Separation technologies for the resource recycling of lithium-ion batteries

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ABSTRACT: Demand for lithium-ion batteries is expected to grow rapidly, especially for automotive and mobile applications, due to their high energy density, voltage, and long cycle life. Therefore, the establishment of their resource circulation is also an urgent task. This presentation will provide an overview of the recycling process for lithium-ion batteries, in which energy-saving and highly efficient separation processes have been developed by combining various separation unit operations such as disassembly, heating, reduction, grinding, physical separation, and hydrometallurgy. I will also introduce a novel original separation technology using the electric pulse method for the direct recycling of lithium-ion batteries.

KEY WORDS: lithium-ion battery, recycling, separation, dismantling, electrical pulsed discharge

1. INTRODUCTION

It is our unquestionable desire to enjoy an economically rich and convenient life while improving the wellbeing of humankind. On the other hand, both environmental impact and resource consumption have been steadily increasing along with these activities. It is well known that the concept of planetary boundary has been organized for environmental burdens, and that some environmental burdens have already exceeded the boundary beyond repair, leading to the adoption of the SDGs. Therefore, "decoupling," in which necessary environmental burdens are reduced and resource consumption is curbed while well-being is improved, is once again being emphasized (Fig.1). However, it has been pointed out that decoupling both this environmental impact and resource consumption is very difficult with the extension of current economic activities.

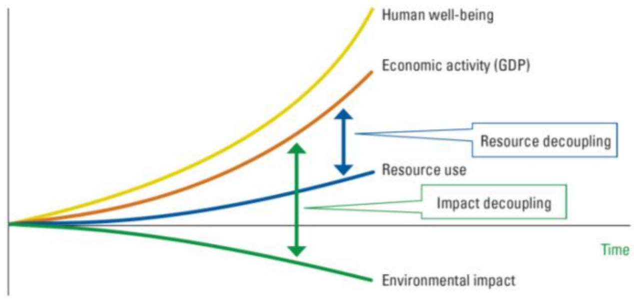

Fig.1 Resources decoupling and Impact decoupling to achieve Human well-being [(1)]

For example, the IEA points out that if the world takes action based on a policy of promoting carbon neutrality, the amount of minerals required will increase rapidly and the supply-demand balance will be disrupted [(2)]. The largest impact is estimated to be from the construction of electric power networks and the introduction of electric vehicles and storage batteries, and there is a concern that the supply-demand balance for lithium, cobalt, nickel, copper, and other minerals will be disrupted. Even for the base metal copper, many researchers point to an imbalance between supply and demand in the near future [(3)]. Lithium-ion batteries have become mainstream, and are essential as a means of energy storage in an electrified society and are one of the key technologies for achieving carbon neutrality. In particular, demand for lithium-ion batteries is expected to expand rapidly for applications such as the electrification of mobility (e.g., electric vehicles), supply and demand adjustment of renewable energy power, and infrastructure functions that support the foundation of a digital society, including various IT devices and backup power sources [(4)].

The Circular Economy is attracting attention as one of the means to achieve this goal, that is, both the environmental impact and resource consumption. The Ellen MacArthur Foundation's Butterfly Diagram (Fig.2), a conceptual diagram of the Circular Economy, shows that the right-hand circulation loop for exhaustible resources and the left-hand circulation loop for renewable resources should be divided and controlled [(5)]. For the circulation of exhaustible resources on the right side, sharing, maintenance, reuse, repair, refurbish, and recycling become multiple loops in order from the inside, and by circulating them in an inner loop as small as possible, a large effect is expected in terms of energy conservation. In other words, first, sharing is used to provide effective services while saving materials, and then maintenance is used to extend the service life, followed by reuse to reutilize functions as much as possible, followed by separation and recycling as materials when functions can no longer be reused. This multiple loop is controlled from the perspective of flow and stock to optimize the overall circulation, and the energy required for the circulation is implemented within the scope of renewable energy, which is an important concept in the circular economy.

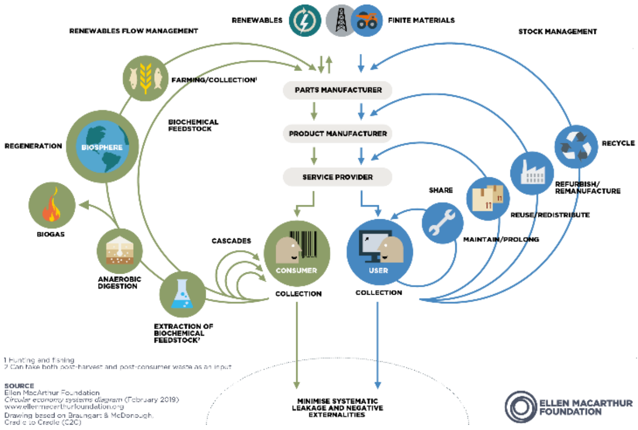

Fig.2 Concept of Circular Economy (5)

In order to apply this concept of circular economy to the life cycle of automotive lithium-ion batteries, first of all, we should try to thoroughly reuse batteries in order to use them to the full extent of their functions. For this purpose, it is necessary to develop a technology to diagnose the deterioration of spent batteries instantly and accurately. Various diagnostic technologies have been developed, but the challenge is to determine the degradation status of batteries in a short time, accurately, and as much as possible on a cell-by-cell and material-by-material basis, without disassembling each individual battery and without removing the battery package. In the case of automobiles, the status of battery usage during use is recorded, and if this information can also be used to diagnose the degradation of used batteries in an appropriate form, it will be useful to select the optimal life cycle for subsequent use. Thus, the use of information in an appropriate form for resource recycling with DX (digital transformation) technology is expected to lead to more efficient resource recycling, not only for batteries.

The disassembly of lithium-ion batteries from automobiles and the dismantling of the battery package into cells after said disassembly currently require heavy manual labor. Although some progress has been made in designing batteries that are easier to disassemble by reducing the number of screws and unifying the orientation of screws, the manual work of disassembling battery packages into battery cells one by one, by removing and cutting wires while changing postures and taking safety measures to prevent short circuits and electric shock is hard work and requires more than 10 minutes per battery package, even for skilled workers. In the near future, there will be a strong demand for the automation of this process.

Spent lithium-ion batteries that have been fully used and no longer function as batteries are separated for recycling and proper disposal. In the following sections, I review the current trends in the development of lithium-ion battery recycling processes and introduce the efforts of the authors towards them .

2. RECYCLING FLOW OF LITHIUM-ION BATTERIES

Separation and recovery of positive electrode materials and other materials from spent lithium-ion batteries can be classified into three types, as shown in Fig.3. In Japan, a combination of pyrolysis and physical separation processes is the mainstream approach, as shown in Fig.3(a). The pyrolysis treatment at 300°C to 900°C has various purposes: first, to burn off the organic solvent in lithium-ion batteries to ensure safety in the subsequent physical separation process; second, to burn off the organic material to concentrate the metal for recycling purposes; third, to burn off the adhesives of positive electrode particles to separate them from the aluminum foil; and fourth, to reduce the chemical form of the recovered positive electrode particles that can be easily leached by acid in the following hydrometallurgical process. The control of temperature, reaction time, and oxygen concentration in the pyrolysis process are the key issues for the optimization of the entire recycling process.

Unlike the process described above, a few major companies have developed a recycling process for lithium-ion batteries that employs a pyrometallurgical process in which metal components are reduced, as shown in Fig.3(b). In this process, copper, cobalt, and nickel are reduced and enriched as metals, while other organic materials are gasified and other materials such as iron, manganese, aluminum, and lithium become slag. These methods yield copper, cobalt, and nickel metals with high purity. On the other hand, since lithium is slagged in the pyrometallurgical furnace, it is necessary to recover lithium separately before and after the furnace by combining with another process.

Recently, some start-up companies have proposed an all-hydrometallurgical process, as shown in Fig.3(c), to separate all materials by disassembly and physical separation processes without using a high-temperature process. In principle, these methods enable the recovery of all types of materials, including resins and lithium. On the other hand, adequate consideration must be given to safety because of the risk of explosions during processing, if appropriate discharge procedures and oxygen control are not implemented.

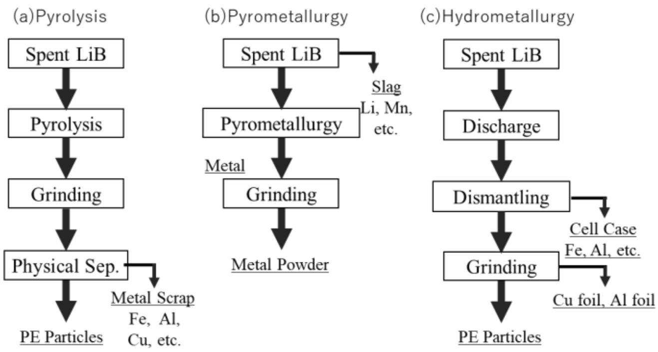

Fig.3 Typical pre-treatment flow of recycling for lithium-ion batteries. LiB: lithium-ion batteries, PE: positive electrode.

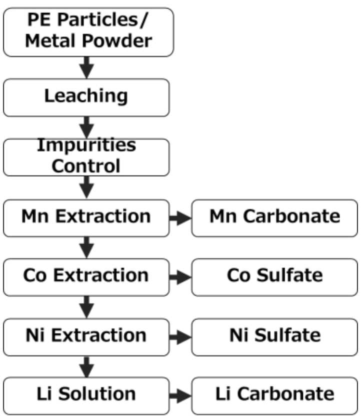

Fig.4 Typical hydrometallurgical process of Co, Ni, and Li recovery from the positive electrode particles.

As shown in Fig.4, the positive electrode particles, also called black mass or black powder, are ionized in solution by acid leaching and then separated into manganese, cobalt, and nickel by solvent extraction after removal of impurities, and refined by into carbonate for manganese and sulfate for cobalt and nickel, respectively. Cobalt and nickel are sometimes further purified by electrolytic extraction to produce cobalt metal and nickel metal. Lithium remains in the residual solution and is recovered as carbonate after purification. Since the key points are the removal of impurities and the improvement of separation accuracy, it is utmost importance to minimize the cost and energy of the entire recycling process by pre-treatment keeping impurities out as far as possible up to the acid leaching. Impurities that can be assumed here include copper, aluminum, fluorine, unburned carbon, and organic matter, depending on the type of the preceding process.

3. ATTEMPT TO DYRECT RECYCLING

The above processes are currently the mainstream mass treatment processes for lithium-ion battery recycling. These resource recycling loops correspond to the outermost recycling loops in the circular economy concept and should be established first to support all resource circulation processes and to properly treat all elements without causing environmental pollution. On the other hand, according to the concept of circular economy, the creation of a further inner recycling loop will lead to the achievement of further energy-saving resource recycling, as shown in Fig.2.

Based on this concept, studies have begun on direct battery recycling, attaining the inner resource circulation loop shown in Fig.5. While the outer recycling loop described in the abovementioned figure is a process to recycle cobalt and nickel sulfates as cathode materials for lithium-ion batteries, the inner direct recycling loop is a process to recover oxide, which is the form of positive electrode material particles and can be reused it as a cathode material after healing.

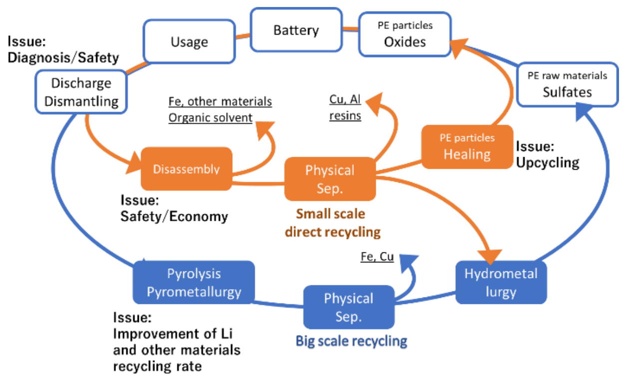

Fig.5 Concept of lithium-ion battery recycling.

To achieve this, it is necessary to construct a process that does not chemically change the cathode active material particles, and processes such as roasting and reduction, which have been widely introduced in current situation, cannot be used. In addition, depending on the type of active cathode material particles, the prolonged exposure to water may also cause chemical transformation. Therefore, to realize such direct recycling, a process that carefully dismantles spent lithium-ion batteries preserving their original state is required. All hydrometallurgical process shown in Fig.3(c) have potential for direct recycling. In addition, automated disassembly processes in air or under inert gas, and processes that separate the aluminum foil and cathode active material particles by grinding, and physical sorting in water are currently being considered.

The issue in these processes is to ensure safety based on reliable discharge and deactivation. In addition, as battery material technology develops, spent materials may become obsolete, so the direct recycling process requires not only regeneration of cathode active materials, but also upcycling technology through healing.

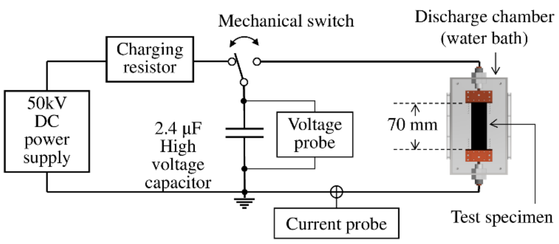

Fig.6 The schematic of the experimental setup of electrical dismantlement of positive electrode particles [4].

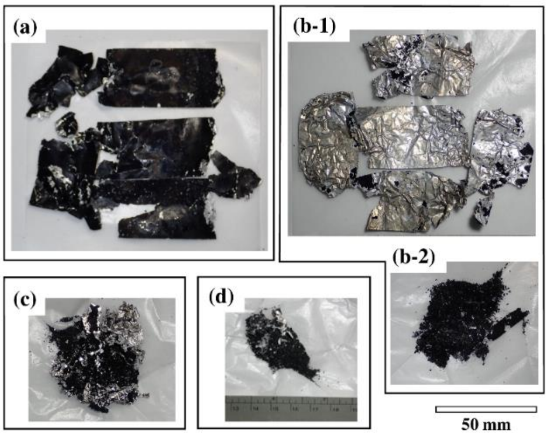

Fig.7 Photographs of the PE material after the pulsed discharge treatment at (a) 20 kV, (b) 25 kV, (c) 30 kV, and (d) 35 kV [6].

The authors are aiming to develop a physical separation method for the separation between the aluminum foil and positive electrode particles with an energy-saving process. To achieve this, we are focusing on electrical pulsed discharge (Fig.6). Electric pulses are applied at several kV to several tens of kV in several nano- to microseconds to achieve the selective separation at the interface by controlling Joule heat due to high current, Lorentz force due to electromagnetic field generation, and expansion and shock wave generation due to plasma generation. The authors have applied the electric pulse method to the cathode material of lithium-ion batteries and succeeded in precisely separating the current-collecting foil and black mass (Fig.7)[5], [6]. It is confirmed that the separated particles were hardly altered in chemical forms. LCA evaluation has also confirmed that the process is energy-saving [8].

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CONCLUSION

I reviewed separation technologies for recycling used lithium-ion batteries and introduced recent efforts to create a new resource recycling loop. The recycling loop is the outermost loop in the conceptual diagram of the circular economy, and is always the final process in the life cycle of a lithium-ion battery. On the other hand, as a business model for the resource circulation of lithium-ion batteries, the inner loop must be created in multiple and diverse ways. To this end, there are also several issues that require more consideration for scheme and system creation, other than the technology development.

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