Materials Recovery and Upgrade from Spent Lithium Ion Batteries

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Abstract

Lithium-ion batteries (LIBs) have been widely used in portable electronics, electric vehicles, and grid storage as the dominant power sources. Especially millions of vehicles have been equipped with or directly powered by LIBs. The rapidly growing demand for LIBs brings 2 major challenges ---- one is the shortage of raw materials of LIBs, and the other is the management of spent LIBs. Recycling of spent LIBs is necessary to solve these 2 problems. Through recycling, low-cost raw materials can be obtained, and environmental concerns of spent LIBs are solved. In the past several years, our team at WPI has developed a closed-loop recycling process and the recovered LiNi1/3Mn1/3Co1/3O2 (NMC 111) has similar or better electrochemical performance than the commercial control NMC 111 powder.

However, due to the low added value, graphite anode materials in spent LIBs are discarded. Currently, the market price of the graphite anode is around \$8–13/kg, which could account to 10–15% of the material cost in typical LIBs. Meanwhile, the graphite content of spent LIBs ranges from 12 to 21 wt. %. As the number of spent LIBs increases, the amount of waste graphite becomes quite large. Therefore, we optimized our closed-loop recycling with a scalable high-quality graphite anode recycling process. After the leaching process, graphite was separated by filtration as a residue with impurities. Then, residual cathode materials, metal impurities, most binder materials, and aluminum oxide were removed after re-leaching and fusion steps. Finally, high-quality graphite powder was obtained, and the recycled graphite exhibits a comparable discharge capacity of 377.3 mAh/g at 0.1 C.

Nowadays, most recycling processes focus on recovering cathode materials with the same composition, structure, and electrochemical properties as the original cathode materials in spent LIBs. However, throughout the rapid evolution of cathode materials, the demand for cathode materials will trend to high energy density and long cycle life cathode materials. It means that to increase competitiveness, make recycling profitable and realize the real sustainable process, recovered cathode materials must keep abreast of the market demand, such as single-crystal Ni-rich cathode materials. Therefore, a universal etching approach is firstly developed to synthesize high-performance single-crystal cathode materials. The rate performance of the obtained single-crystal NMC111 is 10% to 15% more than that of polycrystalline NMC111 whereas the capacity retention of single-crystal NMC111 is enhanced by ~12% after 300 cycles at 0.5 C.

The obtained single-crystal NMC622 exhibits a pronounced improvement in rate performance, especially at high rates (~28.6% better at 5C and ~129% better at 10 C) and has a comparable cycle performance compared to polycrystalline NMC622.

Meanwhile, among the three traditional recycling processes, hydrometallurgical process is the only process that can change the composition of the recycled cathode materials. However, the hydrometallurgical process always involves toxic solvents and concentrated acids for the recovery, which possibly lead to health problems and safety hazards, associated to the dangerous materials handled during the manufacturing process. And direct recycling process has the minimal treatment and low emissions and energy usage to recycle cathode material. Thus, we designed a direct upcycling process to covert spent cathode materials to more current cathode formulations that are more relevant to the marketplace. We obtained single-crystal NMC622 cathode powder from commercial NMC111 cathode powder via a simple molten-salt method. The obtained single-crystal NMC622 shows similar performance at low rate and over 10% better performance at 2C, 5C and 10C. We are working on verification whether this process can apply to upcycle the spent NMC111.