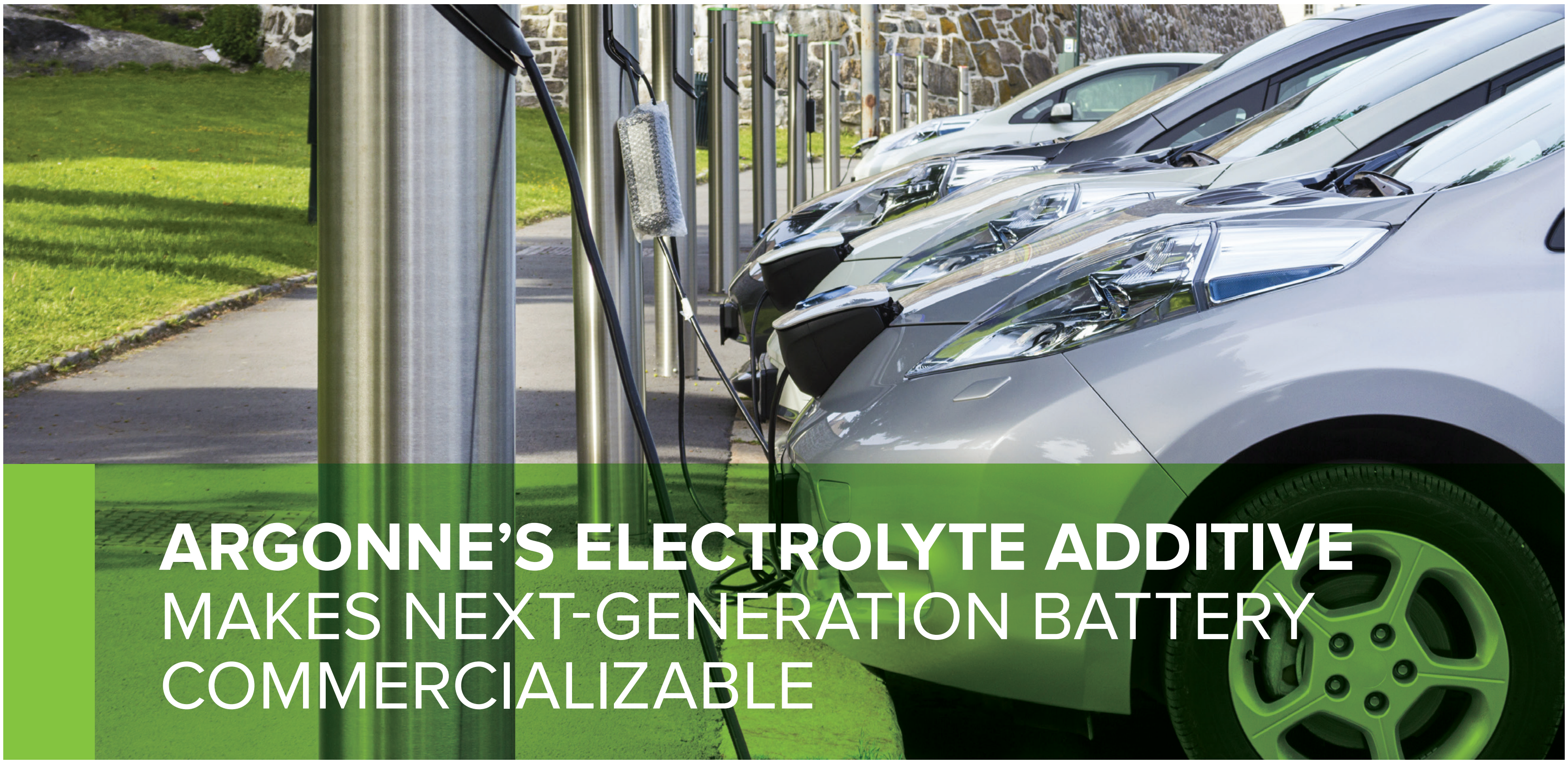
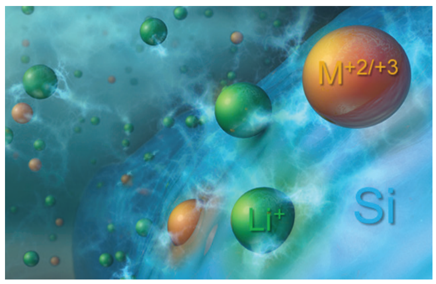
Argonne NATIONAL LABORATORY



ARGONNE’S ELECTROLYTE ADDITIVE MAKES NEXT-GENERATION BATTERY COMMERCIALIZABLE

The present lithium-ion battery has changed our society with the emergence of portable electronics and electric vehicles. But the demand for even greater energy density is driving the search for new battery chemistries.

With more than 250 battery technologies available for licensing and thousands of publications in scientific journals, the U.S. Department of Energy’s Argonne National Laboratory is a global leader in energy storage research. A recent addition of a new Argonne battery technology is the mixed-salt electrolyte for silicon anodes (MESA), developed in the Chemical Sciences and Engineering Division.



Charging results in doubly or triply charged metal cations, such as Mg^{2+} (orange spheres), along with singly charged lithium ions (green spheres) being co-inserted from the electrolyte into the silicon (blue spheres) anode material. This process stabilizes the anode, enabling long term cycling of lithium-ion batteries.

THE SILICON-ANODE BATTERY

Conventional cathodes are already operating near theoretical capacities or energy densities, so many researchers have turned to the anode for the needed boost. Silicon is the most promising alternative to replace the graphite anode, the current state of the art.

Silicon has a significant theoretical energy storage capacity advantage over graphite, being able to store almost ten times the lithium as does graphite. Increasing silicon’s attractiveness commercially is its low cost. It is the second most abundant material in the Earth’s crust, and its prevalence in computing and telecommunications hardware means there exists substantial processing technologies.

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THE CHALLENGE

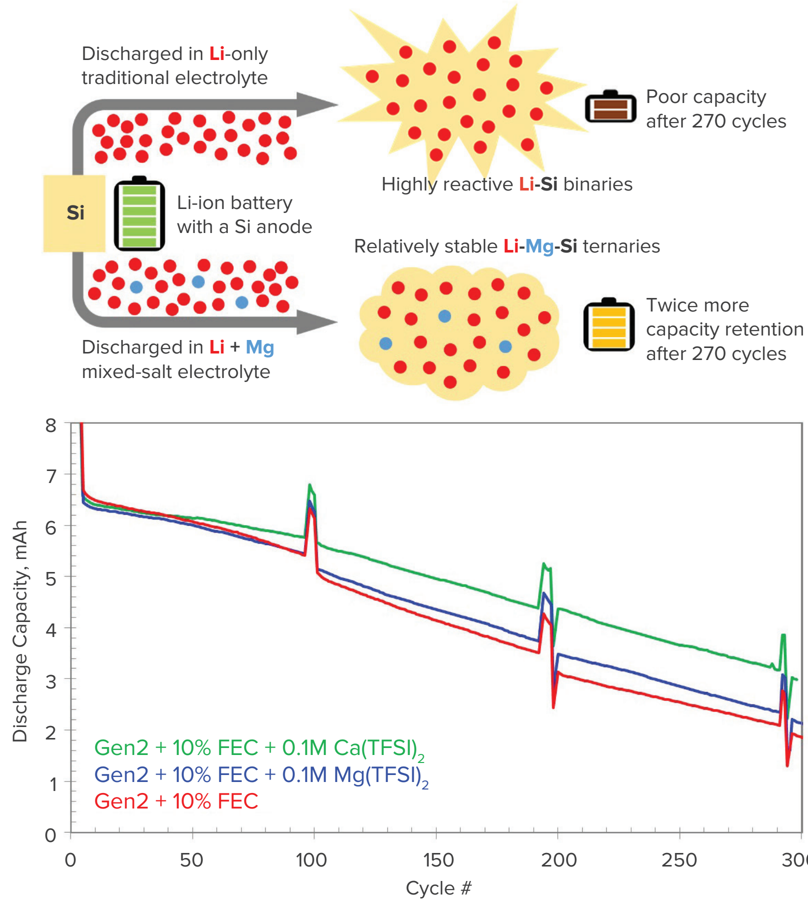
Silicon anodes have multitude problems before they can be widely implemented in commercial batteries. The most critical is their reactivity when charged. This reactivity causes major inefficiencies, which severely reduce cycle life and long-term performance.

THE ARGONNE SOLUTION

Our MESA targets this reactivity with the aim of reducing the detrimental side reactions it causes. We tame the reactive species by replacing them with relatively stable ones. Lithium-ion battery electrolytes currently contain a solvent mixture, with a dissolved lithium salt and at least one, often more than three organic additives. We have developed a unique electrolyte additive strategy — a small amount of a second salt containing any one of several doubly or triply charged metal cations (Mg^{2+}, Ca^{2+}, Zn^{2+}, or Al^{3+}). Our enhanced electrolyte mixtures give silicon anodes increased surface and bulk stabilities, improving long-term cycling and calendar life.

Of the metal salts tested in 2032 coin cells, the added electrolyte salts with either magnesium (Mg^{2+}) or calcium (Ca^{2+}) cations proved to work the best over hundreds of charge — discharge cycles. For instance, in cells with pure silicon anodes coupled with lithium-rich cathodes, the energy densities surpassed those for comparable cells having graphite chemistry by up to 50%, as long as a compatible silicon source is used to allow for multivalent ions to diffuse through the anode.

The benefits also translated to non-optimized xx3450 format single-layer pouch cells made by Argonne's Cell Fabrication Modeling and Prototyping Facility with the magnesium and calcium cations in the MESA. These cells show superior cyclability and higher coulombic efficiencies in both half-cell and full-cell configurations when compared with cell tests of state-of-the-art electrolytes.



Improved performance attained by using MESA in full cells with silicon anodes versus lithium- and manganese-rich composite cathodes (7 mAh, xx3450 format pouch cells). Blue and green lines show performance with Mg^{2+} and Ca^{2+} in MESA, respectively, and red line is for no MESA.

The best-performing cell of quadruplicate sets (for calcium cation) demonstrated 65% capacity retention after 300 cycles at a C/3 discharge rate.

BENEFITS

The MESA formulations are inert, stable with extended cycling, inexpensive, and non-toxic. With the widespread use of MESA formulations, we anticipate commercialization of Li-ion battery anodes composed of silicon in the near future. This will make Li-ion batteries lighter and run longer with a single charge. In addition, since the new additives are mostly inert against other components in the cell, researchers will find their advances in cathodes, binders, electrolytes or silicon sources all synergetic with the gains in performance and stability from this new chemistry. This should accelerate materials discovery for Li-ion battery anodes.

Potential applications for the silicon-anode cell with MESA electrolyte span the energy storage gamut: consumer electronics, transportation, military, and aerospace.

The next step for the silicon-anode battery is to optimize the engineering aspects such as other cell components, for instance, the polymer binder used to make the electrodes or the silicon source.

Further technical details are available in "Using Mixed Salt Electrolytes to Stabilize Silicon Anodes for Lithium-Ion Batteries via In situ Formation of Li-M-Si Ternaries (M=Mg, Zn, Al, Ca)," *ACS Applied Materials & Interfaces* (July 2019).