

AN ORIGINAL OPEN AND CLOSED-LOOP RECYCLING METHOD FOR LI-ION BATTERIES THROUGH PRODUCTION OF METAL-ORGANIC FRAMEWORKS

M. Cagnet, E. Lagae-Capelle, M. Carboni, D. Meyer

Energy storage is one of the biggest challenges for next decades. The management of renewable energy production requires efficient electrochemical energy storage devices to use it anytime and anywhere. In recent years, Li-ion batteries (LiBs) have been developed and successfully commercialized for portable devices (smartphones, laptops ...) or cars. A mixture of cobalt/nickel/manganese has been largely used in the development of the LiB (NMC batteries). Our team has recently proposed a recycling process by selective precipitations of these toxic metals as valuable materials (Metal organic Frameworks (MOFs)) in batteries waste solution.^{1,2} Our previous works have shown an interest to use MOFs as active electrode materials for Li-ion batteries (Electrode material synthesis).³ (Figure 1)

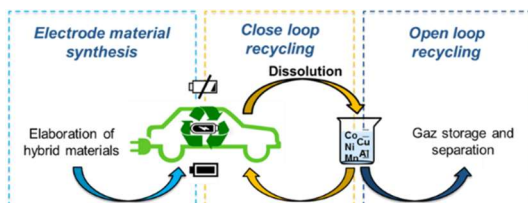


Figure 1: Strategy for the recycling of Li-ion batteries

A CoNiMn MOF obtained from simulant battery waste solution has been tested as electrode in a coin cell. It has revealed capacities as high as 460 mAh/g with a good cyclability over 50 charge/discharge cycles. Our recent studies have been focused on adapting this strategy by using real LiB wastes. It has been possible to obtain in large scale from LiB wastes some known MOFs, based on Al and Cu (the contactors of the battery) reported for their ability for gas storage (open loop recycling). This strategy can create an economical open loop recycling process to develop valuable materials from wastes in large scale.

Recently we also have reported a simple method to recycle plastic-bottle and Li-ion-battery waste in one process by forming MOFs. Poly(ethylene terephthalate) from plastic bottles was depolymerized to produce an

organic ligand source (terephthalate), and Li-ion batteries were dissolved as a source of metals (Figure 2). By mixing both dissolution solutions together, selective precipitation of an Al-based MOF, known as MIL-53 in the literature, was observed.⁴

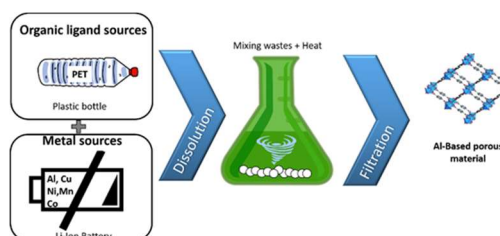


Figure 2: Combining organic and inorganic wastes to form MOFs

This strategy has been recently extended for the recycling of photovoltaic modules.⁵ The adsorption performances of these MOFs on cationic Methylene Blue and anionic Methyl Orange were determined to be ranging from 186.2 to 263.2 mg/g for MB, and 256.4 to 304.0 mg/g for MO. These results therefore suggest the potential of upcycling solar panels waste to form metal-organic framework for application in wastewater remediation to remove cationic and anionic dyes.

State of the art recycling of spent LIBs involving pyrometallurgy and hydrometallurgy processes generates considerable unwanted environmental concerns. Hence, alternative innovative approaches toward the green recycling process of spent LIBs are essential to tackle large volumes of spent LIBs in an environmentally friendly way. Such evolving techniques for spent LIBs recycling based on green approaches, including bioleaching, waste for waste approach, and electrodeposition, have been discussed here⁶ and are still in development with the SCARCE 2 project (collaborative work between CEA and NTU (Singapore)).

¹ Cagnet M., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - Targeted removal of aluminium and copper in Li-ion battery waste solutions by selective precipitation as valuable porous materials - *Materials Letters* (2020) 268, 127564.

² Cagnet M., Condomines J., Cambedouzou J., Madhavi S., Carboni M., Meyer D. - An original recycling method for Li-ion batteries through large scale production of Metal Organic Frameworks - *Journal of Hazardous Materials* (2020) 385, 121603.

³ Cagnet M., Gutel T., Gautier R., Le Goff X. F., Mesbah A., Dacheux N., Carboni M., Meyer D. - Pillared sulfonate-based metal-organic framework as negative electrode for Li-ion batteries - *Materials Letters* (2019) 236, 73-76.

⁴ Lagae-Capelle E., Cagnet M., Madhavi S., Carboni M., Meyer D. - Combining Organic and Inorganic Wastes to Form Metal-Organic Frameworks - *Materials* (2020) 13, 441.

⁵ Pham H. K., Sim Y., Carboni M., Meyer D., Mathews N. - Generating metal-organic frameworks (MOFs) from photovoltaic modules for wastewater remediation - *Journal of Environmental Chemical Engineering* (2022) 10.

⁶ Roy J. J., Rarotra S., Krikstolaityte V., Zhuoran K. W., Cindy Y. D. I., Tan X. Y., Carboni M., Meyer D., Yan Q. Y., Srinivasan M. - Green Recycling Methods to Treat Lithium-Ion Batteries E-Waste: A Circular Approach to Sustainability - *Advanced Materials* (2022) 34, 210334