Spent Lithium-Ion Batteries Recycling

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An urgent demand for recycling spent lithium-ion batteries (LIBs) is expected in the forthcoming years due to the rapid growth of electrical vehicles (EV). To address these issues, various technologies such as the pyrometallurgical and hydrometallurgical method, as well as the newly developed in-situ roasting reduction (in-situ RR) method were proposed in recent studies.

Keywords: Spent lithium-ion batteries ; Recycling ; Pyrometallurgical method ; Hydrometallurgical method ; Utilization

1. Background for Recycling Spent LIBs

Lithium-ion batteries (LIB) have been commercially used from 1990s. Owing to its excellent properties of high energy density, low self-discharge rate, long storage life, and safe handling, LIBs are found in all aspects of our lives, from small portable electronic devices through electric vehicles to energy storage systems [1]. According to statistics from the White Paper on the Development of China's Lithium-ion Battery Industry (2021), the worldwide LIB production has been increased to 294.5 GWh (over 1.6 million tons) in 2020 with a growth rate of 35.8% [2]. However, the capacity of LIBs substantially decays after 800-1500 charging and discharging cycles due to the destruction of electrode structure, the damage of separator, and the volatilization of electrolyte [3][4], leading to the generation of a huge amount of spent LIBs every year.

2. Necessity of Recycling Spent LIBs

A typical LIB are usually composed of shells, current collectors, active materials, organic electrolyte, separators [5]. The main anode materials of LIB are always graphite while the main components of cathode are diverged, mainly $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$, as well as other lithium metal oxides. In addition, LIBs also contain a certain amount of Polyvinylidene Fluoride (PVDF), $LiPF_6$, $C_3H_4O_3$, $C_4H_6O_3$ and other components [6]. Therefore, improper disposal of spent LIBs can cause serious release of toxins such as heavy metals and fluorine-containing organic chemicals, posing potential risks to the environment and human health [7]. On the other hand, valuable metals (e.g. Ni, Co, Li) containing in spent LIBs are at very high levels [3], even higher than those in natural ores. It is reported that China had produced 2.5 billion of spent LIBs with a mass of about 5.0×10^5 t in 2020 [8]. Therefore, it is of great value to recycle the major components from spent LIBs to prevent environmental pollution and to save natural resources of valuable metals. Recently, many countries have established laws and policies to encourage the development of recycling spent LIBs [9]. In 2019, the U.S. Department of Energy launched the Argonne National Laboratory Battery Recycling Research and Development Center and the Lithium ion Battery Recycling Award program. The German government requires battery manufacturers to register the primary responsibility for recycling the LIBs. For China, Development Plan for Energy Saving and New Energy Automobile Industry (2012-2020) issued by the government clearly mentioned that it is necessary to strengthen the cascade utilization and recycling management of batteries and to guide power battery manufacturers to strengthen the recycling and utilization of spent batteries.

3. Methods for Recycling Spent LIBs

There are three major approaches to recycle the spent LIBs: pyrometallurgy, hydrometallurgy, and direct recycling method [10][11][12]. Pyrometallurgy is an established technology that usually smelting spent LIBs with other types of batteries or ores and industrial wastes at a temperature above 1450 °C to produce mixed metal alloys of Co, Cu, Fe and Ni. Usually, pyrometallurgy does not require pre-sorting of the spent LIBs, but the alloy obtained is needed to be separated for further utilization. Umicore, Inmetco, Accurec, etc are the representative companies using this technology for spent LIB recycling [13]. For hydrometallurgical method, metals in cathode materials are leached by acid. The significant advantage of this method recycling of spent LIB is the high metal recovery rate. The representative companies such as GEM High-Tech, Brunp, Retriev Inc. (previously, Toxco), and Recupyl, are engaged in the hydrometallurgical method [14][15]. As for the direct recycling method, the anode or cathode materials of spent LIBs are refurbished directly, then the products are reused as the electrode materials of the new LIBs. This method is still under development and the representiative company is Ganfeng Lithium (China). In addition to the above methods, there are also novel technologies under investigation such as plasma smelting, bioleaching, in situ roasting, redox targeting based material recycling, etc [16]. In all, different methods for LIB recycling have their own cons. For example, the pyrometallurgical method suffers from high energy consumption and greenhouse gas emission, while the commonly used hydrometallurgical approach produces large amounts of acidic or alkaline wastewater. Therefore, development of the recycling method for spent lithium batteries is a hot topic worthy of investigation.

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