

A laboratory-scale lithium-ion battery recycling process

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Abstract

A laboratory process based on simple and environmentally compatible operations, aimed to the treatment and recycling of spent lithium-ion batteries, is described in its various steps. The validity of the process has been evaluated by testing as cathode in a common lithium-ion battery configuration, a lithium cobalt oxide electrode prepared from recycled precursors. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The last decades have seen a tremendous progress in semiconductor technology which brought to the large-scale production of microelectronic components, which are now relatively inexpensive and used in the manufacturing of popular portable electronic devices, such as cellular phones, laptop computers and camcorders. Accordingly, new electrochemical power source systems, based on high energy density electrode materials, have been developed and commercialised to meet the requirements of the evolving electronic technology in terms of volumetric and gravimetric energy density.

Due to their favourable characteristics, lithium batteries are the systems of choice in the consumer electronics market. Lithium primary batteries are presently used for powering sophisticated electronic cameras, while lithium-ion secondary batteries dominate the cellular phones and laptop computer areas. The number of these consumer products is constantly expanding at a very fast rate. Only in Italy, the number of cellular phones has increased three-fold during the last two years. If we consider the expected overall world market evolution of the products and that the average life of the secondary batteries which power them is about 2 years, we can easily understand how the correct disposal of spent lithium batteries may soon become a serious problem.

In general, the utilisation of electric and electronic portable devices is continuously increasing in our everyday life. As a consequence, the amount of primary and secondary

batteries introduced in the global market is also growing. For this reason, their correct disposal is becoming a pressing issue.

Used batteries are explicitly mentioned by the EU regulations on wastes (EU Directives 91/156 and 91/689), this being included in the European community plan for waste management and a sustainable development. However, these regulations mainly refer to ‘conventional’ batteries and thus, quite worryingly, the safe disposal of spent lithium batteries is an issue which is not yet properly addressed. Even though in the last few years recycling plants and protocols are appearing in some countries, e.g. in the US and in Canada¹, much is still to be done with regard to their proper collection and recycling.

Therefore, it has appeared to us of importance to design and test a laboratory-scale, multi-step process for the treatment and the recycling of both primary and secondary lithium batteries. The scope was that of characterizing processes capable of treating the used batteries in order to render them suitable for disposal, by means of safe and environmentally compatible operations. In view of the sustainable management of natural resources, we also aimed at the recovery of all the valuables contained, in the form of pure compounds ready to be used in the manufacture of new batteries, thus achieving a ‘true’ recycling of these materials. With this aim we have previously faced the problem of the recycling and the disposal of used lithium primary batteries, namely Li/MnO₂ batteries, by determining their exact composition and consequently proposing and demonstrating a process which permitted to achieve a good recovery of the

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battery components [1]. In this work, we have extended the study to a process dealing with the disposal and recycling of spent lithium-ion secondary batteries.

2. Experimental

Commercial, cylindrical 18650 size $\text{LiCoO}_2/\text{LiC}_x$ spent batteries, kindly provided by Dr. J.P. Wiaux, Tylalise SA, Switzerland, were used as test systems for our process. These commercial LiCoO_2 -based lithium-ion batteries are standardised and their composition is well known. As an example Table 1 reports the characteristics of a 18650 size lithium-ion secondary batteries, which are among the most commonly sold and thus, the ones which have been selected for our study. Due to these available information, it has not appeared to us necessary to carry out any chemical analysis on the 18650 spent battery samples to determine their composition.

First, the batteries were opened by simply cutting their cases and extracting the active materials. During the cutting we noticed a strong heating, caused by the internal short-circuit of the cell. On an industrial scale, refrigeration during this operation is strongly advisable, e.g. by using liquid nitrogen (see footnote 1), in order to prevent safety hazard due to flames and explosions.

Table 1

Typical design parameters and chemical structure of a C/LiCoO₂ 18650 cylindrical cell [2]

Cathode:	
Active material	LiCoO_2
Binder	PVDF
Loading (total)	11.57 g
Current collector	Al foil (25 μm)
Leads	Al
Thickness (total)	0.018 cm
Cathode length	49.5 cm
Substrate length	52.0 cm
Substrate width	5.4 cm
Area (both sides)	535 cm
Anode:	
Active material	Nongraphitized carbon
Binder	PVDF
Loading (total)	4.92 g
Current collector	Cu foil (25 μm)
Thickness (total)	0.020 cm
Anode length	51.1 cm
Substrate length	53.7 cm
Substrate width	5.4 cm
Area (both sides)	552 cm
Other components:	
Electrolyte	PC/DEC, LiPF_6
Separator	Celgard (25 μm)
Insulator	PP disk
Leads	Aluminum
Case	Nickel-plated steel
Header	Aluminum safety vent
Closure	Crimp

The opened cells were submitted to a series of laboratory tests for defining their recycling and treating process. Among others, these tests included the determination of the concentrations of lithium and cobalt in aqueous solutions. These were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Varian Liberty 150 spectrophotometer.

The recycled lithium cobalt oxide was prepared by first thermally treating on the recovered product, i.e. cobalt hydroxide (see Fig. 1) at 450°C for 3 h, to obtain the Co_3O_4 oxide. This was then stoichiometrically mixed with Li_2CO_3 , i.e. another material which can be recovered from a lithium battery recycling process [1]. This mixture was first heated in a muffle furnace at 400°C for 5 h and then, after homogenizing in a mortar, annealed at 700°C for about 20 h to produce the desired lithium cobalt oxide LiCoO_2 . This was added with carbon (conductive component) and PVC (binder) in tetrahydrofuran (THF), to form a slurry which was sprayed onto an aluminum foil (current collector). The electrode film formed in this way had the following composition (in wt.%): $\text{LiCoO}_2/\text{Super P}/\text{PVC}$, 90/5/5.

The electrochemical characterization of these electrodes was carried out by galvanostatic cycling using an Amel 545

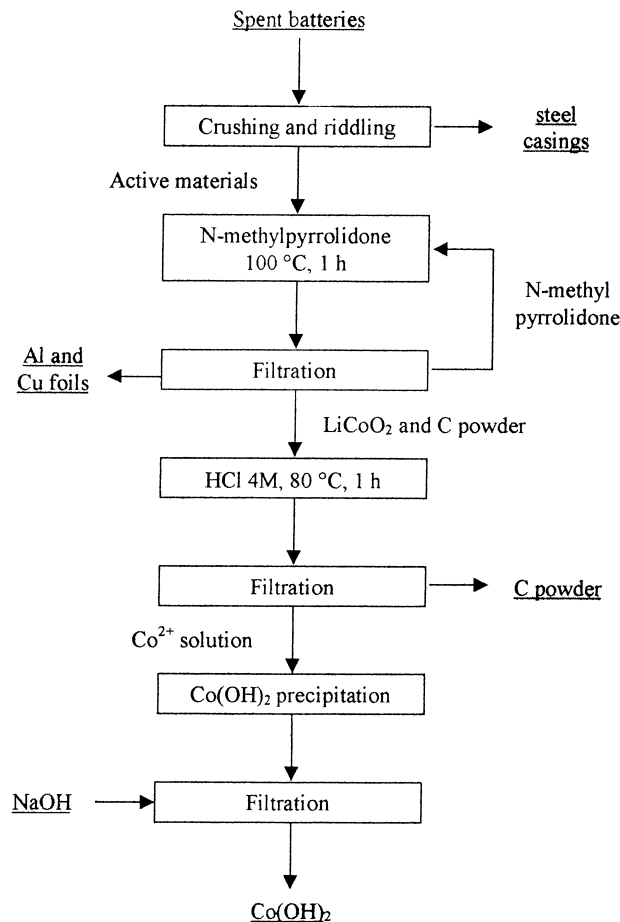


Fig. 1. Flow-sheet of the recycling process.

galvanostat and by cyclic voltammetry using a P.A.R. 362 potentiostat.

3. Results and discussion

Fig. 1 shows the flow-sheet of the process designed in this work; the various step operations are described below.

3.1. Sorting

The preliminary step in the treatment of the spent lithium-ion batteries consists in their separation from batteries of other chemistry which may be present in the waste flow. This can be achieved by the use of adequate sorting machines as those recently developed and commercialised [3].

3.2. Selective separation of the active materials

Fig. 2 shows the appearance of the cell after extraction from the casing. To achieve a good recovery of the active materials, a selective separation of the components is necessary. Except for the aluminum current collector, which appears to be almost self-separated from the rest, the other materials are strictly bound one to each other. We have experimented various separation approaches, the best being a treatment with *N*-methylpyrrolidone (NMP), at about 100°C for 1 h. The choice was motivated by the fact that NMP is a good solvent (solubility around 200 g/kg of solvent) for PVDF, i.e. for the binder used to hold the electrode films on the substrate, and that its boiling point is high (about 200°C). Indeed, this treatment allowed to achieve the effective separation of the films from their support and thus, the recovery of both copper and aluminum in

Table 2

ICP analysis results of a 1:5000 diluted aqueous solution

Li (ppm)	Co (ppm)	Cu (ppm)	Al (ppm)
1.30	7.23	–	–

their metallic form by simply filtrating them out from the NMP solution. This is particularly convenient since the two metals, after adequate cleaning, can be directly reused.

The separation by filtration of the other electrode film components, e.g. carbon and lithium cobalt oxide powders, is more difficult, due to the low size of the particles (order of magnitude of 1 µm). We have accomplished this operation by decanting the solution and then repeatedly washing with water the separated powders. The recovered NMP is then recycled since, thanks to its high solubility for PVDF, it can be reused for many cycles.

3.3. Lithium cobalt oxide dissolution

The dissolution of lithium cobalt oxide was achieved by treating the separated residual powders with a small volume of 4 M HCl for 1 h at about 80°C. The quantitative dissolution of cobalt and lithium from the oxide was obtained by using an acid/sample ratio of about 10 [4]. This was tested by inductively coupled plasma emission spectroscopy (ICP) analyses operated on the sample after a dilution of 1:5000. The results, reported in Table 2, give a concentration which in fact confirms the quantitative dissolution of the lithium cobalt oxide.

The side product, i.e. the carbon powder settling on the bottom, was separated and recovered by solution decantation.

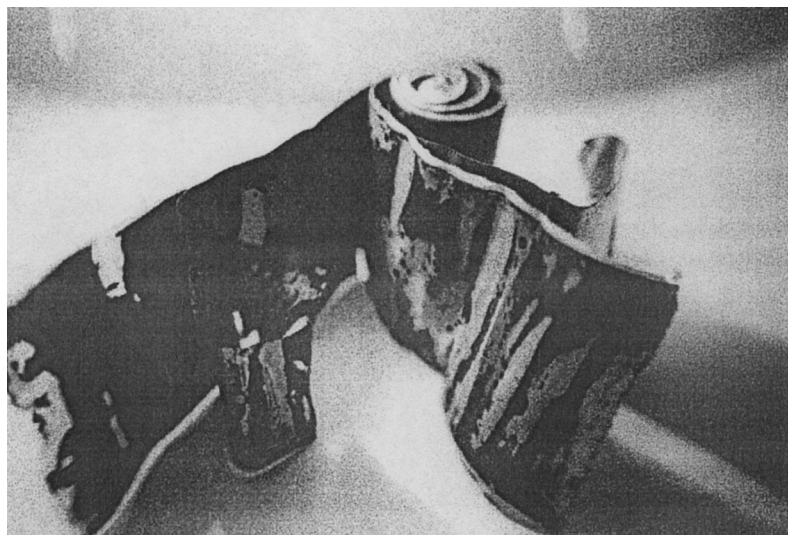


Fig. 2. Appearance of the electrode package of a lithium-ion battery once extracted from the casing.

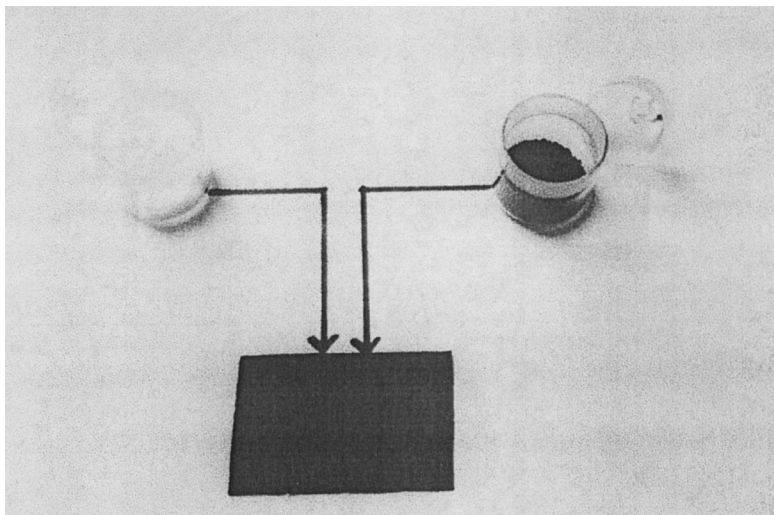


Fig. 3. Appearance of the LiCoO_2 -based electrode film prepared starting from recycled materials.

3.4. Cobalt hydroxide precipitation

The cobalt dissolved in the hydrochloric solution was recovered as cobalt hydroxide $\text{Co}(\text{OH})_2$ by addition of one equivalent volume of a 4 M NaOH solution. The solubility product of cobalt hydroxide is about 10^{-16} ; consequently, its precipitation begins at a pH value of 6 and can be considered to be completed at $\text{pH}=8$. Ideally, one could obtain $\text{Co}(\text{OH})_2$ precipitation by using an ammonia solution, i.e. by a weak base which forms a buffer solution at $\text{pH}=9$. Unfortunately, ammonia forms stable complexes with cobalt causing the partial dissolution of the hydroxide and thus, preventing from a quantitative recovery.

Therefore, NaOH, which is a strong base and which allows to work with small volumes of solution, remains the best choice. On an industrial scale, this step can be controlled by using an adequate pH sensor. The $\text{Co}(\text{OH})_2$

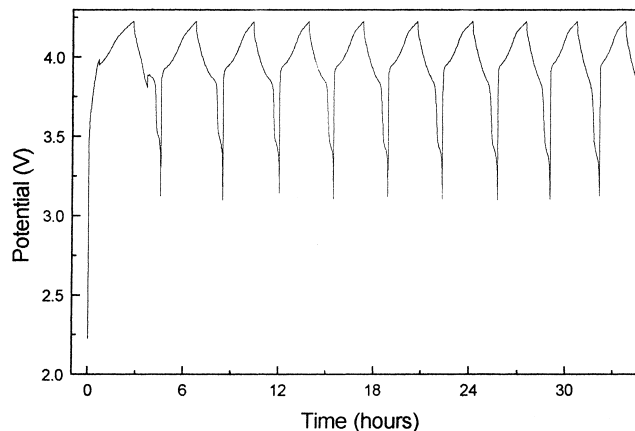


Fig. 4. Li intercalation-deintercalation cycles of a LiCoO_2 electrode in a EC-DMC, LiClO_4 electrolyte. Lithium counter electrode. Room temperature. Cycling rate: $100 \mu\text{A}/\text{cm}^2$.

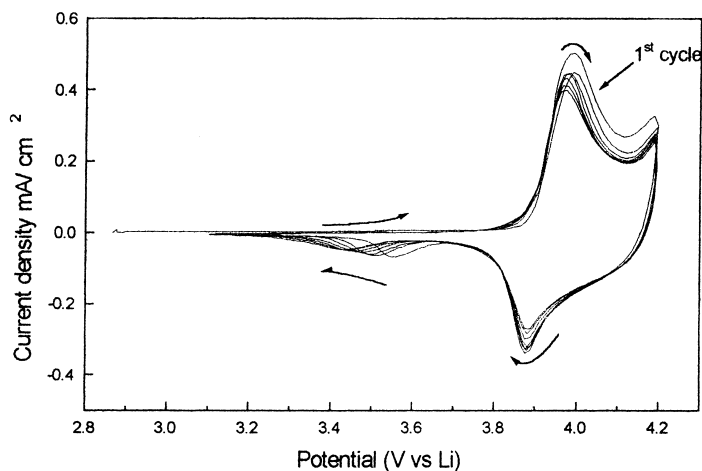


Fig. 5. Cyclic voltammety of a LiCoO_2 electrode in a EC-DMC, LiClO_4 electrolyte. Counter and reference electrode: Li. Room temperature. Scan rate: $100 \mu\text{V}/\text{s}$.

precipitate can be easily separated from the solution by filtration, to be then recycled.

3.5. Electrochemical characterization of a lithium cobalt oxide-based cathode prepared from recycled materials

To evaluate the validity of the process and the grade of the recovered materials, we have used the recycled cobalt hydroxide to synthesise lithium cobalt oxide to be tested as a cathode in a common lithium-ion battery configuration. The appearance of this recycled electrode, prepared as described in the Experimental part, is illustrated in Fig. 3. To test its electrochemical response, this LiCoO_2 electrode film was characterised by galvanostatic cycling and cyclic voltammetry. Figs. 4 and 5 show the results.

The galvanostatic intercalation and deintercalation cycles (Fig. 4) demonstrated the good working capabilities of the electrode, which can undergo various cycles with a good capacity retention. This favourable electrochemical

response is confirmed by the cycling voltammogram which clearly shows the reversibility of the electrode within the expected voltage limits. This allows us to conclude that the process described in this work may indeed provide good quality grade recycled materials which can be directly rerouted to the manufacturers for the production of new batteries.

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