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Designing Polymer Electrolytes for Safe and High Capacity Rechargeable Lithium Batteries

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ABSTRACT: The development of solid polymer electrolytes for lithium battery applications is a challenge of profound technological significance. We have established a collaboration with the aim of understanding and designing improved polymer electrolytes that combines theoretical modeling, polymer synthesis, and experimental characterization. By studying diverse polymer chemistries, we have discovered that ion-solvation-site connectivity is an important feature of polymer electrolytes that is necessary for high lithium-ion conductance. We are employing this insight into search for improved polymer electrolytes, with promising early-stage results.



The importance of rechargeable batteries in the emerging sustainable energy landscape is widely recognized. Society will increasingly depend on renewable sources such as wind and solar energy to produce electrical power. The intermittent nature of these resources, however, requires the development of systems that store excess energy when it is produced and release it to the grid when needed. Rechargeable batteries offer great promise for energy storage and are being used to power electric cars and, more recently, homes and businesses. At the heart of this technology is the lithium-ion battery, which is used in all currently marketed electric vehicles, as well as the Tesla Powerwall for residential energy storage.

Lithium-ion batteries used currently in clean-energy applications were originally developed to power consumer electronics. These batteries are typically comprised of a graphite anode and transition-metal-oxide cathode that reversibly intercalate lithium, with a mixture of liquid alkyl carbonates and lithium salts serving as the electrolyte. The cycle life of current batteries is limited by side reactions that involve the electrolyte, since alkyl carbonates are not stable at the reductive potentials encountered in a lithium-ion battery. The limited stability of the electrolyte also limits the chemistry of electrodes that can be used in the battery. Catastrophic battery failure, triggered by direct contact (or an electrical short) between the cathode and the anode, often begins with venting or combustion of the electrolyte. Such failures, which become more probable as the energy density and size of the battery increases, have resulted in the recall of millions of electronic devices, recently including the Samsung Galaxy Note 7. We believe that deployment of large-scale batteries for clean energy

technologies will be accelerated if an intrinsically safe rechargeable lithium battery can be conceived.

Solid electrolytes have the potential to solve both safety and life cycle issues. The probability of catastrophic failure due to direct contact between the electrodes decreases if the solid is mechanically rigid, nonvolatile, and nonflammable. Solid electrolytes also have the potential to enable high capacity electrodes, for example, the lithium metal anode. Slower side reactions in solids will lead to improved cycle life. Two classes of solids are known to conduct lithium ions: inorganic materials (ceramics and glasses) and polymers. The ionic conductivity of inorganic electrolytes is comparable to that of the conventional electrolytes. However, the brittle nature of the inorganic conductors is likely to preclude large-scale applications wherein mechanical robustness is important; the battery electrolyte must not crack when the car encounters a bump in the road or when they are employed in wearable or foldable electronics that require flexibility. Polymer electrolytes are mechanically robust and well suited for large-scale processing.¹ However, the ionic conductivity of these electrolytes is a factor of 10 lower than that required for practical applications. How to increase the rate of lithium ion transport is thus a question of immense practical interest; it is also fundamentally challenging due to the intrinsic coupling between properties that govern ion transport.

The current state-of-the-art for polymer electrolytes in lithium batteries is poly(ethylene oxide) (PEO),¹ which was first proposed for battery applications in 1973.² For over 40

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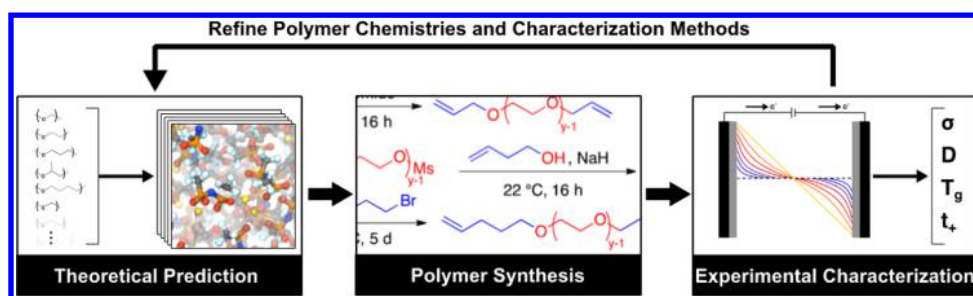


Figure 1. Overview of the collaborative research strategy for characterizing and discovering new polymer electrolytes. Theoretical predictions are used to identify promising polymers for synthesis and characterization, which in turn, informs the refinement of the theoretical methods.

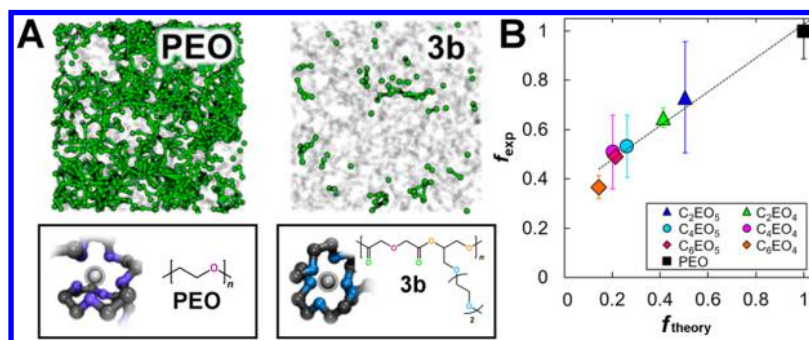


Figure 2. Ion-solvation-site networks are important for high Li-ion transport in polymers. (A) The distribution and connectivity of solvation sites in PEO and representative polyester, with characteristic coordination structures shown above. Poor connectivity of the solvation site networks severely limits Li-ion conductivity in the polyester, even though it has comparable oxygen density to PEO. (B) The theoretically determined site connectivity (f_{theory}) correlates with the Li-ion diffusivity in a range of polymers (f_{exp}), relative to PEO.^{9,11}

years, scientists and engineers have used intuition to search for a significantly more conductive polymer than PEO, with limited success. The historic dominance of PEO and its derivatives among polymer electrolytes has had two notable consequences: First, the general understanding of the solvation and dynamics of ions in polymers is largely based on computer simulations for the specific case of PEO;^{3,4} and second, most strategies for improving the conductivity of polymer electrolytes have been based on mitigating crystallinity or reducing the glass-transition temperature for PEO, including the addition of nanoparticles and plasticizers^{5,6} and the design of ether-based branched polymers.^{7,8} An important conclusion of many decades of work is that the ion transport in an amorphous polymer depends mainly on the mobility of polymer segments, governed by the glass transition temperature. A question worth asking is thus: Can theoretical methods guide the synthesis of improved polymer electrolytes, thereby moving the field beyond the current PEO-centric view of ion conductivity?

A few years ago, we established a collaboration to pursue this goal. The mode of operation for the collaboration, described in Figure 1, is to synthesize polymers that are informed by computer simulations and to test their properties. Discrepancies between simulations and experiment are used to refine the simulations, which then output targets for the next generation of polymer electrolytes. For this strategy to succeed, accurate theoretical models are needed to describe a wide variety of polymer electrolytes. Our first task was to examine if the prevailing theoretical picture for ion transport in polymers was sufficient.

We initially considered a series of polyester-based polymer electrolytes in which the structure of the monomer is systematically varied while keeping the total oxygen density comparable to PEO (Figure 2A).^{9,10} While the measured

conductivities of the polyesters agreed with the molecular simulations, they were well below that of PEO-based electrolytes. Interestingly, we noted that the reduction in conductivity was much larger than would be expected on the basis of differences in the glass transition temperature. Computational analysis was used to explore this anomalous behavior, revealing a generic ion-diffusion mechanism across the full set of polymers in which lithium ions undergo hopping between nascent solvation sites in the polymer structure. It was thus found that a key predictor of ion conductivity among the various polymers is the intrinsic connectivity of this network of nascent solvation sites. In subsequent work,¹¹ we demonstrated that the computationally predicted solvation-site connectivity and the experimentally measured ion conductivity correlate strongly across a striking array of polymers, temperatures, and salt concentrations ranging from the dilute to concentrated regimes (Figure 2B).

The discovery of the important role of solvation-site connectivity is notable for several reasons. First, and most critically, it reveals an essential feature of ion transport that must be considered for future polymer electrolyte design. In the search for improved electrolytes on the “fitness landscape” of candidate polymers, it is clear that high solvation-site connectivity must be included in the search criteria, along with low T_g to ensure polymer-segment mobility and sufficient salt solubility. Second, by demonstrating that the simulations can efficiently determine the solvation-site connectivity (in accurate agreement with experimental metrics), the work indicates that computational methods can play a central role in the screening and identification of promising new polymer electrolytes. And third, it is notable that discovery of the role of solvation-site connectivity was only made possible via the synthesis and detailed characterization of polymer electrolytes

with fundamentally different monomer chemistries than PEO; only by breaking out of the PEO-centric view of polymer electrolytes was this new insight achieved.

Establishment of the connection between ion conductivity and solvation-site connectivity has led to the development of a promising new coarse-grained simulation method for the efficient prediction of ion conductivity in polymer electrolytes. Building upon the earlier work of Ratner and Nitzan,^{12,13} we derived a chemically specific dynamic bond percolation (CS-DBP) model¹⁴ in which ion diffusion occurs via hopping transitions on the network of ion solvation sites. In the CS-DBP model, the hopping rates depend on the distribution and connectivity of solvation sites, which are obtained from short-time scale (1–10 ns) MD (molecular dynamics) trajectories and account for the effects of detailed molecular properties of the polymer, such as monomer topology, composition, and flexibility. The model has been employed to predict the rate of lithium-ion diffusion in a range of polymers, yielding good agreement with long time scale MD simulations. Although the current version of the model neglects local rafting effects on lithium transport due to segmental diffusion of the coordinating polymer chain,^{15,16} such effects may be included as in other theoretical models.⁴ By reducing the required MD trajectories lengths from microsecond to nanosecond time scales and by providing a theoretical framework that allows for the characterization of polymer electrolytes with diverse monomer chemistries, the CS-DBP model creates new opportunities for the large-scale screening and discovery of new polymer electrolytes.

In ongoing simulation studies, we are using the CS-DBP model to predict chemical structures that will result in both rapid segmental motion and high connectivity. This work has already begun to identify promising avenues for investigation. In particular, the simulations provide support for Lewis-acidic polymers as a potential alternative to PEO-based polymers for improved ion-conduction properties.¹⁷ Lewis-acidic polymers exhibit strong polymer–anion interactions, which drive high levels of salt solubility while liberating the lithium cations to diffuse rapidly (Figure 3). Additives based on Lewis-acidic

moieties have previously been used to improve Li⁺ transference, but we find several realizations of Lewis-acidic polymers that simultaneously exhibit substantially enhanced Li⁺ diffusivity, decreased anion diffusivity, and promising overall salt solubility. Although at an early stage, this work suggests that uninvestigated regions of polymer design space may well yield the next-generation polymer electrolyte materials, with improved conductivity and solubility properties.

Critical to our collaborative research effort is that theoretical results and predictions are transmitted to chemists and engineers who work out approaches for synthesizing, purifying, and characterizing the polymers; purification is a particularly important issue, since many impurities that cannot be present in lithium batteries (e.g., water) help ion transport. In future work, we will study the performance of the theoretically predicted polymer electrolytes and their stability and behavior in batteries. Our ultimate goal is to present an all-solid battery that can be charged more quickly than one based on PEO. While we are hopeful that the insights and simulation tools we have developed will lead to the discovery of improved polymer electrolytes, there is no guarantee of success. Already, we have identified solvation-site connectivity as an important bottleneck that limits ion transport in polymer electrolytes, yet other limitations must simultaneously be avoided, including limited redox stability and propensity for dendrite formation at electrodes. Nevertheless, we feel that a fundamental understanding of solid polymer electrolytes is necessary for guiding the design of next-generation materials.

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The authors declare no competing financial interest.

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REFERENCES

- (1) Xue, Z.; He, D.; Xie, X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. *J. Mater. Chem. A* **2015**, *3*, 19218–19253.
- (2) Fenton, D. E.; Parker, J. M.; Wright, P. V. Complexes of alkali-metal ions with poly(ethylene oxide). *Polymer* **1973**, *14*, 589–589.
- (3) Mogurampelly, S.; Borodin, O.; Ganesan, V. Computer simulations of ion transport in polymer electrolyte membranes. *Annu. Rev. Chem. Biomol. Eng.* **2016**, *7*, 349–371.
- (4) Maitra, A.; Heuer, A. Cation transport in polymer electrolytes: A microscopic approach. *Phys. Rev. Lett.* **2007**, *98*, 227802.
- (5) Tarascon, J. M.; Armand, M. Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, *414*, 359–367.

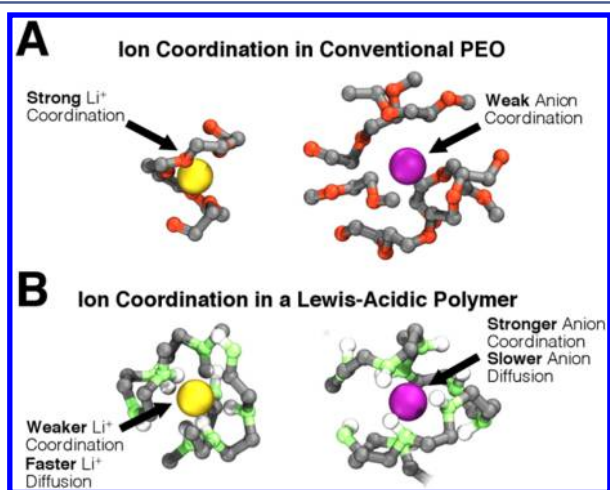


Figure 3. Comparison of cation (left) and anion (right) solvation structures in PEO (A) and a representative Lewis-acidic polymer (B).¹⁷ Strong cation coordination and weak anion coordination in PEO leads to relatively slow Li-ion diffusion and rapid anion diffusion. Lewis acidic polymers reverse this relationship, leading to a favorable increase in Li-ion diffusion while preserving salt solubility.

(6) Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. Nano-composite polymer electrolytes for lithium batteries. *Nature* **1998**, *394*, 456–458.

(7) Wright, P. V. Developments in polymer electrolytes for lithium batteries. *MRS Bull.* **2002**, *27*, 597–602.

(8) Zhang, L.; Zhang, Z.; Harring, S.; Straughan, M.; Butorac, R.; Chen, Z.; Lyons, L.; Amine, K.; West, R. Highly conductive trimethylsilyl oligo(ethylene oxide) electrolytes for energy storage applications. *J. Mater. Chem.* **2008**, *18*, 3713–3717.

(9) Webb, M. A.; Jung, Y.; Pesko, D. M.; Savoie, B. M.; Yamamoto, U.; Coates, G. W.; Balsara, N. P.; Wang, Z.-G.; Miller, T. F. Systematic computational and experimental investigation of lithium-ion transport mechanisms in polyester-based polymer electrolytes. *ACS Cent. Sci.* **2015**, *1*, 198–205.

(10) Pesko, D. M.; Jung, Y.; Hasan, A. L.; Webb, M. A.; Coates, G. W.; Miller, T. F.; Balsara, N. P. Effect of monomer structure on ionic conductivity in a systematic set of polyester electrolytes. *Solid State Ionics* **2016**, *289*, 118–124.

(11) Pesko, D. M.; Webb, M. A.; Jung, Y.; Zheng, Q.; Miller, T. F.; Coates, G. W.; Balsara, N. P. Universal relationship between conductivity and solvation-site connectivity in ether-based polymer electrolytes. *Macromolecules* **2016**, *49*, 5244–5255.

(12) Druger, S. D.; Nitzan, A.; Ratner, M. A. Dynamic bond percolation theory: A microscopic model for diffusion in dynamically disordered systems. I. Definition and one-dimensional case. *J. Chem. Phys.* **1983**, *79*, 3133–3142.

(13) Nitzan, A.; Ratner, M. A. Conduction in polymers: dynamic disorder transport. *J. Phys. Chem.* **1994**, *98*, 1765–1775.

(14) Webb, M. A.; Savoie, B. M.; Wang, Z.-G.; Miller, T. F., III. Chemically specific dynamic bond percolation model for ion transport in polymer electrolytes. *Macromolecules* **2015**, *48*, 7346–7358.

(15) Diddens, D.; Heuer, A.; Borodin, O. Understanding the lithium transport within a Rouse-based model for a PEO/LiTFSI polymer electrolyte. *Macromolecules* **2010**, *43*, 2028–2036.

(16) Hanson, B.; Pryamitsyn, V.; Ganesan, V. Mechanisms underlying ionic mobilities in nanocomposite polymer electrolytes. *ACS Macro Lett.* **2013**, *2*, 1001–1005.

(17) Savoie, B. M.; Webb, M. A.; Miller, T. F. Enhancing cation diffusion and suppressing anion diffusion via Lewis-acidic polymer electrolytes. *J. Phys. Chem. Lett.* **2017**, *8*, 641–646.