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

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7 Abstract

8 Leaching reactions in hydrochloric acid of several cathodic materials used in lithium-ion 9 batteries were investigated between 25 °C and 82 °C. The dissolution rate increased as follows: 10 NMC811 $(LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2) > NMC622 (LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2)$ >>NMC532 $(\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2) > \text{NMC111}$ $(\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2)$. The dissolution of lithium is faster 11 12 than that for nickel, cobalt and manganese. Data analysis demonstrated that NMC dissolution 13 is always a two-step process. In the first step, NMC was transformed very quickly into a new 14 lithium-defficient phase. This phase was subsequently dissolved during a second-rate limiting 15 step. No significant impact of the solid/liquid ratio on the leaching kinetics was observed as far 16 as the solid-liquid ratio remained below the stochiometric composition. Finally, a shrinking 17 core model and a first-order rate law were used to investigate the leaching kinetics of the second 18 rate-limiting step, which is the main step involved during NMC digestion in hydrochloric acid. 19 20 Keywords: Lithium-ion batteries, NMC, hydrochloric acid, leaching, kinetics, recycling. 21 22 *Correspondence should be addressed to: 23 Alexandre Chagnes (alexandre.chagnes@univ-lorraine.fr) 24 25

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 (LiNi_{1-x-y}Mn_xCo_yO₂) are the most widely used material in LIBs. The electrochemical and physicochemical properties of NMC electrodes depend on their compositions (Gong et al. 31 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 $(LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2),$ NMC622 38 (LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂), NMC532 (LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂) and NMC111 (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂).

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 SOx 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 developpement of recycling processes of spent LIBs 53 is challenging (Pagliaro and Meneguzzo, 2019). In particular, many efforts concern the 54 manganese recovery of lithium, cobalt. nickel and from the 55 LiNi_{1-x-y}Mn_xCo_yO₂ cathodic material. Although, several studies addressed leaching of NMC111 (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂), LCO (LiCoO₂), LMO (LiMnO₂), LNO (LiNiO₂) and LFP 56 57 (LiFePO₄), 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 acids such as lactic acid, citric acid, formic acid, and tartaric acid were tested in previous works 61 62 to leach cathodic materials (Ordoñez et al., 2016). Likewise, several studies addressed the use of hydrochloric acid in order to take advantage of its reactivity and the formation of metal 63 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

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

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

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

83
$$\% E_i = \frac{c_f(i) - c_0(i)}{c_f(i)} \times 100\%$$
 (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.

Table 3 shows a comparison of this result with the theoretical liquor composition.
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 DionexTM IonPacTM AS22.

92 **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 LiCoO₂, LiMn₂O₄ or LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ by using
hydrochloric acid. In the case of LiCoO₂, it is usually stated that the leaching mechanism
by HCl can be described by the following equation (Takacova et al., 2016):

97 $2LiCoO_{2,(s)} + 8HCl_{(l)} \rightleftharpoons 2LiCl_{(l)} + 2CoCl_{2,(l)} + 4H_2O_{(l)} + Cl_{2,(g)}$ (2)

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 form 25 °C to 82 °C.

Figure 3 shows the influence of the temperature on the dissolution of nickel, cobalt, 102 103 manganese and lithium from NMC811 as a function of time. The leaching kinetics of 104 the other NMC cathodic materials are reported in the Supporting Information (Figures S1-S16). The NMC materials were fully dissolved under these experimental conditions. 105 106 No significant difference in the dissolution kinetics was observed for nickel, manganese 107 and cobalt. Conversely, the dissolution kinetics of lithium from all cathodic materials 108 were much faster than those obtained for nickel, manganese and cobalt. Furthermore, it 109 was observed that the digestion of the cathodic materials containing high content of nickel 110 or low content of manganese was faster (NMC811 and NMC622). The comparison of the 111 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 >> 112 113 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). 114

115 3.1 Kinetic models

116 *3.1.1 Empirical model based on chloride consumption*

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

119 <u>Step 1:</u>

123

120
$$LiMO_{2,(s)} + \frac{4n-4}{2n-1}HCl_{(l)} \Rightarrow \frac{2n-2}{2n-1}LiCl_{(l)} + \frac{n-1}{2n-1}MCl_{2,(l)} + \frac{n}{2n-1}Li\frac{1}{n}MO_{2,(s)} + \frac{2n-2}{2n-1}H_2O_{(l)}$$

121 (3)

122 <u>Step 2: (rate limiting reaction)</u>

124
$$Li_{\frac{1}{n}}MO_{2,(s)} + 4HCl_{(l)} \rightleftharpoons \frac{1}{n}LiCl_{(l)} + MCl_{2,(l)} + 2H_2O_{(l)} + \left(1 - \frac{1}{2n}\right)Cl_{2,(g)}$$
 (4)

- 125 The overall equation can be written as:
- 126 $2LiMO_{2,(s)} + 8HCl_{(l)} \rightleftharpoons 2LiCl_{(l)} + 2MCl_{2,(l)} + 4H_2O_{(l)} + Cl_{2,(g)}$ (5)
- 127 where the first step results in the formation of an intermediate product $Li_{\frac{1}{2}}MO_{2,(s)}$ 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**).

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

138
$$[Cl^{-}]_{t} = ([Cl^{-}]_{\infty} - [Cl^{-}]_{0})[1 - exp(-at)] + [Cl^{-}]_{0}$$
(6)

where $[Cl^-]_0$, $[Cl^-]_t$, and $[Cl^-]_{\infty}$ denote the chloride concentration in the leach solution at the begining of the experiment, at time t and at infinite time, respectively. In this equation, the initial chloride concentration corresponds to the initial concentration of hydrochloric acid and the theoretical value of the chloride concentration at infinite time can be deduced by the following equation:

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

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

Figure 4 shows the variation of the chloride concentration as a function of time when NMC532 was leached in 4 mol L⁻¹ HCl at 82 °C and S/L= 20 g/L. There is a fair agreement 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
$$[Cl-]_{t,exp} = u [Cl-]_{t,calc}$$
 (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 R² of Eq. (8) are close to the unity (**Table 5**). The theoritical values of [Cl⁻] 159 $_{\infty}$ are in agreement with those calculated by Eq (7): [Cl⁻] $_{\infty}$ =3.7-3.9 mol L⁻¹ at S/L=20 g/L 160 and [Cl⁻] $_{\infty}$ =3.2-3.3 mol L⁻¹ at S/L=80 g/L, whereas the theoretical values are equal to 3.8

- 161 and 3.2 mol· L^{-1} , respectively (**Table 5**).
- 162 The following equations can be written by using Eqs (3)-(4) and Eq (6):

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

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

Eqs (9) and (10) were used to calulate the metal concentration as a function of the leaching time. For the sake of illustration, the comparison of the experimental data and the calculated values are displayed in Figure 5 for NMC532 digested in 4 mol L⁻¹ HCl at 82 °C. The other 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).

The leaching of NMC811 was tested in 4 mol L⁻¹ at 25 °C and three different S/L ratios, i.e. 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 g/L NMC811. Below this stochiometric limit, the leaching kinetics of Li, Co, Ni and Mn hardly depend on the S/L ratio (**Figure 6**).

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

Figure 8 confirms that Eqs (9) and (10) can be used to calculate the concentrations of cobalt,
nickel, manganese and lithium in the leachate at any S/L ratios for the four NMC cathodic
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
$$[Ni]' + [Mn]' + [Co]' = n[Li]' = \frac{[HCl]_0 - [HCl]}{4} = f(t')$$
 (11)

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

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

The transition time t_0 can be determined by using the approach below. According to Eq (3), the following mass-balance equations can be written for step 1 and step 2, respectively:

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

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

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

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

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

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

- Figure 9 illustrates the way to determine the transition concentrations for NMC111 leached in 4 mol L⁻¹ HCl at 54 °C. The intersection of the two straight lines corresponds to the concentrations of lithium ([Li]₀), and the sum of the concentrations of nickel, cobalt and 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 relatioship:

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

In this equation, $\left(\frac{1}{M_{NMC}L} - [Ni]_0 - [Mn]_0 - [Co]_0\right)$ is the theoretical maximum sum of the concentrations of Ni, Mn and Co when all the solid is dissolved, which is calculated by the total number of moles of Ni, Mn and Co from the solid subtracted by the dissolved part during the first step. The constants k₁ and f have been deduced by fitting the experimental data of metal dissolution vs. time with the following general equation used to describe NMC digestion, using solve of Excel:

227
$$[Ni]' + [Mn]' + [Co]' = \left(\frac{1}{M_{NMC}}\frac{s}{L} - [Ni]_0 - [Mn]_0 - [Co]_0\right) [1 - e^{(-k_1t'+f)}]$$
 (17b)

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

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

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

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

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

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

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

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

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

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

244
$$[HCl] = [HCl]_f + ([HCl]_0 - [HCl]_f)e^{-k_1t'}$$
 (23)

where [HCl] is the acid concentration at time t'=t-t₀ (time in the second step), [HCl]₀ is the acid concentration at the transition time t₀ 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
$$[Ni]' + [Mn]' + [Co]' = n[Li]' = (\frac{1}{M_{NMC}} \frac{S}{L} - [Ni]_0 - [Mn]_0 - [Co]_0)(1 - e^{-k_1 t'})$$
 (24)

Figure 10 shows that the first-order rate law can be used to describe the leaching kinetics of the second step given that a good agreement was obtained between the experimental data and the values calculated by using Eq (24) [the same accordance was obtained for all leaching tests

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 completly 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 its reaction rate constant $k_{R,i}$ in the case of chemical reaction control mechanism or its diffusion 269 rate constant $k_{D,i}$ in the case of film diffusion control mechanism. Therefore, one of the 270 271 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
$$1 - (1 - x_i)^{\frac{1}{3}} = \left(\frac{3\beta_{r,i}[HCl]}{\rho_B R_0}\right) = k_{R,i}t$$
 (25)

275 In the case of film diffusion control:

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

where x_i is the extraction fraction of the element i=Li, Ni, Mn or Co, and [HCl] represents the 277 278 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.

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

The Shrinking Core Model described by Eqs (25) and (26) can be applied to the second step by plotting [Li]', [Ni]', [Mn]' and [Co]' as a function of $t' = t - t_0$, as is done with first-order rate law in the previous sub-chapter. For the sake of illustration, Figure 14 shows the plot of the shrinking core model applied to the longest step during the NMC1111 dissolution in 4 mol L⁻¹ HCl at 54 °C, considering both reaction controls and diffusion controls.

The kinetic parameters deduced from Eqs (25) and (26) for the investigated NMC materials at different temperatures are reported in Tables S1-S4 (Supporting Information). The R^2 coefficient corresponding to reaction control is often higher than the R^2 coefficient found for diffusion control. It is therefore reasonable to conclude that the kinetics of the second step is 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 Arrhenius304 equation:

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

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 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 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 energy of I, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (in K).

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

- considering a film dissolution control). According to the literature, activation energies around
 20 kJ mol⁻¹ usually correspond to diffusion-controlled leaching whereas values higher than 40
 kJ mol⁻¹ can be attributed to chemical reaction-controlled leaching (Reid et al., 2017). Therefore,
 the values of the activation energies confirm the previous conclusion, i.e. the second step of
 NMC leaching is controlled by the chemical reaction.
- The following equation deduced by combining Eq (25) [shrinking core model, reaction controls] and Eq (27) [Arrhenius law] can be used to calculate the dissolution yield of each metal contained in NMC at any leaching time and any temperature during the second step:

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

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 J mol⁻¹) is the apparent activation energy of i =Li, Ni, Mn or Co. R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (in K) and t' is the leaching time of the second step in minutes.

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

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

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

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

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

Table 10 gathers the values of the leaching time necessary to reach the full dissolution of lithium, cobalt, nickel and manganese by considering shrinking core model and the first order law in the case of NMC811 dissolution. The duration to complete the full dissolution of NMC622, NMC532 and NMC111 are reported in Table S5-S7 in the Supporting Information. These Tables show a good agreement between the two models. It is possible to determine the residence time needed to reach the full dissolution of NMC by taking into consideration the maximum time of dissolution between the two models and by multiplying this value by 1.1 in order to take into account the first step, which usually represents less than 10% of the globalleaching time (see Table 9).

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

4. Conclusions

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

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

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- 479

TABLES

481 482 **Table 1**: Composition of the main cathodic materials in LIBs.

Abbreviation	Chemical formula
LCO	LiCoO ₂
LMO	LiMn ₂ O ₄
LNO	LiNiO ₂
LFP	LiFePO ₄
NMC111	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
NMC532	LiNi0.5Mn0.3Ni0.2O2
NMC622	LiNi _{0.6} Mn _{0.2} Co _{0.2} O ₂
NMC811	LiNi _{0.8} Mn _{0.1} Co _{0.1} O ₂

		Leaching med	lia	Experimental conditions				Reference
Cathode		Concentration		Temperature	Sol	id/Liquid	Time	
	Acid	(M)	Additive	(°C)	% solids	mass/volume (g/ml)	(h)	
NMC111	H_2SO_4	1		30	4% (w/w)			Billy et al., 2018
NMC111, LCO	H_2SO_4	2	10% H ₂ O ₂	70		1/30	1.5	Chen and Ho, 2018
NMCIII, LCO, LMO	HCl	4		80		1/50	1	Wang et al., 2009
Spent LIBs cathods	HC1	1.75		50	20% (w/v)		2	Barik et al., 2017
NMC532	$\mathrm{H}_2\mathrm{SO}_4$	2	3% (v/v) H ₂ O ₂	60		1/20	1	Liu et al., 2020
LCO, LMO, LNO, NMC	$\mathrm{H}_2\mathrm{SO}_4$	2.5	3.3% (v/v) H ₂ O ₂	90			2.5	Chu et al., 2020
NMC, LFP, LIBs cathodes	HCl	6	$H_2O_2/M^{2+}=$ 2 (mole)	60		1/8	2	Li et al., 2009
Spent LIBs cathodes	HC1	4		80		1/50	1	Dhiman et al., 2019
NMC, LiCoO2	H_2SO_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	$\mathrm{H}_2\mathrm{SO}_4$	2	4% (v/v) H ₂ O ₂	50		1/20	2	Sattar et al., 2019
Spent LIBs cathodes	$\mathrm{H}_2\mathrm{SO}_4$	1	0.075 M NaHSO ₃	95		1/50	4	Meshram et al., 2015
NMC cathode scrap	$\mathrm{H}_2\mathrm{SO}_4$	2.5	0.8 M NH4Cl	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

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

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

Composition % (w/w) NMC Ni Со Li Mn 0 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 36.1 7.16 622 36.3 11.8 12.2 7.33 11.0 11.3 33.7 33.0 532 30.1 12.2 7.27 7.19 17.1 34.1 30.4 11.9 16.6 33.1 19.7 111 20.3 19.2 20.4 7.24 7.20 18.3 19.0 35.5 33.2

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

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)	$[Cl^{-}]_{0} (mol \cdot L^{-1})$	$[Cl^{-}]_{\infty} (mol \cdot L^{-1})$	u	\mathbb{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 R^2 deduced from Eq (7) give information about the quality of the fit.

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

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

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

	Activation Energy (kJ/mol)										
	First-order Rate Law		Shrinking Core Model				Sh	Shrinking Core Model			
NIVIC			Reaction Controls			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	

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

502 that leaching occurs via chemical reaction control, deduced from	Eq	(2'	7)	
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			In(A _i)					
NMC	First-	order Rate Law	Shrinking Core Model Chemical Controls					
	Li	Ni / Mn / Co	Li	Ni	Mn	Со		
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		

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

NMC	Temperature (°C)	t₀ (min)	Total t (min)	to/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

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

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

	Leaching time (min) NMC811							
		Reaction	controls		First order rate law			
(0)	Li	Ni	Mn	Со	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 12 NMC811 in 4 mol L = 1 HCl (Solid even liquid above ratio S/I = 20 eV)

513 NMC811 in 4 mol L⁻¹ HCl (Solid over liquid phase ratio S/L=20 g/L).

FIGURES



- 516 Figure 1: Particle size distribution of NMC811.



- 519 Figure 2: Setup for leaching experiments.



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



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)**].





Figure 5: Li concentration and sum of the concentrations of Ni, Mn and Co in the leachate at









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





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)].



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

551



552

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
- after 5 minutes of leaching in 4 mol L⁻¹ HCl at S/L=2 g/L and 25 °C.





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



Figure 14: Application of the shrinking core model to the second step of NMC 111 dissolution
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 at temperature range between 54 and 82°C according to Eq (27).



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

571 (**30**).