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New insights in the leaching kinetics of cathodic materials in acidic chloride media for lithium-ion battery recycling

Wen Xuan^[a], Antônio Braga de Souza^[a], Chloé Korbel^[a], Alexandre Chagnes^{[a]*}

^[a] *Université de Lorraine, CNRS, GeoRessources, F- 54000 Nancy, France.*

Abstract

Leaching reactions in hydrochloric acid of several cathodic materials used in lithium-ion batteries were investigated between 25 °C and 82 °C. The dissolution rate increased as follows: NMC811 ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$) > NMC622 ($\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$) >> NMC532 ($\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$) > NMC111 ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). The dissolution of lithium is faster than that for nickel, cobalt and manganese. Data analysis demonstrated that NMC dissolution is always a two-step process. In the first step, NMC was transformed very quickly into a new lithium-deficient phase. This phase was subsequently dissolved during a second-rate limiting step. No significant impact of the solid/liquid ratio on the leaching kinetics was observed as far as the solid-liquid ratio remained below the stoichiometric composition. Finally, a **shrinking core model** and a first-order rate law were used to investigate the leaching kinetics of the second rate-limiting step, which is the main step involved during NMC digestion in hydrochloric acid.

Keywords: Lithium-ion batteries, NMC, hydrochloric acid, leaching, kinetics, recycling.

*Correspondence should be addressed to:
Alexandre Chagnes (alexandre.chagnes@univ-lorraine.fr)

26 1. Introduction

27 Lithium-ion batteries (LIBs) are composed of cathode, anode and electrolyte, which
28 contain valuable metals. Among the main cathodes reported in the last decades (**Table**
29 **1**), lithiated nickel-manganese-cobalt oxide electrodes abbreviated as NMC
30 ($\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$) are the most widely used material in LIBs. The electrochemical and
31 physicochemical properties of NMC electrodes depend on their compositions (Gong et al.
32 2017): (i) high nickel content is responsible for high capacity and high charge-discharge rate at
33 the expense of poor safety, (ii) high manganese content improves the safety and increases the
34 lifespan of the electrode, and (iii) high cobalt content stabilizes the NMC layer structure and
35 improves the charge-discharge rate. Four types of NMC cathodes containing nickel, cobalt,
36 manganese and lithium are available to satisfy the needs in terms of stability, charge-discharge
37 rate, cycle ability and capacity: NMC811 ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$), NMC622
38 ($\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$), NMC532 ($\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$) and NMC111 ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$).

39 Therefore, the huge increase in electric vehicle production in the next decade will
40 impact the future demand of cobalt, nickel and lithium, which will likely increase by
41 31%, 69% and 46% between 2017 and 2030, respectively (Chagnes, 2019, Chagnes and
42 Pospiech, 2013). Recycling appears in part as one of the solutions to face up this demand
43 (Pagliaro and Meneguzzo, 2019). Furthermore, the environmental footprint of raw
44 material production can be significantly reduced by processing spent materials rather
45 than primary resources due to the high environmental impact of mining, comminution
46 and ore beneficiation. For instance, the production of transition metals, generally
47 extracted from sulfide ores, contributes dramatically to SO_x emissions, which are
48 drastically reduced by implementing recycling processes. More generally, the closer the
49 recycled material is to its final product, the more the net production impacts can be
50 reduced (Gaines, 2018).

51 In order to face up cobalt, nickel, manganese and lithium demand due to the
52 emergence of electric vehicle, the development of recycling processes of spent LIBs
53 is challenging (Pagliaro and Meneguzzo, 2019). In particular, many efforts concern the
54 recovery of lithium, cobalt, nickel and manganese from the
55 $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ cathodic material. Although, several studies addressed leaching of
56 NMC111 ($\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$), LCO (LiCoO_2), LMO (LiMnO_2), LNO (LiNiO_2) and LFP
57 (LiFePO_4), only few studies investigated the leaching mechanisms of NMC811, NMC622, and
58 NMC532 in spite of their potential uses as new cathodes (**Table 1**).

59 Hydrometallurgy appears to be the best technology to extract and separate metals from spent
60 LIBs (Boyden et al., 2016). Hydrochloric acid, nitric acid, sulfuric acid and several organic
61 acids such as lactic acid, citric acid, formic acid, and tartaric acid were tested in previous works
62 to leach cathodic materials (Ordoñez et al., 2016). Likewise, several studies addressed the use
63 of hydrochloric acid in order to take advantage of its reactivity and the formation of metal
64 chloride species in solution, which may improve the selectivity of the liquid-liquid extraction
65 stage usually implemented to extract and separate metals contained in the leachate (Seeley and
66 Crouse, 1966; Zhu et al., 2017). This paper investigates the leaching kinetics of NMC811,
67 NMC622, NMC532 and NMC111 in hydrochloric acid. Kinetic data were analyzed by means
68 of two models that fairly describe the digestion of NMC cathodic materials in acidic chloride
69 media.

70 2. Material and methods

71 Hydrochloric acid (37% weight) was supplied by Sigma Aldrich. The battery materials
72 NMC811, NMC622, NMC532 and NMC111 were supplied by Xiamen Tob New Technology
73 Co., LTD. **The particle size distribution is reported in Figure 1.** The leaching experiments
74 were performed between 25 °C and 82 °C in a homemade double-jacketed 1L-glassware
75 reactor thermostated with a Lauda thermostat (**Figure 2**). Diluted acid was added into
76 the reactor under agitation before introducing the cathodic material (powder). Samples
77 were withdrawn regularly from the reactor and immediately filtered.

78 Nickel, cobalt, manganese and lithium concentrations were analysed by Microwave
79 Plasma-Atomic Emission Spectrometry with appropriate standards (Agilent 4210 MP-
80 AES).

81 The leaching efficiency of the chemical element *i* was calculated by using the
82 following equation deduced from the mass-balance:

$$83 \%E_i = \frac{C_f(i) - C_0(i)}{C_f(i)} \times 100\% \quad (1)$$

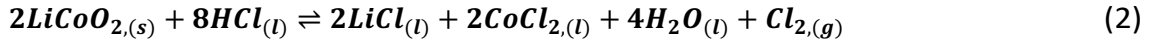
84 where $C_f(i)$ and $C_0(i)$ are the final and initial concentrations of the metal *i* in the leach
85 solution, respectively. The metal concentrations in the residues during leaching and the
86 metal concentrations in the leach solution after full digestion of the cathodic materials
87 were used to recalculate the cathode composition and check the mass-balance.

88 **Table 3** shows a comparison of this result with the theoretical liquor composition.
89 This calculation confirmed the validity of **Eq (1)**.

90 Chloride concentrations in the samples were determined by ion chromatography
91 (ICS-900 Dionex) equipped with the column IC Dionex™ IonPac™ AS22.

3. Results and Discussions

Wang et al. (2009) showed that it was possible to achieve a full dissolution of cobalt, manganese, nickel and lithium from LiCoO_2 , LiMn_2O_4 or $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by using hydrochloric acid. In the case of LiCoO_2 , it is usually stated that the leaching mechanism by HCl can be described by the following equation (Takacova et al., 2016):



In the present study, leaching experiments of NMC532, NMC811 and NMC622 were performed under similar experimental conditions as those reported by Wang et al. (2009) but at different leaching temperatures, i.e. a solid/liquid phase ratio of S/L=20 g/L, an hydrochloric acid concentration of 4 mol L⁻¹ and temperatures ranging from 25 °C to 82 °C.

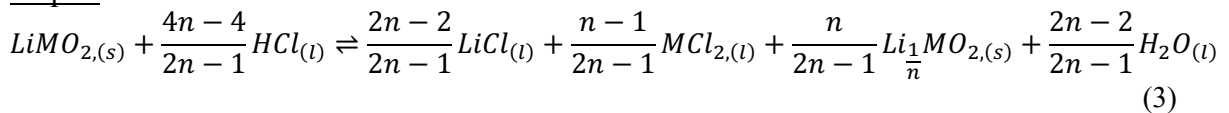
Figure 3 shows the influence of the temperature on the dissolution of nickel, cobalt, manganese and lithium from NMC811 as a function of time. The leaching kinetics of the other NMC cathodic materials are reported in the Supporting Information (Figures S1-S16). The NMC materials were fully dissolved under these experimental conditions. No significant difference in the dissolution kinetics was observed for nickel, manganese and cobalt. Conversely, the dissolution kinetics of lithium from all cathodic materials were much faster than those obtained for nickel, manganese and cobalt. Furthermore, it was observed that the digestion of the cathodic materials containing high content of nickel or low content of manganese was faster (NMC811 and NMC622). The comparison of the leaching curves reported in Figure 3 and Figures S1-S16 (Supporting Information) leads to the conclusion that the leaching kinetics follows this order: NMC811 > NMC622 >> NMC532 > NMC111 at 54 °C. It is in accordance with the stability of the NMC electrodes, which is higher for manganese-rich cathodes (Gong et al., 2017).

3.1 Kinetic models

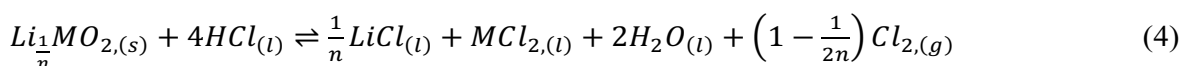
3.1.1 Empirical model based on chloride consumption

In our previous paper (Xuan et al., 2019), it was demonstrated that NMC111 digestion involves the two following steps:

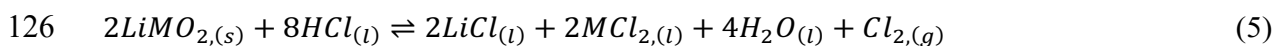
Step 1:



Step 2: (rate limiting reaction)



125 The overall equation can be written as:



127 where the first step results in the formation of an intermediate product $Li\frac{1}{n}MO_{2,(s)}$ with
128 M=Ni, Mn or Co. The parameter n denotes the molar ratio between all transition metals
129 and lithium in the intermediate product, which was calculated by plotting the total
130 concentration of nickel, manganese and cobalt as a function of lithium concentration in
131 the leachate (Xuan et al., 2019). The values of n were found to range from 2.1 to 4.0 when
132 the solid/liquid ratio (S/L) and the temperatures were comprised between 20 and 80 g/L,
133 and between 25 and 82 °C, respectively (**Table 4**).

134 Release of chlorine gas was observed during the NMC digestion due to chloride
135 oxidation (Eq (4)). The chloride concentration in the leach solution can be calculated as
136 a function of the leaching time by using the following semi-empirical equation when the
137 step 2 is predominant:

$$138 \quad [Cl^-]_t = ([Cl^-]_{\infty} - [Cl^-]_o)[1 - \exp(-at)] + [Cl^-]_o \quad (6)$$

139 where $[Cl^-]_o$, $[Cl^-]_t$, and $[Cl^-]_{\infty}$ denote the chloride concentration in the leach solution at
140 the beginning of the experiment, at time t and at infinite time, respectively. In this
141 equation, the initial chloride concentration corresponds to the initial concentration of
142 hydrochloric acid and the theoretical value of the chloride concentration at infinite time
143 can be deduced by the following equation:

$$144 \quad [Cl^-]_{\infty} = [Cl^-]_o - \frac{1}{M_{NMC}} \left(\frac{S}{L} \right) \quad (7)$$

145 where M_{NMC} (in g/mol) is the molecular weight of NMC and S/L (in g/L) is the
146 solid/liquid phase ratio. The chloride concentration at infinite time $[Cl^-]_{\infty}$ is equal to 3.8
147 mol L⁻¹ and 3.2 mol L⁻¹ when 4.0 mol L⁻¹ HCl is used to leach the NMC materials at
148 S/L=20 g/L and 80 g/L, respectively.

149 **Figure 4** shows the variation of the chloride concentration as a function of time when
150 NMC532 was leached in 4 mol L⁻¹ HCl at 82 °C and S/L= 20 g/L. There is a fair agreement
151 between the experimental data and those calculated by using the semi-empirical **Eq (6)**.

152 To assess the relative success of the semi-empirical model applied to various experimental
153 conditions (**Figures S17-S27**), a linear square regression analysis of the form:

$$154 \quad [Cl^-]_{t,exp} = u [Cl^-]_{t,calc} \quad (8)$$

155 was employed where $[Cl^-]_{t,calc}$ and $[Cl^-]_{t,exp}$ represent the calculated and experimental values of
156 the chloride concentration in the leach solution at time t, respectively; u is the conversion factor.

157 **Eq (6)** describes fairly the experimental data as the values of u deduced from Eq. (8) and the
 158 standard deviation R^2 of Eq. (8) are close to the unity (**Table 5**). The theoretical values of $[Cl^-]$
 159 ∞ are in agreement with those calculated by Eq (7): $[Cl^-]_{\infty}=3.7-3.9 \text{ mol L}^{-1}$ at $S/L=20 \text{ g/L}$
 160 and $[Cl^-]_{\infty}=3.2-3.3 \text{ mol L}^{-1}$ at $S/L=80 \text{ g/L}$, whereas the theoretical values are equal to 3.8
 161 and $3.2 \text{ mol}\cdot\text{L}^{-1}$, respectively (**Table 5**).

162 The following equations can be written by using Eqs (3)-(4) and Eq (6):

$$163 [Li] = \frac{1}{M_{NMC}} \left(\frac{2n-2}{2n-1} \right) \frac{S}{L} + \frac{([Cl^-]_{\infty} - [Cl^-]_0)[1 - \exp(-at)] + [Cl^-]_0}{2n-1} \quad (9)$$

$$164 [Ni] + [Mn] + [Co] = \frac{1}{M_{NMC}} \left(\frac{n-1}{2n-1} \right) \frac{S}{L} + \frac{([Cl^-]_{\infty} - [Cl^-]_0)[1 - \exp(-at)] + [Cl^-]_0}{2 - \frac{1}{n}} \quad (10)$$

165 where M_{NMC} (in g/mol) is the molar mass of NMC corresponding to 1 mol of Li and $\frac{S}{L}$ (in g/L)
 166 is the solid/liquid phase ratio.

167 **Eqs (9) and (10)** were used to calculate the metal concentration as a function of the leaching
 168 time. For the sake of illustration, the comparison of the experimental data and the calculated
 169 values are displayed in **Figure 5** for NMC532 digested in 4 mol L^{-1} HCl at $82 \text{ }^{\circ}\text{C}$. The other
 170 results are available in the Supporting Information.

171 It is interesting to highlight that lithium dissolution was faster than that observed for nickel,
 172 cobalt and manganese at the beginning of the reaction. This difference in kinetic behavior might
 173 be explained by the fact that the mechanism of lithium dissolution does not involve any
 174 reduction [**Eqs (3) and (4)**] unlike cobalt, nickel and manganese (Buzatu et al., 2014).

175 The leaching of NMC811 was tested in 4 mol L^{-1} at $25 \text{ }^{\circ}\text{C}$ and three different S/L ratios, i.e.
 176 2 g/L , 20 g/L and 80 g/L . According to **Eq (5)**, 4 mol L^{-1} HCl cannot dissolve more than 97.3
 177 g/L NMC811. Below this stoichiometric limit, the leaching kinetics of Li, Co, Ni and Mn hardly
 178 depend on the S/L ratio (**Figure 6**).

179 **Eqs (9) and (10)** can also be used to investigate the effect of S/L ratios on the leaching
 180 kinetics. **Figure 7** shows the variation of the lithium concentration and the variation of the total
 181 concentrations of cobalt, nickel and manganese as a function of the leaching time at two
 182 different S/L ratios, i.e. 80 g/L for NMC111 at $25 \text{ }^{\circ}\text{C}$, and 20 g/L for NMC 622 at $54 \text{ }^{\circ}\text{C}$. These
 183 experimental results are in fair agreement with **Eqs (9) and (10)**. Therefore, the present model
 184 can fairly predict the leaching kinetics as a function of S/L ratios. Additional results are
 185 available in the Supporting Information (**Figures S28-S38**).

186 **Figure 8** confirms that **Eqs (9) and (10)** can be used to calculate the concentrations of cobalt,
 187 nickel, manganese and lithium in the leachate at any S/L ratios for the four NMC cathodic
 188 materials.

189 3.1.2 First-order rate law

190 The first-order rate law was used to describe the rate of many chemical systems in the
 191 literature. This law was used in the present paper to describe the rate of NMC digestion in HCl
 192 media.

193 The following equation can be written:

$$194 [Ni]' + [Mn]' + [Co]' = n[Li]' = \frac{[HCl]_0 - [HCl]}{4} = f(t') \quad (11)$$

195 where [Ni]', [Mn]', [Co]' and [Li]' represent nickel, cobalt, manganese and lithium
 196 concentrations dissolved in the leach solution during the second step, respectively. The term
 197 [HCl]₀ is the acid concentration at the end of the first step and the term [HCl] denotes the acid
 198 concentration at time t' (where t' is the time during the second step, which is the difference
 199 between the total time t and the transition time t₀ when the first step finishes).

$$200 t' = t - t_0 \quad (12)$$

201 The transition time t₀ can be determined by using the approach below. According to **Eq (3)**, the
 202 following mass-balance equations can be written for step 1 and step 2, respectively:

$$203 [Ni] + [Mn] + [Co] = \frac{1}{2}[Li] \quad (13)$$

$$204 [Ni] + [Mn] + [Co] = n[Li] + b \quad (14)$$

205 where n is defined in **Eq (4)**, and b is an empirical constant. Both n and b can be determined by
 206 plotting [Ni]+[Mn]+[Co] with [Li].

207 These two equations are equal at the transition times corresponding to the end of the first step
 208 and the beginning of the second step. Therefore, the sum of the concentrations of cobalt, nickel
 209 and manganese as well as the lithium concentration in the leach solution at the transition point
 210 can be calculated by using the following equations deduced from **Eqs (15) and (16)**:

$$211 [Li]_0 = \frac{2b}{1-2n} \quad (15)$$

$$212 [Ni]_0 + [Mn]_0 + [Co]_0 = \frac{b}{1-2n} \quad (16)$$

213 **Figure 9** illustrates the way to determine the transition concentrations for NMC111 leached in
 214 4 mol L⁻¹ HCl at 54 °C. The intersection of the two straight lines corresponds to the
 215 concentrations of lithium ([Li]₀), and the sum of the concentrations of nickel, cobalt and
 216 manganese in the leach solution ([Ni]₀+ [Mn]₀+ [Co]₀) at the transition time.

217 The transition time (t₀) can be deduced by using the following empirical equations given that
 218 the values of [Ni]₀ + [Mn]₀ + [Co]₀ were previously determined by using the following
 219 relationship:

$$220 [Ni]_0 + [Mn]_0 + [Co]_0 = \left(\frac{1}{M_{NMC} L} S - [Ni]_0 - [Mn]_0 - [Co]_0 \right) [1 - e^{(-k_1 t_0 + f)}] \quad (17a)$$

221 In this equation, $\left(\frac{1}{M_{NMC L}} S - [Ni]_0 - [Mn]_0 - [Co]_0\right)$ is the theoretical maximum sum of the
 222 concentrations of Ni, Mn and Co when all the solid is dissolved, which is calculated by the total
 223 number of moles of Ni, Mn and Co from the solid subtracted by the dissolved part during the
 224 first step. The constants k_1 and f have been deduced by fitting the experimental data of metal
 225 dissolution vs. time with the following general equation used to describe NMC digestion, using
 226 solve of Excel:

$$227 \quad [Ni]' + [Mn]' + [Co]' = \left(\frac{1}{M_{NMC L}} S - [Ni]_0 - [Mn]_0 - [Co]_0\right) [1 - e^{(-k_1 t' + f)}] \quad (17b)$$

228 The parameters k_1 and f are gathered in **Table 6**.

229 The concentrations of lithium, nickel, cobalt and manganese dissolved at the transition time at
 230 the end of the first step can be calculated provided that the transition time has been calculated
 231 by using the preceding approach:

$$232 \quad [Li]' = [Li] - [Li]_0 \quad (18)$$

$$233 \quad [Ni]' = [Ni] - [Ni]_0 \quad (19)$$

$$234 \quad [Mn]' = [Mn] - [Mn]_0 \quad (20)$$

$$235 \quad [Co]' = [Co] - [Co]_0 \quad (21)$$

236 where $[Li]_0$, $[Ni]_0$, $[Mn]_0$ and $[Co]_0$ denote the concentration of lithium, nickel, manganese and
 237 cobalt at the end of the first step (at the transition time, see previously), respectively, whereas
 238 $[Li]'$, $[Ni]'$, $[Mn]'$ and $[Co]'$ represent nickel, cobalt, manganese and lithium concentrations
 239 dissolved in the leach solution during the second step, respectively.

240 According to **Eq (4)**, the following equation can be written:

$$241 \quad [Ni]' + [Mn]' + [Co]' = n[Li]' = \frac{[HCl]_0 - [HCl]}{4} \quad (22)$$

242 According to the first-order rate law, the kinetics of HCl consumption during the second step
 243 can be described as follows:

$$244 \quad [HCl] = [HCl]_f + ([HCl]_0 - [HCl]_f)e^{-k_1 t'} \quad (23)$$

245 where $[HCl]$ is the acid concentration at time $t'=t-t_0$ (time in the second step), $[HCl]_0$ is the acid
 246 concentration at the transition time t_0 and $[HCl]_f$ is the final acid concentration after full NMC
 247 dissolution. The model is appropriate to follow metal dissolution through acid consumption.

248 Therefore, the combination of **Eqs (4), (22) and (23)** leads to the following relationship:

$$249 \quad [Ni]' + [Mn]' + [Co]' = n[Li]' = \left(\frac{1}{M_{NMC L}} S - [Ni]_0 - [Mn]_0 - [Co]_0\right)(1 - e^{-k_1 t'}) \quad (24)$$

250 **Figure 10** shows that the first-order rate law can be used to describe the leaching kinetics of
 251 the second step given that a good agreement was obtained between the experimental data and

252 the values calculated by using Eq (24) [the same accordance was obtained for all leaching tests
253 as shown in Figure 11.

254 3.1.3 Shrinking core model

255 Figure 1 shows that the particule size distribution is narrow in in the case of NMC811, and
256 the same distribution was observed for all investigated cathodic materials. The SEM images of
257 NMC811 after 5 minutes of leaching at 25 °C and abundant water washing, filtration and drying
258 are reported in Figure 12. The initial spherical morphology of NMC was completely destroyed
259 when 40% of lithium and 80% of nickel, manganese, and cobalt were dissolved. The overall
260 leaching process may be controlled by intrinsic chemical reaction or by external mass transfer
261 (diffusion). Figure 12 shows the leaching process may not be controlled by ash diffusion as the
262 particle size drastically decreased very early. It is more reasonable to consider the shrinking of
263 small particles in Stokes regime, either film diffusion controls or reaction controls.

264 Therefore, the Shrinking Core model can be used to describe the leaching kinetics. In the
265 shrinking core model, the function of the reaction conversion $f(x_i)$ of element i (i =Li, Ni, Mn
266 and Co) is proportional to the reaction time t . The function $f(x_i)$ depends on the mechanism of
267 the reaction (Liddell, 2005). The ratio of $f(x_i)$ over the reaction time t is called the reaction rate
268 constant. In the case of the dissolution of several elements, each element i is characterized by
269 its reaction rate constant $k_{R,i}$ in the case of chemical reaction control mechanism or its diffusion
270 rate constant $k_{D,i}$ in the case of film diffusion control mechanism. Therefore, one of the
271 following equations may describe the leaching kinetics (Levenspiel, 1999; Houzelot et al.,
272 2018; Mgaidi et al., 2004):

273 In the case of chemical reaction control:

$$274 \quad 1 - (1 - x_i)^{\frac{1}{3}} = \left(\frac{3\beta_{r,i}[HCl]}{\rho_B R_0} \right) = k_{R,i} t \quad (25)$$

275 In the case of film diffusion control:

$$276 \quad x_i = \left(\frac{3\beta_{L,i}[HCl]}{\rho_B R_0} \right) = k_{D,i} t \quad (26)$$

277 where x_i is the extraction fraction of the element i =Li, Ni, Mn or Co, and [HCl] represents the
278 hydrochloric acid concentration in the bulk (the variation of hydrochloric acid in the bulk
279 throughout the leaching experiments can be considered constant as shown previously). The
280 parameters $\beta_{L,i}$, ρ_B , R_0 and $\beta_{r,i}$ denote the liquid mass transfer coefficient, the density of solid
281 (in g cm^{-3}), the initial radius of the core (in cm) and the intrinsic chemical reaction rate constant,
282 respectively. The terms $k_{R,i}$ and $k_{D,i}$ are rate constants depending upon the leaching mechanism:
283 $k_{R,i}$ (in min^{-1}) is the apparent rate constant of the surface chemical reaction for i , $k_{D,i}$ (in min^{-1})
284 is the apparent diffusion rate constant of i , and t is the leaching time in minutes.

285 Since the reaction takes place in two steps, it is difficult to analyse the global reaction directly
286 by means of the shrinking core model. **Figure 13** shows that the plots of $f(x_i)$ vs. time in the
287 case of chemical reaction control and in the case of film diffusion control do not pass through
288 the origin (0, 0) when NMC111 is leached in 4 mol L⁻¹ HCl at 54 °C (same observation for all
289 leaching experiments). In order to investigate the second step, which is the limiting step and
290 the longest step, it is necessary to subtract the concentrations of lithium, nickel, cobalt and
291 manganese dissolved during the first step.

292 The Shrinking Core Model described by **Eqs (25) and (26)** can be applied to the second step
293 by plotting [Li]', [Ni]', [Mn]' and [Co]' as a function of $t' = t - t_0$, as is done with first-order
294 rate law in the previous sub-chapter. For the sake of illustration, **Figure 14** shows the plot of
295 the shrinking core model applied to the longest step during the NMC111 dissolution in 4 mol
296 L⁻¹ HCl at 54 °C, considering both reaction controls and diffusion controls.

297 The kinetic parameters deduced from **Eqs (25) and (26)** for the investigated NMC materials
298 at different temperatures are reported in **Tables S1-S4** (Supporting Information). The R²
299 coefficient corresponding to reaction control is often higher than the R² coefficient found for
300 diffusion control. It is therefore reasonable to conclude that the kinetics of the second step is
301 controlled by the chemical reaction.

302 3.1.4 The effect of temperature and residence time

303 The temperature dependance of rate constants is usually described by the Arrhenius
304 equation:

$$305 \quad k_i = A_i \exp\left(-\frac{E_{a,i}}{RT}\right) \quad (27)$$

306 where k_i (in min⁻¹) is the rate constant of i =Li, Ni, Mn or Co ($k_i=k_{R,i}$ in the case of chemical
307 reation control, $k_i=k_{D,i}$ in the case of film diffusion control, $k_i=k_{1,i}$ in the case of first-order rate
308 law). The term A_i is the frequency factor of i (in min⁻¹), $E_{a,i}$ (in J mol⁻¹) is the apparent activation
309 energy of i , R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature
310 (in K).

311 **Figure 15** shows the Arrhenius plots corresponding to nickel dissolution from NMC111 in
312 4 mol L⁻¹ hydrochloric acid at 54 °C. **Table 7** gathers the values of activation energies for the
313 dissolution of lithium, nickel, manganese and cobalt during the lixiviation of NMC811,
314 NMC622, NMC532 and NMC111 by considering the first-order rate law, and the shrinking
315 core model including both reaction control and film diffusion control. It is interesting to
316 highlight that the activation energies are very similar for the three models (first-order rate law,
317 shrinking core model by considering a chemical reaction control and shrinking core model by

318 considering a film dissolution control). According to the literature, activation energies around
 319 20 kJ mol⁻¹ usually correspond to diffusion-controlled leaching whereas values higher than 40
 320 kJ mol⁻¹ can be attributed to chemical reaction-controlled leaching (Reid et al., 2017). Therefore,
 321 the values of the activation energies confirm the previous conclusion, i.e. the second step of
 322 NMC leaching is controlled by the chemical reaction.

323 The following equation deduced by combining **Eq (25)** [shrinking core model, reaction
 324 controls] and **Eq (27)** [Arrhenius law] can be used to calculate the dissolution yield of each
 325 metal contained in NMC at any leaching time and any temperature during the second step:

$$326 \quad x_i = 1 - \left[1 - e^{\left(\ln(A_i) - \frac{E_{a,i}}{RT} \right) t'} \right]^3 \quad (28)$$

327 where A_i is the frequency factor of i =Li, Ni, Mn or Co (in min⁻¹) reported in **Table 8**. $E_{a,i}$ (in
 328 J mol⁻¹) is the apparent activation energy of i =Li, Ni, Mn or Co. R is the universal gas constant
 329 (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (in K) and t' is the leaching time of the second
 330 step in minutes.

331 The time to achieve the full dissolution of i =nickel, cobalt, manganese or lithium in the
 332 second step can be calculated from **Eq (29)** according to the shrinking core model:

$$333 \quad t'_{i,100\%} = e^{\left[\frac{E_{a,i}}{RT} - \ln(A_i) \right]} \quad (29)$$

334 Obviously, the full digestion of NMC will be reached by considering the highest value of $t'_{i,100\%}$
 335 among those calculated for i =Li, Ni, Mn and Co.

336 Likewise, the First-order rate law can be used to calculate the leaching duration for achieving
 337 the full digestion of NMC. The time to reach LE% of extraction efficiency during the second
 338 step ($t'_{i,LE}$) can be deduced from the the first-order law:

$$339 \quad t' = \frac{-\ln(100\% - LE(i)\%)}{k_{1,i}} = \frac{-\ln(100\% - LE(i)\%)}{A_i \exp\left(-\frac{E_{a,i}}{RT}\right)} \quad (30)$$

340 where $LE(i)$ and $k_{1,i}$ are the leaching percentage of i (i =Li, or the sum of Ni, Mn and Co) and
 341 the first-order rate constant of i , respectively.

342 **Table 10** gathers the values of the leaching time necessary to reach the full dissolution of
 343 lithium, cobalt, nickel and manganese by considering shrinking core model and the first order
 344 law in the case of NMC811 dissolution. The duration to complete the full dissolution of
 345 NMC622, NMC532 and NMC111 are reported in Table S5-S7 in the Supporting Information.
 346 These Tables show a good agreement between the two models. It is possible to determine the
 347 residence time needed to reach the full dissolution of NMC by taking into consideration the
 348 maximum time of dissolution between the two models and by multiplying this value by 1.1 in

349 order to take into account the first step, which usually represents less than 10% of the global
350 leaching time (see **Table 9**).

351 **Figure 16** shows the variation of the residence time as a function of the temperature. The
352 leaching kinetics follow the following order when temperature is comprised between 25 °C and
353 90 °C: NMC811>NMC622>>NMC532~NMC111. At high temperature, the behavior of
354 NMC811 becomes close to that of NMC622. This order is in accordance with the fact that
355 nickel decreases the thermal stability and manganese improves the stability of NMC cathodic
356 materials (Gong et al., 2017) because of differences in temperature-dependence of NMC
357 leaching kinetics (**Table 7**).

358 **4. Conclusions**

359 Hydrochloric acid is efficient for leaching NMC811, NMC622, NMC532 and
360 NMC111. The apparent rate constants were calculated for each NMC at different
361 temperatures. At 54 °C, the digestion of NMC811 and NMC622 is faster than the
362 dissolution of NMC532 and NMC111. This observation complies with the fact that
363 nickel is usually expected to increase dissolution rate and manganese stabilises the NMC
364 structure.

365 The solid-liquid ratio does not affect the leaching kinetics as far as the solid-liquid phase
366 ratio does not exceed the stoichiometric limit. The leaching mechanism of NMC involves two
367 steps: the first step is a fast phase transformation leading to the formation of a new lithium-
368 deficient phase. This is in agreement with the XRD patterns, which confirm the presence of a
369 shift of the main peak at the beginning of the leaching reaction, without further shifts during
370 the rest of the reaction (Xuan et al., 2019). This transition phase is afterward dissolved during
371 the second step, which is the rate-limiting reaction. Three semi-empirical kinetic models (semi-
372 empirical model based on chloride consumption, shrinking core model and a model based on
373 the first-order law) have been successfully applied to describe the leaching time of the
374 investigated NMC cathodic materials.

375 The shrinking core model and a model based on the first-order law confirm that the kinetic
376 of the second step is controlled by a chemical reaction. Two equations derived from the
377 shrinking core model and the first order law have been reported to calculate the time necessary
378 to achieve the complete leaching of NMC cathodic materials at any temperatures. Such an
379 equation can be used to assess the optimized residence time in the leaching reactor as a function
380 of the temperature and solid composition during NMC digestion.

381

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390

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479

480 **TABLES**

481

482 **Table 1:** Composition of the main cathodic materials in LIBs.

Abbreviation	Chemical formula
LCO	LiCoO_2
LMO	LiMn_2O_4
LNO	LiNiO_2
LFP	LiFePO_4
NMC111	$\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$
NMC532	$\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_2$
NMC622	$\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$
NMC811	$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$

483

484

485 **Table 2:** Experimental conditions implemented to leach cathodic materials from LIBs.

Cathode	Leaching media			Experimental conditions			Reference	
	Acid	Concentration	Additive	Temperature (°C)	Solid/Liquid			Time (h)
		(M)			% solids	mass/volume (g/ml)		
NMC111	H ₂ SO ₄	1		30	4% (w/w)		Billy et al., 2018	
NMC111, LCO	H ₂ SO ₄	2	10% H ₂ O ₂	70		1/30	1.5	Chen and Ho, 2018
NMC111, LCO, LMO	HCl	4		80		1/50	1	Wang et al., 2009
Spent LIBs cathodes	HCl	1.75		50	20% (w/v)		2	Barik et al., 2017
NMC532	H ₂ SO ₄	2	3% (v/v) H ₂ O ₂	60		1/20	1	Liu et al., 2020
LCO, LMO, LNO, NMC	H ₂ SO ₄	2.5	3.3% (v/v) H ₂ O ₂	90			2.5	Chu et al., 2020
NMC, LFP, LIBs cathodes	HCl	6	H ₂ O ₂ /M ²⁺ = 2 (mole)	60		1/8	2	Li et al., 2009
Spent LIBs cathodes	HCl	4		80		1/50	1	Dhiman et al., 2019
NMC, LiCoO ₂	H ₂ SO ₄	1	1% (v/v) H ₂ O ₂	40		1/25	1	He et al., 2017
Spent LIBs cathodes	H ₃ PO ₄ and citric acid	0.2-0.4		90		1/50	0.5	Zhuang et al., 2019
Spent LIBs cathodes	H ₂ SO ₄	2	4% (v/v) H ₂ O ₂	50		1/20	2	Sattar et al., 2019
Spent LIBs cathodes	H ₂ SO ₄	1	0.075 M NaHSO ₃	95		1/50	4	Meshram et al., 2015
NMC cathode scrap	H ₂ SO ₄	2.5	0.8 M NH ₄ Cl	80		1/10	1	Lv et al., 2018
Mixture of NMC, LCO, LMO, and LFP	H ₂ SO ₄	2.5	20% (v/v) H ₂ O ₂	60		1/33	1	Zheng et al., 2017

486 (see the cathode composition in **Table 1**).

487

488

489 **Table 3:** Comparison between the composition of NMC cathodic materials based on assays of
 490 solids after digestion (Exp. for experimental) and leach liquors (Cal. for calculated).

NMC	Composition % (w/w)									
	Ni		Co		Li		Mn		O	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
811	48.3	48.3	5.65	6.06	7.19	7.13	5.56	5.65	33.3	32.9
622	36.1	36.3	11.8	12.2	7.33	7.16	11.0	11.3	33.7	33.0
532	30.1	30.4	11.9	12.2	7.27	7.19	16.6	17.1	34.1	33.1
111	19.7	20.3	19.2	20.4	7.24	7.20	18.3	19.0	35.5	33.2

491

492 **Table 4:** Calculated values of n based on **Eqs (3) and (4)**.

NMC	Temperature (°C)	S/L (g/L)	n
811	25	80	3.60
811	25	20	2.83
811	35	20	3.55
811	43	20	3.79
811	54	20	4.00
622	44	20	2.67
622	54	20	2.28
622	63	20	2.86
622	72	20	3.11
532	54	20	2.44
532	63	20	2.63
532	72	20	2.28
532	82	20	2.60
111	54	20	2.11
111	63	20	2.38
111	72	20	2.72
111	82	20	2.71

493

494 **Table 5:** Parameters used in **Eq (6)** to calculate chloride consumption during NMC leaching at
 495 various temperatures.

NMC	Temperature (°C)	a (min ⁻¹)	[Cl ⁻] ₀ (mol·L ⁻¹)	[Cl ⁻] _∞ (mol·L ⁻¹)	u	R ²
811	25	0.03	4.06	3.28	0.99	0.96
622	44	0.07	4.07	3.87	1.00	0.95
622	54	0.11	4.01	3.78	0.97	0.97
622	63	0.60	4.06	3.83	1.00	0.98
622	72	2.00	4.13	3.90	1.00	0.92
532	63	0.12	4.10	3.92	1.00	0.94
532	72	0.28	4.06	3.89	1.00	0.97
532	82	0.72	4.08	3.91	1.00	0.97
111	63	0.10	4.02	3.84	1.00	0.93
111	72	0.39	4.06	3.88	1.00	0.97
111	82	0.69	4.06	3.89	1.00	0.95

496 The values of u and R² deduced from **Eq (7)** give information about the quality of the fit.

497 **Table 6:** Determination of the empirical parameters for Eq (17).

NMC	Temperature (°C)	k_1	f
811	25	0.02	-0.42
811	35	0.06	-0.44
811	43	0.15	-0.41
811	54	0.41	-0.47
622	44	0.06	-0.41
622	54	0.20	-0.13
622	63	0.47	-0.33
622	72	1.43	-0.21
532	54	0.04	-0.43
532	63	0.11	-0.45
532	72	0.16	-0.46
532	82	0.86	-0.29
111	54	0.04	-0.44
111	63	0.09	-0.44
111	72	0.25	-0.39
111	82	0.60	-0.36

498

499 **Table 7:** Activation energy ($E_{a,i}$) of $i=Li, Ni, Mn$ and Co deduced from Eq (27)¹.

NMC	Activation Energy (kJ/mol)									
	First-order Rate Law		Shrinking Core Model Reaction Controls				Shrinking Core Model Diffusion Controls			
	Ni / Mn / Co	Li	Ni	Co	Li	Mn	Ni	Co	Li	Mn
811	82.2	72.7	85.3	84.5	87.3	84.5	87.9	87.3	79.5	87.0
622	101	94.8	103	104	95.0	102	95.8	95.6	93.7	95.6
532	96.5	111	102	103	90.5	103	98.6	99.4	95.5	99.2
111	99.5	96.8	101	100	103	101	97.5	97.2	97.4	97.7

500

501 **Table 8:** Neperian logarithm of the frequency factor of i (A_i in min^{-1}) calculated by considering
502 that leaching occurs via chemical reaction control, deduced from Eq (27).

NMC	$\ln(A_i)$						
	First-order Rate Law		Shrinking Core Model Chemical Controls				
	Li	Ni / Mn / Co	Li	Ni	Mn	Co	
811	25.7	29.3	29.9	29.1	28.8	28.8	
622	33.8	35.4	32.1	35.1	34.7	35.4	
532	37.3	32.3	28.9	33.0	33.5	33.5	
111	32.2	33.2	33.1	32.4	32.5	32.1	

503

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506

¹ Leaching conditions of NMC: 4 mol L⁻¹ HCl at S/L=20 g/L.

507 **Table 9:** Time to finish the first step t_0 and total time to finish the whole reaction t , and their
 508 proportion.

NMC	Temperature (°C)	t_0 (min)	Total t (min)	t_0/t
811	25	7.54	220	0.03
811	35	2.32	85.5	0.03
811	43	0.83	32.5	0.03
811	54	0.18	11.9	0.01
622	44	2.20	80.3	0.03
622	54	1.90	25.9	0.07
622	63	0.50	10.6	0.05
622	72	0.21	3.05	0.07
532	54	3.04	111	0.03
532	63	0.56	38.9	0.01
532	72	0.39	29.2	0.01
532	82	0.25	5.84	0.04
111	54	3.46	139	0.02
111	63	0.87	56.7	0.02
111	72	0.56	19.9	0.03
111	82	0.28	8.20	0.03

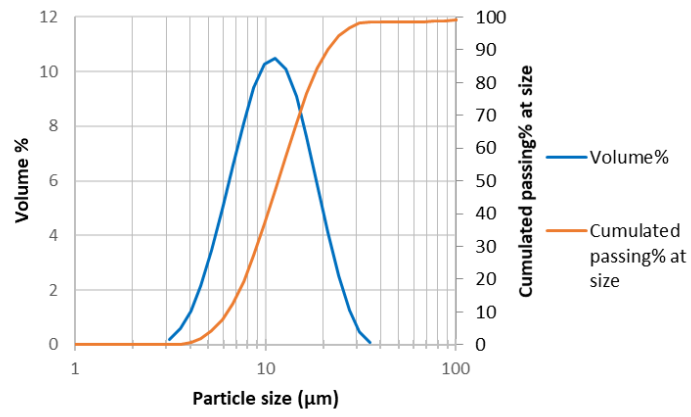
509

510 **Table 10:** Residence time of the whole leaching reaction.

Temperature (°C)	Leaching time (min) NMC811				
	Reaction controls				First order rate law
	Li	Ni	Mn	Co	Ni + Mn + Co
25	207	199	206	199	245
30	116	113	117	113	142
35	66.0	65.0	68.1	65.7	83.4
40	38.3	38.2	40.2	38.8	50.0
45	22.6	22.8	24.1	23.3	30.4
50	13.6	13.9	14.7	14.2	18.8
55	8.28	8.54	9.12	8.80	11.8
60	5.12	5.34	5.73	5.53	7.51
65	3.21	3.39	3.65	3.52	4.84
70	2.05	2.18	2.35	2.27	3.16
75	1.32	1.42	1.54	1.49	2.09
80	0.86	0.93	1.02	0.98	1.40
85	0.57	0.62	0.68	0.66	0.95
90	0.38	0.42	0.46	0.45	0.65

511 The residence time is calculated according to shrinking core model (reaction controls) for Li,
 512 Ni, Mn, Co and first-order rate law for the sum of Ni, Mn and Co, during the dissolution of
 513 NMC811 in 4 mol L⁻¹ HCl (Solid over liquid phase ratio S/L=20 g/L).

514 **FIGURES**



515
516 **Figure 1:** Particle size distribution of NMC811.

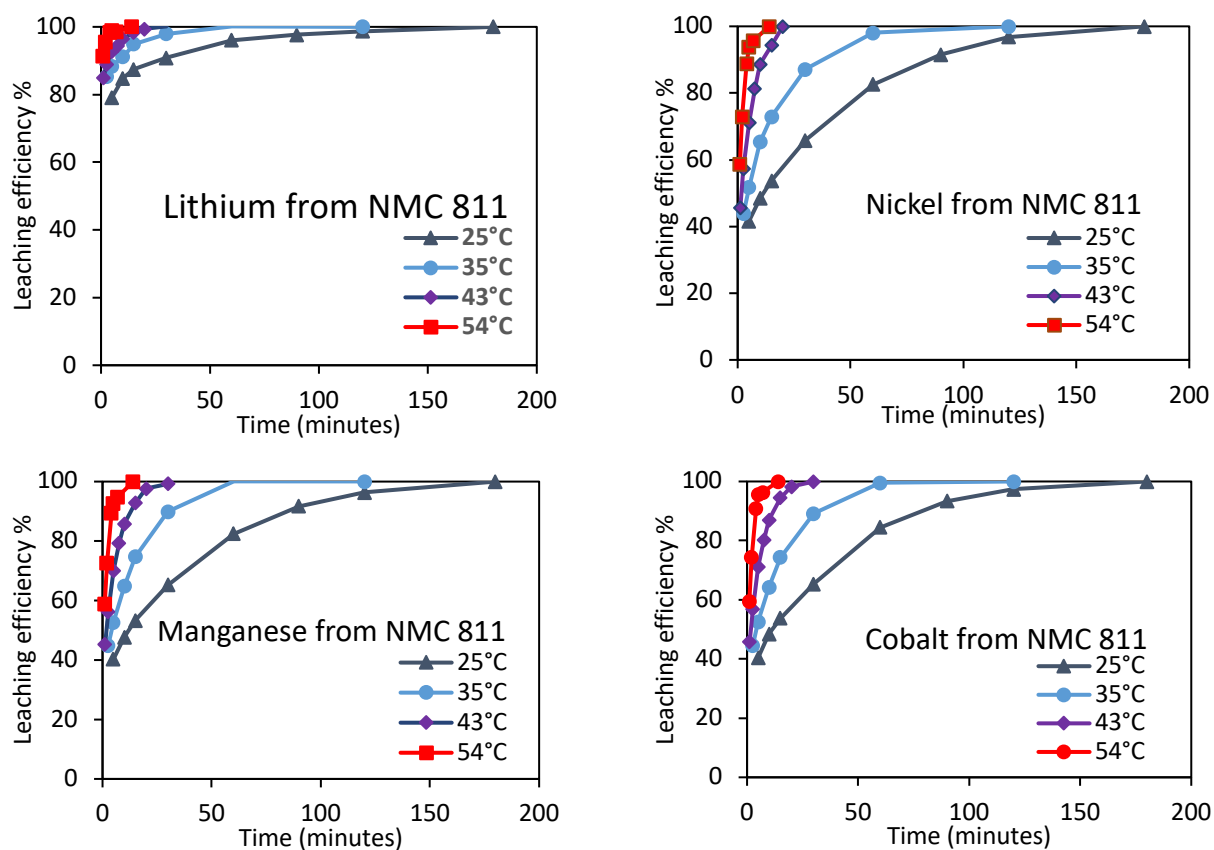
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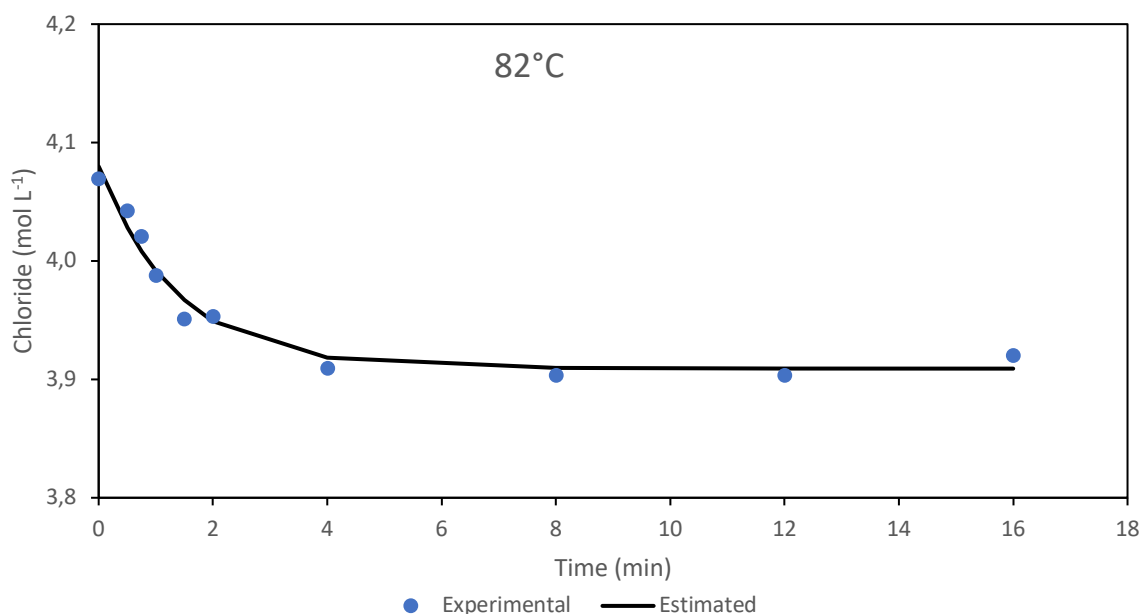
518
519 **Figure 2:** Setup for leaching experiments.

520

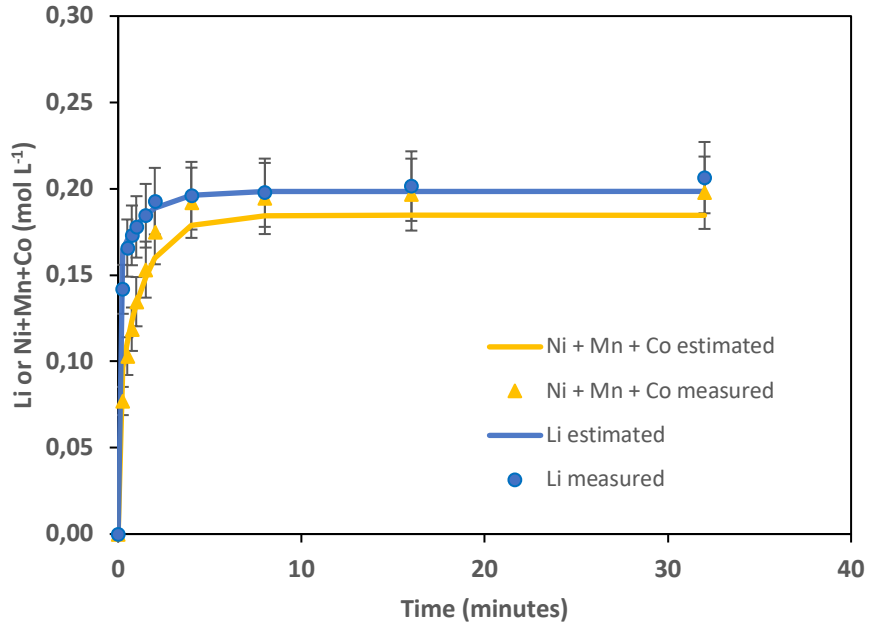
521



522
 523 **Figure 3:** Dissolution kinetics of Li, Ni, Mn and Co from NMC811 in 4 mol L⁻¹ HCl at 25 °C,
 524 35 °C, 43 °C and 54 °C (Solid over Liquid phase ratio S/L=20 g/L).
 525



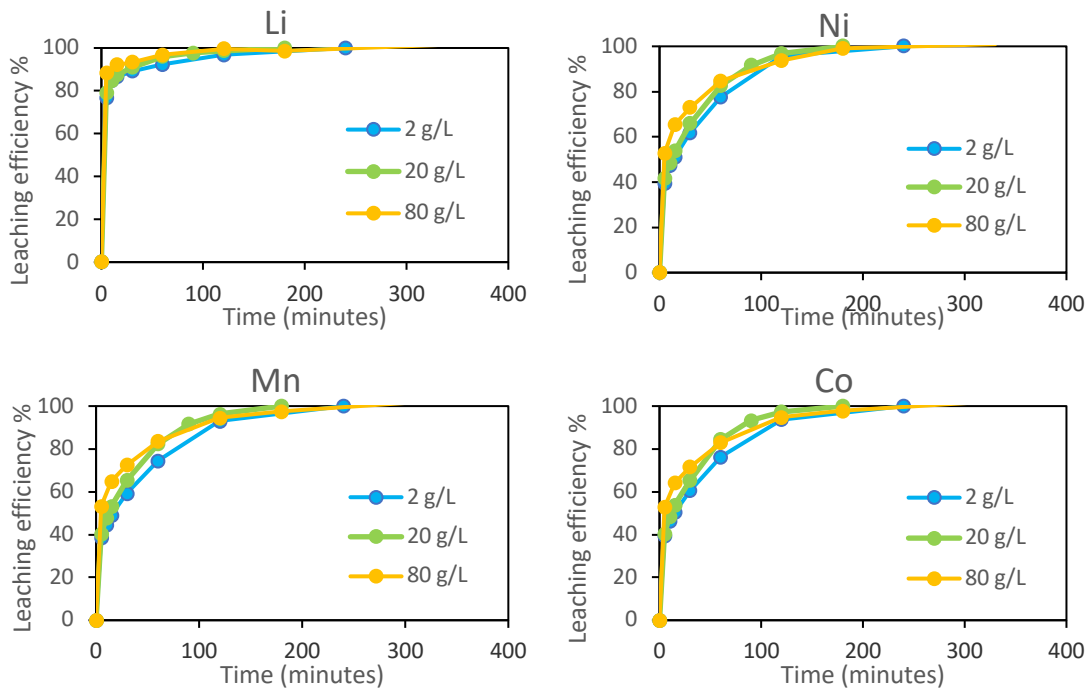
526
 527 **Figure 4:** Chloride concentration in the leachate as a function of NMC532 leaching time in 4
 528 mol L⁻¹ HCl at 82 °C and S/L=20 g/L [see Eq (6)].



529

530 **Figure 5:** Li concentration and sum of the concentrations of Ni, Mn and Co in the leachate at
 531 82 °C and S/L= 20 g/L during NMC532 leaching in 4 mol L⁻¹ HCl. Calculations performed by
 532 using Eqs (9) and (10).

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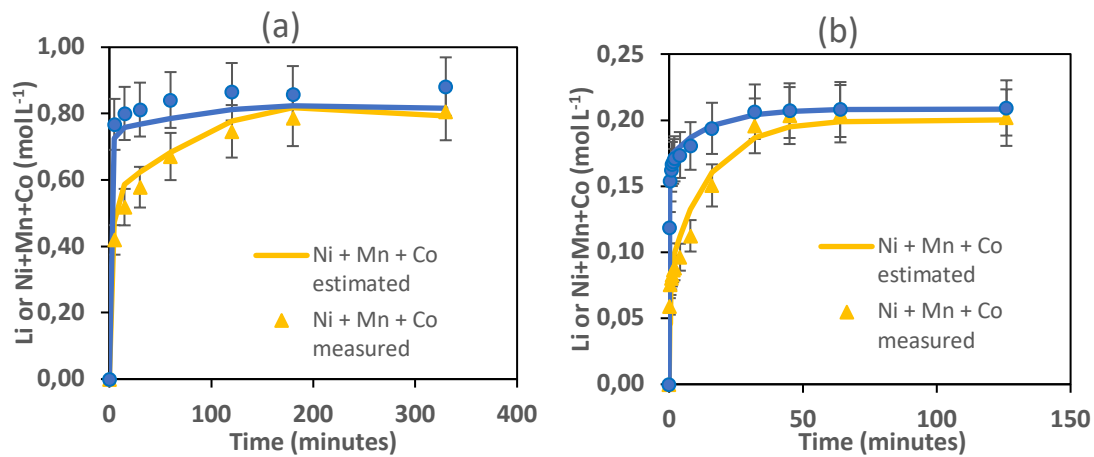


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535

536 **Figure 6:** Effect of S/L on the leaching kinetics of NMC811 in 4 mol L⁻¹ HCl at 25 °C.

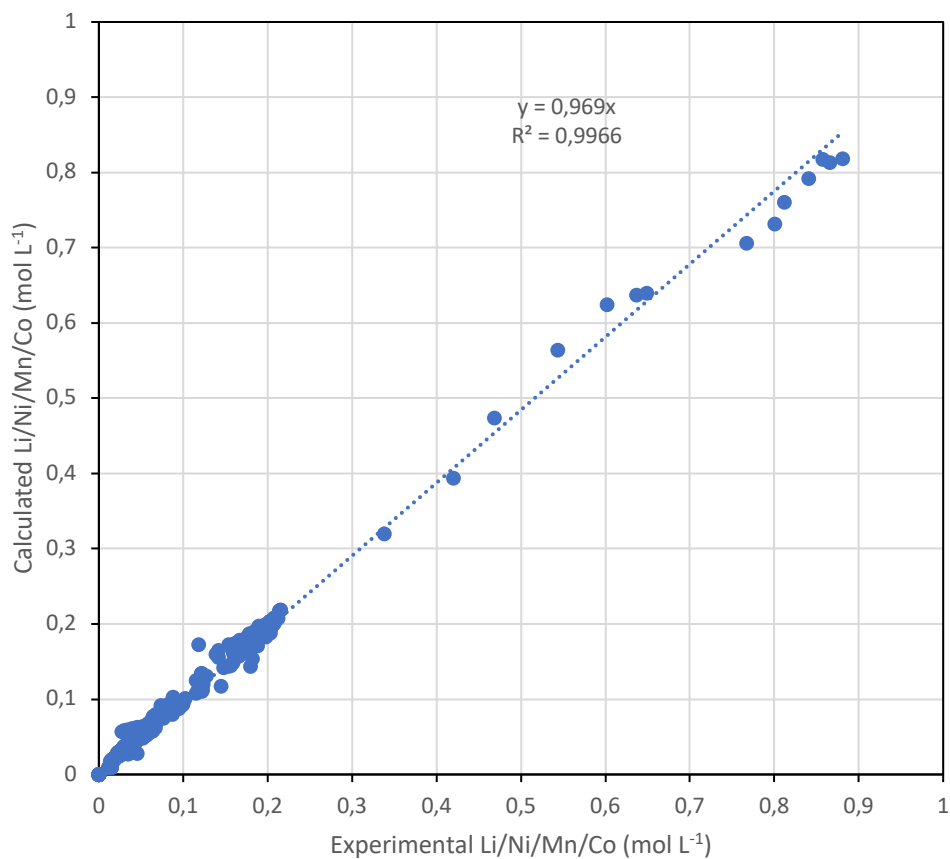
537



538

539 **Figure 7:** Lithium concentration and the sum of the concentrations of Ni, Mn and Co in the
 540 leachate during (a) NMC 811 dissolution at 25 °C and S/L= 80 g/L, and (b) NMC622
 541 dissolution at 54 °C and S/L= 20 g/L. Dissolution were performed in 4 mol L⁻¹ HCl.
 542 Calculations were performed by using Eqs (9) and (10).

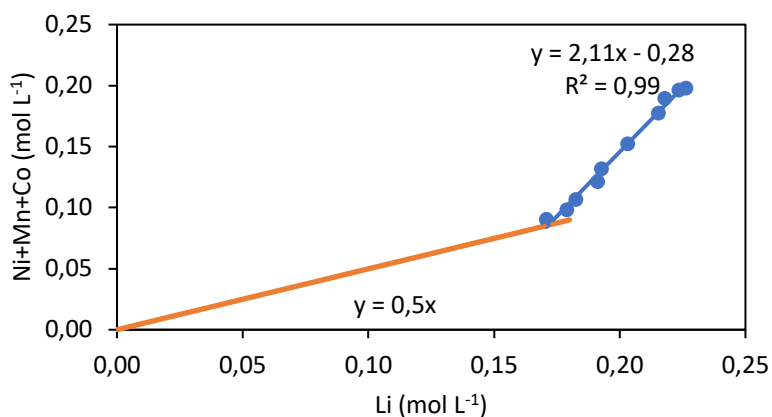
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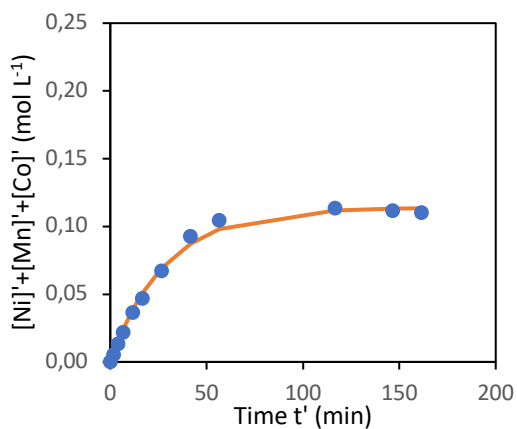
544

545 **Figure 8:** Comparison of the experimental and calculated concentrations of lithium, nickel,
 546 cobalt and manganese in the leach solutions [see Eqs (9) and (10)].

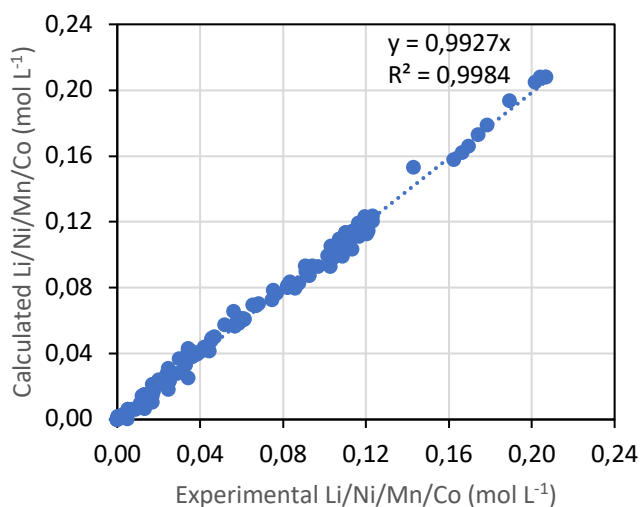
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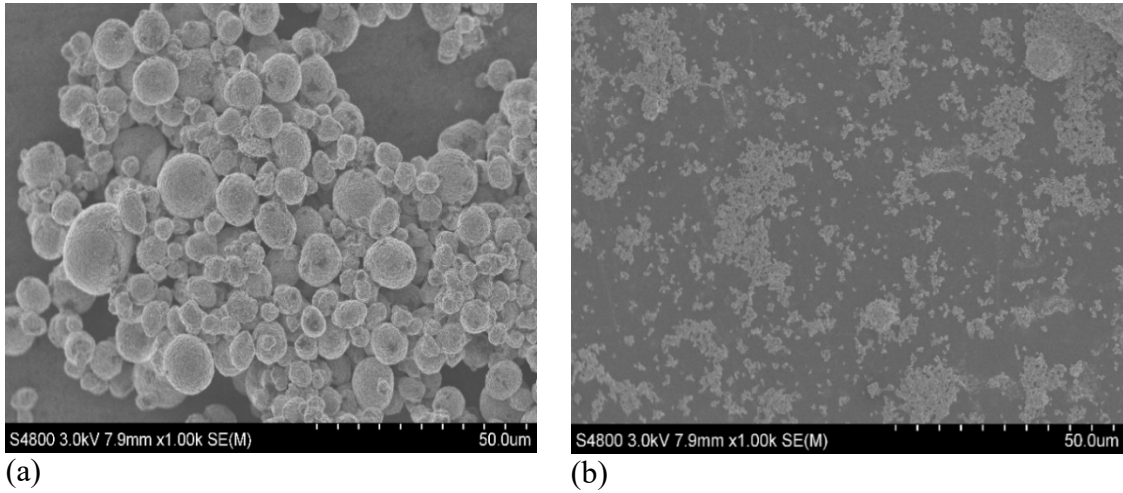
548
 549 **Figure 9:** Determination of the transition point between step 1 (red curve) and step 2 (blue
 550 curve) during the NMC111 dissolution in 4 mol L⁻¹ HCl at 54 °C.
 551



552
 553 **Figure 10:** The sum of the concentrations of Ni, Mn and Co during the second step of NMC
 554 111 dissolution at 54 °C and S/L= 20 g/L. The dissolution was performed in 4 mol·L⁻¹ HCl.

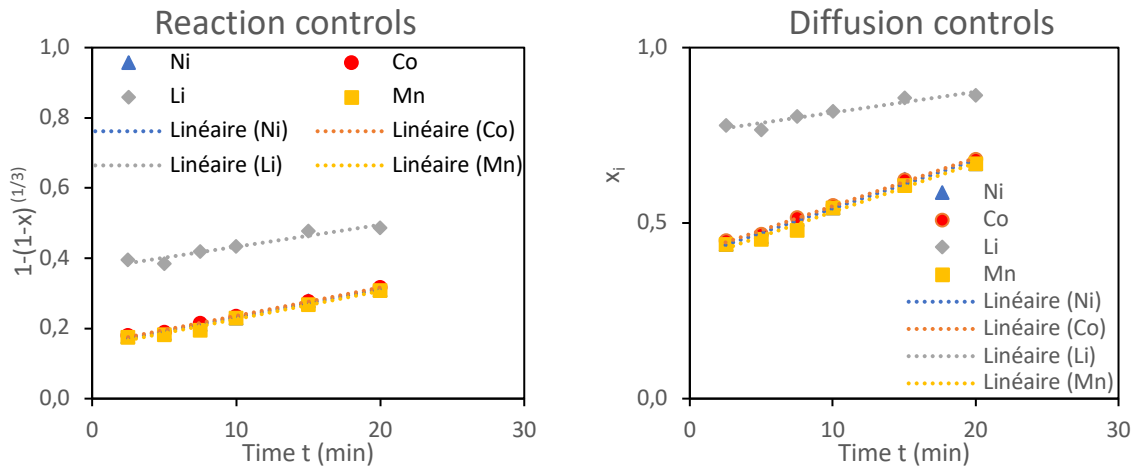


555
 556 **Figure 11:** Comparison of the experimental and calculated concentrations of lithium, nickel,
 557 cobalt and manganese in the leach solutions, generated during the second step.



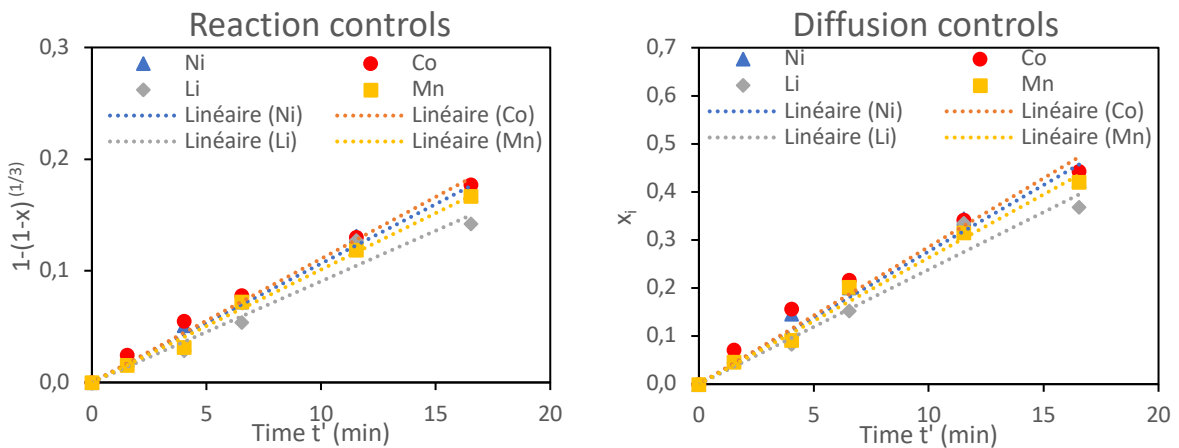
558 **Figure 12:** SEM images of (a) the pristine NMC 811 cathodic material, (b) NMC811 withdrawn
 559 after 5 minutes of leaching in 4 mol L⁻¹ HCl at S/L=2 g/L and 25 °C.

560

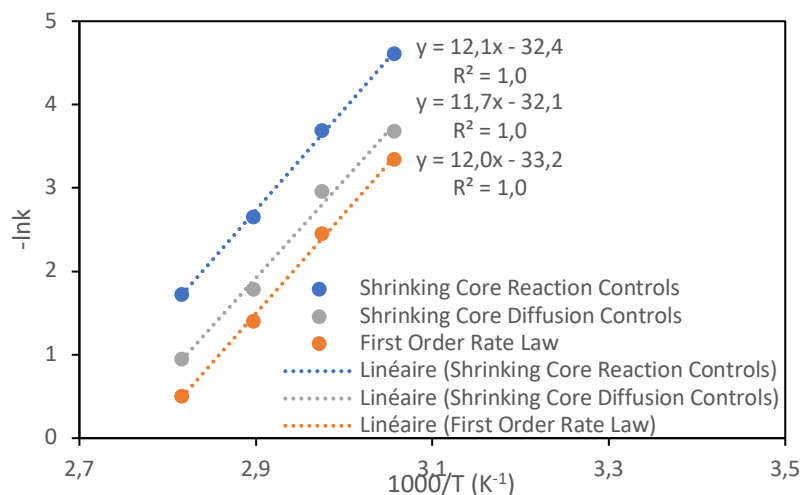


561 **Figure 13:** Application of shrinking core model to the global reaction of NMC 111 dissolution
 562 in 4 mol L⁻¹ HCl at 54°C.

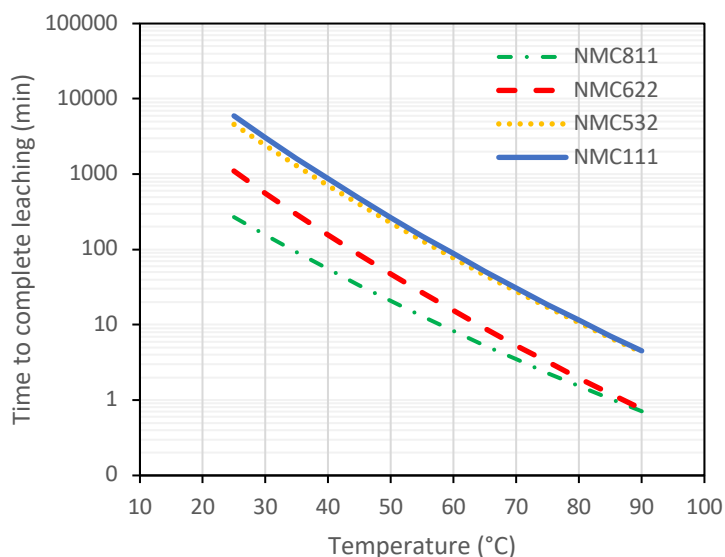
563



564 **Figure 14:** Application of the shrinking core model to the second step of NMC 111 dissolution
 565 in 4 mol L⁻¹ HCl at 54°C.



566 **Figure 15:** Arrhenius plots of Ni in the second step of NMC 111 dissolution in 4 mol L⁻¹ HCl
 567 at temperature range between 54 and 82°C according to Eq (27).



568
 569 **Figure 16:** Leaching time to achieve the full dissolution of NMC materials in 4 mol L⁻¹ HCl as
 570 a function of the temperature at S/L= 20 g/L. The data were calculated by using Eqs (29) and
 571 (30).