with/without water molecules and the Li-CNF system with water molecules on the surface of the CNFs. j, Electrochemical stability window of the Li-Cu-CNF measured by linear sweep voltammogram from 0 V to 5.5 V (vs. Li⁺/Li) at 0.1 mV s⁻¹.

Figure 4

Demonstration of all-solid-state batteries using the Li-Cu-CNF ion conductor. a, Schematic of an all-solid-state full battery consisting of a Li metal anode, the Li-Cu-CNF film SPE, and the solid-state cathode (black spheres) featuring the Li-Cu-CNF as an ion-conducting additive (green fibers). b, Top-view and side-view SEM images of the dense electrolyte made of the 1D Li-Cu-CNF. c, SEM image of the LiFePO₄ cathode with the Li-Cu-CNF ion-conducting additive (false color: grey, LiFePO₄; green, Li-Cu-CNF). d, The ionic conductivity of LiFePO₄ cathodes made with different amounts of Li-Cu-CNF to achieve ion

percolation. e, Photo of the cathode slurry consisting of LiFePO_4 and Cu-CNF additive for casting the electrode and subsequent Li^+ intercalation. f, Cross-sectional SEM images of a 120 μm thick LiFePO_4 cathode made using Li-Cu-CNF and carbon nanotube additives. g, Galvanostatic charge/discharge voltage profiles of the thick LiFePO_4 solid-state cathodes made by filtration-pressing with Li-Cu-CNF or Li-CNF additive and Li-Cu-CNF electrolyte. The arrows indicate the overpotentials at half capacity. h, The cycle performance (0.2 C) of an all-solid-state LiFePO_4 cell made using Li-Cu- CNF ion-conducting additive in the cathode, the Li-Cu-CNF film electrolyte, and Li metal anode. Inset: digital photo of the folded all-solid-state battery based on the LiFePO_4 cathode and Li-Cu- CNF as both the solid-state electrolyte and ion-conducting additive. i, Comparing the performance of the Li-Cu-CNF electrolyte with SPEs and GPEs reported in the literature. j, Digital photos of M-Cu-polymer electrolytes (analogue to Li-Cu-CNF), where M = Li, Na, or Zn, and the polymers include chitosan, carboxymethyl cellulose (CMC), alginate acid, and xanthan gum (XG).