

LITHIUM BATTERIES

High energy and long cycles

All-solid-state lithium batteries typically suffer from low coulombic efficiencies and lithium dendrite growth at high current densities. Now, a silver–carbon composite anode is demonstrated that mitigates some of these problems, even for a prototype cell with a high energy density of over 900 Wh L⁻¹.

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Owing to the high theoretical specific capacity and the lowest electrochemical potential among anode materials, lithium metal has long been viewed as the ideal anode material for rechargeable batteries. However, lithium metal anodes suffer from Li dendrite growth that both poses safety concerns and degrades electrochemical performance. Instead, graphite anodes have dominated the Li-ion battery (LIB) market for the last two decades. Advances in LIBs with graphite anodes have now approached their theoretical energy density limit, prompting the emergence of many new types of post LIBs. All-solid-state lithium batteries (ASSLBs) offer hopes for improved battery safety as well as higher energy and power density^{1,2}. To balance lithium intercalation/de-intercalation and thus achieve high coulombic efficiency (CE) during battery cycling, however, an excess lithium metal anode is often required. Removing excess lithium at anodes would lead to more energy dense and even safer batteries³, but is currently a major challenge in the ASSLBs development.

Now writing in *Nature Energy*, Dongmin Im and colleagues at Samsung design an ASSLB without excess lithium, which is based on an argyrodite (Li₆PS₅Cl) solid electrolyte. Their prototype battery with an unusually large capacity of 600 mAh demonstrates a stable CE greater than 99.8% after 1000 cycles⁴. Because there is no excess lithium at the anode, high volumetric energy density of the ASSLBs (over 900 Wh L⁻¹) is achieved, exceeding that of commercial LIBs⁵. By contrast, the currently reported maximum CE of a lithium metal anode in a liquid electrolyte system is 99.5%⁶ after initial cycling with a large anodic lithium reservoir, decreasing energy density. Although encouraging performance and pioneering work on batteries without excess lithium has recently been reported⁷, those batteries have a much smaller capacity (250 mAh), produce fewer stable cycle numbers (90 cycles) and use a liquid electrolyte instead of a solid electrolyte.

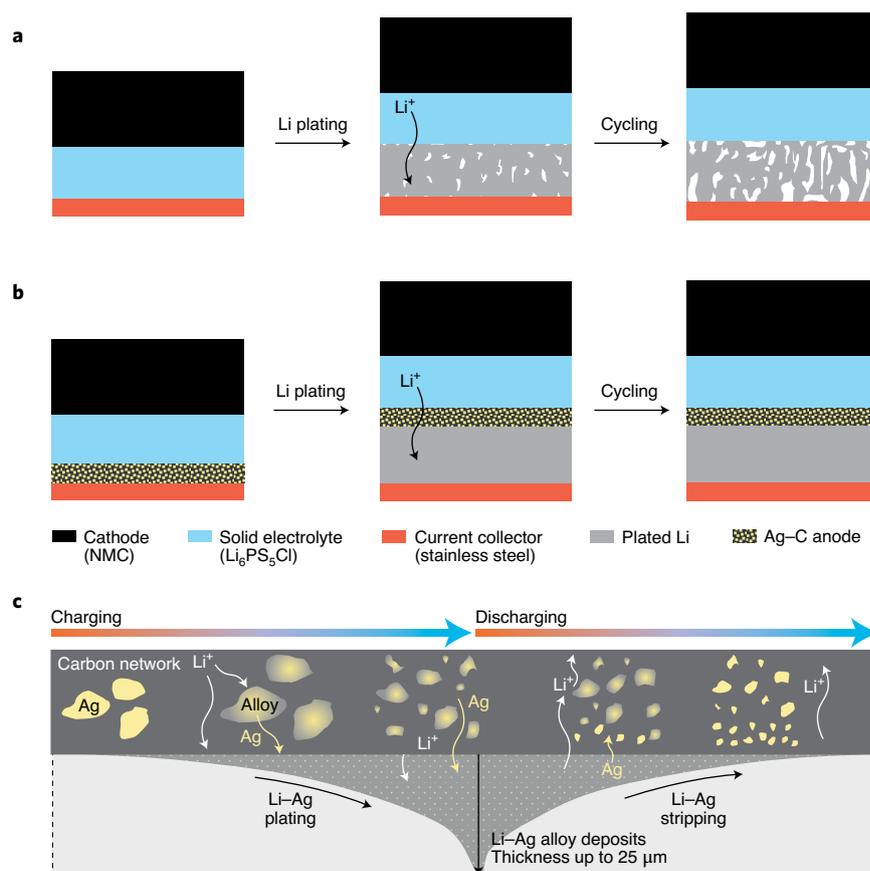


Fig. 1 | Morphological effect of the Ag-C nanocomposite anode in ASSLBs. The ASSLBs consist of a NMC (LiNi_{0.90}Co_{0.05}Mn_{0.05}O₂) cathode, an argyrodite solid electrolyte and a stainless steel current collector. **a–b**, Nonhomogeneous lithium metal growth and resulting poor performance (**a**) are completely mitigated by adding a nanocomposite anode (**b**), resulting in CE of more than 99.8% for 1000 cycles. **c**, Microstructure and compositional changes inside the nanocomposite anode during charge and discharge. Starting from a lithiation of silver and carbon particles, Li–Ag alloying and Li–Ag deposition take place, leading to deposit thickness up to 25 μm. While lithium diffuses back to the cathode in the discharge process, de-alloying and redistribution of silver atoms are observed with localized silver concentration near the bottom in the nanocomposite.

The key to Im and co-worker's cell design is the 5-μm-thick nanocomposite anode between the Li₆PS₅Cl electrolyte and the stainless steel current collector. The anode nanocomposite consists of silver nanoparticles (60 nm average diameter)

supported on carbon black, prepared by conventional screen printing. Im and co-workers show that in the absence of the nanocomposite (Fig. 1a), the lithium morphology after plating at moderate rates (for example, 0.05 C) is thick with

significant void formation between the solid electrolyte and the plated lithium metal. This void formation significantly decreases the contact between the current collector, the plated lithium and the electrolyte, which could lead to lithium dendrite formation⁸. The poor contact results in non-homogeneous growth of lithium deposits, displaying a capacity retention of only 10% after 30 cycles. By contrast, a dense and uniform lithium microstructure is formed in the presence of the nanocomposite silver/carbon black anode even after 1000 cycles with neither isolated lithium nor void formation (Fig. 1b).

Im and team examined the local microstructure and composition inside the nanocomposite during cycling. They uncovered that during the early stage of charging (Fig. 1c), a lithiation of silver and carbon particles takes place, leading to the formation of a Li–Ag alloy and particle densification; near the end of charging, lithium and silver are progressively deposited between the nanocomposite and current collector. Upon discharge, lithium ions return to the cathode through the nanocomposite and electrolyte. Some silver atoms diffuse back to the nanocomposite layer, but many others remain at the bottom part in the nanocomposite to form a

locally-concentrated area of silver. Clearly, the Li–Ag alloy initially formed inside the nanocomposite layer seeds homogenous lithium deposition and minimizes dendrite growth. Furthermore, due to its mixed ionic and electronic conducting properties, the nanocomposite enhances contact between the current collector, the plated lithium and the electrolyte. The anode also acts as a blocking layer between the electrolyte and the lithium metal, mitigating the reduction of the argyrodite solid electrolyte^{9,10}. Lastly, the researchers also optimized the carbon-to-silver ratio to accommodate the pulverization and re-segregation behaviour of the silver nanoparticles, leading to a long cycle life without degradation.

The demonstration of Im and team is an important step toward practical, large-scale ASSLBs. However, more fundamental studies on the alloying and de-alloying mechanism within the nanocomposite will help to further optimize other parameters, such as the amount of silver loading, particle size and nanocomposite thickness. Also, the cause of the silver concentration and the effect of diffusion kinetics at high currents remain to be further explored. A theoretical approach, such as electric field-induced phase modelling under applied bias¹¹, may help to explain the distribution of silver in the

nanocomposite. Furthermore, computational and experimental research to discover better nanocomposite materials as anodes should be considered with an eye toward economical manufacturing of lithium batteries with improved performance. □

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