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Imagining circular beyond lithium-ion batteries

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INTRODUCTION

Cobalt, nickel, and lithium are essential ingredients in today's lithium-ion batteries (LIBs), but their continued use presents economic, ethical, and environmental challenges. Projected shortages of these metals in the coming decades may cause increased prices, exacerbated by highly localized supply chains. The last few years have brought attention to the harsh conditions of and use of child labor in the extraction of some of these materials, adding social and ethical concerns. Compounded with the increasing demand for LIBs brought by the expanding electric vehicle market and rapid digitalization of society, there is an imminent need to address these issues. Society must now begin to consider the implications of a LIB's full life cycle, including the carbon footprint, the economic and environmental costs, and material access. These challenges motivate the case for degradable or recyclable batteries sourced from earth-abundant materials whose life cycle bears minimal impact on the environment.

Current LIBs utilize transition metal oxide and phosphate-based cathodes (e.g., $LiNi_xMn_yCo_zO_2$, $LiFePO_4$) and graphite-based anodes, which are physically separated by a polymer-based separator impregnated with a non-aqueous electrolyte-containing lithium salt. Material acquisition, purification, and production result in the greatest portion of CO_2 emissions at ca. 25 kg CO_2 equivalents per kWh, followed by battery assembly at 17 kg CO_2 equivalents per kWh (Figure 1).[1] Recharging (using electricity from the power grid to charge the battery after use) of the LIB incurs minor CO_2 emissions, whereas recycling produces ca. 8 to 12 kg CO_2 equivalents per kWh.[1] At their end of life, LIBs can be repurposed for a secondary application, recycled, or disposed to an eWaste facility (typically imported to developing countries).[2]

Despite the benefits of LIB recycling, only 5% of LIBs were recycled in the EU in 2017.[3] This may be attributed to recycling's energy cost, safety issues, and the need to further establish the recycling technology. Leading recycling approaches for LIBs include (1) pyrometallurgy, (2) hydrometallurgy, and (3) direct cathode recycling. Pyrometallurgy is used on the complete LIB to separate the components as molten alloys and solid waste (slag) from organic components at high temperature. Hydrometallurgy involves the use of sulfuric acid and hydrogen peroxide extracting desired metals from the cathode. Last, direct recycling of the cathode involves physically removing the whole cathode and reassembly into a new battery.

In attempts to redirect LIBs away from landfills, policies have been enacted by several global economies. A proposal from the EU targets an LIB recycling efficiency of 65% by 2025.[4] Also, China has restricted the import of eWaste from other countries. In contrast, the USA does not have federal policies requiring LIB recycling. However, there are US government-sponsored programs focused on LIB recycling, such as the Department of Energy's supported ReCell Center. Taken together, these policies do not mandate the method of recycling or require a certain net reduction in CO_2 emissions.[1]

The high energy cost, low material recovery, and safety concerns associated with LIB recycling have prompted the investigation of a variety of alternative battery chemistries that are degradable or more easily recyclable. These approaches may offer metal-free or low-metal solutions to energy storage.

Here, we reflect upon recent advances in degradable and recyclable energy storage systems beyond the LIB. We define "degradation" as the chemical

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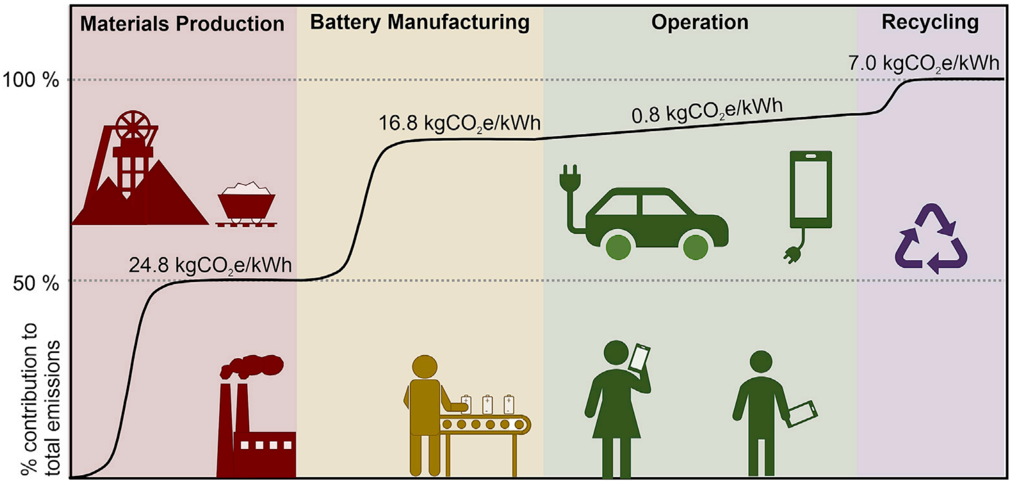


Figure 1. CO$_2$ emissions of LIB production, manufacturing, operation, and recycling
Emissions for the operation (or charging) were estimated using the Greenhouse Gas Emissions from Electric and Plug-In Hybrid Vehicles – Results from US Department of Energy and converted assuming a 40 kWh battery has a range of 226 miles.

decomposition of materials to smaller molecules using acidic, basic, or enzymatic conditions. In contrast, we define "recyclable" as the extraction and recovery of material. Recent demonstrations in full battery cells are the focus.

Degradable and recyclable beyond-LIBs

The landscape for fully circular beyond-LIBs is not fully developed, presenting enormous opportunity for research and innovation. Unlike LIBs, these alternative batteries have a variety of chemistries, which means that not "one" recycling or degradation strategy is appropriate for all (Table 1).

Transient batteries

Much can be learned from the emerging field of transient batteries. These batteries are flexible or stretchable but, most importantly, degradable. Transient batteries tend to deliver less energy due to their intended biomedical application, which is beneficial for short-term sensors since they disappear in days or weeks with the help of enzymes. Although these batteries have a limited useful lifetime, their degradability offers the possibility of recovery and reconstitution of the active materials.

Wang et al.[11] demonstrated a Mg paper anode and Mo paper cathode battery using a gelatin and lemon juice gel electrolyte. The battery fully degraded in 32 days in PBS with cellulase at pH ca. 5.

Jia et al.[7] fabricated a thin-film Mg battery with a Au-based cathode and a silk fibroin ionic liquid solid electrolyte. Crystallized silk was used as the substrate for both the anode and cathode, while the entire battery was packaged in silk. The complete battery degraded enzymatically over 45 days in buffered protease solution at 37°C.

Lee et al.[8] proposed a unique material and device integration strategy for preparing biodegradable sodium-ion batteries (SIBs). The biodegradable composite electrode was fabricated with $Na_4Fe_3(PO_4)_2(P_2O_7)$, pyroprotein-based carbon and a cellulose-based binder. A porous cellulose acetate mesh was used as a separator, and sodium perchlorate in a propylene carbonate solution was selected as a biodegradable electrolyte. Finally, the whole cell was safely protected from water and oxygen by encapsulation in a biodegradable pouch, a multilayered film of carboxymethyl cellulose (CMC), silicon, and aliphatic copolyester (poly(butylene adipate-co-terephthalate); PBAT). The authors demonstrated that each battery component decomposed via hydrolysis and/or fungal degradation into non-toxic compounds or elements already found in nature.

Mei et al.[9] designed a biocompatible fiber battery with a polydopamine/polypyrrole composite anode, MnO_2 cathode, chitosan separator, and body fluid as the electrolyte. The fiber battery was directly injected into the body to power a biosensor. The excellent biocompatibility and biodegradation were systematically investigated by observing the tissue morphology around the fiber batteries, indicating safe and biodegradable properties.

A survey of the latest advances in transient batteries shows promising routes to battery degradation, but several existing challenges show that these batteries cannot be directly translated from biomedical to, e.g., electric vehicle applications. First, transient batteries are suitable for low-power biomedical settings, but not always for high-power ones. Second, although degradation occurs, few studies identify the degradation products, leaving unanswered questions regarding the environmental

Table 1. Selected examples of degradable and recyclable beyond-LIBs

						Degradation/recycling information				
Cathode	Anode	Capacity	Specific energy	Power density	Cycling stability	Conditions	Time	D and/or R[a]	Greenness	Citation
pBQ	H_2BQS	42 mAh/g (with 2 kΩ load)	32 Wh/kg	1.7 mW	N/A	digested sludge[b]	40 days	D	⚪⚪🟢	Esquivel et al.[5]
BiTEMPO polypeptide	viologen polypeptide	37.8 mAh/g (@ 1C)	60 Wh/kg	57 W/kg	7.5 mAh/g (after 250 cycles @ 1C)	1 M HCl at 110°C	24 h	D[c]	⚪🟡⚪	Nguyen et al.[6]
Gold NPs on crystalized silk	Mg on crystalized silk	0.06 mAh/cm^2 (@ 10 $\mu A/cm^2$)	0.06 mWh/cm^2[d]	9 $\mu W/cm^2$[e]	N/A	buffered protease solution at 37°C	45 days	D + R	⚪🟡⚪	Jia et al.[7]
NFP	pyroprotein-based carbon	0.12 mAh/cm^2 (@ 0.15 mA/cm^2)	0.4 mWh/cm^2[d]	0.5 mW/cm^2[e]	0.12 mAh/cm^2 (after 50 cycles @ 0.15 mA/cm^2)	aqueous fungal solution at 25°C	>120 days	D + R	⚪🟡⚪	Lee et al.[8]
MnO_2	polydopamine/PPy	26 mAh/g (@ 1,000 mA/g)	31 Wh/kg	1,200 W/kg	17.7 mAh/g (after 200 cycles @ 1000 mA/g)	PBS at 37°C	84 days	D + R	⚪🟡⚪	Mei et al.[9]
p(g3T2)	P-75	11 mAh/g (@ 5C)	4.5 Wh/kg	3,000 W/kg	10.9 (after 500 cycles @ 60C)	chloroform at 65°C or RT	5 min	R	🔴⚪⚪	Tan et al.[10]
Mo paper	Mg paper	2.9 $\mu Ah/cm^2$ (@ 40 $\mu A/cm^2$)	4.0 $\mu Wh/cm^2$[d]	56 $\mu W/cm^2$[e]	N/A	PBS[f] at pH 5	32 days	R	🔴⚪⚪	Wang et al.[11]

pBQ, *p*-benzoquinone; H_2BQS, hydroquinonesulfonic acid potassium salt; 1C is the current required to charge the battery fully in 1 h; PBS, phosphate buffered saline; NPs, nanoparticles; NFP, $Na_4Fe_3(PO_4)_2(P_2O_7)$; p(g3T2), poly(dialkoxybithiophene) with triethylene glycol side chains; P-75, poly(naphthalenetetracarboxylic diimide-*co*-bithiophene) with 25% branched alkyl side chains and 75% heptakis(ethylene glycol) side chains.

[a] Degradation (D) or recycling (R).

[b] Defined by ISO 11734:1995.

[c] Degradation of only the active material was considered.

[d] Areal energy density.

[e] Areal power density.

[f] With cellulase.

impact of the battery at the end of its life. Third, many transient batteries are designed to operate once or over a short period time, but other applications require a useful life on the scale of years or thousands of cycles.

Toward the notion of fully circular batteries, transient batteries show the possibility of breaking down the battery's components into smaller molecules. To achieve full circularity, those degradation byproducts should be recovered and reused either by reconstitution into the original battery components or by valorization for a second application.

Organic batteries

By expanding the design space to synthetic organic polymers or small molecules, many new options emerge for batteries. Specifically, the metal-containing cathode can be replaced by redox-active organics, which may offer more flexibility in the degradation and recovery of byproducts. Further, organic batteries offer a pathway away from dependencies on lithium, cobalt, and nickel.

With the Wooley group, we demonstrated a metal-free organic battery composed of redox-active synthetic polypeptide cathodes and anodes.[6] Specifically, the cathode polypeptide was decorated with nitroxide radicals, and the anode polypeptide was decorated with viologen groups. The battery yielded a capacity of 37.8 mAh g^{-1}, initially delivering 85% of its theoretical capacity. With the addition of an acid, the battery deconstructed on command, yielding amino acids and other byproducts. Ideally these components could be recovered for reconstruction and full circularity, but we found that the separation step was quite challenging.

Esquivel et al.[5] presented a single-use degradable battery with p-benzoquinone (pBQ) and hydroquinone sulfonic acid potassium salt (H_2BQS) as the catholyte and anolyte, respectively. The as-prepared battery was stable for 2 h and could be disposed in an organic waste container or biotically degraded by bacteria with minimal environmental impact.

Tan et al.[10] showed a promising route toward recycling organic batteries based on diimide and bithiophene polymers using solvent extraction. The electrodes were additive and binder free, making solvent extraction straightforward. However, the cell capacity was quite low at ~10 mAh g^{-1}.

Comparison of LIBs and circular beyond-LIBs

Currently, beyond-LIBs exhibit lower capacities than commercial LIBs; however, there have been major improvements since early reports. Relative to transient batteries, organic-based batteries offer higher capacity and specific energy.[5,6] Additionally, batteries based on conjugated polymers (PPy, p(g3T2), and P-75) offer high specific powers comparable to some LIB chemistries.[9,10] However, additional work on post-degradation separation and active material design is needed for the organic batteries to achieve full circularity.

One additional consideration for commercial viability is the production costs of current LIBs and beyond-LIBs. With current metal prices (cobalt, nickel, and lithium), the production of LIBs is still more economical than the beyond-LIBs chemistries presented here. However, LIBs have been optimized and scaled for decades in commercial production. With beyond-LIBs, cost is still a question. One estimate places the cost of the pBQ/H_2BQS battery as low as €231 or $248 per Wh,[5] which is still higher than that of LIBs. To make them more competitive, the cost for organic beyond-LIBs could be driven down by considering the effects of scaled up production or a move toward easily sourced or bio-sourced feedstocks.

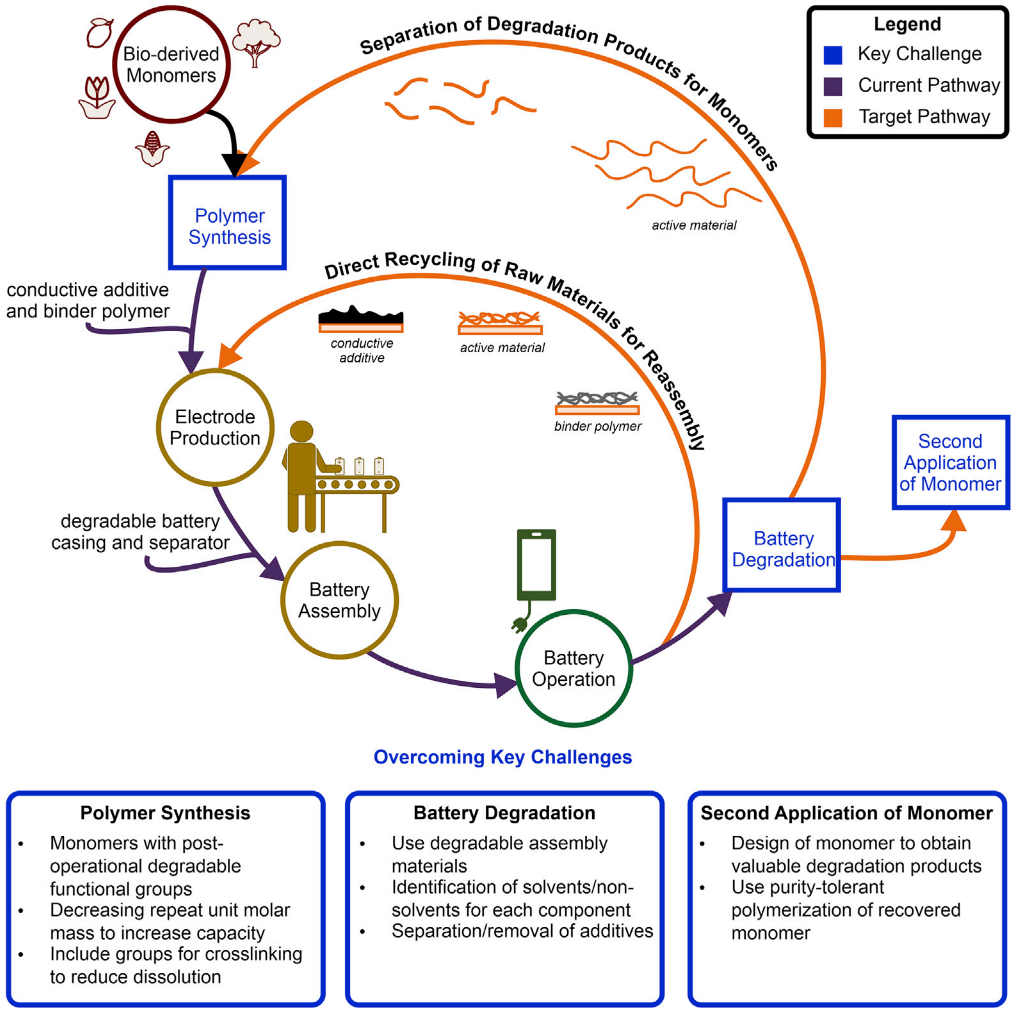
Taken together, the work on degradable, recyclable organic batteries highlights that the capacities, energy, power, and cost should be improved. Further, solubility issues remain important to address for long-term cycling and orthogonal extraction. Recovery and reconstitution of the active materials remains a challenge in improving circularity.

Challenges

Certain technical challenges must be addressed before a commercially viable degradable or recyclable beyond-LIB is feasible.

The primary challenge hindering the advancement of circular beyond-LIBs is the synthesis of active materials with suitable specific capacity and energy. One clear pathway is to focus upon organic materials capable of multi-electron transfer while also minimizing the repeat unit molar mass to improve the capacity. Additionally, special attention to the selection of redox-active groups is needed to result in a high cell voltage and specific energy. Likewise, these materials should be designed to bear on-command degradable functionalities (such as amide or ester groups) for selective extraction.[6] Table 1 shows that the capacities of degradable and recyclable batteries are quite low. For example, the pBQ/H_2BQS battery would have to weigh 3 to 4 times as much as an LIB to deliver an equivalent capacity.

Even if an extraordinary redox-active polymer is identified, its recycling and recovery becomes the next major challenge. Evaluation of the recovery success is difficult because electrodes contain mixed phases (i.e., conductive carbon and polymer binder). Therefore, identification of suitable solvents and non-solvents for all components is needed for separation and extraction. Additionally, the conditions used for separation should not result in chemical damage/degradation to the active materials.



Polymer Synthesis
- Monomers with post-operational degradable functional groups
- Decreasing repeat unit molar mass to increase capacity
- Include groups for crosslinking to reduce dissolution

Battery Degradation
- Use degradable assembly materials
- Identification of solvents/non-solvents for each component
- Separation/removal of additives

Second Application of Monomer
- Design of monomer to obtain valuable degradation products
- Use purity-tolerant polymerization of recovered monomer

Figure 2. A circular methodological study guide identifying key challenges and target pathways for circular battery design

A life cycle of a degradable/recyclable battery with targeted reclamation pathways and key challenges.

In contrast to recycling, degradation offers a simply means to extract components of the original redox-active polymer. Synthetic design should focus upon elegant degradation methods that leave backbones or side chains intact for further manipulation or reconstitution. If the degradation products are of value, they could be utilized to synthesize new materials or refabricate battery components. With the identification of degradation products and mechanisms, stimuli-triggered degradation can be targeted. Previous approaches have mainly investigated degradation in aqueous environments such as PBS, noting that the battery lifetime can be as little as 5 h before failure. By utilizing an external stimulus, operational degradation can be circumvented leading to on-demand degradation and more stable performance.

A circular methodological study guide

Moving forward, it is critical to overcome the presented key challenges. Here, we present a brief study guide that summarizes key factors and parameters to investigate and consider in future studies (Figure 2).

For synthesis of new degradable active materials, one key factor to consider is the stability of the redox active group and any degradable functionalities during battery operation. The selected moieties/functionalities should remain stable during operation and recycling. However, during the design process, cost and scalability should also be considered.

One key factor that must be considered in future studies is complete understanding of degradation/recycling products. To fully understand the environmental impact of the recycling or degradation process, the atom economy must be preserved. This means that any byproducts resulting from the degradation or recycling process should be identified and

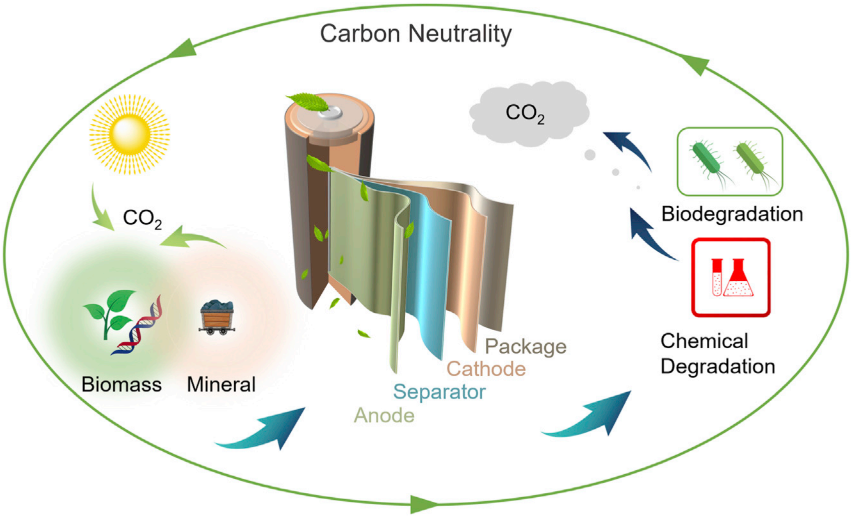


Figure 3. Future targets for next-generation degradable and recyclable batteries
The life cycle of a degradable/recyclable battery with the concept of carbon neutrality.

catalogued. These byproducts should be assessed for biocompatibility.

Accordingly, recycling studies should be considered for any new battery materials. There are many polymer-based chemistries that claim "recyclability" but few actual demonstrations in literature.[10] This is because full extraction of the material of interest from the original battery is difficult. It is our own experience that separation is the most time-consuming step. Material separation and recovery efficiencies for current and target pathways should be presented for complete comparison.

Outlook

Achieving a fully circular battery economy requires openness to new chemistries and new recycling strategies. LIBs represent the current state of the art, and large-scale recycling of them is still developing. With anticipated supply chain shortages and scarcity of critical LIB elements, alternative battery chemistries offer flexibility in domestic sourcing, manufacturing, and recycling. There is no clear front-runner in terms of recyclable beyond-LIB chemistries yet.

In the pursuit of the ideal, recyclable beyond-LIB, it will be important to involve not only chemists and engineers but also technoeconomists. The life cycle and greenhouse gas emissions should be considered and analyzed with the goal of a net neutral future (Figure 3). One way this can be accomplished is through the use of net neutral starting materials, such as CO$_2$ or biomass. These may then be recycled at the battery's end-of-life, to achieve a truly circular life with the vision of a battery never reaching a landfill. Alternatively, these batteries could degrade into value-added or environmentally benign products. Further, the rapidly changing economy and global access to materials should be considered when projecting energy and materials costs.

By pursuing net-neutral batteries, the battery supply chain can become democratized to allow for more global economies to participate in battery manufacturing. Further, the infrastructure in place for recycling plastics might be translated to that of recycling batteries. Implementation of regulations and policies may be needed to push the commercialization and translation of the discussed technologies. To realize this vision, it will be essential to mobilize scientists, engineers, and policy makers to consider not only the performance of a battery but also the human and global imprint throughout the battery's life cycle.

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AUTHOR CONTRIBUTIONS

Conceptualization, A.D.E. and J.L.L.; writing and editing, A.D.E., T.M., and J.L.L.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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