For Teachers

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

Module 1

Degradation of $LiCoO_2$ cathode material from spent Lithium-Ion Batteries for the recovery of Li and Co

Introduction

One of the main challenges of the present day and of the near future is the production and storage of energy. Energy storage devices that allow for accumulation of energy are thus the key components that today allow the production of many portable devices, house appliances, and that are promoting the exploitation of clean renewable energy and the diffusion of electric vehicles. The lithium-ion rechargeable batteries (LIBs) are the most exploited due to their light weight, high energy density, scalability, durability, number of working cycles.

Their widespread diffusion poses the problems of the management and supply of the raw material present in the cathode like lithium (Li), Cobalt (Co), Nickel (Ni), Manganese (Mn) not always abundant, easily available, and cheap. One strategy for the supply of such raw materials is the so called "urban mining" approach, that is the recovery of raw materials from urban waste. For the specific case of LIBs, the recycling of spent LIBs allows to address two problems at the same time: the correct management of this kind of waste, avoiding the disposal in landfills and the recovery of valuable raw materials.

One of the most exploited methods studied in the last year is the hydrometallurgy process that involve the use of an inorganic acid (hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and/or nitric acid (HNO_3)) to dissolve the solid raw materials. The as-obtained solution contains the elements of interest; through extractions and/or selective precipitation steps the single elements can be recovered and are ready to be reused. The problem of using inorganic acids is the production of secondary pollution, such as toxic gas emission (Cl_2, SO_x, and NO_x) and waste acid solution, the huge amount of waste waters. For this reason, in the very last years, many studies appeared in literature proposing alternatives to the inorganic acids. Many studies demonstrated that the use of organic acids such as citric, ascorbic, oxalic is feasible and sustainable. Indeed, high dissolution yields can be obtained under mild conditions, the considered acids are cheap and biodegradable, no toxic waste are generated.
This laboratory experience is focused on the comparison of the results of the dissolution of $LiCoO_2$, the most common cathode material, using inorganic and organic acids. The main aims are the recovery of Li and Co through precipitation steps and push the students to think about the box, considering not only the chemical yields but compare also other relevant factors such as safety of the procedures, costs, sustainability, type of produced waste and the disposal procedure after the lab procedure in the view of the circular economy.

For Teachers

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

Necessities

Reagents	Formula	
Lithium Cobalt Oxide	$LiCoO_2$	
Citric acid	$C_6H_8O_7$	
Tartaric acid	$C_4H_6O_6$	
Succinic acid	$C_4H_6O_4$	
Hydrogen peroxide	H_2O_2	
Nitric acid	HNO_3	
Oxalic acid	$C_2H_2O_4$	
Sodium carbonate	Na_2CO_3	

List of materials/tools

- Protection glasses and disposable gloves,
- Lithium Cobalt Oxide (LCO) powder 98%, cas. 12190-79-3,
- 1 spun,
- 2 syringe (5mL),
- 5 Becker (100mL),
- 4 magnetic stirrers,
- 1 heating plate
- 1 round-bottom flask with two neck (50 or 100mL),
- 1 oil bath,
- 1 Allihn condenser (reffrigerante a bolle),
- 2 rubber tubes,

For Teachers

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

List of Chemical

- Citric Acid powder, Sigma-Aldrich, CAS 77-92-9
- Oxalic Acid powder, Sigma-Aldrich, CAS 144-62-7
- Tartaric Acid powder, Sigma-Aldrich, CAS 87-69-4
- Succinic Acid powder, Sigma-Aldrich, CAS 110-15-6
- Nitric Acid 65% acq solution, Sigma-Aldrich, CAS 7697-37-2
- Lithium Cobalt Oxide 97% powder, Alfa Aesar, CAS 12190-79-3

Lab Procedure

1. *Organic Acids Solutions Preparation*

- *<<For this part you need 1 spun, 4 Becker (100mL), Citric Acid, Oxalic Acid, Tartaric Acid, Succinic Acid, 4 magnetic stirrer, 1 heating plate.>>*
  *Weight the organic acid in a Becker using a weight scale, after adding **20mL of distilled water** and then put the Becker on a magnetic plate with inside a magnetic stirrer so to complete dissolve the organic acid. In the following table are reported the concentration of the solution obtained and the weight to take for every acid:*

Organic Acid	***Weight (g)***	***H_2O Volume (mL)***	***Molarity (mol/L)***
Citric Acid	*4.8*	*20*	*1.25*
Oxalic Acid	*5.4*	*20*	*3*
Tartaric Acid	*6*	*20*	*2*
Succinic Acid	*3.5*	*20*	*1.5*

2. *Inorganic Acid Solution Preparation*

- ***ATTENTION!!** Nitric Acid is dangerous: work with the acid under a hood and carefully.*
  <<For this part you need 1 spun, 1 long syringe, 1 Becker (100mL), nitric acid, 1 magnetic stirrer, 1 heating plate.>>
  *Take a Becker and put **10mL of distilled water**, using a long syringe take **2mL of HNO_3 65%** and put in the Becker (when you work with a strong acid is important **"to not give drink to***

the acid" *this to avoid splashes caused by the strong heat developed), adding* ***10mL more of water*** *(now you can because the acid is diluted), put a magnetic stirrer and stir for few minutes. In the following table are reported the volume to take and the final concentration of the solution*

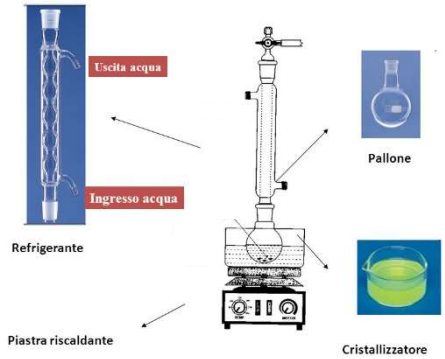
Inorganic Acid	***Volume (mL)***	***H_2O Volume (mL)***	***Molarity (mol/L)***
Nitric Acid	*2*	*20*	*1*

3. Leaching Process

- *Preparation of the heating system*

  <<For this experiment the class we will be separated in 5 groups (1 for each acid), any group require: 1 round-bottom flask with two neck (50 or 100mL), 1 oil bath, 1 Allihn condenser (reffrigerante a bolle), 2 rubber tubes, 1 magnetic stirrer, 1 heating plate, 1 spun, 1 syringe (5mL), filter paper, 1 Becker (100mL), 1 funnel.>>

  In the figure you can see how to assemble the heating system, it's important to block with a tongs the centre of the condenser and the neck of the flask. When all is ok on the water and control if there condenser is ok.



If is don't possible use this system, can replace with a Vial of 100mL without the condenser system.

- *Leaching the Lithium Metal Oxide*

  Put the acid solution and the magnetic stirrer in the flack and set the temperature of the oil bath at ***75°C*** *and with stir on (wait 10 minutes to be sure that the temperature is reached and stable), adding the* ***400mg LCO*** *(Lithium Cobalt Oxide from commercial source will be considered,* ***DO NOT TRY TO OPEN A WASTE BATTERY AS IT CAN CAUSE EXPLOSION AND***

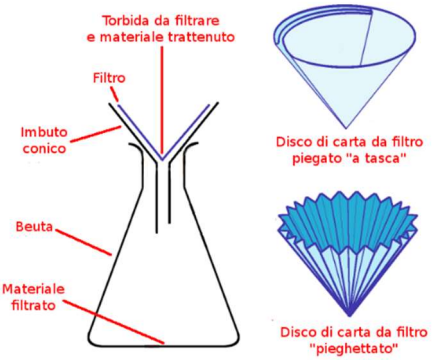
Urban Mining: recycling of Spent Lithium-Ion Batteries chasing raw materials

***FIRE**) and with a syringe a volume of H_2O_2 30%(the volume is reported in the following table). After **1h** stop the reaction removing the flask from the bath and cooling it down naturally. When the solution is cold, using a filter paper separate the solid phase and put the liquid phase in a Becker. Recover the eventual undissolved solid, dry it and weight it. Thus it is possible to calculate the dissolution yields as (W(starting LCO)-W(unreacted LCO)/W(starting LCO))*100.*

Acid	***Volume of H_2O_2 35% (mL)***
Citric Acid	*1*
Oxalic Acid	*/*
Tartaric Acid	*3*
Succinic Acid	*3*
Nitric Acid	*2*

- *Precipitation of Cobalt*

  *Now you will have a colored solution, adding **370mg of Oxalic Acid** (equimolar rate) in the solution and stir, when it starts forming a precipitate count **15min** and let it sit. Using a filter paper, separate the solid phase and put the liquid phase in a second Becker (if is not possible have other Becker you can use the flask used for the leaching) for the precipitation of lithium. The solid phase so obtained is [Co(II)(C_2O_4)]. Weight the powder. Considering the weighted amount of LCO at the beginning it is possible to calculate the Co recovery yield.*



- *Precipitation of Lithium*

  *Now in the remain liquid phase adding **780mg of Sodium Carbonate** (1mol LCO: 1.8mol Na_2CO_3) and stir until formation of a white precipitate. Filter in the same way did before. The solid phase so obtained is Li_2CO_3. Weight the powder. Considering the weighted amount of LCO at the beginning it is possible to calculate the Li recovery yield.*

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

Additional Safety Notes

- Maximus attention when use Nitric Acid (HNO_3)
- Don't touch anything without wearing protective glass and lactic gloves

Conclusion

The idea of the proposed experience is to compare the efficiency of the different degradation solutions, comparing them under the same experimental conditions. This will allow for direct comparison. Push the student to take notes about the similarities and differences in the dissolution rate, colour of the solutions, eventual presence of residual black solids and/or of white precipitate. A quantitative comparison can be done considering the degradation yields, Co recovery yield, Li recovery yield.

During the degradation of the LCO (waiting time 1 hour) stimulate the students to search information about the updated cost of the acids that they are using, safety and risk associated with their handling and disposal, correct disposal way.

As the students to prepare a synoptic table considering the degradation yields, Co recovery yield, Li recovery yield, costs of the acids, notes about the risk during their handling and disposal and ask the students to identify, based on the global evaluation of all these parameters, the best degradation agent, motivating their choice.

This experience can be made by groups with i) each groups preparing all the solutions and comparing all the degradations ii) each group preparing a single solution and highlighting pro and cons in a final discussion with the other groups.

1. **Why is important find new degradation agents 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.

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

3. **Using the formula** $\% = \frac{Starting\ Co\ mass\ (g) - Final\ Co\ mass\ (g)}{Starting\ Co\ mass\ (g)} * 100$ **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 CoC2O4= 146.95g/mol; PM Li2CO3= 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