



## **Advancing the Sustainability of Batteries**

A Tongji University/Nature Sustainability Expert Panel Report

March 2022

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To cite: Huang, Y.H. *et al.* Advancing the Sustainability of Batteries, A Tongji University/Nature Sustainability Expert Panel Report, Shanghai and London, Tongji University and Springer Nature, 2022.



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# Chapter 1

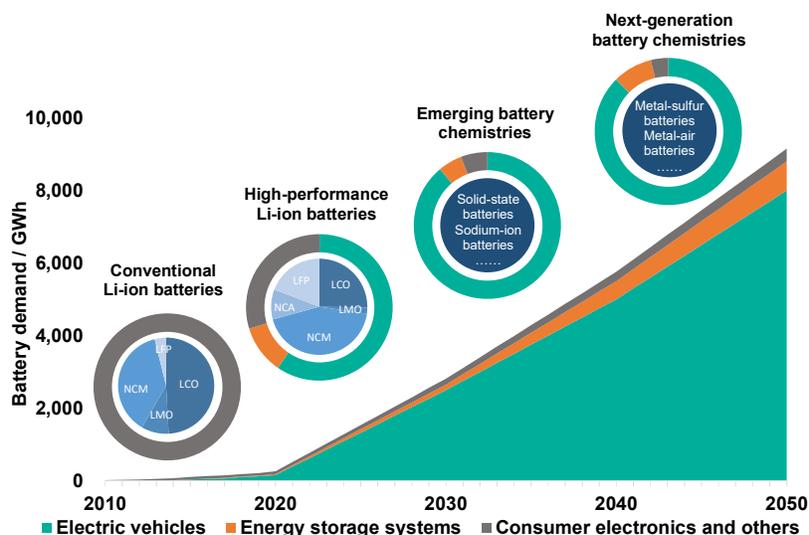
## Life cycle sustainability assessment of batteries

### 1.1 Resource related sustainability analysis based on dynamic MFA

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Driven by the massive deployment of electric vehicles (EVs), global demand for lithium-ion batteries has been growing strongly in recent years. Global lithium-ion battery demand increased from 16 GWh in 2010 to 266 GWh in 2020, implying an over tenfold increase within the past decade. Although uncertainties exist in the scale of future battery demand growth, an order-of-magnitude increase can be generally expected. Figure 1 presents a referential projection of global battery demand in the coming decades by compiling projections from multiple sources ([IRENA 2017](#); [BNEF 2021](#); [IEA 2021](#)). Compared to today's battery demand level, a tenfold increase can be expected by 2030; and a further 2-3 fold increase can be expected by 2050.



**Figure 1.** Battery demand projection categorized by sector and battery chemistry

Battery demand from EVs will be the dominating driving force behind such growth. Global electric car sales reached 3 million in 2020, representing 4.6% of total car sales. In Europe, China and the U.S., the market shares of electric cars reached 10%, 5.7% and 2%, respectively ([IEA 2021](#)). In Norway, the market share of electric cars has reached as high as over 70%, representing the highest level in the world. This trend of fast growth is expected to continue into the coming decades. The EU, China and the U.S. governments have all proposed aggressive targets for EV market penetration for the next decade. The recent monthly electric car sales in 2021 have indicated an electric car market share of over 20% in China and major European countries including Germany, France and the U.K., a significant sign of electric car entering its rapid commercialization phase. At the same time, the single-car battery capacity has also increased in major EV markets in pursuit for higher electric range. Taking China for example, average single-car battery capacity has increased from 28 kWh in 2015 to about 50 kWh in 2020. A further increase in electric car battery capacity can be expected by looking at the EV models to be introduced into the market, which typically features higher electric range and larger battery capacity than the current models. This will also contribute to increasing the battery demand from EVs.

Beyond the light-duty segment, the heavy-duty segment also potentially brings considerable demand for batteries. Unlike the light-duty segment, the technology pathway for the decarbonization of the heavy-duty segment is still not fully clear, with plug-in electric, fuel cell electric, renewable-based internal combustion engine (e.g., renewable power-to-liquid) competing with each other. Still, from the commercialization perspective, plug-in electric powertrains are taking the lead with a number of heavy-duty EV models being or to be introduced to the market ([IEA 2021](#)). Although the number of heavy-duty vehicles is order-of-magnitude lower than light-duty vehicles, the single-vehicle battery capacity is typically much higher because of higher energy consumption rate and high electric range necessary for intensive commercial operation. It was estimated that the battery demand from heavy-duty vehicle electrification could grow to a level comparable to light-duty vehicles if heavy-duty vehicle decarbonization relies heavily on plug-in electric powertrains ([Hao, Geng et al. 2019](#)). Furthermore, in the aviation and marine transport sectors, the electrification process is being triggered by consistent improvement of battery performances ([ICCT](#)

2018). The electrification in these sectors will also invoke considerable battery demand. Under the current battery specific energy, a 100-km-electric-range flying car needs the support of a 50 kWh battery, 3-4 times the requirement from a land-use EV with the same electric range (Ullman 2017). Despite these considerations, the battery demands from transport sectors other than the light-duty segment have not emerged to be significant in the short term, for which such demands have not received enough attentions as compared to the light-duty segment.

Stationary energy storage systems also represent a significant share of battery demand, with a strong growing trend in the coming decades. IEA projected that variable renewable generation, including solar PV and wind power, will account for about 60% of total power generation by 2070 under its Sustainable Development Scenario (IEA 2020). To harness such high-share variable renewable generation, flexibility of electricity systems have to be improved, in which energy storage systems have an essential role to play. Many countries have now explicitly included energy storage in their renewable energy development plans. Among the various forms of energy storage, lithium-ion batteries are gaining popularity owing to their mature technology and decreasing costs. Under IEA's Sustainable Development Scenario as mentioned above, utility-scale energy storage capacity is expected to reach 2100 GW in 2070, mostly of which will be battery-based energy storage. It should be noted that the huge EV fleet to be formed in the coming decades can serve as distributed energy storage devices based on vehicle-to-grid technologies, potentially reducing the demand for dedicated energy storage systems. Furthermore, the retired batteries from EVs can be used in a cascaded way in energy storage systems. These factors add to the complexity in projecting future battery demand from energy storage systems.

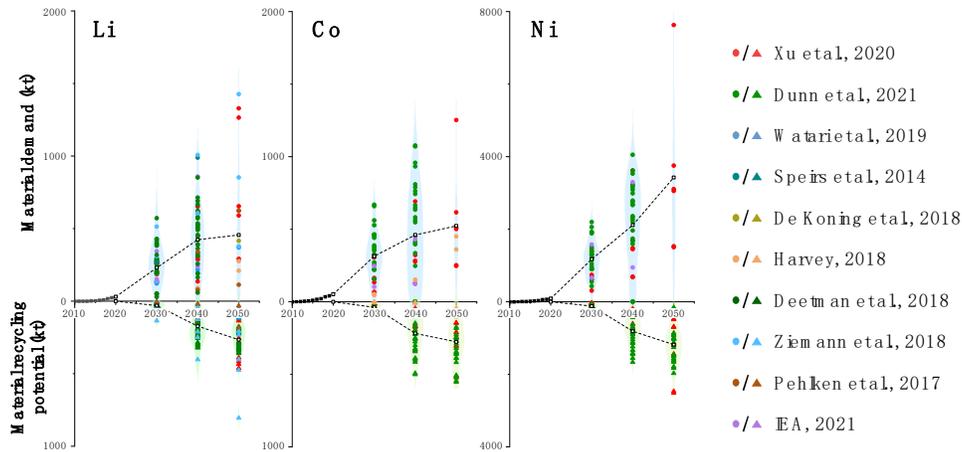
Accompanying the growth of battery demand is the fast development of battery technology. Substantial improvements have been made in terms of battery chemistry, format, packaging, manufacturing processes, etc. Battery chemistry lies in the center of such technology development because it substantially determines battery cost, specific energy, safety, durability, among other battery performances. Figure 1 indicates the history and future trend of battery chemistry evolution. Back in 2010, battery chemistry was dominated by LCO and NCM, which were mostly used in consumer electronics batteries. The shares of LMO and LFP batteries were low at that time. By

2020, NCM and NCA batteries that provide improved specific energy favoring vehicle use have gained significantly higher market shares. LFP batteries also gained popularity owing to its wide use in commercial EVs and a few popular electric car models. Driven by the pursuit for safer, cheaper and longer-range enabling batteries, solid-state and sodium-ion batteries are emerging as candidates for the next-step battery chemistries. Regarding the long term, next-generation chemistries such as metal-sulfur, metal-air batteries are expected to become prominent although significant technology barriers are yet to be overcome.

The fast growth of battery demand brings substantial challenges to resource sustainability. The metals the current generation of lithium-ion batteries relies on, including lithium, cobalt, nickel and manganese, are all considered as critical metals owing to their indispensable roles in modern industry. The U.S. identified lithium, cobalt and manganese as critical in its mineral assessment ([US DOI 2018](#)). The EU's material criticality assessment – conducted in 2011, 2014, 2017 and 2020– consistently mentions cobalt as a critical raw material ([EU 2020](#)). Japan has lithium, nickel, cobalt and manganese categorized within its thirty strategic minerals ([PMOJ 2012](#)). Over the past decade, the battery industry has gradually become dominating in the consumptions of these metals. In 2019, the consumptions of lithium and cobalt for battery production represented 65% and 61% of their respective total mineral consumptions ([Hao and Sun 2021](#)).

Figure 2 summarizes the projections of lithium, cobalt and nickel demands from light-duty vehicles based on selected literatures. Generally, existing literatures all point to a strong growth of demands for all these critical metals. However, the scale of growth projected by different studies spans a big range, especially when regarding the long-term demands. The projections from one study's different scenarios can also be highly different. This highlights the inherent uncertainty in the future demands for critical metals. The causes of such uncertainty are twofold, one from the uncertain battery demand (vehicle sales, EV market penetration, single-vehicle battery capacity) as discussed above; the other from the uncertainty of battery chemistry evolution - each battery chemistry has its own unique critical metal reliance. Even the current battery chemistries adopted by EU, China and the U.S. markets are highly different ([Dunn, Slattery et al. 2021](#)), let alone the future evolution with more battery chemistries

joining in the competition. Relatively, the demand for lithium is robust because of the indispensable role of lithium in the current generation of lithium-ion batteries. The demands for cobalt and nickel are more elastic when considering the existence of cobalt and nickel-free batteries such as LFP batteries. In recent years, the industry has shown strong interests in LFP batteries with numerous popular EV models including Tesla Model 3 equipping LFP batteries.



**Figure 2.** Projections of critical metal demands and recycling potentials in selected studies (Speirs, Contestabile et al. 2014; Pehlken, Albach et al. 2017; Bean, Bhandari et al. 2018; de Koning, Kleijn et al. 2018; Harvey 2018; Ziemann, Müller et al. 2018; Watari, Nansai et al. 2019; Xu, Dai et al. 2020; Dunn, Slattery et al. 2021; IEA 2021)

Recycling critical metals from end-of-life batteries is expected to meet part of future metal demand and reduce the reliance on natural resources. Figure 2 also presents the estimated material outflow from light-duty vehicles, i.e., the potential for material recycling. The material outflow is about ten-year lagging behind material demand, due to the stocking of materials in the in-use vehicles. When considering the fast growth on the demand side and the lagging of material outflow, recycling is not likely to play a significant role in meeting material demand before 2040. Furthermore, whether the material outflow can be effectively used depends critically on the development of recycling technology and the efficiency of collection system, both of which are yet to be improved. Even with recycling considered, most existing literatures reveal high pressures in the supply of these critical metals and call for coping measures to enhance resource sustainability. It should be noted that existing projections of battery-related

critical metal demands are mostly focused on light-duty vehicles. Due to higher uncertainties in battery demand and battery chemistry evolution, the projections of critical metal demands for the heavy-duty segment and energy storage systems are relatively insufficient.

The resource sustainability challenges also lie in the geographical concentration of the supply of these critical metals. For lithium, two thirds of global lithium reserves are distributed in Chile and Australia ([USGS 2021](#)). In 2020, Chile and Australia together were responsible for 71% of global lithium mine productions. The geographical concentration of cobalt mines is even higher, with 51% of global cobalt reserve identified in Congo (Kinshasa) ([USGS 2021](#)), the country suffering from consistent political instability. High concentration of supply can also be found in the downstream processes of lithium-ion battery production ([Sun, Hao et al. 2019](#)). Such concentration implies a higher risk of supply disruption, especially in the context of global-wide supply chain impacts from COVID.

To cope with the resource sustainability challenges needs the support from battery recycling technology development that reduces the reliance on primary resources; and ideally, a transition towards critical metal-free battery chemistries. However, the evolution of battery chemistry and development of recycling technologies are not silver bullets. While addressing the critical metal challenges, they can simultaneously induce a wide range of energy, environmental and resources impacts throughout the whole life cycle of batteries. Under such a circumstance, life cycle assessment is needed to identify the environmental impacts from emerging battery technologies so that a transition towards sustainable batteries can be ensured.

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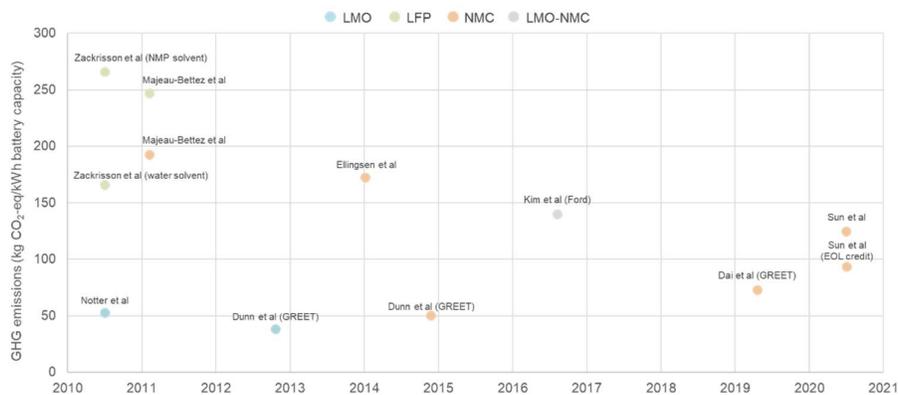
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## 1.2 Status quo of LCAs of Li-ion batteries for mobility

Linda Ager-Wick Ellingsen

The LCA literature of Li-ion traction batteries comprises several studies. However, very few studies provide original life cycle inventory data and even fewer yet have obtained primary industry data for their analysis. Because many of the LCA studies rely on data from a few previously published studies, there is a high degree of interconnectedness in the LCA studies considering cradle-to-gate impacts of Li-ion traction batteries (Peters *et al.*, 2017).

Figure 1 considers cradle-to-gate studies with original inventory data and their reported greenhouse gas emissions per kWh battery capacity. In the figure, the considered cathode material evaluated in the study is denoted blue for spinel lithium manganese oxide (LMO), green for olivine lithium iron phosphate (LFP), orange for layered lithium nickel manganese cobalt oxide (NMC), and violet for blended LMO and NMC (LMO-NMC).



**Figure 1.** Cradle-to-gate studies and reported greenhouse gas emissions

Looking at the reported cradle-to-gate GHG emissions from the various studies providing original data, one can observe a “funneling” effect in the reported results; the discrepancies in reported emissions were particularly high in the early years around 2010 but has gradually diminished moving towards 2020. The “funneling” effect is owed both to improved data availability and quality but also development in the battery technology and production procedures. While there are many parameters that can

explain the differences in the reported cradle-to-gate GHG emissions (Ellingsen, Hung and Strømman, 2017; Peters *et al.*, 2017; Aichberger and Jungmeier, 2020), energy use in cell manufacture and emissions due to cell materials are two of the primary factors and will be elaborated further below.

Much of the observed difference in the reported emissions and discussion in the LCA literature has been concerning energy use in cell manufacture (Ellingsen, Hung and Strømman, 2017; Aichberger and Jungmeier, 2020). In the first studies published around 2010-2012 (Notter *et al.*, 2010; Zackrisson, Avellan and Orlenius, 2010; Majeau-Bettez, Hawkins and Strømman, 2011), data availability on energy use was particularly scarce and studies relied either on own process-based estimates or secondary energy data from industry reports, which resulted in large differences in assumed energy use and consequently emission estimates. A couple of studies published around 2014-2016 obtained primary energy data from commercial cell manufacturers (Ellingsen *et al.*, 2014; Kim *et al.*, 2016), and these studies reported relatively high energy use and associated emissions from cell manufacture, albeit lower than some of the highest preceding estimates relying on older secondary industry data. In more recent years, 2019-2020, a couple of studies have obtained energy data from Chinese cell manufacturers operating on the Gigafactory level (Dai *et al.*, 2019; Sun *et al.*, 2020), and these studies report lower energy use than preceding studies relying on either secondary or primary energy data. An overview of the energy use in battery cell manufacture used in studies based on primary energy data are shown in Table 1.

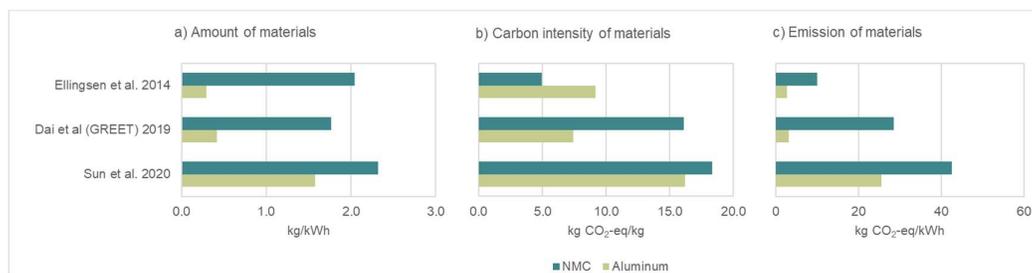
**Table 1** Energy use in battery cell manufacture from studies based on primary energy data

	Ellingsen <i>et al.</i> (2014)	Kim <i>et al.</i> (2016)	Dai <i>et al.</i> (2019)	Sun <i>et al.</i> (2020)
Production scale	Small industrial plant, < 1 GWh	Gigafactory, ~3-4 GWh	Gigafactory, 2 GWh	Gigafactory, ~30 GWh
Energy demand (MJ/kWh cell)	586	530	170	106
Of which is electricity	100%; from South Korean mix	Unknown; South Korean mix	18%; from US mix	68%, from Chinese mix
Of which is heat		Unknown; heat from natural gas	82%; from natural gas	32%; from steam

The reported energy use among the studies varies with a factor of five to six. The most likely explanation for the significant difference is due to the transition to large-scale production with higher energy efficiency and material utilization (Dai *et al.*, 2019; Sun *et al.*, 2020; Chordia, Nordelöf and Ellingsen, 2021). It is also likely that production processes for specific cell production steps have matured and contributed to this overall development with time (Chordia, Nordelöf and Ellingsen, 2021). Notice that the studies

also report different shares of energy from electricity and heat; both total energy demand and energy shares may affect the GHG emissions.

While much of the observed difference in reported emissions can be ascribed to energy use estimates in cell manufacture, differences also stem from other inventory data pertaining to cell materials, particularly to aluminum and the NMC material. Figure 2 provides an overview of the amount of aluminum and NMC materials, carbon intensity of the materials, and the resulting emissions of the materials from three of the studies relying on industry data (note that such details could not be obtained from the study by Kim *et al.*, (2016)).

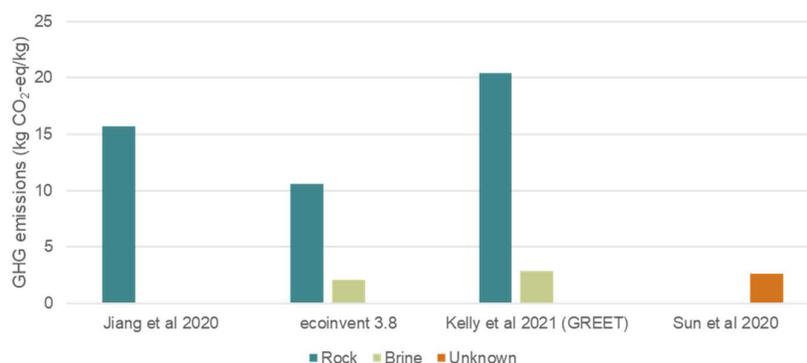


**Figure 2.** Differences in a) material use, b) carbon intensity of materials, and c) reported emissions of materials.

The difference in reported emissions stems from both assumed amount of materials as well as the carbon intensity of these. Sun et al., (2020) reports significantly higher use of aluminum compared to both Ellingsen *et al.*, (2014) and Dai *et al.*, (2019). Note that both Dai et al., (2019) and Sun et al., (2020) assess an aluminum prismatic cell container while Ellingsen et al., (2014) assess an aluminum composite pouch material. Thus, the difference in cell containers may explain the difference in aluminum use between Sun et al., (2020) and Ellingsen et al., (2014), but not between Sun et al., (2020) and Dai et al., (2019). The higher use of aluminum combined with the highest aluminum carbon intensity explains why Sun et al., (2020) obtains the emissions associated with aluminum. The second part of the explanation for the difference in cell material emissions lies with NMC material. While all three studies report similar use of NMC, the carbon intensity of the NMC material differs somewhat between Sun et al., (2020) and Dai *et al.*, (2019) but significantly between Ellingsen *et al.*, (2014) and the other two studies. Both Dai *et al.*, (2019) and Sun *et al.*, (2020) obtained data for

industrial NMC production, while Ellingsen *et al.*, (2014) relied on an inventory based on lab-scale production of NMC (Majeau-Bettez, Hawkins and Strømman, 2011) that is likely to underestimate the energy use in material production and consequently the carbon intensity of NMC production.

Furthermore, both modelling choices (e.g., background data, characterization method, mineral source) and actual differences in supply chains (e.g., resource quality, processes, and technology) as well as battery technology and design may result in different emission estimates. For instance, estimated cradle-to-gate GHG emissions of battery production will depend on both modelling choices and actual difference in lithium carbonate supply chains. Lithium carbonate is primarily produced from spodumene rock in Australia and salt brines in South America. However, the actual difference in supply chains is only one factor that will affect the estimated GHG emissions, the inventory data and characterization methods are others. Figure 3 reports cradle-to-gate GHG emissions of lithium carbonate from different data sources and supply chains.



**Figure 3.** Cradle-to-gate GHG emissions for lithium carbonate production

The cradle-to-gate results reported in Figure 3 differ widely between the different data sources and supply chains. In general, the results indicate that lithium carbonate from brine has lower cradle-to-gate emissions than lithium carbonate from spodumene rock. Jiang *et al.*, (2020) estimated the cradle-to-gate emissions of lithium carbonate from spodumene rock extracted in Australia and processed in China based on primary industry data. *Ecoinvent* based their rock-based inventory on Jiang *et al.*, (2020), but estimates lower cradle-to-gate emissions. Kelly *et al.*, (2021) modelled the same

extraction route based on assumptions for production in Australia and data from an environmental impact assessment report for a Chinese cathode plant and report the highest cradle-to-gate emissions for lithium carbonate from rock. For lithium carbonate from brine, *Ecoinvent* based their inventory on an environmental survey from SEIA-CONAMA (2006) as well as environmental reports from a Chilean company (Ecoinvent Centre, 2021). Kelly *et al.*, (2021) estimated the production emission of lithium carbonate from brines based on primary data. The *ecoinvent* database reports about half the cradle-to-gate emission of lithium carbonate from both rock and brine compared to Kelly *et al.*, (2021). This brief review of lithium carbonate demonstrates that both data sources and supply chains matter to the results of LCA of Li-ion batteries. The point about differences in emissions due to supply chain, brings us to the fact that batteries are not created equal; one must expect actual, not just modelled, differences in cradle-to-gate battery impacts. Differences may be due to supply chains but also due to battery design and chemistry. As numerous aspects affect the results, providing transparent and complete inventories is important to allow for full understanding of the reported LCA results.

Through this brief literature review, we see that many of the studies with original data are now several years old and may not be viewed as representative for the current battery technology and production practices. Unfortunately, some of the more recent studies relying on primary industry data only provide part of the inventory data used in the analysis. Moving forward, LCA studies should consider and incorporate progresses in the continuously evolving battery technology and production practices and provide transparent and complete inventory data to further advance our environmental understanding of Li-ion traction batteries.

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## **1.3 A common, modular and transparent LCA model for Li-Ion batteries**

Roland Hischer

*EMPA*

Sustainability got a key issue in the development of new technologies over the past few years, and in order to make the environmental sustainability measurable (allowing taking decisions towards more sustainability), Life Cycle Assessment (LCA) is considered nowadays as the most appropriate methodological approach (Ness et al., 2007). LCA is a standardized systems-thinking approach, used to assess the environmental challenges along the life cycle of products and services (ISO, 2006).

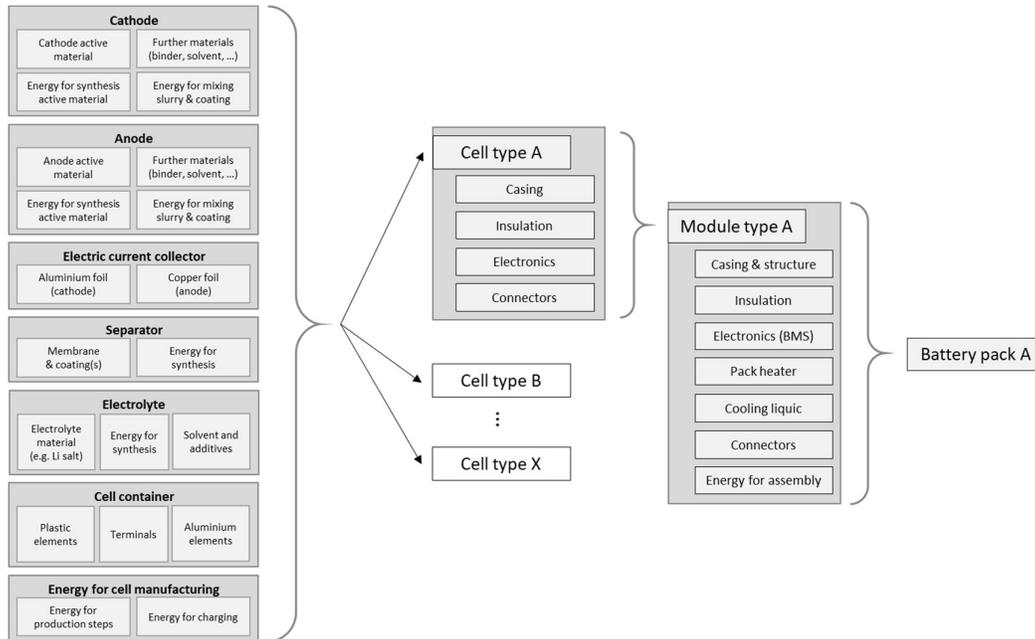
Looking into the LCA literature, batteries (and their environmental impacts) are a topic since more than two decades – the big review work of Peters and co-workers (Peters et al., 2017) ended up with over hundred publications having been analysed. However, only few of these studies are actually based on their proper inventory data (i.e. coming from a clearly identifiable source) and report those numbers in a transparent and reproducible manner. As shown in Peters et al., 2017, already these few "original" studies lead in the end to a great variability in terms of the environmental impacts related to the production of a battery. A key factor for this wide variability in the results lies on one hand side in the fact, that these studies assess not all the same chemistry. Furthermore, the studies make use of data from a variety of different technology readiness levels (ranging from pilot operation to full production lines), hand in hand with varying modelling approaches (e.g. top-down vs bottom-up) and with differences in the further assumptions in order to model such a battery (see e.g. Romare & Dahllöf, 2017; Ellingsen et al., 2017; Cerdas et al., 2018; Peters & Weil, 2018; Raugei & Winfield, 2019). One of the elements showing huge differences – i.e. up to three orders of magnitude – is the energy consumption of the production of a single battery; ranging from almost 600 MJ/kWh storage capacity (Ellingsen et al. 2014) down to about 3 MJ/kWh (Notter et al. 2010). In the end, all these differences are highly visible in the overall impacts – often expressed per kWh battery capacity. Looking on the highly debated issue of the Global Warming Potential (GWP), the results are going

from 50 up to about 500 kg CO<sub>2</sub> eq per kWh battery capacity (see Ellingsen et al., 2014; 2017). Applying these data in another technology, such as electric vehicles, obviously leads then – again – to a broad variety in the results ... variety that is partly due to the use of different electricity mixes in the use phase of these vehicles – but partly also due to these assumptions behind the life cycle inventory (LCI) of the battery (Notter et al. 2010, Cox et al. 2018). Especially in the field of non-scientific literature (i.e. grey reports, journal articles, online news, ...) this resulted over the past years in contradicting headlines (see e.g. Jungmeier et al. 2019 and Choudhury 2021).

In order to overcome these issues, and to allow decision makers to take well-informed decisions in relation to Li-Ion batteries, one of the key points is to make high-quality LCI data for these batteries easily accessible. One possible place for such an easy accessibility of respective data are the specific tools and databases used by the LCA practitioners. Among such databases, the ecoinvent database (Wernet et al. 2016) is one of the few general LCI background databases offering a high transparency and modularity within its content; being important attributes in order to achieve a high level of comparability among different products, technologies and materials. Crenna and co-workers followed in a recently published work these rules for transparency and modularity of ecoinvent (Crenna et al. 2021) – heading for setting a new baseline for a modular, transparent and comprehensive modelling of modern Li-ion batteries. Key characteristics of this new modelling approach are the following points:

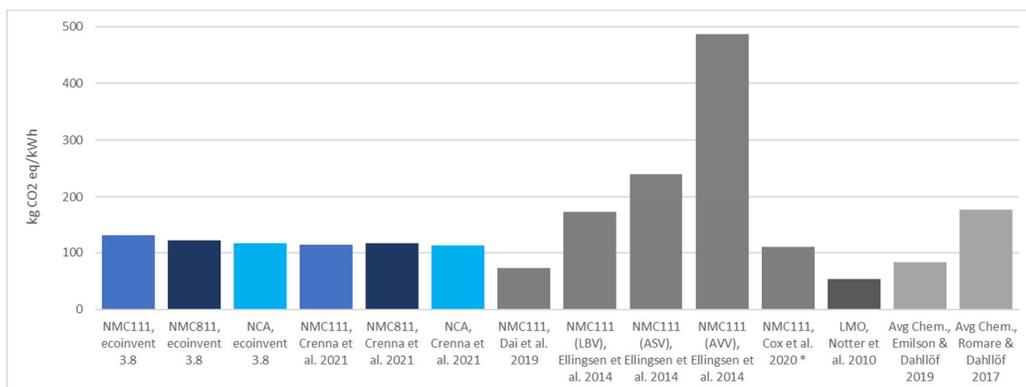
- Approach is independent from a single chemistry – but applicable to all types of chemistries;
- Approach is highly transparent and modular (i.e. representing a gate-to-gate modelling – details, see Figure 1) – being able to cover today's as well as future Li-Ion battery chemistries;
- Approach is making use of the most recent information and data from industry – complemented by further (scientific) sources in order to end-up with a comprehensive, transparent and thus traceable quantification of the various production steps;
- Approach is in line with the quality requirements of the ecoinvent database, resulting in an integration of respective datasets into the database;

- Approach can be integrated into other database environments due to its modularity (i.e. the gate-to-gate approach), allowing the LCA community to use a common baseline.



**Figure 1.** Modular scheme of materials and energy for the Li-ion battery pack production (Figure representing a simplification of Figure 1 from Crenna et al. 2021)

With these inventory data published in the supporting materials of Crenna et al. (2021), and also being part of version 3.8 of the ecoinvent database (version published in September 2021), a new baseline for NMC111 batteries (considered being representative for currently used batteries), NMC811 as well as NCA batteries (both being seen as next generation batteries) has been created. Taking the most recent LCA impact assessment method from the European Commission – the EF method 3.0 – the three baseline batteries as integrated in ecoinvent 3.8 show a carbon footprint in a range of 18.1 to 18.6 kg CO<sub>2</sub>-Eq/kg of battery; values that are slightly higher compared with the values for the same models of Li-ion batteries in Crenna et al. (2021), but remain in the lower range compared with older data sources (see Figure 2).



**Figure 2.** Carbon footprint per kWh of stored energy (Updated and expanded figure from Crenna et al. 2021), (Legend: LBV=low band value for electricity consumption; ASV=asymptotic value for electricity consumption; AVV= average value for electricity consumption; Avg Chem. = unspecified average chemistry; \* graph interpretation, based on the average energy requirement in current battery production).

The differences between Crenna et al. (2021) and ecoinvent 3.8 is mainly due to an update of, among others, the underlying cobalt data within ecoinvent – visible by the fact that the NMC111 shows a much higher difference (in the order of 15%) than the NMC811 battery (only about 4% of difference), containing much less cobalt.

According to Crenna and co-workers, the three datasets represent the currently best available mix of primary data from commercial-scale manufacturer of such batteries, completed with further information from literature and/or from battery experts in order to have the entire value chain covered in a comprehensive and complete manner. One of the objectives of Crenna and co-workers is it indeed to "achieve the highest degree of modularity possible, allowing for a complete traceability of data sources". These data are setting a baseline also due to the fact that the entire modelling of their respective supply chains follow the requirements and the rules of ecoinvent (Wernet et al. 2016); resulting in three battery datasets that fit perfectly well together with all the other data within the ecoinvent database, one of the most popular LCA background databases used on a global scale.

This complete traceability goes hand in hand with a high degree of transparency – offering a variety of areas of (further) improvements. First, it allows battery specialists and engineers to further specify and improve the (current) modelling approach. Not all the information used in Crenna et al. 2021 is actually directly based industry data; but

it is partly based on (oral) expert feedback and/or on further literature sources. Secondly, this approach can obviously be used for the modelling of additional, new battery compositions – being it with other cathode materials (e.g. cobalt-free materials such as lithium iron phosphate, LFP), with other anode compositions (e.g. anodes with a high(er) silicon content) or with solid instead of liquid electrolytes. Third, the modularity of the approach allows investigating changes in production properties (e.g. different electricity mixes in the production phase – representing either other production places or individual changes e.g. in the electricity supply of a production site, by switching from grid-electricity to own photovoltaic panels on the roof). Crenna and co-workers themselves have given a first outlook into this direction in form of an online presentation at the Green Batteries Conference 2021 (Crenna et al. 2021b).

Using such a common, transparent and comprehensive modelling approach will allow getting a more complete picture of the sustainability of Li-ion batteries – as a product, as well as in a specific application context – today and tomorrow. The transparency of the model is in the same time a clear invitation to the community to build upon and to contribute to the further refinement and development of this model – allowing to achieve a more and more adequate modelling of this highly relevant product that batteries represent for our society turning towards a more sustainable energy system.

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## 1.4 Future oriented LCA of batteries

Christian Bauer

Batteries represent a technology that is experiencing ever broader mobile and stationary application and is subject to rapid technological progress. Therefore, their environmental performance must be assessed not only from today's perspective, but also from a future-oriented one. Such a prospective LCA must take into account not only changes in battery technology per se, but also in the background LCI system. A coupling of the LCA database ecoinvent with so-called Integrated Assessment Models is suitable for this purpose. With this coupling, consistent future-oriented versions of ecoinvent can be created that depict differently ambitious climate protection scenarios and thus decarbonisation paths. A first application of this coupling, taking into account transformations in the electricity, transport, steel and cement sectors towards low-carbon technologies, shows that the modification of the LCA background data has a significant impact on the life cycle assessment of battery production: depending on the specific climate protection scenario, a reduction of greenhouse gas emissions from battery production of up to 50% can be achieved until 2050 by changing the LCA background system alone. The coupling algorithms are being continuously developed by PSI together with international partners and are available to the scientific community in open source format.

# 1.5 Production and recycling of lithium and post-lithium batteries

Jens Peters

The quest for new cell chemistries has long been driven by the need for increasing energy density and reducing costs. This has led to stunning progress in the sector, and corresponding improvements in performance and price decreases (Figure 1).

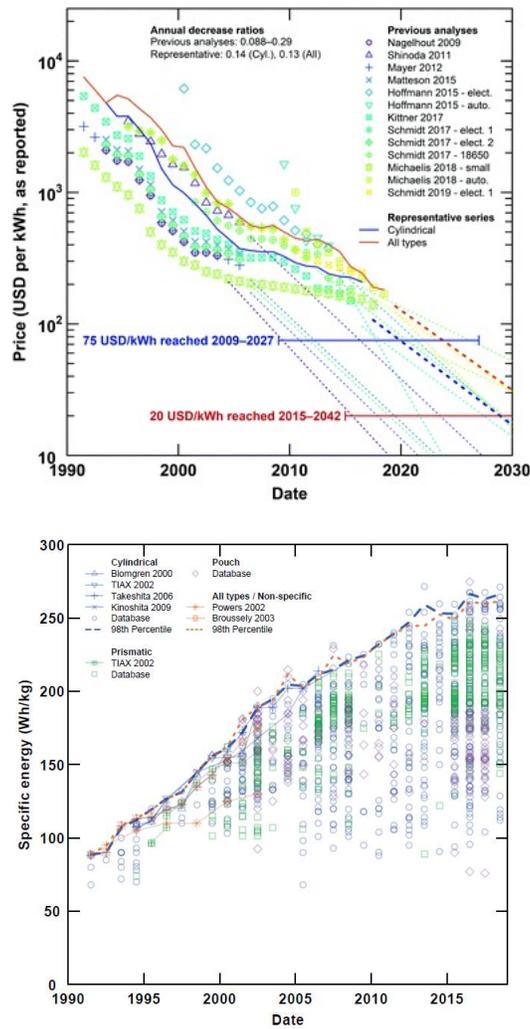


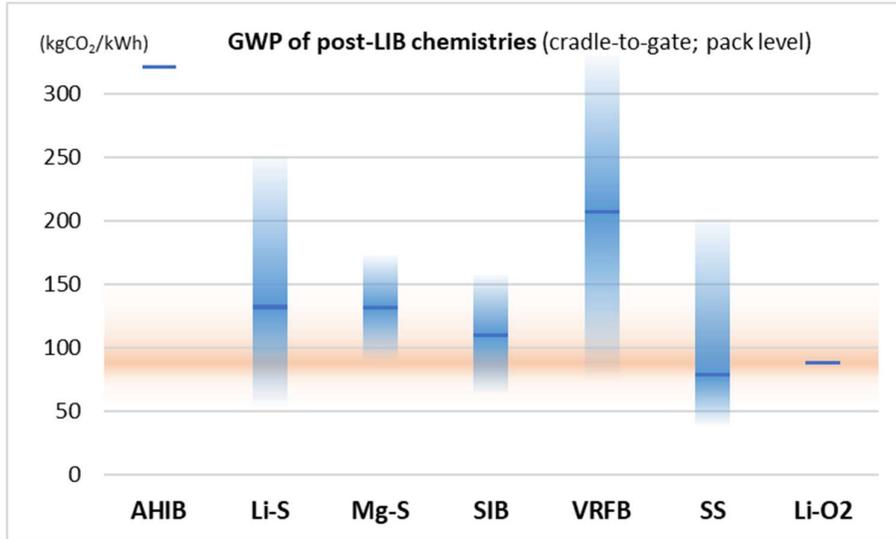
Figure 1. Evolution of price and specific energy density of LIB over time <sup>1</sup>

LIB are foreseen to continue dominating the EV sector also in medium future, with a clear trend towards LIB cell chemistries based on abundant, low value materials, thus reducing the cost and resource impacts associated with battery production.<sup>2,3</sup> The NMC111 chemistry, prevalent until recently, is increasingly being substituted by low cobalt chemistries like NMC622 NMC 531 or even NMC811.<sup>4</sup> LFP also experienced important improvements in performance, and, while limited to more robust applications where energy density is less an issue like forklifts or stationary systems (and a few Chinese car makers), they recently caught up and might become a more important player also for the vehicle market.<sup>5</sup> In fact, Tesla recently announced to use LFP cells in some of its models,<sup>6</sup> and a recent study for the EU foresees a relevant share of LFP for EV batteries also in future.<sup>2</sup> Silicon-doped anodes (or, in farer future, even silicon or metallic lithium anodes) might push the boundaries of the current LIB technology even further.<sup>7</sup> Apart from that, other battery chemistries that go beyond the classic LIB scheme are being researched intensively, so-called post LIB systems. These include solid state batteries, but also new cell chemistries like Na-Ion, Mg-Ion, Al-Ion and others [Ref to corresponding chapter]. Except Na-Ion batteries, which are starting to be commercialised in pilot scale, they are however far from commercial application, all suffering from some still fundamental problems like short lifetime or very poor performance in terms of energy density or efficiency.<sup>4</sup>

While costs and performance aspects are usually the main drivers for these developments, a second, increasingly relevant aspect are concerns regarding the environmental impacts and resource demand of (majorly electric vehicle / EV) batteries. These have been brought into society by a series of reports and news articles based on the most recent LCA studies on batteries, starting a debate about the GHG backpack associated with batteries and the time EV require for amortizing it.<sup>8-12</sup> At the same time, it also drove LCA research to improve modelling precision and reduce uncertainty in the results.<sup>8,13</sup> Main concerns in this regard are GHG emissions and resource depletion, though other environmental impacts associated above all with the mining phase might be equally relevant.<sup>14</sup> This, in combination with the expected increasing flow of returning end-of-life (EoL) batteries, triggered also interest in the environmental impacts and benefits of battery recycling, disregarded in many of the existing LCA studies until recently.<sup>15,16</sup> However, while costs and energy density are rather

straightforward indicators, this is more complex for environmental and resource aspects. First, data is often scarce and requires substantial efforts for modelling process chains and collecting reliable data on inputs and outputs associated with each process stage. This is especially challenging for emerging battery chemistries, where information about synthesis routes, raw material markets and process technology are mostly unavailable. Second, the actual performance that emerging cell chemistries might reach in future once established can only be guessed, though these parameters are highly relevant under a full life cycle perspective<sup>14</sup>. Still, such prospective studies are highly relevant for foreseeing potential environmental hotspots and avoiding burden shifting, allowing to provide recommendations about eco-design and potential problems already in an early design stage.

Despite their early stage of development, several **LCA studies of emerging battery chemistries** are available. These are, despite the mentioned simplifications and uncertainties, highly valuable for obtaining a first picture of potential hotspots and for applying eco-design criteria already from an early stage of development. So far, LCA studies are available for AHIB, Li-S, Mg-S, SIB and VRF batteries. The results from these studies in terms of GHG emissions from battery manufacturing in comparison with the current benchmark (NMC-type LIB; average value from recent reviews<sup>8,14,17</sup> are displayed in **Figure 1**. Comparison is limited to GHG emissions, being other categories often disregarded or not directly comparable due to different impact assessment methodologies applied.<sup>14</sup> Current LIB (NMC type) batteries are taken as reference, with the average benchmark value for these cell chemistry taken as 85 kgCO<sub>2</sub>eq/kWh<sup>8</sup>, significantly lower than the average value reported by a review in 2017.<sup>14</sup> This can be attributed to improvements in cell manufacturing technology, in LCA modelling precision and also cell energy density.[Ref to chapter 3a]



**Figure 2.** Global warming potential (GWP) associated with the production of post-LIB based on published literature as discussed in the text. The bars mark the standard deviation, the dark line the average value. The area shaded in orange marks the values of current (NMC) LIB, considered as benchmark. AHIB = aqueous hybrid ion batteries, Li-S = Lithium-Sulphur; Mg-S = Magnesium-Sulphur; SIB = Sodium-Ion batteries; VRFB = vanadium redox flow batteries. Results on pack level; when values were given on cell level in the underlying work, these were divided by the factor 0.8 to account for the impact of the pack components (making up on average 20% of an EV battery).

While **Solid state batteries (SSB)** cannot be considered a battery chemistry in the narrower sense but rather a radically different cell concept, relying on the same cathode materials as current LIB but avoiding the need for a liquid electrolyte and the graphite host structure on anode side. Using metallic lithium at the anode, they can achieve theoretically very high energy densities.<sup>18,19</sup> The first LCA study on SS cells published in 2015<sup>20</sup> assesses eight different Li-SSB cell chemistries, obtaining very competitive GWP impacts in a broad range of between 30-70 kgCO<sub>2</sub>e/kWh on cell level. Best results are found for a LiNMO cathode chemistry, followed by LVO and LCO. Key parameter for a good environmental performance is energy density. However, the upstream processes i.e., mining and processing of minerals are not modelled comprehensively or disregarded completely (no further information disclosed in this regard), what might cause a certain underestimation of the actual impacts. A more

recent work found pyritic Li-SSB to show comparably high GWP (199 kgCO<sub>2</sub>eq/kWh), which would be above the current benchmark of around 85 for current high energy NMC cells (85 kgCO<sub>2</sub>eq/kWh). A third study used a laboratory process for assessment and obtained unrealistically high values of 1 ton CO<sub>2</sub>eq per kWh due to extremely high energy demand for cell production (probably due to the use of laboratory data for this purpose), which is why it is not considered in **Figure 2**. Overall, there is still a very high uncertainty in the results, and more thorough and transparent modelling is required in combination with better data of the future cell performance in terms of lifetime and efficiency.

For **Sodium-Ion Batteries (SIB)**, at an already higher TRL, several works are available.<sup>16,21,22</sup> The first study, published in 2016, assessed a NaNMMT – hard carbon type SIB,<sup>21</sup> and found the SIB to be not yet competitive with LIB but to have the potential if achieving similar or higher cycle lives. Apart from high cycle lives, a key for reducing environmental impacts was found to be the hard carbon material, initially modelled to be produced from sugar and associated with significant environmental impacts.<sup>21</sup> Petroleum-coke based HC was suggested as alternative with high yields and low process inputs. A follow-up work, relying on the same cell model, analysed different HC precursors and found biogenic waste material, coke and waste tyres to be promising raw materials for HC production.<sup>22</sup> Mohr et al.<sup>16</sup> updated minor parts of the inventory of the same NMMT cell, analysing it in terms of recyclability, finding the recycling of SIB cells with current hydrometallurgical treatment processes to show comparably low environmental benefits for this type of SIB cell. The GWP was found to be 106 kgCO<sub>2</sub>eq/kWh on cell level, and 93 kgCO<sub>2</sub>eq/kWh when accounting for recycling credits. Finally, a very recent publication evaluated five different SIB cell chemistries in comparison with current NMC<sup>622</sup> and LFP LIB.<sup>[Ref]</sup> With a thorough cell modelling based on electrochemical considerations and a cell-specific recycling model it obtained GWPs of between 51 and 93 kgCO<sub>2</sub>eq/kWh, with the best results obtained for NMMT and MMO cathodes (in combination with petroleum coke derived hard carbon). However, under a full life cycle perspective also the cells with Prussian-blue based cathodes showed promising results due to higher cycle lives.

**Aqueous hybrid ion batteries (AHIB)**, first developed by Aquion Inc, a now bankrupt spin-off of Carnegie Mellon University, are currently being commercialised

for stationary energy storage.<sup>23,24</sup> Their unique selling point is their simple technology (layout similar to lead-acid batteries) and the exclusive use of abundant, non-toxic materials. Despite their comparably high technological maturity, only one study is available on this type of batteries.<sup>25</sup> With 320 kgCO<sub>2</sub>eq/kWh, its GWP was found to be significantly higher than for current LIB due to the low energy density and corresponding high material intensity. However, end-of-life handling was disregarded in the study, though a good recyclability could make up for part of the additional impacts.<sup>26</sup> The study concluded interesting applications especially for countries where no sophisticated recycling technology is available, being the batteries easy to disassemble and to separate into components even manually and without toxic exposure.

Until today **Lithium-Sulphur (Li-S) Batteries**, promising due to their high theoretic gravimetric energy density, have not managed to fulfil the expectations, with several problems still unsolved.<sup>27,28</sup> These are the low coulombic efficiency due lithium polysulfide (LiPS) shuttling and huge volume change, leading to quick degradation of electrode materials and poor cycle lives.<sup>29</sup> In addition, several still unsolved issues, above all the poor cycle lifetime are major drawbacks also under environmental aspects. Three studies are available for Li-S batteries to-date. The first one from 2017, assessing a Li-S battery with sulphur-graphene cathode based on a very detailed and thorough electrochemical modelling of the cell.<sup>30</sup> The GWP on battery pack level was found to be 146 kgCO<sub>2</sub>eq/kWh, better than the reference LIB assumed by the authors, but above the current average (see Figure X). The main drivers for GHG emissions in the production stage were the energy demand for cell manufacturing, contributing 2/3 to the total impacts, followed by electrode materials. Energy demand for cell manufacturing was taken from a pilot production stage, and the authors state that in larger scale production it could be at least halved, if not reduced to a quarter, with the corresponding reduction of GWP impacts. A specific recycling process was modelled as well but no credits for recovered materials are indicated. Based on a prototype cell layout, a study by Arvidsson et al.<sup>31</sup> assessed Li-S battery with carbon-sulphur composite cathode and found its GWP to be between 230 and 30 kgCO<sub>2</sub>eq/kWh. The highest value was obtained for pilot-scale production with corresponding high energy demand and coal electricity, while the lowest value assumed large scale production using PV electricity. A more recent study evaluates a set of 8 different cathode materials,

with mass balances and cell layout compiled from different independent publications.<sup>29</sup> The S-CNT cathode is found to show the highest GWP (248 kgCO<sub>2</sub>eq/kWh), mainly due to the energy intensity of the CNT production. The best value was achieved by the pure sulphur cathode (53 kgCO<sub>2</sub>eq/kWh) and a Li<sub>2</sub>S cathode material (100 kgCO<sub>2</sub>eq/kWh). Energy for cell manufacturing only contributed around 20%, while the electrolyte made up between 35 and 45%, depending on the cell chemistry. Potentially different performance of the individual cathode materials in terms of cycle stability were disregarded, assuming identical cycle life for all.

**Magnesium-Sulphur (Mg-S) Batteries**, promising due to the bivalent nature of the Mg Ion and corresponding high theoretical energy density, share some major shortcomings with Li-S, more precisely those related with the sulphur cathodes: poor cycle lives and efficiency.<sup>7,32</sup> Despite their very early stage of development, there is one recent study assessed the environmental performance of a prototype Mg-S battery<sup>33</sup>. The prototype cell itself was found to be not competitive with LIB yet due to its thick separator, large amount of electrolyte and corresponding low energy density, achieving values of 190 kgCO<sub>2</sub>eq/kWh. However, a hypothetical evolution assuming similar separator thickness and electrolyte loading like in current LIB reduced this value to 90 kgCO<sub>2</sub>eq/kWh, comparable to the NMC benchmark. The high energy intensity of metallic magnesium production was identified as one of the main drivers of GHG emissions. The work disregarded end-of-life handling and use phase (and with this cycle life assumptions).

Similar to Li-S, **Lithium-Air or Lithium-Oxygen (Li-O<sub>2</sub>) batteries** have extremely high theoretical energy densities, while their actual performance is still comparably poor.<sup>34,35</sup> Being sensitive to impurities in the air, they need to be fed with pure oxygen, either generated on site or stored in a tank (closed systems). Both solutions drastically lower energy density and increase environmental impacts, and Li-O<sub>2</sub> are currently not considered as promising technology on medium term.<sup>36</sup> To-date, two studies are available that assess Li-O<sub>2</sub> systems. One is based on an existing prototype cell, but with the scope limited to the actual cell, disregarding oxygen tank and peripheral components like pumps or electronics.<sup>37</sup> This results in an extremely high energy densities of 2700 Wh/kg for the prototype cell and 10.800 for a hypothetical established Li-Air technology, and correspondingly low GWP of 55 and 3.4 kg

kgCO<sub>2</sub>eq/kWh, respectively, though with low cycle lives of 50 and 200 full cycles. Due to the incompatible scope, the results from this work are not included in Figure 1. A second work modelled a hypothetical Li-O<sub>2</sub> battery, using a detailed cell dimensioning approach based on electrochemical considerations.<sup>38</sup> The authors obtain a GWP of 86 kgCO<sub>2</sub>eq/kWh, below their reference NMC LIB. Main driver for GWP impacts are cell manufacturing energy demand, while for other impact categories the CNT and metallic lithium are most relevant.

**Aluminium-Ion (Al-Ion) batteries** are another approach substituting lithium by more abundant materials. Following a similar concept as LIB, Al-Ion batteries rely on metallic Aluminium anodes in combination with e.g., Graphite cathodes.<sup>39</sup> Despite the use of abundant materials, its very low energy density leads to a poor environmental performance, with a GWP of 2600 kgCO<sub>2</sub>eq/kWh on cell level, far from current LIB. Nevertheless, the authors point out that with a lifetime of 5000 cycles and an energy density of >60Wh/kg, the Al-Ion technology could start to become competitive with LIB under environmental aspects. Also, the comparably high GHG emissions associated with aluminium production can be expected to decrease in future with ongoing decarbonisation of the economy.

**Redox-Flow Batteries (RFB)** are, like AHIB unsuited for mobile applications due to their low energy density. While there are several LCA on stationary batteries that include an RFB in their comparison,<sup>40-44</sup> these are at least partially based on an extremely simplified LCA study from 1999<sup>45</sup> that considered V<sub>2</sub>O<sub>5</sub> as a waste material available free of burden, or do not disclose comprehensive and transparent inventory data.<sup>46</sup> In consequence, the results from these works are not considered in Figure 1. The first detailed LCA of a RFB that also modelled upstream processes and disclosed all inventory data modelled an 8MWh vanadium based system and found the associated GHG emissions to be 328 kgCO<sub>2</sub>eq/kWh.<sup>46</sup> Main driver for these impacts was the electrolyte production, especially the vanadium production and corresponding upstream processes. Being the electrolyte almost 100% recyclable, also the potential benefit from recycling is high: When accounting for recycling credits, total GWP is reduced by over 75% to a very competitive 80 kgCO<sub>2</sub>eq/kWh. He et al.<sup>47</sup> assess three different types of RFB (vanadium, zinc-bromine and iron flow battery; or VRFB, ZBFB and IFB, respectively) under a cradle-to gate perspective (excluding recycling). They

find the IFB to show the lowest GWP (75 kgCO<sub>2</sub>eq/kWh), while VRFB and ZBFB obtain similar results (172 and 180 kgCO<sub>2</sub>eq/kWh). The authors find a high sensitivity on the type of vanadium production process and therefore the origin of the V<sub>2</sub>O<sub>5</sub> for VRFB. If it is obtained from crude oil burning residue instead of vanadium-bearing magnetite, the GWP of the VRFB decreases to values similar to those of the IFB. A third work comparing a small-scale VRFB with LIB for stationary applications find the GWP to be 274 kgCO<sub>2</sub>eq/kWh when assuming virgin V<sub>2</sub>O<sub>5</sub>.<sup>48</sup> Again, the electrolyte was found to be main driver of impacts in the majority of the assessed categories, but to decrease when using recycled electrolyte, again highlighting the importance of accounting for the end-of-life stage.

**The development of LIB and post-LIB is driven by the three key indicators performance, environment/resources and cost.** These are often opposed (e.g., a higher energy density increases prices; low-cost, abundant materials based cell chemistries (like LFP) achieve lower energy densities), but can also be synergic (e.g., a higher energy density reduces the material intensity per unit of storage capacity provided, thus decreasing environmental impacts from production). In addition, the indicators environment and performance embrace several components that are often not synchronous as well: high energy density might be achieved for the price of lower cycle lifetime, the use of less critical resources might increase GHG emissions. Together with the previously mentioned uncertainties regarding the production process, this makes the evaluation of emerging cell chemistries a challenging task.

Except some SSB LIB chemistries, none of the assessed post-LIB seems to be able to challenge present LIB, which are a mature and highly optimised technology. However, many battery types have the potential to do so in future, given that technological challenges like e.g., poor lifetimes are overcome. Also, only GHG emissions have been considered here, though other environmental impacts, but also resource issues might be at least as important. In addition, while a comparison of manufacturing impacts is relevant, only a full life cycle perspective can give a meaningful picture, considering also aspects of lifetime and the very different recyclability of the technologies. For example, AHIB and VRFB, associated with high GHG emissions from the manufacturing stage, also obtain particularly high benefits from recycling. In consequence, a meaningful assessment of any cell type requires

thorough definition of the foreseen application, which determines the requirements in terms of power, energy density, cycle and calendric lifetime, and the impacts associated with charge-discharge inefficiencies and standby consumption. Especially for emerging chemistries, studies focusing on the manufacturing stage prevail, disregarding use and disposal. These studies provide important information about possible environmental hotspots and improvement potentials including the upstream processes but should be used cautiously when comparing different cell chemistries. Only a full life cycle approach can give meaningful recommendations, being e.g., the EoL /recycling stage fundamentally different between different cells. A standardised assessment framework including a set of standard application cases could help to harmonize future studies and to make their results better comparable.

The soaring demand for lithium and other battery metals is triggering a **new mineral goldrush**.<sup>49,50</sup> Mining projects are explored also in Europe, but with often heavy opposition by local population.<sup>51</sup> A better knowledge of both the environmental impacts, but also the societal implications (potentially both negative and positive i.e., beneficial) of mining activities is required for creating acceptance within society and allow for an evidence-based decision making. In consequence, there is a **need for broader sustainability assessment** with a higher spatial resolution, also including social aspects, relating mining activities with local value generation and employment. The accelerating uptake of EV in combination with circular economy policies and corresponding mandatory recycling targets has triggered a steeply increasing interest in **battery recycling**.<sup>52,53</sup> Numerous studies have been published recently in this area, although most of these focus on describing the existing recycling technologies and the progress made in this regard, while major knowledge gaps in the field of LCA are still given.<sup>16,54-60</sup> Still, there is general agreement that recycling is one of the keys for minimising the environmental impacts of future batteries.<sup>53,54,57</sup>

1. While substantial efforts are being made in the R&D of new recycling technologies, a major challenge in the field is the **economic viability of battery recycling**. Currently, recycling efforts are driven mainly by legislative obligations than by economic considerations, with vast majority of current battery systems not being recyclable economically (i.e., costs are higher than benefit from the recovered materials).<sup>61,62</sup> This might lead to a tendency for avoiding the associated costs and

to recycle batteries informally or to export them, like it is the case with waste electric and electronic devices. Although in major economies LIB are characterized as hazardous and recycling is mandatory, this is not the case in many countries where no legislation exists in this regard.<sup>62</sup>

Recycling benefits are usually higher the better a process is adapted to a specific cell chemistry. For portable batteries (IT and power tools), standard pyrometallurgical or hydrometallurgical processes are applied, with a focus on recovering the most valuable materials cobalt, nickel, copper, but also metallic aluminium and lithium. Portable batteries are usually made up of a mix of different cell chemistries, dominating LCO, but the exact composition of each cell is impossible to determine. Therefore, robust processes like pyrometallurgy are required that are tolerant to contamination with other battery cell types.<sup>63</sup> However, these are likely not to comply with future recycling targets, recovering only the most valuable materials from the processed cells.<sup>64</sup> Vehicle batteries on the other hand will be returned in a more controlled way, allowing to tailor the recycling process according to a specific cell chemistry and thus to optimize recovery and process inputs.<sup>52</sup> Here, main obstacles for an economic recycling are the dismantling steps, with current EV batteries often not designed for recyclability, requiring substantial effort for opening the welded battery packs.<sup>56,61</sup> This is often one of the main cost drivers for recycling, and OEM slowly start working on improving dismantling of their battery packs. However, prevailing criteria are costs and safety, which is why battery packs continue to be welded and not designed for easy and quick dismantling.

This increases process costs and inputs and reduces economic sustainability.<sup>17,56</sup> From an economic point of view, decreasing the costs of the recycling process (e.g., by allowing automatization of sorting and disassembly, by better adjusting the processes to the specific cell chemistry, but also by designing simpler processes) while recovering high-value products is therefore of paramount importance.<sup>63,65</sup> However, the current trend in battery development is going into an opposite direction, aiming at reducing the content of high value metals like copper, but also nickel, in turn also reducing the economic viability of recycling processes. In an extreme case, this can lead to landfilling batteries to be associated with lower

costs than recycling.<sup>66</sup>

For the most part, the products of recycling processes are less valuable than the batteries being processed and not all valuable components of the battery are being recovered. The business model for current recycling technologies is not robust; (2)

Also under **environmental aspects**, the specific cell chemistry needs to be considered. Highest benefits are obtained for the materials that are associated with the highest impacts from mining and beneficiation, leading to **high recycling benefits for LCO, NMC and other cobalt and nickel containing cells.**<sup>[Ref], 16,67</sup>

The recovery of metals in their elementary form (mainly aluminium, steel and copper) by simple mechanical processes (usually not performed in pyrometallurgical treatments of battery cells) is correspondingly highly beneficial for all types of batteries.<sup>68,69</sup> Correspondingly, for post LIB, where the avoidance of copper for the anode current collector leads to a reduction of impacts in many impact categories for the manufacturing stage, also the corresponding recycling benefit is low. As under economic aspects, the more environmentally friendly are the battery materials, the lower the environmental benefit from recycling, and maximum recycling depth does not necessarily mean a maximum reduction of environmental impacts. Especially for low-value chemistries like LFP, but also for SIB or Li-S, recycling with prevailing hydrometallurgical processes is not always associated with environmental benefits. In some cases, breaking down the recovered active material into their constituents (metal salts) even increases total impacts i.e., the benefit of recovering the metal salts are lower than the credits obtained for avoiding their production from virgin materials.<sup>16</sup> Here, new low cost and low-input processes need to be developed, making also the recovery of these materials attractive. This might also require a shift away from the prevailing closed loop recycling, finding alternative more suitable applications for the recovered materials (e.g., graphite and sulphur in case of Li-S batteries, or iron and phosphorous salts in case of LFP) in other sectors of the economy.<sup>70</sup> A second alternative is so-called direct recycling, aiming at maintaining the crystal structure of the active materials instead of breaking them down into their constituents ('refurbishment' of active materials). This way, higher-value products are obtained,

increasing economic benefit while at the same time saving the environmental impacts associated with breaking down the materials and re-synthesizing them.<sup>63,67</sup> However, the cathode chemistries of Li-ion batteries are constantly evolving, making it difficult for recycling companies to adapt, which is more challenging the better a specific process is optimised for a given cell chemistry.<sup>62</sup>

**Thorough EoL modelling requires information about the whereabouts of current batteries.** In existing assessments, recycling or end-of-life handling is either neglected (cradle to-gate approaches that are, as previously mentioned, of only limited significance), or complete recycling with recent recycling technologies is assumed. Both do not reflect reality, since only a fraction of current waste LIB are actually being returned for recycling.<sup>66</sup> While recycling rates (i.e., the fraction of input that is recovered by a given recycling process) for EV batteries are known and provided by battery recyclers and are also stated as mandatory targets in the European Battery Directive,<sup>71,72</sup> these reflect only one part of the process chain i.e., the recovery efficiency regarding the battery materials at the recycling plant. The return rate i.e., the share of batteries that actually returned from the market to recycling is not accounted for in this calculation, although it is at least as important. In fact, return rates are below 50% on average in the EU (with one of the most ambitious battery recycling policies worldwide) for portable batteries,<sup>73</sup> and even lower for portable LIB (e.g., below 10% in Germany)<sup>74,75</sup>. For EV, reliable numbers are not available (and maybe also not meaningful due to the strong growth of the market, making a meaningful calculation of return rates difficult (for other batteries, return rates are calculated as the relation out of batteries recovered and put on the market annually). However, when taking the conventional vehicle market as reference, an important share of old or decommissioned vehicles disappears in the EU with unknown whereabouts, assumed to be illegally exported into third countries or to be dismantled illegally and under circumvention of any legal obligations in terms of environment or recovery rates.<sup>76</sup> While these practices are widely known but hardly tackled, it cannot be discarded that similar structures will establish in the EV and second-hand battery sector, with all corresponding environmental impacts. Since these vehicles do not appear in the official statistics, they also are not captured by the recycling targets according to EU legislation. These aspects are not

considered yet at all, and interdisciplinary work is required for filling this gap, combining different methods like MFA, LCA and big data. [Ref to MFA Chapter]

2. It is common practice to account for resource depletion at the beginning of the life cycle i.e. at the mining site. This is straightforward, but does not always grasp the actual problem associated with resources, which is twofold: **Resource extraction is not equal to resource depletion**, since the extracted minerals or metals are then incorporated into the Technosphere, where they are readily available as functional materials, often in much higher concentration than in its initial state as ore or mineral.<sup>77</sup> The problem arises when these materials are lost from there by dissipation and diluted to a concentration where they cannot be recovered again. This would call for a change in scope towards a dissipation-oriented resource depletion assessment.<sup>78,79</sup> Initiatives in this regard are ongoing, but the dominance of existing databases likeecoinvent creates a strong inertia. A second aspect is the quality of materials recovered in recycling processes. Especially for metals recovered in their metallic form, impurities can accumulate and reduce the quality of the recycled / remelted material. This limits the amount of recycled material that can be contained in a product, requiring a certain share of virgin material for maintaining quality standards.<sup>80</sup> Assuming a closed loop recycling as usually done might therefore overestimate the true recycling potential. In a growing market like it is the case for batteries, this is less an issue since additional material is required anyway for maintaining the growth and since spent batteries return with a delay determined by their lifetime. However, for future-looking LCA this might be a highly relevant aspect, limiting the potential circularity of the battery sector, but also causing possible overestimation of recycling benefits in current studies assuming closed-loop recycling processes.

The **reuse of spent batteries in secondary stationary, mainly industrial applications ('second life')** has attracted a lot of attention ultimately <sup>81,82</sup>[Ref]. Many companies have initiated pilot projects for testing the viability of such approaches, using stockpiled old EV batteries for providing grid services. However, these are currently R&D projects subsidized by research funds; up to what point commercial applications would be viable in future is yet to be seen.<sup>17</sup> Lack of knowledge about the actual state of health of used vehicle batteries, different

formats and sizes (requiring to pick used batteries of only one specific vehicle model for reasons of compatibility, need for simulating a complex vehicle environment etc. might be major hurdles.<sup>82</sup>

Several publications assessing the benefits of second life use have been published ultimately, majorly finding a positive balance for such projects, reducing the need for additional, new batteries in grid applications and therefore the impacts caused by up-ramping the required battery stock<sup>17,59,83</sup>. However, the amount of batteries actually available for second-life applications is not yet foreseeable, and neither is the actual economic attractiveness (without subsidies or promotional considerations), taking into account the high diversity of vehicles batteries in terms of package, connectivity and interfaces, and the insufficient knowledge about their state of health and remaining lifetime.[Ref]<sup>82,84</sup> When looking at the second-hand vehicle marked as now, used cars and used car parts are usually either scrapped or sold as replacement parts for the same application. For instance, vehicle engines are sold either as second-hand engines for the same vehicle type (replacement of broken parts), or scrapped, but not used for e.g., stationary electricity generators. From a circular economy perspective, refurbishment and re-use in the same vehicle application via the second-hand vehicle marked would be the first choice. Also, if second life applications are used to ‘park’ old EV batteries for saving costs associated with recycling, this could lead to an unnecessary increase in absolute stocks and corresponding impacts from resource extraction. In any case, there are certain trade-offs related with second life applications, like delayed return of used batteries to recycling facilities or shift of producer product responsibility that might have detrimental effects of the overall environmental performance of the batteries over their whole life cycle. Minimizing the stock of vehicles should therefore be the overarching objective, making best use of the existing battery stock.

**Vehicle-to-grid** is one of the key technologies for minimizing the required total amount of battery capacity, allowing to use the available battery park as efficient as possible. Instead of being parked without use the major part of its lifetime (vehicle are parked on average 95% of the time)<sup>85,86</sup>, batteries can be connected to the grid and provide (part of) the service that stationary batteries would. The benefit would be a more intensive usage of the existing battery park and a

smaller overall battery park, with the corresponding benefits in terms of manufacturing impacts and resource demand. However, research activity in this field is currently low, and the lack of regulatory schemes and a broader policy support hinder their development.<sup>87</sup>

R&D in the battery sector is increasingly taking into account material issues. Driven above all by economic, but more and more also by environmental concerns, battery developers seek to reduce the content of scarce and critical raw materials by developing new cathode materials, but also completely new battery chemistries based exclusively on abundant and/or non-toxic materials. While this can be considered a progress in terms of environmental impacts in the upstream processes, care has to be taken to avoid environmental trade-offs further down the ‘path of life’ e.g., due to lower efficiency or life-time (use-phase) or poor recyclability (end-of-life). A good example are aqueous lithium- or sodium-ion batteries that avoid the use of organic electrolytes and scarce metals in the cathode, but that also have significantly lower energy densities, thus requiring substantially higher amounts of battery mass to be produced for a certain storage capacity. Also, recycling of batteries based on abundant materials is economically less attractive and the recovery of certain elements might in some cases be associated even with higher environmental impacts than their mining from primary sources. Direct recycling i.e., the recovery of active materials while maintaining their molecular / functional structure might be a big step forward in this regard, but quality issues (and their corresponding impacts on the environmental performance of the batteries made from these) are yet widely unassessed. On the other hand, batteries based on abundant and non-toxic materials (like the mentioned aqueous ones) might be the advantageous when proper recycling with modern technology cannot be assured like it is the case for batteries exported into developing countries (be it as second-hand electric vehicles or stationary systems for local energy communities). There, recycling is often done in artisanal ways and without proper measures for protecting exposure of workers and the environment, making the avoidance of toxic or scarce substances in the battery significantly more relevant. Only a full life-cycle approach including an up-to-date modelling of material flows (origin of raw materials and destiny of spent batteries) will provide a realistic picture of the potential

environmental impacts of competing battery technologies, but the vast majority of existing assessments fall short in doing so. The quickly changing markets and prices, together with rapid progress in battery and recycling technology and the often insufficient availability and re-usability of data from previous studies are one of the main challenges for sustainability assessment in this regard.

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## Chapter 2

### Sustainable grid-scale lithium-ion battery energy storage

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#### 1. Background and key challenges

The demand for energy rises rapidly with growing electrification of the modern world. Currently, the burning of fossil fuels contributes to ~ 80% of the world's electricity generation, while accounting for more than 95% of the energy sector's emission of CO<sub>2</sub>, a major greenhouse gas responsible for global warming<sup>1,2</sup>. To reduce CO<sub>2</sub> emission while maintaining energy generation growth, the decarbonization of energy is crucial and has gained wide support. A key component of decarbonization is the substitution of fossil fuels by low-carbon renewable energy sources such as wind and solar energy. While these sources have nearly unlimited amount in the nature, they are highly regional and intermittent<sup>3</sup>. This requires a significant expansion in the storage capability of the energy grid to allow rational distribution of electricity spatially and temporally. To date, several technologies have been explored as candidates for energy storage, including pumped hydro, compressed air, flywheels, supercapacitors, vanadium redox flow, hydrogen, sodium sulfur batteries and lithium-ion batteries. Among these, lithium-ion batteries (LIBs) make up the largest market share for their advantages of high energy density, good energy efficiency and long cycle life. The competitiveness of LIBs are further examined in a detailed study by Schmidt *et al.*<sup>4</sup>, where they assessed a leveled cost efficiency of all energy storage technologies by factoring in twelve stationary application scenarios such as energy arbitrage, black start, management, power quality and reliability, and etc., and found that LIBs will remain dominant in energy storage in future decades.

To outcompete and eventually replace fossil fuels in the long term, renewable energy combined with LIB storage has to achieve greater reliability and cost efficiency. Past research efforts on LIBs have mainly been focused on improving cycling stability<sup>5</sup> and reducing raw materials/manufacturing costs<sup>6,7</sup>. Presently, lithium-ion battery packs have already been demonstrated to withstand 7000 deep charge/discharge cycles in industry<sup>8</sup>. With continued efforts in electrode materials, electrolyte, pack design and battery management, it is technically feasible to push towards 10,000 or even 20,000 deep cycles, which corresponds to an attractive 10-20 years of LIB lifetime in stationary storage. The reduced installation and management costs for replacement brought by the

prolonged cycle life, together with efforts in reducing raw materials cost (e.g., using inexpensive redox-active Mn or Fe and thicker electrodes) and manufacturing costs (e.g., aqueous processing of electrodes, dry electrode coating, and reducing wetting/formation time<sup>7</sup>), the cost of batteries have come down dramatically in the course of a decade, from US\$1160/kWh in 2010 to US\$156/kWh in 2020 on the pack level<sup>9</sup>. Bloomberg predicts this number to be lower than US\$100/kWh by 2025 and even lower in the years beyond<sup>10</sup>. A recent study by Ziegler *et al.*<sup>11</sup> shows that the target cost for renewable energy storage needs to be below US\$20/kWh to fulfill 100% of baseload demand, and if other sources can meet 5% of the demand (renewable energy filling in 95%), the target energy storage cost rises to US\$150/kWh, a goal we have already achieved in recent years<sup>10</sup>. With ongoing efforts in improving cyclability and reducing cost in both academia and industry, the push towards 100% energy decarbonization seems to be only a time issue.

The real challenges nowadays are not cycling and cost concerns, but rather safety and recycling, which are the two factors that have been overlooked in the past, and can be game changers to the field of renewable energy storage. This report focuses on recent progresses on the safety and recycling of LIBs for stationary storage.

## 2. Fire safety

Although LIBs lead other energy storage technologies in comprehensive performance, they are far behind in safety, which has been widely criticized. Over the years, there has been repeated reports of fire incidents on mobile devices, electric vehicles and stationary storage. For instance, in November 2017, the fire at a LIB energy storage site in Belgium forced thousands of residents to stay at home; in April 2019, the explosion at a LIB storage facility in Arizona caused many severe injuries; between the years of 2017 and 2019, there were 28 cases of fire incidents at energy storage sites in South Korea, resulting in the suspension of more than 500 additional facilities<sup>12</sup>.

To prevent such incidents, it is essential to understand the origins and stages of battery failure (summarized in the upper part of Fig. 1). The initial stage of failure occurs within the individual cell, where heat can be generated by degradation of different components inside the battery and by side reactions between them, including breakdown of the anode solid-electrolyte interface (SEI) layer, reaction between anode and electrolyte, melting or penetration of the separator, reaction between cathode and electrolyte and etc.<sup>13</sup> As individual cells rise in temperature and pressure, flammable gases escape from the cell and can lead to thermal runaway, igniting adjacent cells and eventually the whole battery pack. Therefore, it is critical to make safety improvements on both battery materials and extrinsic safety devices.

Significant efforts have been made on battery materials such as cathodes, anodes and electrolytes. For cathode materials, high energy density is often pursued. To achieve high energy density, high-capacity and high-voltage layered cathodes (such as LiCoO<sub>2</sub> and LiNi<sub>1-x-y</sub>Co<sub>x</sub>Mn<sub>y</sub>O<sub>2</sub>) are favored over the more thermally-stable olivine cathodes (such as LiFePO<sub>4</sub>). To reach even higher capacity, recent efforts focus on

charging layered cathodes to higher voltages. This increases the participation of oxygen redox and subsequent oxygen gas release, which is very dangerous considering its possible combustion reaction with organic solvents and thermal runaway triggered by this exothermic process<sup>14</sup>. To improve thermal stability of high-voltage layered cathodes, doping and coating are the two main methods. It has been proven effective to substitute Co, Ni or Mn in common layered materials by dopants such as Mg<sup>15,16</sup>, B<sup>17,18</sup>, Al<sup>19,20</sup>, La<sup>19</sup>, Zr<sup>18</sup>, and etc., which act as structural stabilizers by being redox-inactive or forming strong bonding with oxygen. It is also beneficial to coat an electrochemically-inactive and structurally stable surface layer, such as AlF<sub>3</sub><sup>21</sup>, MgO<sup>22</sup>, ZrO<sub>2</sub><sup>23</sup>, Al<sub>2</sub>O<sub>3</sub><sup>22,24</sup>, AlPO<sub>4</sub><sup>25</sup> and LiFePO<sub>4</sub><sup>26</sup>. In an intriguing recent work, Yoon *et al.*<sup>27</sup> coated a Co<sub>x</sub>B metallic glass on LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811), and achieved stable cycling for 500 cycles in pouch-type full cells against graphite anode. The Co<sub>x</sub>B metallic glass infused into the grain boundaries of NCM811 and formed strong bonding with oxygen, which suppressed oxygen activity and stress-corrosion cracking at grain boundaries of the NCM811 secondary particles.

Graphite is the most commonly used anode in LIBs. The thermal stability of graphite anodes is controlled by the SEI layer that is formed in the initial cycles via reactions with electrolyte salts such as LiPF<sub>6</sub> or LiBOB<sup>28</sup>. Decomposition of the SEI layer dramatically degrades battery performance and thermal stability<sup>29</sup>. Efforts on improving graphite anode stability include using electrolyte additives<sup>30</sup>, mild oxidation<sup>31</sup>, coating<sup>32</sup>, morphological modifications<sup>33</sup> and etc. Other anode materials with higher energy density and stability are also being explored, including silicon nanowires<sup>34,35</sup>, Fe<sub>3</sub>O<sub>4</sub><sup>36</sup> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub><sup>37</sup>. Researchers have also been investigating the possibility of using lithium metal, the ultimate anode material with the highest energy density, but have met tough barriers due to the catastrophic lithium dendrite growth, which leads to poor cycling performance and poses serious safety issues due to short circuiting<sup>38</sup>. General methods on suppressing lithium dendrite growth include electrolyte engineering, artificial SEI design, using stable hosts and etc.<sup>38,39</sup>

Electrolyte engineering is another important area to improve safety. Organic solvents in liquid electrolytes are highly flammable, especially when the battery undergoes abuse conditions such as penetration, crushing, impact and overcharging<sup>40</sup>. Ignition of the organic solvents are highly exothermic and leads to thermal runaway. Over the past two decades, various strategies have been adopted to improve the safety of electrolytes, including replacing LiPF<sub>6</sub> and carbonate-based solvents with more stable ones<sup>41,42</sup>, using functional additives<sup>40,43</sup>, and switching to ionic liquids<sup>44</sup>, gelled polymer-based electrolytes<sup>45</sup> or inorganic solid electrolytes<sup>46</sup>. Recent progress has seen significant improvements in electrolyte safety, especially under high voltages. For example, Suo *et al.*<sup>47</sup> found LiF to be stable against high-voltage cathodes and lithium metal, and that increasing the amount of donatable fluorine in the electrolyte improves coulombic efficiency, and achieved stable cycling in a 5-V Li metal full cell by utilizing a full-fluoride electrolyte composed of highly concentrated Li bis(fluorosulfonyl)imide (LiFSI) in fluorinated carbonate (FEC) solvent. Xue *et al.*<sup>48</sup> demonstrated that a

sulfonamide-based electrolyte, composed of LiFSI in liquid aprotic N,N-dimethyltrifluoromethane-sulfonamide (DMTMSA) solvent, can stabilize NCM811 cathode charged to 4.7 V by suppressing stress-corrosion cracking, and is beneficial to the lithium metal anode by forming a thinner and more uniform SEI layer. A variety of combinations of different types and amounts of salts, solvents and additives can be used for liquid electrolytes, which requires thousands of experimental trials. Recently, our group is using robotic arms and automatic testing apparatus paired with active learning algorithms to conduct high throughput electrolyte testing (ongoing)<sup>49</sup>. This eliminates the need for tedious experiments and human error, and dramatically speeds up the search for the optimal liquid electrolyte for both performance and safety. To bypass the flammability issues in liquid electrolytes, solid electrolytes are a good alternative. The field has seen significant progress over the past few years, with ionic conductivities reaching or even surpassing that of liquid electrolytes<sup>50</sup>. The parasitic reactions and poor mechanical contact between solid electrolytes and the anode remain a tough challenge, but has also seen some light in recent works. For instance, Chen *et al.*<sup>51</sup> showed reversible Li stripping and plating inside a mixed ionic-electronic conductor host made of carbon hollow tubules, which presents great promise on the use of safer solid electrolytes by stabilizing Li metal SEI production, and maintaining good mechanical contact between anode and solid electrolyte. Improvements have also been done on the separator and current collectors, which are reviewed elsewhere<sup>52,53</sup>.

Fire hazards not only originates from battery materials, but can also stem from bad cell design or poor battery management systems. Therefore, improvements on extrinsic safety devices are also critical for grid storage safety, which include safety vents<sup>54</sup>, current interrupt device<sup>55</sup>, positive temperature coefficient device<sup>56</sup>, shutdown separator<sup>57</sup>, gas sensors<sup>58</sup>, battery management system<sup>59</sup> and etc.<sup>13,60</sup> These technologies have progressed tremendously over the past few years, and now researchers are even incorporating them with state-of-the-art machine learning methods. For example, Hsu *et al.*<sup>61</sup> used deep neural network to predict battery life and state of health by only using data from the first cycle. This allows better battery management for more rational utilization of individual cells, which not only lengthens battery life but also reduce fire hazards due to battery abuse. The combination of these extrinsic devices enables early detection of safety threats, balanced cell utilization in battery packs and timely shutdown of thermal runaway events, and together with the advancement in battery materials, safe and reliable LIB stationary storage will be made possible in the near future (solutions for fire safety are summarized in the lower part of Fig. 1).

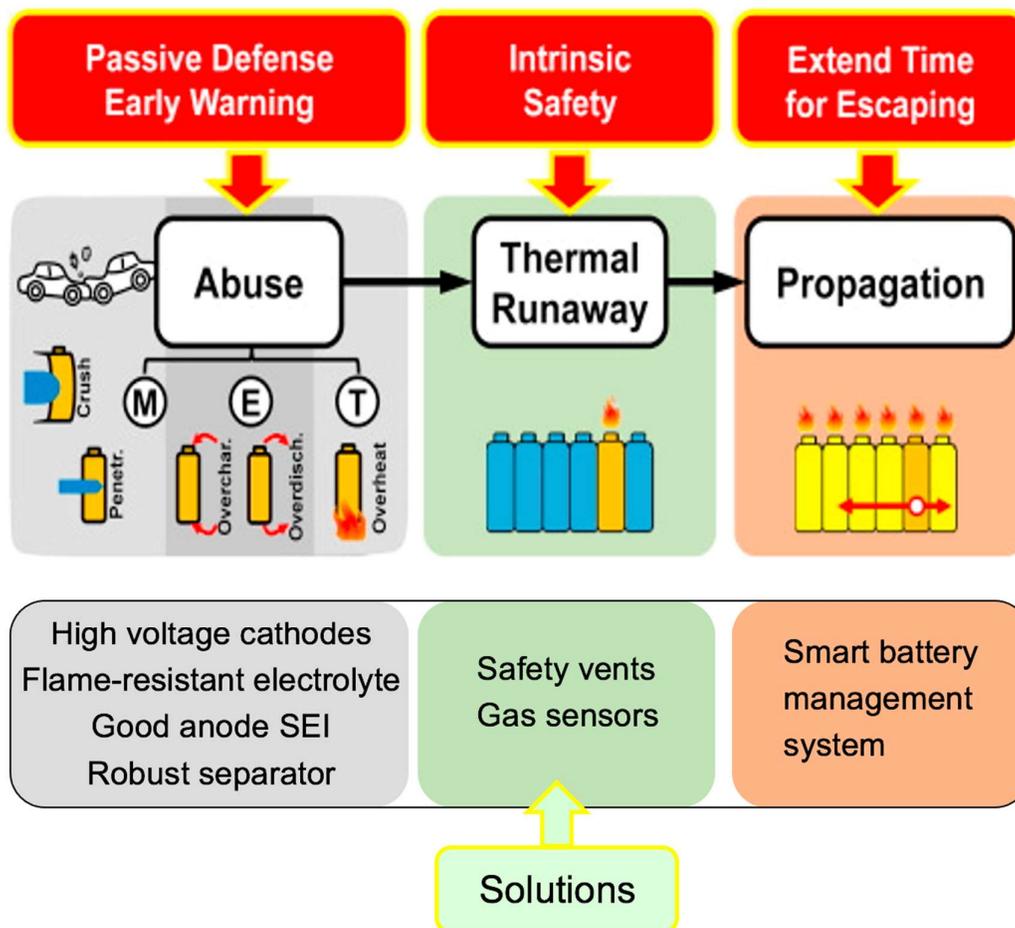


Figure 1. Origins of fire hazards and solutions to enhance LIB safety. Adapted from reference<sup>62</sup>.

### 3. Recycling

Apart from safety concerns regarding LIB stationary storage, people have always questioned whether renewable energy is truly ‘green’. The production of wind turbines, solar arrays and LIBs are highly mineral-intensive, which is a serious concern for supply chains and Earth’s limited mineral deposits. For instance, LIB production today accounts for 40% and 25% of all lithium and cobalt mining capacities, respectively, and will be even more demanding in the future.<sup>63</sup> Additionally, mineral mining and LIB production both produce large amounts of CO<sub>2</sub>, and the retired green devices mostly end up in landfills or oceans, generating massive amounts of waste plastic and heavy metals that threatens our environment. Thus, it is important to focus on recycling of these devices to create a sustainable mineral supply chain and reduce pollution.

The recycling rate for LIBs is considerably low, around 5% worldwide as of 2019<sup>64</sup>. This is due to various factors such as absence of regulations, complex/expensive recycling processes and lack of recycling facilities<sup>65</sup>. Currently, the two major recycling methods are pyrometallurgy and hydrometallurgy, both of which focus on the

extraction of valuable metals such as Co, Ni, Mn in their metallic form. However, these techniques are energy-consuming and neither environmentally nor economically-friendly<sup>66</sup>. Studies show that these methods may even bring negative CO<sub>2</sub> emission reduction compared to not recycling at all<sup>65</sup>.

To address these issues, direct recycling methods have been recently developed, which features the recovery of cathode or anode materials as a whole instead of extracting individual metals. The most common strategy is to heat treat the spent active materials with new active materials or new lithium sources in order to recover lost lithium or repair the damaged crystal structure. The reconditioned cathode and anode materials can be directly reincorporated into new electrodes for battery remanufacture, greatly reducing the cost and emissions of recycling and resynthesis of active materials. Other facile and inexpensive methods include hydrothermal regeneration<sup>67</sup>, selective healing<sup>68</sup>, mechanochemical activation<sup>69</sup> and etc. In our own recent collaborative work (ongoing), we show that heavily cycled LiFePO<sub>4</sub>/C cathode powders can be regenerated with microwave plasma in the order of seconds and minutes. Ultra-nanocrystalline LiFePO<sub>4</sub> around the size of 10 nm are formed after microwave treatment for 30 seconds, and the treated material has similar capacity and rate performance compared to new commercial LiFePO<sub>4</sub>, and much better than the untreated material. This rapid regeneration by microwave plasma is potentially much better in cost efficiency and environmental friendliness than other direct recycling and conventional metallurgical processes. Such extreme processing can also be applied to other green technologies such as converting hydrocarbon wastes into useful fuels and chemicals<sup>70</sup>. Direct recycling can also be used in combination with metallurgical processes, which could greatly extend the lifetime of LIBs and result in less resource consumed per unit energy stored. A schematic of the recycling processes in the lifetime of LIBs is shown in Figure 2.

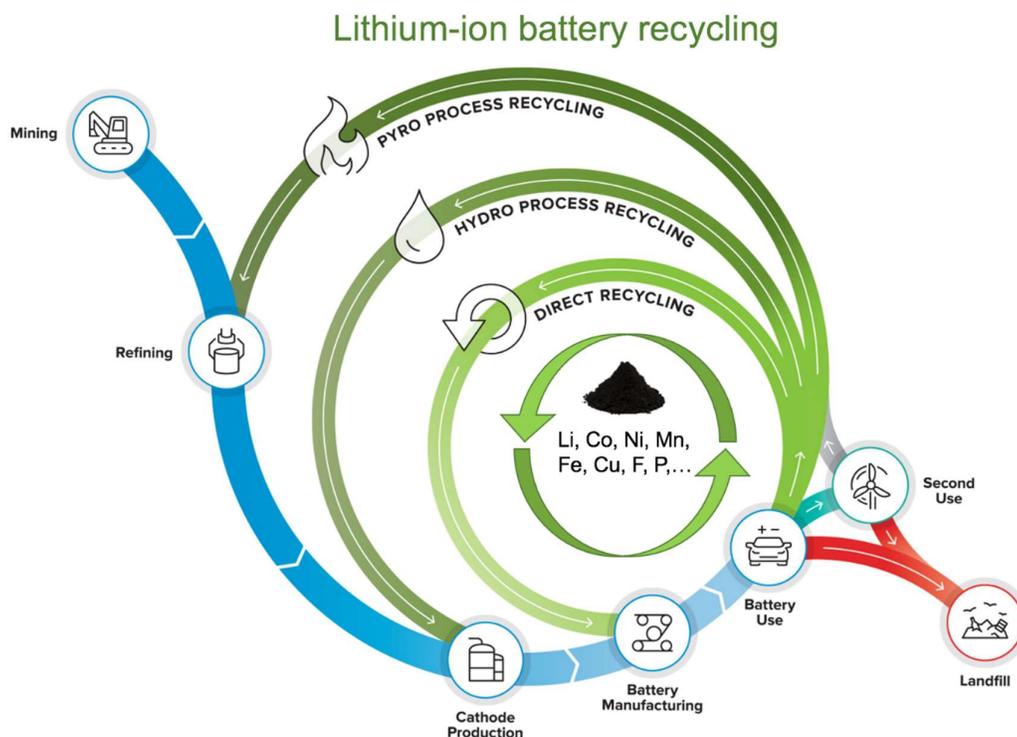


Figure 2. Schematic of closed-loop recycling of lithium-ion batteries. Imaged adapted from Argonne National laboratory ReCell Center<sup>71</sup>.

#### 4. Conclusion and outlook

With continuous improvements in energy density, cost efficiency and cycle life of lithium-ion batteries, the principal challenges of grid storage lie in safety and recycling. These two areas have been overlooked in the past but are critical for ensuring the reliability and true environmentally-friendliness of renewable energy. Fortunately, they have attracted growing attention over the past few years and have seen significant progress. For safety, deeper understandings of the origins of heat generation and thermal runaway have been made<sup>72</sup>, and better designs are developed on both materials and engineering levels, including stable high-voltage cathodes, anodes with stable SEI, flame-resistant liquid electrolytes, solid electrolytes with good cyclability, better extrinsic safety devices and smarter battery management systems. For recycling, people are working towards more economically and environmentally-viable metallurgical processes, as well as innovative ways of direct recycling. The combination of these methods could result in better efficiency economically and environmentally, forming a closed loop of valuable elements such as Co, Ni, Mn and Li within the renewable energy field, which greatly alleviates resource and mining burdens under the rapid growth in energy storage demands. Together with continuous improvement in safety and cyclability, we are moving closer towards the goal of having reliable US\$90/kWh battery packs with stable cycling up to 20,000 cycles and beyond for grid storage, but

there are still tons of work to be done across the fields of materials, chemical and computer engineering.

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## Chapter 3

### Na-ion batteries

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#### 1. Introduction

In spite of the huge success of Li-ion batteries (LIBs) in portable electronics and electric vehicles, resource issues related to the abundance and geographical distribution of lithium drive us to explore new options as strategic relevance for future energy storage. In this regard, Na-ion batteries (NIBs) in particular are proving to be a very promising technology for stationary grid storage not only due to the low-cost and abundant resources with secure supply chains but also the easy scale up of materials and cells production as a “drop-in” technology of LIBs<sup>[1, 2]</sup>. Despite fast advancement in NIBs, the higher atomic mass (23 vs. 6.9 g/mol), larger ionic size (1.02 vs. 0.76 Å) and higher standard electrode potential (-2.71 vs. -3.02 V) of sodium than lithium arouse concerns in whether NIBs can outperform LIBs in terms of the cost per kilowatt hour. It has been generally recognized that simply exchanging Li with Na in electrodes and replacing Cu current collectors with Al analogues are not enough for cost reduction taking the lower energy density of NIBs into account.<sup>[3, 4]</sup> Materials innovation and manufacture advance are highly demanded to highlight the low-cost feature of NIBs and promote the quick transition from proof-of-concept to commercial products. This report will introduce the current status of NIBs including the new discovered electrode/electrolyte materials, the battery prototypes of several start-up companies and the cost assessment compared with LIBs, discuss challenges and strategies for the improvement of battery performance to cater diverse demands, and provide an outlook for the research and development of NIBs in the future.

#### 2. Current Status

##### 2.1 Materials innovation

The choice of NIB constituent materials has a significant impact on electrochemical performance and battery cost. The set of materials that can be used for NIBs covers a wide variety of chemical families. The main categories studied as cathode materials comprise sodium-containing layered transition metal oxides, polyanionic compounds and Prussian blue analogues. The scope of anode materials is proposed according to sodium storage mechanisms of insertion, conversion and alloying, including carbonaceous materials, transition metal oxides/sulfides, Na-metal alloying compounds of group 14 or 15 elements and organic compounds. The development of electrolytes for NIBs in general follows that of LIBs with common solvents and salts, but found to have higher kinetics due to the smaller desolvation energy for  $\text{Na}^+$  ions. Besides electrodes and electrolytes, properties and functionalities of interface between them also captures the major interest due to the considerable potential influence on the whole performance of battery system.

As the source of  $\text{Na}^+$  charge carries, the investigation of cathode materials mainly focuses on the increase of redox potential and specific capacity<sup>[5]</sup>. Early investigation of two-dimensional layered oxides ( $\text{Na}_x\text{MO}_2$ , M: transition metal) by Delmas et al.<sup>[6]</sup> defined the crystal structure, where typical configurations are P2 and O3 according to the geometry of  $\text{Na}^+$  surroundings (P: prismatic and O: octahedral) and the number of unique oxide layer forming the vertically aligned repetitive unit. A criterion for predicting the equilibrium stacking arrangement was recently developed<sup>[7]</sup>. Generally, O3 layered oxides with higher sodium stoichiometry ( $\sim 1$  mol) enable to release more  $\text{Na}^+$  ions and result in higher specific capacity; P2 layered oxides have lower sodium content (typically  $\sim 2/3$  mol) but higher diffusion coefficients to support higher charge and discharge rate due to the facile ionic mobility through rectangular faces. The hybrid of the two structures could make a balance of the overall performance. As 3d transition metals from Ti to Cu are all electrochemically active in Na-based layered oxides, cathode materials of this type are highly diverse given double, triple and even multiple transition metals can be included. In view of element abundance, it is clear that the use of Fe-, Mn-, Cu-rich compounds are the preferred choice<sup>[8]</sup> (e.g. O3- $\text{Na}_{0.9}[\text{Cu}_{0.22}\text{Fe}_{0.30}\text{Mn}_{0.48}]\text{O}_2$ <sup>[9]</sup>). Ni-based cathodes (e.g. O3- $\text{Na}[\text{Ni}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ <sup>[10]</sup>) are also preferred to improve the energy density due to the relatively high redox potential and multi-electron reactions of  $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$  redox couples<sup>[11]</sup>. Based on the

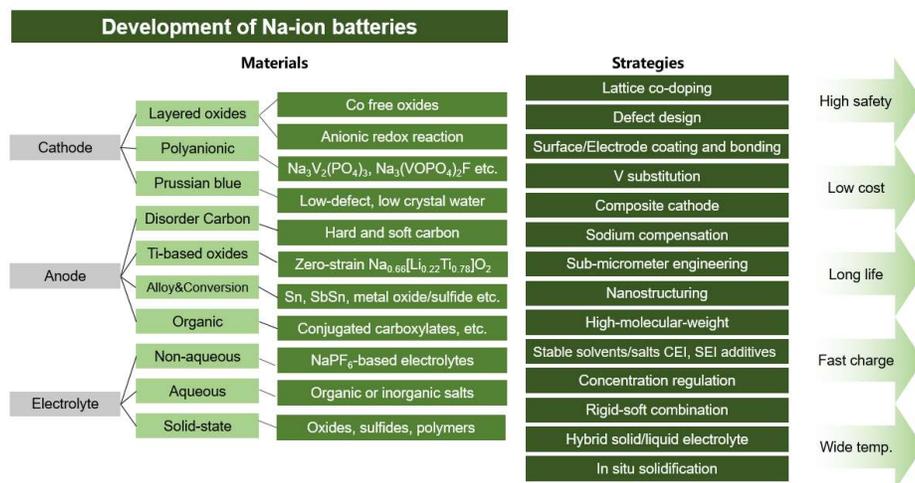
charge compensation of transition metals, layered oxides typically show an average voltage of 2.8-3.3 V (vs. Na<sup>+</sup>/Na) and a specific capacity of 110-150 mAh/g over a desodiation cycle, although the Ni-containing compositions can reach 3.2 V with capacity up to 190 mAh/g<sup>[3]</sup>. Besides, the anionic redox reaction can also contribute to the capacity (e.g. P2-Na<sub>0.72</sub>[Li<sub>0.24</sub>Mn<sub>0.76</sub>]O<sub>2</sub><sup>[12]</sup>, 270 mAh/g), leading to a further increase in energy density. Polyanionic compounds (Na<sub>x</sub>M<sub>y</sub>(X<sub>a</sub>O<sub>b</sub>)<sub>z</sub>Z<sub>w</sub>, M: metals; X: Si, S, P etc.; Z: F, OH) containing multiple Na<sup>+</sup> and polyanions have diverse open-framework crystal structures. They present higher redox potentials than that of layered oxides due to the inductive effect of polyanionic groups. For instance, NASICON-type Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> can reversibly intercalate two Na ions at a potential of 3.4 V and sodium vanadium fluorophosphate family Na<sub>3</sub>(VO<sub>1-x</sub>PO<sub>4</sub>)<sub>2</sub>F<sub>1+2x</sub> (0≤x≤1) display high operation voltage in two pseudoplateaus at 3.6 and 4.1 V.<sup>[13]</sup> However, the heavy polyanion groups limit their specific capacity within the range of 80-130 mAh/g. Prussian blue analogues consist of a metal-organic framework with the general composition of Na<sub>x</sub>M<sub>a</sub>[M<sub>b</sub>(CN)<sub>6</sub>]<sub>1-y</sub>·□<sub>y</sub>·nH<sub>2</sub>O (0≤x≤2, 0≤y<1; M<sub>a</sub>, M<sub>b</sub>: Fe, Mn, Ni, among others; □: [M<sub>b</sub>(CN)<sub>6</sub>] vacancy)<sup>[14]</sup>. The variability of available transition metals to be incorporated into the structure leads to a wide range of potentials and capacity, with hexacyanoferrates delivering a capacity of around 160 mAh/g at 3.1 V<sup>[3]</sup>.

As the cathode counterpart, the search of appropriate anodes for NIBs is even challenge because graphite and silicon the conventional anode materials for LIBs have limited sodium storage capacity as well as Na metal with low melting point and dendrite growth tendency is ineligible as anode. Disordered carbons are a form of nongraphitic carbons normally divided and defined as “hard carbon” and “soft carbon” according to their capability of being graphitizable when annealed at high temperatures (e.g. 2800°C)<sup>[15,16]</sup>. Consisting of graphene nanosheets with significant turbostratic disorder and curvature, the sodium storage process of hard carbons universally demonstrates a sloping region at higher voltages and a plateau process just above 0 V (vs. Na<sup>+</sup>/Na) while the short-range ordered soft carbons exhibit a sloping region very similar to that of hard carbons but do not display the typical low voltage plateau curve. Thus the former generally has a lower average oxidation voltage (0.2-0.5 V vs. 0.5-1.0 V) and higher sodium storage capacity (250-400 mAh/g vs. 100-250 mAh/g) compared with the latter, with the record capacity up to 480 mAh/g<sup>[17]</sup>, beneficial for energy density

improvement of NIBs. Alternatively, reports of very good rate capability in some soft carbons make them appealing substitutes for hard carbons for high power application<sup>[18]</sup>. Similar to carbonaceous anodes, titanium-based anodes with the insertion reaction are also widely studied due to their reasonable operation voltage (0.3-2 V) for avoiding sodium plating issue and the inorganic scaffold conferring superior stability. In addition to various common polymorphs such as TiO<sub>2</sub>, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, Na<sub>x</sub>Ti<sub>y</sub>O<sub>z</sub>, recent reported P2 type (e.g. Na<sub>0.66</sub>[Li<sub>0.22</sub>Ti<sub>0.78</sub>]O<sub>2</sub><sup>[19]</sup>) anodes also bring about broad interest due to the “zero-strain” feature to induce excellent cycling performance. However, the relatively high molar mass sacrifices the specific capacity to fall in the range of 100-180 mAh/g. Different from the above-mentioned insertion-type anodes, conversion and alloying anodes are able to deliver even high specific capacity (>500 mAh/g), but the drawback is obvious as well owing to the severe volume change and large voltage hysteresis during sodium storage to deteriorate the cycling stability. One possible way to alleviate the limitations of large-scale use involves compositing with carbon materials<sup>[20]</sup>. In the case of organic anodes, conjugated carboxylates-, imides and quinones- and Schiff base-groups are widely investigated, among which carboxylates bonded to aromatic systems whose  $\pi$ -conjugation can lead to the insertion of excess charges and the secondary functional groups expected to provide additional interaction sites for Na<sup>+</sup>, are the most popular moieties, generally resulting a specific capacity above 200 mAh/g with adjustable redox potential between 0.2 V and 0.5 V<sup>[21]</sup>.

In regard to electrolytes, non-aqueous liquid electrolytes containing solvents (linear and cyclic carbonates, ethers, etc.), salts (NaPF<sub>6</sub>, NaBF<sub>4</sub>, NaClO<sub>4</sub>, NaFSI, NaTFSI, etc.) and certain additives (film-forming and fire-retardant, etc.) are still the mostly used type, the importance of which has been emphasized recently. Not only on regulating the composition and concentration to tune the ionic conductivity but also on understanding the formation of solid electrolyte interphase (SEI) on both cathodes and anodes to suppress the lasting decomposition of electrolytes and dissolution of electrodes. For solid-state electrolytes,  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, Na<sup>+</sup> super ionic conductor (NASICON), sulfides, polymers etc. all have their own cons and pros, combining inorganic and organic electrolytes to exert their respective advantages is widely investigated<sup>[22]</sup>. The ionic conductivity of some solid-state electrolyte is comparable to or even surpass that of aprotic liquid electrolytes, reaching  $3.2 \times 10^{-2}$  S/cm (e.g.

$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_4$ <sup>[23]</sup>). For aqueous electrolytes, extend the electrochemical window and inhibit side reactions of hydrogen and oxygen evolutions are still directions needing endeavor.



**Figure 1.** Current materials and effective strategies for the development of Na-ion batteries.

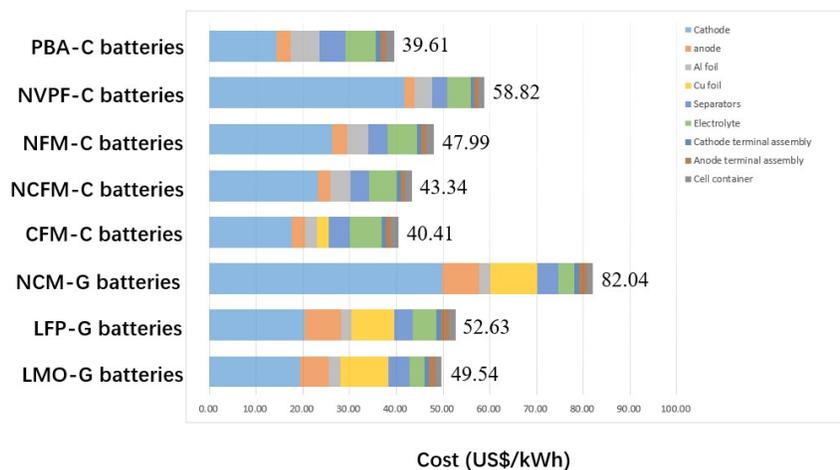
## 2.2 Manufacture advance<sup>[3, 24]</sup>

Materials innovation also attracts interest to accelerate the commercialization of NIBs. More than twenty start-up companies are established to develop and manufacture NIBs until now, most of which choosing carbon anodes and non-aqueous electrolytes given the demonstrated comprehensive performance. The UK company Faradion used the mixed-phase O3/P2 layered cathode  $\text{Na}_4\text{Ni}_{(1-x-y-z)}\text{Mn}_x\text{Mg}_y\text{Ti}_z\text{O}_2$  to develop a 32 Ah pouch cell with energy density of 160 Wh/kg, but the cycle life is not published. Tiamat in France developed cells based on  $\text{Na}_{3+x}\text{V}_2(\text{PO}_4)_2\text{F}_3$  cathodes. The 1Ah 18650 cylindrical cell are reported to have operation voltage of 3.7 V and cycle life of 4000 at 1C. The USA Novasis's Mn-Fe Prussian Blue analogue based NIB can deliver 100-130 Wh/kg in 0.5-5 Ah pouch cells at an average discharge voltage of 3.4 V. The Chinese HiNa Battery Technology is developing cells based on the copper based layered oxides cathode, where the pouch cells show an average voltage of 3.2 V, a specific energy of 145 Wh/kg,  $\geq 83\%$  capacity retention after 4500 cycles at 2C and a working temperature down to  $-40^\circ\text{C}$ . They also demonstrated the first mini-electric vehicle powered by  $\sim 5.5$  kWh NIB pack in 2018, first energy storage power station based on the 100 kWh and 1 MWh NIB systems in 2019 and 2021, respectively<sup>[25, 26]</sup>. Other companies that are

developing NIBs include Natrium Energy (using  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode), Star Sodium (using  $\text{Na}_2\text{Fe}_2(\text{CN})_6$ ) and Natron Energy (using Prussian blue analogues). To be noted that the leading LIB company CATL also launched their first generation NIB technology this year and aroused broad attention.

### 2.3 Cost assessment

Based on the Battery Performance and Cost (BatPaC) model created by the Argonne National Laboratory<sup>[27]</sup>, cost of the 1 kWh model LIBs and NIBs with various cathode-anode combinations are assessed, where the anodes for LIBs and NIBs are graphite and coal derived disordered carbon, respectively. Meanwhile, the cost of electrolyte, separator, current collector and other components like cell container are all considered. It is obvious that NIBs based on layered oxide cathodes have cost advantage over that of LIBs in general with the Cu-Fe-Mn system among the best. Even though NIBs with the Prussian blue cathode and carbon anode is competitive in cost, the removal of crystal water from the lattice is still difficult in the short time. It should be noted that NIBs have not been produced on a comparable scale to LIBs and the cost would be further reduced at that time. Also, the lifetime (shelf life and cycle life), energy conversion efficiency and safety substantially together will influence the cost of the final batteries, the impact of which has not been considered in the above cost analysis yet.



**Figure 2.** Cost comparison of model Li-ion and Na-ion batteries. The model systems are 1kWh batteries, and all costs are in US\$. (PBA, Prussian blue analogues; C, disordered carbon; NVPF,  $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ ; NFM,  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; NCFM,  $\text{NaNi}_{2/9}\text{Cu}_{1/9}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; CFM,

$\text{Na}_{0.9}\text{Cu}_{0.22}\text{Fe}_{0.30}\text{Mn}_{0.48}\text{O}_2$ ; NCM333,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ; G: graphite; LFP,  $\text{LiFePO}_4$ ; LMO,  $\text{LiMn}_2\text{O}_4$ ) (Data of each component based on the price in 2019)

### 3. Challenges & Strategies<sup>[2, 21, 28, 29]</sup>

The urgency for large-scale energy storage opens the door for the development of NIBs, which have undergone rapid advances and progresses both in academia and industry. Nevertheless, there are still some critical problems must be solved and scientific issues must be studied in the development of next generation NIBs.

For cathode materials, layered oxides with high energy density and easy scale-up synthesis are the favorite choice, but complex structural evolution including phase transition at charged state, gliding of transition metal layers, transition metal migration, irreversible anionic redox, etc. will take place to degrade the performance during cycling<sup>[30]</sup>. Besides, most of materials are hygroscopic, requiring meticulous handling and moisture-free conditions to avoid the formation of insulating  $\text{NaOH}$ ,  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  species. As such, the design and synthesis of novel layered oxide cathodes with high structural stability via lattice co-doping, surface coating, core-shell structure, multiphase composite, etc. can potentially solve the above problems. Polyanionic materials possess better thermal stability compared to those of oxides, and the high voltage, high structure durability together with fast charging channels make them superior to high power applications. However, most of polyanionic compounds are based in the toxic and expensive V element and the electronic conductivity is poor. Replacing V with environmental friendly elements to bring down the noxiousness and cost (for example,  $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$  and  $\text{Na}_3\text{MnZr}(\text{PO}_4)_3$  were first proposed by Hu et al. in 2013)<sup>[1]</sup>, tuning compositions to induce more than two electrons transfer as well as carbon-coating and sub-micrometer engineering to improve insertion kinetics could present a route towards the practical use. Regarding to PBAs, the presence of water remains a hindrance, which limits the maximum capacity, reacts with electrolytes and oxidized inside the cell at high potential. Optimizing synthesis method to minimize interstitial water, inventing feasible approach to remove water and modifying electrolytes are avenues for future studies to explore.

In terms of anode materials, the disordered carbon is regarded as the better candidate. However, debated Na storage mechanisms couldn't give a direct guidance

for the effective design of suitable microstructures for sodium storage, and the structure-performance correlation needs further clarifying via advanced characterization techniques. Besides, maximize the initial and average Coulombic efficiency by manipulating the surface/electrolyte interphase is the key for practical application. The main factors limiting the application of titanium-based oxides lie in the low specific capacity and interfacial stability. Potential and capacity regulation via tuning crystal structure and surface coating strategies have been extensively developed. The commercialization of conversion and alloying type anodes are even challenging given the generation of multi-phase intermediates and the pulverization of electrodes. Low Coulombic efficiency at the first cycle is another critical issue to be studied further. Strategies for these anode materials includes carbon composite fabrication and nanostructuring, aiming to improve the ionic and electronic transport pathways and accommodate the stress and strain in electrodes. Main problems faced by organic anodes are poor tap density, easy solubility, which has much room for improvement.

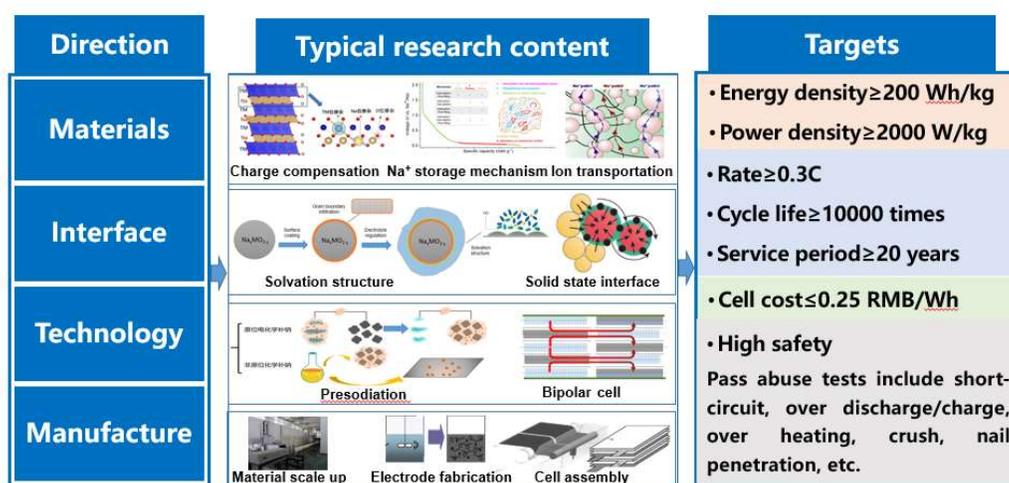
As far as electrolytes, identifying suitable formulation or structure configuration is complicated but indispensable, where comprehensive parameters ranging from physical properties (wide liquidus range, low viscosity, high ionic conductivity, good thermal stability, low cost, environment-benign, etc.), chemical characteristics (simple synthesis, inert toward inactive or active components, etc.) and electrochemical requirements (wide electrochemical stability window, thin and stable SEI, etc.) should be taken into account. Regulation of liquid electrolyte concentration (dilute, concentrated, local-concentrated) and formula (salt and solvent additive), rational design of hybrid solid/liquid electrolyte and inorganic-organic composite electrolyte as well as forming solid electrolyte via in-situ solidification are all significant to tune the physicochemical properties at the interface, therefore improving the compatibility of electrodes and electrolytes and reducing the interfacial resistances.

#### **4. Outlook<sup>[25, 31]</sup>**

Continuous materials innovation and manufacture advance help decrease the cost while improve the performance, making NIBs an appealing energy storage technology for large-scale stationary application. The first-generation of NIBs have already hit the market by pioneer companies and how to make full use of their advantages to

become real competitors for LIBs and be accepted by consumers is crucial for future development. To highlight the low-cost feature of NIBs, besides choosing abundant and low-cost raw materials, improving energy density and cycle life are also important to decrease the cost per kWh. In order to achieve a 200 Wh/kg pouch cell, it should operate with a cathode of 200 mAh/g coupled with a 400 mAh/g anode with an average cell voltage of 3 V, where layered oxide cathodes featured with both transition metal and oxygen redox reactions and disordered carbon anodes with plateau region could help realize the goal. Polyanionic cathodes with rigid open framework can potentially provide long cycle life to reduce the cost per kWh and high safety. Develop materials similar to  $\text{LiFePO}_4$  without containing precious and toxic transition metals is meaningful. According to cost assessment, Prussian blue cathode is promising for cost reduction, remove the lattice water in a simple, low-cost way is critical for its wide use. Carbonaceous anodes are the best candidate until now, understanding the Na storage mechanism to reach the capacity limit or compositing with alloying or conversion materials is still promising for future application. Besides, low-strain anode materials analogous to  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  with a Na storage voltage of 1-1.5 V and without forming SEI are worth to explore to realize high power and long cycle life of NIBs. In addition to electrode materials, exploit low-cost, environmental-friendly and fluorine-free Na salts, functional electrolyte additives and non-flammable electrolytes can also help reduce the cost and improve safety. Moreover, developing simple and effective Na compensation (presodiation) technology to help realize even higher energy density and longer cycle life of 10,000 times is vital for grid energy storage. Additional advantages beyond cost and electrochemical performance are that NIBs have no potential safety issue during over-discharge and are suitable for bipolar design to improve volumetric energy density. Furthermore, we should bear in mind that it is very ideal for a single NIB type to fulfill all requirements of high energy density, high power density, long cycle life, wide operation temperature, etc., intentionally select and combine various electrodes and electrolytes to cater diverse application scenarios have the practical significance. Thus, not only improving the existing material systems via adopting smart strategies but also discovering novel materials with the help of “Material Genome Engineering” to satisfy the diverse demands. Meanwhile, developing solid-state NIBs via improving the ionic conductivity of solid-state

electrolytes ( $>10^{-2}$  S/cm at room temperature) and addressing the electrode/electrolyte interface problems, as well as aqueous NIBs via expanding electrochemical window and inhibiting electrode dissolution also attracts research interest at the same time. We fully believe that with joint effort from government, academia and industry, NIB technology would develop at a fast pace to take over its role in energy storage to mitigate climate change. We expect to see the NIB powered electric bicycles, vehicles and boats, etc. in the market and NIB equipped renewable energies, data centers, communication base stations, household/industrial energy storage systems etc. all over the world.



**Figure 3.** Research directions, contents and targets for Na-ion batteries.

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## Chapter 4

### Emerging zinc battery technologies for large scale energy storage application

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#### 1. Introduce

The rapid development of renewable energy technologies is a vital cog in building a sustainable society in the future. To make efficient use of renewable energy, there is an urgent need to develop high-performance, low-cost, and safe energy storage systems. Among them, the battery storage system is highly effective and promising that can integrate intermittent renewable resources into power systems (Nature 2015, 526, S92). Lead-acid batteries are widely used due to the advantages of cost-effectiveness, high element abundance, good low-temperature performance, and efficient recovery process (more than 95% of lead can be recovered). In view of large-scale energy storage that requires long-term cycling at a reasonable depth of discharge (DOD), however, further technical breakthroughs are needed for lead-acid batteries since the formation of insulating lead sulfate and potential hydrogen evolution. Although lithium-ion batteries have been successfully commercialized, the shortage of lithium resources triggered by the continuous expansion of the electric vehicle market, costly price, and safety problems still restrict them to become the pillar of large-scale energy storage technology. Hence, it is proposed that other high-performance battery systems are needed to meet the requirement of large-scale energy storage and cope with the changes in the energy situation. Given this, zinc-ion batteries are expected to be the first multivalent ion battery technology applied in the field of large-scale energy storage.

Zinc batteries are of great expectation due to several merits. First of all, zinc is the fourth ordinary metal after iron, aluminum, and copper with abundant reserves (~154 ppm vs. Li ~37 ppm) and can be recovered from zinc ores by the mature zinc hydrometallurgy technology. Accordingly, zinc has a relatively low bulk metal market price (about \$85/t in 2020). Besides, the adoption of aqueous electrolytes is one of the

most attractive aspects of zinc batteries, which brings about reliable safety. In terms of performance, zinc has a desirably low redox potential (-0.76V vs. standard hydrogen electrode) and high theoretical specific/volumetric capacity (820 mAh/g and 5855 mAh/cm<sup>3</sup>). In addition, no heavy metals such as cobalt are included in the electrode materials of zinc batteries, providing environmental friendliness. Beyond these, the stability of zinc metal in atmosphere simplifies the assembling of zinc batteries. These characteristics determine that zinc batteries have the prospect of taking the lead in the field of large-scale energy storage.

Zinc batteries have a long application history of about 200 years (Daniel invented copper-zinc battery in 1836) including zinc-air batteries, alkaline zinc-manganese batteries, zinc-nickel batteries, and have occupied one-third of the world battery market. Nonetheless, the use of alkaline electrolytes leads to serious side reactions and dendritic growth and thus poor reversibility. It is necessary to develop rechargeable secondary batteries with high performance and a long lifespan to meet the goal of sustainable development. In 1986, Yamamoto et. al. first reported the aqueous Zinc-ion battery (Zn||ZnSO<sub>4</sub>||MnO<sub>2</sub>) using neutral ZnSO<sub>4</sub> electrolyte and proved the chargeability of Zn-MnO<sub>2</sub> battery system using neutral electrolyte (Inorg. Chim. Acta 1986, 117, 27–28). In 2012, Kang et. al. introduced the concept of rechargeable zinc ion battery (ZIB) and revealed the possible charging and discharging mechanism based on MnO<sub>2</sub> cathode. (Angew. Chem. 2012, 124, 957–959), which has aroused extensive research and attention on ZIBs.

## 2. Cathode

To make ZIBs technology competitive on an industrial scale, cathode materials must have a large reversible charge capacity and maintain high cycling stability. The existing cathode materials can be divided into four categories: manganese-based, vanadium-based, Prussian blue analogs-based (Adv. Energy Mater. 2015, 5, 1400930), and organic-based cathodes (Energy Environ. Sci. 12 (2019) 3288–3304). Manganese oxides are the most studied due to their high theoretical capacity (308 mAh/g, based on single-electron transfer between Mn<sup>4+</sup> and Mn<sup>3+</sup>), high voltage (about 0.8 V~1.9 V), non-toxicity, and natural abundance. Vanadium has also been widely studied in metal-ion devices in recent years, as the multivalent state (V<sup>2+</sup>, V<sup>3+</sup>, V<sup>4+</sup>, V<sup>5+</sup>) of vanadium

can supply higher capacity and rich redox chemistry through the multi-electron transfer (Adv. Energy Mater. 2020, 10, 2000477). However, the dissolution of vanadium- and manganese-based materials leads to serious capacity attenuation. For manganese-based materials, the structure and phase transition/deformation and the disproportionation reaction of  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and  $\text{Mn}^{2+}$  are the main reasons for the dissolution. To tackle this problem, several strategies have been put forward including using electrolyte additives (e.g.  $\text{MnSO}_4$ ) (Nat. Energy, 2016, 1, 16039), forming solid electrolyte interface (SEI) membrane (e.g.  $\text{CaSO}_4$  SEI film formed on the  $\text{Ca}_2\text{MnO}_4$  cathode) (ACS Nano 2019, 13, 13456–13464) and introducing metal ions into the structure to inhibit the dissolution of the cathode (J. Power Sources 1998, 72, 150-158).

In addition to the dissolution of the cathode, the structural instability will also seriously affect the capacity and stability of the cathode. Compared with monovalent lithium ions, when embedded into host materials, zinc ions with larger atomic mass and higher charge density will produce large electrostatic repulsion force and poor transmission dynamics, giving rise to increased layer spacing and accelerated bending vibration of crystal structure, which can consequently lead to crystal structure collapse. Taking the  $\text{MnO}_2$  cathode as an example, during the cycle, the initial  $\text{MnO}_2$  structure will suffer a serious structural transformation into a layered manganese oxide phase with interlayer water molecules. The formation of layered compounds is attributed to the dissolution of cathodes and the insertion of hydrated zinc ions and  $\text{H}^+$  (Nat. Commun., 2018, 9:2906). Therefore, finding suitable cathode materials for zinc ion deintercalation is an important challenge for zinc-ion batteries development. The use of the pillared effect can effectively enhance the stability of the structure. For example, using  $\text{Zn}^{2+}$  pillared layered vanadium-based materials, about 450Wh/g high energy density and 80% capacity retention can be obtained for 1000 cycles (Nat. Energy 2016, 1, 16119). PBAs materials and organic materials themselves have excellent structural stability. However, for PBA materials, low capacity and high operating voltage are issues to be solved. Organic materials are in their infancy, and the mechanism of charge storage needs to be further studied to improve the performance.

Despite great advances, the existing performance is far from the commercial performance standard for a battery storage system (cycle > 5000 times with 100% DOD, round-trip efficiency > 72%) (Energy Storage Technology and Cost Characterization

Report). Moreover, the low mass loading ( $< 2.5$  mg) of the reported cathodes cannot satisfy the demand for practical applications, which is critical for achieving high cell-level energy and power density. In general, many excellent electrochemical properties including energy density, rate capability, and cycle life obtained at low loadings cannot be scaled with mass loading. (Current Opinion in Electrochemistry 2021, 30:100801).

### 3. Anode

Although zinc has been the most common electrode in primary batteries, its practical application in aqueous rechargeable zinc batteries as metal anode has been hindered by its poor cyclability for detrimental issues of dendrite growth and side reactions. Although the use of neutral and weakly acidic electrolytes has alleviated this issue to a great extent, it is not completely solved and is still a limiting factor. Apart from that, part of zinc dendrites will fall off and form the "dead zinc", resulting in the decrease of Coulomb efficiency (CE). To this point, a large body of works already exist to tackle these problems intensively focusing on electrolyte optimization, novel separators, electrode structural design and surface engineering. Recently, Archer et. al. reported an epitaxial electrodeposition strategy (Science 2019,366,645–648). Firstly, graphene was deposited on the surface of the stainless steel electrode to make its epitaxy match the substrate (002) surface of metal zinc, to minimize the lattice strain. Then, metal zinc was electrodeposited on the graphene epitaxial substrate. The crystal orientation of zinc was preferentially parallel to the electrode to form a plate-like stacking structure rather than dendrites. The cycle stability of metal zinc anode is greatly enhanced ( $CE \approx 99.7\%$  over 2000 cycles with  $3.2 \text{mAh/cm}^2$ ). Zhao et al reported a polyamide (PA) coating, which can prevent direct contact between zinc anode and the electrolyte (Energy Environ. Sci. 2019, 12, 1938). The PA layer can also destroy the solvation sheath of zinc ions to increase the migration number of zinc and limit the two-dimensional diffusion of zinc ions to obtain uniform zinc plating. The zinc anode protected by PA shows excellent reversibility and cycle stability (over 8000 cycles).

Although great progress has been made in zinc anodes, there is still much room to improve for the accomplishment of rechargeable zinc anodes. Considering practical applications, it is imperative to further develop advanced zinc anodes with high zinc

utilization (DOD > 50%), high CE (with efficiency > 80%), and long lifespan (Energy Environ. Sci., 2020, 13, 3917).

#### 4. Electrolyte

The electrolyte is an important part of energy storage devices, which provides a channel for the movement of carriers between anodes and cathodes and determines the working voltage window of the battery. Aqueous electrolyte systems have the advantages of eco-friendliness, security, high ionic conductivity, and buffers the charge density of zinc ions to benefit the intercalation and delamination of charge transport. However, the hydrogen evolution reaction can be more serious in neutral and weakly acidic electrolytes, making decreased CE and expansion of batteries. At the same time, zinc ions will exist in the form of solvation in the electrolytes of the water system, which will slow down the deposition kinetics of zinc ions. Tremendous efforts have been exerted to solve the aforementioned problems including the use of high concentration electrolytes to form "water in salt" electrolyte (the high concentration electrolyte can adjust the pH to about 7 and inhibit the formation of  $(\text{Zn}-(\text{H}_2\text{O})_6)^{2+}$  to reduce the occurrence of side reactions.) (Nat. Mater. 2018,17,54–549), additives (Nat. Commun. 2018, 91656), and functional groups to guide zinc ion transport (Angew. Chem. Int. Ed. 2019, 58, 15841–15847).

Although the traditional liquid electrolyte has high ionic conductivity (7~60 mS/cm), problems such as electrolyte leakage, hydrogen or oxygen evolution, cathode dissolution, zinc anode corrosion/passivation cannot be ignored. Considering these, the emergence of gel electrolytes may offer a new way. Unfortunately, low ionic conductivity, low electrode/electrolyte interface, and high overpotential are the issues of gel technology. Yi et. al. grafted water-absorbent polyacrylamide (PAM) onto natural biopolymer gelatin, added inorganic salts, and compounded with two-dimensional electrospun polyacrylonitrile (PAN) membrane to obtain a multi-layer polymer electrolyte with high ionic conductivity. The zinc battery assembled with the electrolyte has a specific capacity of 306mAh/g and exhibits excellent cycle stability. It still maintains 97% of the initial capacity after 1000 cycles (Energy Environ. Sci., 2018, 11, 941).

Although the reversibility of zinc in aqueous electrolytes can be enhanced by optimizing electrolytes, the understanding of the electrochemical reaction process at the electrode/electrolyte interface should be further strengthened, such as the effect of electrolyte on the solvation structure of zinc ions and the structure of the electric double layer on the electrode surface.

## **5. Zinc-Air battery**

Except for zinc-ion batteries, zinc-air battery has become the most promising new energy battery of the next generation due to its high energy density and environment-friendly trait. Zinc-air batteries have a high energy density (1350 Wh/kg) and the actual values can reach 300-400 wh/kg. Primary alkaline zinc-air batteries have been commercialized in medical and communication applications, such as hearing aids and wireless information transmission devices. Currently, the zinc-air battery is the only type of air battery technology applied to large-scale energy storage applications at this stage. Many enterprises are developing high-performance rechargeable zinc-air batteries including EOS Energy Storage, NantEnergy and Fluidic Energy. For instance, a new kind of rechargeable zinc-air flow battery technology for commercial power grid invented by WATTECH POWER INC. has achieved commercial production capacity. Its technology completely adopts a single liquid flow modular design and can be applied to work in the temperature range of 40°~80°, with an initial manufacturing cost of \$80~\$120/kWh and a design life of more than 20 years (<http://www.itdcw.com/news/guojj/0Z1495432015.html>).

At present, the disadvantage of zinc-air batteries is that the system design is complex, the product production automation is low, and the system efficiency is still low (less than 75%). Breakthroughs in technology and performance will help to improve these shortcomings. From the perspective of battery chemistry, the strong alkaline electrolyte is the key to hinder the commercialization of rechargeable zinc-air batteries. In 2021, Wang et. al. invented a highly electrochemically reversible non-alkaline zinc-air battery (Science, 2021, 371,46–51). To break the bondage of alkaline electrolytes on zinc-air batteries, this breakthrough work provides a new understanding and research idea for the follow-up research and development of highly reversible secondary metal-air batteries. Despite the current progress, zinc-air batteries have not

fulfilled their full potentials as limited by challenges associated with the metal anode, air cathode and electrolyte. These challenges would have to be properly resolved before zinc-air batteries can become a practical reality and be deployed on a large scale.

## **6. Applications and Outlook**

It can be seen that the development of technologies has begun to pave the way for the industrialization of zinc-ion batteries. In a patent from Salient Energy (Canada), the modular aqueous ZIB can reduce the storage cost by about 30%~50%, achieve a prolonged service life of about 15~20 years, and provide similar performance to lithium batteries. This becomes the only non-lithium technology that can adopt the manufacturing process of lithium-ion batteries, providing an attractive solution for renewable energy storage. At the same time, according to the report of Yueqing Power Supply Company of State Grid, a new aqueous zinc-based battery jointly developed by the company and the electrochemical energy storage team of Tianjin University was put into use in Wenzhou, China for the first time in November 2020, which has high capacity about 2.6 times that of a lead-acid battery with the same volume and can work at -40 °C with the high power density and excellent cyclability.

Although a few applications are already available, the performance factors limit the further commercialization of zinc batteries. Additionally, according to the statistics of the International Zinc Association, 70% of the zinc in the world comes from mined zinc ore and 30% comes from recycled zinc. Therefore, improving the reversibility and cyclability of zinc batteries to realize large-scale energy storage is of great significance. At the same time, attention should be paid to the recovery and reuse of zinc to complete the industrial closed-loop and further promote industrial applications.

In summary, in the fixed energy storage mode, the weight of the battery is not a serious threat. The more decisive factors are the volumetric energy density, cycle life, and cost (including production and maintenance cost). Based on this, zinc batteries are far more attractive in the field of large-scale energy storage. Due to the existing technology is not as good as commercial lithium-ion batteries, there is a lot of research required on electrode materials and electrolytes to further improve the performance. It is reasonable to believe that in the near future, safe, clean and high-performance zinc batteries will realize great application in the field of large-scale energy storage and

greatly help the transition from the existing energy system to a sustainable energy system.

## Chapter 5

### Challenges and perspectives for sustainable lithium battery industry

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#### 1. Background

The population growth, economic growth and technological development have triggered a rapid increase in global energy demand.[1-3] The massive exploitation of the fossil fuels and the consequent emission of greenhouse gases and pollutants result in the climate changes and other environmental issues. Battery is one of the most common energy storage systems. Due to its high specific capacity, high energy density and good cycling stability. Li-ion battery has the dominant share of the rechargeable batteries and is widely applied in many areas. The EV ownership has increased greatly and the value of global LIB market is projected to reach 50 billion dollars by 2020.[1-3] New EV seals in China has increased sharply, from 207.4 thousand in 2013 to 1362.5 thousand in 2020.[1-3] China's EV sales accounted for more than 50% of global electric vehicle sales in 2019, and China has become the world's largest new EV market.[1-3]

China's power LIB production has increased from 16.9 GWh in 2015 to 80 GWh in 2020, and is expected to reach 431 GWh in 2020. Major battery manufacturers are concentrated in the southeast of China. CATL is the largest LIB manufacturer in China. Its installed capacity of power density in China has reached 31.79 GWh in 2020, accounting for more than 50%.[4]

Future demand on LIB mainly from EVs. Power demand for EV is estimated to be 96.9 GWh by 2020, a growth of 41% from 2016-2020. There is significant material demand on  $\text{Li}_2\text{CO}_3$ , cobalt and graphite.[5]

In 2013, about 0.003 GWh LIB was scrapped in China, compared with 5.3 GWh in 2019, and it is expected to increase to 111.7 GWh in 2025.[6-8] Spent power batteries contain a lot of metal elements, such as Ni, Co and Mn. LIB production is strongly dependent on the aforementioned mineral resources.[6-8]

However, China lacks cobalt and nickel ores. The reserves of Ni and Co of China account for only 3.4% and 1.1% of the global reserves, respectively. Our country has to import Co, and that in 2020 our external dependence will reach 97%.[9] The metal resources of battery materials are seriously insufficient, and it is difficult to support the sustainable development of new EVs. The recycling of retired traction batteries is the only way for the NEV's sustainable development. [9]

In addition, as the production and sales of electric vehicles increase year by year, the demand for batteries has increased sharply, and battery prices have continued to rise. This is mainly due to the shortage of raw materials for the production of lithium batteries and the increase in raw material prices. The global distribution of raw material that produces lithium batteries is very uneven, mainly in South America, and the production technology level is difficult to meet the market's demand for raw materials. Therefore, the recovery of valuable components in waste lithium batteries is of great value, which can not only alleviate the shortage of raw materials but also reduce battery production costs. More importantly, if the heavy metals in waste lithium batteries cannot be recycled, the environment will be seriously polluted. Therefore, the recycling of valuable components in lithium batteries not only recovers resources but also avoids environmental pollution, showing high economic value.

The waste lithium battery is composed of positive electrode material, negative electrode material, separator, electrolyte and metal casing. The positive electrode material contains a large amount of valuable metals, such as nickel, cobalt, and manganese. The recovery of the positive electrode is also the most widely researched topic at present, showing a good development prospect. The recovery methods of cathode materials include pyrometallurgy, hydrometallurgy and pyrohydrometallurgy combined. Pyrometallurgy is a simple treatment method. The recovered lithium battery is smelted in a high temperature environment to the final alloy, and then the alloy is separated. Hydrometallurgy mainly uses a combination of sulfuric acid and hydrogen peroxide to dissolve the cathode material, and then separates it through impurity removal and solution extraction. The combination of pyrometallurgy and hydrometallurgy is the use of pyrometallurgy to separate the positive electrode material from the aluminum foil in the first stage of pretreatment, and the use of solvent leaching to recover the metal in the second half of the treatment. The negative electrode material

is mainly composed of graphite. With the expansion of the lithium battery market, the demand for high-quality graphite has increased sharply. The recovery of graphite can meet the environmental market demand to a certain extent. There are also many teams working on the electrolyte at present, and it is in the laboratory research and development stage. The recovery of electrolyte not only recovers resources but also protects the environment. Metal casings can be recycled very well at present, this is mainly because metal casings are magnetic. Currently battery separators are very expensive, and many research teams are currently working on the recycling of separators. If commercialized use is achieved, battery costs will be further reduced.

The progress in recycling of spent LIBs include the significance of materials recovery from spent LIBs, the hydrometallurgical method for materials recovery from spent LIBs, the combined hydrometallurgy-pyrometallurgy technology for materials recovery from spent LIBs, regeneration of graphite from spent LIBs and the pollution control.

## **2. Progress in Recycling of Spent Lithium Batteries**

### **2.1 Significance of materials recovery from spent LIBs**

The significance of materials recovery from spent LIBs can be include four points. (1) spent LIBs include large of valuable metals, such as Co, Ni, Mn et al. The resource distribution of Co, Ni and Mn is very uneven, mainly concentrated in the Congo and other areas. Due to the limitation of the local production technology level, the development of Co, Ni and Mn is difficult to meet the increasing market demand. With the rapid expansion of the lithium battery market, the price of Co, Ni and Mn resources has risen rapidly. In China, due to the high difficulty of mining cobalt and nickel resources, high mining costs and small resource reserves, almost 97% of cobalt in China's battery production needs to be met by imports, and 85% of manganese resources are met by imports. However, China is also the largest battery producer. Due to resource constraints, it is difficult to meet market demand for battery production. Resource constraints have led to rising battery prices. The recycling of Co, Ni and Mn not only greatly reduces the cost of the battery but also avoids environmental pollution. (2) Spent LIBs is a valuable Urban mine.[10] (3) Decrease the pollution of spent LIBs. The electrodes have a lot of heavy metals and electrolyte has corrosive nature. In

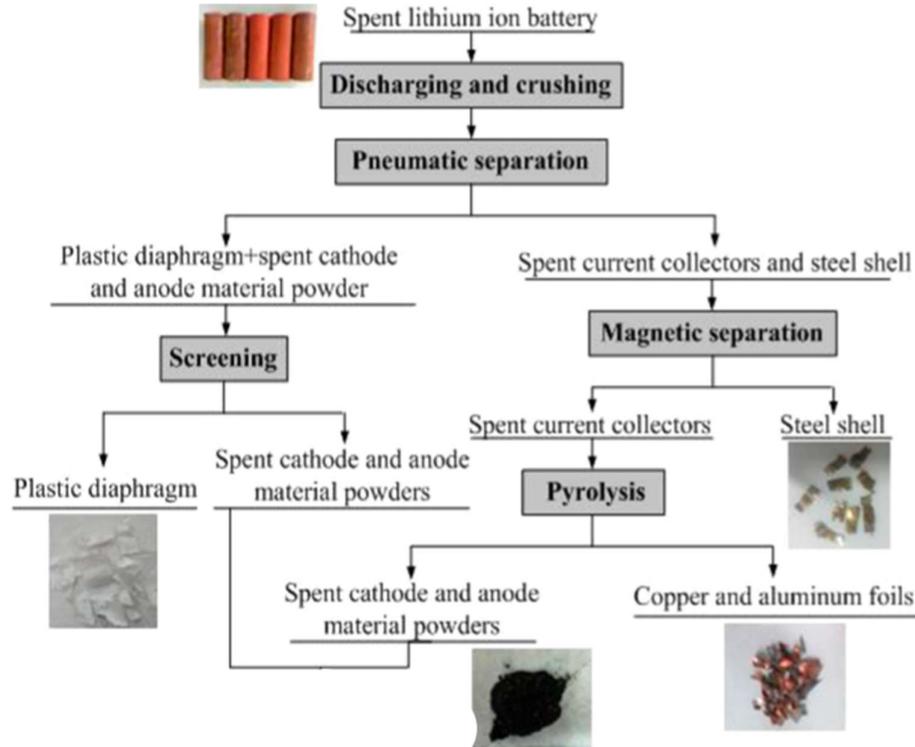
addition, the emission of HF will happen during charging and discharging process. HF is very corrosive, if it is directly discharged, it will cause huge disasters to the environment. (4) The cascade utilization and recycling of spent lithium-ion batteries have cost advantages over the entire life cycle of lithium-ion batteries.[11] Therefore, if the spent LIBs can't be recycled, the soil, water and air maybe polluted.

## **2.2 Hydrometallurgical method for materials recovery from spent LIBs**

The recycling process of spent LIBs include three steps: (1) physical processes, there are pretreatment (discharge of battery), mechanical processes (crushing and separation) and thermal treatment. (2) Chemical processes, there are pyrometallurgical processes (such as smelting), hydrometallurgical processes and mechanochemical processes (crushing or milling in chemical solution). In hydrometallurgical method, first is the physical processes and the chemical processes including hydrometallurgical processes, the leaching, solvent extraction and precipitation.

The typical hydrometallurgical processes can be described as following: (1) pretreatment (discharging, dismantling, crushing and sorting), (2) Using NaOH to remove Al, (3) Using H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> to leach, (4) purification, using solution extraction to remove impurities. (5) metal recovery, (6) the products.

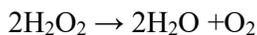
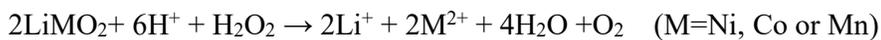
After pretreatment, a positive electrode material containing binder, conductive carbon black, active material and aluminum foil can be obtained. In pre-treatment-physical separation, the spent Li-ion battery is first discharged and crushed. The spent current collectors were treated by pyrolysis to separate active materials and metal foils. Using the difference in the decomposition temperature of the active material, the binder and the conductive carbon black, the binder and the conductive carbon black can be decomposed first at a high temperature without the active material being affected. The plastic diaphragm was removed by pneumatic separation. Because steel shell is magnetic, steel shell was recovered by magnetic separation. Spent current collectors were treated by pyrolysis to separate active material and metal foils.[12] The treatment of the anode collector is similar to that of cathode collector.[13]



**Figure 1.** Pre-treatment physical separation flow chart.[12]

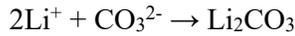
The cathode material is completely separated from the Al foil. The obtained material particles are dispersed. Aluminum hardly enters the positive electrode material (AL content is less than 5%).[13] Optimal conditions for separation of cathode material and AL foil: 600°C, 30min.

After pre-treatment-physical separation, the acid leaching will be needed. The leaching agent (Sulfuric acid) and reducing agent (hydrogen peroxide) can be used. During this process, the reactions as following:[14]



After acid leaching, separation process will be needed. Separation process can be divided into four kinds. The first is Co-extraction of manganese and cobalt, especially suitable for treating spent high nickel LIB materials.[14] The second is Ni-Co coprecipitation. Introducing organic functional groups to improve the difference between S and Co, Ni and its bonding ability with Mn.[15] Especially suitable for treating spent high manganese LIB materials. The next is co-extraction of nickel, cobalt

and manganese. The optimum conditions are pH=3.5, extraction time 6min and 40% D2EHPA. By a counter-current extraction process wherein almost 100% manganese, 99% cobalt and 85% nickel were co-extracted into organic phase and about 70.0% Li remain in aqueous phase after a three-stage extraction. The last is lithium recycling. The reaction as following.



### **2.3 Combined hydrometallurgy-pyrometallurgy technology for materials recovery from spent LIBs**

#### 2.3.1 Reduction smelting (Take $\text{LiCoO}_2$ as an example)

Reductive smelting is the use of reducing materials mixed with the positive electrode material, and the reduction is carried out at high temperature and under the protection of an inert atmosphere. There are three types of reductive smelting. The first is to use aluminum foil to reduce the positive electrode material, the second is to use waste graphite as a reducing agent to reduce the positive electrode material, and the third is to use alkali as a catalyst to accelerate the high-temperature reduction of the positive electrode by the waste graphite. The base catalyst includes sodium hydroxide or potassium hydroxide. In the field of lithium battery recycling, reductive smelting mainly uses waste graphite as a reducing agent and mixed with positive electrode materials for high-temperature reduction. The positive electrode materials can be reduced to oxides that are easily dissolved in weak acids. The use of sulfuric acid and hydrogen peroxide can be avoided, which saves costs and avoids environmental pollution caused by the use of sulfuric acid. In addition, in the field of battery recycling, the reductive smelting process will also introduce alkali as a catalyst. The use of alkali can accelerate the reduction of the positive electrode material and lower the reduction temperature. Reduction smelting have three advantages [16]: (1) Using spent graphite as reducing agent to make full use of its heat and reducibility, (2) Recovering lithium resources preferentially, (3) Leaching nickel and cobalt without reductant. Lithium is converted to lithium carbonate, trivalent cobalt is converted to divalent cobalt. The selective leaching efficiency of lithium is higher than 80%, and the purity of regenerated lithium carbonate is 99%.

Leaching Ni, Co and Mn after lithium extraction. The leaching condition: temperature is 90 °C, the stirring speed is 500 rpm, the liquid-solid ratio is 8 ml/g, the H<sub>2</sub>SO<sub>4</sub> concentration is 4 mol/L and the leaching time is 2 h. Leaching efficiency can up to 98.5% Ni, 99% Co and 85% Mn.

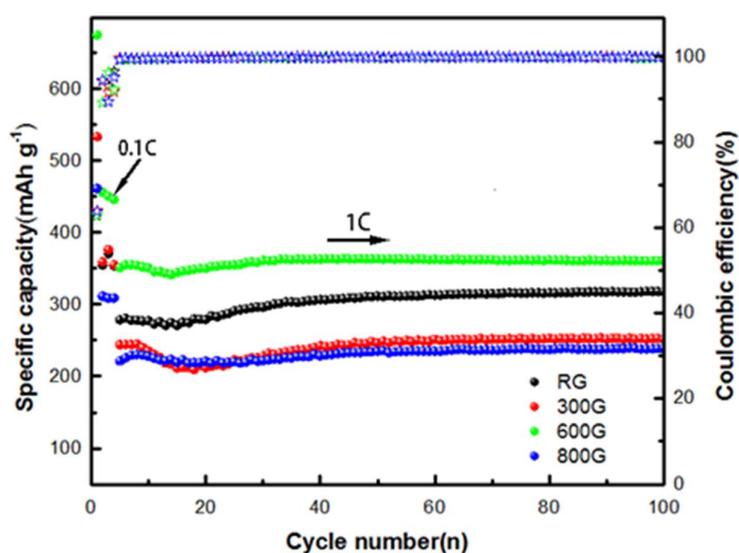
### 2.3.2 Material regeneration

Regenerated materials exhibit good electrochemical properties similar to those of raw materials. regenerated materials obtained through physical and chemical methods can be directly applied to lithium-ion batteries. Can realize the closed-loop utilization of raw materials, alleviate the pressure of resource shortage. In addition to getting the metal solution, material regeneration is another method of recycling. This method can avoid the long process and high cost of separating nickel, cobalt and manganese. In addition, directly obtain regenerated products of lithium battery cathode materials to achieve high-value utilization of nickel, cobalt and manganese.[17] In material regeneration, waste lithium-ion batteries still need to undergo pretreatment (dismantling, crushing and screening), leaching, impurity removal and extraction separation. Sulfuric acid and hydrogen peroxide still need to be used. In material regeneration, adjusting composition of Ni, Co and Mn in leachate, ammonia as a complexing agent and sodium hydroxide as a precipitating agent. Co-precipitation of nickel, cobalt and manganese is achieved by controlling the ratio of complexing agent and precipitating agent, regulating crystal nucleation and growth.[18-19] Recycled material is a dense spherical shape: particle size 9-12 $\mu$ m.[20] The regenerated cathode material has good electrochemical rate and cycle performance. The regenerated materials are as good as new materials synthesized directly from pure materials.[20]

### 2.3.3 Regeneration of graphite

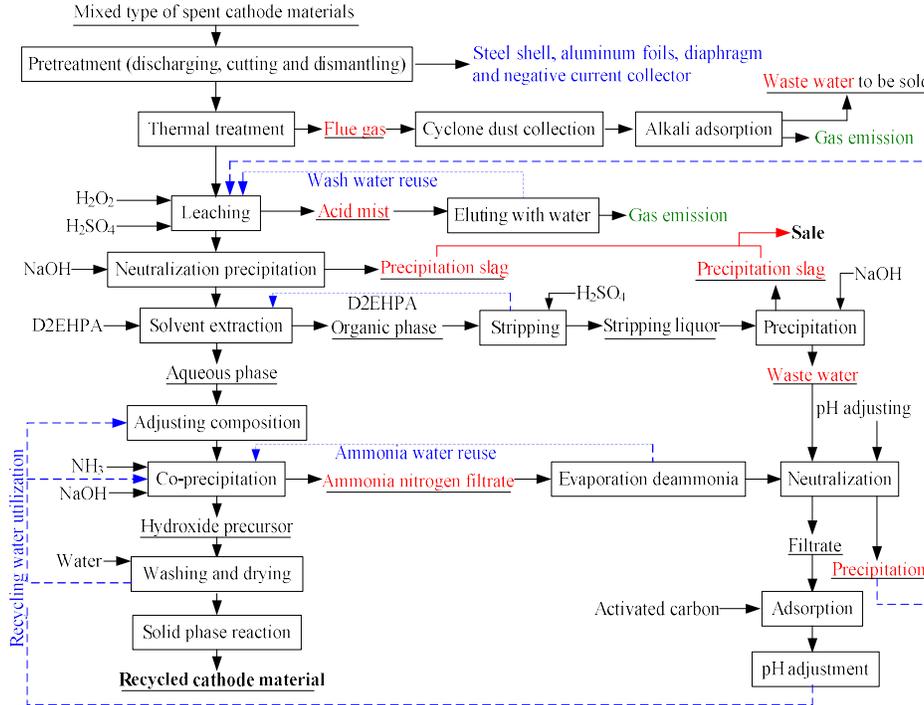
According to previous studies, the recovery of one ton of graphite requires 1.644 tons of hydrochloric acid, 0.602 tons of sodium hydroxide and 10,000 KWh of electricity. The total cost of recycling one ton of graphite is 13,364 CNY. According to the current market price, 1 ton of graphite requires 15000 CNY. And while recovering graphite, copper and lithium can also be recovered. Therefore, the recovery of graphite is economically feasible.[21] More importantly, the recovered graphite exhibits good

cycle performance and high specific capacity (the electrochemical performance of the recovered graphite is almost the same as that of the original graphite). The recovered graphite can be directly used in batteries, and the recycling of graphite can be realized. The demand for high-quality graphite in the commercial market grows by 10%-20% every year. Graphite used in batteries is very expensive. Recycling graphite is not only recycling resources but also reducing the environment pollution. Graphite from waste lithium batteries has high recycling value. If graphite can be reused in lithium batteries after a series of physical and chemical treatments, and the anode material can be recycled, the cost of battery production will be further reduced. The spent graphite can be collected by two-step calcination.[21] Firstly, Separate the waste graphite from the negative electrode of the waste lithium battery by physical or other mechanical methods. Physical methods include dismantling, crushing and screening. The copper and lithium can be recovered and the graphite can be regenerated. The process included adding binder to granulate, high temperature crystal reconstruction and physical screening separation. After high temperature reconstruction of graphite, the surface is smooth and the crystal crystallization is good. The graphite is separating deeply from impurities such as copper, phosphorus, lithium and fluorine. The discharge capacity of recycled material can reach 360mAh/g at 1 C, and the material has good cycle performance.[21]



**Figure 2.** The cycle performance of regenerated graphite under 1C.[21]

### 3. Pollution control



**Figure 3.** The flow chart of recycled cathode material.[22]

This is the flow chart of recycled cathode material.[22] The mixed type of spent cathode materials need to go through the pretreatment (discharging, cutting and dismantling), thermal treatment, leaching, neutralization precipitation, solvent extraction, adjusting composition, co-precipitation, washing and drying, solid phase reaction. The final production can be obtained. During this process, there are several links will lead to pollution. First is thermal treatment, which will lead to flue gas. In order to solve this pollution, cyclone dust collection and alkali adsorption will be proceeded. The waste water can be sold. And the gas can be directly discharged. The second is leaching process, which will lead to acid mist and the gas emission. In this process, the wash water can be reused. The third is neutralization precipitation, which will produce precipitation slag. The precipitation can be sold. Next is solvent extraction,

which will produce waste water. The waste water need to go through neutralization by PH adjusting, filtrate, adsorption by activated carbon and the last pH adjustment. The waste water can be recycled. The last is co-precipitation, which will lead to ammonia water. The ammonia water need neutralization process and reuse again.

#### **4. Perspectives for sustainable lithium battery industry**

The waste lithium battery industry has a large commercial market. At present, the market is rapidly expanding, waste lithium batteries urgently need to be properly disposed to avoid environmental pollution and economic losses. The recycling and regeneration of waste lithium battery can realize the maximum utilization of resources. Recycling can not only avoid heavy metal pollution in waste lithium batteries, but also reduce the cost of battery production.

Waste lithium batteries are mainly composed of positive electrode material, negative electrode material, separator, electrolyte and metal casing. Both the positive electrode material and the negative electrode material are composed of active components, binders and conductive carbon black. The current recycling methods mainly include pyrometallurgy, hydrometallurgy and combined pyrohydrometallurgy. The positive and negative materials can be recycled and reused, effectively avoiding resource waste and environmental pollution. The recovery of diaphragm and electrolyte also shows good application prospects, but it is still in the laboratory research stage, and there is still a certain distance from commercialization. The metal casing can be recycled very well by magnetic separation. Lithium battery recycling shows a good commercial prospect. However, in order to achieve high-efficiency and large-scale disposal of waste lithium batteries, there are still many technologies that require further breakthroughs.

In the future, the following problems should be dissolved. (1) Technical bottleneck of Echelon Utilization and Intelligent Disassembly Technology of Retired Powder Batteries. Mixing different types of batteries will cause difficulties in subsequent processing. (2) Focus and difficulty of Anode and cathode materials recovery from spent batteries. (3) Regeneration and Pollution control of spent batteries. Recycling technology can avoid the long process of metal recycling and improve recycling efficiency. The recycling process will produce a lot of polluting gases and waste

residues, and it is a problem that needs to be solved to achieve pollution-free treatment of waste lithium-ion batteries.

Project backgrounds-common problems in the Industry are the following points: (1) Research on Dismantling Technical Knowledge. (2) In-Depth Smart Decision Making on Dismantling. (3) Intelligent Scheduling of Material Control. (4) Research and Development of Flexible Dismantling Equipment.

Retired Traction Battery Module Dismantling and Intelligent Transfer Technology have a good development potential. The 3D industrial camera is used for positioning, and the distance between the connecting pieces of the module is automatically identified. The industrial computer reads the traceability module information, compares the real-time acquisition information of the module, and gives the best tool information. The robot automatically selects the corresponding tool in the tool library. The tracking database automatically identifies the welding thickness, and the motorized spindle uses a high-precision servo control system to control the milling depth to achieve accurate milling and ensure that the milling damage rate is less than 2%.

Separation of positive and negative electrodes of Retired Power Battery. High-speed intelligent visual identification methods and devices have been developed to achieve accurate and efficient separation of positive and negative electrode pieces, laying a solid foundation for the restoration and recovery of materials

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## Chapter 6

### **Current situation and sustainable lithium supply to power the EV industry supporting carbon free society**

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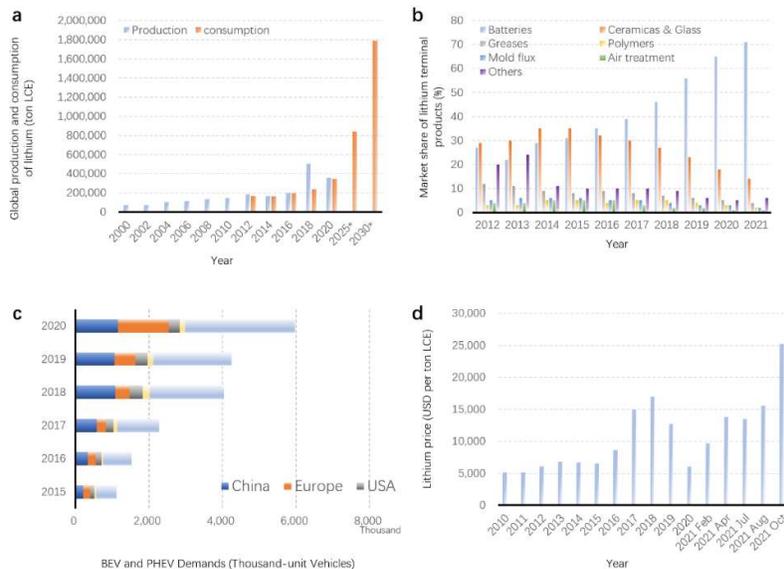
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#### **1. Global lithium demand and lithium market**

Human society emerged over 6 million years of hominid evolution, of which the essence was in fact the evolution of productive force. We humans had been through Stone Age, Bronze Age, and Iron Age, and stepped into Industrial Age from 18th century. Coal and petroleum successively pillared the Industrial Age in the past two centuries, which were described as “black gold”. It is commonly believed that the Industrial Age will be fully supplanted by the Information Age in the current 21st century. What will be the “contemporary gold” pillaring the incoming Information Age? One of the most powerful competitors is certainly lithium, also known as “white gold”. Twenty years ago (2000), the global lithium demand was just ca. 87 thousand metric tons (lithium carbonate equivalent, LCE), which were mainly consumed by the fields of glass and ceramic. The increment rate of lithium demand was so slow at the beginning of 21<sup>st</sup> century that it took 15 years for global lithium demand to reach double (167 thousand metric tons LCE, 2015).<sup>1</sup> However, the global lithium demand sky-rocketed to another double in the following five years, reaching 345 thousand metric tons LCE in 2020. Batteries become the largest oligarch and consume 71% of global lithium in 2021. The powerful driver of this soaring lithium demand is the determination of governments to reach their net zero carbon emissions targets, and the concerns about environmental degradation due to the emissions of greenhouse gas, particulate matter < 2.5  $\mu\text{m}$  (PM2.5) and NO<sub>x</sub> from vehicles. More than 20 countries/regions have issued legislations to bring forward a ban on the sale of new petrol and diesel cars from 2030 - 2050. In this context, the amount of electric vehicle (EVs) went from close to zero in 2012 to 1.2 million units just four years later (2015),

to 3.29 million just three years later (2018), and to 10.0 million just two year later (2020).<sup>2</sup> Affected by the Covid-19, global economy growth decreased by 4.4%, and the sales of vehicles decreased by 6.0%, while the sales of EVs dramatically increased by 41%. It is expected that the amount of EVs will reach ca. 0.145 billion in 2030. Pushing by the strong demand and growing rate of EVs, the lithium demand will reach to 1.4–1.7 million metric tons LCE in 2030, and while the current lithium reserves are expected to be exhausted by 2080.

In the aspect of supply, the price of lithium carbonate had been stable at ca. \$6,000 per metric ton for a long time. Stimulated by the skyrocketed global lithium demand from 2016, the price doubled passing from \$8,650 to \$17,000 per metric ton in three years. The miners responded by massively ramping up production, halving the price to \$8,000 per metric ton again in 2020. However, even the Covid-19 epidemic is not over yet, the global lithium supply is rapidly expended by the robustly growing demand, and the price reach to \$25,000 per metric ton in ten months (254.84% increase since the beginning of 2021). It has been widely accepted that the increase of lithium prices is absolutely not temporary. Many investment banks and bourses have upgraded their assessment of lithium price since the lithium supply failed to be stretched to meet the demand in 2021. And “a long-term perpetual deficit” is employed to describe the supply-demand relationship. The deficit of lithium supply is estimated to 2,900 metric tons LCE in 2021, and expand to 61,000 in 2023. Although some new supply additions may temporarily lighten the market, the supply deficit should widen more and more significantly. New supply sources must come online to support demand after 2025.



**Figure 1.** (a) Global production and consumption of lithium; (b) Market share of lithium terminal products; (c) BEV and PHEV demands; (d) Lithium price.

## 2. Lithium on Earth

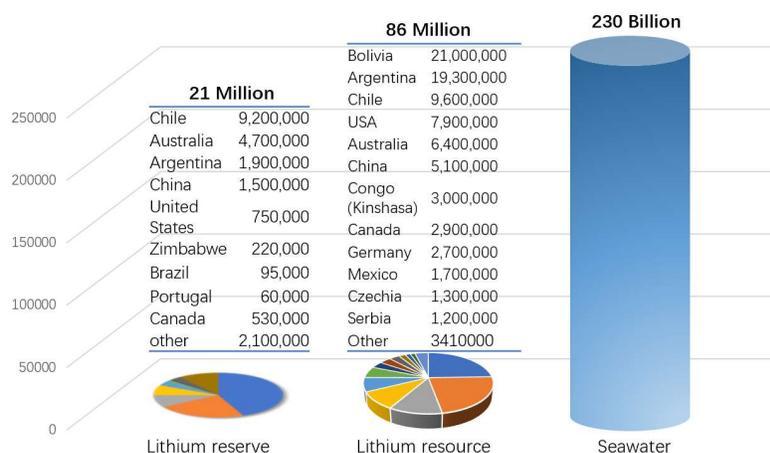
Lithium is the 33rd most abundant element in nature, and the abundance of lithium presenting in the Earth's crust is 0.002–0.006 wt% and is distributed widely in rocks, soils, basin, ground, and sea waters. According to the concentration, the lithium on Earth can be divided into three parts: lithium reserves, lithium sources and lithium inventories.<sup>3</sup>

The lithium reserves are the lithium deposits that could be economically extracted or produced at the time of determination, including the high-quality lithium ores (with lithium concentration of 10,000 – 30,000 ppm) and the high-quality lithium brine (with a lithium concentration above hundreds of ppm and Mg/Li ratio less than 10). Lithium reserves are proven to 21 million metric tons until 2021, are geographically uneven. Most of lithium reserves locate in Australia (ores) and Latin America (lithium brines). Australia is biggest worldwide lithium producer, and affords the 49% lithium demand in the world. It has the biggest reserve of lithium ores, as well as the second-biggest lithium reserves (4.7 million metric tons, 22.32% of the world). Commercial ores are usually spodumene ( $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ ), lepidolite ( $\text{KLi}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$ ), petalite ( $\text{LiAlSi}_4\text{O}_{10}$ ), amblygonite ( $\text{LiAlPO}_4(\text{OH})$ ), and eucryptite ( $\text{LiAlSiO}_4$ ), which contain a

high lithium concentration of 10,000 – 30,000 ppm.<sup>4</sup> Salt lake brine is another important lithium reserve. Chile, Argentina and Bolivia are famous as “lithium triangle” because of the rich salt lakes with Li concentrations from 220 to 3800 ppm and Mg/Li ratio less than 10.0. According to the U.S. Geological Survey 2021, these three countries, possesses ca. 53% of proven global lithium reserves. Thereinto, Chile has the largest lithium reserves worldwide, which is ca. 44% of the global lithium reserves (9.2 million metric tons). The interference component are salts such as chlorides and sulfates of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , with minor amounts of carbonate and borates.<sup>4</sup> Lithium reserves, no matter ores or brines, are perfect for utilization, except for the annoyingly limited amount.

Lithium sources are the lithium deposits with a concentration that economic extraction of a commodity is currently or potentially feasible, such as the low-quality salt-lake water (generally with dozens ppm of lithium concentration, and more than dozens of Mg/Li ratio),<sup>5</sup> geothermal brines (10 - 20 ppm lithium with several arsenic, mercury, and boron etc.),<sup>6</sup> oilfield brines (4.6 - 150 ppm lithium with organic matters, inorganic salts etc.)<sup>7</sup>. Lithium resources is proven to 86 million metric tons until 2021, which is three times higher than lithium reserves. Therefore, in the medium-term, developing new technique with low cost to commercially utilize the lithium sources is efficient and necessary to meet the rapidly increased lithium demand. Bolivia and Argentina possess the biggest lithium resource in the world, which is 21 and 19.3 million metric tons, respectively. Salar Uyuni in Bolivia is the world largest lithium resource, but it has not been steadily and commercially exploited yet. The biggest problem faced by Uyuni is the relatively high Mg/Li ratio (21),<sup>8</sup> which makes the extraction of lithium much more difficult in technique and inviable in economics. This problem is also faced by China and USA. The lithium sources of salt lakes in Chinese Qinghai-Tibet Plateau are three times more than the rest lithium reserves of whole China, but the Mg/Li ratio of Chinese lithium sources usually 100 – 10,000 impedes the commercial exploitation. It is easy to separate  $\text{Li}^+$  from  $\text{Na}^+$ ,  $\text{K}^+$  due to the great solubility difference of corresponding carbonate salts.  $\text{Ca}^{2+}$  content is not high the lithium sources (few hundreds to dozens of ppm), and is easy to be removed by chemical precipitation, ion exchange, extraction, membrane separation or absorption due to the great chemical difference between  $\text{Li}^+$  and  $\text{Ca}^{2+}$ . Annoyingly, the separation

of Li/Mg quite difficult. The chemical properties of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  are similar owing to their diagonal relationship in the periodic table, particularly the similar ion radius (72 pm for  $\text{Mg}^{2+}$  and 76 pm for  $\text{Li}^+$ ).<sup>5, 9</sup> Thus, developing efficient and economically feasible method to achieve Li/Mg separation is the key for utilization of lithium sources in medium-term.



**Figure 2.** The lithium on earth (unit is ton in the figure)

Maybe the exploitation of lithium resources can meet the lithium demand in medium-term, the amount of 86 million metric ton is far from satisfying lithium demand in long-term. For example, only in the aspect of EVs market, based on the global decarbonization policy, most of the major countries have deployed plans to phase out combustion vehicles by the year 2040 - 2050.<sup>10</sup> EVs is the only commercial alternative, and each EV needs at least 8 kg lithium metal.<sup>11</sup> That means the lithium resources can only maximumly afford ~ten billion EVs, regardless of lithium regeneration and recycling. The current market of motor vehicles is ~1.4 billion, and it is expected to grow to 2.8 billion by 2035.<sup>12</sup> At this rate, if the global decarbonization policy reinforces, lithium will be exhausted by in this century. This timing also matches with the predictions by Sverdrup<sup>13</sup> and Speirs et al.<sup>14</sup> Thus, for a long-term consideration, developing more advanced lithium extraction technology is of great importance.

The lithium inventories are the solids, liquids, or gaseous materials in which the lithium concentration is very low, and the Mg/Li is extra high. Lithium is widely distributed in rocks, soils, basin, ground, and sea waters. However, the exploitation of lithium from solid lithium inventories are almost economically impossible due to the

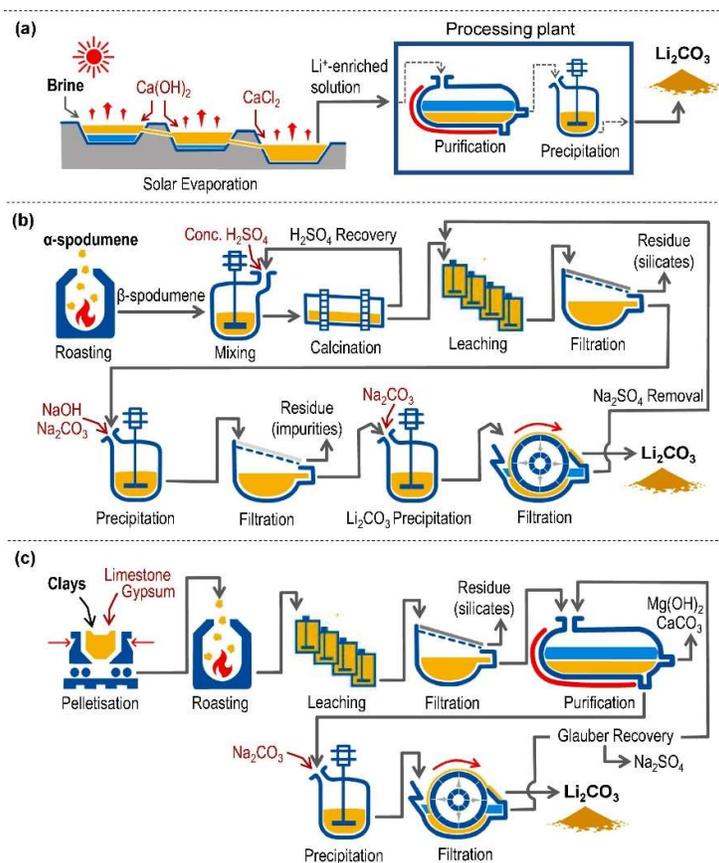
huge consumption of energy and chemicals required by the calcination or dissolution of solids. The most comparable example is the mining of gold, which is extra high-cost due to the low concentration ( $> 8$  ppm for rich gold mine, and 1-4 ppm for normal gold mine). Although praised as “white gold”, it is very hard for us to accept the lithium stock with a price equal to gold. Conversely, the extraction of lithium from seawater is relatively more executable, because the cost required by calcination and dissolution of solids are exempted. For convenience, the lithium inventories in this portion of chapter refer in particular to the lithium in seawater. The total amount of lithium in seawater is estimated to more than 230 billion metric tons (5,000 times higher than that of lithium resources).<sup>15</sup> Extracting lithium from seawater is expected to be very promising and regarded as the ultimate solution to meet the lithium demand in long-term. However, the lithium concentration in seawater is generally 0.17 – 0.25 ppm, with interference ions including  $\text{Na}^+$  (ca. 12,000 ppm),  $\text{Mg}^{2+}$  (ca. 13,50 ppm),  $\text{K}^+$  (ca. 380 ppm),  $\text{Ca}^{2+}$  (ca. 400 ppm) etc.<sup>16</sup> Seawater can be deemed to be a kind of inferior lithium brine, and shares the problems faced by lithium sources. Besides, the extra low lithium concentration renders a big problem of removing interference ions. Thus, two key factors should be addressed for utilization of lithium inventories in long-term:  $\text{Li}^+/\text{Mg}^{2+}$  and  $\text{Li}^+/\text{Ca}^{2+}$  separation, and enriching lithium to an operable concentration.

### **3. Current production technique for lithium reserves**

To extract lithium from ores, ores should be crushed to achieve the reactive phase, and dissolved by acid to form brine. Lithium is extracted from the brine by a “lime-soda evaporation process”. In detail,  $\text{Mg}^{2+}$  is precipitate in the form of  $\text{Mg}(\text{OH})_2$  after adding lime, and  $\text{Ca}^{2+}$  is precipitated in the form of  $\text{CaCO}_3$  using soda. After filtration, the pH of brine is adjusted by adding sulfuric acid. Finally, more soda is added into the brine at above 70 °C to precipitate lithium carbonate.<sup>4, 17</sup> The crude lithium carbonate product is further purified by redissolving in supersaturated carbon dioxide solution, filtrating to remove the insoluble impurities, and driving carbon dioxide away at elevated temperature to reprecipitate the purified product. However, great cost and energy are required due to the complex extraction process containing calcination, dissolution, precipitation, and purification. A number of chemicals should be used, and

abundant hazardous wastes will be generated. These two issues render this method can only be used for high low-quality lithium reserves.

The lithium extraction from brine reserves is based on a revised “lime-soda evaporation process”, combined with “evaporitic technology”.<sup>17, 18</sup> The brine is pumped into some large salt pond, where the lithium will be concentrated to above 6000 ppm by solar evaporation. The following operation are similar to that of refine brine of ores. Owing to exempting calcination and dissolution processes, the cost of lithium extraction from brine is only half of that from ores, rendering a high profit. However, extracting lithium from brine still have many disadvantages. The biggest problem is the slow production cycle as it is based on solar evaporation, and highly depends on natural environment including the solar radiation, humidity, winds, and rainfall. Half a million liters of water should be evaporated to produce one ton of  $\text{Li}_2\text{CO}_3$ , which takes 12-24 months, although most of the brine lakes are located in torrid desert areas with strong solar radiation and intense wind.<sup>2</sup> In addition, this lag time is a synonym that lithium from brines is not a reliable source for dealing with sudden surges in demand.



**Figure 3.** (a) a simplified process flowchart for the recovery of  $\text{Li}^+$  from Salt Lake brines, involving pre-concentration via solar evaporation followed by multiple purification processes like cation-exchange and solvent extraction to achieve high purity, battery-grade  $\text{Li}_2\text{CO}_3$  (b) the conventional flowchart used in lithium extraction from spodumene concentrate, and (c) a generalised process flowchart for the recovery of lithium from Li-bearing clay minerals. Copyright © Elsevier 2021.<sup>19</sup>

## 4. Potential technique for lithium sources

The lithium reserves are quite limited to meet the sharply increased global lithium demand. Stimulated by the doubled price in 2016-2017, miners worked at full capacity to massively ramp up production. Unfortunately, the increased capacity is rapidly disposed in just two years. The deficit of lithium supply will be widened more and more significantly if we only rely on the high-quality reserves. Thus, researchers have devoted abundant efforts on developing new technique with low cost to commercially for utilizing the lithium sources in medium-term. Three methods will be most possible for commercialization: liquid–liquid extraction, adsorption and membrane separation.

### 4.1 Liquid-liquid extraction

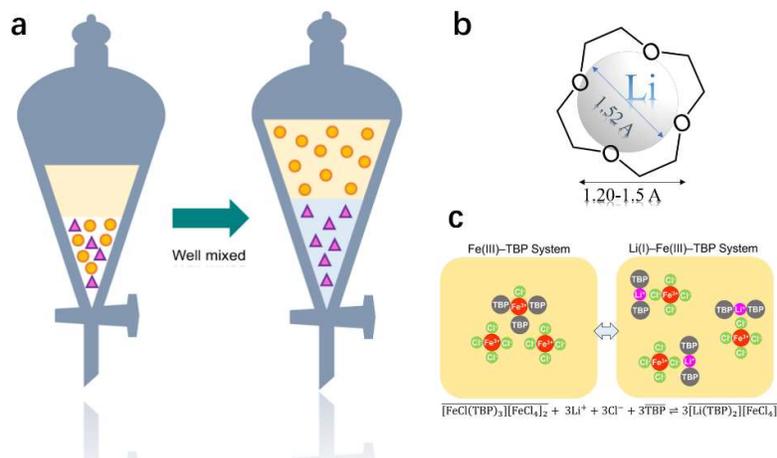
Liquid-liquid extraction is based on the different solubilities of ions in two different immiscible liquids. By employing lithium ionophore dissolved in non-polar organic solvent as extractant, lithium ion can be captured into the extracting solution, and the impurity ions remain in the brine. Lithium ionophore is the key for extraction, and two kind of compounds are worth mentioning: crown ethers, tributyl phosphate (TBP) and its derivatives.

Crown ethers can be regarded as the “cyclic ethylene glycol oligomer”, which strongly bind certain cations through coordination of cyclic-distribution oxygen atoms. The 12-crown-4 (Lithium ionophore V) is an excellent lithium ionophore because its cyclic cavity of 0.6-0.75 Å (radius) is similar to the radius of lithium ion (0.76 Å). Unfortunately, serious loss caused by the high solubility in water hampers the usage of 12-crown-4 in liquid-liquid extraction. Many analogues of 12-crown-4 with no aqueous solubility is developed, such as 6,6-Dibenzyl-14-crown-4 (lithium ionophore VI), dibenzo-14-crown-4, dibutyl-phenanthroline, crown ether-grafting polymers. Although the selectivity of Li vs. reference ions is easy to achieve hundreds or thousands, the

price of these analogues are very expensive. For example, the price of lithium ionophore VI is even surprising \$500 per 100 mg. It is a long way to commercially apply crown ether in lithium extraction. Exploiting low-cost approach to synthesize high-performance crown ethers maybe a potential future direction.

TBP and its derivatives had been studied for several decades, such as tributyl phosphate,<sup>20</sup> triisobutyl phosphate,<sup>21</sup> N,N-bis(2-ethylhexyl)acetamide (N523),<sup>22</sup> Lithium ionophore II - IV, and Lithium ionophore VIII. TBPs usually collaborates with non-polar organic solvents (fatty alcohol, kerosene, methyl isobutyl ketone, ionic liquid etc. as diluent) and FeCl<sub>3</sub> (as co-extractant). In extraction process, TBPs, lithium ion and water generate a coordination cation ([Li(TBP)<sub>x</sub> nH<sub>2</sub>O]<sup>+</sup>) in the organic phase, and meanwhile FeCl<sub>3</sub> will coordinate with Cl<sup>-</sup> to form [FeCl<sub>4</sub>]<sup>-</sup> anion.<sup>23</sup> The interference ions are remained in the brine phase. By optimizing the extraction parameters, like TBPs concentration, Fe/Li ratio, brine acidity, organic phase/brine ratio, the extraction rate of lithium from brine can reach to 96% with a Li/Mg selectivity of 32,000.<sup>22</sup> TBPs extraction processes are the most promising in practical commercialization due to their relatively low cost. For example, Solvay recently launched CYANEX®936P, a commercialized phosphorus-based lithium extractant for lithium extraction. However, several problems should be solved before the practical commercialization of extraction processes, such as the corrosivity to equipment, toxicity to environment, and micro-solubility of extractant in brine.

Ionic liquids are also widely reported as lithium extractant.<sup>21, 24</sup> However, they usually act as auxiliaries, and collaborate with crown ether or TBPs to achieve better performance.



**Figure 4.** (a) Illustration of liquid-liquid extraction; Copyright © Springer 2021.<sup>25</sup> (b) Coordination between lithium ion and 12-crown-4. (c) Lithium extraction using TBP; Copyright © AMERICAN CHEMICAL SOCIETY 2021.<sup>23</sup>

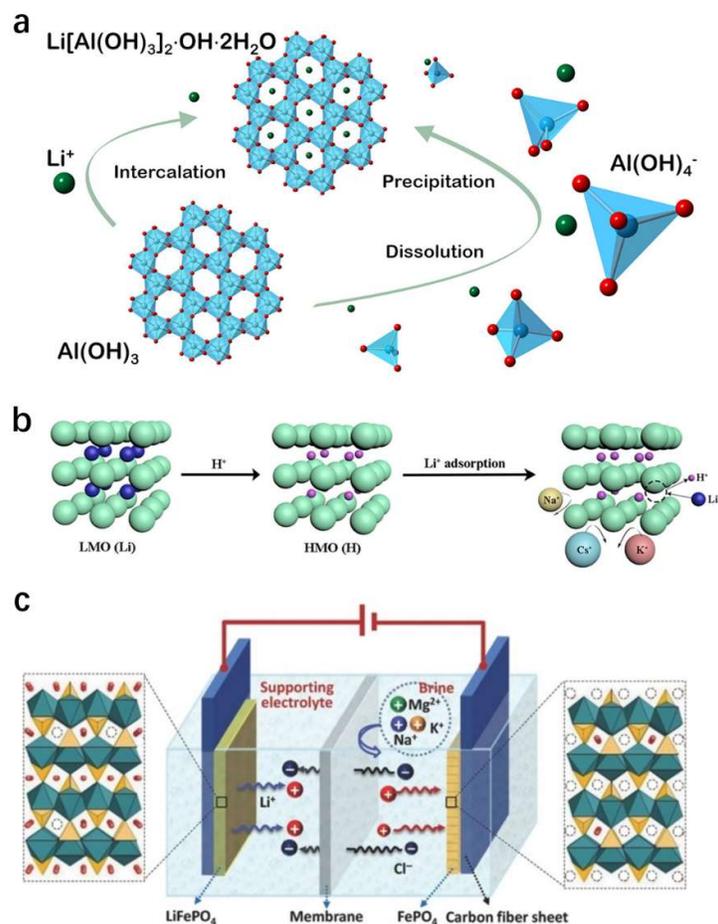
## 4.2 Adsorption

The key factor of adsorption processes is the adsorbents. High stability in acid or high-salinity solution, high selectivity, adsorption capacity and good reproducibility are the most important parameters required for adsorbents. Two kind of adsorbents are worth being mentioned: aluminum-based adsorbents, lithium-intercalation materials.

Aluminum-based adsorbents are usually used as flocculant in water purification. The active constituent of aluminum-based adsorbents is the amorphous  $\text{Al}(\text{OH})_3$  generated by hydrolyzation.<sup>26</sup> Amorphous  $\text{Al}(\text{OH})_3$  can coordinate with  $\text{LiCl}$  to form a  $\text{LiAl}$ -layered double hydroxide complex based on gibbsite structure ( $\text{LiCl} \cdot x\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ ), whereas the other ion cannot due to the larger ion radius or the higher hydration free energy. Aluminum-based adsorbents are very cheap, and had been commercialized in the other field for many decades. For convenience on separating and recovering, aluminum-based adsorbents usually collaborate with superparamagnetic nanoparticles, mesh grid membrane, fixed bed columns etc. However, biggest problem faced by the aluminum-based adsorbents is the low capacity of < 10 milligram lithium per gram adsorbent.<sup>5</sup> Further optimization on capacity is required to achieve requirement of industrial performance.

Lithium-intercalation materials are mainly manganese-based adsorbents (LMO, such as  $\text{LiMn}_2\text{O}_4$ ,<sup>27</sup>  $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ <sup>28</sup>), titanium layered-based adsorbents (LTO, such as  $\text{Li}_2\text{TiO}_3$ ,<sup>29</sup> spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ <sup>30</sup> etc.) and lithium iron phosphate (LFP,  $\text{LiFePO}_4$ )<sup>31</sup>. LMOs and LTOs have crystal frameworks consisting of oxygen and transition metal. The cavity spaces and electric charge of crystal lattices are rather limited that only lithium and proton can intercalate. Before use, LMOs or LTOs are treated by acid to generate the proton form (HMOs or HTOs, respectively). Then HMOs or HTOs can absorb lithium ion in brine by ion. The capacity of LMOs and LTOs are one order of magnitude higher than that of aluminum-based adsorbents, but the absorption processes usually spend several hours to several day, especially in the situation where the lithium concentration of brine is low.

Interestingly, it can be noted that lithium-intercalation materials just happen to be the electrode materials for lithium ion battery. Thus, the absorption/desorption process can be substantially facilitated by electrochemistry, just like the charge/discharge process of lithium ion battery. The electro-adsorption/desorption are usually finished in few hours. Besides, if dividing the electrolytic cell to dual compartments using an anion exchange membrane (AEM), the adsorption and desorption can be simultaneously operated.<sup>31</sup> For example,  $\text{LiFePO}_4$  and  $\text{FePO}_4$  can be employed as anode (in Na salt or K salt based aqueous electrolyte) and cathode (in brines), respectively. Time consumption can be halved, meanwhile the side reactions of counter electrodes, such as hydrogen evolution, oxygen evolution, are substantially exempted, which reduces the energy consumption by more than half. We think this technology must be the most potential to be commercialized near-term.



**Figure 5.** (a) Aluminum-based adsorbents; Copyright © AMERICAN CHEMICAL SOCIETY 2019.<sup>26</sup> (b) Extracting lithium using lithium-intercalation materials; Copyright © Willey 2017.<sup>27</sup> (c) Electro-absorption using  $\text{LiFePO}_4/\text{FePO}_4$  electrode; Copyright © Willey 2018.<sup>31</sup>

### 4.3 Membrane separation

The membrane processes are one of the most promising separation methods due to its high efficiency, continuous operation and, and easiness on scale up. In this report, we will introduce the nanofiltration and selective electro dialysis.

The radius of hydrated  $\text{Mg}^{2+}$  (428 pm) is higher than that of hydrated  $\text{Li}^+$  (382 pm), and the charge of  $\text{Mg}^{2+}$  is double as much as that of  $\text{Li}^+$ .<sup>32</sup> By rationally designing the pore sizes and the charge distribution in membrane, nanofiltration membrane can easily intercept  $\text{Mg}^{2+}$  based on steric hindrance and Donnan exclusion.<sup>6</sup> The nanofiltration system is very simple, and the operation is easy. However, the selectivity of  $\text{Li}^+/\text{Mg}^{2+}$  is usually order of magnitudes lower than the Lithium-intercalation materials.

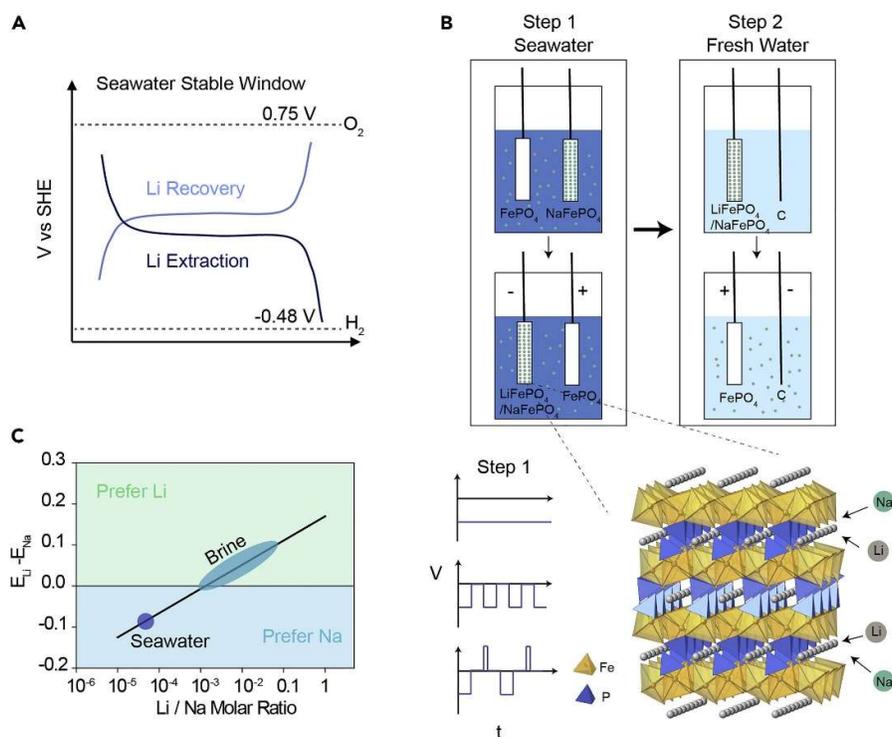
Multistage process must be set up to achieve a satisfactory effect. Meanwhile, membrane fouling is another significant issue leading to degradation in permeability, selectivity and lithium recovery. High pressure is required as the driving force of nanofiltration, thus the high operating cost and energy consumption are another important issue to be addressed.

Selective electrodialysis can efficiently separate monovalent ions from multivalent ions.<sup>33-37</sup> The key of selective electrodialysis is the monovalent selective ion-exchange membrane. Various mechanisms have been proposed to explain the monovalent selectivity, including the pore-size sieving effect, the electrostatic repulsion effect and hydration energy difference. The driving force of selective electrodialysis is electricity. Thus, membrane stacks can be easily fabricated by alternately arrange the monovalent selective ion-exchange membrane and anion exchange membrane, which greatly increased the handling capacity. However, the monovalent selective ion-exchange membrane cannot separate different monovalent ions from each other, thus the existence of monovalent ions ( $\text{Na}^+$ ,  $\text{K}^+$ ) usually renders a reduced current efficiency. In addition, further efforts should be devoted to the development of monovalent selective ion-exchange membrane with high conductivity.

## **5. Future technique for lithium inventories**

Despite huge difficulty, researchers still devote abundant efforts to explore the possibility of lithium extraction from seawater due to the concern on the long-term lithium supply. Researchers tried to directly use the aforementioned lithium-intercalation materials (LMOs,<sup>38</sup> LTOs<sup>30</sup> etc.) in lithium extraction from seawater, but the performance still needs to be improved greatly, especially the rate of adsorption. The time-consuming is usually in weeks while the adsorption capacity are just several milligram lithium per gram adsorbent. Electricity is necessary to facilitate the adsorption for lithium extraction from seawater. However, the application of electricity will render a serious problem in selectivity. For example,  $\text{Li}^+$  can intercalate into  $\text{FePO}_4$  with an intercalation potential of  $\sim 0.36$  V versus SHE in standard conditions, while  $\text{Na}^+$  also can intercalate into  $\text{FePO}_4$ , with an intercalation potential of  $\sim 0.19$  V versus SHE in standard conditions. According to Nernst equation, the intercalation potential of  $\text{Li}^+$  will reduce to lower than that of  $\text{Na}^+$  if the  $\text{Na}^+/\text{Li}^+$  molar ratio is higher than

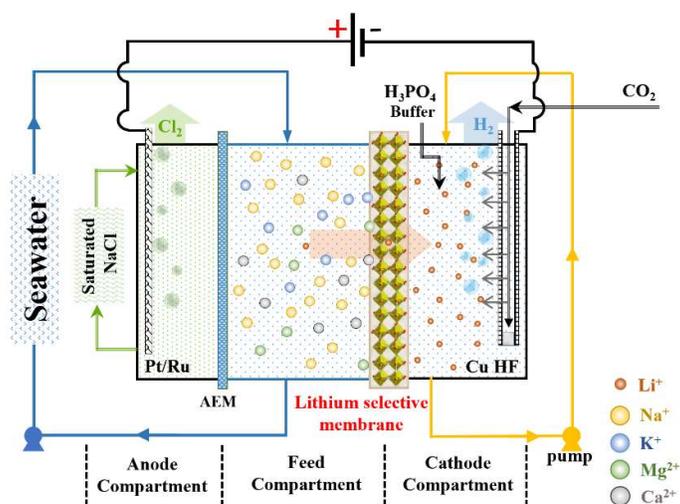
747.73, resulting in a preferential adsorption of  $\text{Na}^+$ .<sup>15</sup> In seawater, the  $\text{Na}^+/\text{Li}^+$  molar ratio is as high as 15,500. Thus, researchers must modify the lithium-intercalation materials with  $\text{Li}^+$  selective coating to ensure the preferential adsorption of  $\text{Li}^+$ , such as polydopamine,  $\text{TiO}_2$  etc. Stable  $\text{Li}$  extraction with 1:1 of  $\text{Li}$  to  $\text{Na}$  can be achieved after the electrode modification. However, the time-consuming is still 3 - 6 times higher than that of extraction from brine.



**Figure 6.** (a) Schematics showing the seawater stability window. (b) Schematics showing the  $\text{Li}$  extraction using  $\text{TiO}_2$  coating electrode. (c) The  $\text{Li}$  and  $\text{Na}$  intercalation potential difference at difference initial  $\text{Li}$  to  $\text{Na}$  molar concentration using  $\text{FePO}_4$  electrode. Copyright © Elsevier 2018.<sup>15</sup>

For membrane technology, some special membrane with high selectivity had been exploited to realize the selective electro dialysis in seawater. These membranes are fabricated by inorganic crystals like LLTO,<sup>16</sup> LAGP,<sup>39</sup> NASICON,<sup>35</sup> LLTZO<sup>40</sup> etc. The size of  $\text{Li}^+$  is similar to the crystal lattice of these materials, where other ions present in seawater are obstructed due to the larger ion sizes or incompatible charge. Selectivity of thousands can be easily achieved to realize the effective extraction of lithium from seawater. However, a high voltage of 3 – 6 V are usually required to push the permeation of lithium through membrane due to the low concentration, which results

in several times in the energy consumption. The electric consumption is estimated to be 18 – 75 kW h per kilogram lithium. By combining the lithium extraction with other industries is a feasible solution for this issue. For example, selective electro dialysis requires the movement of ions in solution, disregarding the reaction on electrodes, while chlorine alkali industry requires the reaction on electrodes, disregarding the movement of ions in solution. By combining the lithium selective electro dialysis with the chlorine alkali industry, it can be simultaneously operated to achieve the lithium selective extraction and the manufacture of hydrogen and chlorine gas. Electric cost can be fully compensated by the by-produced hydrogen and chlorine gas, implying the profitability of this joint production.



**Figure 7.** Combining the lithium selective electro dialysis with the chlorine alkali industry to pursue the benefit maximization. Copyright © Royal Society of Chemistry 2020.<sup>16</sup>

Currently, the top global lithium miners are SQM, Albemarle, Ganfeng, Tianqi, Livent and among others. Due to the standardization in the mining process and a much faster ramping up rate than the brine peers, hard-rock miners were able to respond much more efficiently to the current rapid-growing lithium demand in the past few years since 2015. However, much more lithium resources residues in brine, especially in the ocean. Due to the different merits owned by the various brine resources, many advanced lithium extraction technologies are also under development. Once the advanced lithium extraction technologies from ocean are becoming mature, lithium supply might be the

strong support for the EV industry which is similar as people are able to successfully utilize the shale gas thanks to the modern mining technologies.

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## Chapter 7

### Biomaterials for greener batteries

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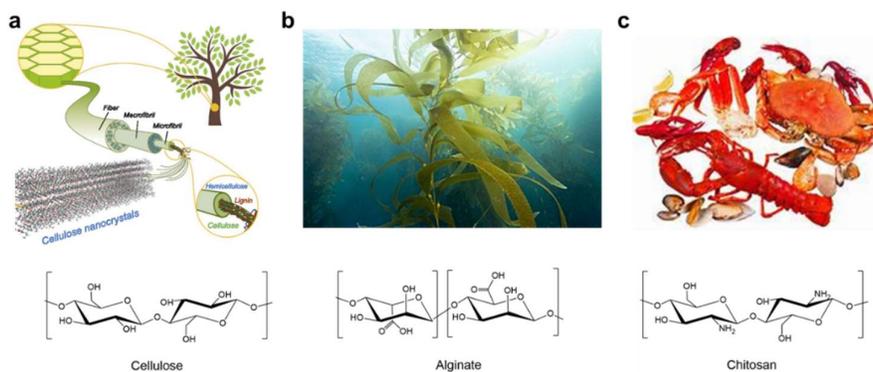
#### 1. Introduction

Rechargeable batteries, especially Li-ion batteries, are playing a critical role in curbing the dependence on fossil fuels and reducing the emission of greenhouse gas. While being designed for clean energy storage, Li-ion batteries generally use metal-containing active materials (Li, Co, etc.), flammable organic electrolytes, and non-degradable polymeric separators (PP, PC, etc.). However, the ever-growing demand for the Li-ion batteries, mainly in portable electronics and electric vehicles, has greatly increased the prices of Co and Li and may eventually strain the raw material resources. Thus, existing materials for batteries fail the needs for sustainable development of energy utilization. For sustainable usage of renewable energy, it is necessary to develop battery materials made of renewable, sustainable, and green resources<sup>1</sup>. In this regard, natural biomaterials are attracting increasing interest for greener batteries, as biopolymers are sustainable, renewable, and eco-friendly.

Biomaterials refer to materials obtained from biological systems, including cellulose, chitin, proteins, etc. Due to the great abundance, wide accessibility, and unique biopolymer molecular structures, biomaterials have been frequently investigated in batteries. Many studies have been devoted to developing organic electrode materials derived from biomaterials such as lignin-derived materials, polydopamine, melanin, purpurin, and so on<sup>2-5</sup>. Since extensive Reviews have summarized biomaterial-based electrodes<sup>6-9</sup>, in this Report, we will focus on the use of biomaterials in sustainable batteries as non-electrode components, such as binders, separators, electrolytes, and substrate materials (ion-transport hosts and structural matrices).

Natural polysaccharides, which are carbohydrates consisting of monosaccharide molecules, are the largest component of biomass widely existing in starch, cellulose, etc. Cellulose, alginate, and chitosan are three typical types of polysaccharides (Figure

1), which we will mainly discuss their applications in batteries in this Report to show the use of biomaterials for greener energy storage. Cellulose is the most abundant biopolymer on Earth present in trees, plants, and so on. More importantly, cellulose holds strong mechanical properties, rich polar functional groups, and 1D long-chain structure, which make cellulose promising for structure host and ion transport. Similar to cellulose, chitosan, which is derived from chitin in crustacean shells, and sodium alginate, which is a major constituent of brown algae. Cellulose, chitosan, alginate, and other biomass have found extensive applications in batteries as binders, separators, and so on, which play critical roles in producing renewable and sustainable batteries. The use of these biomaterials with unique molecular structures, source abundance, environmental friendliness, and low cost will greatly promote the development the next-generation “greener” batteries.



**Figure 1.** Scheme or photos of biopolymers (or their resources) that are widely used for energy-storage applications: (a) cellulose, (b) alginate, and (c) chitosan, and their molecular structures.

## 2. Biopolymer binders for electrode fabrication and 3D printed batteries.

Many biomaterials contain rich carboxy groups, which can form strong hydrogen bonding with electrode materials (e.g., Si anode), and can thus be applied as effective binders in electrodes. The typical biomaterial binders are carboxymethyl cellulose (CMC) and sodium alginate. The biopolymer binders (CMC and alginate) are water-soluble and thus eco-friendly and cost-effective for fabricating sustainable battery electrodes, in place of the traditional PVDF binder, which uses a toxic organic solvent (NMP). The biopolymers with enormous hydrogen bondings also enhances the electrolyte performance, particularly for those anode materials with large volumetric

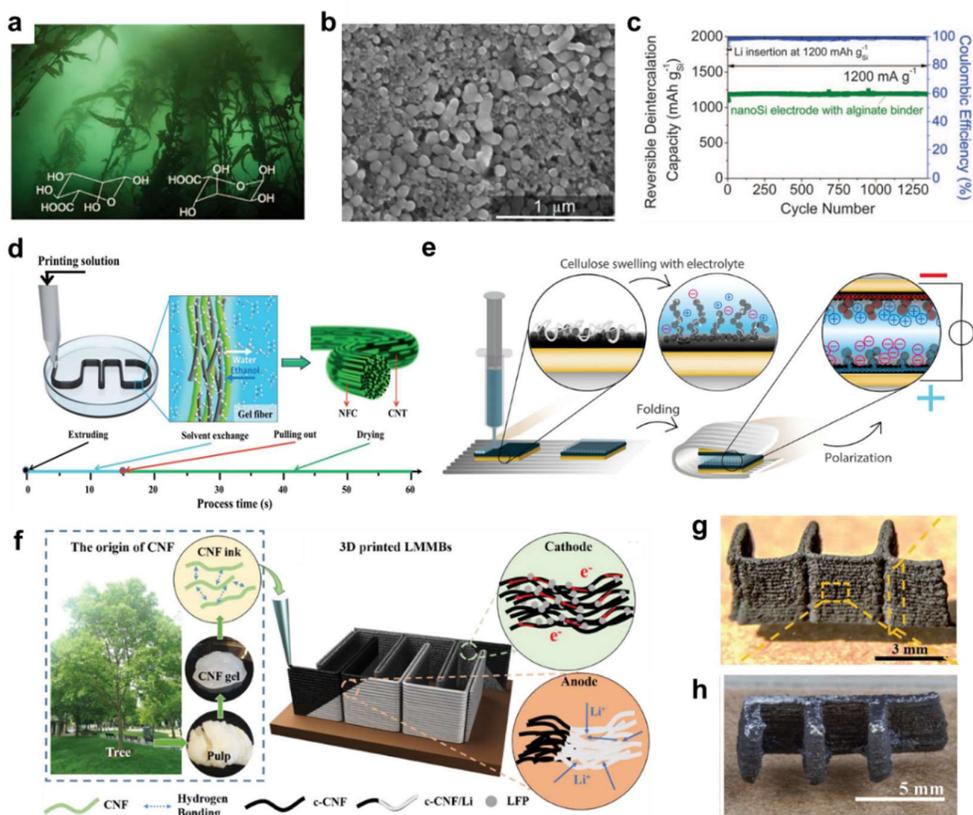
change during cycling. For example, when using a CMC binder with the Si anode, the hydrogen bonds between the carboxyl groups and the SiO<sub>2</sub> on the Si surface were reported with a self-healing effect and reformation if locally broken<sup>10</sup>. Yushin and co-workers first reported alginate extracted from brown algae as a high modulus binder for stable Si anodes. Alginate (or alginic acid) is a linear polysaccharide consisting of  $\alpha$ -L-glucuronic acid and  $\beta$ -D-mannuronic acid residues connected via 1,4-glycosidic linkages (Figure 2a). Using the sodium alginate as a binder for the Si anode (Figure 2b), the alginate carboxylic moieties of the sodium alginate and the hydroxylated Si surface forms strong hydrogen bonding. The strong interaction between the alginate and the Si anode plays a critical role in the stability of the Si anode. With the sodium alginate binder, the Si anode shows a stable capacity of 1200 mAh/g for more than 1300 cycles (Figure 2c). Compared with the CMC binder, the alginate has more concentrated and uniformly distributed carboxylic groups along the chain. Thus, the alginate molecules have more polar groups than CMC, leading to a stronger interaction between the binder and the active materials, as well as the binding of the electrode to the current collector.

Due to the strong binding effect and high mechanical strength of the cellulose, cellulose (mainly nanofibril cellulose (NFC), also named cellulose nanofibril (CNF)) is further applied for scalable, 3D printed energy-storage devices. 3D printing is an “additive” manufacturing process whereby layers of materials are built up to create a 3D object, integrating materials, structures, and functions. This technique is known for its versatility, accuracy, and low cost compared with traditional manufacturing techniques. NFC is an excellent building block for 3D printing, as the natural abundant NFC has a high Young’s modulus of 145–150 GPa, which is crucial to maintain the structural integrity of the printed materials. The NFC is also excellent dispersion agent for 3D printing. When dispersed in an aqueous solution, the strong hydrogen bonding between NFCs and water improves the water retention and increases the viscosity, which is needed for effective 3D printing. For example, Hu and co-workers<sup>11</sup> demonstrated NFC for improved 3D printability by printing CNT-NFC composite microfibers (Figure 2d). NFC serves as an excellent dispersion agent (surfactant) to effectively disperse CNTs in a water solution with a high viscosity, which is suitable for scalable 3D printing. The NFCs and CNTs in the printed microfibers in the 3D-printing process are dual-aligned, leading to excellent mechanical strength ( $247 \pm 5$

MPa) and electrical conductivity ( $216.7 \pm 10 \text{ S cm}^{-1}$ ). The fast yet scalable 3D-printing technology promises the NFC a strong candidate for printed energy-storage devices.

NFC has been frequently studied for fabricating printed energy-storage systems, such as supercapacitors and batteries. Using nanocellulose as a rheology modifier, agent for dispensing, gelling, and network forming, a fully printed electrical-double-layer-capacitor (EDLC) was fabricated by direct-ink-writing technique (Figure 2e)<sup>12</sup>. The direct-ink-writing technique extrudes gel ink line-by-line and layer-by-layer to produce the 3D object. The biomaterials are crucial in all components of the printed EDLC. In the substrate, the nanocellulose provides structural integrity. In the current collector ink, shellac (a renewable biopolymeric resinous substance) was used as an electron-conducting matrix. The electrolyte ink is also made from nanocellulose, which induces gelling and prevents electrolyte evaporation or leaking. The nanocellulose provides gelling for the electrode ink, preventing particle agglomeration and precipitation. In particular, the nanocellulose also functions as a binder that swells with the electrolyte, allowing ion transport in the printed electrode. The fully printed EDLC exhibits the state-of-the-art electrochemical performance of supercapacitors, excellent stability. Moreover, as the biomaterial comprises the most solid content of the printed EDLC, the EDLC is biodegradable, disintegrated over a few weeks.

The CNF-based inks are also employed for 3D printed Li metal batteries. In a 3D printed  $\text{LiFePO}_4$  battery (Figure 2f)<sup>13</sup>, the  $\text{LiFePO}_4$  cathode was printed using CNF as a surfactant and viscosifier for the cathode ink. The Li metal anode was infused into a carbonized 3D printed NFC scaffold. The carbonized NFC scaffold provides not only a 3D structure for the Li metal anode accommodating the volume change of Li during Li plating/stripping but also access for the electrolyte. A planar Li metal battery with the printed  $\text{LiFePO}_4$  cathode (Figure 2g) and Li metal anode (Figure 2h) was successfully assembled to demonstrate the possibility of the CNF-printed high-energy-density batteries. Combining the 3D printing technique and natural biomaterials are expected to construct green batteries rapidly with different customized formats.



**Figure 2.** Biomaterials as binders and for use in printable batteries. (a) Photo of brown algae (giant kelp in the ocean), which is the source of sodium alginate. (b) SEM of nanoSi electrode with the sodium alginate binder. (c) Cycling performance and Coulombic efficiency of the nano-Si electrodes with the sodium alginate binder. (d) Schematic of 3D printing the CNT–NFC microfiber network formation and the processing time. (e) Schematic of the printed disposable electrical-double-layer-capacitors (EDLC) using nanocellulose as a rheology modifier, dispersing agent, gelling, and network former. (f) Schematic showing the CNF ink derived from trees, 3D printed LMMBs with a high-aspect ratio, the  $\text{LiFePO}_4$  particles linked with c-CNF, and the 3D printed c-CNF for hosting Li. Photographs of (g) c-CNF/ $\text{LiFePO}_4$  electrode and (h) c-CNF/Li electrode by 3D printing. Data source: Li et al. 2017; Aeby et al. 2021; Cao et al. 2019.

### 3. Biomaterial-based thick electrodes and 3D batteries

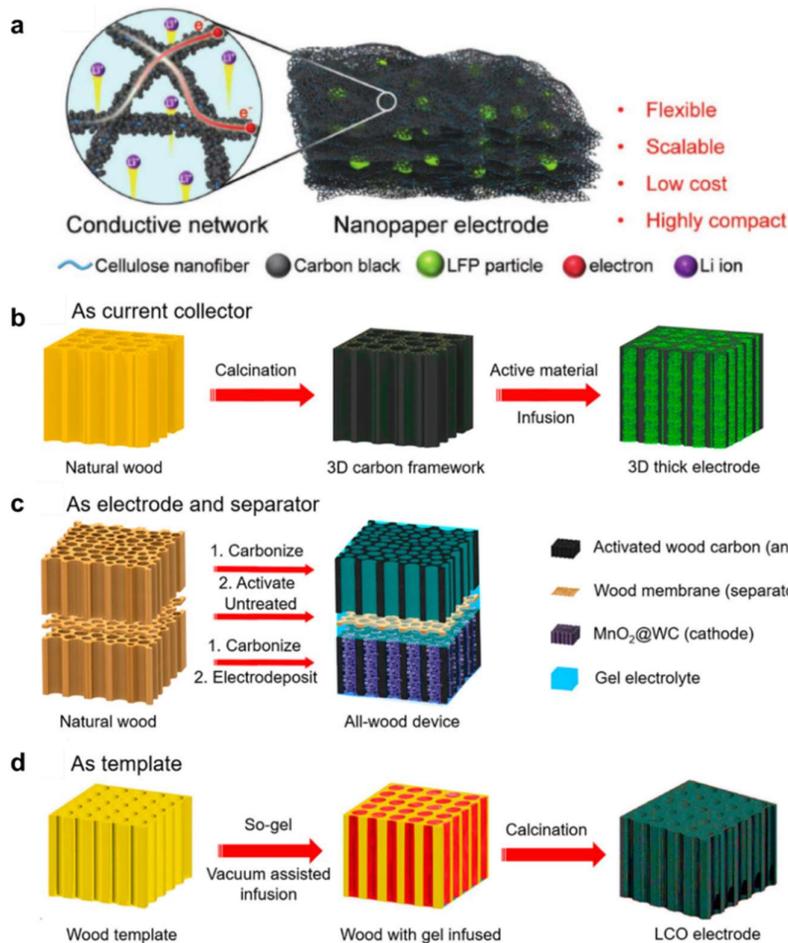
Due to the strong bonding effect, CNF can also aid in constructing thick, 3D electrodes toward a high energy density. To establish thick electrodes, their charge (electrons and ions) transfer kinetics and mechanical stability must be improved.

Biomaterials have a great potential for utilization in thick electrodes as a scaffold component, due to their advantages of high mechanical strength and capability in creating structures with a low tortuosity for rapid ion and electron transport, as well as their natural abundant, renewable resources. The most abundant biopolymer, cellulose, has outstanding mechanical strength and flexibility, which can enable mechanically robust thick electrodes. The biomaterials with high aspect ratio and rich polar functional groups can form strong interaction with electrode particles. The 1D CNFs can be assembled into a 3D ion-conductive network for thick electrodes. For example, negatively charged CNF was used to build a conductive nanofiber network by a spontaneous electrostatic self-assembly technology (Figure 3a)<sup>14</sup>. The CNF network tightly wraps the active materials such as  $\text{LiFePO}_4$  as a robust backbone. The nanoporous CNF network with high electrolyte retention forms a continuous ion transfer pathway, combined with an electron-conducting network by carbon black, ensuring fast kinetic properties through the thick electrode. In addition to the wood-derived cellulose, bacterial cellulose has also been processed to thick, porous, and large-surface carbon nanofiber aerogels for various energy storage devices.

Wood is an attractive biomaterial for the top-down designing of 3D thick batteries for high energy density, owing to not only the natural abundance and sustainability, but also the unique structure of wood. The wood has a naturally aligned, hierarchical, and low-tortuosity porous structure, which allows wood or wood-derived carbon to host an ideal 3D host. When the wood is carbonized, the unique porous structure can be maintained, providing a fast electronic perpendicularly transferring pathway for thick electrodes. The low-tortuosity macropores in the 3D carbonized wood framework can accommodate high-mass-loading active materials and the mesopores in wood allows electrolyte infusion for ionic conductivity (Figure 3b)<sup>15</sup>. Thus, the carbonized wood can serve as a current collector (or matrix material) for thick electrodes. This wood-hosted thick electrodes have been realized with a variety of electrode materials, such as  $\text{LiFePO}_4$ , sulfur, Li metal, and Na metal. The cathode materials can fill in the 3D carbonized wood to build cathodes with high mass loading (up to  $60 \text{ mg cm}^{-2}$ ) while the metal anodes can be melted and diffused into the 3D framework forming thick anodes (up to millimeter), producing ultrathick and high-energy-density wood-based batteries. If not used as a host for active materials, the wood can also be processed as

membranes to serve as a separator hosting liquid or gel electrolytes. In addition, the carbonized wood with a large surface area can also serve as an anode material for  $\text{Li}^+$  storage or supercapacitor. As a result, the natural wood can be utilized as an electrode, thin separator, and matrix structure for thick electrodes, producing “all-wood” energy-storage devices (Figure 3c).

In addition, the wood can also serve as a (sacrificial) template for building 3D, wood-like thick electrode material. For example, Yu and co-workers reported a thick electrode design inspired by natural wood, in which 3D cathode ( $\text{LiCoO}_2$ ) replicates the unique porous structure of wood (Figure 3d). Using the wood as a sacrificial template, the produced ultrathick  $\text{LiCoO}_2$  cathode successfully duplicates the vertical microchannels of natural wood. The low tortuosity replicated from the wood is proven beneficial to the electronic transport through ultrathick electrodes. The wood-inspired thick  $\text{LiCoO}_2$  cathode delivers an extremely high areal capacity of up to  $22.7 \text{ mAh/cm}^2$  (5 times that of existing electrodes). With these possibilities of wood utilization in batteries, including electrodes, host structures (current collectors), separators, and templates, wood deserves more research for developing green batteries.



**Figure 3.** Biomaterials for thick electrodes and 3D batteries. (a) Conductive cellulose nanofiber network and neutral carbon black building hierarchical network structure with decoupled ion and electron transfer pathways for a thick electrode. Wood-based 3D batteries: (b) wood-derived carbon as a 3D current collector; (c) wood as a separator and wood-derived carbon as a current collector for a 3D thick battery; (d) Wood as a template for fabricating a 3D thick electrode. Data source: Kuang et al. 2018; Chen et al. 2018.

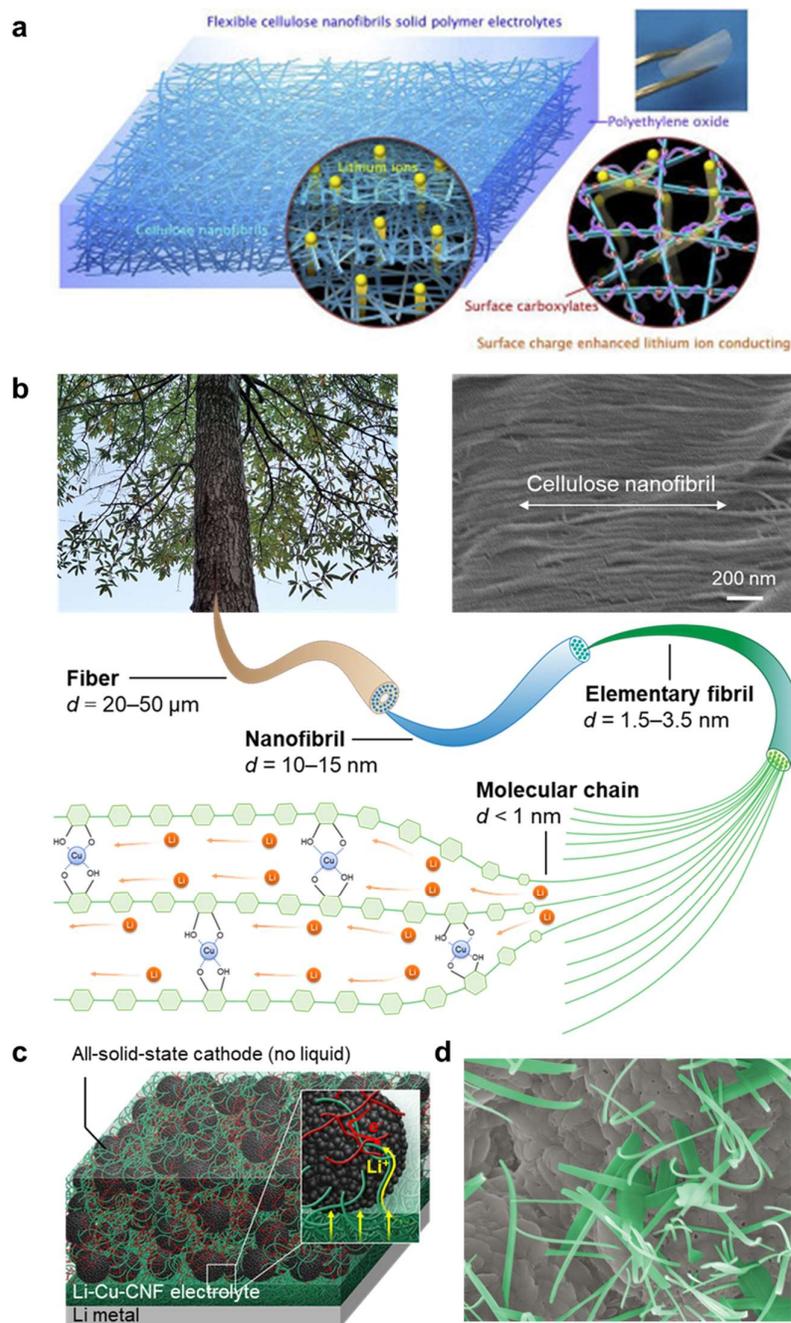
#### 4. Biomaterial-based gel and solid-state electrolytes

Due to the rich polar groups (carboxyl, amine, etc.) that can attract ions, there have been extensive studies of using biomaterials, including cellulose, chitosan, etc., for ion transport in batteries. As the most abundant biopolymer, cellulose has been frequently designed as separators (filled with liquid electrolytes) and gel electrolytes (soaked with organic or aqueous electrolytes).<sup>16</sup> As a separator, the cellulose membrane is fabricated with high porosity to ensure high electrolyte uptake. For example, Cui and co-workers

fabricated CNF-reinforced cellulose separators with tunable pore size and improved working stability<sup>17</sup>. The nanosized CNFs play a crucial role in optimizing the pore size (~0.8  $\mu\text{m}$ ) of the separator to achieve a high electrolyte uptake of 95.7–142.3% for high ionic conductivity. For use as gel polymer electrolytes, the cellulose-based gel enables a high uptake of electrolyte (70–650 wt%) for high ionic conductivity. Similarly, chitosan and other biomaterials have also been investigated as gel electrolytes for  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  conduction. These biomaterial-based separators and electrolytes not only promote the ion transport properties but also benefit the eco-compatibility, especially when using aqueous electrolyte is coupled with the biopolymers.

Compared with the liquid electrolytes and gel electrolytes, solid-state electrolytes are more attractive due to their enhanced safety and promised high energy density when used in Li metal batteries. However, the cellulose itself does not conduct ions due to insufficient salt dissolution capability. To use cellulose-based SPEs<sup>18-21</sup>, cellulose is generally cross-linked with or blended with other polymers that can dissolve and conduct ions (e.g., polyethylene oxide (PEO)). With the added polymers,  $\text{Li}^+$  can transport with the segmental motion of the added polymer that fills the spaces and pores of the cellulose fibers. The cellulose matrix serves as structural support for the ion-conducting polymer. For example, NFC has been used to reinforce the thermal, mechanical, and electrochemical properties of PEO solid polymer electrolytes. PEO is a widely investigated polymer electrolyte, due to its high dielectric constant ( $\epsilon = 8$  at the amorphous region) for dissolving Li salt, ability to form membranes, and its good interfacial contact with electrodes. However, PEO-based electrolyte can only enable reasonable ionic conductivity in its amorphous state and at elevated temperature, holding a poor mechanical property. CNF is promising for fabricating polymer composites to enhance the mechanical properties and thermal stability of PEO electrolyte<sup>22</sup>. In the PEO-CNF composite electrolyte, the CNF nanofibers form a continuous  $\text{Li}^+$  transfer network in PEO. The surface charge of CNFs significantly improves the ionic conductivity of PEO SPE (reaching  $3.1 \times 10^{-5} \text{ S cm}^{-1}$  at 25 °C). In addition, the CNFs also enhance the thermal stability, mechanical robustness, and flexibility of the polymer electrolyte, creating the potential to be used in flexible solid-state batteries.

Recently, Hu and co-workers<sup>23</sup> reported Cu<sup>2+</sup>-coordinate cellulose as solid-state Li<sup>+</sup> conductors. By expanding the nanochannels naturally available in cellulose with Cu ions, the cellulose molecules are open for Li<sup>+</sup> ion transport. The open molecular channels of cellulose with rich oxygen-containing form multiple Li-O, which is beneficial to the Li-salt dissociation and Li<sup>+</sup> transport. The open molecular channels also allow hosting and bounding a small amount of H<sub>2</sub>O molecules, which further aids in the Li<sup>+</sup> movement. The resulting Li-Cu-CNF solid-state ion conductor presents a high ionic conductivity of  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  along the CNF fiber direction. The 1D CNF ion conductor can not only be assembled into thin paper electrolytes but also for an ion-conducting network in a solid-state cathode with an excellent ionic percolation behavior. As a result, the Li-Cu-CNF presents great promise to build solid-state batteries with the natural abundant cellulose biomaterial. The strategy to process the cellulose toward a high-performance electrolyte via such simple coordination chemistry sheds a light to the utilization of the biomaterials in green batteries for sustainable energy storage.



**Figure 4.** Biomaterials for solid-state batteries. (a) Schematics and photo of the CNF/PEO solid polymer electrolyte. CNF aerogel was used as a scaffold and PEO LiTFSI was infiltrated into the CNF aerogel to form the nanocomposite SPE. (b) The schematic of the Li-Cu-CNF solid-state ion conductor and SEM image of naturally aligned CNFs. The CNFs are derived from wood cellulose fibers and are composed of elementary fibrils, which can be further broken down into individual cellulose molecular chains. The spacing between cellulose molecular

chains open by  $\text{Cu}^{2+}$  coordination serves as  $\text{Li}^+$  conducting pathways. (c) Schematic of solid-state full battery made of the Li-Cu-CNF electrolyte, solid-state cathode (black spheres) mixed with the Li-Cu-CNF additive (green fibers), and a Li metal anode. (d) SEM image of the Li-Cu-CNF ion-conducting additive interconnecting  $\text{LiFePO}_4$  cathode (false color: green, Li-Cu-CNF; grey,  $\text{LiFePO}_4$ ). Data source: Qin et al. 2020; Yang et al. 2021.

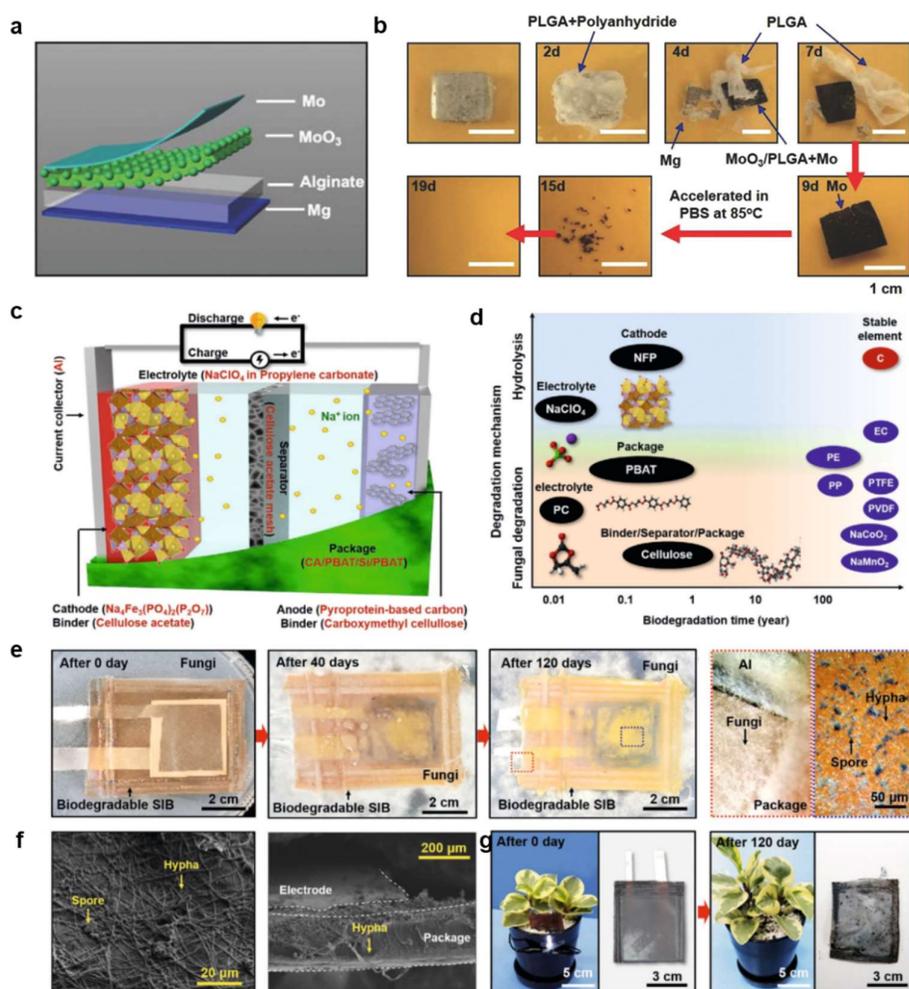
## 5. Bio-degradable batteries

Although Li-ion batteries are designed as clean energy-storage devices (compared with lead-acid batteries), the ever-increasing production of batteries could still pose threat to the environment. It is estimated that 11 million tons of Li-ion batteries will be spent by 2025, inducing a heaving disposal burden. The organic electrolytes in Li-ion batteries are potentially pollutive. Moreover, the polymer separators (mainly polypropylene and polycarbonate) take hundreds or thousands of years to degrade. Recycling batteries cost money ( $\sim \$1/\text{kg}$ ) and time (recycling valuable materials takes 5 times longer than extracting from raw sources).

Biodegradable batteries can degrade safely in the natural environment, significantly relieving the burden of used batteries. Some biodegradable batteries are also designed for “transient devices”, which can be controllably degraded and vanish with time or by a passive trigger. Transient devices are attractive in fields such as medical therapeutic/diagnostic processes, data-secure hardware systems, and so on. Thus, biodegradable electronics are attracting increasing interest, whereas the investigation on biodegradable batteries is still inadequate, due to the limitation of materials used in batteries. In traditional Li-ion batteries, the component materials are generally non-degradable (e.g., carbon, stainless steel, oxides, and polymeric separator) or even harmful to the environment (e.g., organic electrolyte). Using biomaterials as the main components, “green” batteries are expected, which will be environment-friendly, sustainable, and biodegradable.

Yin and co-workers<sup>24</sup> fabricated a fully biodegradable magnesium-molybdenum trioxide battery with alginate hydrogel electrolyte and polyanhydride/poly(lactide-co-glycolide) coating (Figure 5a). The battery was degradable in phosphate-buffered saline, where the encapsulation polymer swelled and degraded first, followed by the dissolution of Mg, sodium alginate hydrogel, and active materials (Figure 5b). Recently,

Kang and co-workers<sup>25</sup> proposed a fully biodegradable sodium-ion secondary battery (SIB) (Figure 5c). They extensively screened biodegradable materials for all components of the battery, including the cathode, anode, binder, separator, electrolyte, and package. They also carefully investigated the fabrication biodegradation time (Figure 5d) to fabricate fully biodegradable SIBs. None of the components of the SIB produced toxic substances or non-degradable wastes after hydrolysis and/or fungal biodegradation (Figure 5e). The non-toxicity of the SIB was confirmed using living microorganisms (Figure 5f) and plants (Figure 5g). These findings suggest that using biomaterials (alginate, cellulose, etc.) together with biodegradable materials will greatly push forward the development of fully biodegradable batteries to minimize the impact of batteries on our environment.



**Figure 5.** Biomaterials for solid-state batteries. (a) Structural schematic of a biodegradable battery with alginate hydrogel electrolyte. (b) Photos of the battery in (a) dissolved in

phosphate-buffered saline at various stages. (c) Schematic of the materials in a fully biodegradable SIB. (d) Biodegradation mechanism and biodegradation times for various battery components. (e) Photos of a biodegradable rechargeable SIB pouch cell after fungal degradation for 0, 40, and 120 days. (f) Top-view and cross-sectional SEM images of biodegradable battery after fungal degradation for 120 days. (g) Photos of a plant and a battery (right frame) and their photos after burying the SIB in the plant-soil for 120 days. Data source: Huang et al. 2018; Lee et al. 2021.

It is noteworthy that fabricating truly biodegradable batteries should also consider the process of biomaterials. For example, although organic electrode materials are often claimed biodegradable, their synthesis needs toxic agents, which compromises the sustainability and biodegradability of the green battery. Conversely, some inorganic electrode materials, such as Zn, Mg, are naturally biodegradable. It is necessary to develop facile and green procedures to produce biomass-based electrodes, electrolytes, binders, and so on for true biodegradability. In addition, the biomaterials do not necessarily guarantee battery biodegradability. For fully biodegradable batteries, the batteries need to be designed at the system level including all components and processes. The biodegradability of the batteries should be verified by biodegradation tests in conditions approximating commercial composting.

## **6. Conclusion.**

The natural-available and sustainable biomaterials have been extensively studied for energy-storage systems. This report mainly presents promising and cutting-edge applications of biomaterials in batteries, including printed batteries, 3D thick batteries, solid-state batteries, and bio-degradable batteries. The successful commercialization of CMC binder for anodes is an example of biomaterial-based batteries. However, despite the natural abundance and low cost, the biomaterials have not been fully utilized in commercial large-scale green batteries. This could be due to the limitation of the material manufacturing and structural engineering of the biomaterials. For example, the large-scale utilization of wood is restricted by the size of the wood slice or wood trunk. The production of chitosan is on a limited scale due to the difficulty and low economic effect of preparing chitosan from the relatively inert chitin. While the biomaterials are

eco-friendly and sustainable, the processing process, which could involve reactions such as harsh basic solution treatment and calcination, leaves a significant impact on the environment. Further research on biomaterial-based greener batteries should be devoted to the massive production of biomaterials with environment-friendly procedures. Via advanced engineering techniques, such as 3D printing as discussed, the biomaterials can be integrated into batteries as critical sustainable components for clean energy storage.

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