Stretchable Battery Underpinned by Supramolecular Chemistry

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The rapid development of wearable electronics requires compatible energy storage components to power device operation. High-energy density, state-of-art Li-ion batteries however are typically in rigid form factors which limits the design space of wearable devices and the use of flammable liquid electrolytes causes potential safety concerns. Further innovation is urgently necessary to incorporate flexibility, stretchability and safety into existing Li-ion battery technology for applications in emerging wearable electronics.

Solid-state polymer electrolytes that are ionically conductive and mechanically robust serve as ideal building blocks for such next-generation batteries. Replacing the flammable organic liquids with solid electrolyte also enhances the device safety. In contrast to brittle inorganic ion conductors, using soft polymer electrolytes reduces material cost while offering facile processability. Despite being pursued for decades, developing new polymer electrolytes is always confronted with a canonical trade-off between mechanical robustness and ionic conductivity. Conventional approaches focus on enhancing the ion transport in polymer electrolyte by decreasing the glass-transition temperature (T_g), which in turn compromises the mechanical integrity of solid electrolytes. Other strategies are employed to enhance the mechanical properties such as using block polymers or ceramic fillers, but they all end up with stiff polymers that cannot be stretched under large and continuous strain.

Decoupling of ionic conductivity and mechanical robustness

To address this long-standing dilemma in polymer electrolytes, an interdisciplinary research team led by **Prof. Zhenan Bao** (Bao Group) and **Prof. Yi Cui** (Cui Group) leveraged their expertise of supramolecular chemistry to rationally customize new dynamic polymers for stretchable batteries. In their *Nature Communications* paper, one distinct innovation showcased by the team is to decouple the ionic conductivity and mechanical toughness by incorporating orthogonally functional segments into the same supramolecular network.

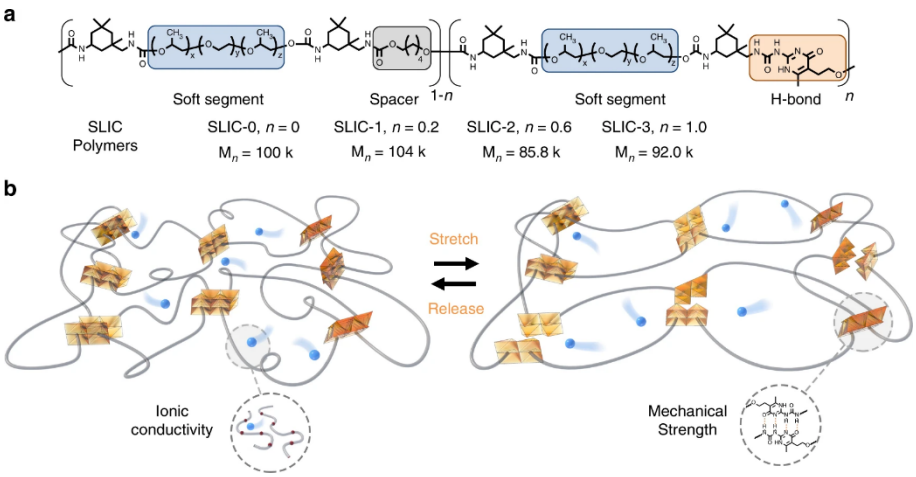
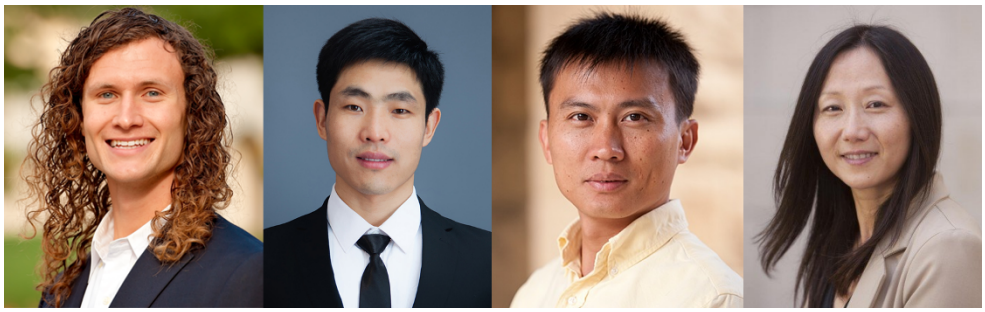


Figure 1. Schematics of (a) chemical structure of SLIC with varied ratios of dynamic H-bonding units and (b) decoupled ionic conductivity and mechanical robustness in a SLIC electrolyte upon stretching. Image credit: Mackanic, D.G., Yan, X., Zhang, Q. *et al.* Decoupling of mechanical properties and ionic conductivity in supramolecular lithium-ion conductors. *Nat Commun* **10,** 5384 (2019). https://doi.org/10.1038/s41467-019-13362-4

Specifically, a soft polyether backbone with low T_g dictates fast transport of Li ions whereas a 2-ureido-4-pyrimidone (UPy) segment with dynamic hydrogen bonding ensures mechanical robustness, as shown in **Figure 1**. The crosslinking between different polymer chains by the H-bonding creates dynamic supramolecular networks. The overall mechanical properties of polymers can be effectively optimized by tuning the relative ratio of dynamic units versus the non-dynamic ones. By varying the ratios of dynamic units, the researchers demonstrated that incorporation of H-bonding allows fully reversible elastic behavior of polymers under large tensile strain, achieving high stretchability and toughness. Combination of a Li salt (lithium bis(trifluoromethanesulfonyl)imide, LiTFSI) with the supramolecular network produces robust solid-state electrolytes, whereas the addition of plasticizer (diethylene glycol dimethyl ether, DEGDME) further elevates the ionic conductivities to as high as ~2×10^{-4} S cm^{-1} at room temperature. Interestingly, despite the impressive mechanical robustness, the measured T_g values and ionic conductivities remained nearly constant among polymers with different ratios of dynamic units, confirming the decoupling of ion-conducting and mechanical functions within the supramolecular network.



Lead authors, Dr. David Mackanic and Dr. Xuzhou Yan, and team leaders, Pro. Yi Cui and Prof. Zhenan Bao (from left to right).

SLIC as both solid electrolyte and binder

Consisting of the polymer, Li salt and additives, the rationally formulated supramolecular lithium-ion conductors (SLIC) exhibit compelling performances for stretchable batteries. Firstly, no change in ionic conductivity was found for the SLIC electrolyte when stretched reversibly between 0 and 200%. A record high toughness of 29.3 ± 1.4 MJ m^{-3} was realized when compared to other reported electrolytes in literatures. The high ionic conductivity ensures its effective operation in Li-ion batteries. These excellent characteristics also allow it to be used as a binder with electrode materials such as $LiFePO_4$ (LFP) to produce monolithic electrode with high stretchability of > 400 %, contrasting conventional rigid binders like polyvinylidene fluoride (PVDF) that can only be stretched to ~20% strain. Moreover, the high adhesion energy of SLIC resulting from H-bonding leads to intimate contact at electrode/electrolyte interface which can avoid delamination of different electrode layers under continuous strain-release cycles. Combining all these advantages, the research team finally demonstrated stable and efficient operation of an all-stretchable Li-ion battery with high capacity using the SLIC as both electrolyte and binder, which showed minimal capacity loss even under up to 70 % strain.

Overall, this work represents one of the first demonstrations of an intrinsically stretchable Li-ion battery, highlighting a supramolecular design to resolve the trade-off between ion transport and mechanical properties. Most importantly, the dynamic H-bonding within the supramolecular network lays solid foundation for not only high stretchability and roughness but also seamless interfacial contact of polymer electrolytes. Judicious combination of this supramolecular network with other salts and additives allows fast ion conduction without compromising its mechanical integrity. The composite solid electrolyte can be easily integrated with widely adopted techniques in battery industry such as slurry casting, for low-cost and large-scale manufacturing of stretchable batteries.

Today, this technology has been licensed and leveraged by Anthro Energy to commercialize the conformal battery for powering real-world wearable electronic devices.

Original Article: Mackanic, D.G., Yan, X., Zhang, Q. *et al.* Decoupling of mechanical properties and ionic conductivity in supramolecular lithium ion conductors. *Nat Commun* **10,** 5384 (2019). https://doi.org /10.1038/s41467-019-13362-4

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