

# ELECTROCHEMICAL METHODS FOR THE RECYCLING OF BATTERIES AND ELECTRONIC WASTE

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## Abstract

The recycling of batteries is currently based on pyro- or hydrometallurgical processes that are energy and chemical-intensive. [1] Therefore, novel strategies using electrochemical methods are investigated. By in situ generation of leaching reagents the need for chemicals can be minimized and the handling of dangerous substances like hydrogen peroxide is avoidable. The separation of extracted metals requires several complex steps that need additional chemicals for solvent extraction, stripping and precipitation. Thus, using electrowinning for the recovery and separation of metals is an alternative.

As sustainable leaching reagent peroxydisulfate was generated in situ from sulfuric acid on boron-doped diamond electrodes. This solution was used for ex-cell leaching of battery cathode materials like lithium cobalt oxide (LCO) and lithium nickel cobalt manganese oxide (NCM) as well as industrial black mass. The leaching rate is increased by up to 100 % for LCO and NCM compared to not electrolyzed solutions and a substantially faster conversion rate is observed for black mass with full extraction of all metallic components. [2]

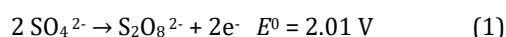
Mechanistic studies revealed that hydrogen peroxide is formed in situ from persulfate and is responsible for the improved reactivity. To further improve the method, a flow cell setup was designed to use currents up to 4 A to generate 1 M persulfate concentrations.

In addition, we investigated the electrowinning and separation of cobalt and nickel from solution. By using varying conditions (pH, temperature, potential) a controlled low reduction potential was most beneficial for a high selectivity reaching over 90 % cobalt content. The use of organic additives further increased the cobalt selectivity up to 97 %.

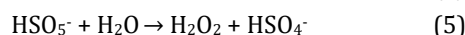
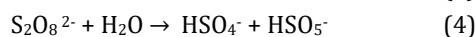
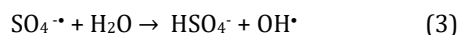
## Introduction

The growing waste stream of batteries is increasing the urge to find sustainable recycling methods to preserve valuable resources as well as to prevent ecological effects. Current recycling strategies for these materials are based on pyro- or hydrometallurgical methods as well as direct recycling. [1,3–7] Direct recycling is especially suitable for production scraps and LiFePO<sub>4</sub> type batteries while spent NCM and LCO batteries usually require metallurgical treatment and resynthesis of the material. In pyrometallurgical processes e-waste and batteries are subjected to high temperature above 1000 °C to melt transition metals that are forming an alloy fraction together with a slag fraction that contains oxides of metals like Al and Li. To separate the metals further hydrometallurgical treatment is required. This can also be done directly by leaching metals from waste using acids. However, typically further reagents are required, oxide materials as in battery waste are treated with hydrogen peroxide or sulfites as reducing agent. The recovery and separation of the metals in solution requires further processing and complex procedures like solvent extraction with organic reagents and precipitation. These processes require substantial amounts of chemicals and generate additional waste streams. [1,8–10]

Therefore, novel strategies using electrochemical methods were investigated by several researchers. [11–13] By in situ generation of leaching reagents the need for chemicals can be minimized and the handling of dangerous substances is avoidable. One potential reagent is peroxydisulfate (PDS) that can be produced on boron doped diamond electrodes from sulfuric acid. [14,15] The formation of PDS follows a radical pathway on the electrode surface according to eq. (1) with high current efficiency of up to 90 %. [14–16]



When peroxydisulfate is activated by heat or radiation, it forms sulfate radicals, which can further react to hydroxyl radicals (eq. 2-3). [17] More importantly, in acidic solution PDS undergoes hydrolysis to peroxymonosulfate (PMS) and hydrogen peroxide (eq. 4-5). [18,19] These reactive oxygen species can enhance the reactivity of the leaching solution to yield higher conversion rates.

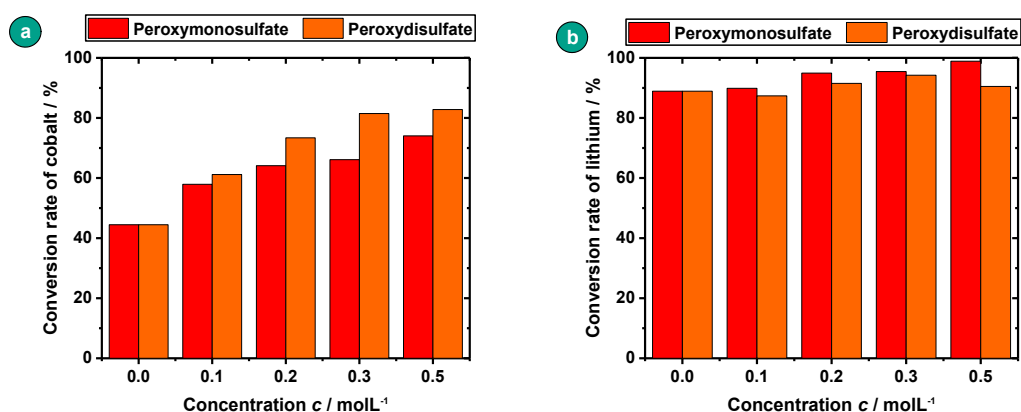


This reactivity allows it to generate oxidizing (PDS, PMS,  $\text{H}_2\text{O}_2$ ) as well as reducing ( $\text{H}_2\text{O}_2$ ) reagents with one electrochemical process. Thus, it is well-suited for our investigation as reagent in hydrometallurgical processes.

For the recovery and purification of metals electrochemistry is established on a large scale, e.g. copper refining and Ag electrowinning. In addition, by using potential controlled methods a separation of elements can be achieved according to their standard redox potentials. Separate electrowinning after solvent extraction is well established in the literature as well as in industrial processes. [20–24] Recently, approaches with polymer coated electrodes have been made to achieve selective electrodeposition as well as obtaining Co/Ni alloys from leaching solutions. [25,26] This concept of coupled electrochemical leaching and electrowinning was also previously used for the recovery of silver and copper from photovoltaic waste with high recovery rates. [27]

## Results and Discussion

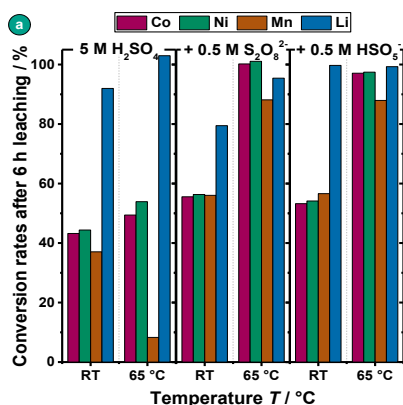
To demonstrate the suitability of persulfates for leaching pre-studies with commercial persulfate salts were performed. Lithium cobalt oxide (LCO) was investigated initially as it is one of the most stable active materials as well as having the highest value and even though nowadays it finds little application it is still contained in end-of-life batteries. Different acid concentrations were used at room temperature (RT) as well as 65 °C with varying amounts of PDS and PMS in 5 M sulfuric acid that was found to be most suitable and the conversion rate of Li and Co was determined as displayed in Figure 1. RT leaching was not suitable to achieve high conversion remaining below 40 % and 70 % for Co and Li, respectively. At 65 °C an increasing amount of persulfates clearly increases the leaching of Co from 45 to over 80 % and leaching of Li increases slightly from 80 % to 90–100 %.



**Figure 1:** (a) Influence of different peroxymonosulfate and peroxydisulfate concentrations on the conversion rate of cobalt. (Leaching parameter: 5 M Sulfuric acid, 65 °C and  $s/l = 5 \text{ gL}^{-1}$  for 6 h) (b) Influence of different peroxymonosulfate and peroxydisulfate concentrations to the conversion rate of lithium.

The higher leaching rate for Li is based on the facile deintercalation of Li from the LCO structure. The strongly delithiated LCO structure is relatively stable and resists leaching without the addition of further reducing agents.

NCM as the commercial most employed material nowadays, was investigated in the next step using PDS at 0.5 M and PMS at 0.3 M in 5 M sulfuric acid. As displayed in Figure 2, the addition of PDS or PMS significantly improves the leaching rate for Co, Ni and Mn, especially at elevated temperatures. Nearly complete leaching is achieved, only the conversion rate of Mn is not quantitative which can be attributed to the formation of insoluble  $\text{MnO}_2$ . The lower Co content clearly facilitates the leaching of this material, thus, reducing the amount of additional reagents required. The difference between PDS and PMS is small as it was also observed for LCO. The likely explanation is that the reaction from PDS to PMS is substantially faster than the formation of hydrogen peroxide which is the active reagent.

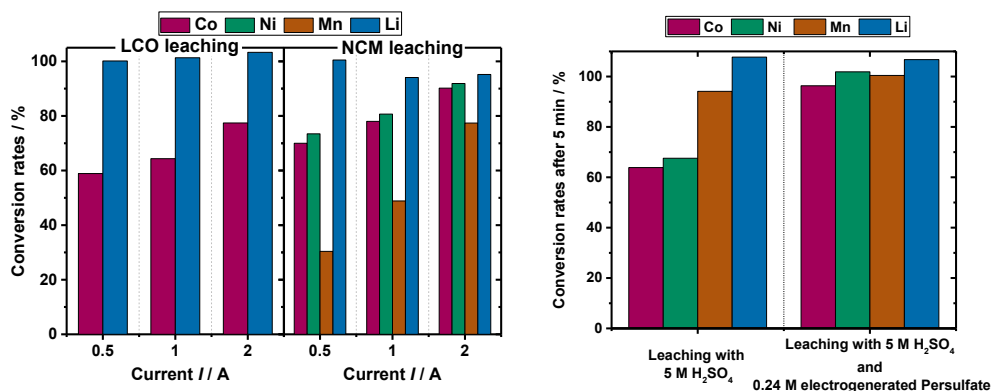


**Figure 2:** (a) Conversion rates of cobalt, nickel, manganese and lithium for the leaching of NCM with and without the addition of 0.5 M peroxydisulfate or 0.5 M peroxymonosulfate at ambient temperature and 65 °C. Leaching parameter: 5 M sulfuric acid with a  $s/l = 5 \text{ gL}^{-1}$  for 6 h).

By further investigations it was observed that the conversion of PDS to PMS and finally  $\text{H}_2\text{O}_2$  according to eqs. 4-5 is the reason for the improved reactivity. The successful demonstration of the positive influence of PDS and PMS on leaching is followed by the in situ generation in an electrochemical cell with consecutive leaching.

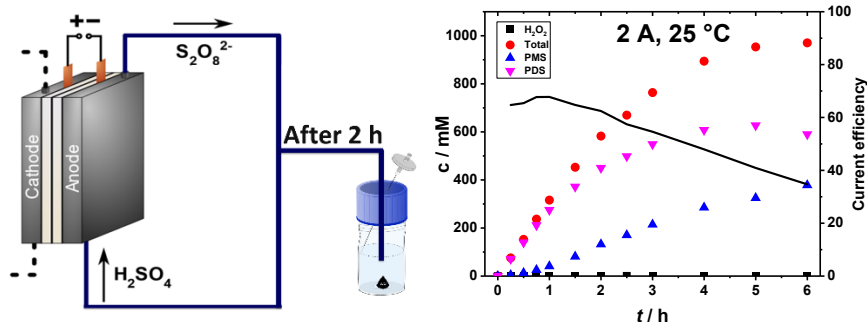
### Electrochemical leaching

Electrochemically generated persulfates were used to leach LCO, NCM and black mass from an industrial source. The electrolysis was carried out in an H-cell with a membrane to separate anodic and cathodic compartments. Currents between 0.5-2 A ( $25\text{-}100 \text{ mA/cm}^2$ ) were employed to generate persulfate in concentrations of up to 0.26 M. Leaching with an in-cell approach was found to be ineffective as faradaic efficiency was low due to the formation of Co(III) as side reaction. Instead, the persulfate solution was used in a separate reaction vessel. The results displayed in Figure 3 show the improved conversion rates for LCO and NCM for higher currents as a result of higher persulfate concentrations. The obtained conversion rates are only slightly lower than those for persulfate salts because of the lower concentrations in the electrochemical reaction. For the leaching of black mass nearly complete conversion was achieved within 5 minutes which shows a significant improvement compared to leaching with sulfuric acid only.



**Figure 3:** Left: Conversion rates for the leaching of LCO and NCM with electrogenerated persulfates in 5 M sulfuric acid with  $s/l = 15 \text{ gL}^{-1}$  at 65 °C and varying amounts of persulfate depending on the current during electrolysis. Right: Conversion rates of cobalt, nickel, manganese and lithium for the leaching of black mass with and without the addition of 0.243 M electrogenerated persulfates after 5 min. Leaching parameters: 5 M sulfuric acid with  $s/l = 15 \text{ gL}^{-1}$  at 65 °C.

In the next step, a flow cell setup was used to generate PDS more efficiently and at higher quantities. The setup used for electrolysis and leaching is displayed in Figure 4 together with concentrations of persulfates and  $\text{H}_2\text{O}_2$ . Significantly higher concentrations up to 1 M of persulfates can be generated with this method. With prolonged reaction time a rise in PMS concentration is clearly visible due to the hydrolysis reaction.



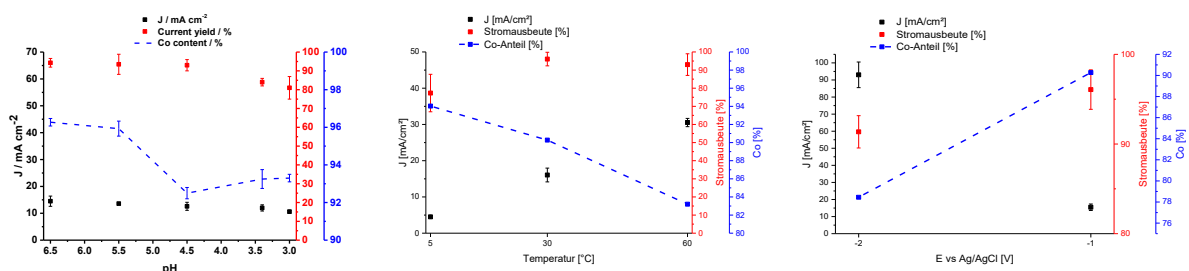
**Figure 5:** Scheme of an electrochemical flow cell leaching setup (with BDD as anode) combined with a leaching experiment (reaction vessel with LCO powder).

To improve the leaching rate further, it is possible to include a step for conversion of persulfates to hydrogen peroxide prior to introducing it into the leaching reactor. This reduces side reaction of persulfate with  $\text{Co}^{2+}$  that lead to catalytic decomposition of persulfates, thus, limiting the beneficial effects.

## Electrochemical recovery

The electrochemical recovery of Co and Ni is established after separating the metals by solvent extraction. Direct electrochemical separation has not been demonstrated. The Co deposition was studied using rotating disk electrode measurement to reduce the influence of mass transport limitations. By varying the deposition parameters, we have aimed to achieve a high Co selectivity by studying the effect of pH, temperature and deposition potential. The results are displayed in Figure 6. In general, a high current efficiency of 80-95 % can be observed from a solution containing 0.1 M Co and Ni sulfate. The solutions pH has only a minor influence on the Co selectivity and a high Co content of over 90 % is found in the deposit. However, the current efficiency of the process decreases for  $\text{pH} < 4.5$  from 95 % to 82 % at pH 3 for currents of approximately  $15 \text{ mA/cm}^2$ . The temperature of the solution has a more profound influence on selectivity. Increasing the temperature to  $60 \text{ }^\circ\text{C}$  decreases the Co content substantially to 83 % while at  $5 \text{ }^\circ\text{C}$  the deposit contains 94 % Co. Yet, low temperature also results in a reduced current density of only  $5 \text{ mA/cm}^2$  and reduced current efficiency of below 80 %. The electrode potential was found to have a major influence on the electro-winning selectivity. By applying a more negative electrode potential of  $-2 \text{ V}$  instead of  $-1 \text{ V}$  (vs. Ag/AgCl) the Co selectivity drops below 80 %. This coincides with a significant increase in current density up to  $90 \text{ mA/cm}^2$ , indicating a much higher deposition rate.

From these results it can be concluded that the Ni reduction shows slower kinetics and thus is disfavored despite being the slightly more noble metal. Therefore, conditions that slow the kinetics in general like low temperature and low overpotential benefit the Co deposition over Ni.



**Figure 6:** Influence of pH, temperature and potential on the Co content of the deposit, the current and current efficiency.

To further improve selectivity organic additives were added in order to form complexes that shift the redox potential of the metals. The experiments were conducted in a batch cell with two parallel electrode plates to scale up the process as shown in Figure 7. Different organic acids and amino acids have been investigated, the results for alanine are displayed in Figure 7 showing a high dependency on the pH of the electro-winning solution containing equimolar amounts of Ni and Co. In this setup, a cobalt selectivity of 88 % was achieved which is slightly lower than for rotating disk electrode experiments. This can be attributed to a less efficient mass transport in this setup. While at pH 5 and 9 the Co selectivity is lower than the reference, at pH 7 nearly 97 % Co content can be achieved. The much higher pH dependence when using complexing agents is a result of the degree of protonation and thus allows the formation of different complexes of Ni and Co which can benefit the selectivity.



**Figure 7:** Image of the used cell for Co deposition. Center: Deposits of Co/Ni. Right: Cobalt content of the deposit dependent on varying parameters with added alanine.

This demonstrates that the selective recovery of Co from Co/Ni solutions is possible by electrochemical deposition by taking advantage of the small differences in kinetics and reactivity of Co and Ni. The high selectivity is comparable to other published methods with higher complexity. [25] Further investigation is required to achieve even higher selectivity under quantitative deposition conditions.

## Experimental

Leaching experiments are performed by adding LCO, LNO, NCM powder (TCI Chemicals GmbH) or black mass, provided from Accurec Recycling GmbH, and the oxidation agents  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  or  $\text{KSO}_5\text{H}$ , obtained as Oxone<sup>®</sup>-salt into sulfuric acid (dilution from 75%). A sulfuric acid volume of 50 mL is placed in the reaction vessel with 250 mg of the corresponding cathode powder, to obtain a solid-liquid ratio of  $5 \text{ gL}^{-1}$ , if not specified otherwise, with varying concentrations of the corresponding oxidation agent. The leaching compound and the oxidation agent are added simultaneously to the solution, while the stirring speed is 250 rpm. If the sulfuric acid must be heated, the temperature of the solution is kept constant for minimum 45 min prior to the experiment. The cathode powder and the oxidation agent are added subsequently. For reactions at ambient temperature, the chemicals are added directly. In both cases, the leaching time starts when the leaching compound is added into the solution. Conversion rates are calculated as described in eq. 6.

$$\text{Conversion rate metal (in \%)} = \frac{c_{\text{Me,t}}}{c_{\text{Me}}} \cdot 100 \quad (6)$$

$c_{\text{Me}}$  is defined as the overall concentration of metals, which can be potentially leached based on the weight of the cathode material and  $c_{\text{Me,t}}$  is defined as the concentration of metals leached after a certain period of time. Samples are taken and stored during leaching in timed intervals. This sample solution has been diluted with 2%  $\text{HNO}_3$  to achieve the same solution matrix used for the ICP-OES system. These solutions are examined with the Agilent 5800 ICP-OES (Agilent Technologies) to obtain the concentration of  $\text{Li}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ . If the concentration of the sample cannot be determined with UV-Vis, an ICP-OES analysis has been performed with samples that were taken out of the solution after a certain leaching duration.

The electrochemical experiments are carried out in either an H-cell setup with a total volume of  $2 \times 100 \text{ mL}$  or a flow cell setup. A boron-doped diamond electrode (W&L Coating Systems) with a geometric surface area of  $20 \text{ cm}^2$  ( $2 \times 10 \text{ cm}^2$ , front and back, expanded metal for H-cell and  $20 \text{ cm}^2$  flat for the flow cell) serves as anode and carbon fiber felt as cathode with an interelectrode distance of approximately 10 cm. A  $\text{Hg}/\text{HgSO}_4$  electrode was used as reference electrode for the 3-electrode H-cell setup. The electrolyte in both half-cells is 5 M sulfuric acid, and the half-cells are separated with a cation exchange membrane F-930rfd (Fumatech BWT). The potentiostat Ivium-n-Stat (Ivium) has been used to apply the current. The concentrations of formed peroxydisulfate and peroxymonosulfate have been determined with the titration procedure of Thompson.[28] The metal concentration is examined with the same methods described above.

Electrowinning experiments were conducted using a rotating disk electrode made of Pt or Ti controlled by a Metrohm potentiostat. As reference electrode a  $\text{Ag}/\text{AgCl}$  electrode was used. Solution containing 0.1 M of  $\text{NiSO}_4$  and  $\text{CoSO}_4$  and 0.1 M boric acid as buffer were used and the pH adjusted using  $\text{H}_2\text{SO}_4$  or  $\text{NaOH}$ . The deposits were dissolved by nitric acid and diluted for measurement with the Agilent 5800 ICP-OES (Agilent Technologies) to obtain the concentration of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ . Experiments using a batch cell were performed using the same conditions, but the working electrode was changed for a stainless-steel plate with a surface area of  $3.75 \text{ cm}^2$ .

## Conclusion

The electrochemically assisted leaching by in situ formation of persulfates and hydrogen peroxide was shown to be a promising alternative to conventional leaching methods. The addition of persulfate can double the leaching

rate for LCO from (42 % to 78 % Co) and NCM ( $\approx$  40 % to > 90 % for Ni, Co, Mn). The electrolyzed sulfuric acid solutions show a significantly increased reactivity allowing nearly quantitative leaching of NCM and industrial black mass (> 95 % for Li, Ni, Co, Mn). By improving the setup, the persulfate generation was increased further to achieve concentration > 1 M in order to further improve efficient leaching rates.

Electrowinning was used to deposit Co from Co/Ni solutions with a selectivity of up to 95 % by optimizing the parameters using low temperature and overpotential. The utilization of organic additives like alanine allowed an even higher Co content in the deposit of 97 % at a pH of 7. Precise control of the conditions was found to be crucial for obtaining the best results.

For future studies we plan to combine both steps, the anodic persulfate generation with the cathodic metal deposition within one electrochemical cell and optimizing the full system.

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