Preemptive sustainable strategies could assist in next-generation energy storage.

Sustainable design of fully recyclable all solid-state batteries*

By **Darren H.S. Tan** and **Zheng Chen**

With today's rapidly increasing demand for lithium-ion batteries (LIBs) for emerging applications, such as electric vehicles (EVs) and large-scale grid storage, it begs the question of how sustainable batteries really are. Proponents of increasing electrification of our modern society often tout the environmental benefits of using battery energy storage over traditional fossil fuels, citing direct reductions in greenhouse gas emissions, especially when paired with renewable energy generation. Unfortunately, these often leave out considerations for the "dark side" of LIBs that few manufacturers in the battery industry have addressed: how to deal with batteries at their end of life. As the world accelerates toward displacing conventional vehicles with EVs, methods of handling large volumes of spent LIBs when these devices reach their end of life have not been fully developed. This potentially results in the accumulation of battery waste that will ultimately undo the environmental benefits batteries originally sought to achieve.

Unlike conventional waste generated from consumer commodities such as paper, plastics, or metals, spent battery packs cannot be treated in the same category. They need to be collected, transported, stored, and treated using specialized processes and avoiding potential fire/hazards arising from embedded chemical energy within. Additionally, we do not want to simply dispose of LIBs, as they contain economically valuable materials, such as lithium, cobalt, nickel, and other transition metals. However, existing technologies used to recover and recycle batteries tend to be energy-intensive, costly, and use copious amounts of toxic chemicals, which can be difficult to handle. Conventional recycling technologies, such as pyrometallurgy or hydrometallurgy's recovery efficiencies as a ratio of the entire battery, also remain relatively low because of poor recovery rates of other components in the cell.

The biggest obstacle faced in LIB recycling today is not a lack of good technology but the fact that LIBs are not designed to be recycled. This naturally creates technical hurdles to engineer processes to dismantle, separate, and recover materials from within. To avoid repeating the same problem with the next generation of batteries, it is vital to explore strategies to incorporate recycling-friendly designs before they enter the market. In the extended version of this work published in *MRS Energy & Sustainability**, researchers adopted the concept of "design for recycling," developing a sustainable and scalable strategy for next-generation all solid-state batteries (ASSBs). It was demonstrated that such an approach dramatically reduces the sophistication, energy/material input, and environmental impact of ASSB recycling compared to conventional LIBs. In traditional pyrometallurgical or hydrometallurgical methods to recycle batteries, cathode materials are typically broken down into their precursor forms and subsequently leached to recover valuable elements. Moreover, the electrolytes are often decomposed and cannot be recycled for further use. Taking a different approach, the team adopted a direct regeneration strategy, avoiding the breakdown of core chemical components to produce recycled materials that can be directly used to make fresh batteries without additional resynthesis steps. Moreover, this was experimentally demonstrated for both the spent cathode and solid electrolytes, increasing the material recovery rates relative to the entire battery. The new batteries made with recycled cathodes and electrolytes were found to achieve similar performance to the pristine state, completing the recycling loop.

To design the improved process, several guiding principles were selected: (1) design chemistries that favor component separation during disassembly; (2) eliminate the use of any toxic, expensive, or difficult-to-handle organics; (3) recover other components in the cell; and (4) ensure scalability/relevance to a variety of ASSB cell configurations. The figure illustrates the five-step procedure involving cell/pack disassembly, solution processing, phase separation, recovery, and direct regeneration.

At the onset, ASSB recycling offers several advantages compared to conventional liquid-electrolyte-based LIBs. Its intrinsic nonflammability reduces potential safety hazards arising from dealing with organic liquids. Additionally, fewer components from the absence of polymeric separators or lithium salts/additives reduce separation steps needed prior to recycling. In this case, the battery was not separated and was directly treated whole in ethanol, a nontoxic and relatively low-cost solvent. This allows the sulfide-based solid electrolyte (Li_6PS_5Cl) to be fully dissolved and with the cathode particles as the precipitate. After dissolution in ethanol, the solid electrolyte in the solution phase was separated from the cathode using gravity-based decanting. Subsequently, the solvent was removed under vacuum, and the solid electrolyte was mildly annealed to regain its original electrochemical properties. An ionic conductivity of 1.48 mS cm^{-1} was measured after recycling, which is within the same order of magnitude as its pristine form

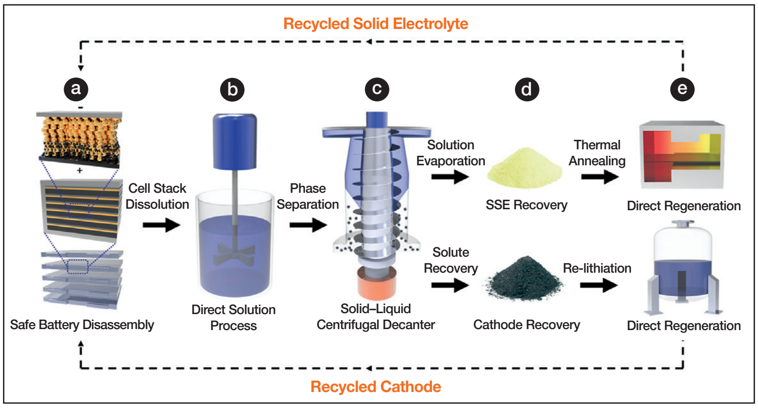
---

Darren H.S. Tan, Department of NanoEngineering, University of California, San Diego, USA
Zheng Chen, Department of NanoEngineering, Sustainable Power & Energy Center, and Program of Chemical Engineering, University of California, San Diego, USA; zhengchen@eng.ucsd.edu

*This article originally appeared in its entirety in *MRS Energy & Sustainability*: doi.org/10.1557/mre.2020.25.

(1.62 mS cm^{-1}). This represents an unsophisticated, low energy/low material input method to recycle solid electrolytes.

For the electrodes, the solid cathode particles harvested after decanting were surface treated using de-ionized water to remove the interfacial products formed. Unlike LIBs, interfacial products formed on electrode surfaces in ASSBs are inorganic in nature, such as S, P_2S_5, and LiCl, and can be washed away with water. As spent cathodes ($LiCoO_2$ in this case) are lithium deficient, a consequence of battery cycling, their lithium content needs to be compensated in order to regain its electrochemical properties. To do so, a direct hydrothermal regeneration process using an aqueous solution of lithium hydroxide (LiOH) was completed, followed by thermal annealing. Subsequent measurements found that the cathode resumed its original lithium content and microstructure, and thus became fully regenerated. One of the key benefits of using hydrothermal regeneration is its inherent robustness and ability to be applied to cathodes with varying degrees of degradation. As the re-lithiation is self-saturating, there is no need to evaluate the degree of lithium loss within spent cathodes prior to regeneration, enabling a “one pot” regeneration for cathodes harvested from different spent battery sources.



Schematic of the proposed all solid-state battery (ASSB) recycling procedure at an industrial scale, based on the principles of direct recycling. Cell packaging of the ASSB is first removed before the entire cell stack is processed in a solution without further component separation. Solids and liquids are then separated and recovered for direct regeneration via thermal annealing for the solid electrolyte and direct re-lithiation for the cathode. SSE, solid-state electrolytes. Credit: Tan et al.

To close the recycling loop, both regenerated solid electrolytes and cathodes were used to fabricate new ASSBs and cycled under similar conditions as the original cell. Both cells display comparable first cycle charge- and discharge-specific capacities as well as overall cell polarization. Additionally, both cells achieved high capacity retention and average Coulombic efficiencies of >99.9%. While these results demonstrate the effectiveness of recycling the spent ASSBs, it should be noted that this has yet to be conducted in a full commercialized cell pack at large capacities and material quantities (>2 Ah). Thus, it is not entirely clear how future multilayer stacked cells, which may contain carbon additives, binders, and other additional components, may influence the recycling approach. Nonetheless, the recycling principles of separation, recovery, and direct regeneration can also be applied to alternative cell chemistries with ease, also using inexpensive and relatively safe solvents such as acetonitrile, water, or methanol, allowing cathode materials to be readily separated from the dissolved solid-state electrolytes during recovery. Likewise, direct regeneration methods can be applied to alternative cathodes as well, using either solid-state sintering methods or molten eutectic salts, to enable direct re-lithiation of materials such as lithium nickel cobalt aluminum oxide (NCA)- or lithium nickel manganese cobalt oxide (NMC)-type chemistries commonly used in EVs.

Despite LIB’s commercialization in the 1990s, the urgency of battery sustainability did not occur until the early 21st century, where applications ventured beyond the small capacity (and easier to handle) personal device markets. With the advent of EVs, the size and volume of battery packs at the device’s end of life presented a growing logistical and environmental nightmare for manufacturers and third-party waste collectors. Unfortunately, to re-design recycling-friendly batteries will require battery manufacturers to modify their existing production protocols, with evident cost and performance consequences. As such, we should look toward preparing future technologies and enable sustainable production-to-recycling manufacturing processes that meet both environmental and consumer device target specifications. Among various contenders, ASSBs are regarded as a front-runner of the future energy-storage technologies, owing to their potential for improved safety, higher energy density, and lower costs. While media spotlights have been placed on breakthroughs in ASSB technologies, both in industry and academia, comparatively little attention has been placed on their potential recyclability thus far. It is prudent to avoid similar mistakes.

Developing a good technology is not enough. Many challenges associated with battery recycling are due to the complex logistics of battery handling. The lack of a battery collection infrastructure today is just as important if not more so than developing better recycling technologies. As an example, transporting used batteries over long distances to recycling centers would typically be done via trucking. This requires a Class 9 Hazardous status, which increases transport costs by 50–100 times that of regular cargo. To this end, ASSBs, with much improved safety, may allow us to circumvent these problems and to be treated like regular cargo during transport. Likewise, this translates into safer long-term storage in urban environments, reducing incidents of fire and allowing workers to handle them with reduced safety hazards faced in LIB disassembly.

While ambitious, setting high standards for battery recycling and sustainable processes are not out of reach. Lead-acid batteries commonly used in internal-combustion engine vehicles today have achieved more than 99% collection and recycling rates in most countries. Through the principles of design for recycling, such goals are not only conceivable, but necessary for LIBs and next-generation batteries. □