# Effect of deep eutectic solvents and organic acids use during the electrodialytic lithium extraction from aluminium-lithium alloy waste

ORAL
Ph.D. Student: N
Journal: JECE

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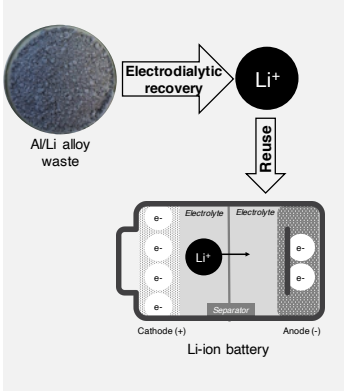


The transport sector contributes to a quarter of the global greenhouse gases emissions. To alleviate these environmental burdens, policies were developed to support the uptake of electric vehicles (EV) and promote transport decarbonization. In the clean energy transition, lithium (Li) is a strategic element that is applied during EV battery production. However, Li consumption and price have increased abruptly during the past decade, and the EU included Li in the 2023 critical raw materials list. Aiming to improve Li recovery in a circular perspective, while mitigating the negative impacts from primary Li exploitation, the present work tested the electrodialytic process to extract Li from an Al/Li alloy waste. Six bench-scale experiments were conducted for three days, using a two-compartment electrodialytic reactor at 100 mA, as well as organic acids and deep eutectic solvents as adjuvants. The results demonstrated a maximum Li recovery of 91.5%.

## Introduction

The transportation sector accounts for approximately 25% of global greenhouse gases (GHG) emissions, being the top priority of decarbonisation policies [1]. Under the “Fit for 55” package, the European Union (EU) has set straight targets to decrease net emissions by at least 55% by 2030 (compared to 1990 levels) to turn the EU climate-neutral by 2050 [2]. Moreover, the technological progress in renewable energy and battery storage is accelerating the development of innovative power systems with sustainable energy sources. This has leveraged the electric vehicle (EV) market, which is now a key factor in achieving carbon neutrality. In 2030, it is foreseen that EV account for about 60% of total vehicle sales [3].

Lithium-ion batteries (LIB) play an important role as energy storage devices in mobility and renewable energy systems. However, the raw materials that comprise a LIB, such as lithium (Li), nickel (Ni) and cobalt (Co), are included in the 2023 EU critical raw materials (CRM) list due to their high risk of supply, economic value and importance to product performance [4]. Furthermore, 96% of primary Li global production comes from China, Chile, Argentina and Australia, with deposits forecast to be depleted by 2055 [5]. To decrease EU dependency on imported battery chemicals and raw materials, while improving EU competitiveness in the value chain of battery storage, sustainable alternatives are desirable. The effective reuse and recycling of secondary raw materials across all stages of production and use cycles can ensure maximum usage of available resources cost-effectively, while mitigating environmental risks.

Aluminium lithium (Al/Li) alloy is widely used in the aerospace field. These alloys have lower density than conventional Al alloys, reducing the weight of components. However, the methods for producing finished metal products by machining, transformation and cutting of intermediate products contribute to large amounts of machine scraps [6]. This waste is generated during the production of structural elements from rolled, drawn or forged semi-finished products and during the scalping of ingots for rolling or skinning of billets in the aluminium plant. Additionally, the recycling of Al/Li alloy waste is often difficult due to the mixture with other alloys of aluminium or other materials, such as stainless steel and titanium [7].

The reuse of Al/Li alloy waste may allow to recover Li contents in a circular economy perspective, while reducing waste generation in the aerospace sector. Electro-based technologies have been used to recover CRM from a wide range of environmental matrices. In the electrodialytic (ED) process, a low-level current density is applied, between two electrodes, mobilizing species through transport mechanisms in the presence of ion exchange membranes [8]. The present work aimed to test electro-based technologies to recover Li from an Al/Li alloy waste untreated and treated with super critical $CO_2$. A 2-compartment (2C) ED reactor with a cation-exchange membrane was used. Organic acids and deep eutectic solvents (DES) were also tested to improve the Li extraction from the Al/Li alloy waste.

## Material and Methods

The ED reactor set up was a 2C acryl XT cell (RIAS A/S, Roskilde, Denmark). The internal diameter of the reactor was 8 cm (electrolyte end = 5 cm and sample = 10 cm length). The compartments were

separated by a cation exchange membrane (CEM), CR67, MKIII, Blank (Ionics, USA). The electrodes were made of Ti/MMO (titanium/ metal mixed oxide) Permaskand wire: Ø = 3 mm, L = 50 mm (Grønvold & Karnov A/S, Denmark). A power supply E3612A (HewlettPackard, Palo Alto, USA) was used to maintain a current of 100 mA in the ED reactor and stirring (Heidolph, Germany) was applied in the sample compartment, at 200 rpm (Figure 1).

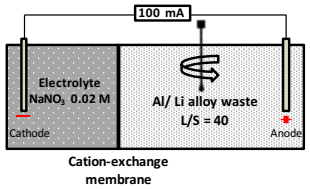


**Figure 1.** Electrodialytic reactor configuration.

Suspensions were prepared with deionised water and Al/ Li alloy waste treated and untreated at a liquid/solid (L/S) ratio of 40. A solution of $NaNO_3$ at 0.02 M was prepared for the electrolyte.

The study tested the ED process coupling organic acid and DES: (1) choline chloride/malonic acid (1:1) and (2) choline chloride/oxalic acid (1:1). The experiments were operated for 3 days.

Microwave-assisted acid extraction was carried out in a microwave Ethos (Milestone S.r.l, Bergamo, Italy) according to EPA 3051 A. Total concentrations of Li were determined by Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) (HORIBA Jobin-Yvon Ultima, Japan).

## Results and Discussion

The Al/Li alloy waste is composed of 4106.1 mg Li/kg of sample. The pH is 12.7 and the conductivity is approx. 22.1 mS/cm (in water at a L/S=40).

At the end of the ED process was applied, in the anode and cathode compartments, pH values were acid and alkaline, respectively. This was expected since water electrolysis promotes the generation of $H^+$ at the anode and $OH^-$ at the cathode end. Furthermore, the conductivity in the sample compartment decreased after all the experiments, suggesting the electromigration of ions from the sample compartment to the electrolyte end.

The maximum Li extraction from the Al/ Li alloy waste was achieved when oxalic acid alone was added to the sample compartment. Around 92% of Li was solubilized in the liquid phase of the sample compartment, where 18% electromigrated to the electrolyte end. On the other hand, when a pre-treatment with supercritical $CO_2$ was applied to the initial sample, 81% of Li was solubilized, and the highest electromigration was observed towards the electrolyte compartment (69%).

The properties of the bidentate oxalate ion may have contributed to forming oxalate complexes, since oxalic acid may react with solubilized elements, releasing Li ions. From the electrolyte compartment, Li can be further separated and reused in Li-ion batteries. This can leverage CRM circular economy while mitigating the environmental impacts of waste disposal from aerospace industries.

## Conclusions

The recovery of Li from secondary resources can alleviate the environmental impacts of primary Li production and the dependency on EU imports of raw materials. The application of the ED process with organic acids and DES to Al/Li alloy waste suggested new possibilities for the recovery of Li (maximum Li recovery of 91.5%) in a circular perspective.

***Acknowledgements***

This work has received funding from the Horizon Europe program, grant agreement number 101069789: project RELiEF – Recycling of Lithium from secondary raw materials and further, and Portuguese Foundation for Science and Technology (FCT) through grant UIDB/04085/2020 (strategic project for CENSE). This research was anchored by the RESOLUTION LAB, an infrastructure at NOVA School of Science and Technology. Disclaimer: Funded by the European Union. Views and opinions expressed are however those of the authors only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

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