

Preliminary tests for lanthanum and cobalt recovery from waste SOC cathodes

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Introduction

Solid Oxide Cells (SOCs) are efficient and clean power systems destined to be highly exploited in the next future [1], having a predicted market growing from 1.09 billion USD in 2021 to 5.31 billion USD in 2028 [2]. According to the economic forecast, high amounts of waste cells will be generated in the next years; however, an efficient strategy for the management of waste SOC cathodes still does not exist.

Thanks to their economic importance and criticality, REEs and cobalt were included in the list of Critical Raw Materials (CRMs) in 2020 [3]. The development of an efficient strategy for the recovery of valuable metals from waste SOC cathodes is crucial to reduce the consumption of virgin raw materials, lowering the costs and the environmental impacts, and supporting the SOC value chain in EU [4]. This work has the aim to provide some preliminary results for the development of hydrometallurgical processes for the recovery of lanthanum and cobalt from the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) perovskite cathodes of waste SOC cathodes.

Materials and methods

The explored hydrometallurgical process was made of consequent phases: acid leaching (eventually with a hydrogen peroxide as reducing agent) of lanthanum and cobalt from waste SOC cathode dry powders, precipitation after the addition of oxalic acid at 25°C, and recovery via centrifugation. The recovered and dried powders were further characterized through X-Ray Diffraction (XRD). Four leaching agents were tested: nitric, sulfuric, oxalic, and citric acids. For each leaching process, the operative conditions (acid concentration, solid/liquid ratio, temperature, and contact time) were selected according to previous literature studies concerning the recovery of lanthanum and cobalt from different sources (waste batteries, spent cracking catalysts) [5-10].

Results and discussion

The experimental parameters (acid concentration, presence of reducing agents, solid/liquid ratio, temperature, and contact time) (Table 1) adopted for the leaching processes were derived from literature [5-10].

Table 1. Experimental conditions adopted for the leaching processes

Leaching agent	Acid concentration	Reducing agent (concentration)	S/L ratio	Temperature	Contact time
Nitric acid	2M	H ₂ O ₂ (1.7%v)	10 g/L	80°C	3 h
Sulfuric acid	First stage: 2 M Second stage: 1 M	-	150 g/L	80°C 25°C	3 h 1 h
Oxalic acid	1M	-	50 g/L	80°C	2 h
Citric acid	2 M	H ₂ O ₂ (1%v)	50 g/L	70°C	4 h

When nitric acid was employed as leaching agent [5,6], a pink solution rich in lanthanum and cobalt, and a mixture of lanthanum cobalt oxide and strontium oxide were obtained. An excess of oxalic acid was added to the leachate to recover lanthanum and cobalt while the pH of the solution was controlled adding 10 M NaOH. A lanthanum-rich solid precipitated at low (<1.2) pH values, while at higher pH (5.7) powders rich in cobalt and strontium were obtained (the mixture contained cobalt oxalate hydrate and sodium strontium oxalate hydrate).

The use of sulfuric acid allowed to carry out a more selective process, exploiting the different solubility of cobalt and lanthanum in the acid lixiviant depending on temperature [7]. A leaching process with sulfuric acid was conducted at 80°C to dissolve most elements except REEs. Then, a second leaching step was performed at 25°C, maximizing REEs' solubility. Adding NaOH step by step to the leachates, Co-rich powders were obtained from the first process while sodium lanthanum sulfate hydrate was recovered from the second.

Oxalic acid was investigated, attempting leaching and recovery with one reagent [8]. The grey powder obtained was a mixture of unreacted LSC and cobalt and lanthanum oxalates. This process looks attractive, being based on a single chemical, but an efficient method for the separation of lanthanum and cobalt-rich compounds from the powder mixture is needed.

When citric acid was employed as leaching agent [9,10], a pink liquor was obtained while the residual solid phase mainly consisted of strontium oxide. Adding a stoichiometric amount (with respect to La concentration in LSC powders) of oxalic acid, lanthanum oxalate hydrate was recovered. The further addition of an excess of oxalic acid (referred to the concentration of cobalt in LSC) led to the precipitation of a Co-rich solid.

Conclusions

This work preliminary investigated the recovery of lanthanum and cobalt from waste SOC's cathodes through different leaching agents. In the processes based on nitric and citric acids the leaching stage was followed by the recovery of the valuable metals from the liquor through the addition of oxalic acid, observing a partially selective precipitation. The first precipitate (pH <1.2) was rich in lanthanum, while the second (obtained at pH 5.7 with nitric acid or dosing higher concentration of oxalic acid for the process with citric acid) was rich in cobalt. The process employing sulfuric acid required two leaching phases but provided an enhanced separation between lanthanum-rich and cobalt-rich products. The process based on oxalic acid was simpler, but the resulting mixture of oxalates of valuable metals needs to be recovered from the unreacted LSC powders. In conclusion, this preliminary study suggests different procedures for the recovery of lanthanum and cobalt from waste SOC's cathodes. In the proposed processes cobalt and lanthanum precipitated as oxalates, sulfates, hydroxides, and oxides, but the further research is needed to optimize of the yields and selectivity of the processes, and to improve the purity of the products.

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