

A laboratory-scale lithium battery recycling process ¹

M. Contestabile ², S. Panero, B. Scrosati ^{*}

Dipartimento di Chimica—Sezione di Elettrochimica, Università di Roma ‘La Sapienza’, 00185 Rome, Italy

Received 21 December 1998; accepted 9 March 1999

Abstract

After reviewing the status of the lithium battery waste treatment and, in particular, outlining the technical and practical aspects of this operation, we describe some preliminary activity in progress in our laboratory mainly directed to the development and evaluation of a multi-step recycling process. Although this process is still in an exploratory phase, the preliminary results obtained in our laboratory suggest that the process may be of some practical interest since it gives promises of obtaining a good recovery of the battery components by rather efficient and easily achievable operations. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium battery; Waste treatment; Recycling process

1. Introduction

During the last decade a great increase in environmental awareness took place and legislation on wastes developed consequently. At the end of 1980s restrictions on heavy metals like mercury, cadmium and lead were imposed. This led battery manufacturers to make great efforts in developing ‘green’ batteries. In fact, since the early 1990s, nearly all of the market primary dry batteries became mercury-free. At present, due to a further increase in environmental sensibility, attention is addressed to sustainable management of natural resources, in addition to concern related to the hazardous properties of metals and substances. This means that more efforts are expected to be devoted to the collection and recycling of batteries of any kind, despite the possibility that they may present a low content in heavy metals.

In the rechargeable battery field, Ni-MH and lithium batteries are progressively inserted in the consumer market, as alternatives to the more polluting and less performing Ni-Cd batteries. However, rechargeable batteries also

have a limited life and their proper disposal is an issue which is not yet properly addressed. According to European regulation, all batteries must be regarded as hazardous wastes and thus they require treatment before disposal. European directives on hazardous wastes and sustainable development point at the following tasks to be pursued, in order of priority:

1. waste reduction at the origin, by means of cleaner products and processes;
2. recovery of valuables from wastes, where possible;
3. treatment of non-recoverable wastes, to make them safe and disposable.

According to these directives, several recycling plants are in operation or in project phase in various European countries. However, the majority of them are presently restricted to the treatment of dry primary cells and of rechargeable Ni-Cd batteries, while little attention has so far been devoted to the collection and the recycling of lithium batteries.

This is somewhat surprising since lithium batteries represent one of the most promising technology in battery development. Both primary and secondary lithium cells are invading the market due to their favourable characteristics and performances. Even though in the last few years protocols and recycling plants came to existence in some countries, e.g., in the United States and Canada [1], much is still to be done about their collection and recycling.

To our knowledge, no such plants are in operation in Europe or, at least, in Italy. It has, therefore, appeared to

^{*} Corresponding author. Tel.: +039-6-4462866; E-mail: scrosati@uniroma1.it

¹ This work has been presented as an invited talk at the 4th International Battery Recycling Congress, Hamburg, Germany, 1–3 July, 1998.

² E-mail: contestabile@axrma.uniroma1.it.

us of interest to develop a laboratory-scale lithium recycling process with the main goal of evaluating its characteristics and thus, of determining its practical value.

2. Collection and sorting of exhausted lithium batteries

The first problem which we met in our research was the collection and the sorting of exhausted lithium batteries.

Proper sorting and identification of the battery's chemistry is a major issue in the treatment and recovery of lithium batteries and, more generally, of any kind of battery. In fact, to develop an efficient recycling process, it is necessary to know the composition of the batteries subjected to the treatment. Indeed, the more specific the process is, the more effective the recovery of materials is. The chemistry and technology of lithium batteries are still evolving, making their recycling more difficult than other simpler and better established electrochemical systems.

With regard to the problem of sorting, although recently sorting machines have been developed [2], some problems are still waiting for answers. They are:

- differences in composition even for the same type of battery (e.g., different electrolytes) from different manufacturers;
- changes in the battery structure due to the introduction of new models or the development of the existing ones.

Possibly, sorting of lithium batteries may generally benefit by a higher degree of standardisation. Ideally, batteries of the same kind should have almost the same chemical composition and be marked with an easily understandable code, although this is difficult to expect because manufacturers achieve competitive edge by using slightly different chemistries.

As for our research project, we decided to face the problem from an empirical point of view. With the help of some retailers selling batteries, films and small electronic devices for consumers' use, like shavers, cameras, etc., we were able to screen the battery waste stream in Rome. In fact, we noticed that, despite their little knowledge of the hazards related to these items, they organised on a voluntary basis the collection of the batteries they dealt with, in order to avoid their improper disposal. This demonstrates a good level of environmental awareness, especially considering that no consisting information campaigns are held by the municipality. From the screening that we have performed, a strong presence of used lithium primary batteries emerged. We could not find any used lithium secondary cell; this can be explained by their very recent entrance in

Table 1
Basic composition of Li/MnO₂ lithium primary batteries [3]

System	Cathode	Electrolyte	Solvent	Separator
Li/MnO ₂	MnO ₂ /C	Li salt	organic mixture	polypropylene

Table 2

Electrolyte salts and organic solvents for lithium primary batteries [3]

Lithium salts	LiAsF ₆ ; LiClO ₄ ; LiPF ₆ ; LiBF ₄ .
Organic solvents	PC–DME; BL–THF; 1,3-D.

PC = propylene carbonate; DME = dimethoxyethane; BL = γ -Butyrolactone; THF = Tetrahydrofuran; 1,3-D = dioxolane.

our market and by their longer life compared with primary systems.

The next problem we met was the identification of the batteries' type and chemistry. To solve this, we referred to the 'Battery International Type Code' [3] reported on their wrappings and we determined that the lithium primary batteries collected in several different retailers were all of the Li/MnO₂ type, used for cameras and other portable devices. No other types of lithium primary cells were found. According to their manufacturers, these batteries have the composition reported in Table 1.

The information available to us on the composition of the battery was not complete, since the nature of the electrolyte and of the organic solvent employed was not known. The most common lithium salts and organic solvents for lithium primary batteries are reported in Table 2.

Thus, we had to determine it by chemical analysis. For the batteries collected for this study we have found by inductively coupled plasma atomic emission spectrometry and by gas chromatography-mass spectrometry that the electrolyte is formed, depending on the make of the batteries, by LiAsF₆ in PC–DME and probably LiClO₄ in 1,3-D. It would be highly desirable that more detailed information on the chemistry of a given cell were provided by the manufacturers, particularly concerning the case when toxic or harmful substances are used.

Moreover, by examining the collected Li/MnO₂ cells, we noticed that almost all of them still presented a very high voltage, close to the nominal voltage value. This clearly suggested that a large fraction of these batteries were still in a partially charged state when disposed, probably because they were replaced when the battery indicator of the electronic device turned on. Most of the times this happens long before the battery is fully discharged. The consequence is that a considerable amount of lithium metal is expected to be present in the scrap battery, as indeed confirmed by our experiments.

3. The treating process

We have conceived a process which is expected to treat and recycle exhausted lithium batteries by a series of easily performing and low-cost steps. These steps are summarised in Fig. 1 and briefly described below.

3.1. Crushing

This can be generally accomplished by using a hammer mill. In our laboratory project, we have opened the batter-

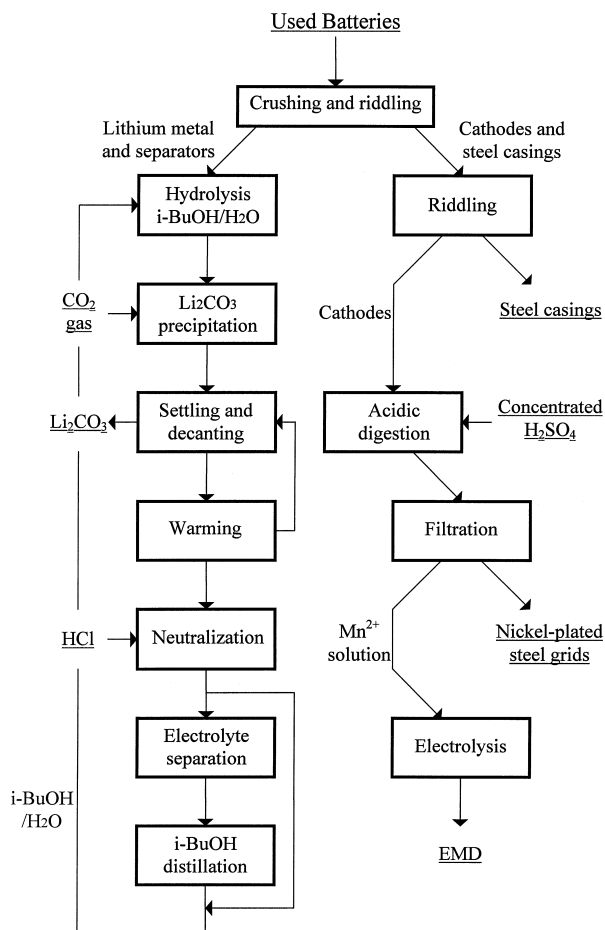


Fig. 1. Flow-sheet of the lithium battery recycling process.

ies by cutting the steel cases and removing the inner parts. During this step cooling of the batteries is advisable, in order to reduce the risk of explosions due to the reactivity of their components, e.g., by using liquid nitrogen [1]. In fact, during the opening of the casings, we detected a strong warming of the batteries, caused by internal short-circuits. It is also advisable to scrub the gases evolved during this step since, originating from the thermal decomposition of the solvent and the electrolyte, they may be toxic.

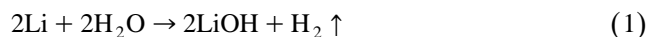
3.2. Riddling

Due to their different specific weight, mechanical riddling may allow to achieve the separation of the steel casings and of the cathode assembly (MnO_2/C supported on nickel-plated steel grids) from the rest of the active materials (lithium anodes and polypropylene separators). The latter may be directed to the hydrolysis step, while the steel casings can be recovered or properly disposed. Finally, the cathodic materials can be treated to recover highly pure manganese dioxide.

3.3. Hydrolysis

The active materials of the samples examined in this work contained a large amount of lithium metal, the

presence of which constituted the main source of hazard in the treatment of our lithium batteries. Accordingly, these materials were introduced into an *iso*-butyl alcohol/water, *i*-BuOH/ H_2O , biphasic system, which allowed to achieve a mild oxidation of lithium metal. In fact, the direct reaction of lithium metal in water, represented by:



cannot be used since it occurs very quickly, also due to the high solubility of lithium hydroxide in an aqueous solution. Since the reaction is highly exothermic, the resulting hydrogen gas can ignite, with consequent high safety risk. A possible alternative is to conduct the operation in a pure alcoholic medium. However, the solubility of lithium hydroxide in this medium is so low that passivation occurs on the metal surface and its oxidation soon stops.

Looking for a compromise between these two media, we tested various different alcohol/water mixtures. One possible example is the ethyl alcohol–water, $\text{EtOH}/\text{H}_2\text{O}$ monophasic system, where the two components are miscible in a wide range of composition. However, the reaction rate in this medium strongly depended on the $\text{EtOH}/\text{H}_2\text{O}$ ratio and, in any case, it was very difficult to control. We found that the *i*-BuOH/ H_2O biphasic system represented a favourable alternative. Since this system consists of two phases, the alcohol/water ratio did not affect the reaction rate. Moreover, the low solubility of water in the upper alcoholic phase allowed a mild lithium oxidation reaction to happen. In fact, we have experimentally noticed that parts containing lithium metal initially floated on the upper phase and then, the formed lithium hydroxide precipitated in the lower aqueous phase, where it dissolved.

The final solution became strongly alkaline, due to hydroxonium ion consumption during the completion of reaction (1). The solution also contained the electrolyte salt and its original organic solvent.

Polypropylene separators could be easily removed by filtration or by floating of the solution.

3.4. Lithium carbonate precipitation

This step was performed by bubbling CO_2 gas through the solution. As a result, the formation of a precipitate consisting of almost pure Li_2CO_3 was readily observed. Moreover, because of the acidic properties of the CO_2 gas, the pH of the medium decreased toward neutrality. The precipitation process was achieved in a few minutes since the ionic concentration in the solution decreased below the solubility product value for lithium carbonate, also due to the fact that the solubility of the CO_2 gas in water decreases along with the loss of alkalinity of the medium. The full separation of the precipitate was accomplished by a proper decantation process.

3.5. Warming and neutralising

It is advisable to recycle the *i*-BuOH/H₂O biphasic system in order to minimise the use of solvents and the amount of wastewater produced. For this reason, the quantitative removal of the dissolved inorganic carbon has appeared appropriate. This could be simply achieved by warming the solution, to promote the following equilibrium sequence:



It is expected that an increase in the temperature depresses the solubility of CO₂ and causes the acidic gas to leave the solution, thus raising the pH value. Consequently, by heating the solution the above equilibrium could be shifted to the formation of the carbonate ion (CO₃²⁻) which in turn precipitated as Li₂CO₃ since no other cations which could form poorly soluble carbonates were present in solution. By operating this second precipitation, quantitative recovery of lithium could be achieved.

The thermal energy resulting from lithium oxidation could be used to accomplish the warming step. The Li₂CO₃ product so obtained was separated by settling and decantation. After completion of this step, the neutralisation of the solution was achieved by addition of a small amount of hydrochloric acid and controlling the resulted pH by an adequate sensor.

3.6. Lithium salt separation

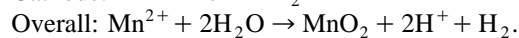
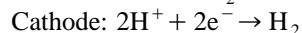
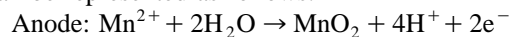
As previously mentioned, one of the lithium salts used in the electrolyte of the batteries tested in this study is LiAsF₆ (see Table 2). The toxicological properties of arsenic are well known and thus its concentration in the wastewater must be reduced to less than 1 ppm to meet the acceptable releasing limits. Moreover, arsenic accumulating in the *i*-BuOH/H₂O biphasic system during several cycles can coprecipitate together with lithium carbonate, this affecting the purity of the precipitate. Thus, removal of arsenic from the solution is advisable. So far, we have not developed any experimental process to satisfactorily achieve this goal. However, the use of ion exchanging resins appears to be an adequate approach [4].

3.7. Organic solvent separation

The organic solvents used in the original electrolytes of the tested batteries, which essentially consisted of ether mixtures (see Table 2), distributed mainly in the alcoholic phase rather than in the aqueous one. Since the concentration of these solvents is very low, they should not cause any problem in the overall recycling process. If required, the alcoholic phase can be purified from these organic compounds by distillation.

3.8. Cathodic materials recovery

Cathode mixtures are composed of MnO₂/C powder supported on nickel-plated steel grids. We have treated them with concentrate sulphuric acid, in order to obtain the quantitative solubilization of manganese in the reduced Mn²⁺ state. Moreover, after some time carbon powder was released from the grids, and so they could be recovered as well. No relevant concentration of nickel was found in the sulphuric solution, as detected by qualitative test using dimethylglyoxime that forms a strongly coloured, red complex with nickel. Manganese could be recovered as Electrolytic Manganese Dioxide (EMD) by an electrochemical process which is well established and widely reported in literature [5]. It consists in the electrolysis of a neutralised and purified solution of MnSO₄ (80–180 g/l), acidified with H₂SO₄ (50–100 g/l). The electrochemical reaction can be represented as follows:



EMD is highly pure, 'battery grade' manganese dioxide and may be used in the manufacturing of high energy density batteries, such as the same lithium batteries.

We also tried to attack this materials with other acids, however, with no good results. In fact, both nitric and hydrochloric acid led to the solubilization of nickel from the grids, which interferes with the recovery of manganese. Moreover, MnO₂ in hot hydrochloric acid causes the quantitative evolution of Cl₂ gas, which is dangerous.

4. Conclusion

We report the description of a multi-step process for the treatment and the recovery of exhausted lithium primary batteries. Although similar processes are probably used by commercial battery disposal companies, no detailed information is published. The preliminary results suggest that the process developed in our laboratory may be of some practical interest since it gives promises of obtaining a good recovery of the battery components by means of rather efficient and easily achievable operations.

References

- [1] Lithium Battery Recycling Facility, Toxco, 3200 E. Frontera Street, Anaheim, CA 92806, USA.
- [2] J.P. Wiaux, Spent Battery Sorting: The Future, 4th International Battery Recycling Congress, Hamburg, Germany, July 1–3, 1998.
- [3] D. Linden, Handbook on Batteries, 2nd edn., McGraw-Hill, New York, 1995.
- [4] J.W. Patterson, Industrial Wastewater Treatment Technology, 2nd edn., Butterworth–Heinemann, New York, 1985.
- [5] Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 15, 4th edn., Wiley-Interscience, New York, 1995, pp. 1013–1017.