SULZER

White Paper

April 2024

Ultra-pure ethylene carbonate

Drive OPEX down to 1/3 with crystallization

Cut your OPEX costs by 3 with crystallization

To achieve ambitious CO_2 reduction targets set by the Paris Agreement, energy decarbonization, particularly through electrification, is crucial. This shift is expected to drive double-digit growth in the lithium-ion battery market. Organic carbonates, such as ethylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, fluoroethylene carbonate, and vinylene carbonate, play a crucial role as electrolyte solvents and additives in lithium-ion batteries. The demand for these compounds in energy storage and conversion technologies requires a higher purity level than their current applications. Traditionally utilized as solvents and additives in the plastic industry, these organic carbonates are now subjected to heightened purity standards to meet the rigorous requirements of advanced electrochemical applications. The tailored combination of distillation and falling film crystallization is vital to reach the electronic grade purity while ensuring high energy efficiency and recovery yield.

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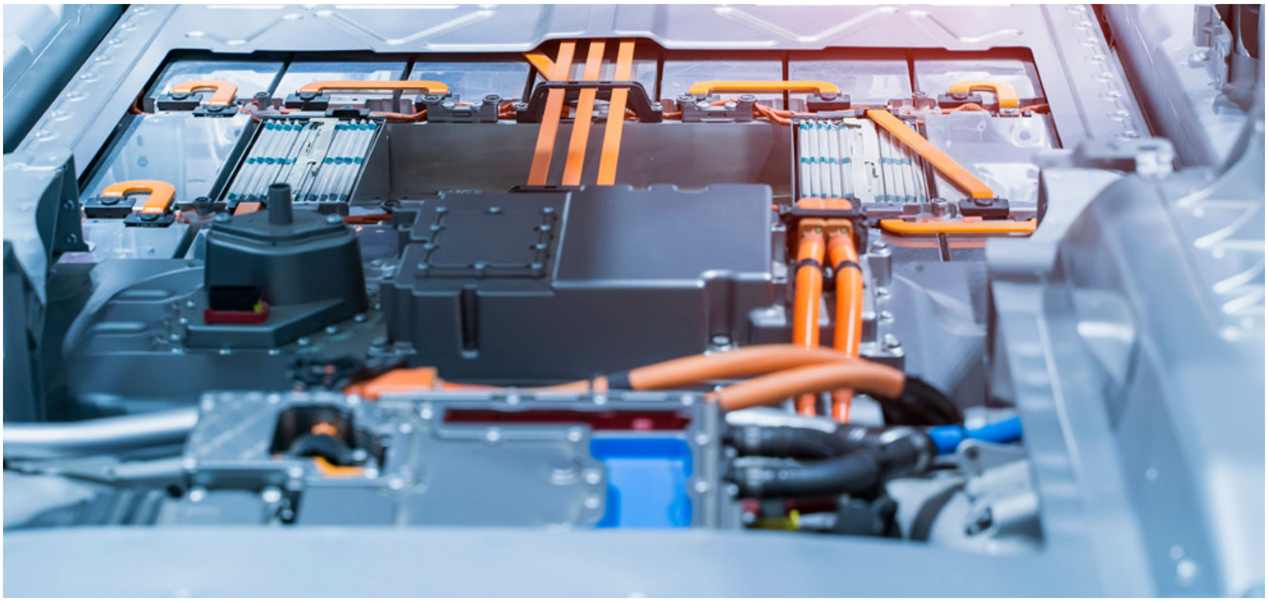
Introduction

Electrification reduces overall CO_2 emissions and enables the use of CO_2 as input in the production of organic solvents such as ethylene carbonate and dimethyl carbonate, further reducing already emitted CO_2. The Sulzer process of organic solvent purification centers around minimizing energy consumption, cutting the OPEX cost by 3 with crystallization, and ensuring high reliability and low maintenance solutions.

Due to resource scarcity in Europe and North America, recycling of battery material is becoming increasingly important. This paper will present how Sulzer mass transfer technologies, namely distillation and falling film crystallization, are deployed to meet the new demanding purity targets and energy constraints of ethylene carbonate production and how this can be extended to other organic solvents, including reclaimed streams.



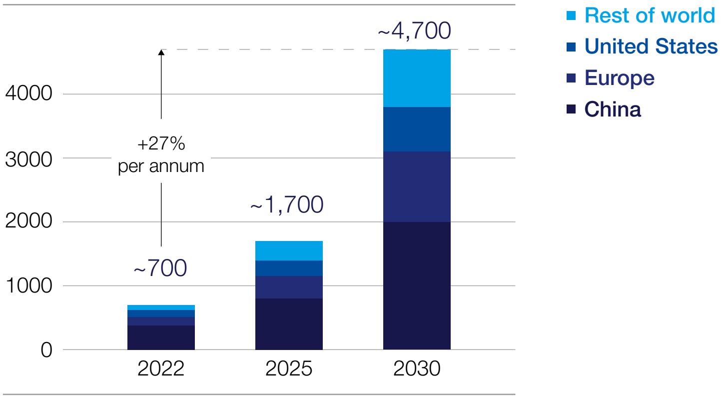
Market growth for lithium-ion batteries

Strongly driven by the rise of electric vehicles, lithium-ion (Li-ion) batteries demand should increase by 27% per year, from 2022 to 2030, according to McKinsey Battery study [1].

Global Li-ion battery cell demand by region, GWh, Base case

Including passenger cars, commercial vehicles, two-to-three wheelers, off-highway vehicles, and aviation.

Source: Lithium-ion battery demand forecast for 2030 | McKinsey [1].

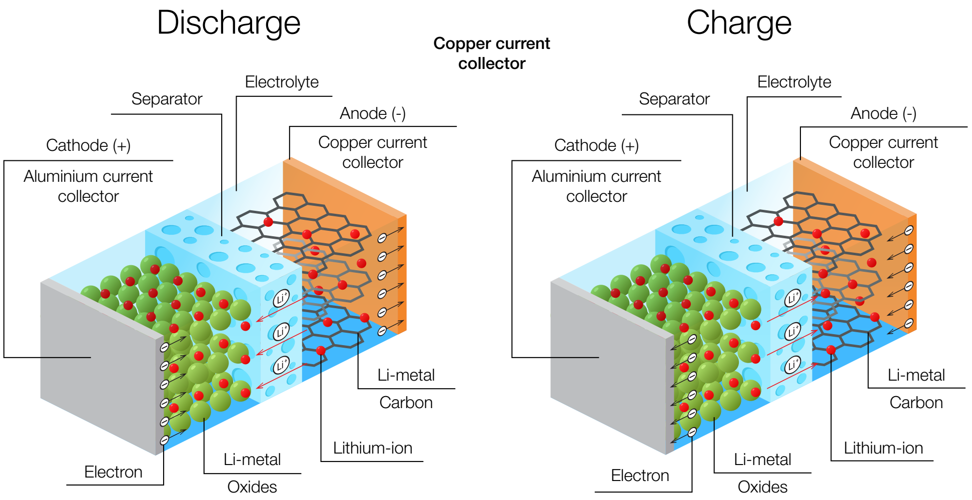


Due to its strong battery supply chain, China is expected to maintain its leading role in battery production along with a boost in production capacity in Europe and the United States. The Western World is forecasted to increase its battery production substantially, leading to an expansion of its share of the global production from the current 20% to 33% in 2030 (i.e. 1 out of 3 battery cells is expected to be produced in Europe or in the United States in 2030, according to the latest public capacity announcements) [1]. Mobility is by far the largest industrial sector contributing to the expansion of Li-ion battery demand in the coming years.

Battery composition

In technical terms, a battery is a device that generates electric power through one or more electrochemical cells. Its composition is tailored to meet specific application needs and varies according to different manufacturers' designs. Essentially, a standard battery comprises a cathode (positive electrode) and an anode (negative electrode), separated by a porous material and immersed in a liquid or solid electrolyte, as illustrated in the schematic below:

Lithium-ion battery



Among the diverse types of batteries available or under development in the energy storage sector are Li-ion, sodium-ion, redox-flow, and solid-state batteries. Currently, Li-ion batteries stand out as the most prevalent type. These batteries are characterized by their varied cathode compositions, which include Lithium Iron Phosphate (LFP), Lithium Nickel Manganese Cobalt Oxide (NMC), Lithium Nickel Cobalt Manganese Aluminium Oxide (NCMA), and Lithium Manganese Oxide (LMO), among others. Each composition offers unique benefits, shaping the battery's performance characteristics for different applications. Li-ion batteries are available from 1kW to 1MW and can discharge their electricity within minutes.

In Li-ion batteries, the electrolyte, despite representing only 10-15% of the battery's weight, holds a crucial function. It enables the essential movement of lithium ions between the cathode and the anode. The electrolyte's composition is critical in ensuring the battery's optimal performance over time. This mix consists of carefully selected organic solvents, specialized additives, and lithium salts, with each component contributing to the battery's overall efficiency, longevity, and safety.

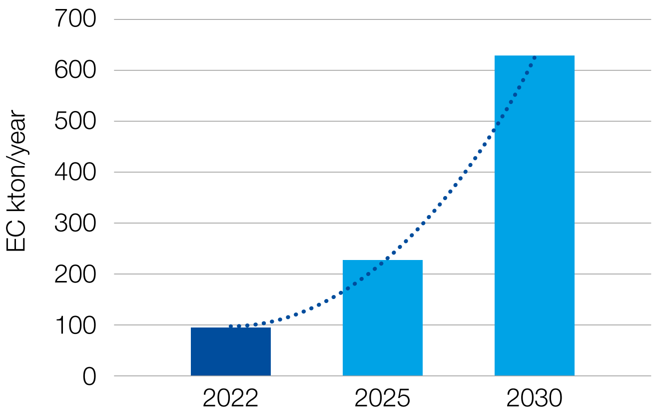
The most utilized organic carbonates (also known as organic solvents) in Li-ion batteries include ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC). Other organic carbonates, such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC), are often incorporated as additives. FEC is known for fostering a stable and protective Solid Electrolyte Interface (SEI), essential for battery longevity.

The specific recipes and precise compositions of these electrolyte mixtures are closely guarded secrets, forming part of the proprietary knowledge of manufacturing companies. This area is dynamic and continuously evolving, driven by the need to meet specific customer requirements, particularly in enhancing battery operability across a broader temperature range.

In the literature, the ratios of organic solvents are commonly mentioned for both ternary and quaternary systems. For a ternary system, a typical ratio by weight might be 1:1:1 (e.g., EC/DMC/EMC), whereas for a quaternary system, a ratio like 6:6:6:1 by weight (e.g., EC/DMC/EMC/DEC) is often cited. These ratios are pivotal in determining the electrolyte's overall performance characteristics [2, 3].

This paper focuses on ethylene carbonate, which is used as the basis for the case study, but the findings are also, in general, applicable to other organic carbonates.

Based on the abovementioned Li-ion batteries expansion and common electrolyte composition, the expected market demand for ethylene carbonate (EC) is expected to show a significant growth higher than 25% per annum in the coming decade.



Source: Estimated EC required in the marked based on battery demands as given above [1].

Benefits of high-quality ethylene carbonate and other carbonates

In Li-ion batteries, the purity of electrolytes is paramount. It impacts the battery's life, its efficiency, and safety. This chapter focuses on EC, as it is one of the most important solvent components in Li-ion batteries.

Graphitic carbon surfaces can form a Solid Electrolyte Interface (SEI) when exposed to ethylene carbonate, which is one of the main organic solvent capable of facilitating this process. The SEI is crucial for enabling the graphite anode to engage in reversible reactions with lithium ions over hundreds of cycles [4]. A higher purity level of ethylene carbonate in the electrolyte, characterized by extremely low impurities (such as metallic ions), enhances the cycling efficiency of the graphite anode.

Companies established different purity grades for solvent carbonates used in their battery cell (i.e. different definitions of battery grade). Typically, battery-grade ethylene carbonate is expected to surpass 99.99% purity, with water content restricted to less than 50 ppm, and often reduced further to less than 10 ppm [5]. It is widely acknowledged that the higher the purity, the better the battery performance and safety, as highlighted in the following paragraphs.

Effects of water on battery performance and battery safety

Water can react with lithium salts, such as lithium hexafluorophosphate (LiPF6), to form unstable and reactive compounds, which can lead to the decomposition of the electrolyte, causing the release of harmful gases and contributing to the formation of deposits on battery electrodes. These deposits can hinder the movement of lithium ions, reducing the battery's capacity and efficiency.
It is well known that organic carbonates are hygroscopic. This is especially true for EC, which not only shows high affinity with water, but it also reacts with it and forms ethylene glycol and carbon dioxide (hydrolysis). This reaction is worsened in the presence of hydroxide ions (OH-), as also mentioned in [6]. Water can also reduce the electrolyte's ionic conductivity, making it less effective at transporting lithium ions. This can lead to slower charging and discharging rates, reduced cycle life, and increased heat generation.

Finally, water can initiate side reactions that degrade the battery's materials, including the cathode and anode electrodes, compromising the battery's performance and safety.

Even trace amounts of water can affect battery safety by increasing the hygroscopicity of the electrolyte, making it even more likely to absorb moisture from the environment. This increased moisture content can further accelerate the reactions mentioned above, leading to higher temperatures and potential thermal runaway.

Water can also undergo electrolysis in the presence of lithium salts, generating hydroxyl radicals (•OH), which can initiate further degradation of battery materials, increasing the risk of fire or explosion [7].

Effects of methanol and acid impurities on battery performance and safety

Methanol can react with lithium metal to form lithium aluminum hydride ($LiAlH_4$), a highly flammable and volatile compound. It can also react with the organic solvents in the electrolyte, such as ethylene carbonate (EC) or dimethyl carbonate (DMC), forming decomposition products that can reduce their solubility and conductivity. Moreover, it can oxidize to carbon monoxide (CO) and carbon dioxide (CO_2) on the electrodes, contributing to the formation of carbon deposits. Side reactions that consume lithium ions reduce the battery's capacity and efficiency in the presence of methanol.

Organic solvents like EC can also contain acidic impurities, such as hydrochloric and acetic acids. These acids can corrode essential battery components, drastically reducing the efficacy of the electrolyte. In addition, they can react with lithium salts, causing the formation of harmful gases and further degradation of battery materials. The presence of these acids not only impairs battery performance but also poses risks to the overall battery integrity.

Less energy is required to support decarbonization: a combination distillation and crystallization to purify EC

Achieving the electronic grade purity of EC, also called ultra-high purity or Electrical Vehicle (EV) grade, involves a careful balance between maintaining high energy efficiency and ensuring a substantial recovery yield. The optimal method for this is combining distillation and fractional melt crystallization.

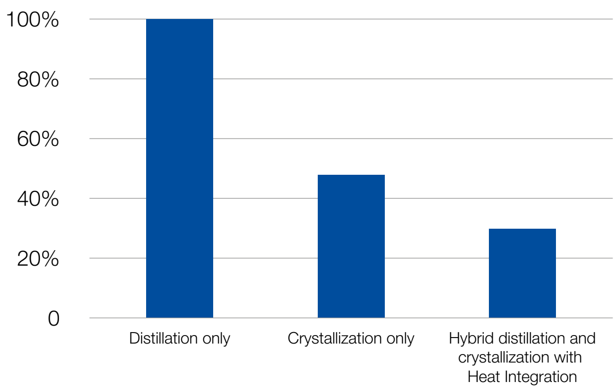
The three fundamental aspects to consider in this process are the purity targets, recovery yield and energy consumption, and their interconnection.

Distillation technology has the potential to achieve a purity level of 99.99%, although with some difficulties, such as energy efficiency, thermal degradation of the product, and challenges on the yield. Because of the nature of impurities (co- and/or close boilers), it is extremely energy-intensive to use distillation to achieve such high purity requirements. This is particularly true for EC, as boil-up and reflux ratios need to be pushed to the limit to meet the specification, leading to lower recovery yield, high energy consumption, and extended residence time, further promoting product degradation. As an alternative, slightly relaxing the specifications at the distillation outlet offers a dual advantage: significantly lowering energy consumption and enhancing recovery yield. While distillation technology excels in providing high purity, it needs careful management to balance energy efficiency and product quality.

On the other hand, fractional melt crystallization, in particular falling film crystallization, can purify to more than 99.999% while also ensuring water content lower than 10 ppm. For the operational expenditure (OPEX) associated with crystallization, the most energy-efficient approach when aiming for ultra-high purity involves starting with a partially purified feed. This not only optimizes the working range from an energy perspective but also reduces the capital expenditure (CAPEX) of the crystallization unit, as achieving the final purity requires fewer crystallization stages.

The crystallization process relies on partially freezing the initial liquid mixture by gradually decreasing its temperature. The frozen-out solid phase exhibits a different chemical composition than the remaining residual liquid. This phenomenon is the basic physical rule of the fractional melt crystallization process. More information is available in the public domain, such as in the Chemical Engineering FAYF publication (March 2023) [8]. Falling film crystallization technology is the perfect solution for the purification of EC: it can handle high throughput and achieve very high purity. It is robust and extremely easy to operate, without maintenance or replacements needed throughout its lifetime. Thanks to these characteristics, it has already been used for more than 30 years in the chemical industry where extremely high purities need to be obtained, for instance, glacial acrylic acid, food grade benzoic acid, and optical grade BPA. By combining the strength of both distillation and crystallization separation technologies, it is possible to achieve the highest quality (targeting 99.999%), not only without any compromise on the yield but also, most importantly, with a minimized energy consumption (lower overall OPEX), and optimized initial investment (CAPEX).

With distillation and crystallization technologies available in its portfolio, Sulzer can develop a fully integrated and optimized solution. Moreover, heat integration between the utilities of the two mass transfer processes can further foster the reduction of external energy consumption. This is achieved using the heat recovered at the condensers of the distillation process as a heat source for the crystallization melting phase.

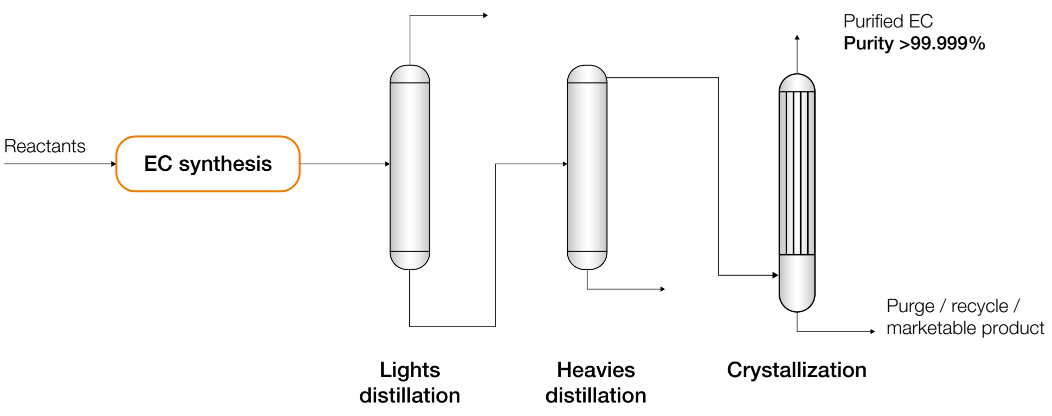


Thermal energy to produce 1 ton of EC at 99.99 wt.%

For comparison, the chart above represents the energy required to purify a post-reaction EC stream to 99.99% by distillation only, crystallization only, and hybrid with heat integration. Clearly, the hybrid system substantially outperforms both single technology processes, with an overall OPEX reduction of 3 folds compared to a single distillation solution.

Calculating the optimal distillation/crystallization interface point is key to reducing energy consumption, optimizing the yield, reducing the waste stream, and maximizing production while keeping the size of the equipment small.
The simplified flow diagram below illustrates the process, incorporating upstream distillation technology to purify the complex reaction mixture into an intermediate purified material. The downstream process involves melt crystallization, focusing on achieving ultra-pure ethylene carbonate.

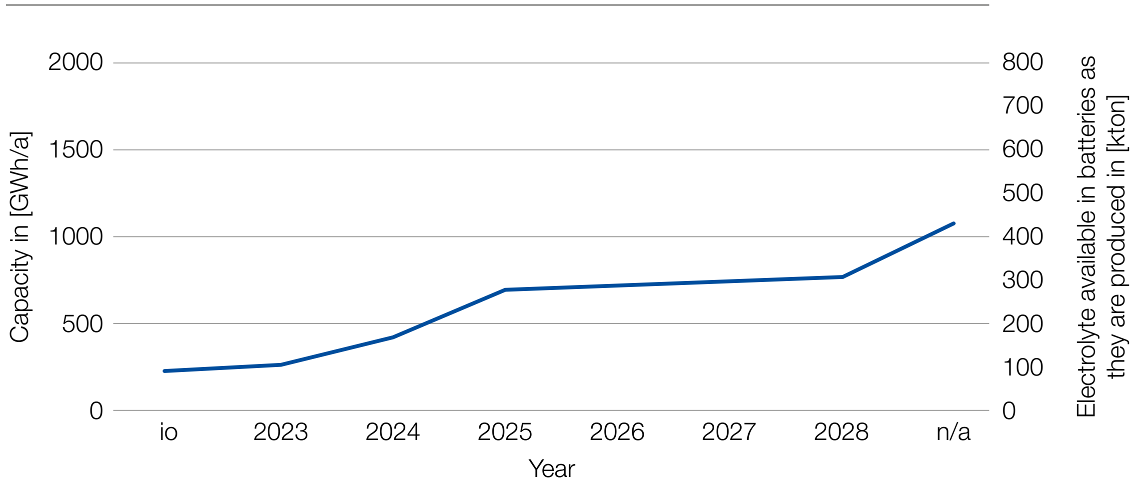
EC purification through hybrid distillation-crystallization method



Recycling of organic solvents: challenge and opportunity

With an ever-increasing number of electric vehicles produced yearly, recycling volumes of batteries and electrolytes must increase rapidly to achieve net-zero targets. For example, European installed capacity follows the world trend, and more and more gigafactories are in operation (io) or in the construction phase [9].

Europe: installed capacity in GWh/a and equivalent of kton of electrolyte (at the time of battery production)



Source: Estimated European capacity of gigafactories in operation or forecasted, based as above [7].

In addition, in the European Union, one of the largest markets for batteries, there's a growing focus on recycling used Li-ion batteries. This approach is not just economically attractive but also essential due to the scarcity of raw materials in the region. The European Union's legislation, in particular the "Regulation of the European Parliament and of the council concerning batteries and waste batteries" (further referred to as "The Regulation" [10]), underscores the importance of a circular economy in battery development. It sets ambitious targets for battery recycling, aiming for a 65% recovery of lithium-based batteries by 2025, increasing to 70% by 2030. Additionally, The Regulation mandates efficient material recycling, targeting a 95% recovery rate for lithium by 2030, and ensures that recycled materials like cobalt, lithium, nickel, and lead are reintegrated into new batteries.

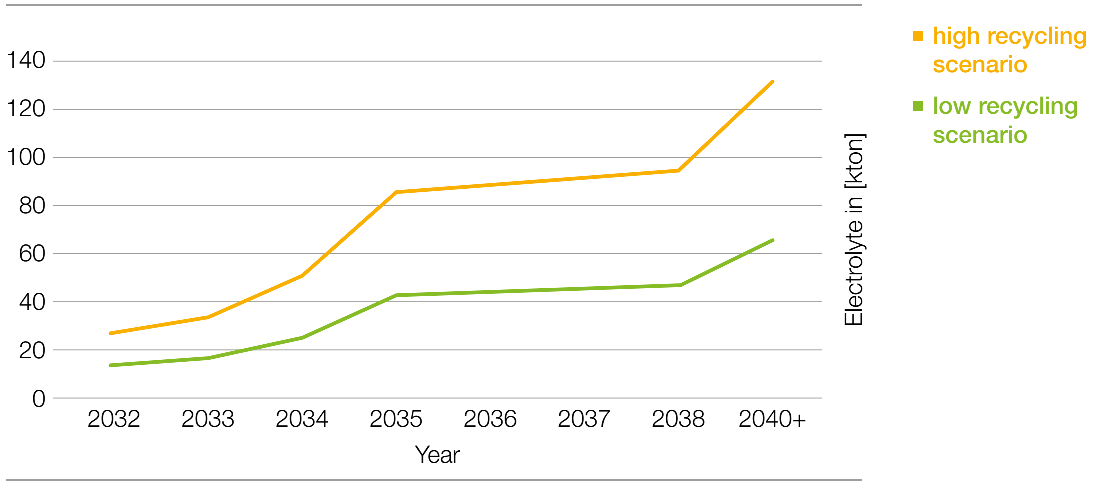
A striking testament to the power of regulatory frameworks driving innovation is the case of lead-acid battery recycling. In the early 1990s, lead-acid battery recycling was virtually non-existent. However, spurred by robust regulations and technological advancements, the industry witnessed a remarkable transformation. By the end of that decade, the recycling rate had soared to an impressive 98%. This rapid progress not only highlights the effectiveness of targeted environmental policies but also demonstrates their capacity to yield substantial results within a relatively short span of time.

Presently, battery recycling employs three primary methods: direct, pyrometallurgical, and hydrometallurgical processes, essentially focusing on recovering cathode materials from spent Li-ion batteries [11, 12]. However, there is a trend towards recycling electrolytes and reclaiming their valuable components. Emerging companies are investing in advanced recycling technologies, such as the mechanical thermodynamic Duesenfeld Recycling process, which claims high efficiency in recovering battery materials and electrolytes [13], and the newly established European project, HORIZON, the target of which is to recover not-active material from the end-of-life battery (amongst them solvents such as EC, DEC, DMC, etc) [14]. This evolution in recycling technologies is key to strengthening the EU's battery supply chain and sustainability efforts.
To get forecast for the growth of the electrolyte recycling market, several factors need consideration. First, the lifespan of batteries varies based on usage: typically, 8-12 years for personal vehicles and 15-20 years for commercial applications. This variation indicates a substantial and increasing volume of electrolyte materials in Europe destined for recycling, conversion, or landfill disposal, as stipulated by The Regulation.

To capture the potential of this market, two scenarios have been formulated: low recycling and high recycling. These scenarios are derived from key factors considered in the analysis of the battery recycling framework, including the composition of the electrolyte, initial and enhanced electrolyte recycling rates, and the recycling recovery rate.

These scenarios provide context for understanding the potential scale and evolution of the electrolyte recycling market in the context of Europe's growing focus on sustainable battery use and disposal.

Europe: kton of electrolyte available for re-purifying, high recycling and low recycling scenarios



The composition of the electrolyte mixture is typically around 80% organic solvent, complemented by 5% additives and 15% lithium-based salts.

Upon reaching a recycling facility, the material undergoes a thorough purification process. It's estimated that from every ton of used organic solvent processed, about 900 kg can be successfully reclaimed and repurposed for use in new battery electrolytes. This high recovery rate underscores the efficiency of modern recycling techniques.

The recycling process is also possible due to the combination of distillation and crystallization, which would lead to the split and purification of the organic solvent. The theoretical study shows promising results, and the experimental phase will be undertaken in the near future. The recycling process is expected to decrease costs, energy consumption, water use, and SO_x emissions, and more emphasis is given to building up efficient processes throughout the battery production chain. However, the challenges of battery recycling involving the extraction of electrolytes bear some risks that need to be duly addressed. One of the many challenges is the potential formation of hydrogen fluoride (HF) due to lithium salts, especially LiPF6, which is the cause of material corrosion and the formation of extremely toxic material.

Conclusion and take-away

The demand for battery materials is increasing due to the growing popularity of electric vehicles and other electronic devices. High-purity organic solvents, such as ultra-pure ethylene carbonate (EC), are required to ensure high performance of a battery and can be obtained with high yield and minimizing energy consumption, thanks to the optmized Sulzer combination of distillation and falling film crystallization technologies.

Recycling of batteries, including their electrolytes, is also becoming increasingly important to reclaim valuable materials and reduce environmental pollution. In the future, the recycling of electrolytes will become even more crucial as the number of spent batteries increases and the overall recycling chain is better established.

At Sulzer, we are excited to be at the forefront of innovation in this field. Collaboration between technology and research has allowed us to reach new heights in the development of ethylene carbonate of ultra-high purity, while cutting the OPEX cost by a factor 3. We are committed to continuing our work in this area to provide the best possible solutions for our customers.

References

[1] McKinsey Battery Insights – supply model, team analysis Q4 2022
https://www.mckinsey.com/industries/automotive-and-assembly/our-insights/battery-2030-resilient-sustainable-and-circular

[2] Electrolyte Solutions for Rechargeable Li-Ion Batteries Based on Fluorinated Solvents by Ortal Lavi, Shalom Luski, Netanel Shpigel, Chen Menachem, Zvika Pomerantz, Yuval Elias, and Doron Aurbach
https://pubs.acs.org/doi/10.1021/acsaem.0c00898

[3] Liquid electrolyte development for low-temperature lithium-ion batteries by Dion Hubble, David Emory Brown, Yangzhi Zhao, Chen Fang, Jonathan Lau, Bryan D. McCloskey and Gao Liu

[4] Primitet specification available at
https://primetlab.com/battery-grade-ethylene-carbonate-ec-high-purity/

[5] Challenges in Development of Low Cost Lithium Ion Battery Materials for Grid Applications by Dee Strand, Ke Zhang, Ye Zhu
https://www.huntsman.com/docs/Documents/Impact%20of%20Purity%20in%20UPEC%20on%20Battery%20Performance.pdf

[6] Lithium ion battery degradation: what you need to know by Jacqueline S. Edge, Simon O'Kane,Ryan Prosser, Niall D. Kirkaldy,Anisha N. Patel, Alastair Hales, Abir Ghosh, Weilong Ai, Jingyi Chen, Jiang Yang, Shen Li, Mei-Chin Pang, Laura Bravo Diaz, Anna Tomaszewska, M. Waseem Marzook, Karthik N. Radhakrishnan, Huizhi Wang, Yatish Patel,Billy Wu and Gregory J. Offer
https://pubs.rsc.org/en/content/articlehtml/2021/cp/d1cp00359c

[7] Hydrolysis of Ethylene Carbonate with Water and Hydroxide under Battery Operating Conditions by Michael Metzger, Benjamin Strehle, Sophie Solchenbach and Hubert A. Gasteiger https://iopscience.iop.org/article/10.1149/2.0411607jes

[8] https://www.chemengonline.com/facts-at-your-fingertips-fractional-solvent-free-melt-crystallization/

[9] Build-up of the battery industry in Europe – status quo and challenges in Market Analysis Update Q2 2023 available at
https://www.ipcei-batteries.eu/fileadmin/Images/accompanying-research/market-updates/2023-07-BZF_Kurzinfo_Marktanalyse_Q2-ENG.pdf

[10] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52020PC0798
ANNEX XII Treatment and recycling requirements

[11] European battery recycling: an emerging cross-industry convergence by Rodrigo P. Navarro, Dr. Philipp Seidel, Michael Kolk, Alexander Krug, Luca Lenz
https://www.adlittle.com/en/insights/viewpoints/european-battery-recycling-emerging-cross-industry-convergence

[12] A qualitative assessment of lithium ion battery recycling processes by Roberto Sommerville , Pengcheng Zhu , Mohammad Ali Rajaeifar, Oliver Heidrich, Vannessa Goodship Emma Kendrick https://www.researchgate.net/publication/344948988_A_qualitative_assessment_of_lithium_ion_battery_recycling_processes

[13] Ecofriendly recycling of lithium-ion batteries https://www.duesenfeld.com

[14] HORIZON-CL5-2024-D2-01-01: Advanced sustainable and safe pre-processing technologies for End-of-Life (EoL) battery recycling (Batt4EU Partnership)
https://ec.europa.eu/info/funding-tenders/opportunities/portal/screen/opportunities/topic-details/horizon-cl5-2024-d2-01-01

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