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1 **Role of transport in the first atomic layers of the nanoparticles in lithium batteries**

2
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4
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11 12 13 14 **Abstract**

15
16 A theoretical approach of the insertion/deinsertion of lithium in host materials is proposed to
17 take into account some phenomena not included in classical analyses of lithium battery
18 operation. This is mainly related to the variation of the transport properties in the first atomic
19 layers in the vicinity of the interface which can give rise to rapid storage phenomena. These
20 processes are of great importance in the case of electrodes made of nanoparticles as a result of
21 the considerable development of the interfacial surface. For example, they can be at the origin
22 of the important capacitive behavior of the system. A model based on the numerical integration
23 of transport equations is presented to describe these complex mechanisms. The theoretical
24 analysis is illustrated on the model case of lithium insertion in electrodes made of nanoparticles
25 of anatase and fluorinated anatase.

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Introduction

The pressing need for transportable electrical energy sources has given rise to a great deal of work in recent decades. Among these, lithium-based batteries occupy a prominent place due to the electrochemical properties of this element joined to its low density. This sector has benefited from intensive research which has improved performance¹⁻³. A large part of the research was devoted to the development of electrode materials which exhibit a suitable free energy of formation and thus a high open circuit voltage for a high performance battery. In order to improve the battery power, they also should allow a rapid transport of lithium atoms. A device commonly used to fulfill these criteria is based on the lithium insertion in a host material, generally a metal oxide such as V_2O_5 , Nb_2O_5 , $LiCoO_2$, TiO_2 , etc⁴.

However, a weakness of the system comes from the very slow transport of lithium atoms in the crystal lattice of the host material. An effective way to overcome this difficulty is to reduce the size of host particles which reduces the diffusion length and promotes faster transport⁵. Hence the idea of using particles of reactive material at a nanometric dimension, which considerably increases the contact surface and facilitates the lithium storage; an issue of nanoparticles is accelerated side reactions. The study of these systems has given rise to a large number of research work which focus on the nature of the host material, its preparation and the properties of lithium intercalation. Various systems have been developed which are essentially characterized by the nature of the host material in order to obtain the best lithium intercalation qualities. This work has led to a lot of research to get a more accurate view of the reaction mechanisms. Here is a brief overview of the main work in this area.

The insertion of Li-ions within cathode materials during the discharging of a battery oftentimes brings about one or more structural transformations⁶. A theoretical investigation of the effects of elastic coherency strain on the thermodynamics, kinetics, and morphology of intercalation in single $LiFePO_4$ nanoparticles yields new insights into this important battery material⁷. The kinetics of a two-phase electrochemical reaction in Li_xFePO_4 indicates that the phase transition proceeds with a one-dimensional phase-boundary movement⁸. The core-shell, the

69 compositional striping modulations and the resulting strain gradients point to the need to design
70 cathode materials and electrode architectures to mitigate such pronounced local
71 inhomogeneities in Li-ion intercalation and diffusion⁹.

72

73 The different specific constraints of the batteries have given rise to many analytical descriptions
74 of transport phenomena from conventional models. For example, concentration dependent
75 diffusion coefficients are found to be necessary to match experimental results¹⁰. On the other
76 hand, in a finer way, it was suggested to represent the phase transitions as moving boundary
77 points where jump discontinuities in concentration occur; the question of when it is necessary
78 to include these effects in a transport model is difficult to resolve, because the measured values
79 of the open-circuit voltage for real materials are never completely flat and always exhibit a
80 small dependence on state of charge; it was shown that the jump discontinuities arise as a
81 singular limit of a nonlinear diffusion equation when chemical potentials are used as the driving
82 force for transport¹¹. It was also pointed out that variations in the chemical diffusivities over a
83 significant range of lithiation are shown to be explained by the inclusion of both the
84 thermodynamic factor and the flux of lithium due to bulk motion of material^{12, 13}.

85

86 In addition to the influence of the thermodynamic properties and of the structural changes of
87 the materials described above, it is important to pay our attention to an essential characteristic
88 of the batteries, namely the nanometric dimension of the active particles. As already pointed
89 out, the use of nanoparticles has the advantage of significantly increasing the electroactive
90 surface. The increase in surface area is generally taken into account by the introduction of a
91 roughness factor in the calculation elements^{14, 15}. But this correction does not take into account
92 the specific nature of the transport in the very first atomic layers of the surface thus introduced.
93 Indeed, another consequence of the use of nanoparticles is to considerably shorten the path of
94 lithium transport, which is now reduced to distances of the order of atomic dimensions.
95 Attention should be drawn to the fact that much of the transport is no longer carried out in the
96 compact layers but remains confined to the first atomic layers of the substrate. In the superficial
97 region the transport properties are greatly affected by the loosening of the surface structure of
98 the material. This phenomenon is generally negligible for large conventional systems but
99 becomes predominant when transport does not exceed a few atomic layers.

100

101 The purpose of this paper is to analyze and highlight the important role of transport phenomena
102 in the surface layers of the substrate material: given the nanometric nature of the particles, the

103 influence of transport kinetics in these few superficial atomic layers becomes significant. To
104 tackle in a more structural way the origin of these phenomena it seems interesting to take
105 inspiration from already developed models dealing with the analysis of the transport kinetics in
106 the first atomic layers of the host material¹⁶.

107
108 After a brief description of the materials and of the experimental setup, we will describe the
109 elementary principles involved in the reaction mechanisms. Particular emphasis will be placed
110 on deviations from ideality, on the variation of transport properties in the surface layers, and on
111 the formation of storage layers at the interface; then, to interpret the modifications thus
112 introduced we will briefly recall the principle of the integration of basic equations by the finite
113 difference method^{17, 18}. Finally, the investigations will be illustrated on the model case of
114 lithium insertion in anatase or fluorinated anatase crystallites.

115

116 **Experimental**

117

118 *Synthesis.* The experimental study examined nanoparticles of anatase and fluorinated anatase;
119 in fact, the action of a fluorinated agent improves the storage properties of the battery. The
120 materials were synthesized using the sol-gel chemistry without and with a fluorinating agent,
121 as described in a previous report¹⁹. The degree of fluorination may vary depending on the
122 procedure employed; we used a compound with 22 % cationic vacancies, corresponding to
123 $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$, where \square represents a cationic vacancy. For more details
124 concerning this formulation see ref. (19).

125

126 *Electrochemistry.* Electrochemical measurements were carried out with three-electrode
127 Swagelok-type cells. The working electrode was prepared with 80 wt.% active materials, 10
128 wt.% Super P and 10 wt.% polyvinylidene difluoride (PVDF), and lithium metal was used as
129 counter and reference electrodes. 1M LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate
130 (DMC) (1:1, v/v) was used as the electrolyte. The electrode is made of a thin layer of a mixture
131 of anatase (2.5 mg/cm^2) and carbon (0.32 mg/cm^2) nanocrystals with PVDF (0.32 mg/cm^2). The
132 theoretical capacity of the material is 3.02 C/cm^2 . Cyclic voltammetry was performed at
133 different scan rates within a potential range of 1.0-3.0 V vs Li^+/Li . Galvanostatic intermittent
134 titrations were carried out after one galvanostatic discharge/charge cycle, a constant-current
135 discharge pulse of $84 \mu\text{A cm}^{-2}$ was applied for 20 minutes, followed by a relaxation duration of
136 20 h; the current pulse corresponds to a capacity fraction of 1/30.

137

138 **Results and discussion**

139

140 **Transport equations.** A specific advantage of electrochemical techniques is to provide an easy
141 measurement of the reaction flux, J , at the electrode surface and of the concentration, c , of the
142 active species during the electrochemical process. The flux at the electrode surface is given by
143 the current density, i

$$144 \quad J^{\circ} = -\frac{i}{nF} \quad (1)$$

145 For an ideal and reversible reaction, $Ox + ne^{-} \rightarrow Red$ (such as, $Li^{+} + e^{-} \rightarrow Li$), the concentration,
146 c , of the *Red* species is deduced from the electrode potential from the Nernst law, the
147 concentration of *Ox* species is assumed to be constant,

$$148 \quad c = \exp\left(\frac{nF}{RT} (E^{\circ} - E)\right) \quad (2)$$

149 where, $E^{\circ} = RT/nF \times \ln c^{\circ}$; E is the electrode potential vs the pure *Red* species, c° is the
150 concentration of pure *Red*.

151 However, most systems exhibit large deviations from ideality; the Nernst equation gives access
152 to the activity, a , of the electroactive species which is linked to the concentration by a factor f
153 called the activity coefficient f :

$$154 \quad a = fc = \exp\left(\frac{nF}{RT} (E^{\circ} - E)\right) \quad (3)$$

155 The activity coefficient demarcates the equilibrium (thermodynamic) response under
156 concentrated conditions. The intercalation electrodes represent very high concentrations (of the
157 order of 50 M) that the activity coefficient becomes a strong function of concentration. Various
158 theoretically consistent treatments were used to recover activity coefficient from the open
159 circuit potential (OCP) curves²⁰. Here we refer to a previous work dealing with the system Li-
160 V_2O_5 which exhibits various phase transformations²¹. It was shown²² that the large changes in
161 the activity factor vs the concentration were correctly described by the series:

$$162 \quad \ln f = \sum_{j=1}^n 0.5(\ln f_j - \ln f_{j-1}) \operatorname{erfc}\{\psi_j (c - c_{Tj})\} \quad (4)$$

163 $\ln f_j$ is the activity factor corresponding to the plateaus of the potential curves; since the reference
164 is the pure compound, $\ln f_0 = 0$; the complementary error function, erfc , was used to describe
165 the change from one factor to the next, c_{Tj} is the concentration at the inflexion points of the

166 potential curve. ψ_i is the steepness of the change of the activity factor around the concentration
 167 c_{Tj} . The various parameters $\ln f_i$ and ψ_i were adjusted to obtain a suitable representation of the
 168 OCP curves. The driving force for diffusion is the gradient of the chemical potential $\mu = \mu^\circ +$
 169 $RT \ln fc$; the flux, J , of the electroactive species inside the electrode matrix writes:

$$170 \quad J = -\tilde{D} \left(1 + c \frac{\partial \ln f}{\partial c} \right) \frac{\partial c}{\partial x} \quad (5)$$

171 where \tilde{D} is the component diffusion of the active species, it is related to the chemical diffusion
 172 coefficient, D , by the equation^{23, 24}

$$173 \quad D = \tilde{D} \left(1 + \frac{\partial \ln f}{\partial \ln c} \right) \quad (6)$$

174 As pointed out by Levi et al.²⁵ this expression may be modified according to the thermodynamic
 175 model; to examine the influence of the gradient of the activity coefficient a damping factor, φ ,
 176 is introduced in the calculation

$$177 \quad D = \tilde{D} \left(1 + \varphi \frac{\partial \ln f}{\partial \ln c} \right) \quad (7)$$

178 The term Γ is called enhancement factor

$$179 \quad \Gamma = 1 + \varphi \frac{\partial \ln f}{\partial \ln c} \quad (8)$$

180 In a non-stationary state the concentration changes obey the mass balance equation

$$181 \quad \frac{\partial c}{\partial t} = -\nabla J = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (9)$$

182 The integration of transport equations has been solved for different boundary conditions
 183 corresponding to galvanostatic or potentiostatic regimes. For a constant value of D algebraic
 184 equations are available in literature to interpret the results obtained from transient electro-
 185 chemical techniques²⁶.

186

187 However, in nanoparticles the transport occurs over a few atomic layers and the specificity of
 188 the motion in this region must be taken into account. Indeed, in the interfacial domain, the
 189 looseness of the crystal lattice enlarges the mass transport facilities. In other words it is possible
 190 to consider that over these short distances interfacial energy affects the dynamic response. Thus,
 191 as a first approximation, it can be considered that the intercalation of ions in the very first atomic
 192 layers is extremely rapid and corresponds to an accumulation process occurring instantaneously
 193 over a distance δ . This analysis is in good agreement with the concept of relevant surface

194 activity thickness (RSAT) introduced by Verbrugge and Tobias²⁷ to calculate by electro-
195 chemical techniques the surface activity of metallic alloys.

196

197 From a dynamic point of view, this approach amounts to considering that, in this film of
198 thickness δ , the coefficient of diffusion D has an infinite value. Of course, within the material,
199 the diffusion coefficient has a constant finite value which is usually the only one taken into
200 consideration; indeed, generally the diffusion phenomena last long enough and affect the deep
201 mass of the material; the amount of material involved in the surface film becomes negligible.
202 To refine our model it was considered that in the few atomic layers in the vicinity of the storage
203 layer, of thickness δ , the diffusion coefficient evolves to reach the classical value of the
204 coefficient in the mass of the material. Here, as in our previous articles^{16,28}, it was assumed that
205 D obeys the equation

$$206 \quad D = D^* \exp(\delta'/x) \quad (10)$$

207 where D^* is the bulk diffusion coefficient and δ' is a characteristic distance called relevant
208 rapid diffusion thickness (RRDT). A diagram is proposed to illustrate the evolution of transport
209 in the surface layers (Fig. 1).

210

211 The current density is linked to the flux at the electrode surface J^o (Eq. 1). Now, the
212 accumulation process at the interface has to be taken into account

$$213 \quad J^o = \delta \frac{\partial c_0}{\partial t} - D \left(\frac{\partial c}{\partial x} \right)_{x=\delta} \quad (11)$$

214 c_0 is the concentration in the surface layer of thickness δ . The introduction of metal ions in the
215 matrix of the crystal creates a volume change of the electrode deduced from the partial molar
216 volume of the electroactive component \bar{V}_M . It results that during the electrolysis the interface
217 moves with a velocity v

$$218 \quad v = J \bar{V}_M \quad (12)$$

219 The quantity \bar{V}_M takes account of the constraints introduced by the insertion of the active
220 element M into the substrate. In general \bar{V}_M is clearly lower than the molar volume V_M ; under
221 the action of strong stresses, \bar{V}_M can even become negative.

222

223 The displacement of the interface is introduced in the diffusion equation which becomes

224 $J = -D \frac{\partial c}{\partial x} + v c$ (13)

225 D depends on the distance, x , (Eq. 10) and, according to Eq. 9, the concentration change obeys
 226 the equation

227 $\frac{\partial c}{\partial t} = -\nabla J = D \frac{\partial^2 c}{\partial x^2} - D^* \frac{\delta'}{x^2} \exp\left(\frac{\delta'}{x}\right) \frac{\partial c}{\partial x} - v \frac{\partial c}{\partial x}$ (14)

228 However, in contrast with the classical treatment, it is no more possible to integrate the
 229 complete diffusion equation into an algebraic form. It is proposed to solve the problem by
 230 numerical integration of the diffusion equation according to a procedure already developed to
 231 study the electrowinning of refractory metals²⁸. The technique requires an analytical
 232 representation of the thermodynamic and kinetic properties of the system.

233

234 **Integration of the diffusion equations.** The digital simulation technique used to calculate the
 235 transient curve consists in solving the partial differential equation by numerical calculation¹⁷.
 236 A numerical model is set up within a digital computer and the model is allowed to evolve by a
 237 set of algebraic laws deriving from equations defining the mass transport. The space (x
 238 coordinate) is divided in small intervals, Δx , and the time into small time steps, Δt . The
 239 concentration of the electroactive reagent at the electrode surface, at the time t , is given by the
 240 Nernst equation, and the current density is related to the concentration gradient at the electrode
 241 surface

242 $J^o = \delta \frac{c(0,t) - c(0,t - \Delta t)}{\Delta t} - D \frac{c(0,t) - c(\Delta x,t)}{\Delta x} + v c(0,t)$ (15)

243 $c(\Delta x,t)$ is the concentration at the time t at the distance Δx from the electrode surface. D obeys
 244 Eq. 10. Concentrations as a function of time and concentration profiles in the bulk of the
 245 substrate were calculated from the diffusion equation (Eq. 14). In finite difference scheme the
 246 continuous functions are finitized with centered finite scheme for space derivative:

247 $\frac{\partial c}{\partial x} = \frac{c(x+\Delta x,t) - c(x-\Delta x,t)}{2\Delta x}$ (16)

248 $\frac{\partial^2 c}{\partial x^2} = \frac{c(x+\Delta x,t) - 2c(x,t) + c(x-\Delta x,t)}{(\Delta x)^2}$ (17)

249 It must be pointed out that the stability conditions of the finite difference calculation require
 250 that the space interval Δx be greater than the diffusion path during the time step: $\Delta x > \sqrt{2D \Delta t}$;
 251 but, on the other hand, to correctly integrate the evolution of the diffusion coefficient (Eq. 10),
 252 it is necessary that the space interval, Δx , be less than the length RRDT, $\delta' > \Delta x$. For large time

253 intervals, such as in voltammetry at low sweep rate, these conditions may be difficult to meet.
254 More details concerning the calculation procedure can be found in previous papers^{17, 21}.

255

256 **Application to lithium insertion in anatase nanocrystals**

257

258 *Electrode structure* – Anatase TiO₂ has been extensively studied over the past decade due to its
259 application as electrode material for Li batteries^{29, 30}. In a simplifying assumption and in
260 agreement with the known structure of the nanoparticles, the electrode material will be
261 considered as a collection of nano-platelets of parallelepiped shape³¹ (Fig. 2) in contact with
262 the electrolyte and with the carbon powder which provides the electric contact. For an electrode
263 containing m gram of active compounds per unit surface the number of particles is

$$264 \quad n_p = m/(\rho \times a \times a \times b) \quad (18)$$

265 where ρ is the specific mass of the compound. It is assumed that the lithium diffusion occurs
266 only in one direction perpendicular to the surface $a \times a$.³¹ The real active surface for the
267 electrochemical reaction is

$$268 \quad S_p = n_p \times a \times a \quad (19)$$

269 The electrochemical reaction occurring in the battery is described by the reaction



271 where y is the lithium intercalation ratio. Upon lithiation to Li_{0.5}TiO₂, anatase is observed to
272 undergo a tetragonal to orthorhombic phase transition³². The thermodynamically stable ordered
273 phase at $y = 0.5$ can accommodate excess Li in vacant sites up to $y = 0.6$ ³³; in agreement with
274 the model developed above, it was shown that the diffusion in this phase is strictly one
275 dimensional³¹. In order to improve the storage capacity of the electrode, fluorinated anatase
276 crystals were also investigated. The samples used in the present description correspond to the
277 fluorinated anatase, Ti_{0.78}□_{0.22}O_{1.12}F_{0.40}(OH)_{0.48}, as described in previous papers^{19, 34}.

278

279 An estimate of the particle sizes is deduced from microscopic investigation showing that the
280 anatase grains have a dimension of the order of ten nanometers^{19, 35}. In our study, as a first
281 approximation, they will be assimilated to parallelepipeds according to the representation of
282 Fig.2, with, for dimension: $a = 3$ nm and $b = 12$ nm.

283

284 According to the synthesis of the electrodes, the cathodic layer has a thickness of 10 μm . In this
285 layer the weight of anatase or fluorinated anatase unit is 2.5 mg/cm^2 ; the number of particles,
286 n_p , and their active electrochemical area, S_p , deduced from Eqs 18, 19 are reported in Table 1.

287

288 *Electrochemical analysis* – The electrode potential, E (vs pure lithium metal), corresponding
289 to the electrochemical reaction (Eq. 20) is given by the Nernst's equation

$$290 \quad E = E^\circ - \frac{RT}{F} \ln f_{Li} c_{Li} \quad (21)$$

291 with

$$292 \quad E^\circ = \frac{RT}{F} \ln c_{Li}^o \quad (22)$$

293 c_{Li}^o is the concentration of pure lithium metal. The index y (Eq. 20) and c_{Li} are linked through
294 the equation

$$295 \quad c_{Li} = y/V_{Li_yTiO_2} \quad (23)$$

296 $V_{Li_yTiO_2}$ is the molar volume of the compound

$$297 \quad V_{Li_yTiO_2} = V_{TiO_2} + y\bar{V}_{Li} \quad (24)$$

298 \bar{V}_{Li} is the partial molar volume of lithium. The above relation assumes that \bar{V}_{Li} remains constant
299 in the concentration range studied; however, the imprecision eventually introduced is very
300 small; indeed, as indicated above, \bar{V}_{Li} is much smaller than the molar volume of lithium ($\bar{V}_{Li} \approx$
301 $0.1 V_{Li}$). As a result, the variations in volume of the substrate during the insertion of lithium are
302 always small.

303

304 The value of the activity coefficient, f_{Li} , is deduced from the Eq. 4; the parameters, f_j and ψ_j , the
305 index j varying from 1 to 4, are adjusted in order to obtain a good fit between the calculated
306 curve and experimental OCP curve (Fig. 3). The goodness-of fit values of the parameters
307 involved in the calculation are shown in Table 2.

308

309 *Analysis by cyclic voltammetry, pseudo-capacitive contribution* – The cyclic voltammograms
310 on anatase, or fluorinated anatase $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.4}\text{OH}_{0.45}$ particles are reported in Figs 4-5.

311 To analyze the voltammograms it was assumed that the electrochemical response depends of
312 two components³⁶: the faradaic current, i_F , coming from the lithium insertion process and from

313 the charge-transfer process with surface atoms (pseudo-capacity), and the non-faradaic current,
314 i_C , arising from double layer capacitance, which corresponds, in our field of study, to a very
315 small current³⁷; it can be neglected³⁶. In the literature it is generally accepted that the faradaic
316 contribution is the sum of two terms^{36, 38}:

$$317 \quad i_F = k_1 v^{1/2} + k_2 v \quad (25)$$

318 where v is the scan rate; k_1 and k_2 are two constants, the first term arises from the diffusion
319 controlled insertion, and the second one from the pseudo-capacitive effect.

320

321 It is now proposed to interpret the cyclic voltammetry response in a more precise way by taking
322 into account the characteristic features of atomic-scale transport.

323

324 *Surface transport and capacitive effect* – The pseudo-capacitive behavior arises from the
325 transport properties in the first atomic layers and from the fast storage of the active material at
326 the surface of nanoparticles. These effects come from the properties of the interface at atomic
327 scale which result in a variation of the diffusion velocity (Eq. 10) and in the existence of an
328 instantaneously charged layer of thickness δ (RSAT).

329

330 The finite differences technique is used to calculate the current response during a cyclic
331 potential scan rate corresponding to lithium insertion (Figs 4-5). The morphological change of
332 the crystal lattice due to the lithium insertion induces a change of the thicknesses δ and δ' . It is
333 assumed that these values reach a maximum for $c = c_p$; for anatase: $c_p = 15.9 \times 10^{-3} \text{ mol/cm}^3$, for
334 fluorinated anatase: $c_p = 12.3 \times 10^{-3} \text{ mol/cm}^3$. The corresponding intercalation ratios (Eq. 20)
335 are respectively: $y = 0.34$ and $y = 0.26$. To make it easier to implement the calculation, it was
336 assumed that δ and δ' obey the equations

$$337 \quad \delta = \delta_{max} \exp - \frac{(c - c_p)^2}{3c_p^2} \quad (26)$$

338 and

$$339 \quad \delta' = 0.25 * \delta \quad (27)$$

340 The two above empirical relations, and the values of D^* and δ_{max} are adjusted in order to obtain
341 the best fit with the experimental curves (Table 3). It should be noted that the δ_{max} values are of
342 the same order of magnitude as those obtained during the electrochemical preparation of metal
343 alloys^{28, 39} (a few nanometers).

344

345 The storage process can be interpreted in terms of pseudo capacitance, C . The charge density
346 q , stored in the RSAT layer is

$$347 \quad q = F \delta S_p c(0) \quad (28)$$

348 $c(0)$ is the concentration at the electrode surface at a potential, E . The value of the capacitance,
349 C , is deduced from the classical formula, $C = dq/dE$. The charge increment, dq , induced by a
350 potential increment, dE , can be deduced from concentration change, $dc(0)$, calculated from the
351 Nernst equation (Eq. 3); then

$$352 \quad C = dq/dE = F \delta S_p dc(0)/dE \quad (29)$$

353 In Table 3 are reported the maximum values C_{max} of the capacitance, which occurs when $\delta =$
354 δ_{max} , so, according to Eq. 26, when $c = c_p$. The values of the so-called capacitance may seem to
355 be enormous. However, they are in good agreement with the experimental observations. For
356 example, in the fluorinated anatase at a scan rate of 10 mV/s, almost all the current has a
357 capacitive origin (Fig. 6); thus, to obtain a current density, i_c , of the order of 10 mA/cm² with a
358 scan rate, v , of 10 mV/s, a capacitive constant, C , of the order of one Farad is required (reminder
359 of the formula: $i_c = C \times v$).

360

361 Due to the large increase in the electroactive surface it has sometimes been suggested that the
362 double-layer capacity could account for the large values obtained. This suggestion is hardly
363 conceivable: for usual solvents, the order of magnitude of the double-layer capacity⁴⁰ is at most
364 around 18 $\mu\text{F}/\text{cm}^2$, which corresponds, even for an area of around 550 cm^2 , to a capacity of 10
365 mF, a value much lower than those obtained experimentally (Table 3). For that matter, a large
366 part of this paper has been written in an attempt to analyze this phenomenon. The importance
367 of the so-called capacitive response is also underlined by the work of Wang et al.³⁶ which show
368 that, even at low scan rates (0.5 mV/s), the capacitive response is not negligible.

369

370 This model also makes it possible to link the variations of the so-called capacity to the size of
371 the particles. Indeed, the capacitive effect depends directly on the contact surface, S_p , which is
372 inversely proportional to the particle size as can be deduced from Eqs 18, 19. This suggests that
373 the capacitive effect will also be inversely proportional to the particle size. This dependence is
374 well observed experimentally³⁶. At lower sweep rates the influence of the capacitive current
375 decreases, concentration profiles indicate a deeper penetration of lithium atoms into the bulk of

376 the electro material, the electrochemical response is getting closer to the classical laws of
377 diffusion.

378
379 *Diffusion and thermodynamics* – In order to obtain a more accurate determination of the
380 diffusion into the bulk of anatase particles dependence a galvanostatic intermittent titration
381 technique is used. The procedure consists of a series of current pulses, each followed by a
382 relaxation time, in which no current passes through the cell. The digital simulation technique is
383 used to calculate the electrode response from the model presented above. As deduced from the
384 cyclic voltammetry investigations the surface storage capacity is taken into account and the
385 bulk diffusion coefficient is adjusted to obtain the best fit with the experimental results. As
386 shown in Fig. 7, the fitted curves correctly represent the experimental curves. The values of the
387 diffusion coefficients are shown in Fig. 8.

388
389 It should be noted that wide fluctuations in the diffusion coefficient are obtained as a function
390 of the degree of lithium insertion. These variations reflect the change in structure of the anatase
391 crystals; they can result in a change in the thermodynamic properties of the system that is
392 reflected in the evolution of the enhancement factor (Eq. 7). The curves of Fig. 8 show that
393 there is some correlation between the evolution of this factor and that of diffusion coefficients.
394 This approach makes it possible to envisage a reasoned study linking the structural,
395 thermodynamic and kinetic properties of the system. The anatase OCP curve (Fig. 3) exhibits
396 two potential plateaus at $E_1 = 1.808$ V, and $E_2 = 1.605$ V, which correspond respectively to the
397 compounds TiO_2Li_y , with $y_1 = 0.302$ and $y_2 = 0.635$. The Gibbs energies of lithium insertion in
398 the compounds are $\Delta G_1 = -52.7$ kJ and $\Delta G_2 = -98.4$ kJ. The formation of these compounds leads
399 to a large departure from ideality during the insertion of lithium. This results in significant
400 variations in the activity coefficient, f , which according to Eq. 5, influences the diffusional
401 behavior of lithium.

402

403 **Conclusion**

404

405 The analysis of lithium insertion, in a host material made of nanoparticles shows that special
406 attention needs to be given to the study of transport phenomena in the first atomic layers of the
407 interface. In this region the looseness of the crystal lattice enlarges the mass transport facilities.
408 It results in additional effects not included in the classical analyses. To describe the system
409 behavior it is required to introduce the characteristics of surface transport in the diffusion

410 equation which can be solved by numerical calculation. This model takes into account the actual
411 contact surface and includes the concept of storage layer correlated with the increase of the
412 diffusion coefficient in the vicinity of the interface. In addition, the variations of transport
413 kinetics are related to the thermodynamic properties of the medium.

414
415 This work highlights the primary and complex role of atomic-scale transport phenomena in the
416 surface layers of electrode materials. The analysis thus developed can be a useful tool for
417 directing research towards structure with rapid charge kinetics and thus increase the available
418 power. This is how the idea of fluorination of anatase came about: this treatment improves
419 diffusivity, surface storage and pseudo-capacitance (Table 3). In addition, the study focuses
420 directly on the capacitive properties of the electrode; it can thus be useful for the research,
421 development and processing of materials for super-capacitors

422
423 The significant effect of transport in the first atomic layers of the substrate is highlighted. To
424 facilitate the implementation of the model, simplifying assumptions were arbitrarily introduced:
425 shape of particles, variation of the thickness of the storage layers (Eqs 26, 27); in addition, the
426 finite difference treatment could be refined. Nevertheless, this study can be adapted and may
427 provide a useful basis for more accurate analysis of the electrochemistry of nanoparticle
428 systems. In the present work we have endeavored to develop a method of analysis of these
429 mechanisms. The theoretical procedure is illustrated on the model case of lithium insertion in
430 anatase nanoparticles studied by cyclic voltammetry or by galvanostatic titration; in particular,
431 it accounts for the high values of the observed capacitive effects. Moreover, it can be easily
432 extended to the analysis of charge-discharge processes under various experimental conditions.

433

434

435 **Acknowledgement**

436

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442 **References**

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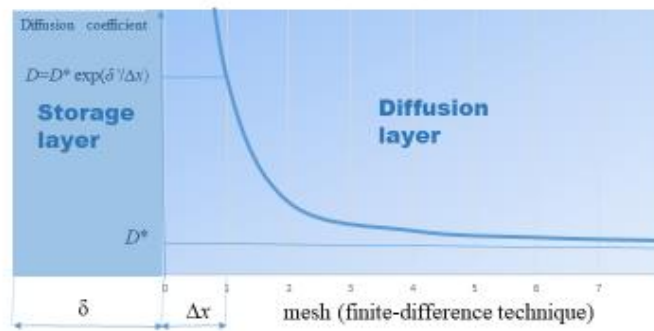
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525 **Figures**

526



527

528 **Figure 1.** Diagram illustrating the transport in surface layers.

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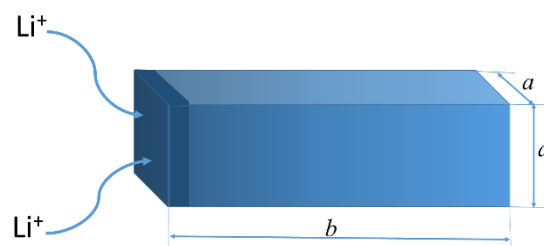
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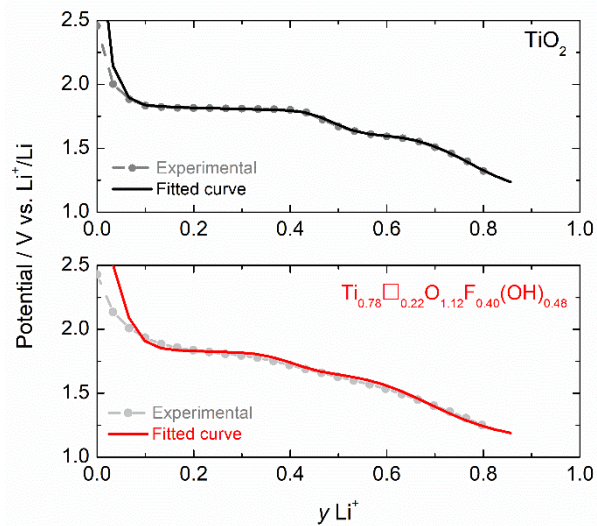
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536 **Figure 2.** Platelet-like nano-particle³¹, simplified form used for the calculation.

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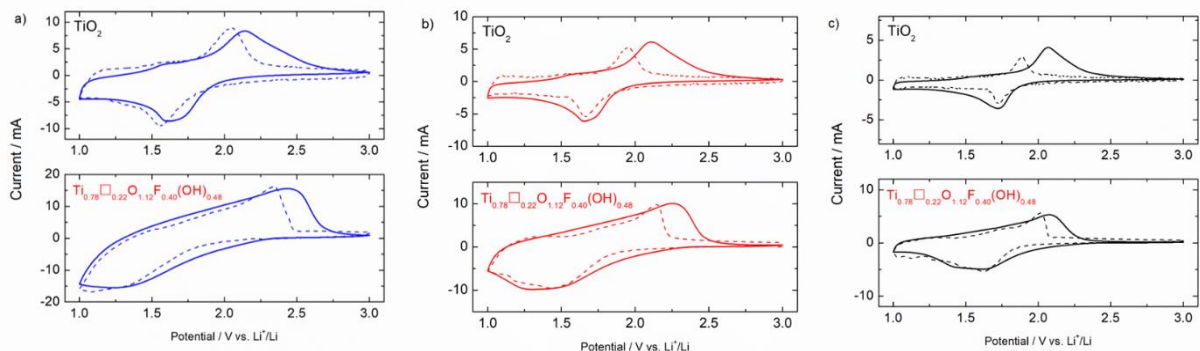
539 **Figure 3.** Open circuit potential curve, anatase and fluorinated anatase ($y\text{Li}^+$ is the intercalation
540 ratio).

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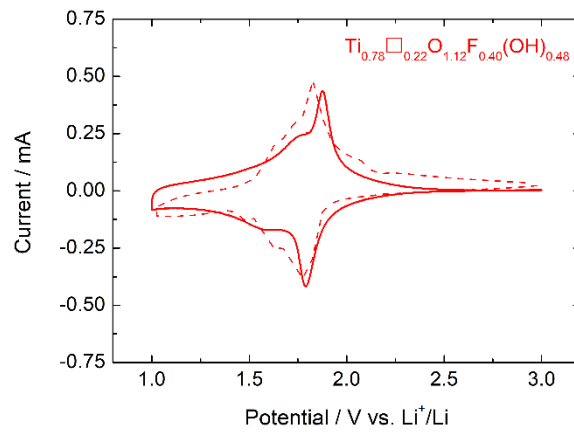
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546 **Figure 4.** Experimental (continuous line) and fitted (dashed line) cyclic voltammograms of
547 lithium insertion/deinsertion in anatase and fluorinated anatase; electrode surface: 0.78 cm^2 .

548 Sweep rates: (a) $v=10 \text{ mV s}^{-1}$, (b) $v=5 \text{ mV s}^{-1}$, (c) $v=2 \text{ mV s}^{-1}$.

549

550



551

552 **Figure 5.** Experimental (continuous line, after 2 cycles activation) and fitted (dashed line)
 553 cyclic voltammograms of lithium insertion/deinsertion in fluorinated anatase; electrode surface:
 554 0.78 cm^2 ; scan rate: $v=0.05 \text{ mV s}^{-1}$.

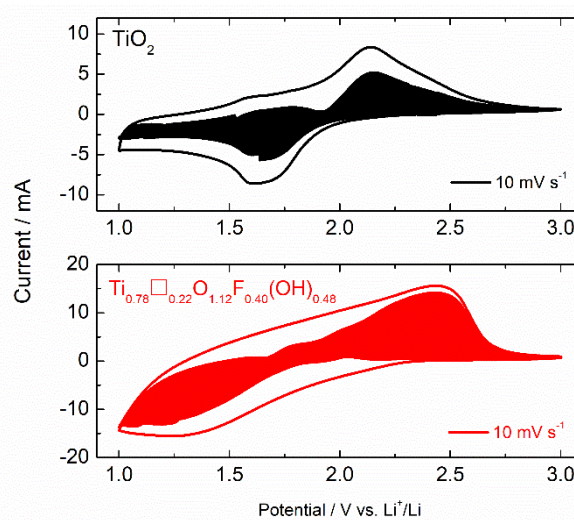
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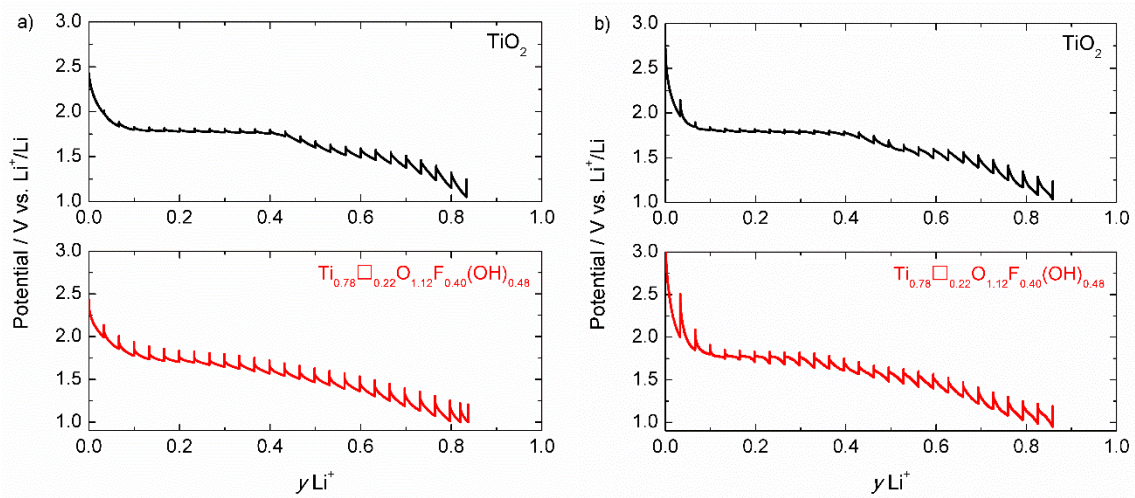
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561 **Figure 6.** Cyclic voltammograms of lithium insertion/deinsertion in anatase and fluorinated
 562 anatase; electrode surface: 0.78 cm^2 ; shaded region, capacitive current determined from the
 563 procedure using Eq. 25 at $v=10 \text{ mV s}^{-1}$.

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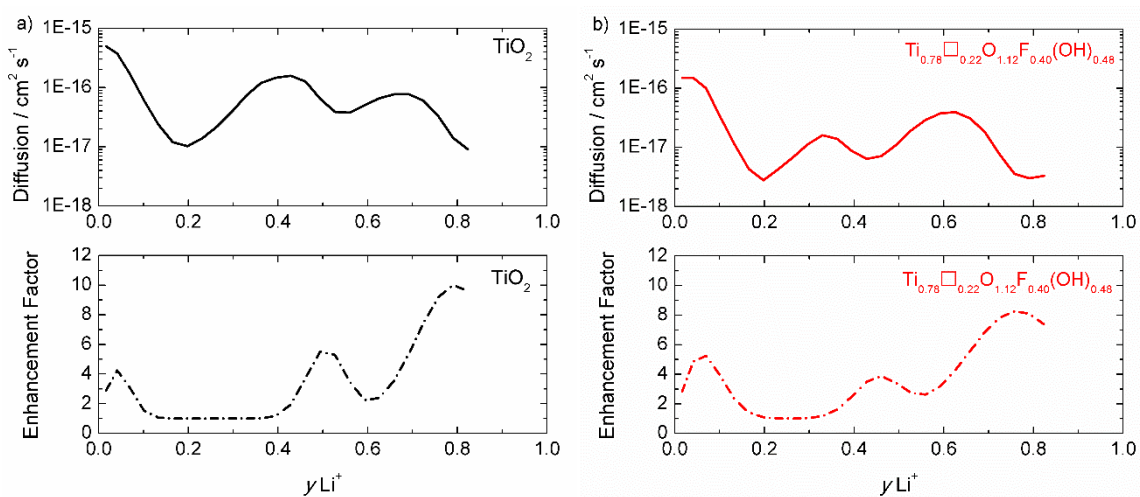
568 **Figure 7.** Galvanostatic intermittent titration. (a) Experimental and (b) fitted curves in anatase
569 and fluorinated anatase; current density: $84 \mu\text{A cm}^{-2}$, duration of the galvanostatic charge: 1200
570 s, relaxation time: 20 h (γLi^+ is the intercalation ratio).

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575

576 **Figure 8.** Diffusion coefficient deduced from the different sequence of the galvanostatic
577 intermittent titration curves. Calculated enhancement factors (Eq. 8, with $\phi = 0.26$). (a): TiO_2 ;
578 (b): $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$.

579

580

581 **Table Content**

582

583 **Table 1.** Characteristic quantities of the system.

584

Dimension of nano-particles		For 1 cm ² (electrode surface)	
<i>a</i> (nm)	<i>b</i> (nm)	<i>n_p</i> , number of nano-particles	<i>S_p</i> , electrochemical interface, (cm ²)
3.0	12	6.18×10 ¹⁵	556

585

586 **Table 2.** Values of the parameters used to describe the evolution of the activity coefficient (Eq. 4).587 F--TiO₂ represents Ti_{0.78}□_{0.22}O_{1.12}F_{0.40}(OH)_{0.48}.588 Logarithms of the activity coefficients, ln *f_j*.

	ln <i>f₁</i>	ln <i>f₂</i>	ln <i>f₃</i>	ln <i>f₄</i>
TiO ₂	-41	-57	-63	-138
F-TiO ₂	-40	-58	-63	-172

589

590 Concentrations at the transition points, *c_{Tj}* (mol cm⁻³)

	<i>c_{T1}</i>	<i>c_{T2}</i>	<i>c_{T3}</i>	<i>c_{T4}</i>
TiO ₂	0.057	0.035	0.025	0.0004
F-TiO ₂	0.057	0.033	0.019	0.0002

591

592 Steepness factors to describe the changes of the activity coefficient, *Ψ_j* (cm³ mol⁻¹)

	<i>Ψ₁</i>	<i>Ψ₂</i>	<i>Ψ₃</i>	<i>Ψ₄</i>
TiO ₂	83	195	333	338
F-TiO ₂	91	143	257	273

593

594

595 **Table 3.** Values of the diffusion coefficient at the interface, *D** (Eq. 10). Maximum value of the
596 storage thickness, *δ_{max}* (Eq. 26), and pseudo-capacitance associated to that thickness (Eq. 29).

597

	<i>D*</i> (10 ⁻¹⁷ cm ² s ⁻¹)	<i>δ_{max}</i> , (nm)	<i>C_{max}</i> (mF cm ⁻²)
TiO ₂	1.3	2.0	283
F-TiO ₂	4.0	4.7	978

598