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# Recovery of metallic nickel from NiMH battery waste

An investigation of the dissolution step from a hydrometallurgical recycling route using hydrochloric acid

Master of Science thesis in the Master Degree Program, Nuclear Science and Technology

# FREDRIK NYHLÉN

Department of Chemistry and Chemical Engineering Industrial Materials Recycling CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2017

MASTER'S THESIS 2017:NN

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#### FREDRIK NYHLÉN

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Supervisor and Examiner: Britt-Marie Steenari, Industrial Materials Recycling Supervisor Assistant: Filip Holmberg, Industrial Materials Recycling

Master's Thesis 2017:NN Department of Chemistry and Chemical Engineering Division of Energy and Materials Industrial Materials Recycling Chalmers University of Technology SE-412 96 Gothenburg Telephone +46 31 772 1000

Cover: Scanning Electron Microscope picture of undissolved material, showing dendritic nickel particles, after 5 hours leaching of mixed electrode material with HCl. (3000x magnification)

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### Abstract

The market for batteries is growing and is expected to continue to do so. The increasing need for transporting electric energy in the electrification of the car fleet is a large contributing factor to this. In order to keep the materials of the batteries in a sustainable closed loop cycle, the recycling demand will increase at the same rate. Nickel Metal Hydride (NiMH) batteries serves as a replacement to the former Nickel Cadmium (NiCd) batteries and are expected to hold a relatively small, but important role of the battery market in a near future. The complex construction of metals in a battery makes the constituent components suitable for chemical recycling. With a previously developed hydrometallurgical recycling route for NiMH batteries as starting point, the dissolution step of NiMH battery material originating from batteries produced by Nilar AB was in the current project studied.

Dissolution titration experiments performed at pH 1 using hydrochloric acid (HCl) showed selective leaching of everything but metallic nickel, which was the only remaining undissolved specie after five hours leaching time. Terminating the dissolutions at this point could decrease the dissolution time significantly compared to total dissolution, which was completed first after 30 hours. Furthermore, a fraction of undissolved nickel with a purity of above 99.5% by mass could be collected. This fraction amounts to five sixths ( $\approx 83\%$ ) of the initial amount of metallic nickel in the batteries.

Results from upscale experiments confirmed that selective leaching also occurs during dissolution using highly concentrated solutions. It was also indicated that it might take even shorter time to dissolve everything but metallic nickel during these conditions, but this needs to be confirmed with further studies before any conclusions can be drawn.

Keywords: NiMH batteries, Recycling, Dissolution, HCl, Selective leaching, Nickel

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# 1 Introduction

One of the major environmental issues today is considered to be the amplified global warming, which is according to IPCC fifth assessment report (2013) extremely likely to be caused by emissions of greenhouse gases from human activities[1]. This contribution comes mainly from combustion of fossil fuels which generates anthropogenic carbon dioxide ( $CO_2$ ). A sustainable vision to avoid a large part of these emissions is to aim towards a more electrified society, where electricity is used as an energy carrier instead of fossil fuels[2]. This requires of course that the electricity generation in the future's grid will be produced from carbon neutral energy sources, such as nuclear-, biomass-, wind- and solar power etc. Going towards a more electrified society and one of the ways to achieve that is with batteries.

The transport sector could be the most intuitive sector which to a large extent relies on the battery technology in the conversion from fossil fuels as energy carrier towards electric energy. But there are also other future possible applications for batteries. A large scale use of batteries as energy storing technologies for the electric grid, would enable a large expansion of the intermittent renewable energy sources windand solar power[3]. This could be achieved by charging the batteries during hours when the supply of electric energy is larger than the demand. This excess energy could later be used during hours when the demand is larger than the supply.

The total world demand of batteries is forecasted to grow by 7.7% annually and amount to US\$120 billion in 2019[4]. At the same time, the European Commission reports that approximately 160000 tons of consumer batteries, 190000 tons of industrial batteries and 800000 tons of automotive batteries enters the market in the European Union each year[5].

Since the production of batteries has increased and is expected to increase in the near future, the amount of battery waste will also increase at the same rate. This leads to an increasing recycling demand of the batteries. Recycling is important for many reasons such as environmental, limited availability of resources and economical reasons. According to legislation within the European Union (Directive 2006/66/EC), batteries or accumulators with a mercury or cadmium content above a certain value (0.0005% by weight for mercury and 0,002% for cadmium) are prohibited[6]. Furthermore, the legislation promotes collection and recycling of battery and accumulator waste. It also promotes a reduction of the environmental impact from all processes involved in their life-cycles, including disposal and recycling.

There are currently many different types of batteries on the market. One of them is the Nickel Metal Hydride batteries. These batteries have been introduced to replace the highly toxic and environmental unfriendly previously used Nickel Cadmium batteries[7, 8]. NiMH batteries can also provide higher specific energy than its forerunner. NiMH batteries are currently used in different applications, such as telecom and back-up applications, electric mobile equipment and hybrid vehicles as well. They are also available as AA and AAA for consumer use. With a share of 3%, NiMH batteries holds a small but important part of the global battery market[4].

The main components of the batteries, that are also of most concern regarding environmental impact and has largest economical potential when recycled, are the metals. The concentration of metals are in many cases larger in the waste streams of metal-containing products than in primary metal ore. Metal recovery from primary sources consumes therefore in many cases more energy than production of metals from recycled waste[9].

NiMH batteries contains a lot of nickel, but also some cobalt and rare earth elements (REE). The waste stream of NiMH batteries could therefore potentially become a resource of these technically important elements. In particular, relatively pure nickel components are used to increase conductivity of the electrodes. To increase the economical gains of recycling NiMH batteries, it is useful to extract this component separately. The price of nickel (purity >99.9%) has the last year been fluctuating around US\$10000 per metric ton[10]. Cobalt is also associated with a high price. The price of cobalt has increased from US\$20000 to US\$50000 per metric ton during the last year (from March 2012). There has been a frequent debate the last six years concerning the scarcity of the rare earth elements. Several technologies associated with sustainable energy recovery and usage (e.g. batteries, energy saving light bulbs, solar cells, wind turbines etc.) requires certain amounts of the RREs. The issue and costs related to the RREs lies not necessarily in the supply of these elements, but in obtaining a pure enough fraction of the individual elements for certain applications [11]. The RREs are namely usually found together in the earths crust and they have similar chemical and physical properties, which makes separation difficult.

A possible recycling procedure of the active (metal containing) material in batteries is to dissolve this material in acid and subsequently extract the dissolved species to an organic phase. This has previously been studied by Larsson et.al. for the NiMH batteries in the Toyota Prius hybrid cars[12, 13, 14, 15]. One of the components in NiMH batteries is metallic nickel and the proposed process enables selective leaching of everything but metallic nickel using hydrochloric acid as leaching agent. With this process as a starting point, the dissolution of battery waste originating from the company Nilar AB, has in the current project been investigated. There is a significant difference in which form the metallic nickel is constructed in the two types of batteries and this is the reason why it is interesting to investigate a different version of NiMH batteries using a former developed process.

# 1.1 Aim and approach

The aim of the current project is to investigate the dissolution process of the active material from spent NiMH batteries using hydrochloric acid as leaching agent. An evaluation of the process itself as well as an investigation if the material can be selectively leached with respect to everything but metallic nickel will be performed. If selective leaching and a subsequent separation of this nickel component appears to be possible, the undissolved nickel will be characterised in order to investigate if this recovered fraction could be reused in the production of new batteries. Alternatively, it should be recycled for other uses (i.e. steels).

The current work focuses on the dissolution step, which is the first step to treat NiMH waste using hydrometallurgical methods. The conditions of the produced aqueous solutions will affect subsequent separation procedures.

#### 1. Introduction

# 2

# Theory

## 2.1 Chemistry of batteries

A battery is an energy storing device consisting of several electrochemical cells, each with an anode, cathode and electrolyte[16]. The circuit is closed and a current arise once a load is connected between the anode and cathode. Energy is consequently extracted from the battery and it is said to be discharged. During this process the anode material is being oxidised, producing electrons which flows through the circuit and to the cathode, where the material is reduced and therefore absorbs the electrons. The anode and cathode are physically and electrically separated, only connected through the electrolyte, which allows ionic transfer between them in order to allow the electrochemical reactions to arise.

#### 2.1.1 NiMH batteries

The anode material of NiMH batteries consists of a hydrogen storing alloy denoted  $AB_5$ , where A is a mixture of lanthanides (lanthanum, cerium, neodynium and pradeodynium) and B is mainly nickel, but also small amounts of cobalt, manganese and aluminum[16]. The cathode material consists, in its discharged state, mainly of Ni(OH)<sub>2</sub> and with smaller amounts of cobalt and zinc. The electrolyte is an alkaline aqueous solution of KOH.

Both the anode and cathode materials from the batteries investigated in the current project also contains metallic nickel as dendritic (star-shaped) particles. The role of these particles is to form a network of metallic nickel, which in combination with its high electric conductive properties forms "highways" for the electrons. This increases the conductivity of the active materials as a whole, which enables faster charging and possibility to extract more energy per unit of time from the battery. As a comparison to the NiMH batteries investigated by Larsson (2012), the metallic nickel constructing the active material in those batteries is a foam-type mesh structure of metallic nickel. The working principle of both constructions is still the same.

The reaction of discharging is for NiMH batteries a reversible reaction, which means it can be pushed in the reversed direction. This is done by connecting an external electric energy source to the battery. The chemical reactions occurring in a NiMH battery during charging and discharging are shown in the equations 2.1-2.3 below. The forward reactions refers to discharging and the backward reactions corresponds to charging of the battery [7, 17]. Anode reaction (M is the hydrogen absorbing AB<sub>5</sub>-alloy):

$$MH + OH^{-} \rightleftharpoons M + H_2O + e^{-}$$
(2.1)

Cathode reaction:

$$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH_2) + OH^-$$
(2.2)

Overall reaction:

$$MH + NiOOH \rightleftharpoons M + Ni(OH_2)$$
(2.3)

#### 2.2 Recycling

The environmental impact of waste management is highlighted in the waste management hierarchy, where the different ways of waste treatment are rated with respect to sustainability. The very best is of course if the waste was never produced and the next best lies as a responsibility from the producers to design products which minimises the amount of waste. This project considers though the waste once it has been formed and the most sustainable way to treat waste is in descending order; reuse, recycling, energy recovery and landfilling. Recycling of batteries have been pointed out as an energy intensive process so favourable would be if there are components that can be reused directly without any treatments instead of being recycled in terms of material recovery.

One reason why recycling of batteries is considered to be energy intensive is because a major component in many batteries is alloys and it is difficult to mechanically separate the constituent metals from an alloy. But metals are actually relatively suitable for being recycled chemically, since it is comparably easy to change their oxidation state which changes their chemical properties completely[16]. Oxidising a metal atom to its ion will for instance increase its solubility in aqueous solutions dramatically. This phenomena is utilised in the hydrometallurgical recycling route, which is more closely described in section 2.3. There is also no theoretical limit how many times metals can be recycled this way, since they do not undergo any degradation.

#### 2.3 Hydrometallurgical recycling route

Hydrometallurgy is known as the aqueous chemical processing for metal recovery and purification, which can be used both in ore treatment and metal waste recycling[18]. This process involves dissolution of the metals in an aqueous solution, separation using solvent extraction or ionic exchange and recovery of the separated metals as salt precipitation or electrolysis[19].

The beauty of the hydrometallurgical process is that it can be performed at room temperature and no external energy needs to be added in order for the process to proceed. One of the main drawbacks is though that it requires external addition of chemicals in relatively large amounts. Another drawback is that it can take long time for the metals to completely dissolve in the dissolution step. These are important aspects to consider when designing a hydrometallurgical process.

Utilising selective leaching in the dissolution step and using as concentrated solutions as possible throughout the process are two solutions to minimise the effect of the above explained issues. The separation of metals in the solvent extraction step will also be more efficient with higher ionic strengths, which means using more concentrated solutions. The volumes of chemicals needed is thereby reduced, which means the facilities can be smaller and the process will also be more cost effective.

#### 2.3.1 Dissolution chemistry

In the current project, the electrode materials are dissolved using hydrochloric acid as leaching agent. The reaction formulas for dissolution of any of the constituent metals (here denoted M) and  $Ni(OH)_2$  are shown in equation 2.4 and 2.5[20].

$$M(s) + nH^+(aq) \longrightarrow M^{n+}(aq) + \frac{n}{2}H_2(g)$$
 (2.4)

$$Ni(OH)_2(s) + 2H^+(aq) \longrightarrow Ni^{2+}(aq) + 2H_2O(l)$$
(2.5)

The reaction explained in equation 2.4 is a redox reaction, where the metal atom is being oxidised and the hydrogen ion is being reduced. All constituent metals in the current material have a standard potential below zero, which means they will dissolve and develop hydrogen gas in contact with hydrochloric acid[17, 20]. They are all so called base metals or hydrogen developing metals.

The second reaction consists strictly speaking of two equilibrium reactions, which are also known as hydrolysis of a metal ion. Which of the species  $Ni^{2+}$ ,  $Ni(OH)^+$ or  $Ni(OH)_2$  that dominates in a solution is strongly dependent on the pH of that solution. The dissolved metal ions from equation 2.4 can also undergo hydrolysis and form hydroxides. But at the low pH conditions used during the investigations in the current project (pH 0-2), hydrolysis of the dissolved metal ions is assumed to be negligible. This means that reaction 2.5 is expected to be completely shifted to the right and all constituent metals are expected to occur as free ions (M<sup>+</sup>).

In both reactions, the amount of hydrogen ions consumed during the reaction is equal to the oxidation state of the dissolved ion after dissolution. This observation makes it simple to calculate the theoretical amount of acid needed to completely dissolve a certain amount of material, if the metal composition of the material is known. This is utilised in section 4.2.

#### 2.3.2 Dissolution kinetics

The above knowledge only gives us the information that the material should dissolve in acidic media, but it gives us no information about the dissolution kinetics[16]. According to Ross (2011), the reaction mechanism for a dissolution reaction like the one explained above occurs in several steps[21]. Hydrogen ions are first transported to the metal surface, where they are adsorbed onto the surface. Once they are adsorbed, the actual reaction can take place. Subsequently, the oxidised metal ions along with hydrogen gas desorbs from the metal surface and the dissolved ions can finally be transported away to the liquid solvent.

Geankoplis (2003) describes that the rate determining step when dissolving a solid in a solvent solution is the mass transport from the solid surface to the liquid[22]. In the case of a batch system where the solute A is being dissolved in a solution of volume V, the rate of accumulation of A in the solution can be described by equation2.6;

$$\frac{Vdc_A}{dt} = A_s k_L (c_{AS} - c_A(t)) \tag{2.6}$$

where  $A_s$  is the total surface area of the particles,  $k_L$  is a mass transfer coefficient,  $c_{AS}$  is the saturation concentration of A in the solution and  $c_A$  is the concentration of A in the solution at time t. It can be seen that as the dissolution proceeds, the dissolution rate decreases both as the total particle area decreases and as the concentration of the solution approaches saturation with respect to A. The mass transfer coefficient can be increased for example by introducing stirring. Solving equation 2.6 with respect to  $c_A$  gives the expression;

$$\frac{c_{AS} - c_A}{c_{AS} - c_{A0}} = e^{(-\frac{k_L A}{V})t}$$
(2.7)

A leaching curve can be obtained by plotting  $c_A$  against t [23]. It can be seen from equation 2.7 that the solution approaches saturation exponentially. But if the amount of the solid solute is relatively small so that everything will dissolve, the total particle area A will decrease dramatically during dissolution. This will thus, according to equation 2.7, give rise to a dissolution curve with the same shape, see figure 2.1.

The above reasoning holds when the mass transport from the solid surface to the solvent is the rate determining step. But for metallic nickel, the case is a bit different. Even if nickel should dissolve in hydrochloric acid as previously described, nickel has been reported to be corrosion resistant to non oxidising acids like HCl due to slow desorption of hydrogen gas from the metal surface[24][16]. In presence of oxidising species, metallic nickel will dissolve rapidly though[24]. This means, by using HCl as leaching agent and avoiding other oxidising agents in the current project, selective leaching with respect to everything but metallic nickel should be possible.

It is of great interest to investigate if and to what extent, selective leaching occurs during dissolution of mixed material in the current project. If metallic nickel is the



Figure 2.1: Typical shape of a leaching curve of a solid solute when the mass transfer of from the solid surface to the liquid is the rate determining step.

only solid specie present in the solution after a certain time, the dissolution could be terminated at that point followed by separation of the undissolved material. This would reduce the dissolution time and a fraction of metallic nickel could also be collected. The mechanical separation of solid particles should in that case be possible to be carried out using a magnet, since nickel is a ferromagnetic metal and is therefore attracted to an external magnet. This would though not be an evidence that nickel is the only element in the undissolved material, since cobalt is also a ferromagnetic metal.

#### 2.3.3 pH-measurements

The dissolution process of the active material relies on the access of hydrogen ions, since these are consumed in the reactions (see section 2.3.1). It is therefore convenient to control the concentration of hydrogen ions in the solution during the dissolution and this is in the current project done using a pH electrode. This measuring device consists of two electrodes; a reference electrode which is in contact with a reference solution and a sensing electrode which is in contact with the measured solution[25]. Each electrode is equipped with a sensing membrane and what is measured is the potential over this membrane arising from a gradient in activity of hydrogen ions across the membrane. Nernst equation describes the measured value of the potential E in a solution, see equation 2.8[25].

$$E = E_0 + \frac{2.3RT}{nF} log(a[H^+])$$
(2.8)

 $E_0$  refers to the potential of the reference electrode, (2.3 RT/nF) is the Nernst factor, a is the activity factor and  $[H^+]$  is the concentration of hydrogen ions. The factors  $a[H^+]$  and  $log(a[H^+])$  are also known as the activity of hydrogen ions and the pH of the solution, respectively. By calibrating the electrode to buffer solutions with defined pH-values, a dependence between the recorded potential and pH can be

correlated. It can be seen from equation 2.8 that the recorded potential has a significant temperature dependence, which makes it important to control the temperature during measurements. The other quantities in the Nernst factor are constants.

The activity factor *a* for diluted solutions has a value close to unity, which means the activity of hydrogen ions can be approximated with the concentration[26][27]. An issue arises for concentrated solutions with high ionic strengths. Ions that are relatively close in size to hydrogen ions can affect the result from the electrode. This means that the measured values from the electrode will be affected by other dissolved ions as the dissolution proceeds. According to Grenthe et al. (2000) it is possible to compensate too high recorded activities due to high ionic strengths, but that lies beyond the scope of this project since the correct and absolute values of pH is of minor importance.

#### 2.3.4 Solvent Extraction

The proposed separation unit operation in the hydrometallurgical recycling route for NiMH batteries explained by Larsson et.al. (2012) is solvent extraction[16]. This method utilises the distribution of a solute between two immiscible phases, an aqueous phase and an organic phase. Changing the chemical and physical conditions of the system, such as pH, temperature, concentrations, presence of organic extractants etc, will change the constituent species affinity for the two liquids. An extractant is one or a mixture of several organic molecules which role is to selectively extract species from the solute in the aqueous phase to the organic. This is achieved by complex binding these to an active cite of the extractant molecules and thereby achieve a separation. The extracted species in the organic phase are thereafter back extracted to an aqueous phase, completing the separation. For more detailed information about Solvent Extraction, see Rydberg et.al. (2004)[28].

Cyanex 923 is an extractant that has been reported by Larsson et.al (2012) to extract all metals but nickel, potassium and magnesium from highly concentrated chloride solutions of dissolved mixed NiMH battery waste[14]. Out of these three metals, only nickel is relevant in the current project. A slightly acidic nitrate solution has by the same author been reported to subsequently strip cobalt and manganese from the organic phase, enabling a group separation of these two metals as well. Increasing the acidity of the system during back extraction increases the fraction of lanthanides being stripped to the aqueous phase. It is therefore important to keep the pH of the aqueous feed from the dissolution step not too low, since this will load the organic phase with hydrogen ions during extraction. In the subsequent stripping step, these hydrogen ions will leave the organic phase along with the lanthanides. The extractant Cyanex 923 is not a single molecule, but consists of a mixture of trihexylphosphine, octyldihexylphosphine, dioctylhexylphosphine and trioctylphosphine oxides and branched isomers of these[29].

# Methods and experimental outline

There were three analytical instruments frequently used in the current project; X-ray diffraction (XRD), inductively coupled plasma-optical emission spectrometry (ICP-OES) and scanning electron microscope (SEM). Detailed descriptions how these analytical methods were carried out is described in section 3.4.

The dissolution behaviour of the materials was investigated in the current project with a titration method using HCl as titrant, which is described in section 3.2.

For the practical work, the following list of aspects were investigated;

- Characterisation of the work-up starting material using XRD, ICP-OES and SEM (section 3.1)
- Elemental dissolution kinetics by titration at pH 1 (section 3.2.1)
- Characterisation of undissolved material after 5h dissolution time (section 3.2.2)
- The effect of pH during titration including reproducibility tests (section 3.2.3)
- Elemental dissolution kinetics in 8 M hydrochloric acid including characterisation of undissolved material (section 3.3)

A detailed list of the chemicals used in the project can be found in appendix A.1.1. A contribution report for the experimental work can be found in appendix A.3.

# 3.1 Work-up and characterisation of the starting material

The starting material in the current project was the anode and cathode materials as separated dry powders originating from spent NiMH batteries, provided by the company Nilar AB. The batteries were dismantled, after which the anode and cathode materials were removed separately, washed with MQ-water (>18 M $\Omega$ /cm, Milli-Q, Millipore, i.e MQ) and finally dried.

Characterisations of the anode and cathode starting material were separately performed using XRD, ICP-OES and SEM.

## 3.2 Materials and procedure for dissolution titration

In the current project, the dissolution behaviour of a mix of the cathode and anode starting materials was investigated using the proportions of cathode to anode materials as approximately 1:1.2 based on mass. This proportionality was used to mimic the real proportions between the electrode materials, which are used in practical battery applications.

The titration dissolution experiments were carried out with a miscellany of equipment from Metrohm's 800-900 series and with the software Tiamo for monitoring the process. The dissolution was carried out at a constant potential, which was measured on-line with a pH-meter (854 iConnect, Metrohm).

The electrode measures the potential of the solution and gives feedback to a titrator, which add corresponding amount of acid through a dosing device in order to keep the potential at the fixed value. Since the dissolution of material consumes  $H^+$  ions and therefore results in a pH increase, acid needs to be added continuously throughout the dissolution process. The volume acid added during the titration as a function of time was therefore used to quantify how much material that had been dissolved. The experimental set-up can be seen in picture 3.1.



Figure 3.1: Experimental setup for dissolution titration experiments

The dissolutions were carried out in a 120mL double wall glass vessel, which was connected to a heating bath, in order to control the temperature of the solution during titration. HCl was used as titrant and added to the aqueous suspension of mixed material. A propeller was used as stirring device in order to achieve a

homogeneous mix of the dissolving material in the solution. The stirring rate was set to an appropriate value to receive a well-mixed suspension without the risk for splash from the solution.

Before each experiment, the electrode was calibrated with a tripel-point calibration with buffer solutions at pH 1, 4 and 7. The dissolutions were carried out at 25°C and at the potential corresponding to a desired pH value, according to the performed calibration. A solution of approximately 1M NaCl in 50mL MQ-water was pre-set to the desired pH with HCl before 1.1g of mixed material was added, after which the titration could start. NaCl was added to increase the conductivity of the solution in order to speed up the dynamic response of the pH-electrode. No corrections were made to compensate the measured pH for the increasing ionic strength during the dissolution. Triplicates were performed for all experiments.

#### 3.2.1 Kinetic study of elemental dissolution at pH 1

A kinetics study with respect to the dissolution of elements from the material was carried out. These experiments were carried out by titration at pH 1 using 1M HCl. Samples of 1.5mL were taken continuously throughout the dissolution process. The samples were filtrated through a syringe filter of  $0.45\mu$ m polypropylene membrane, diluted with 0.7M suprapur nitric acid and subsequently analysed with ICP-OES. The slurry of dissolving material in the solution was assumed to be homogeneously distributed in the reaction vessel, so that the final data could be corrected for the loss of undissolved material trapped in the filter.

#### 3.2.2 Characterisation of undissolved material after 5 hours titration time at pH 1

Preliminary studies showed that a fast initial dissolution regime was followed by a slow dissolution regime. Large batch dissolution experiments were performed and terminated after the fast dissolution regime, after which the undissolved material was separated from the solution and characterised.

Approximately 5g of mixed material in the proportions of cathode to anode materials as 1:1.2 was added to the reaction vessel together with 50mL MQ-water. Solid to liquid ratio was kept the same as the other experiments, by increasing the concentration of the titrant from 1M to 5M. The dissolutions were terminated after approximately 5 hours. The undissolved material appeared to be attracted by an external magnet so it could mechanically be separated from the solution using a magnet. The collected material was subsequently washed with 0.1M HCl-solution, MQ-water and dried in an oven (55°C). The undissolved material was investigated using XRD, ICP-OES and SEM.

#### 3.2.3 Dissolution titrations at different pH values

The effect of acid concentration during dissolution was investigated by carrying out dissolution experiments at potentials corresponding to pH 0, 0.5, 0.75, 1 and 2, according to the associated calibrations. The aim of that was to investigate how the acid concentration would affect the dissolution kinetics of the material and if the equipment could handle the low pH (< 1) conditions.

The addition of titrant was logged in respect to time. To compare between experiments, the amount of acid have been normalised in respect with the sample mass. From the initial and final pH-values and the amount of acid added, the consumed amount of hydrogen ions for each replicate was calculated. These values were compared to the theoretical amount of  $H^+$  needed for total dissolution, which was calculated based on the most common oxidation states in aqueous solution for the dissolved metals.

The reproducibility of the titration experiment was tested. It was also tested if the same results could be obtained with simpler sample preparation (no salt used or preset of the pH of the initial solution).

### 3.3 Dissolution of electrode materials in 8M HCl

As described in section 2.3, highly concentrated solutions with respect to metal ions is desired in the hydrometallurgical process from an industrial point of view in order to handle as small volumes of chemicals as possible. To simulate that, scale-up dissolution experiments were carried out with the aim to produce 4M NiCl<sub>2</sub> solutions. This was achieved by adding approximately 17g of mixed electrode material to the dissolution vessel containing 52mL 8M HCl with continuous stirring. The temperature of the heating bath was set to  $25^{\circ}$ C. As it was noted that the reaction would be too violent if all material would be added at once, it was instead added at a rate of approximately 0.5g each 30 seconds during approximately 17min. The stirring rate was set significantly higher than for the more diluted dissolution experiments due to the larger rate of sedimentation. The stirring rate was also increased throughout the addition of material due to the viscosity increase. Once the last portion of material had been added, a timer was started.

Samples were thereafter taken continuously until the dissolution experiments were terminated after 2h, 5h and 7h respectively. The samples were filtered, diluted and measured with ICP-OES in the same way as described in section 3.2.1. The undissolved material was mechanically separated using Büchner funnel filtration with a  $10.0\mu$ m polypropylene filter. The collected material was subsequently washed, dried and investigated using XRD, ICP-OES and SEM.

# 3.4 Analysis methods

In the current project, three main analysis instruments were used; X-ray diffraction (XRD), inductively coupled plasma-optical emission spectrometry (ICP-OES) and scanning electron microscope (SEM).

XRD was used to identify the crystal structure of the material, which could give an indication of what substance it was. ICP-OES was used to confirm the information from XRD and to determine the elemental composition and purity of the actual elements in the material. SEM was used to investigate the morphology of the undissolved material, which was compared to the morphology of unused dendritic nickel particles.

### 3.4.1 XRD

The XRD-unit used was a Siemens D5000 diffractometer using a Cu K<sub> $\alpha$ </sub> source with a scintillation detector. A thin layer of the material was applied on the sample holder by dropping a suspension of the material in acetone and letting the acetone evaporate. A step size of 0.05°was used during measurement and to identify crystalline compounds, the database JCPDS-ICCD (PDF-4+,2010) was used.

#### 3.4.2 ICP-OES

Liquid samples were analysed with ICP-OES (Thermo iCAP 6500) for quantitative elemental determination. The samples were diluted with 0.7M suprapur nitric acid to an expected concentration of each element within the interval 1-50ppm. Calibration solutions were prepared from calibration standards diluted with the same matrix solution as used for the samples around the expected concentration of each metal.

Liquid samples, from solid starting material and collected residues, were produced by acid digestion. Approximately 6mL of aqua regia, prepared from concentrated HCl and concentrated HNO<sub>3</sub> in the proportions 3:1, was dropped into a plastic beaker with approximately 0.5g of material in 20mL MQ-water and magnetic stirring. The lid of the beaker had some drilled holes in order to allow the rapid reaction when the aqua regia was dropped into the suspension of material and water. 0.5mL of hydrogen peroxide was subsequently added each 30 minutes during two hours. The reaction was allowed to continue with magnetic stirring for the night and on the following day it was heated in a heating bath during approximately one hour. The produced liquid samples were filtered, diluted and subsequently measured.

#### 3.4.3 SEM

Undissolved residual material from terminated dissolution experiments and unused dendritic nickel particles were investigated with SEM (FEI Quanta 200 FEG ESEM). One picture for each magnification of approximately 1000, 3000 and 10000 times was taken for each sample, using high vacuum and an acceleration voltage of 12.5kV. The samples were prepared by careful tapping of a spoon with tiny amounts of material above a double-sided carbon tape attached on a sample holder and subsequently remove unattached powder by shaking the sample holder upside down.

4

# **Results and discussion**

In this chapter are the results from characterisation of the staring material, titration dissolution experiments, high concentration dissolution experiments and characterisation of undissolved material after terminated dissolution experiments presented and discussed.

### 4.1 Characterisation of the starting material

Material from different batches of used anode and cathode material were used in the current project. Table 4.1 shows the elemental composition of these batches. These results are fairly similar to the results reported by Larsson et.al. (2012)[12].

Table 4.1: Elemental composition of the starting material. Values reported as mg metal/g material, with 95% confidence interval. nd - not detected or below detection limit.

	Cathode 1	Anode 1	Cathode 2	Anode 2	
Al	$1.27{\pm}0.01$	$12.70 \pm 0.13$	$2.14{\pm}0.03$	$14.48 \pm 0.19$	mg/g
Ce	nd	$42.72 \pm 0.64$	nd	$44.35 \pm 0.57$	mg/g
$\mathrm{Co}$	$38.50 {\pm} 0.37$	$53.70 {\pm} 0.17$	$41.91 {\pm} 0.55$	$55.04 {\pm} 0.75$	mg/g
La	nd	$165.29 \pm 0.54$	nd	$166.22 \pm 2.03$	mg/g
Mn	$0.14 {\pm} 0.003$	$36.39 {\pm} 0.12$	$0.53 {\pm} 0.03$	$37.03 {\pm} 0.39$	mg/g
Nd	nd	$28.18 \pm 0.16$	nd	$28.68 {\pm} 0.36$	mg/g
Ni	$617.46 {\pm} 4.56$	$564.79 \pm 1.93$	$605.20 \pm 4.16$	$564.92 \pm 7.41$	mg/g
$\Pr$	nd	$10.29 {\pm} 0.09$	nd	$10.30 {\pm} 0.16$	mg/g
Zn	$20.97 \pm 0.04$	nd	$20.71 \pm 0.09$	nd	mg/g
tot	678.34	914.31	670.49	921.16	mg/g

It can be seen that the metal content in the materials does not sum up to 1000 mg/g, due to presence of minor amounts of other elements as well. This can probably partly be explained by oxidation of the metals by atmospheric oxygen, forming metal oxides. The reason why the metal content of the cathode material in particular is well below 1000 mg/g is that one of the main components in this material is  $Ni(OH)_2$ , see section 2.1.1.

The crystal structure of the starting material was investigated by XRD-analysis on the second batch of starting material (Anode 2 and Cathode 2), see figures 4.1 and 4.2.



Figure 4.1: Evaluated XRD diffractogram of the anode starting material.



Figure 4.2: Evaluated XRD diffractogram of the cathode starting material.

The hydrogen storing alloy of the anode material was identified as a hexagonal structured alloy with space group P6/mmm(191) with composition  $AB_5$ , where A is a mix of lanthanides (lanthanum, cerium, neodymium and praseodymium) and B is nickel with substitutions of aluminum, cobalt and manganese. The average composition of this alloy was found to be Ni<sub>3.6</sub>La<sub>0.5</sub>Ce<sub>0.3</sub>Pr<sub>0.1</sub>Nd<sub>0.1</sub>Mn<sub>0.4</sub>Co<sub>0.7</sub>Al<sub>0.3</sub>. The

nickel particles were identified as cubic structured metallic nickel with space group Fm-3m(225). Minor amounts of hexagonal structured  $Ce(OH)_3$  with space group P63/m(176) and with substitutions of cerium with the other lanthanides previously mentioned was also detected.

The cathode material was identified as nickel hydroxide with substitutions of nickel with cobalt and zinc, with the average composition  $Ni_{0.972}Co_{0.025}Zn_{0.003}(OH)_2$ . The same metallic form of nickel was found in the cathode material as in the anode material.

SEM pictures of unused anode and cathode material are shown in figure 4.3. Small, star-shaped particles can be seen in both pictures, indicating that these are the dendritic particles of metallic nickel. It can be seen that these particles form a network, connecting other particles to each other, as explained in section 2.1.1. The big particle seen in the anode material must therefore be a piece of the hydrogen absorbing  $AB_5$  alloy and the spheres in the cathode material are thereby particles of Ni(OH)<sub>2</sub>.



(a) Anode, magnification 3200x

(b) Cathode, magnification 750x

**Figure 4.3:** SEM images of unused (a) anode and (b) cathode electrode material using SSD-detector.

### 4.2 Total dissolution by titration

#### 4.2.1 Dissolution kinetics with respect to elements at pH 1

Figure 4.4 shows the dissolution kinetics in terms of mass dissolved (wt%) as a function of time at pH 1 for the different elements. During these dissolution experiments, samples were taken continuously and subsequently analysed using ICP-OES. The mass of dissolved material was normalised using data from the elemental composition of the material. The reason why the graphs do not reach exactly 100% is probably caused by experimental fluctuations, material loss, evaporation of solution

during dissolution or incorrectness of the total dissolution assumption before ICP-OES measurements. The reason why there are no data points between 7h and 24h of ongoing experiment is because no samples taken during evenings and nights.



**Figure 4.4:** 0.5 g cathode and 0.6 g anode dissolution in hydrochloric acid at pH 1 and 25°C.

The results show that the dissolution process starts at a rapid rate for all elements, where the curves have a parabolic shape and approaches complete dissolution exponentially. This means that the mass transfer of dissolved ions from the solid surface to the liquid solvent is the rate determining step during this part of the dissolution process. The results also show that nickel is the elements which takes longest time to dissolve and that all other elements are more or less completely dissolved after 5-7 hours. Suspicions exists that the slow dissolution rate of nickel is caused by dissolution of the metallic nickel particles, for which the dissolution process should be inhibited by slow desorption of hydrogen gas from the particles surfaces[16, 24].

Initially, also nickel has the parabolic dissolution curve. This is probably caused by dissolution of  $Ni(OH)_2$  from the cathode material, where the dissolution process does not generate any hydrogen gas and is therefore not inhibited by hydrogen desorption (see equation 2.5). Zinc is a constituent in the cathode hydroxide core that is not present in the anode material. For this reason, this element is useful to demonstrate the dissolution kinetics of the cathode material. The amount of dissolved zinc surpass that of nickel after 3h. After 7 hours the dissolution of zinc appear almost 98wt%, and therefore the amount of dissolved hydroxide material should be equal. The lanthanides have all dissolved to more than 90wt% within one hour and to almost 100wt% after 5-7 hours. Since they have such similar properties and follow the same dissolution kinetics, they are in this graph represented by lanthanum, to make the figure easier to survey. The reason to choosing lanthanum for this purpose is because it is the most abundant of the lanthanides in the material, which means its results should be the most representative. This also eliminates the nonaccurate values of cerium (see explanation in appendix A.2). The remaining elements (manganese, cobalt and aluminium) all dissolves slower than the lanthanides, but faster than nickel. Since elements that are constituents of the hydrogen storing alloy is dissolving fast, it is an indication that the alloy dissolves faster than the hydroxide material. According to these results, manganese is the next most abundant element after nickel in the undissolved material after the initial fast dissolution regime.

Nickel appear to be least dissolved (approximately 84wt%) after 7 h and it has been indicated that most other elements are completely dissolved (> 95wt%), except for manganese (approximately 93wt%), at this point. From a practical point of view it may not be necessary, or beneficial, to dissolve the remaining material that has not dissolved after this time. The transition between fast and slow dissolution regimes could be the end criteria of the dissolution process. This would decrease the dissolution time significantly compared to total dissolution. By separating the undissolved material mechanically, a relative pure fraction of nickel would also be obtained, which could potentially be reused directly in the production of new batteries. The hypothesis of nickel being the only metal remaining in the undissolved material was further investigated and these results can be seen in section 4.2.2.

#### 4.2.2 Characterisation of undissolved material after 5 hours titration time at pH 1

Three replicates of dissolution at pH 1 were terminated after 5h, whereafter the undissolved material was separated and analysed using XRD, ICP-OES and SEM. The aim of this section was to investigate if the undissolved material consists of metallic nickel. Furthermore, the elemental composition and the morphology was characterised. This was done in order to study if the suggested nickel particles are visually damaged or if they have maintained their dendritic shape and form the characteristic network. From the 5.5g of mixed material used, approximately 0.7g of undissolved material was collected after 5h of leaching.

#### 4.2.2.1 XRD analysis of solid residual material

Figure 4.5 shows the results from the x-ray diffraction analysis of undissolved material, collected after 5h from pH 1 solutions. The three peaks indicate that the material consists of cubic structured metallic nickel with space group Fm-3m(225). No other crystal phases were detected in these diffractograms. However, other compounds present may not be detectable due to non-crystallinity and/or too low concentration within the samples. These results confirm previous suspicions that metallic nickel is the main component that dissolves slow after 5 hours in these solutions.



Figure 4.5: XRD diffractograms of undissolved material from three replicates of pH 1 dissolution titrations terminated after 5 hours.

#### 4.2.2.2 ICP-OES analysis of solid residual material

Table 4.2 shows the composition of the undissolved material from the ICP-OES investigation. Details on how the values were calculated from raw data are shown in appendix A.2.2. These results shows that the nickel content of the undissolved material is considerably high, with a purity of 99.7wt% with respect to the investigated metals. The reason why the metal content does not sum up to 1000mg metal/g material is probably caused by oxidation of the metals. Another contribution to this could be material losses during the total dissolution by acid digestion prior the ICP-OES measurements. As seen from the results of the dissolution kinetics with respect to elements in section 4.2.1, the lanthanides all dissolve considerably fast and are thereby not found in the undissolved material. Al, Co, Mn and Zn take longer time to dissolve and traces of these elements, mainly Co, were found in the undissolved material.

**Table 4.2:** Composition of undissolved material from pH 1 dissolutions, terminated after 5h. Values reported as mg metal/g material, nd - not detected or below detection limit.

	Al	Ce	Co	La	Mn	Nd	Ni	$\mathbf{Pr}$	Zn	
average	0.12	nd	2.46	nd	0.37	nd	965.95	nd	0.19	mg/g
st dev	0.02		0.31		0.05		10.82		0.04	mg/g

#### 4.2.2.3 SEM analysis of solid residual material

Since preliminary studies showed that most of the undissolved material appeared to consist of metallic nickel, SEM pictures of undissolved material as well as unused dendritic nickel particles were taken. Their morphologies were compared in order to be able to make a qualitative evaluation if the particles that have been exposed to acids had been damaged or if they still stuck together, forming a characteristic network.

Figure 4.6 shows SEM pictures of dendritic nickel particles, which have not been used in a battery. These particles stick to each other and form a network for electron transfer, which increase the conductivity of the active material in the batteries (see section 2.1.1).



(a) Magnification 1000x

(b) Magnification 10000x

**Figure 4.6:** SEM images of unused dendritic nickel particles with different magnification using ETD detector.



(a) Magnification 800x

(b) Magnification 8000x

**Figure 4.7:** SEM images of collected undissolved material after fast dissolution regime from replicate 2 using SSD detector.



(a) Magnification 1000x

(b) Magnification 10000x

**Figure 4.8:** SEM images of collected undissolved material after fast dissolution regime from replicate 3 using ETD detector.

Figures 4.7 and 4.8 show pictures of the undissolved material, which previously have been confirmed to consist of metallic nickel with high purity. A visual inspection indicates that these nickel particles have the same dendritic shape and form the same network with each other as the unused nickel particles in figure 4.6. Pictures of two different batches of undissolved material, taken with two different detectors, are presented to show that the external circumstances do not affect the visual observation.

This observation indicates that it may be possible to reuse the undissolved nickel after the fast dissolution regime directly in the production of new batteries. If the metallic nickel particles are assumed to dissolve at a constant rate throughout the

whole dissolution process, not only during the slow dissolution regime, approximately five sixths (83%) of the metallic nickel in the batteries can potentially be recovered with this method.

#### 4.2.3 Dissolution kinetics at different pH values

The results from these total dissolution experiments are considered to be the added amount of acid as a function of time as well as the total amount of  $H^+$  consumed. These results are presented and discussed in this section.

#### 4.2.3.1 Dissolution at pH 0, 0.5 and 0.75

Dissolution experiments at pH values lower than 1 did not give reproducible results, both with respect to dissolution curves and the consumed amount of  $H^+$ . It is believed that this is due to limited practical pH range of the pH electrode. An example of non-reproducible results are shown in figure 4.9, originating from dissolution experiments carried out at pH 0.5.



**Figure 4.9:** 0.5g cathode and 0.6g anode dissolution in hydrochloric acid at pH 0.5 and 25°C.

The dissolution curves indicate that total dissolution was reached after 2h for the first replicate and after 7h for the second. However, there was still undissolved material in the dissolution vessel at these points. Even for a long time after 30h (when everything was dissolved for the pH 1 and 2 titrations), there was still undissolved material left. Since nickel seem to be the element which takes longest time to dissolve completely, it is reasonable to assume that this undissolved material should be nickel. But the material did not show the same characteristics as the undissolved nickel from experiments explained in section 4.2.2. For example, it stuck more to the walls of the vessel and the devices in the solution and it sedimented slower. It was also not attracted to an external magnet, as a ferromagnetic metal should be.

From XRD results it was indicated that this "mystical" residual material was only elemental nickel though, see figure 4.10.



**Figure 4.10:** Evaluated XRD diffractogram of the undissolved "mystical" material from pH 0.5 dissolution.

#### 4.2.3.2 Dissolution at pH 1

Figure 4.11 shows the dissolution of mixed electrode material at pH 1. The dissolution curves lies almost on top of each other, which means the method is adequately reproducible. These results confirms that the dissolution starts with a  $5 \pm 0.5$  hours long fast dissolution regime, where the curves seem to follow a parabolic shape. This region is followed by a  $25 \pm 2$  hours long slow dissolution regime, where the dissolution kinetics appears to follow a linear trend until everything is dissolved after approximately  $30 \pm 2$  hours. According to previous reasoning, this slow dissolution rate is caused by dissolution of the solid nickel particles.



Figure 4.11: 0.5g cathode and 0.6g anode dissolution in hydrochloric acid at pH 1 and  $25^{\circ}$ C

The last part of the dissolution curve appears to follow a linear trend indicating that the dissolution rate is constant. Therefore the dissolution rate does not depend on the total particle surface area or the particle size. This dissolution rate is possible to calculate from the slope of a linear regression of the dissolution curves in this region. Eliminating one of the three replicates, which linear regression had a value of the slope which differed significantly from the other two, the average dissolution rate becomes 0.205mmol consumed HCl/h.

The total amount of hydrogen ions consumed in the dissolution process was calculated from the initial and final pH-values along with the added amount of acid. Normalised to the mass of dissolved material, the average value with a 95% confidence interval from the three replicates is  $26.43 \pm 0.55 \text{ mmolH}^+/\text{g}$  material. The results from the elemental composition investigation along with data of the most common oxidation states of the current elements (see section 4.1 and appendix A.2.1 respectively) allows the calculation of a theoretical value of the H<sup>+</sup> consumption for total dissolution. This value becomes  $26.40 \text{ mmolH}^+/\text{g}$  material. The experimental obtained average seems to match this theoretical value considerably good, which gives an indication that the used method is not only reproducible (as confirmed earlier), but also reliable and accurate.

Further investigation of the method showed that the same results as presented above could be obtained even if the solution was not preset to pH 1 prior the addition of the material. The dissolution curve followed the same trend and the total amount of consumed hydrogen ions had the value of  $26.27 \text{mmolH}^+/\text{g}$  material, which lies within one standard deviation from the average of the previous results. The dissolved NaCl, on the other hand, was needed in order to increase the dynamic response of the pH electrode and consequently obtain a smooth dissolution curve. The experimental

preparation of the experiments hereinafter did therefore not include a preset of the pH value but did include the addition of salt to the solution.

#### 4.2.3.3 Dissolution at pH 2

Figure 4.12 shows the dissolution curves from dissolution experiments at pH 2, which also appear to have high degree of reproducibility. These obtained dissolution curves does not show a distinct inflection point between the fast and slow dissolution regimes, as the respective ones from dissolution experiments using pH 1 solutions did. At pH 2 the apparent faster dissolution is prolonged to 15h. Though it appears that the fast dissolution regime is clearly affected by the ten times smaller concentration of  $H^+$  and continues to 15h (instead of 5h). It is reasonable to assume that the rate determining step of the dissolution in this region is the mass transport of dissolved ions from the solid surface to the liquid solvent since the dissolution curves have the characteristic parabolic shape. But it is also, according to equation 2.4 and 2.5, likely that the concentration of  $H^+$  effects the dissolution rate significantly.



Figure 4.12: 0.5g cathode and 0.6g anode dissolution in HCl at pH 2 and 25°C.

Since the pH was not preset to 2 prior the addition of the material during this series of dissolution experiments, the obtained dissolution curves starts from no added acid at all. Furthermore, slightly less than 30mmol HCl/g material was added to reach total dissolution. This can be compared to the dissolution curves obtained from the dissolution experiments performed at pH 1, which starts at 5mmol HCl/g material and reaches almost 35mmol HCl/g material for total dissolution. The total amount of H<sup>+</sup> consumed for total dissolution, however, is similar in the two cases. For total dissolution at pH 2, 27.36mmolH<sup>+</sup>/g material with a standard deviation of 0.15mmolH<sup>+</sup>/g material was consumed, which is reasonable similar to the corresponding value for the dissolution experiments performed at pH 1 (26.43mmolH<sup>+</sup>/g material, with a standard deviation of 0.27mmolH<sup>+</sup>/g material).

Total dissolution at pH 2 takes only slighter longer time than at pH 1 and the slow dissolution regime shows also in this case a linear trend. The average value of the dissolution rate during this regime with 95% confidence interval is  $0.190\pm0.0025$ mmol HCl/h. This can be compared to 0.205mmol HCl/h for pH 1. Since the dissolution rate during the slow dissolution regime at pH 2 is so similar to the dissolution rate at pH 1, it is reasonable to suspect that the rate determining step during dissolution in the current region is the desorption of hydrogen gas from nickel particles. This process is clearly not as affected by the lower concentration of H<sup>+</sup> as the fast dissolution process is.

### 4.3 High concentration dissolutions

A dissolution kinetic study using highly concentrated solutions with the aim to produce  $4M \operatorname{NiCl}_2$  solutions was carried out. Experiments were terminated after 2h, 5h and 7h, whereafter the undissolved material was analysed using XRD, ICP-OES and SEM.

#### 4.3.1 Dissolution kinetics with respect to elements

Figure 4.13 shows the dissolution kinetics for each element during two hours of dissolution. As can be seen from this figure, many of the elements appear to not be completely dissolved. As previously mentioned, it is believed that the reasons for this are material losses, evaporation, incorrectness in the total dissolution assumption or that the samples taken for characterisation of the starting material were not representative. Furthermore, the evolution of hydrogen bubbles were significant. it is therefore believed that it was more difficult to reach a homogeneous mixture in the reaction vessel during the experiment. It is also reasonable to believe that the matrix is more difficult to analyse than anticipated. Nonetheless the general dissolution of all elements except that of nickel is high ( $\geq 90 \text{ wt\%}$ ) and does not increase after 0.5 h, which indicate that the alloy and hydroxide materials are completely dissolved.



Figure 4.13: 7.7g cathode and 9.3g anode dissolution in 52mL 8M hydrochloric acid at 25°C.

The results indicates that everything but nickel has been completely dissolved after 30min and that a considerably large amount of the material have been dissolved already at the first sample collection point, which occurred 2min after the last portion of material had been added to the solution. However, it should be noted that the first addition of sample occurred 17min before the reported time of the experiment started. Similarly to previous results, the dissolution of the alloy appear to be instantaneous and complete, as 100 wt% of lanthanum is dissolved meanwhile the acid concentration is at its maximum of 8 M. As the dissolution proceeds, acid is consumed and the dissolution will proceed at a slower rate the further the dissolution has proceeded. The equivalent fast dissolution regime lasts in this case 30min, after which the dissolution curve corresponding to nickel, in consistency with the previous results, seem to follow a linear trend. The value of the slope in this region is though not comparable to the values of the slope from the dissolution titrations, since they have different units (wt% dissolved/h vs mmol HCl added/h).

#### 4.3.2 Characterisation of undissolved material

The undissolved material from the high concentration dissolution experiments was characterised using XRD, ICP-OES and SEM. The diffractograms from the XRDmeasurements (figure 4.14) shows, for all three replicates, only peaks corresponding to the same metallic form of nickel as described earlier.



Figure 4.14: XRD diffractograms of undissolved material from three replicates of high concentration dissolutions terminated after 2, 5 and 7 hours.

Compositional analysis using ICP-OES of this undissolved material only showed measurable concentrations of nickel and cobalt (see table 4.3). The nickel contents above 1000mg metal/g material for replicate 2 and 3 are unrealistic and one explanation to why these high values could be obtained is given below. Nonetheless, the purities of nickel were calculated using these values. Cobalt was, except nickel, the element which was present in largest amounts (0.74-2.03 mg/g) also in the undissolved material from the dissolution titrations described earlier. Neither aluminum, manganese or zinc were detected.

Table 4.3: Composition of the undissolved material from high concentration dissolutions, terminated after 7h, 5h and 2h. Amounts are reported as mg metal/g material and nickel purities are reported as wt% of the measured elements.

	rep 1 (7h)	$\operatorname{rep} 2 (5h)$	$\operatorname{rep} 3$ (2h)	
amount Ni	950,8	1079,9	1144,0	mg/g
amount Co	2,03	1,92	0,74	mg/g
purity Ni	99,79	99,82	99,94	wt%

During the acid digestion of the undissolved material prior to the ICP-OES measurements, relatively large losses of material was observed as particles stuck to the walls of the beaker and on the inside of the parafilm covering the opening of the beaker. This observation was largest for replicate 3, smaller for replicate 2 and almost nonexistent for replicate 1. Suspicious exists that this phenomena could be coupled to evaporation of the acid solvent, which could be an explanation why the values of metal content in the material lies above 1000mg metal/g material for replicate 2 and 3.

The results in terms of absolute values are, however, not especially reliable. But one conclusion that most certainly can be drawn is that the undissolved material mainly contains of metallic nickel and to a purity of above 99.7%. This also matches the previous results from the characterisation of undissolved material from the dissolution titrations. Another conclusion is that traces of mainly cobalt can be present. Neither aluminum, manganese or zinc were detected here, but we have seen trace levels of them in the undissolved material from previous results. The amounts of the trace metals varies though and the actual concentrations of these elements in the undissolved material have not been certainly determined and depend most probably on when the dissolution experiments are terminated.

SEM pictures of undissolved material from high concentration dissolutions are shown in figure 4.15.



(a) Magnification 1000x

(b) Magnification 10000x

**Figure 4.15:** SEM images of undissolved material after terminated high concentration dissolution experiments using ETD detector.

In consistency with previous findings, it can be seen that the metallic nickel also here consists of the dendritic particles, which forms the characteristic network. Nothing else was found in the undissolved material from dissolutions terminated after 5h and 7h. But in the one terminated after 2h, a small piece of material that visually looks different from the rest of the material was found after a careful visual examination of the sample. A picture of that particle can be seen in figure 4.16.



Figure 4.16: SEM image of traces of unknown material in the undissolved material from high concentration dissolution terminated after 2h. Magnification 15000x.

A comparison with the pictures of unused anode and cathode material (figure 4.3) indicates that this particle could be a piece of the  $AB_5$  alloy from the anode material. This observation was unexpected and not observed for other samples. Results from the XRD or ICP-OES analyses did not indicate that this was a systematic result and more information is needed to be able draw any conclusions.

The above findings in this section confirms that collected undissolved material, even in upscaled laboratory experiments can potentially be reused as nickel in new batteries. Further investigations need to be performed to determine at which point the dissolutions should be terminated in order to recover the most nickel, with high purity, in the undissolved material.

#### 4. Results and discussion

# 5

# Conclusions

The dissolution method developed by Larsson (2012) for leaching of spent NiMH battery material was feasible for dissolution studies of the NiMH battery material studied in the current project as well. Selective leaching of everything but metallic nickel did occur during dissolution of mixed electrode material using hydrochloric acid as leaching agent. As a consequence, it was possible to reduce the dissolution time for titration dissolution experiments performed at pH 1 from 30 hours to 5 hours. This means a reduction by a factor of six can be achieved compared to total dissolution by terminating the process and mechanically separate the undissolved material. For scale up experiments performed with highly concentration solutions, the results indicates that the selective leaching was complete after even shorter dissolution time.

The separated undissolved material after selective leaching was a fraction of metallic nickel with a purity of above 99.5wt%, both from pH 1 dissolution experiments as well as from high concentration dissolution experiments. The size of this fraction is expected to amount to five sixths ( $\approx 83\%$ ) of the initial fraction of metallic nickel in the material. Furthermore, the dendritic metallic nickel particles does not appear to be damaged, from a visual inspection. This means they could not only be recycled, but potentially also reused directly in the production of new batteries.

## 5.1 Future work

One of the most obvious fields for future work is to investigate if the dissolution of metallic nickel can be further avoided and by that, further increase the yield of recovered undissolved nickel. Perhaps this can be achieved by carrying out the dissolutions in non-oxidising atmosphere, for example using  $N_2$ . Correlating the rate of dissolution during the slow dissolution regime (i.e. dissolution of metallic nickel) to a theoretical model describing hydrogen desorption would also be interesting, but from a more philosophical point of view.

Further investigations of the concentrated system is needed to determine how fast the selective leaching is actually completed. This could be performed by taking samples from the solution during dissolution experiments and subsequently analyse the undissolved material, obtaining a correlation between the content of metallic nickel in the undissolved material and dissolution time. There is also room for improvements of the practical performance during the highly concentrated dissolution experiments. One of the major drawbacks of the methodology used in that part of the current project is that the material was continuously added to the acid during 17 minutes. In order to be able investigate the really short time scales, this period needs to be shortened. Perhaps it is possible to avoid it completely by adding all material to the acid and subsequently start the stirring.

In order to make the hydrometallurgical recycling process complete, separation using solvent extraction and metal recovery also needs to be investigated. Up-scaling of the process using a mixer settler is thereafter required in order to make the process ready for industrial applications. But since the main difference between the material investigated in the current project and the material described by Larsson (2012) is the structure of the metallic nickel, there should be no significant difference between the composition in the solutions from respective process once the material has been selectively leached. This means that the solvent extraction process described by Larsson (2012) could potentially be applicable to the system investigated in the current project as well, without any changes. It is of great interest to investigate if that is the case.

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## A.1 Experimental

This section provides additional experimental details, such as chemical specifications and wavelengths used in the ICP-OES analysis.

#### A.1.1 Chemical specification

A list of the used chemicals in the experimental performance of the current project can be found in table A.1 below.

Chemical	Company	Purity
MilliQwater	MilliQ, Millipore	18.2 M $\Omega$ cm at 25°C
NaCl	VWR	$99.7 \mathrm{wt\%}$
HCl (titrations)	Sigma Aldrich-FIXANAL	$37 \mathrm{~wt}\%$
conc HCl	Sigma Aldrich	$37  { m wt}\%$
$suprapur HNO_3$	Merck KGaA	$65 \mathrm{wt\%}$
$H_2O_2$	Sigma Aldrich	$30\mathrm{wt\%}$
Buffer solutions	Metrohm Ltd.	$\pm 0.02$ pH-units
ICP-OES standards: Al	Ultra Scientific	$1000 \ \mu g/mL$
Ce	Ultra Scientific	$1000 \ \mu \text{g/mL}$
Co	Ultra Scientific	$1000 \ \mu g/mL$
La	Ultra Scientific	$1000 \ \mu { m g/mL}$
Mn	Ultra Scientific	$1000 \ \mu { m g/mL}$
Nd	Ultra Scientific	$1000 \ \mu { m g/mL}$
Ni	Ultra Scientific	$1000 \ \mu { m g/mL}$
$\Pr$	Ultra Scientific	$1000 \ \mu { m g/mL}$
Zn	Ultra Scientific	1000 $\mu g/mL$

Table A.1: Chemicals with purity, used in the current project

#### A.1.2 ICP-OES analysis

The emission wavelengths used in the ICP-OES analyses are presented in table A.2.

$\mathbf{Element}$	Wavelength (nm)
Al	308.2
Al	396.1
Ce	404.0
$\mathrm{Co}$	228.6
$\mathrm{Co}$	231.1
La	333.7
La	379.4
Mn	257.6
Mn	259.3
Mn	279.4
Nd	406.1
Nd	430.3
Ni	216.5
Ni	221.6
Ni	231.6
$\Pr$	417.9
$\Pr$	422.5
Zn	202.5
Zn	206.2

 Table A.2: Emission wavelengths used in the ICP-OES analyses

For cerium, only one wavelength was used. The reason for this was that all other peaks were overlapping and therefore affected by the relative high concentration of nickel. The used wavelength (404.0nm) is the best available one, but does also not represent cerium perfectly. The values for cerium are therefore not sufficient reliable in the current project.

### A.2 Calculation details

#### A.2.1 Theoretical H<sup>+</sup> consumption for total dissolution

The theoretical consumption of hydrogen ions during dissolution was calculated for the total dissolution experiments. The most common oxidation states of the current elements used in these calculations are presented in table A.3[30, 31].

Table A.3: Most common oxidation states of the current elements

Al Ce Co La Mn Nd Ni Pr Zn +2+3+2+3+3+3+2+3+2

### A.2.2 ICP-OES

The ICP-OES instrument reports the concentrations of the elements as ppm of the measured solutions. But the results from these analyses are in this report presented as a content of the different metals in the initial material, mg metal/g material. These values were obtained by first compensating the reported values in ppm from the instrument by the dilution factor, multiply these new values with the initial used mass of material and subsequently divide by the volume of liquid used during acid digestion.

# A.3 Contribution report

Most of the practical work and all writing was done by the author Fredrik Nyhlén. The following practical work was done by PhD student Filip Holmberg:

- Dismantling of the batteries
- Removal, washing and drying of the anode and cathode materials
- Characterisation of the starting material using XRD, ICP-OES and SEM

Everything else was done by the author.