Teachers' Card

Urban Mining: recycling of Spent Lithium-Ion Batteries chasing raw materials

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Acknowledgement……………………………………………………………………………………………...................……….

General Introduction

Nowadays, Lithium-Ion Batteries (LIBs) make up the lion's share of low-to-mid scale energy storage systems. This is due to the outstanding properties of energy and power density guaranteed by lithium's mass and dimension[1]. The core components of LIBs are a negative electrode mainly made of graphite, an electrolyte composed by an organic liquid in which a lithium salt is dissolved, and a positive electrode made by $LiCoO_2$ (LCO) or similar compounds (in which cobalt is partially substituted with Ni and Mn, generally called NMC).

The proposed activity is addressed to 14 years old students and older, who will recycle the positive electrode of a LIB, starting from commercial powders, in place of the active material already mechanically separated from the other components of the battery that is difficult to obtain under safe condition. The students will prepare and deploy mild organic acid or strong inorganic acid solutions to dissolve the electrode's material. Then, lithium and cobalt ions will be separated by precipitation with different reactants.

Key words:

Recycling, Batteries, Waste, Lithium, Circular Economy, Sustainability

Extended background information

A Lithium-Ion Battery (LIB) is a secondary electrochemical cell (featuring a reaction that can be reversed by providing electrical energy) made by three components: two electrodes in which oxidation and reduction occur alternately, and an ion-conductor called electrolyte. The circuit is then close by connecting the two electrodes together *via* an electron conductor (wire) connected to a power source (so to charge the battery) or a power-requiring device. The first official definition of a LIB is that proposed by Yoshino in his patent (1985) where it is defined as a "*nonaqueous secondary battery using transition-metal oxides containing lithium ion such as* $LiCoO_2$ *as a positive electrode and carbonaceous materials as a negative electrode*"[2][3]. The outstanding properties of lithium (low standard reduction potential, low atomic weight, and small dimension) make LIBs difficult to replace with similar technologies that does not include lithium-ions. Moreover, the use of cobalt, which is toxic and rare, makes the sole concept of LIBs' disposal an environmental problem. With the advent of electric cars to devices dependent on LIBS, the production of waste electrical and electronical equipment (WEEE), of which LIBs are part, is expected to grow to values around 45 million tonnes per year.[4]. For all the reasons explained above, inserting LIBs in recycling processes is to be considered a mandatory step in the path of a greener and sustainable future. Due to the presence of strategic metals such as cobalt (5-20 wt%) and lithium (5-7 wt%), spent LIBs can, in fact, be seen as valuable sources of many of the chemicals needed to produce new lithium-ion batteries[5].

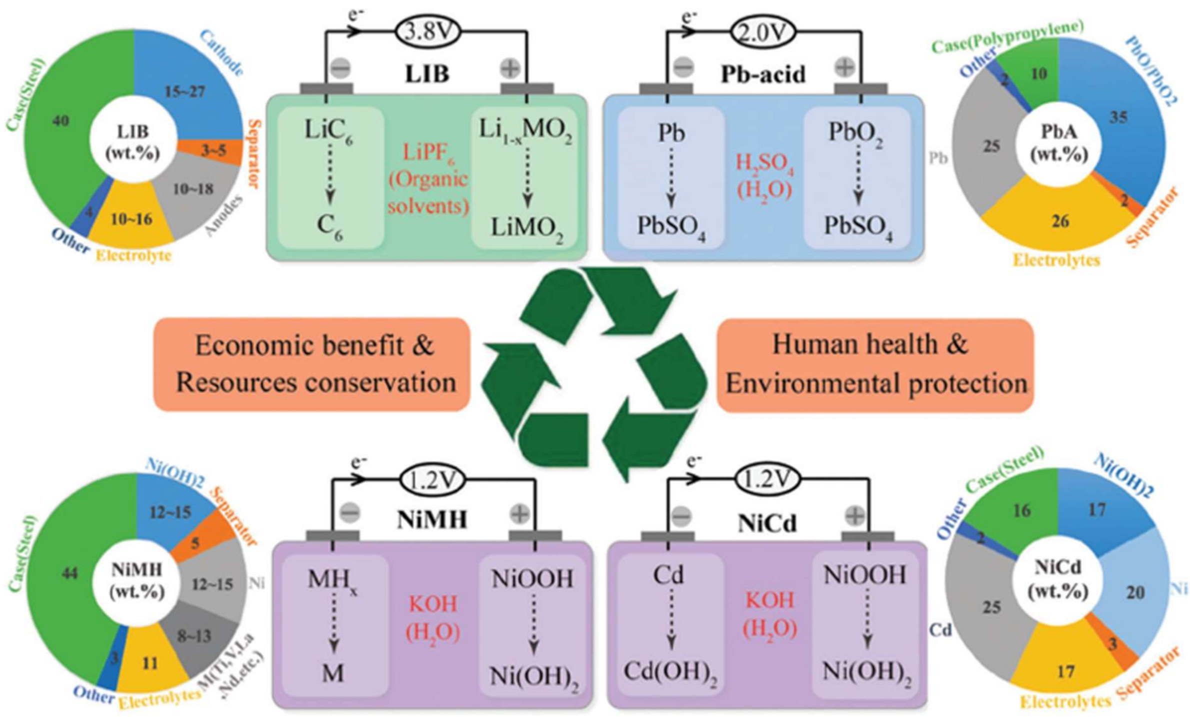

Figure 1: Structure and composition of the four main types of rechargeable batteries

Learning Outcomes

By the end of the lesson the students will be able to:

- Using some of the conventional glassware present in chemical labs (flasks, pipettes, etc.)
- Apply the methods and verify their efficiency though systems
- Be critical in the evaluation of lab results

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Key Competence European Framework

Literacy competence
S1. Ability to understand and interpret concepts, feelings, facts or opinions in oral and written form.
S3. Ability to interpret the world and relate to others.
Multilingual competence
S7. Ability to use technical language accordingly to the field of work.
Mathematical competence and competence in science, technology and engineering
S5. Capacity for quantitative thinking.
S6. Ability to extract qualitative information from quantitative data
S8. Ability to design experimental and observational studies and analyse data resulting from them.
S9. Ability to formulate complex problems of optimisation and decision making and to interpret the solutions in the original contexts of the problems
Citizen competence
S3. Ability to work effectively and collaborate with other team members
Cultural awareness and expression competence
S2. Creativity/innovation

United Nations' Sustainable Development Goals

The Sustainable Development Goals are the blueprint to achieve a better and more sustainable future for all. They address the global challenges we face, including those related to poverty, inequality, climate change, environmental degradation, peace and justice.

Please indicate which goal/s can be linked to this activity

	1 NO POVERTY 2 ZERO HUNGER Enable access to basic services		10 REDUCED INEQUALITIES Equal access to global expertise
	3 GOOD HEALTH AND WELL-BEING Safe medical devices		11 SUSTAINABLE CITIES AND COMMUNITIES Sustainable urbanization
	4 QUALITY EDUCATION Access to education	✓	12 RESPONSIBLE CONSUMPTION AND PRODUCTION Responsible consumption and production

	5 GENDER EQUALITY — Less hardship, more opportunities	✓	13 CLIMATE ACTION — Strengthen resilience, reduce disaster impact
	6 CLEAN WATER AND SANITATION — Safe and affordable water		14 LIFE BELOW WATER — Reduce marine pollution
✓	7 AFFORDABLE AND CLEAN ENERGY — Energy – the golden thread	✓	15 LIFE ON LAND — Sustainable use of terrestrial ecosystems
✓	8 DECENT WORK AND ECONOMIC GROWTH — Safety of workers and economic growth		16 PEACE, JUSTICE AND STRONG INSTITUTIONS — Promote peaceful and inclusive societies
	9 INDUSTRY, INNOVATION AND INFRASTRUCTURE — Resilient infrastructure and sustainable industrialization		17 PARTNERSHIPS FOR THE GOALS — Better access to technology and innovation

Contents – Theoretical principles

Recycling processes of a LIB all start with some pre-treatments necessary to separate each component of the battery itself, then such components are treated to recover the main chemicals in form that can be used again. Such processes slightly differ from lab- to industrial-scale (figure 2). In this document, only one lab-scale route will be explored: that of the hydrometallurgical process with acid leaching[6], as it is the one proposed in this toolkit for the students to execute.

Generally, the recycling process starts with the discharge of the battery in salt solution. This is done to remove the remaining energy that the battery might retain. If the potentials of the positive and negative electrode exceed those at which water oxidates and reduces:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^0 = 0.00V\ vs\ RHE$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1.23V\ vs\ RHE$$

oxygen and hydrogen will be evolved at the two electric poles of the battery, thus reducing the energy that still is stored in the device[7]. Then, the battery is manually dismantled using knives and saws and the components (external case, separator, positive and negative electrode) are collected. The active material on the positive electrode (LCO or NMC) is then separated from the aluminium foil on which it is deposited by crushing using blade mills (for lab-scale purposes, a simple mixer used in kitchen is enough).

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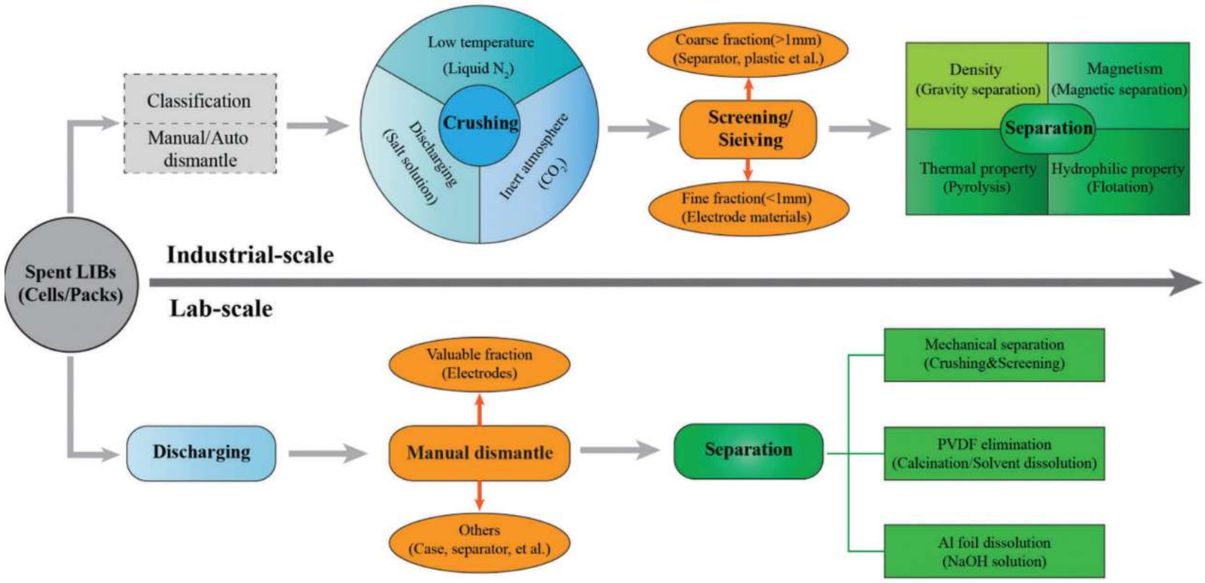

Figure 2: Pretreatment processes and technologies of LIBs from perspectives of industrial scale and lab scale

This step allows for a coarse separation of the active material from the aluminium, which is sufficient for the next steps. Finally, the active material of the positive electrode is treated using acidic solutions at high temperature (generally from 80 to 150 degrees). With this process, both lithium and cobalt (and also nickel and manganese if present) remain dissolved in solution, allowing for their separation (further details in Student's Card 1). Although more efficient in terms of energy needed to complete the leaching process, inorganic acids tend to be much more hazardous, both for the environment and the operators that need to use them. Therefore, mild organic acids (e.g. citric acid, oxalic acid) are preferable. These in fact can be as efficient as the inorganic ones in terms of dissolution of the active material at the cost of an increase in the energy expenditure (i.e. higher temperature of longer times)[6].

Lab Procedure

The activity is composed of one module, where students will evaluate one of the most promising route in recycling the most critical component of exhaust lithium-ion battery (the cathode material). They will also understand how different chemicals impact on the leeching's result.

Module 1 - Recycling of Lithium- Ion Batteries Waste

Teachers' Card

Learning Pathway

Step 1- Time & Activity: *i.e.* 45 minutes - Teachers do a short introduction with a prepared PowerPoint presentation (see among the supporting materials)

Step 2 – Time& Activity*:* 1h - Students are divided into groups (preferably the number of students in one group is 3-4) and starts the first part of the experience, which consist in preparing the acid solutions, preparing the instrumentation, and starting the leaching process

Step 3 – Time& Activity*:* 1h – Wait for the leaching process to be completed

Step 4 – Time& Activity*:* 30 min – Students continue the second part of the activity, which consists in filtering and washing the precipitate, which will be therefore dried

Step 4 – Time& Activity*:* 30 min – Students will end the procedure by weighing the dried powder so to evaluate the yield of the leaching process

Step 5 – Time& Activity*:* follow-up: Students are invited to study chemical aspects and new processes for the LIBs recycling.

Evaluation

1. **Why is important find new solvents to substitute the traditional inorganic acid?**
Inorganic acids could cause considerable secondary pollution, such as toxic gas emission (Cl_2, SOx, and NOx) and waste acid solution, the focus of the last years is to find new propose an environmentally friendly recycling process using organic acids to replace the typically used acids without sacrificing the leaching efficiency.

2. **What is the solid phase present at the end of the leaching process? And what it means its presence?**
The solid phase is Lithium Cobalt Oxide that doesn't react with the acid, this means that the acid it was able to full dissolve the cathode at this condition of time, temperature, and rate between the solid and the liquid.

3. **Using the formula $\% = \frac{Final\ Co\ mass\ (g)}{Starting\ Co\ mass\ (g)} * 100$ to determine the yield of cobalt recovery after the precipitation with oxalic acid, do the same thing for the Li. (PM $LiCoO_2$=97.87g/mol; PM CoC_2O_4= 146.95g/mol; PM Li_2CO_3 = 73.89g/mol PM Co=58.93g/mol; PM Li = 6.94g/mol).**

4. **Why we need to add in the solution H_2O_2?**
To permit the dissolution of the Lithium cobalt oxide we need to change the oxidation of the Cobalt from 3+(III) to 2+(II) because Co(II) is more stable in liquid phase and so the pass form

the solid is more easy and require less energy. Hydrogen peroxide is using as a reductive agent able to give an electron (charge -1) to the Cobalt.

5. **Compare the different acidic solutions filling this table, discuss with your colleagues the pro and cons of different acids**

Acid	Reaction Yield	Co recovery Yield	Li recovery Yield	Acid cost	Safe Handling conditions	Disposal condition

Description of Student's Cards

The Student's Card associated to this toolkit contains the explanation of the activity tailored to students. **Student's Card 1 - Recycling of Lithium- Ion Batteries Waste**

Sources

[1] J.M. Tarascon, Is lithium the new gold?, Nat. Chem. 2 (2010) 510. doi.org/10.1038/nchem.680.

[2] A. Yoshino, Secondary battery, US patent 4668595A, United States Pat. (1987) 9. doi/10.1021/acsnano.7b04646.

[3] A. Yoshino, The birth of the lithium-ion battery, Angew. Chemie - Int. Ed. 51 (2012) 5798–5800. doi.org/10.1002/anie.201105006.

[4] M. Roshanfar, R. Golmohammadzadeh, F. Rashchi, An environmentally friendly method for recovery of lithium and cobalt from spent lithium-ion batteries using gluconic and lactic acids, J. Environ. Chem. Eng. 7 (2019) 102794. doi.org/10.1016/j.jece.2018.11.039.

[5] R. Golmohammadzadeh, F. Faraji, F. Rashchi, Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review, Resour. Conserv. Recycl. 136 (2018) 418–435. doi.org/10.1016/j.resconrec.2018.04.024.

[6] X. Zhang, L. Li, E. Fan, Q. Xue, Y. Bian, F. Wu, R. Chen, Toward sustainable and systematic recycling of spent rechargeable batteries, Chem. Soc. Rev. 47 (2018) 7239–7302. doi.org/10.1039/c8cs00297e.

[7] J. Li, G. Wang, Z. Xu, Generation and detection of metal ions and volatile organic compounds (VOCs) emissions from the pretreatment processes for recycling spent lithium-ion batteries, Waste Manag. 52 (2016) 221–227. doi.org/10.1016/j.wasman.2016.03.011.

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