Researchers flip script for Li-Ion electrolytes to simulate better batteries

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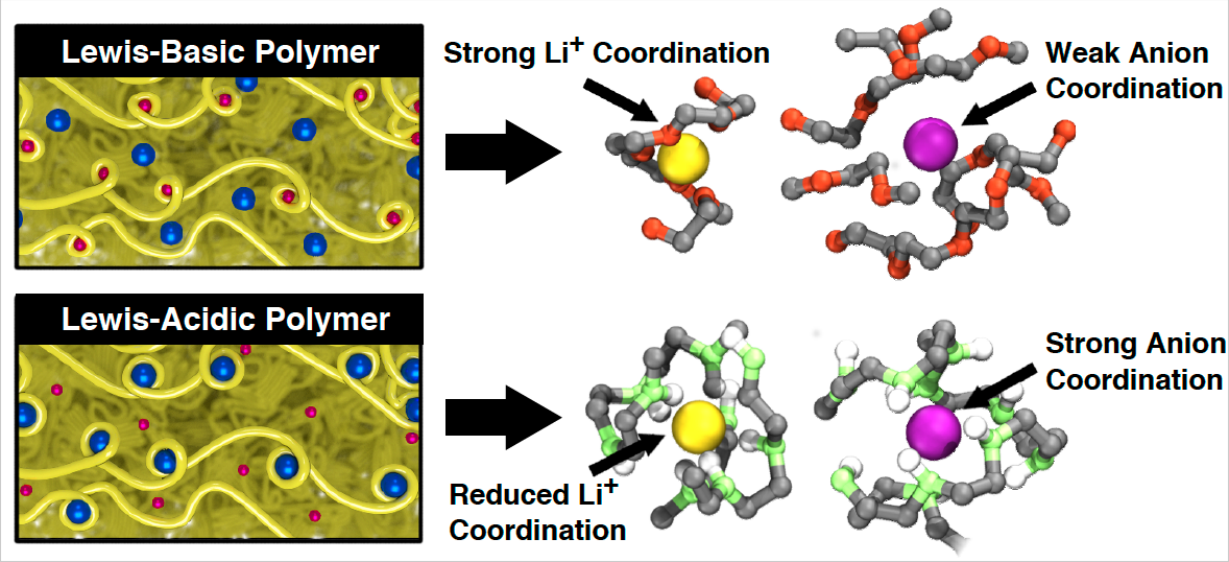

Contrasting solvation strategies in conventional electrolytes (top-left) and a new class of Lewis-acidic polymer electrolytes (bottom-left). Strong lithium ion coordination and weak anion coordination in Lewis-basic polymers (top-right) leads to a slow conduction of lithium ions and an unfavorably fast conduction of anions. Reduced lithium ion coordination and strong anion coordination in Lewis-acidic polymers (bottom-right) allows for rapid conduction of positive lithium ions -- a property that lithium-ion batteries require to maintain efficiency during discharge/charge cycles. Credit: ORNL

Ever since Italian physicist Alessandro Volta invented the first battery out of a stack of copper and zinc disks separated by moistened

cardboard, scientists have been searching for better battery materials.

Lithium-ion batteries, which are lighter, longer-lasting, and functional under a wider range of temperatures than standard batteries, power everything from cell phones to aircraft carriers to electric cars. Their ubiquitous use makes their stability, efficiency, and safety important for businesses and consumers alike.

One of the main challenges researchers face in dealing with battery components, however, is finding novel, nonflammable materials for the electrolyte. The electrolyte is the crucial battery component that shuttles lithium ions during charging and discharging, transferring the energy that enables a battery's use. Now, scientists are looking for electrolytes that are not only stable but also conductive to lithium ions, a property that lithium-ion batteries require to maintain efficiency during charge cycles.

A team led by the California Institute of Technology's (Caltech's) Thomas Miller used the Cray XK7 Titan supercomputer at the US Department of Energy's (DOE's) Oak Ridge National Laboratory (ORNL) to identify potential electrolyte materials and predict which ones could enhance the performance of lithium-ion batteries. Using Titan, the researchers ran hundreds of simulations—each consisting of thousands of atoms—on possible new electrolytes. The work led them to the identification of new electrolytes with promising properties for lithium-ion conduction.

Miller, a professor of chemistry at Caltech and the principal investigator on the project, said a leadership-class supercomputer was essential to meeting the project's goals because the simulations ran on timescales that ranged from a femtosecond (one quadrillionth of a second) up to a microsecond (one millionth of a second), spanning nine orders of magnitude. "These calculations are extremely demanding in terms of computational resources," he said. "We are dealing with—from a

molecular perspective—very big systems and long timescales." Miller said the team needed to rapidly describe complex materials to screen across multiple candidate electrolytes. Luckily Titan—part of the Oak Ridge Leadership Computing Facility (OLCF), a DOE Office of Science User Facility located at ORNL—enabled them to do just that.

Electrodes, Electrons, and Electrolytes

All batteries contain an electrolyte, a liquid or solid that insulates the flow of electrons but promotes the flow of ions between the anode and cathode, which are the two electrodes that conduct electrical current. Electrons inside the battery move through a circuit out of the battery and power a device on the way to the cathode, the battery's positive electrode. When the electrons leave the anode, the positively charged ions (the lithium ions) move across the electrolyte to the cathode. This process continues until the reactants are depleted (meaning the battery loses its charge) or the circuit is disconnected.

In rechargeable batteries the cycle can be reversed, with the lithium ions diffusing back to the anode during charging. The lithium ions are conserved during charging and discharging, diffusing back and forth between the electrodes by an hourglass-like mechanism in which the lithium ions are like the grains of sand that change direction when the reaction reverses.

Typically lithium-ion batteries feature liquid electrolytes, but new research is focusing on polymeric electrolytes, which are known to be more stable, less flammable, and less volatile. Plastics, rubber, and proteins are polymers, or long chains of sequentially repeating molecules, that are used in many different technologies due to their diverse functionality and reliability.

"The polymers that we are studying are made of one molecular unit that's

repeated tens of thousands of times," Miller said.

Historically the best polymer electrolyte for lithium-ion batteries has been polyethylene oxide (PEO), a versatile polymer with various applications in both medicine and science. The addition of lithium salts to polymers like PEO enables these polymers to be used as solid polymer electrolytes. The salt contains lithium cations, positively charged ions that get shuttled back and forth in the battery, and some negatively charged anions to balance the charge.

An ideal electrolyte is one that readily dissolves and then conducts lithium ions. The problem with PEO is that it conducts lithium ions poorly in comparison to liquid electrolytes, meaning the ions travel slowly to the cathode thereby limiting the current the battery can produce. It also conducts the anions too quickly. While the anions are useful for balancing the charge of lithium ions, their rapid conduction creates a loss in battery voltage.

Using this knowledge Miller's team began a hunt for more efficient polymers. Brett Savoie, a postdoctoral fellow at Caltech, thought reversing the typical solid polymer electrolyte dynamic would help Miller's team find more ideal polymers. "You want to conduct the positive lithium ions," Miller said. "You don't want to conduct the negative ions in the salt."

The team set out in search of polymers that would conduct lithium ions more quickly than PEO. Using high-performance computing, Miller's team created the chemically specific dynamic bond percolation model, a coarse-grained simulation protocol that was developed and validated by the group, to screen electrolyte materials based on short molecular dynamics trajectories. They first screened a set of 500 diverse classes of polymers to find ones that were better conductors of lithium ions.

One group of polymers, in particular, fit the bill.

Simulating Lewis-Acidic Polymers

Lewis-acidic molecules are ones that hold a positive charge and strongly interact with anions. Miller's team designed simulations using Lewis-acidic polymers for electrolytes in hopes that they would slow down anion conduction. These polymers, Miller said, have not been simulated or studied experimentally.

The team found that, in the simulation, this class of polymers not only conducted the anions more slowly than PEO but also conducted the positive lithium ions more quickly. Because Lewis-acidic chemical groups' positive regions are contained in a small amount of space and their negative regions are spread out over a large amount of space, they give positive lithium ions more opportunities to dissolve, Miller said. "It was known that Lewis-acidic molecules slowed down anions," Savoie said. "What was surprising here was that by using a purely Lewis-acidic system, we also sped up the lithium."

The simulations showed that these polymers may be capable of producing an eight-fold increase in desired lithium conduction and a marked decrease in the unwanted anion conduction. This would be—given the historically slow pace of discovering new polymer materials—a very large jump.

The team tracked the molecular evolution on timescales that ranged from a femtosecond to a microsecond. The ability to span this vast range of timescales was made possible with Titan, which can compute at a rate of 27 petaflops, or 27 quadrillion calculations per second.

The team used LAMMPS, an open-source classical molecular dynamics code, to run its simulations, looking at several dozen polymer-salt

combinations under different salt concentrations. About 400 simulations at a time were run in parallel, with each simulation using 16 CPUs and 1 GPU. Each simulation consisted of around 3,000 atoms periodically replicated in three-dimensional space to create the effect of a bulk polymer material, with a certain concentration of ions per unit of periodic replication.

Supercomputers Conducive to Polymer Screening

Though Miller's team is continuing to screen promising polymer sequences with the goal of completing its 5,000th candidate electrolyte by the end of 2017, the project has already led to the identification of polymers that may favor lithium-ion conduction.

"These new polymers are exciting because they seem to overcome some of the main problems with other polymer materials," Miller said. "The predictions indicate that these polymers might exhibit a substantial increase in conductivity. It would be a tremendous improvement from the current lithium-ion conductivity that PEO affords," Miller said.

The researchers continue to run their simulations on Titan under an Innovative and Novel Computational Impact on Theory and Experiment award, for which they've been allocated 40 million core hours.

Miller said next-generation supercomputers like the OLCF's Summit, scheduled to come online in 2018, will greatly expand their research capabilities, allowing his team to explore even larger areas of chemical space.

"With faster computers we'll be able to do this with even better accuracy," Miller said. "We'll also be able to look at more polymers more reliably and on longer timescales. Improved computers are going to rapidly accelerate the pace of discovery for materials of this kind."

More information: Brett M. Savoie et al, Enhancing Cation Diffusion and Suppressing Anion Diffusion via Lewis-Acidic Polymer Electrolytes, *The Journal of Physical Chemistry Letters* (2017). DOI: 10.1021/acs.jpclett.6b02662