

The Pitfalls of Deep Eutectic Solvents in the Recycling of Lithium-Ion Batteries

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The exponentially increasing demand for lithium-ion batteries and their limited lifetime lead to a significant increase in spent batteries. With the goal to address the sustainability and recyclability to minimize negative effects for the environment, an efficient process is vital to recover valuable materials from spent batteries by recycling. In this regard, deep eutectic solvents (DESs) have attracted huge interest, due to their unique ability to efficiently extract valuable metals from spent batteries, while also being rendered greener and more cost-effective compared to current pyrometallurgy and/or hydrometallurgy. However, the DES approach also has its own set of challenges and drawbacks, which hinder the widespread use in the industry, including its restricted recyclability, high viscosity, low thermal and chemical stability, complex chemistry, as well as limited scalability. In this perspective, it is claimed that ongoing future research on the recycling of lithium-ion batteries requires the exploration of alternative processes including modification of current hydrometallurgy processes, if the consistent improvements cannot be achieved in DES system for recycling valuable elements.

1. Introduction

Lithium-ion batteries (LIB) have reconstructed the modern world offering high capacity, high energy density, and a longer lifetime for portable consumer electronics compared to other batteries.^[1,2] Furthermore, the global transition from fossil fuel-based vehicles to electric vehicles (EVs) relies heavily on the production


of LIB, which uses resources like the functional metals Ni and Co, as well as Li, Mn, and Al. It is estimated that by 2030, if all EV targets are met, there will be ≈ 140 million EVs on the road.^[2] As a result, a vast amount of spent LIB will be accumulated in the near future.^[3] Therefore, it is crucial that the recycling processes be understood, optimized, and scaled to minimize environmental impacts and to maximize the usage of already mined and used materials. Currently, the most common practices of LIB recycling are pyrometallurgy and hydrometallurgy. The pyrometallurgy approach involves high-temperature processes, such as smelting and roasting to extract metals. It is energy intensive and only few selected metals can be recovered in alloy form. Hydrometallurgy utilizes acids and extractants to leach metals and then to precipitate into high-purity precursors for new cathode materials.^[4,5]

Hydrometallurgy does not require as much energy as pyrometallurgy along with reduced CO₂ emissions. However, the process poses potential risks to workers and the environment.^[6] More research is needed to lower the negative impact of hydrometallurgy on the environment. Pyrometallurgy and hydrometallurgy have been widely employed in the industrial recycling chemistry, and combined processes are typically adopted with its own set of advantages and limitations. Other more environmentally friendly approaches include direct recycling. The primary goal of direct recycling is to repair the cathode active material by healing the defects that cause the major problems of capacity loss instead of complete disintegration of the LIB. It is a promising alternative to conventional recycling processes, since low energy and chemical input are anticipated. Similar to direct recycling, it is possible to develop nondestructive recycling processes taking spent LIB as second raw material that otherwise would be waste.^[5,7] With the utilization of the residual value of retired batteries, in contrast, the spent battery is repurposed to other stationary energy-storage devices, if the capacity does not meet the requirements for EV batteries.^[8] The hydrometallurgy approach currently seems to be the most attractive approach for extracting valuable metals from LIB with high selectivity and facile industrial implementation, but the resulting large amounts of slag deposits will be a burden to the environment.^[9]

Deep eutectic solvents (DESs) have been proposed as novel alternative green solvents for metal leaching from LIB, replacing

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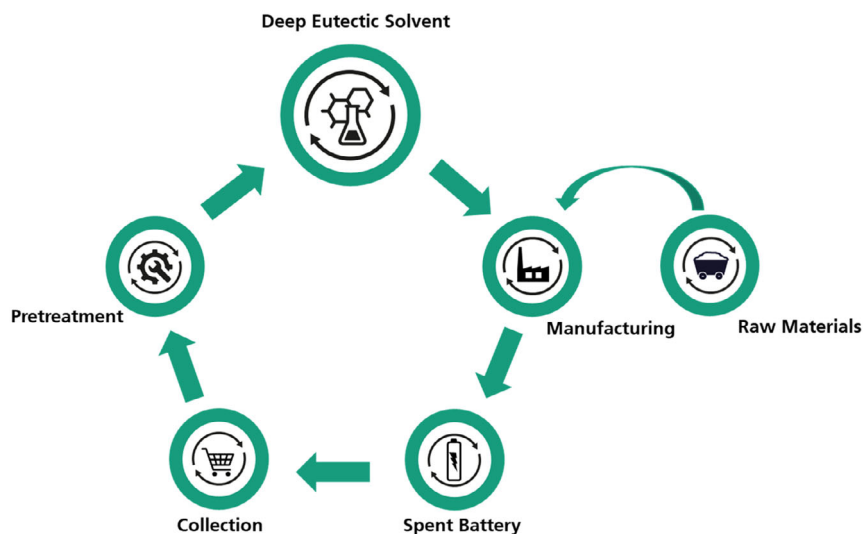


Figure 1. Battery recycling by using deep eutectic solvent from raw materials into secondary raw materials.

conventional acidic or organic solvents as shown in **Figure 1**. This process is termed as ionometallurgy.^[10] DES is a binary or ternary eutectic mixture, consisting of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA) linked through hydrogen bonding. The melting point of the DES mixture is much lower than the pure components alone and is usually liquid at room temperature.^[11] They have several advantages like adjustable polarity, low volatility, facile synthesis, as well as rational design and tunability in compositions.^[11,12] The most prominent DES for the extractive metallurgy of cathode active materials consists of mostly quaternary ammonium salts like choline chloride (ChCl) as HBA in combination with ethylene glycol (EG) or urea as HBD.^[13] Tran et al., e.g., have achieved leaching efficiencies of 89.8% for Li and 50.3% for Co from spent LiCoO₂ (LCO) with a DES based on ChCl and EG at 180 °C for 24 h.^[14] For lithium nickel manganese cobalt oxide (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂), leaching efficiencies as high as 70.8% for Li and 31.7% for Co were obtained under same conditions, which are overall lower compared to traditional hydrometallurgy processes.^[15] Generally, extraction efficiencies can be varied by using different HBD in DES, but similar efficiencies could be also achieved by using other type of DES such as urea or oxalic acid as HBD.^[16,17] In case of oxalic acid, extraction efficiencies are comparatively higher compared to other HBDs to be used. Zhu et al. reported that over 90% of Li and Co can be fast leached within 4 min in the ChCl–EG–urea/lactic acid DES system by using microwave-assisted heating method.^[18] By using DES, recovery and regeneration of anode graphite from spent LIBs have been also proposed as novel alternative.^[19] However, DES reveals disadvantages that prevent its broad usage for the battery recycling industry. In this perspective, the challenges of DES are discussed. Unjustified reusability, high viscosity, and low thermal and chemical stability are described more in detail.^[11,17,20] Due to these disadvantages, the broad use of DES in LIB recycling is limiting the practical applications in closed-loop battery recycling. Judging from the current situation, careful and special attention must be paid to

the potential drawbacks and challenges associated with DES in LIB recycling.

2. Discussion

2.1. Recyclability

The recycling and reuse of DES after the leaching process in industrial settings is a significant barrier and influenced by various factors. Typically, the solution after hydrometallurgy process contains acid or base. Research on the reusability of the solution after the hydrometallurgy process has been crucial for current LIB recycling. Notably, this is one of the important issues in terms of sustainable development of recycling technology. Likewise, reusability of solution becomes more important for the overall cost reduction when DES is considered as it is relatively more expensive than conventional acidic solvents. In our understanding, solution reuse after hydrometallurgy process is not a standard procedure yet. From the literature, it can be inferred that the leaching process consumes and decomposes components of the DES, thereby reducing its capability and may lead to decreased chemical stability.^[20,21] Over subsequent recycling cycles, consumed DES may result in decreased interaction between DES and materials in contact, which could ultimately impact the effectiveness of leaching and jeopardize the sustainability of the recycling process. The question is whether or not a purification step can restore the original properties of the DES after leaching and also its performance after multiple cycles can be retained. The original composition of DES could be partially restored, but full recovery of the DES characteristics is still not proven to be possible. For example, Morina et al. reported that the DES system consisting of ChCl and lactic acid could be recycled up to three times after leaching and extraction before its capacity begins to decline.^[22] The multiple recyclability of DES to more than several tens of cycling times has not been reported. The calculation of the life cycle costing relies on a robust data set for the process, i.e., on the exact number of cycles required for a

cost-efficient process for commercialization. Further research would be needed to have a better understanding of the limiting chemical processes for reduced cycle counts. Nevertheless, the recyclability of even less than 10 times shown in the previous studies will be one of the challenges for an industrial perspective, especially given the high cost of DES components. Therefore, more focus should be paid to the recycling of DES for multiple cycles to assess the overall reusability, instead of focusing only on several times leaching and its efficiency improvement, since this is pivotal for the future of DES in the extractive metallurgy of cathode active materials. Keeping the ratios of chemical species constant throughout the recycling process is also critical for the recycling of DES. Any variation from the original ratios of HBA and HBD can drastically affect the DES characteristics reducing its leaching efficiency. Degradation or loss during recycling may be brought on by chemical reactions, contaminations, or unintentional changes in its composition, which in the end makes it even harder to recycle. Nevertheless, it should be mentioned that facile tunability of composition is one of the advantages demonstrating that DES can be still recovered for well-designed leaching and extraction of LIB with different cathode compositions.

2.2. High Viscosity

One of the other major issues of DES as leaching agent is its high viscosity. For example, one of the most extensively utilized DESs based on ChCl and urea exhibited a viscosity of ≈ 750 cP at 25 °C, which is much higher compared to other traditional solvents.^[23] Mass transport is limited, which in turn slows the kinetics of leaching. This restriction may lower the overall efficiency of the metal extraction.^[12] Slow diffusion rates make it difficult for DES to reach particle surfaces, lengthening the leaching procedure and in the end lowering metal recovery yields. The high viscosity matrix hinders the transfer of extracted metals, making the following separation procedure more difficult. The higher the solid to liquid ratio is, the stickier system is produced. This is naturally harder to handle, stir, and pump from an engineering perspective.^[17] Although low volatility of DES is frequently mentioned as a benefit, this characteristic paradoxically makes it more difficult to separate metals from the solvent without washing since it is not possible to evaporate the solvent from the resulting solution. As extracted metals accumulate, the viscosity of DES may further rise, aggravating mass transfer and impeding effective leaching.^[20] Particularly when aiming for high metal recovery rates, this amplifying viscosity might constitute a serious bottleneck for the industrial implementation. Research introducing water or other organic liquids into DES formulations to reduce the high viscosity has been investigated.^[17] By altering viscosity, these additives can speed up mass transfer rates and make metal separation easier. When EG is used as HBD, DES showed a viscosity of 48 cP at 25 °C, which is much lower than that of urea DES.^[24] Nonetheless, part of its unique advantages of DES would be lost, and an additional step is needed to eliminate the dilutant. Hence, the goal of ongoing research is to pinpoint the ideal solvent mixtures that may effectively leach metal ions while also keeping low viscosity without losing unique properties of DES.

2.3. Thermal and Chemical Stability

The lack of thermal and chemical stability poses another challenge. For example, low thermal stability at high temperature is one of the critical issues in DES. Peeters et al. showed that DES of ChCl and EG is not stable and form toxic decomposition products at 180 °C, where the leaching efficiency is the highest.^[25] Research and development are currently underway to address the chemical stability. The decomposition products were found to be present for the DES of ChCl and EG.^[26] Hence, further studies would be necessary to clarify the thermal and chemical stability of each DES with varied composition and its respective leaching mechanism, so the leaching efficiency and selectivity can be kept constant throughout the entire recycling process. Achieving higher efficiencies at lower temperature was possible for some DES. For instance, Luo et al. showed that the leaching rate of Ni, Co, Mn, and Li can reach 99% at 140 °C within 10 min by using the DES of betaine hydrochloride (BCL) and EG.^[27]

2.4. Complexity

Hydrometallurgy has achieved better leaching efficiencies than DES in all types of cathode active materials. Currently, hydrometallurgy has been developed and deployed as mature industrial processes. To achieve the efficiency of state-of-the-art hydrometallurgy, DES-based leaching techniques should be further improved. The recycling of LIB by using DES is still in the early stages, but it is gaining momentum. Several research institutes, universities, and companies are working on DES. DES-based approach depends on the composition and chemical conversions of the deployed DES type, process and cathode active materials. Designing efficient extraction methods by using DES has to be adjusted to the dynamic changing interactions between DES components and metal ions in LIBs. Due to the distinctive characteristics of each DES and of each cathode active materials with its own properties, the leaching efficiency and the selective recovery of metals are found to be significantly varied although different types of DES in general have a similar leaching mechanism.^[13] For a widespread application, DES should be compatible with a varied chemistry of cathode active materials. Research progress has been made recently to further understand the leaching mechanism in DES with ChCl and EG.^[13,28] Wang et al. suggested a novel screening method by using electrochemical principles that can be used for the determination of suitable DES systems to recycle LIB.^[29] Further studies are in progress and requested for future breakthrough in new type of DES for a better understanding of the kinetics in the context of process complexity in LIB recycling.

2.5. Sustainability and Feasibility

Although DESs show the feasibility in metal recovery in LIB recycling, potential environmental issues should be addressed. DES are typically regarded as greener substitutes for conventional acidic solvents, but the production and disposal needs to be investigated in terms of environmental criteria together with waste management for a comprehensive eco inventory.

The environmental impact has to be further investigated and evaluated for each DES depending on the individual compositions. Although DES consists of nontoxic materials, it can be converted to more toxic components when it decomposes due to the poor chemical stability at elevated temperatures.^[25] Reducing the environmental impact is vital for a sustainable transition toward green battery recycling and a carbon emission-free industry. Therefore, potential environmental loads and resources consumed in each process needs to be monitored and evaluated. Life cycle assessment studies and toxicological data would be in the end crucial for the evaluation of environmental impacts of the DES approach to recycle LIBs. Lastly, frequently overlooked is the cost of DES. In general, they are less expensive than ionic liquids, although the cost is greatly influenced by the individual components of DES.^[30] Nonetheless, the cost of DES alone is not effectively lower than traditional acid-based metal-extraction systems, which should be evaluated in terms of the economic feasibility.^[13] Converting current industrial processes and equipment to handle DES process will be an additional capital-intensive expenditure. Therefore, it is not clear if such a process using DES would be feasible in large scale operations, since there are no pilot-scale plants to be proven otherwise. Hence, efforts to go from lab-scale studies to pilot-scale tests are needed as a first step to verify the feasibility of DES in LIB recycling. In the end, future efforts should be devoted for a comprehensive description of the reaction mechanism related to thermodynamic and kinetic data of the leaching process in DESs at a molecular level. Newly discovered DES by the research community would result in more sustainable and feasible recycling process.

3. Conclusion

DESs have been regarded as potentially useful leaching agents for LIB recycling. In this perspective, practical obstacles preventing widespread utilization of DES are discussed in industrial settings. DES is not a solution that can address all LIB recycling issues allowing the energy transition to be clean and more sustainable. The arguable reusability, high viscosity, poor thermal and chemical stability, complex chemistry, as well as high-cost and scale-up issues have remained a bottleneck for practical applications. Industries are reluctant at the moment to consider adopting new DES-based recycling methods although significant scientific advancements have been continuously reported. Not only the scientific understanding and knowledge accumulation on DES for LIB recycling, but also the development and deployment of scalable and economically persuasive technologies that industry can adopt with the promise of potential benefits are anticipated.

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Conflict of Interest

The authors declare no conflict of interest.

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