# DEVELOPMENT OF PIGMENTS FROM END-OF-LIFE LITHIUM-ION BATTERY CATHODES

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## 1. ABSTRACT

Today, we are facing a shortage of certain raw materials considered critical by the European Union, which are used to synthesise ceramic pigments, such as oxides of Co, Ni, and Mn.

Furthermore, the generation of electronic waste grows steadily, including discarded lithium-ion batteries which, apart from lithium, contain elements such as Co, Mn or Ni in their composition. Therefore, recovering those metals for reuse in the manufacture of ceramic pigments would provide a twofold benefit: firstly, lesser dependence on third countries for the supply of such raw materials and, secondly, the ensuing environmental benefit.

In this study, a method has been designed for separating the different components of a lithium-ion battery. Cathodes of differing chemistry, separated by this process, were then used to synthesise ceramic pigments, specifically a blue, a green and a black pigment.

## 2. INTRODUCTION

The use of energy storage systems has increased exponentially in recent years, mainly due to the need to achieve a low-carbon economy in order to reduce greenhouse gas emissions and improve air quality. That calls for an energy transition involving the use of renewable energies that need to be stored, lithium-ion batteries being one of the most widely used storage systems.

A lithium-ion battery is a complex system. It consists mainly of a cathode, an anode, an electrolyte and a separator. The cathode is an aluminium foil coated with a mixture of active material, an electrical conductor, a binder and a solvent. The active material present in the cathode is the most valuable material in a battery, as it accounts for more than 50% of its cost and determines the charging efficiency as well as the cost of the batteries. The compound typically used is a double oxide of lithium and one or more transition elements, including $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_zO_2$ (NMC) ($x+y+z=1$), compounds containing scarce elements with high added value that are used in the ceramic pigment making industry [1,2].

High consumption of electronic devices has led to two problems appearing: on the one hand, increased generation of electronic waste and, on the other, a scarcity of certain raw materials required for their manufacture, such as lithium, cobalt, nickel and/or manganese.

In 2011, the European Union published a list of Critical Raw Materials (CRM), which included a series of raw materials considered critical for two reasons: their economic importance and/or the precariousness of their supply. Cobalt was listed as one of them. The main supplier of cobalt is the Democratic Republic of Congo, a country with high geopolitical instability and thus a threat to the supply chain. The list is updated every three years. Lithium was added to the list in 2020 and manganese in 2023. Moreover, nickel has also been included on the list because, even though it does not qualify as critical, it is considered a strategic raw material for the European Union [3].

With regard to increased generation of electronic waste, in 2006, the European Union approved Directive 2006/66/EC of the European Parliament and of the Council of 6 September 2006 on batteries and accumulators and waste batteries and accumulators, which repeals Directive 91/157/EEC, with a view to reducing the negative impact that such waste will have on the environment [4]. The impact assessment in the Directive concluded that battery recycling had been encouraged but not at the desired level. In 2023, Regulation 2023/1542 was approved, repealing the previous Directive and establishing that batteries manufactured from 2031 onwards must contain a minimum percentage of recycled material, namely 16% cobalt, 6% nickel and 6% lithium [5].

Battery recycling is therefore a booming enterprise, not just from an environmental viewpoint but also from an economic standpoint, as discarded lithium-ion batteries can become a secondary source of raw materials such as cobalt, nickel, manganese or lithium.

The ceramic industry, though not the main consumer of such raw materials, also contributes to increased consumption of cobalt, nickel and/or manganese in the synthesis of ceramic pigments, such as: Co-Al blue ($Co_2Al_2O_4$ spinel), Co-Zn-Al-Cr greenish blue ($(Co,Zn)(Al,Cr)_2O_4$) spinel), Co-Zn-Al-Cr-Fe dark turquoise ($ZnCr_2O_4$ and $CoAl_2O_4$ spinels), Zn-Ni-Co-Ti bright green ($(Zn,Ni,Co)_2(Co,Ni,Ti)O_4$ spinel), Co-Cr green ($CoCr_2O_4$ spinel), and Fe-Co-Cr-Mn-Ni black ($(Co, Fe, Ni, Mn)(Fe,Cr)_2O_4$ spinel) [6].

Cobalt, nickel and manganese recovered from lithium-ion batteries can be introduced as raw materials in the manufacture of ceramic pigments either in the form of oxides, after subjecting the active cathode material from discarded batteries to a hydrometallurgical process, or by direct use of the recovered cathode.

Recovery of these metals in the form of oxides calls for a series of chemical reagents and thermal processes that consume a considerable amount of energy which, on the one hand, leads to an increase in secondary raw material costs and, on the other, generates an environmental problem, given that they require chemical reagents that are often toxic [7].

Therefore, interest has turned to studying the feasibility of using the active material from cathodes recovered from lithium-ion batteries at the end of their service life directly in the formulation of ceramic pigments, a usage that will necessarily be conditioned by the level of contamination in the composition of the active cathode material.

The aim of this research consisted of designing a process for separating active materials from cathodes with as little contamination as possible from the rest of the components that make up a battery. Furthermore, the system designed had to be easily scalable to an industrial level to make the process economically viable. This research was carried out with batteries from laptop computers.

In addition, since batteries can have cathodes with different chemistries, it was first necessary to carry out the chemical characterisation of active cathode materials from a sufficiently large number of batteries in order to build a database and be able to sort them prior to the actual process of separating the components.

The active cathode material obtained from the separation process was then used to synthesise three ceramic pigments: one blue, one green and one black, by replacing all or part of the primary raw materials with secondary raw material recovered from discarded lithium-ion batteries, thus enhancing circularity in the economy.

## 3. EXPERIMENTAL PART

The work was carried out in different stages. The first stage was to separate the different components in the battery after first sorting the cathodes by type. The second stage was to control the composition of all separated material, and the final stage involved developing the different pigments selected.

### 3.1 MANUAL SEPARATION OF THE CATHODE MATERIAL

This stage of the process is necessary to be able to sort batteries by the chemical composition of their cathode, which may vary, such as: $LiCoO_2$ (LCO), $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111), $LiNi_{0.5}Mn_{0.2}Co_{0.3}O_2$ (NMC 523), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC 622) or $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC 811). Pre-sorting of the batteries guarantees the constant chemical composition of the by-product obtained after the separation process.

For that purpose, 240 discarded batteries from laptop computers of different makes and models were analysed.

### 3.2 CHARACTERISATION OF THE SEPARATED CATHODES

Chemical characterisation was carried out by wavelength dispersive X-ray fluorescence (WD-XRF), inductively coupled plasma optical emission spectroscopy (ICP-OES), and carbon, oxygen, nitrogen and sulphur analysers.

In addition, mineralogical characterisation was carried out using X-ray diffraction (XRD) and morphological characterisation using scanning electron microscopy (SEM).

The information gained during this stage meant that batteries could be sorted by the chemistry of their cathodes and a database built and furthermore, information was obtained with which to develop an automatic component separation process.

### 3.3 DEVELOPMENT OF A METHOD FOR AUTOMATIC SEPARATION OF BATTERY COMPONENTS

Considering the chemical composition and microstructure of each of the components that make up the battery, a separation process was designed, which was later scaled up to a pilot plant and protected under patent [8], to automatically separate the components of a battery by using mechanical and thermal processes.

The process produces three by-products in addition to the active material of the cathode which, in this study, was going to be used to synthesise pigments. One of the by-products that comes from the electronics of the battery has considerable concentrations of Au and Ag; the second by-product mainly comprises metal Ni and comes from the cell casing, while the third by-product is formed of metal Cu and comes from the collector plates.

### 3.4 SYNTHESIS OF CERAMIC PIGMENTS FROM RECOVERED CATHODES OF DISCARDED LITHIUM-ION BATTERIES

After characterising the chemistry of the cathodes in the batteries under analysis, they were sorted into two types: batteries with an LCO-type cathode which, in addition to Li and O, has a single transition element (Co in this case); and batteries with an NMC-type cathode, including in this group the different NMC chemistries mentioned above which, in addition to Li and O, have Co, Ni and Mn in their composition.

The recovered LCO-type cathode was used to develop a blue ($CoAl_2O_4$ spinel) and a green pigment ($(Co,Zn)(Al,Cr)_2O_4$ spinel). A black pigment $(Co,Fe,Ni,Mn)(Fe,Cr)_2O_4$) was developed using recovered NMC-type cathodes.

These pigments were synthesised by replacing the commercial oxide completely or partially with the recovered cathode and they were also synthesised in parallel using commercial Co, Ni and Mn oxides. Moreover, the calcination cycle in a laboratory muffle kiln was optimised, performing various heat treatments applied up to maximum temperatures ranging from 900ºC to 1300ºC and residence times at maximum temperature between 60 and 240 minutes.

The formation of the characteristic crystalline phase of each synthesised pigment was furthermore determined by X-ray diffraction (XRD) to confirm that the synthesis process for each pigment was suitable [9].

Finally, the pigments synthesised with cathodes recovered from lithium-ion batteries were included in the formulation of a coloured glaze for porcelain stoneware tile and its colour development studied.

### 3.5 MATERIALS

- Samples under study: discarded lithium-ion batteries from laptop computers of different makes and models.
- Reagents and standards used in the chemical characterisation: $LiCoO_2$ from Tob New Energy, $Co_3O_4$ from Alfa-Aesar, NiO from Alfa-Aesar, CuO from Merck, SRM 25d Manganese Ore from NIST, CERAM AN-27 alumina from LGC Standards, SRM 120c Florida phosphate rock from NIST, BCS-CRM No. 392 Fluorspar from the Bureau of Analyzed Samples (BAS).
- Reagents used in pigment synthesis: $Co_3O_4$, $Al(OH)_3$, $Al_2O_3$, ZnO, $Cr_2O_3$ and $Fe_2O_3$

# 4 RESULTS

## 4.1 SORTING OF LITHIUM-ION BATTERIES BY THEIR CHEMISTRY

The chemical composition of the active cathode material was determined in a total of 240 batteries to build a database with the batteries in our study, sorted by make, model and type of chemistry used in their cathode. Figure 1 shows the results.

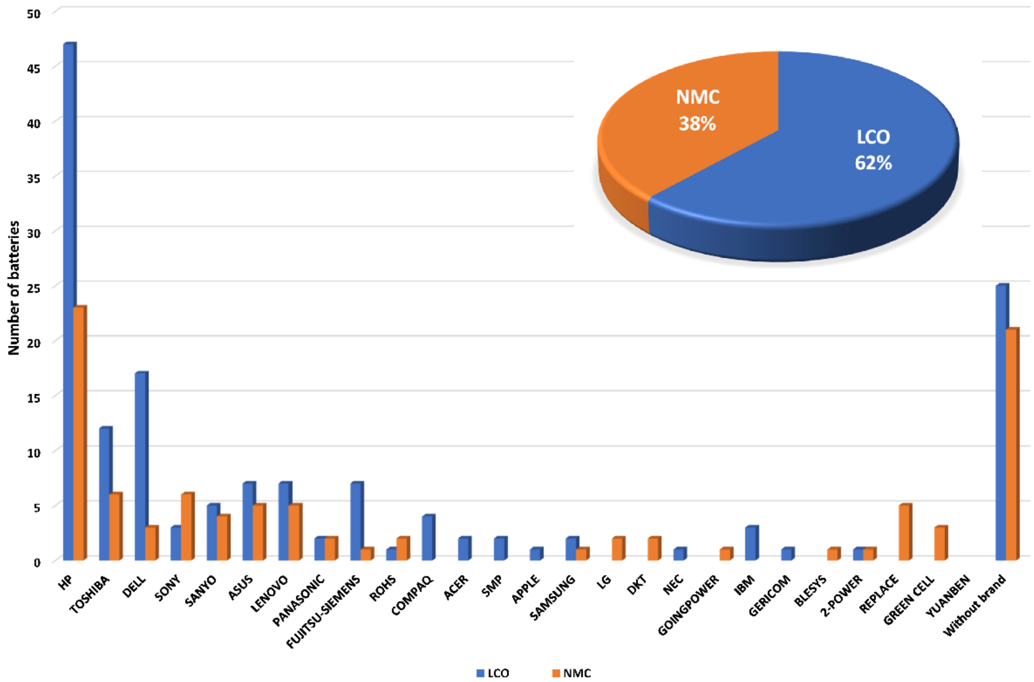


***Figure 1.*** *Classification of discarded computer batteries according to the chemistry of their active cathode material*

It should be noted that brands such as Hewlett-Packard (HP), for example, have a wide range of models. Specifically, this study analysed 63 different models, of which 43 had LCO chemistry while 20 of them had been manufactured with an NMC-type cathode. The reason for mentioning this is to highlight the fact that it is not enough to structure a database by make of battery but rather it needs to contain information on each of the models marketed by each computer brand.

In regard to the composition of the cathodes analysed, nowadays, the percentage of batteries discarded with LCO chemistry is found to be greater than the percentage of batteries discarded with NMC chemistry, although this circumstance may change over time.

## 4.2 AUTOMATIC SEPARATION OF ACTIVE MATERIAL FROM THE CATHODE AND OTHER BY-PRODUCTS

Once the batteries had been sorted and separated according to their chemistry (LCO and NMC), the different components were separated in the pilot plant and, apart from the actual cathode, three other by-products were obtained, with considerable concentrations of other high-added value metals, as shown in figure 2 below.

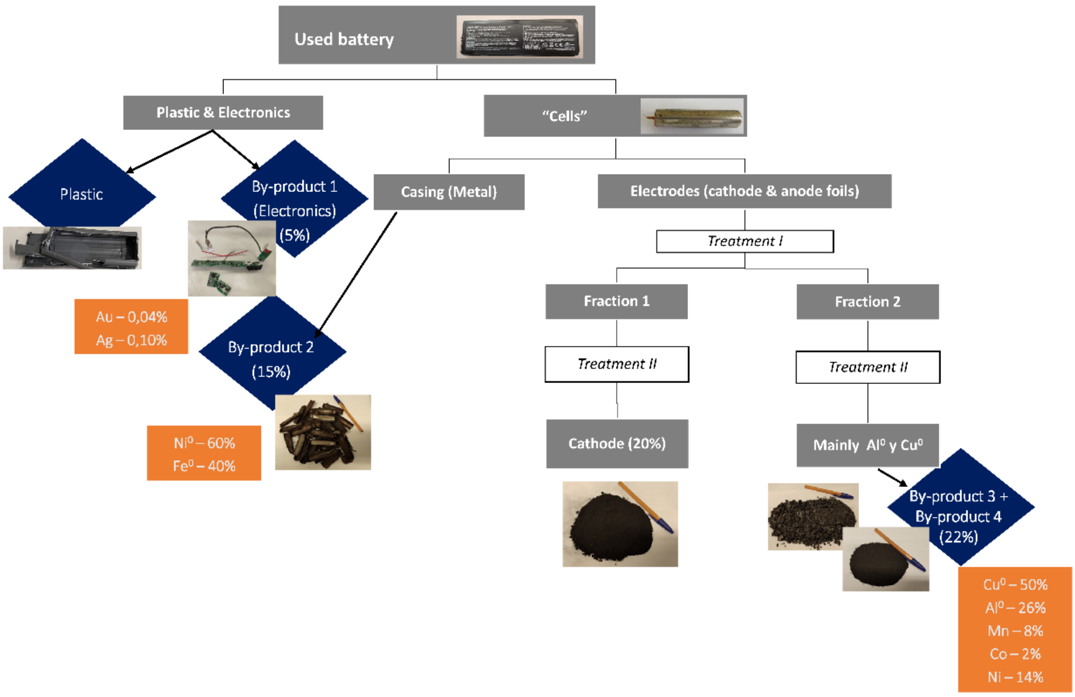


***Figure 2.*** *Scheme of the different products obtained when the components of a lithium-ion battery are separated.*

The recovered cathode accounts for 20% of the battery's weight, the Au- and Ag-rich by-product for 5%, the Ni-rich by-product for 15% and the Cu-rich by-product for 22%.

Table 1 shows the chemical composition of the LCO and NMC cathodes and Figure 3 shows the diffractograms and micrographs of both types of cathodes.

| | LCO-type cathode | NMC-type cathode |
|---|---|---|
| **$Co_2O_3$ (%)** | 74.4 | 54.0 |
| **NiO (%)** | 1.20 | 13.3 |
| **MnO (%)** | 0.50 | 11.1 |
| **$SiO_2$ (%)** | 0.04 | 0.1 |
| **$Al_2O_3$ (%)** | 1.46 | 1.48 |
| **$Fe_2O_3$ (%)** | 2.29 | 2.04 |
| **CaO (%)** | 0.06 | 0.11 |
| **MgO (%)** | <0.01 | <0.01 |
| **$Na_2O$ (%)** | <0.01 | 0.04 |
| **$K_2O$ (%)** | <0.01 | <0.01 |
| **$Li_2O$ (%)** | 11.2 | 11.4 |
| **$P_2O_5$ (%)** | 1.11 | 1.03 |
| **CuO (%)** | 4.20 | 3.03 |

***Table 1.*** *Chemical composition of the separated cathodes*

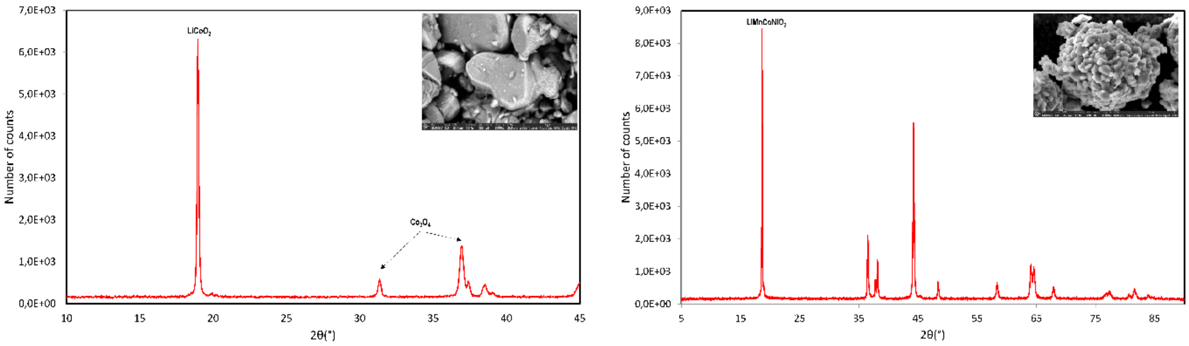


***Figure 3****. Mineralogical and morphological characterisation of the LCO- and NMC-type cathodes*

The chemical composition shows that, in addition to the elements from the cathode, there are elements from the collectors and from the cutting material, a fact that must be taken into account when formulating the pigments. The microstructure of the cathodes indicates particle size, which is crucial in the designed separation process, although our phase characterisation shows that there are no phases apart from those of the active material.

### 4.3 DEVELOPED PIGMENTS

Two pigments were developed by replacing the raw material $Co_3O_4$ with the LCO-type raw material: a Co/Al spinel blue pigment and a $(Co,Zn)(Al,Cr)_2O_4$ spinel-type green pigment. Moreover, a black pigment with a spinel-like $(Co,Fe,Ni,Mn)(Fe,Cr)_2O_4$ structure was also developed, where an NMC-type cathode was used as the source of Ni, Co and Mn. Table 2 shows the raw materials used in the synthesis of the three selected pigments, together with an image of the pigment obtained from the synthesis process.

| | Raw materials | Pigment obtained |
|---|---|---|
| **Co/Al blue** | LCO-type cathode<br>$Al(OH)_3$ |  |
| **$(Co,Zn)(Al,Cr)_2O_4$ green** | LCO-type cathode<br>$Cr_2O_3$<br>$Al_2O_3$<br>ZnO |  |
| **$(Co,Fe,Ni,Mn)(Fe,Cr)_2O_4$ black** | NMC-type cathode<br>$Cr_2O_3$<br>$Al_2O_3$<br>$Fe_2O_3$ |  |

***Table 2**. Raw materials used in the formulation of the selected pigments*

Once the pigments had been synthesised, mineralogical characterisation was carried out to confirm development of the characteristic crystalline structure of each pigment. Figure 4 shows the diffractograms of the three synthesised pigments.

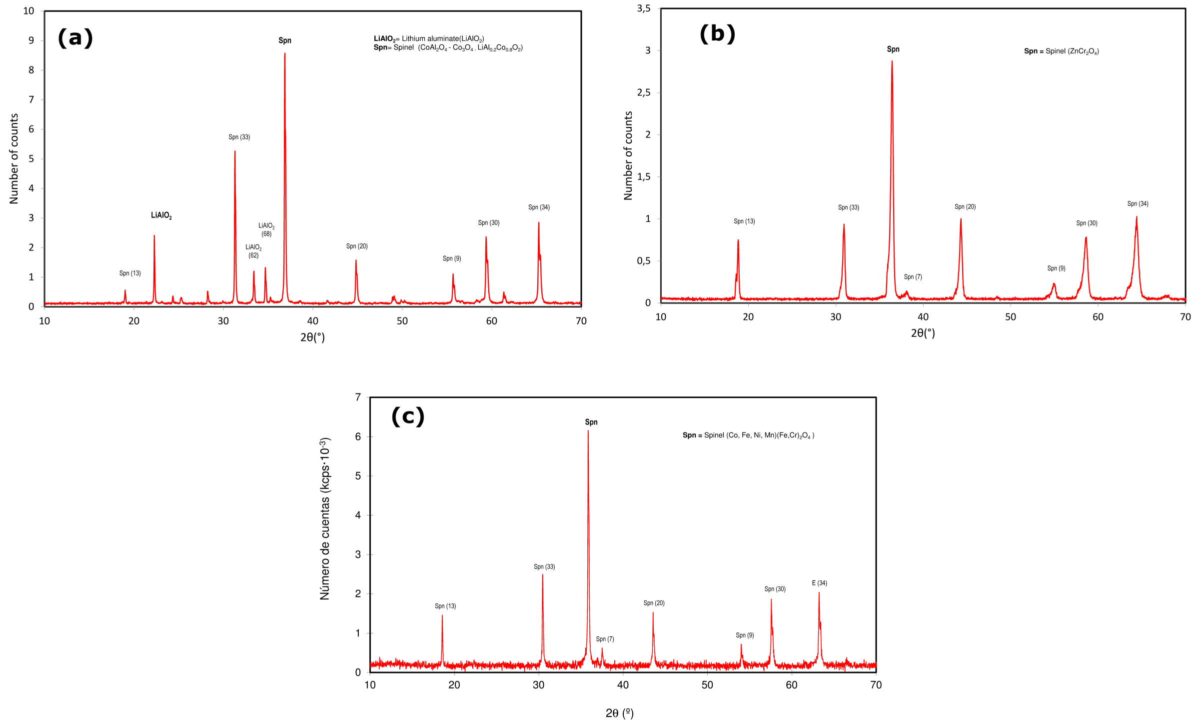


***Figure 4.*** *Phase identification of the synthesised pigments: (a) blue, (b) green, (c) black*

Subsequently, the developed pigments were included in the formulation of a coloured glaze for porcelain stoneware tile and the colour coordinates were measured. The glazes obtained were luminous and exhibited no pinholes or surface heterogeneities. A photograph of the resulting glazes is shown in Figure 5.

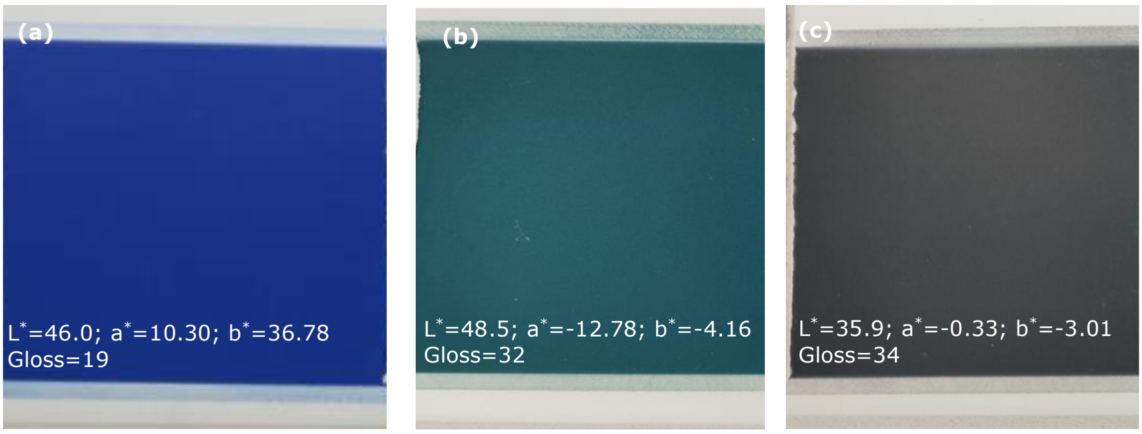


***Figure 5****. Colour development of the synthesised pigments: (a) blue, (b) green, (c) black*

The pigments were synthesised by totally substituting the Co, Ni and Mn raw materials with LCO- and NMC-type raw materials. However, this primary raw material substitution may be just partial rather than complete if the aim is to develop a pigment with specific characteristics.

## 5 CONCLUSIONS

1. A large number of used laptop batteries have been analysed and a database prepared that enables batteries to be sorted according to their type of cathode.
2. An automatic process for separating the components of a battery has been developed and a pilot plant for the process designed.
3. The active material of the cathode accounts for 20% of the weight and is the part of the battery with the highest added value. In addition, three by-products can be recovered during the separation process. Each of them is rich in an element that can be recovered. Thus, the electronics contain Au and Ag in their composition, the casings that cover the cells have a high content of metal Ni and, finally, the by-product that is formed by the collector plates has a high concentration of metal Cu.
4. With the active cathode material, a series of ceramic pigments has been developed, in which the primary raw materials - Co, Ni and Mn - have been fully substituted. However, such substitution can be partial in order to produce a certain colour shade.
5. The development of ceramic pigments from by-products obtained from waste such as used lithium-ion batteries has two important advantages, one from an economic point of view regarding dependence on third countries, and the other from an environmental standpoint, as it contributes to reducing toxic waste generation.

## 6 ACKNOWLEDGEMENTS

This study has been funded by the Generalitat Valencia, through the Valencian Institute for Business Competitiveness (IVACE) (dossier IMAMCA/2023/1).

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