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# Lithium Intercalation in Anatase Titanium Vacancies and the Role of Local Anionic Environment

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## Abstract

The structure of bulk and non-defective compounds is generally described with crystal models built from well mastered techniques such the analysis of an x-ray diffractogram. The presence of defects, such as cationic vacancies, locally disrupt the long-range order, with the appearance of local structures with order extending only a few nanometers. To probe and describe the electrochemical properties of cation-deficient anatase, we investigated a series of materials having different concentrations of vacancies, i.e.,  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ , and compared their properties with respect to defect-free stoichiometric anatase  $\text{TiO}_2$ . At first, we characterized the series of materials  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  by means of pair distribution function (PDF),  $^{19}\text{F}$  nuclear magnetic resonance (NMR), Raman and x-ray photoelectron spectroscopies, to probe the

35 compositional and structural features. Secondly, we characterized the insertion electrochemical  
36 properties vs. metallic lithium where we emphasized the beneficial role of the vacancies on the  
37 cyclability of the electrode under high C-rate, with performances scaling with the concentration  
38 of vacancies. The improved properties were found to be due to the change of the lithium  
39 insertion mechanism induced by the vacancies, which act as host sites and suppress the phase  
40 transition typically observed in pure  $\text{TiO}_2$ , and further favor diffusive transport of lithium within  
41 the structure. NMR spectroscopy performed on lithiated samples provides evidence for the  
42 insertion of lithium in vacancies. By combining electrochemistry and DFT-calculations, we  
43 characterized the electrochemical signatures of the lithium insertion in the vacancies.  
44 Importantly, we found that the insertion voltage largely depends on the local anionic  
45 environment of the vacancy with a fluoride and hydroxide-rich environments, yielding high and  
46 low insertion voltages, respectively. This work further supports the beneficial use of defects  
47 engineering in electrodes for batteries and provides new fundamental knowledge in the insertion  
48 chemistry of cationic vacancies as host sites.

49

## 50 **Introduction**

51 Introducing defects, particularly cationic vacancies, into host intercalation compounds has been  
52 shown to be a viable way to modify the electrochemical properties of electrode materials for  
53 lithium storage.<sup>1</sup> Works on defect chemistry for battery materials are, however, rare.<sup>2</sup> Up to now,  
54 the stabilization of cation vacancies has been achieved in certain metal oxides (manganese, iron  
55 and vanadium) by synthetic procedures, including oxidative electrodeposition at high current  
56 density,<sup>3</sup> doping a fraction of the native metal cations with higher oxidation state dopants,<sup>4-5</sup> and

57 heating ordered oxides at high temperature in a defect-inducing environment.<sup>6</sup> Recently, we  
58 reported on a novel methodology for modifying the chemical composition of titanium dioxide,  
59 which stabilizes cation vacancies.<sup>7-8</sup> Cation vacancies were introduced by substituting divalent  
60 oxides with monovalent fluorides and hydroxides, yielding the general chemical formula  $Ti_{1-x-}$   
61  $y\Box_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y}$ , where  $\Box$  represents a cationic vacancy. When used as an electrode for  
62 lithium-ion battery, this compound showed a modified and enhanced Li activity compared to the  
63 stoichiometric  $TiO_2$ , illustrating the beneficial effect of defects.

64 A better understanding of the relationship between defect chemistry and electrochemical  
65 performance is an essential task to generalize the use of vacancies in improving Li-ion batteries.  
66 Such a task requires the fine characterization of cationic vacancies, which is, however, particularly  
67 challenging.

68 In the present study, we intended to understand how cationic vacancies impact electrochemical  
69 properties vs. Li. This work was motivated by the possibility of controlling the vacancy  
70 concentration in anatase  $Ti_{1-x-y}\Box_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y}$ . We first provide detailed characterization of  
71 materials with distinct vacancy concentrations, by means of pair distribution function (PDF), <sup>19</sup>F  
72 solid-state nuclear magnetic resonance (NMR), Raman spectroscopy, and X-ray photoelectron  
73 spectroscopy (XPS) analyses. Thereafter, the role of the cationic vacancies with respect to lithium  
74 intercalation properties was studied by electrochemistry, NMR, and DFT calculations, allowing us  
75 to identify the electrochemical signatures of lithium intercalation in vacancies. Our work further  
76 emphasizes the impact of the anionic environment of the vacancy, with the redox potential  
77 decreasing as the local intercalation environment changes from purely fluorinated to purely  
78 hydroxylated. Finally, we demonstrate superior lithium transport within vacancy-containing

79 electrode materials, which can be due to the concomitant formation of percolating network  
80 favoring the lithium diffusion and the suppression of the phase transition typically observed in  
81 pure TiO<sub>2</sub>.

## 82 EXPERIMENTAL SECTION

83 **Synthesis.** Anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  featuring different compositions/vacancy  
84 concentrations have been prepared following a previously reported method.<sup>2</sup> Briefly,  
85 solvothermal process was carried out in a stainless steel autoclave with a 45 mL Teflon liner cup  
86 inside. 1.2 mL aqueous hydrofluoric acid (*CAUTION: HF solutions are highly hazardous, and*  
87 *special protective equipment is required*) solution was added to the mixture of 24.8 mL  
88 isopropanol and 4 mL titanium isopropoxide in the Teflon liner cup. After sealing the autoclave,  
89 the mixed solution was heated inside an oven at different temperatures, *i.e.*, 90 °C, 110 °C and  
90 130 °C for 12 h. After cooling down to room temperature, the obtained white precipitate was  
91 washed with ethanol and centrifuged, then dried at 100 °C under air for 10 h. For comparison  
92 purpose, anatase TiO<sub>2</sub> was synthesized without HF.

93  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples were further outgassed at 150 °C overnight under primary  
94 vacuum prior to chemical lithiation and electrochemical analyses.

95 Chemical lithiation were carried out using n-butyl lithium (Sigma-Aldrich, 1.6 M in hexanes).<sup>9</sup>

96 After dispersing anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  powder prepared at 90°C in hexane, an excess  
97 of n-butyl lithium (0.2, 0.5 and 0.8 Li<sup>+</sup> per formula unit) was slowly added under stirring. The  
98 solution was stirred for 48 hours at room temperature. Lithiation process produces a color  
99 change from white to dark purple. After reaction, the products were washed several times with  
100 hexane and dried under vacuum. All operations were carried out in an argon-filled glove box.

101 **Characterization methods.** X-ray powder diffraction analysis were carried out using a Rigaku  
102 Ultima IV X-ray diffractometer equipped with a Cu K $\alpha$  radiation source ( $\lambda = 1.54059 \text{ \AA}$ ).  
103 Total scattering data were collected at the 11-ID-B beamline at the Advanced Photon Source at  
104 Argonne National Laboratory, using high energy X-rays ( $\lambda = 0.2128 \text{ \AA}$ ) with high values of  
105 momentum transfer  $Q_{\text{max}} = 22 \text{ \AA}^{-1}$ .<sup>10-11</sup> One-dimensional diffraction data were obtained by  
106 integrating the raw 2D total scattering data in Fit2D.<sup>15</sup> PDFs,  $G(r)$ , were extracted from the  
107 background and Compton scattering corrected data following Fourier transform within  
108 PDFgetX2.<sup>12</sup> The PDFs were subsequently modeled using PDFgui.<sup>13</sup> PDF peak fitting was  
109 performed using Fityk.<sup>14</sup>

110 Raman spectroscopy. Raman spectra were recorded at room temperature using a micro-Raman  
111 system with a Labram HR800 (Jobin-yvon-Horiba) spectrometer including Edge filters and  
112 equipped for signal detection with a back illuminated charge-coupled device detector (Spex CCD)  
113 cooled by Peltier effect to 200 K. A He–Ne laser (633 nm) was used as the excitation source. The  
114 spectrum was measured in the back-scattering geometry with a resolution of about  $0.5 \text{ cm}^{-1}$ . A  
115 100 $\times$  objective was used to focus the laser beam to a spot of  $1 \text{ }\mu\text{m}^2$  size on the sample surface.  
116 The laser power was adjusted to 0.2-0.5 mW with neutral filters of various optical densities to  
117 avoid local heating of the sample.

118 X-ray photoelectron spectroscopy. XPS chemical analysis was carried out using a VG ESCALAB 250  
119 spectrometer operating at a residual pressure of  $10^{-9}$  mbar. An Al K $\alpha$  monochromatized radiation  
120 ( $h\nu = 1486.6 \text{ eV}$ ) was employed as X-ray source. The spectrometer was calibrated against the  
121 reference binding energies (BE) of clean Cu (932.6 eV), Ag (368.2 eV) and Au (84 eV) samples. The  
122 photoelectrons were collected at a  $90^\circ$  take-off angle with respect to the substrate surface.

123 Survey and high resolution spectra were recorded with pass energy of 100 and 20 eV,  
124 respectively. Binding energies were calibrated versus the C1s signal ( $-\text{CH}_2-\text{CH}_2-$  bonds) set at  
125 285.0 eV. The data processing was performed with the Advantage software version 5.954 using  
126 a Shirley background and Gaussian/Lorentzian peak shapes at a fixed ratio of 70/30.

127  $^{19}\text{F}$  and  $^7\text{Li}$  Solid-State NMR Spectroscopy.  $^{19}\text{F}$  and  $^7\text{Li}$  solid-state magic angle spinning (MAS) NMR  
128 experiments were performed on a Bruker Avance 300 spectrometer operating at 7.0 T ( $^{19}\text{F}$  and  
129  $^7\text{Li}$  Larmor frequencies of 282.2 and 116.7 MHz, respectively), using a 1.3 mm and a 2.5 mm CP-  
130 MAS probe head, for recording  $^{19}\text{F}$  NMR spectra of the  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples and  $^{19}\text{F}$   
131 and  $^7\text{Li}$  NMR spectra of the chemically lithiated samples, respectively. The 2.5 mm rotors  
132 containing the chemically lithiated samples have been filled in glove-box. The room temperature  
133  $^{19}\text{F}$  MAS spectra of the  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples were recorded using a Hahn echo  
134 sequence with an interpulse delay equal to one rotor period. The  $90^\circ$  pulse length was set to 1.25  
135  $\mu\text{s}$  or 1.55  $\mu\text{s}$ , and the recycle delay was set to 20 s. The room temperature  $^{19}\text{F}$  MAS spectra of  
136 the chemically lithiated samples were recorded using a single pulse sequence. The  $90^\circ$  pulse  
137 length was set to 1.75  $\mu\text{s}$ , and the recycle delay was set to 10 s. The room temperature  $^7\text{Li}$  MAS  
138 spectra of the chemically lithiated samples were recorded using a single pulse sequence. The  $90^\circ$   
139 pulse length was set to 0.8  $\mu\text{s}$ , and the recycle delay was set to 10 s.  $^{19}\text{F}$  and  $^7\text{Li}$  spectra are  
140 referenced to  $\text{CFCl}_3$  and 1 M  $\text{LiCl}$  aqueous solution, respectively, and they were fitted by using the  
141 DMFit software.<sup>15</sup>  $^{19}\text{F}$  solid-state NMR spectroscopy was also used to quantify the fluorine  
142 content of the  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples following a previously reported method.<sup>7</sup>

143 **Electrochemistry.** Electrochemical measurements were carried out with CR2032-type coin cells  
144 and three-electrode Swagelok-type cells. The composition of the electrode was 80 wt.% active

145 materials, 10 wt.% Super P, and 10 wt.% polyvinylidene difluoride (PVDF). Copper was used as  
146 the current collector. The electrolyte was 1 M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate  
147 (EC) and dimethyl carbonate (DMC) (1:1, v/v). The cells were assembled and tested with lithium  
148 metal as the anode and the reference electrode in the voltage range of 2.5–1.0 V vs. Li<sup>+</sup>/Li.

149 **Density Functional Theory (DFT) calculations.** Our density functional theory (DFT) calculations  
150 were performed using the code VASP<sup>16-17</sup>, with valence electrons described by a plane-wave basis  
151 with a cutoff of 500 eV. Interactions between core and valence electrons were described using  
152 the projector augmented wave (PAW) method<sup>18</sup>, with cores of [Ar] for Ti, [He] for O, [He] for F,  
153 [He] for Li, and [H<sup>+</sup>] for H. The calculations used the revised Perdew-Burke-Ernzerhof generalized  
154 gradient approximation function PBEsol<sup>19</sup>, with a Dudarev +*U* correction applied to the Ti d states  
155 (GGA+*U*).<sup>20-21</sup> We used a value of  $U_{\text{Ti},d}=4.2$  eV, which has previously been used to model  
156 intercalation of lithium and other metal ions in anatase TiO<sub>2</sub> and TiO<sub>2</sub>(B).<sup>21-24</sup> To model anatase  
157 TiO<sub>2</sub>, we first performed a full geometry optimisation on a single Ti<sub>4</sub>O<sub>8</sub> unit cell, with optimized  
158 lattice parameters obtained by fitting a series of constant volume calculations to the Murnaghan  
159 equation of state. All subsequent calculations were fixed to the resulting optimised lattice  
160 parameters. Intercalation into stoichiometric anatase TiO<sub>2</sub> was modelled using a 3 × 3 × 1  
161 supercell (108 atoms), with a single Li ion inserted at an interstitial site (LiTi<sub>36</sub>O<sub>72</sub>). To identify the  
162 preferred positions of F<sup>-</sup> and OH<sup>-</sup> anions in relation to a cationic Ti vacancy, we performed a series  
163 of calculations in 4×4×2 supercells, with 1 Ti vacancy, and 4 charge compensating X<sub>O</sub> species, with  
164 X=(F, OH), giving cell stoichiometries of Ti<sub>127</sub>O<sub>252</sub>X<sub>4</sub>. These calculations agree with previous  
165 studies, that reported that fluoride ions preferentially occupy sites adjacent to the titanium  
166 vacancy<sup>7, 25</sup>, in equatorially-coordinated sites. We find the same trend for OH units (**Figures S11**



167 **and S12, Supporting Information).** Intercalation into  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  was modelled  
168 using  $3 \times 3 \times 1$  supercells, with 1 Ti vacancy, and 4 charge compensating  $X_{\text{o}}$  species ( $X=\text{F}, \text{OH}$ )  
169 occupying the four equatorial anion sites adjacent to the vacancy. Lithium intercalation energies  
170 were calculated for  $4X=(4\text{F}, 3\text{F}+\text{OH}, 2\text{F}+2\text{OH}, \text{F}+3\text{OH}, \text{and } 4\text{OH})$ . In the case of  $4X=2\text{F}+2\text{OH}$ , we  
171 considered like anions arranged in adjacent (cis) and opposite (trans) equatorial site pairs.  
172 Individual calculations were deemed optimised when all atomic forces were smaller than  $0.01 \text{ eV}$   
173  $\text{\AA}^{-1}$ . All calculations were spin polarized, and used a  $4 \times 4 \times 2$  Monkhorst-Pack grid for sampling  $k$ -  
174 space in the single unit cell, a  $2 \times 2 \times 2$  grid for the  $3 \times 3 \times 1$  cells, and only the gamma-point for  
175 the  $4 \times 4 \times 2$  cells. To calculate intercalation energies, reference calculations for metallic Li was  
176 performed using the same convergence criteria as above. We considered a 2-atom cell for Li, with  
177 a  $16 \times 16 \times 16$  Monkhorst-Pack grid for  $k$ -space sampling. A data set containing all DFT calculation  
178 inputs and outputs is available at the University of Bath Data Archive<sup>26</sup>, published under the CC-  
179 BY-SA-4.0 license. Analysis scripts containing intercalation energy calculations, and code to  
180 produce Figure 9 are available as an open-source repository as reference [27], published under  
181 the MIT license.

182

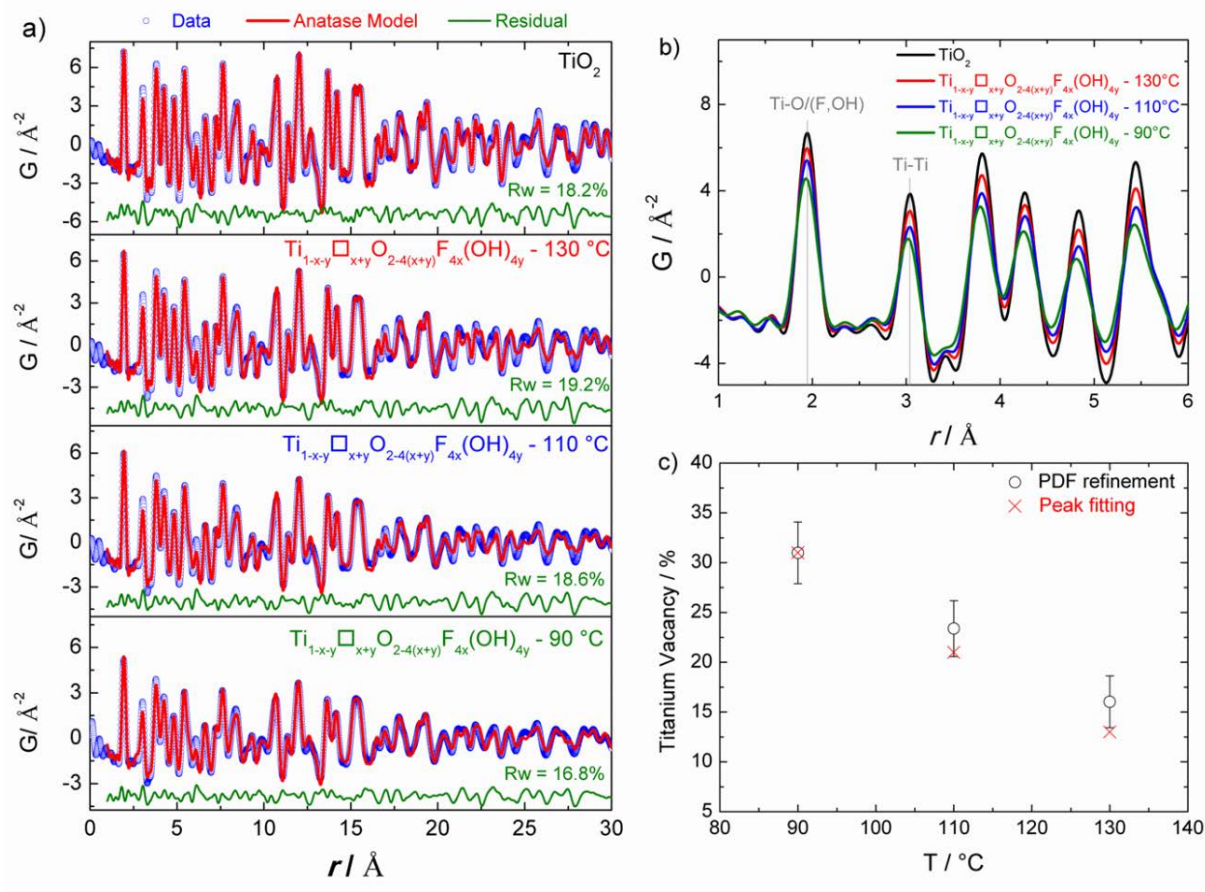
## 183 RESULTS AND DISCUSSION

### 184 **Chemical and physical characterizations.**

185 To control the vacancy concentration in anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ , we performed  
186 solvothermal synthesis at three different temperature that are 90, 110 and 130 °C.<sup>28</sup> The phase  
187 purity was confirmed by x-ray diffraction analysis revealing similar patterns characteristic of  
188 tetragonal symmetry ( $I4_1/amd$  space group) of anatase crystal structure (**Figure S1, Supporting**

189 **Information**). To determine the chemical composition of the series of samples, we assessed the  
190 vacancy content by structural analysis of total scattering data, evaluated the fluorine content  
191 using solid-state  $^{19}\text{F}$  NMR and the OH content was deduced according to the general chemical  
192 formula  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ .

193 Structural analysis was performed by measuring total scattering data from which we obtained  
194 the pair distribution function, a technique suitable to study nanostructured materials at the  
195 atomic scale.<sup>29</sup> To assess the titanium vacancy concentration, we used and compared two  
196 approaches that are (i) the real-space refinement of PDF data and (ii) individual peaks fitting.  
197 First, PDF data were refined against structural model based on the tetragonal symmetry of  
198 anatase using a real-space refinement (**Figure 1a and Table 1**). The refinement of the Ti (4a  
199 Wyckoff site) rate occupancy confirmed that the titanium vacancy concentration decreases upon  
200 increasing the synthesis temperature.<sup>28</sup> All the samples show similar unit cell parameters values  
201 and close particle sizes (coherence length).<sup>28</sup>



202

203 **Figure 1.** (a) PDF refinements of anatase  $\text{TiO}_2$  and  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  prepared at  $90^\circ\text{C}$ ,  $110^\circ\text{C}$  and  $130^\circ\text{C}$ . (b)  
 204 Zoom on the short-range order of PDF data for anatase samples. (c) Determination of the titanium vacancy concentration  
 205 using real-space refinement and peak fitting for anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ .

206

207 To determine the vacancy concentration, we also used the intensity of the peak located at  $1.93$   
 208  $\text{\AA}$  corresponding to Ti-O/F(OH) bond length (**Figure 1b**). Because the intensity of a PDF peak is  
 209 related to the atomic density, atom occupancy can be deduced by comparing peak intensity with  
 210 respect to a stoichiometric sample. Using the first peak intensity, we obtained Ti occupancy of  
 211 69, 79 and 87 % for the samples prepared at 90, 110 and  $130^\circ\text{C}$ , respectively. A comparison  
 212 between the vacancies content assessed by real-space refinement and peak fitting (**Figure 1c**)  
 213 shows a good agreement for high vacancy content while we expect that peak fitting becomes  
 214 more accurate for low concentration vacancy containing materials.<sup>30</sup>

215 **Table 1.** Structural parameters obtained by real-space refinement of the PDF data of anatase TiO<sub>2</sub>  
 216 and Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> samples prepared at 90 °C, 110 °C and 130 °C.

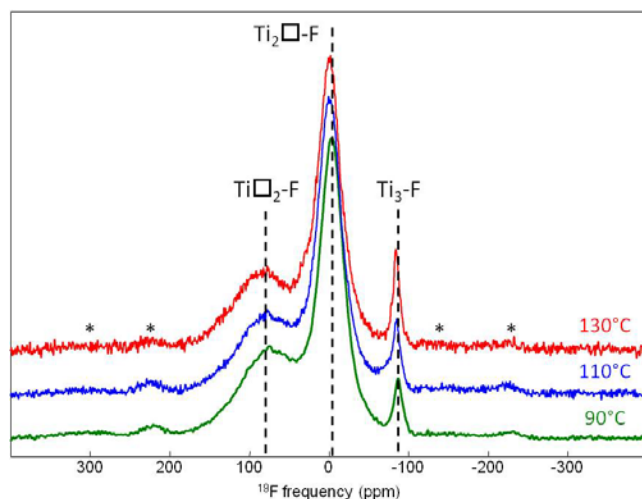
Samples	Lattice constant (Å)	Ti occ.	O occ.	Cohenrence length (nm)
TiO <sub>2</sub>	a=b=3.788(1) c=9.489(2)	1.00(1)	1.00(1)	6.8(3)
T= 90 °C	a=b=3.795(1) c=9.489(5)	0.69(3)	1.00(1)	4.8(2)
T= 110 °C	a=b=3.791(1) c=9.491(4)	0.77(3)	1.00(1)	5.5(2)
T= 130 °C	a=b=3.789(1) c=9.494(5)	0.84(3)	1.00(1)	6.5(2)

217  
 218 Fluorine was quantified by <sup>19</sup>F NMR for samples prepared at different temperatures (**Table 2**).  
 219 Upon increasing the reaction temperature, the weight percentage of fluorine decreases.<sup>28</sup>  
 220 Chemical compositions were determined by using the general chemical formula Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-</sub>  
 221 <sub>4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> (**Table 2**) where the fluorine and vacancy contents were assessed as  
 222 aforementioned.  
 223 **Table 2.** Estimated vacancy concentration (□), fluorine content and chemical composition of  
 224 anatase Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> samples prepared at different temperatures.

T (°C)	□	F (wt%)	Composition
90	0.31	13.3	Ti <sub>0.69</sub> □ <sub>0.31</sub> O <sub>0.76</sub> F <sub>0.48</sub> (OH) <sub>0.76</sub>
110	0.21	11.9	Ti <sub>0.79</sub> □ <sub>0.21</sub> O <sub>1.16</sub> F <sub>0.44</sub> (OH) <sub>0.40</sub>
130	0.13	8.8	Ti <sub>0.87</sub> □ <sub>0.13</sub> O <sub>1.48</sub> F <sub>0.36</sub> (OH) <sub>0.16</sub>

225

226 Insight into the fluorine local environments in  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples was obtained  
227 using  $^{19}\text{F}$  solid-state MAS NMR spectroscopy (**Figure 2**). The spectra show three distinct lines that  
228 were previously assigned to fluorine in the vicinity of different numbers of titanium atoms and  
229 titanium vacancies, *i.e.*, species  $\text{Ti}_3 - \text{F}$ ,  $\text{Ti}_2\square - \text{F}$  and  $\text{Ti}\square_2 - \text{F}$ .<sup>7</sup> Upon increasing the reaction  
230 temperature from 90 °C to 130 °C, the relative intensities of the  $^{19}\text{F}$  NMR lines assigned to the  
231 species  $\text{Ti}_3 - \text{F}$  (from  $\approx 3\%$  to  $\approx 5\%$ ) and  $\text{Ti}_2\square - \text{F}$  (from  $\approx 60\%$  to  $\approx 65\%$ ) increase, whereas  
232 the relative intensity of the  $^{19}\text{F}$  NMR lines assigned to the species  $\text{Ti}\square_2 - \text{F}$  (from  $\approx 37\%$  to  $\approx 30$   
233 %) decreases (**Figures S2-4, Tables S1-3, Supporting Information, Table 3**). The concentrations  
234 of these species point toward a preferential localization of F atoms close to vacancies. Moreover,  
235 the average number of neighboring Ti atoms of the F atoms increases only slightly, from  $\approx 1.66$   
236 to  $\approx 1.74$ , when the reaction temperature increases from 90 °C to 130 °C, whereas the amount  
237 of titanium vacancies decreases from 0.31 to 0.13. Accordingly, the average number of  
238 neighboring Ti atoms of the O atoms and OH groups increases from 2.20 to 2.80 in relation with  
239 the increase of the  $\text{O}/(\text{O}+\text{OH})$  ratio (**Table 3**).



240  
 241 **Figure 2.**  $^{19}\text{F}$  solid-state MAS (64 kHz) NMR spectra of  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples  
 242 prepared at 90 °C ( $\text{Ti}_{0.69}\square_{0.31}\text{O}_{0.76}\text{F}_{0.48}(\text{OH})_{0.76}$ , green), 110 °C ( $\text{Ti}_{0.79}\square_{0.21}\text{O}_{1.16}\text{F}_{0.44}(\text{OH})_{0.40}$ , blue)  
 243 and 130 °C ( $\text{Ti}_{0.87}\square_{0.13}\text{O}_{1.48}\text{F}_{0.36}(\text{OH})_{0.16}$ , red). The dashed lines indicate the three NMR lines  
 244 corresponding to the three-fluorine species occurring in these samples.

245 **Table 3.** Estimated proportions of fluorine species (%), average F coordination number (F CN),  
 246 O/(O+OH) ratio and O(OH) coordination number (O(OH) CN) of anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples.

Sample	$\text{Ti}_3\text{-F}$	$\text{Ti}_2\square\text{-F}$	$\text{Ti}\square_2\text{-F}$	F CN	O/(O+OH)	O(OH) CN
$\text{Ti}_{0.69}\square_{0.31}\text{O}_{0.76}\text{F}_{0.48}(\text{OH})_{0.76}$	2.6	60.5	37.0	1.66	0.50	2.20
$\text{Ti}_{0.79}\square_{0.21}\text{O}_{1.16}\text{F}_{0.44}(\text{OH})_{0.40}$	4.3	66.0	29.7	1.75	0.74	2.55
$\text{Ti}_{0.87}\square_{0.13}\text{O}_{1.48}\text{F}_{0.36}(\text{OH})_{0.16}$	4.6	64.8	30.6	1.74	0.90	2.80

248  
 249 Raman spectroscopy is a sensitive tool to detect the structural distortions at the scale of the  
 250 chemical bond. According to the factor group analysis<sup>31-32</sup>, six fundamental transitions are  
 251 expected in the Raman spectrum of anatase, with the following wavenumbers<sup>32-33</sup>:  $E_g(1)$  at 144

252  $\text{cm}^{-1}$ ,  $E_g(2)$  at  $197 \text{ cm}^{-1}$ ,  $B_{1g}(1)$  at  $399 \text{ cm}^{-1}$ ,  $B_{1g}(2)$  at  $519 \text{ cm}^{-1}$ ,  $A_{1g}$  at  $513 \text{ cm}^{-1}$  and  $E_g(3)$  at  $638$   
253  $\text{cm}^{-1}$ . The overlapping between  $B_{1g}(2)$  and  $A_{1g}$  prevents the detection of the weaker  $A_{1g}$   
254 component in unpolarized measurements at room temperature. The doubly degenerate  $E_g$   
255 modes involve atom displacements perpendicular to the  $c$  axis, while for the other modes, atoms  
256 move parallel to the  $c$  axis.<sup>31-32, 34</sup> Most of the modes are predicted to involve both Ti and O atom  
257 displacements, except the  $B_{1g}(1)$  that is dominated by Ti atom motions and the  $A_{1g}$  that is a pure  
258 oxygen vibration.<sup>34-36</sup>

259 Raman phonon modes belonging to anatase  $\text{TiO}_2$  phase (tetragonal  $D_{4h}^{19}$  ( $I4_1/amd$ ) space group)  
260 are clearly identified for the  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples (**Figure 3a**). While  $\text{TiO}_2$  exhibits  
261 the five characteristic Raman bands at  $143$ ,  $196$ ,  $397$ ,  $517$  and  $639 \text{ cm}^{-1}$ , several changes can be  
262 detected upon increasing the vacancy concentration: the  $E_g(1)$  Raman peak is continuously  
263 broadened and blue-shifted (**Figure 3b**); the  $B_{1g}(2)$  and  $E_g(3)$  modes are gradually red-shifted  
264 (**Figure 3c**); the intensity of the  $B_{1g}(1)$  mode decreases progressively.

265 The most intense  $E_g(1)$  Raman feature is largely investigated in the literature. Many works focus  
266 on the variation of position, width and shape of this peak in relation to several effects: defects in  
267 the stoichiometry, phonon confinement in nanoparticles, presence of minority phases, pressure  
268 and temperature effects, substitutional dopant atoms, O or Ti vacancies, charge carrier density.<sup>37</sup>

269 It is not straightforward to distinguish the influence of a single effect among the others because  
270 they are often simultaneously present in the investigated sample. However, according to the  
271 phonon band structure of anatase<sup>31</sup>, a shift toward higher wavenumbers is expected for the  $E_g(1)$   
272 peak as soon as the fundamental Raman selection rule is relaxed. The presence of a growing local  
273 disorder of the perfect crystalline structure in the  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples induced by

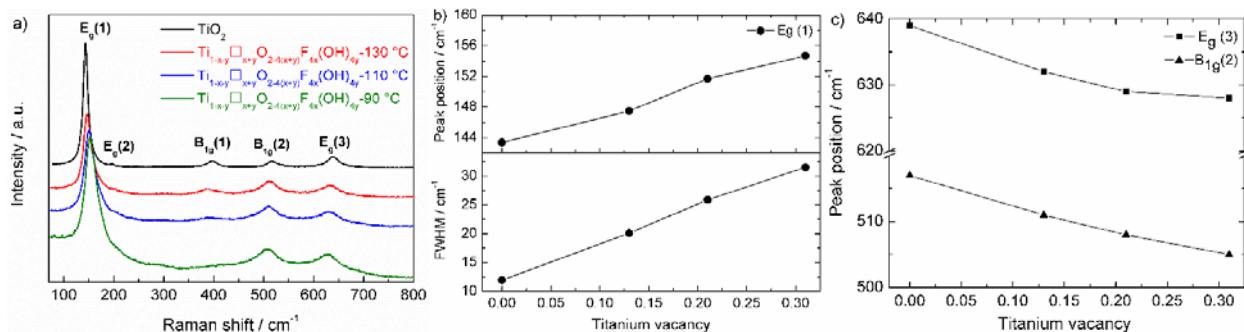
274 the presence of titanium vacancies, probably explains the blue shift from 143 to 155  $\text{cm}^{-1}$   
275 observed when the titanium vacancy increases from 0 to 0.3 (**Figure 3b**). On the other hand, the  
276 existence of up to three types of anions yielding to multiple X-Ti-X (X=  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ) bending  
277 vibrations, may account for the broadening of this peak upon increasing the anionic doping.  
278 The evolution toward lower wavenumbers of the  $\text{B}_{1g}(2)$  (517 to 505  $\text{cm}^{-1}$ ) and  $\text{E}_g(3)$  (639 to 628  
279  $\text{cm}^{-1}$ ) vibrations (**Figure 3c**) which are mixes of both X-atom and Ti-atom motions, is indicative of  
280 an overall decreasing of the Ti-X bond strength. This can be understood by considering the higher  
281 electronegativity of the fluorine anion leading to a greater ionicity of the Ti-X bond as compared  
282 to the Ti-O bond.

283 Finally, the progressive intensity decline of the pure Ti-atom  $\text{B}_{1g}(1)$  vibration can be easily  
284 related to the decreasing amount of vibrating Ti species as the concentration of vacancies  
285 increases.

286 X-ray photoelectron spectroscopy was performed on anatase  $\text{TiO}_2$  and  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$   
287 samples (**Figure 4**). On one hand, the spectrum of  $\text{TiO}_2$  displays a Ti  $2p_{3/2}$  peak that can be fitted  
288 with a single component centered at 458.8 eV characteristic of the binding energy for  
289 stoichiometric  $\text{TiO}_2$ .<sup>38</sup> On the other hand, the Ti  $2p_{3/2}$  peak of  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples  
290 is red-shifted to 459.1 eV probably due to the presence of the more electronegative environment  
291 *i.e.*,  $\text{F}^-$  anion. Furthermore, upon increasing the monovalent doping ( $\text{F}^-$  and  $\text{OH}^-$ ), *i.e.*, the  
292 heterogeneity of anionic environment in the vicinity of Ti atoms, the full width at half maximum  
293 (FWHM) increases. In  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples, the F 1s core spectra were  
294 reconstructed using a broad single component (FWHM=1.7 eV) centered at 684.6 eV

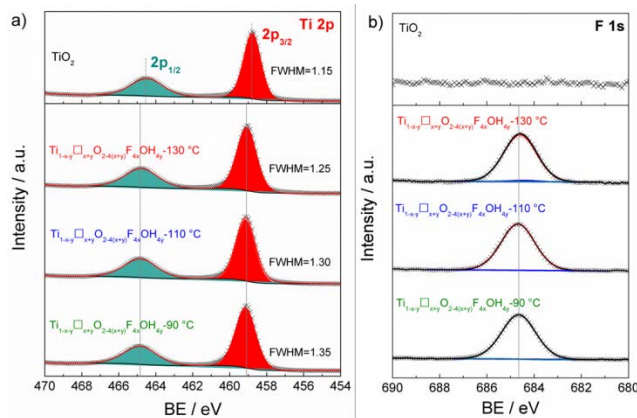


295 characteristic of Ti-F bonds.<sup>39-41</sup> The broadness of the F 1s core peak expresses the various F  
 296 environments in these samples.



297  
 298 **Figure 3.** (a) Raman scattering spectra of TiO<sub>2</sub> (reference nanocrystalline anatase powder) and Ti<sub>1-</sub>  
 299 <sub>x-y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> anatase samples prepared at 90 °C, 110 °C and 130 °C, (b) and (c) peak  
 300 position and full width at half maximum (FWHM) of the TiO<sub>2</sub> and Ti<sub>1-x-y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub>  
 301 anatase samples as a function of the titanium vacancy concentration.

302



303  
 304 **Figure 4.** High resolution (a) Ti 2p, and (b) F 1s XPS spectra of TiO<sub>2</sub> and Ti<sub>1-x-y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub>  
 305 anatase samples prepared at 90 °C, 110 °C and 130 °C.

### 306 Electrochemical properties.

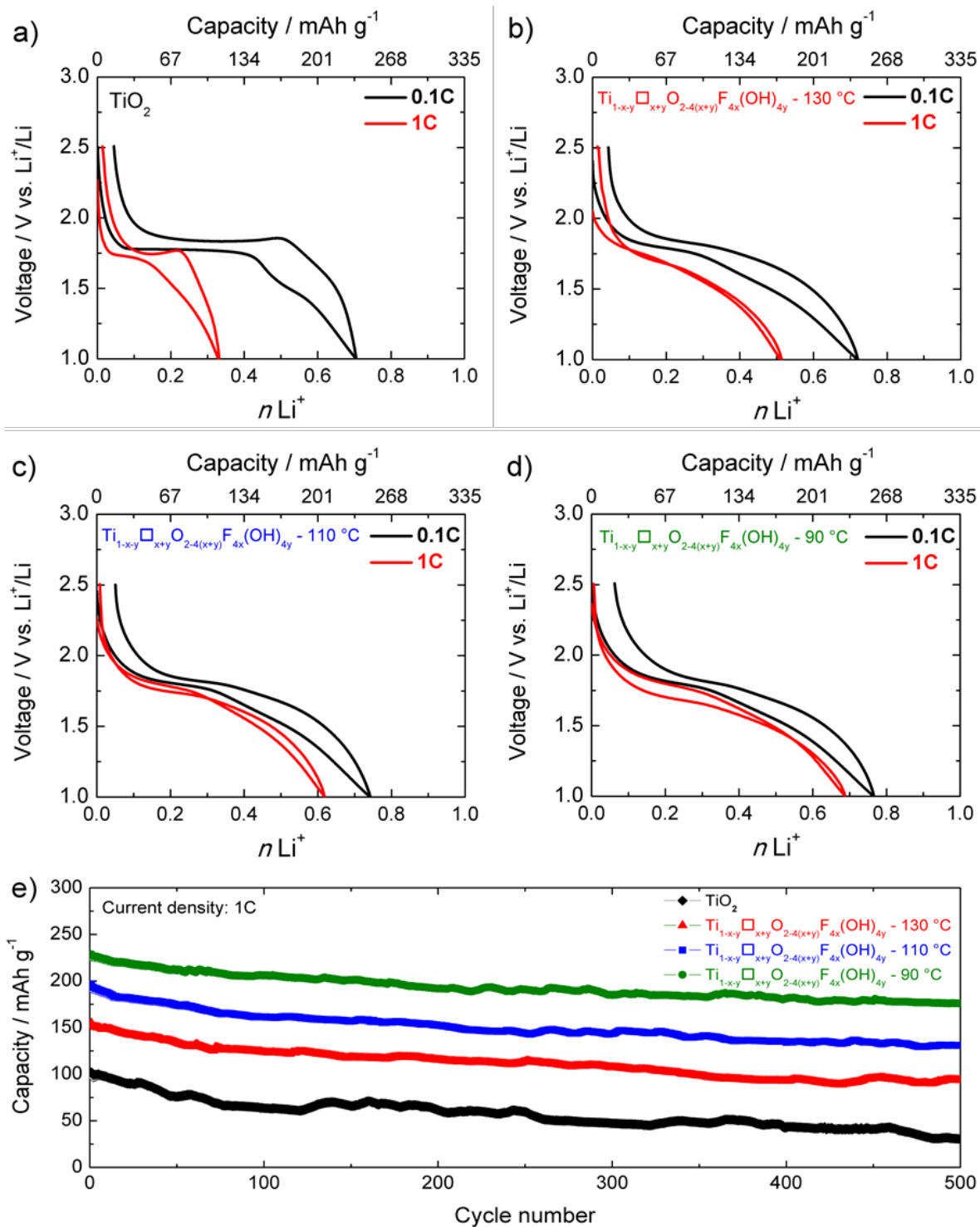
307 The electrochemical properties of anatase Ti<sub>1-x-y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> were evaluated and  
 308 compared with the stoichiometric anatase TiO<sub>2</sub> using galvanostatic discharge/charge

309 experiments. **Figure 5** shows the discharge/charge cycles obtained under galvanostatic  
310 conditions within a range of 2.5 and 1.0 V at 0.1 C and 1 C rates (note that 1 C = 335 mAh g<sup>-1</sup>).  
311 Under 0.1 C rate, the samples Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> prepared at 90 °C, 110 °C and 130 °C  
312 show slightly higher discharge capacities with 255 mAh g<sup>-1</sup>, 248 mAh g<sup>-1</sup> and 241 mAh g<sup>-1</sup>,  
313 respectively (corresponding to 0.76, 0.74 and 0.72 Li<sup>+</sup> per formula unit), in comparison with 234  
314 mAh g<sup>-1</sup> (corresponding to 0.70 Li<sup>+</sup> per formula unit) for TiO<sub>2</sub>. Under 1C rate, the samples Ti<sub>1-x-</sub>  
315 y□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> prepared at 90 °C, 110 °C and 130 °C maintain high discharge capacities of  
316 229 mAh g<sup>-1</sup>, 208 mAh g<sup>-1</sup> and 174 mAh g<sup>-1</sup>, respectively (corresponding to 0.68, 0.62 and 0.52  
317 Li<sup>+</sup> per formula unit). In contrast, a capacity decreases down to 110 mAh g<sup>-1</sup> (corresponding to  
318 0.33 Li<sup>+</sup> per formula unit) is observed for TiO<sub>2</sub>. Overall, higher capacities are obtained for  
319 anatase containing vacancies. Such a trend is also observed for long-term cycling experiments,  
320 shown in Figure 5e. The samples Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> prepared at 90 °C, 110 °C and 130 °C  
321 show stable cycling performance over 500 cycles with superior capacity retention on cycling of  
322 80%, 70% and 62% compared to 30% for TiO<sub>2</sub> anatase after 500 cycles.

### 323 **Intercalation mechanism.**

324 The lithium intercalation mechanism that takes place in anatase Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> and  
325 TiO<sub>2</sub> electrodes was first investigated using the quasi-equilibrium voltage obtained by the  
326 galvanostatic intermittent titration technique (GITT) shown in **Figure 6**. As expected, a constant  
327 voltage plateau is observed for anatase TiO<sub>2</sub> corresponding to the phase transition from  
328 tetragonal to orthorhombic Li-rich phase.<sup>42-44</sup> Upon increasing the vacancy concentration, the  
329 plateau region characteristic of the phase transition progressively vanishes indicating a change  
330 toward a solid solution behavior. The latter was tentatively explained by the presence of

331 vacancies<sup>7</sup> acting as additional sites for lithium ions that can minimize the formation of the  
332 edge-shared  $\text{LiO}_6$  octahedra driving the phase transition.<sup>22</sup> In this study, anatase  $\text{TiO}_2$  and  $\text{Ti}_{1-x}$ -  
333  $\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples present similar particle size/coherence length suggesting that the  
334 presence of titanium vacancies is the predominant factor influencing the lithium storage  
335 mechanism, *i.e.*, phase transition vs. solid solution.<sup>45</sup>

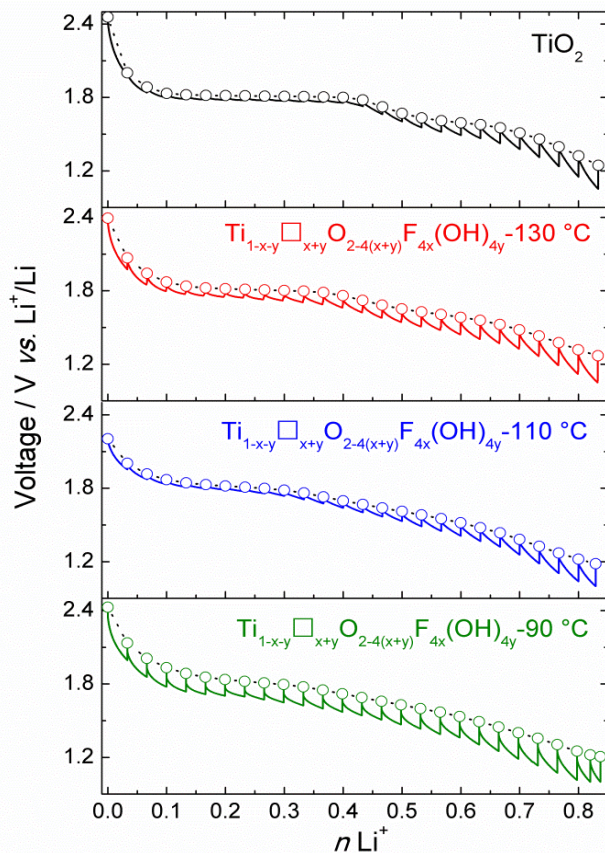


336

337 **Figure 5.** (a, b, c, d) Galvanostatic discharge-charge curves (2<sup>nd</sup> cycle) at 0.1C and 1C rates, and

338 (e) long cycling performance at 1C rate for anatase TiO<sub>2</sub> and Ti<sub>1-x-y</sub>□<sub>x+y</sub>O<sub>2-4(x+y)</sub>F<sub>4x</sub>(OH)<sub>4y</sub> prepared

339 at 130 °C, 110 °C and 90 °C (the cells were activated at 0.1C for the first cycle).

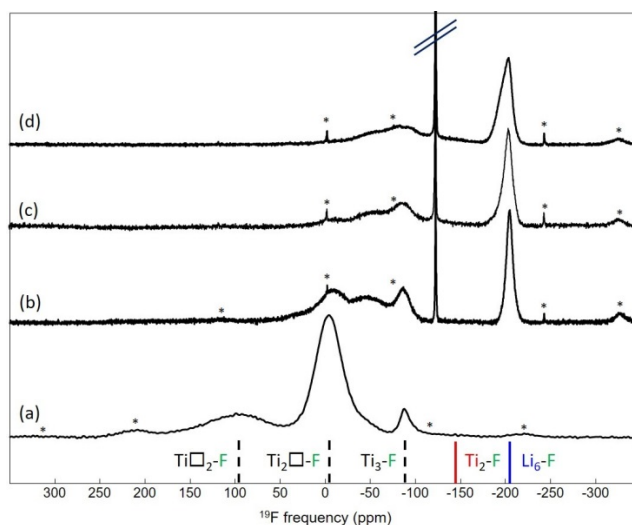


340

341 **Figure 6.** Voltage-composition profiles obtained using the galvanostatic intermittent titration  
 342 technique (GITT) recorded during the second discharge for anatase  $\text{TiO}_2$  and  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$   
 343 prepared at 130 °C, 110 °C and 90 °C electrodes.

344 To attest for the lithium intercalation within the vacancy sites, we used  $^{19}\text{F}$  solid state NMR  
 345 performed on chemically lithiated samples prepared from the sample obtained at 90 °C. Prior  
 346 to lithiation reactions, the sample was outgassed at 150 °C which induces a modification of the  
 347 chemical composition from  $\text{Ti}_{0.69}\square_{0.31}\text{O}_{0.76}\text{F}_{0.48}(\text{OH})_{0.76}$  to  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ .<sup>2</sup> **Figure 7**  
 348 shows the  $^{19}\text{F}$  MAS NMR spectra of the pristine and lithiated samples. Several chemical  
 349 lithiation were performed at increasing lithium concentrations that are 0.2, 0.5 and 0.8  $\text{Li}^+$  per  
 350 formula unit (**Figures 7b-d**).  $^7\text{Li}$  solid state MAS NMR spectra of the chemically lithiated samples

351 showed that the signal increases when the concentration of n-butyl lithium increases  
352 confirming the increasing insertion of lithium (**Figure S5, Supporting Information**). Moreover,  
353 we note the presence of LiF upon lithiation as revealed by X-ray diffraction analysis (**Figure S10,**  
354 **Supporting Information**). The  $^{19}\text{F}$  MAS NMR spectra of the pristine and lithiated samples (fits  
355 are given as **Supporting Information, Figures S6-8 and Tables S5-7**) confirm the presence of LiF  
356 and show the appearance of adsorbed  $\text{F}^-$  ions which suggest that chemical lithiation damages  
357 the material. Based on the  $^{19}\text{F}$  isotropic chemical shift ( $\delta_{\text{iso}}$ ) values of the environments  $\text{Ti}^{\text{IV}}\square_2\text{-F}$ ,  
358  $\text{Ti}^{\text{IV}}_2\square\text{-F}$  and  $\text{Ti}^{\text{IV}}_3\text{-F}$  in  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ ,  $\text{Li}_6\text{-F}$  in LiF (-204.3 ppm)<sup>46</sup> and in  $\text{TiF}_3$  (-144.8  
359 ppm,  $\text{Ti}^{\text{III}}_2\text{-F}$ )<sup>47</sup> and on the decrease of the  $\delta_{\text{iso}}$  value of fluoride anions when the number of  
360 surrounding cations increases, the insertion of  $\text{Li}^+$  ion in a titanium vacancy and/or in an  
361 interstitial site and the reduction of a  $\text{Ti}^{4+}$  ion into a  $\text{Ti}^{3+}$  ion are both expected to induce a  
362 decrease of the  $\delta_{\text{iso}}$  value of the neighboring fluorine. When the concentration of n-butyl lithium  
363 increases, the relative intensities of the NMR resonances of higher (smaller) chemical shift  
364 decrease (increase) and the NMR lines assigned to  $\text{Ti}^{\text{IV}}\square_2\text{-F}$  and  $\text{Ti}^{\text{IV}}_2\square\text{-F}$  vanish (from 0.2  $\text{Li}^+$  per  
365 formula unit and from 0.5  $\text{Li}^+$  per formula unit, respectively), evidencing the insertion of lithium  
366 in vacancies. However, considering the number of species which may exist (**see discussion in**  
367 **Supporting Information and Table S4**) and the low resolution of the  $^{19}\text{F}$  NMR spectra, the  
368 assignment of the NMR lines is complex and could not be achieved.

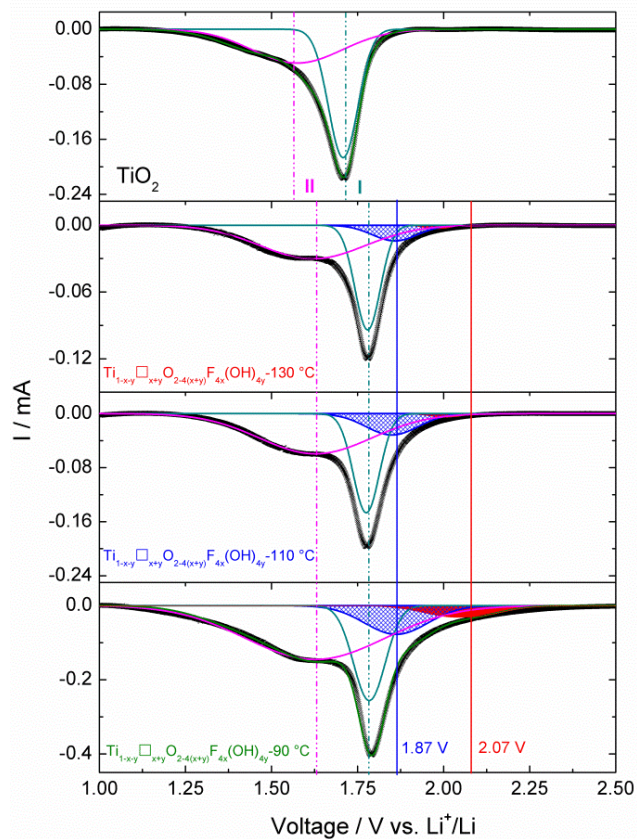


369  
 370 **Figure 7.**  $^{19}\text{F}$  solid-state MAS NMR spectra of (a)  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$  (60 kHz) and  
 371 chemically lithiated ((b) 0.2, (c) 0.5 and (d) 0.8  $\text{Li}^+$  per formula unit samples) (34 kHz). The  
 372 asterisks indicate the main spinning sidebands. The dashed lines indicate the  $^{19}\text{F}$   $d_{\text{iso}}$  values of  
 373 the  $\text{Ti}^{\text{IV}}_3\text{-F}$ ,  $\text{Ti}^{\text{IV}}_2\square\text{-F}$ , and  $\text{Ti}^{\text{IV}}\square_2\text{-F}$  environments in  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ . Solid lines indicate  
 374 the  $^{19}\text{F}$   $d_{\text{iso}}$  values of the  $\text{Ti}^{\text{III}}_2\text{-F}$  environment in  $\text{TiF}_3$  and the  $\text{Li}_6\text{-F}$  environment in  $\text{LiF}$ .  $\text{Ti}^{\text{IV}}$  are in  
 375 black and  $\text{Ti}^{\text{III}}$  are in red. The narrow lines observed on the spectra of the lithiated samples are  
 376 assigned to adsorbed  $\text{F}^-$  ions.

377 Slow scanning linear sweep voltammetry was used to investigate the electrochemical  
 378 signatures of the lithium insertion in the various host sites of anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$   
 379 and  $\text{TiO}_2$ . A slow-scan rate of  $0.05 \text{ mV s}^{-1}$  at the condition approaching equilibrium was applied,  
 380 which allows excluding the capacitive contribution.<sup>48</sup> **Figure 8** shows the anodic part of the Li  
 381 insertion process obtained after one activating cycle. For anatase  $\text{TiO}_2$ , the cyclic  
 382 voltammogram was reconstructed using two signals (signal I and II) at 1.71 and 1.56 V vs.  $\text{Li}^+/\text{Li}$ .  
 383 The higher redox potential corresponds to the lithium insertion reaction in the interstitial sites  
 384 of anatase.<sup>49</sup> The occurrence of a second peak at lower potential can be due to a concentration



385 dependence of lithium insertion in anatase. Particularly, this second peak can be related to the  
 386 insertion of lithium in the lithium-rich orthorhombic phase  $\text{Li}_{0.5}\text{TiO}_2$ .<sup>50</sup>  
 387 The introduction of Ti vacancies yields significant changes in slow scan rate cyclic  
 388 voltammograms. Upon increasing the vacancy concentration, we observed the appearance of  
 389 new redox peaks occurring at a broader potential window. Moreover, the signals I and II were  
 390 observed at higher potentials ( $\Delta E=0.07\text{ V}$ ) in anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ . Furthermore,  
 391 the signal II was reconstructed using a broad line suggesting that the lithium insertion occurred  
 392 in sites featuring different energies which can be related to the heterogeneous anionic  
 393 environment found in  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  samples.



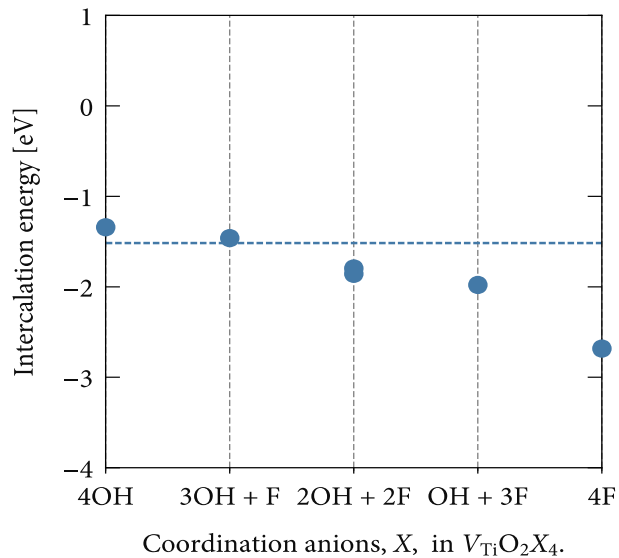
394



395 **Figure 8.** Slow scanning liner sweep voltammetries of  $\text{TiO}_2$  and  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$   
396 anatase prepared at 130 °C, 110 °C and 90 °C electrodes at a scan rate of  $0.05 \text{ mV s}^{-1}$  (obtained  
397 after one activating cycle).

398 To better understand the effect of local anion environment on the insertion of lithium in  
399 anatase  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$ , we performed a series of DFT calculations. We have  
400 previously calculated insertion energies of lithium at the octahedral interstitial site in  
401 stoichiometric anatase  $\text{TiO}_2$ , and at titanium vacancies in fluorine-substituted anatase  $\text{TiO}_2$ .<sup>7, 24</sup>  
402 For Li insertion into stoichiometric anatase, we found intercalation energy of -1.23 eV. For the  
403 cation-deficient anatase  $\text{TiO}_2$  system, we considered systems with one single vacancy  
404 ( $\text{Ti}_{35}\square_1\text{O}_{68}\text{F}_4$ ) and two adjacent vacancies ( $\text{Ti}_{126}\square_2\text{O}_{248}\text{F}_8$ ), which gave favorable intercalation  
405 energies of -2.68 eV and -2.88 eV, respectively. These more favorable insertion energies  
406 translate to higher redox potentials of 2.68 and 2.88 V which is, however, higher than the redox  
407 potentials observed in CV, *i.e.*, 1.87 and 2.07 V. To supplement these previous results, we  
408 considered the single vacancy system ( $\text{Ti}_{35}\square_1\text{O}_{68}\text{X}_4$ ) with X varied from fully fluorinated (with  
409 the Ti vacancy coordinated by 2O and 4F), through hydroxyfluorinated (coordination by 2O,  
410 xOH, and (4-x)F), to fully hydroxylated (coordination by 2O and 4OH) environments. In each  
411 case we consider the four X anions to occupy equatorial sites around the Ti vacancy (see  
412 **Supporting Information, Figures S11 and S12**, and the supporting data in the reference [<sup>27</sup>]).  
413 **Figure 9** shows the variation in lithium insertion energies with changes in the local anionic  
414 environment surrounding the vacancy. The redox potential progressively drops from 2.68 V for  
415 4F to 1.2 V for 4OH demonstrating a significant impact of the anionic environment on the redox  
416 potentials. This result emphasizes the inductive effect of fluoride ions on the redox potential.<sup>51</sup>

417 The presence of protons, however, tends to decrease the redox potential, which is possibly due  
 418 to steric effects. The occurrence of a higher potential for the signal I ( $\Delta E=0.07$  V) in anatase  $\text{Ti}_{1-x-y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$   
 419  $\text{Ti}_{1-x-y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  can therefore be explained by the presence of fluoride ions in the  
 420 vicinity of the interstitial site as revealed by the presence of  $\text{Ti}_3\text{-F}$  species observed by  $^{19}\text{F}$  NMR.



421  
 422 **Figure 9.** Intercalation energy of lithium in a  $\text{Ti}_{35}\square_1\text{O}_{68}\text{X}_4$  supercell with  $X = \text{F}, \text{OH}^-$ . The  
 423 horizontal dashed line shows the intercalation energy for lithium in stoichiometric anatase  $\text{TiO}_2$ .  
 424 *Source:* The data set and code to generate this figure, and the figure file, are available under the  
 425 MIT licence as part of [ref 27].

426 **Kinetic aspects.**

427 The evolution of the diffusion coefficients for  $\text{Li}^+$  in both  $\text{TiO}_2$  and  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$   
 428 electrodes was followed during the discharge process (**Figures 10a** and **d**) using GITT.<sup>52-53</sup> The  
 429 variation of the diffusion coefficients as a function of the  $\text{Li}^+$  concentration was plotted in **Figures**  
 430 **10b** and **e**.

431 At the early stage of lithiation of anatase  $\text{TiO}_2$ , the diffusion coefficient decreases from  $8.3 \times 10^{-12}$   
432  $\text{cm}^2 \text{s}^{-1}$  for  $x \sim 0.03 \text{ Li}^+$  to  $1 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$  for  $x \sim 0.2 \text{ Li}^+$ . The origin of such a decrease is related to  
433 the reduction of  $\text{Ti}^{4+}$  causing the progressive shortening of the O-O pairs through which  $\text{Li}^+$   
434 diffuses, further increasing the site migration barriers.<sup>54</sup> Upon increasing  $x$  to  $0.5 \text{ Li}^+$ , the diffusion  
435 coefficient increases back to  $2.5 \times 10^{-12} \text{ cm}^2 \text{s}^{-1}$  which is caused by the structural transition toward  
436 the ordered lithiated orthorhombic phase. Thereafter, it further decreases during the solid  
437 solution lithiation in the orthorhombic phase. Finally, we observed a subsequent increase of the  
438 diffusion coefficient to  $9 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$  which can be related to a second phase transition toward  
439 the Li-rich tetragonal phase. We note that the diffusion coefficients obtained in this study differ  
440 from the literature values due to the different thickness of the electrode films. In the case of  
441  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ , the evolution of the lithium diffusion coefficient showed less  
442 pronounced variation. At the early stage of lithiation, the diffusion coefficient decreases from  $8.0$   
443  $\times 10^{-12} \text{ cm}^2 \text{s}^{-1}$  for  $x \sim 0.03 \text{ Li}^+$  to  $4.6 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$  for  $x \sim 0.26 \text{ Li}^+$ . Thereafter, the diffusion  
444 coefficient value remains stable with a value of  $8.3 \times 10^{-13} \text{ cm}^2 \text{s}^{-1}$  for  $x \sim 0.8 \text{ Li}^+$ .

445 The above-mentioned results clearly show that the crystal structural features such as vacancies  
446 largely impact the lithium diffusion. We showed that the presence of vacancies in anatase  
447 modifies the insertion mechanism by suppressing the phase transition toward a solid solution  
448 behavior. At the early stage of lithiation ( $x \sim 0.03\text{-}0.2 \text{ Li}^+$ ), it is striking how the presence of  
449 vacancies that act as host sites can mitigate the structural impact of the  $\text{Ti}^{4+}$  reduction and in turn  
450 the migration barriers with a decrease of the diffusion coefficient by a factor of 83 and 10 in  
451 anatase  $\text{TiO}_2$  and  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$ , respectively. The absence of the phase transition

452 suppresses the large variation of the diffusion coefficient observed for TiO<sub>2</sub> which can be at the  
453 origin of the higher rate capability observed for vacancies containing materials.

454 **Thermodynamic considerations.**

455 In order to establish a link between the thermodynamic properties and the electrochemical  
456 behavior of the batteries it is worth to introduce the analysis previously developed to describe  
457 the lithium insertion in solid substrates.<sup>55</sup> The electrochemical investigation shows that the  
458 studied systems exhibit large deviations from ideality. Then, an activity factor,  $f_{Li}$ , must be  
459 introduced in the Nernst's equation that binds the open circuit voltage,  $E$ , to the concentration  
460 of the active material,  $C_{Li}$

$$461 \quad E = E^0 - \frac{RT}{F} \ln(f_{Li}C_{Li}) \quad (1)$$

462 where

$$463 \quad E^0 = \frac{RT}{F} \ln C_{Li}^0 \quad (2)$$

464  $C_{Li}^0$  is the concentration of lithium metal. The values of  $f_{Li}$  can be deduced from the potential  
465 curve  $E$  vs.  $C_{Li}$  or  $E$  vs.  $n$ , where the lithium compound is written as TiO<sub>2</sub>Li <sub>$n$</sub> ;  $n$  and  $C_{Li}$  are linked  
466 through the equation

$$467 \quad C_{Li} = \frac{n}{V_{TiO_2Li_n}} \quad (3)$$

468  $V_{TiO_2Li_n}$  is the molar volume of the compound.

469 The activity factor,  $f_{Li}$ , is an important physical value since it represents the excess Gibbs energy  
470 ( $\Delta G_{Li}^E$ ) of formation of the lithium insertion in the substrate, which is the heart of the battery  
471 operation. For a compound TiO<sub>2</sub>Li <sub>$n$</sub> , the insertion of one mole of Li, i.e. formation of (TiO<sub>2</sub>) <sub>$z$</sub> Li (with  
472  $z = \frac{1}{n}$ ) is

473  $\Delta G_{Li}^E = -RT \ln f_i$  (4)

474 the more negative  $\Delta G_{Li}^E$  is, the more positive the electrode potential is.

475 The deviation from ideality has a direct influence on the kinetic properties of the battery; indeed

476 the real diffusion driving force is the gradient of the chemical potential and, as shown by

477 Darken,<sup>56</sup> an enhancement factor,  $\zeta = \varphi \left( 1 + \frac{d \ln f_{Li}}{d \ln C_{Li}} \right)$  should be introduced in the diffusion

478 equation; then the diffusion flux writes

479  $J_{Li} = D \varphi \left( 1 + \frac{d \ln f_{Li}}{d \ln C_{Li}} \right) \frac{d C_{Li}}{d x}$  (5)

480 where  $D$  is the chemical diffusion coefficient,<sup>57</sup> and  $\varphi$  is a damping factor introduced to take

481 account of the thermodynamic properties of the system.<sup>55, 58</sup>

482 In previous papers<sup>59-60</sup>, it was shown that a suitable representation of the variation of the activity

483 factor was given by the series:

484  $\ln f_{Li} = \sum_{j=1}^n (\ln f_j - \ln f_{j-1}) \operatorname{erfc} \{ \psi_i (C_{Li} - C_{Tj}) \}$  (6)

485  $\ln f_j$  is the activity factor corresponding to a plateau of the potential curve, the complementary

486 error function, *erfc*, was used to describe the change from one factor to the next;  $C_{Tj}$  is the

487 concentration at the inflexion point of the potential curve.  $\psi_i$  is the steepness of the change of

488 the activity factor around the concentration  $C_{Tj}$  (**Table S9, Supporting Information**).

489 The various parameters  $\ln f_j$  and  $\psi_i$  were adjusted to obtain a suitable representation of the OCV

490 curves (**Figures 10a and d**): four terms in the sum ( $n=4$ , Eq.6) were used, the first one (index 1)

491 and the last one (index 4) are relative to the high and very low lithium concentrations

492 respectively. The other two correspond to the operative range of the battery.

493 These theoretical considerations have a major impact on the analysis of the system:

494 - The two potential plateaus of the potential curve (clearly visible on the Li-TiO<sub>2</sub> system, (**Figure**  
495 **10a**) correspond to the composition TiO<sub>2</sub>Li<sub>0.65</sub> and TiO<sub>2</sub>Li<sub>0.3</sub>.

496 In order to consider the implementation of one mole of lithium, the compounds can be written  
497 as Li(TiO<sub>2</sub>)<sub>1.54</sub> and Li(TiO<sub>2</sub>)<sub>3.33</sub>. The excess Gibbs energy of formation of that compounds, deduced  
498 from the value of the activity coefficient  $f_2$  and  $f_3$ , are: -144 kJ and -156 kJ, respectively.

499

500 - The classical formula used to analyze the GITT curves<sup>52-53</sup> (**Figure 6**) is based on the Fick's law  
501 which states that, for an ideal system, the lithium flux  $J_{Li}$  is proportional to the concentration  
502 gradient:

503

$$504 \quad J_{Li} = D_{Fick} \frac{dC_{Li}}{dx} \quad (7)$$

505

506 However, in this determination the important departure to ideality of the system was neglected.  
507 Then, as shown by the analysis of the diffusion process (Eq. 6), the quantity  $D_{Fick}$  is linked to the  
508 chemical diffusion coefficient  $D$  through the equation:

509

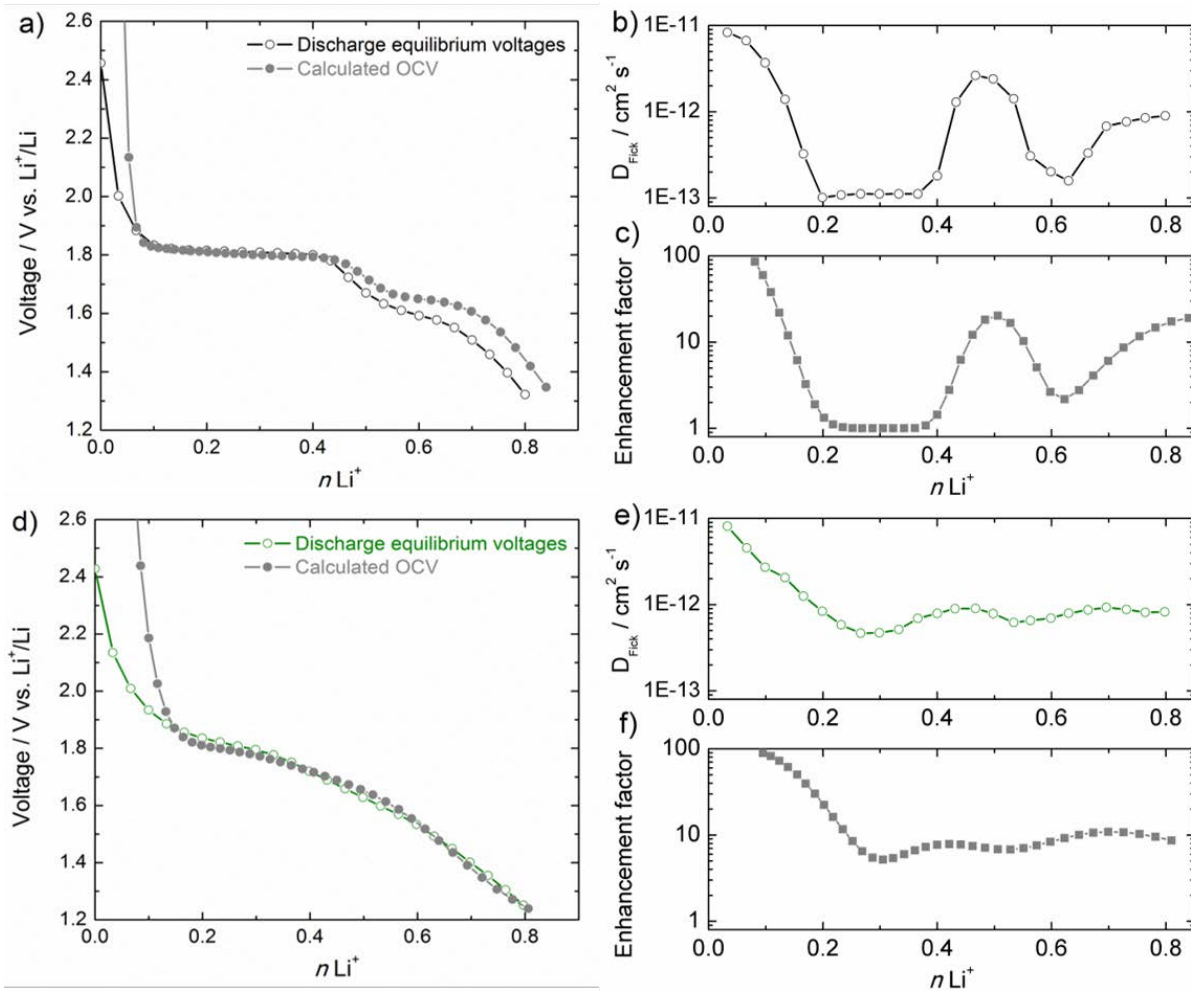
$$510 \quad D_{Fick} = \zeta D \quad (8)$$

511

512 According to the curves in **Figures 10b** and **e**, it should be noted that the important variations of  
513 the  $D_{Fick}$  versus the lithium concentration arise mainly from the thermodynamic properties of  
514 the system as shown by the concomitant values of the enhancement factor **Figures 10c** and **f**.

515 For the Li-TiO<sub>2</sub> system, the lithium insertion gives rise to well defined phases, and the transition

516 from one potential plateau to the other is quite sharp that induces a very large change in the  
 517 enhancement factor; the lithium transport is enhanced by a factor greater than ten (**Figure**  
 518 **10c**). The structural changes in the fluorinated compounds are less marked; the steepness  
 519 factors become smaller, and various structures can coexist. It results in a more continuous  
 520 value of the enhancement factor, concomitant to a continuous value of the diffusion coefficient  
 521  $D_{Fick}$  (**Figures 10e and f**). The thermodynamic properties of the lithium intercalation into  
 522 anatase or fluorinated anatase described in the above study are useful to establish a link  
 523 between the structural properties of the electrode material and their influence on the  
 524 electrochemical behavior of the system.



526 **Figure 10.** (a) and (d) Equilibrium voltage profiles via GITT and calculated OCV profiles, (b) and  
527 (d) extracted diffusion coefficient for  $\text{TiO}_2$  and  $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$  electrodes. (c) and (f)  
528 corresponding calculated enhancement factor profiles.

## 529 CONCLUSION

530 In this work, we prepared cation-deficient anatase having different concentration of vacancies  
531 *i.e.*,  $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$  whose chemical formulae were determined using PDF analysis  
532 (both using real-space refinements and peak fitting methods) and  $^{19}\text{F}$  NMR spectroscopy.  
533 Raman spectroscopy confirmed the presence of titanium vacancies while x-ray photoelectron  
534 spectroscopy attests of the broad anionic heterogeneity in the samples. Galvanostatic  
535 experiments showed the beneficial role of the vacancies on the cyclability of the electrode  
536 under high C-rate, with performances scaling with the concentration of vacancies. Deeper  
537 understanding of the vacancy's insertion chemistry was obtained using low scan rate cyclic  
538 voltammetry showing the appearance of new and shifted redox peaks. The assignment of these  
539 peaks was done using DFT calculations performed on vacancies featuring fluoride- to hydroxide-  
540 rich anionic environment in the vicinity of the vacancy. Moreover, we found that the presence  
541 of vacancies favors the diffusion transport of lithium within the structure in part due to the  
542 suppression of the phase transition typically encountered in pure  $\text{TiO}_2$ . This work further  
543 supports the beneficial use of defects engineering in electrodes for batteries and provides new  
544 fundamental knowledge in the insertion chemistry of cationic vacancies as host sites.<sup>47</sup>

## 545 ASSOCIATED CONTENT

546 **Supporting Information.** Additional information such as XRD patterns and fits of  $^{19}\text{F}$  MAS NMR  
547 spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.



548

549 **Data Access Statement.** The DFT dataset supporting this study is available from the University  
550 of Bath Research Data Archive (doi:10.15125/BATH-00473) [44], published under the CC-BY-SA-  
551 4.0 license. This dataset contains all input parameters and output files for the VASP DFT  
552 calculations, and Python scripts for collating the relevant data used in our analysis. Jupyter  
553 notebooks containing code to produce Figs 9, S11 & S12 are available (Ref [27], doi:  
554 10.5281/zenodo.1181872), published under the MIT license.

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559

### 560 **Notes**

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