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► **To cite this version:**

Jiwei Ma, Wei Li, Benjamin J Morgan, Jolanta Swiatoska, Rita Baddour-Hadjean, et al.. Lithium Intercalation in Anatase Titanium Vacancies and the Role of Local Anionic Environment. *Chemistry of Materials*, 2018, 30 (9), pp.3078-3089. 10.1021/acs.chemmater.8b00925 . hal-02048259

HAL Id: hal-02048259

<https://hal.science/hal-02048259v1>

Submitted on 18 Oct 2024

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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 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}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 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.¹ Works on defect chemistry for battery materials are, however, rare.² 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,³ doping a fraction of the native metal cations with higher oxidation state dopants,⁴⁻⁵ and

57 heating ordered oxides at high temperature in a defect-inducing environment.⁶ Recently, we
58 reported on a novel methodology for modifying the chemical composition of titanium dioxide,
59 which stabilizes cation vacancies.⁷⁻⁸ 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), ¹⁹F
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 TiO₂.

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.² 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 TiO₂ 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).⁹
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⁺ 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 α 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 $Q_{\text{max}} = 22 \text{ \AA}^{-1}$.¹⁰⁻¹¹ One-dimensional diffraction data were obtained by
106 integrating the raw 2D total scattering data in Fit2D.¹⁵ PDFs, $G(r)$, were extracted from the
107 background and Compton scattering corrected data following Fourier transform within
108 PDFgetX2.¹² The PDFs were subsequently modeled using PDFgui.¹³ PDF peak fitting was
109 performed using Fityk.¹⁴

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 cm^{-1} . A
115 100 \times objective was used to focus the laser beam to a spot of 1 \mu 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 α 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° 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}F and ^7Li Solid-State NMR Spectroscopy. ^{19}F and ^7Li solid-state magic angle spinning (MAS) NMR
128 experiments were performed on a Bruker Avance 300 spectrometer operating at 7.0 T (^{19}F and
129 ^7Li 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}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}F
131 and ^7Li 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}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° pulse length was set to 1.25
135 μs or 1.55 μs , and the recycle delay was set to 20 s. The room temperature ^{19}F MAS spectra of
136 the chemically lithiated samples were recorded using a single pulse sequence. The 90° pulse
137 length was set to 1.75 μs , and the recycle delay was set to 10 s. The room temperature ^7Li MAS
138 spectra of the chemically lithiated samples were recorded using a single pulse sequence. The 90°
139 pulse length was set to 0.8 μs , and the recycle delay was set to 10 s. ^{19}F and ^7Li spectra are
140 referenced to CFCl_3 and 1 M LiCl aqueous solution, respectively, and they were fitted by using the
141 DMFit software.¹⁵ ^{19}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.⁷

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 LiPF₆ 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⁺/Li.

149 **Density Functional Theory (DFT) calculations.** Our density functional theory (DFT) calculations
150 were performed using the code VASP¹⁶⁻¹⁷, 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) method¹⁸, with cores of [Ar] for Ti, [He] for O, [He] for F,
153 [He] for Li, and [H⁺] for H. The calculations used the revised Perdew-Burke-Ernzerhof generalized
154 gradient approximation function PBEsol¹⁹, with a Dudarev +*U* correction applied to the Ti d states
155 (GGA+*U*).²⁰⁻²¹ 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 TiO₂ and TiO₂(B).²¹⁻²⁴ To model anatase
157 TiO₂, we first performed a full geometry optimisation on a single Ti₄O₈ 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 TiO₂ was modelled using a 3 × 3 × 1
161 supercell (108 atoms), with a single Li ion inserted at an interstitial site (LiTi₃₆O₇₂). To identify the
162 preferred positions of F⁻ and OH⁻ 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_O species, with
164 X=(F, OH), giving cell stoichiometries of Ti₁₂₇O₂₅₂X₄. These calculations agree with previous
165 studies, that reported that fluoride ions preferentially occupy sites adjacent to the titanium
166 vacancy^{7, 25}, 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_{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 eV
173 \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 Archive²⁶, 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

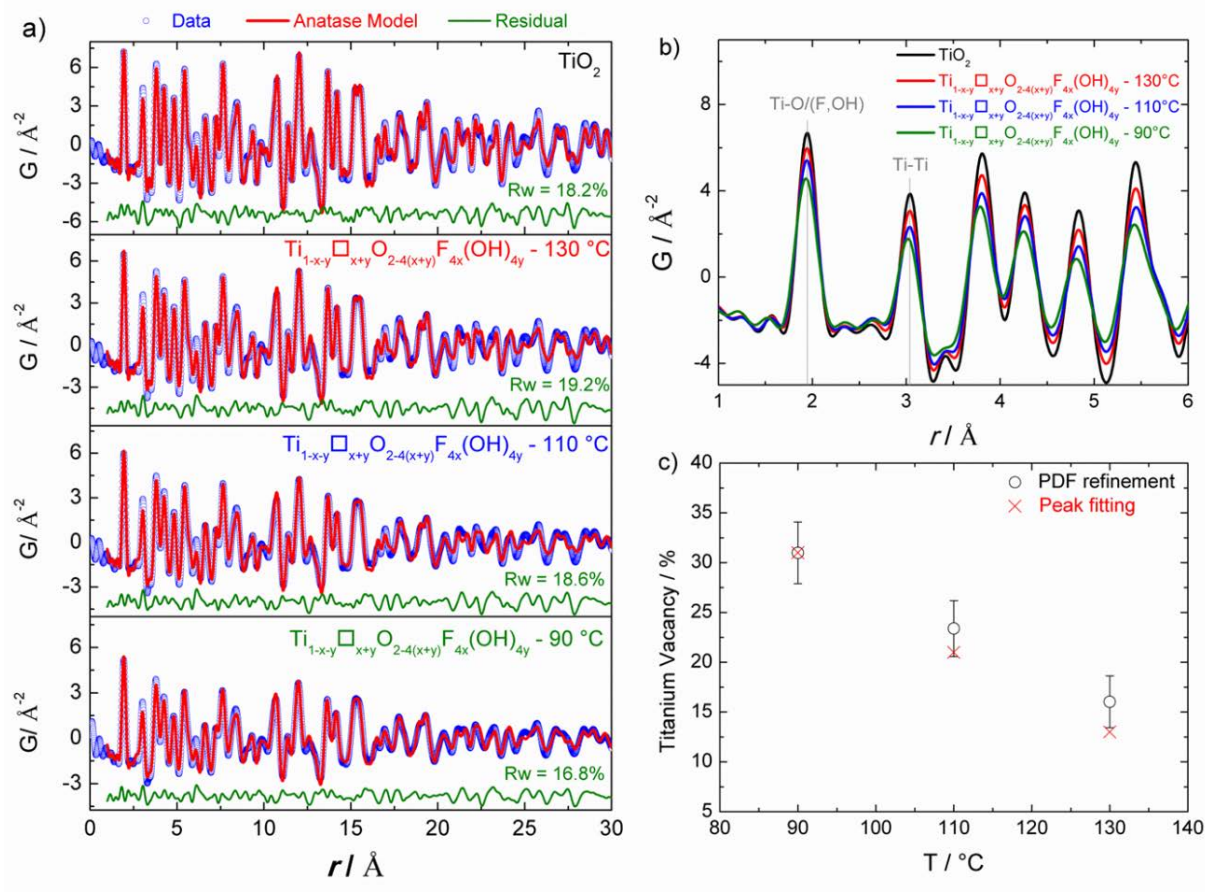
183 RESULTS AND DISCUSSION

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.²⁸ 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}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.²⁹ 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.²⁸ All the samples show similar unit cell parameters values
201 and close particle sizes (coherence length).²⁸



202

203 **Figure 1.** (a) PDF refinements of anatase 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 °C, 110 °C and 130 °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 Å 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 °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.³⁰

215 **Table 1.** Structural parameters obtained by real-space refinement of the PDF data of anatase TiO₂
 216 and Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} samples prepared at 90 °C, 110 °C and 130 °C.

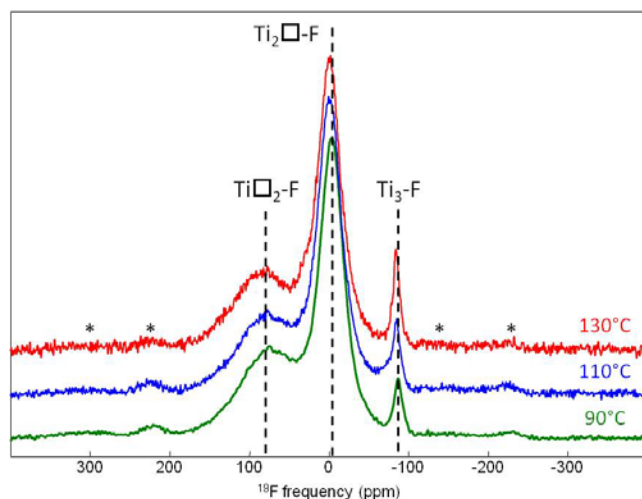
Samples	Lattice constant (Å)	Ti occ.	O occ.	Cohenrence length (nm)
TiO ₂	a=b=3.788(1) c=9.489(2)	1.00(1)	1.00(1)	6.8(3)
T= 90 °C	a=b=3.795(1) c=9.489(5)	0.69(3)	1.00(1)	4.8(2)
T= 110 °C	a=b=3.791(1) c=9.491(4)	0.77(3)	1.00(1)	5.5(2)
T= 130 °C	a=b=3.789(1) c=9.494(5)	0.84(3)	1.00(1)	6.5(2)

217
 218 Fluorine was quantified by ¹⁹F NMR for samples prepared at different temperatures (**Table 2**).
 219 Upon increasing the reaction temperature, the weight percentage of fluorine decreases.²⁸
 220 Chemical compositions were determined by using the general chemical formula Ti_{1-x-y}□_{x+y}O₂₋
 221 _{4(x+y)}F_{4x}(OH)_{4y} (**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_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} samples prepared at different temperatures.

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

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}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 $\text{Ti}\square_2 - \text{F}$.⁷ Upon increasing the reaction
230 temperature from 90 °C to 130 °C, the relative intensities of the ^{19}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}F NMR lines assigned to the species $\text{Ti}\square_2 - \text{F}$ (from $\approx 37\%$ to ≈ 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 ≈ 1.66
236 to ≈ 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}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	Ti ₃ -F	Ti ₂ □-F	Ti□ ₂ -F	F CN	O/(O+OH)	O(OH) CN
Ti _{0.69} □ _{0.31} O _{0.76} F _{0.48} (OH) _{0.76}	2.6	60.5	37.0	1.66	0.50	2.20
Ti _{0.79} □ _{0.21} O _{1.16} F _{0.44} (OH) _{0.40}	4.3	66.0	29.7	1.75	0.74	2.55
Ti _{0.87} □ _{0.13} O _{1.48} F _{0.36} (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 analysis³¹⁻³², six fundamental transitions are
 251 expected in the Raman spectrum of anatase, with the following wavenumbers³²⁻³³: E_g(1) at 144

252 cm^{-1} , $E_g(2)$ at 197 cm^{-1} , $B_{1g}(1)$ at 399 cm^{-1} , $B_{1g}(2)$ at 519 cm^{-1} , A_{1g} at 513 cm^{-1} and $E_g(3)$ at 638
253 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.^{31-32, 34} 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.³⁴⁻³⁶

259 Raman phonon modes belonging to anatase 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 TiO_2 exhibits
261 the five characteristic Raman bands at 143 , 196 , 397 , 517 and 639 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.³⁷

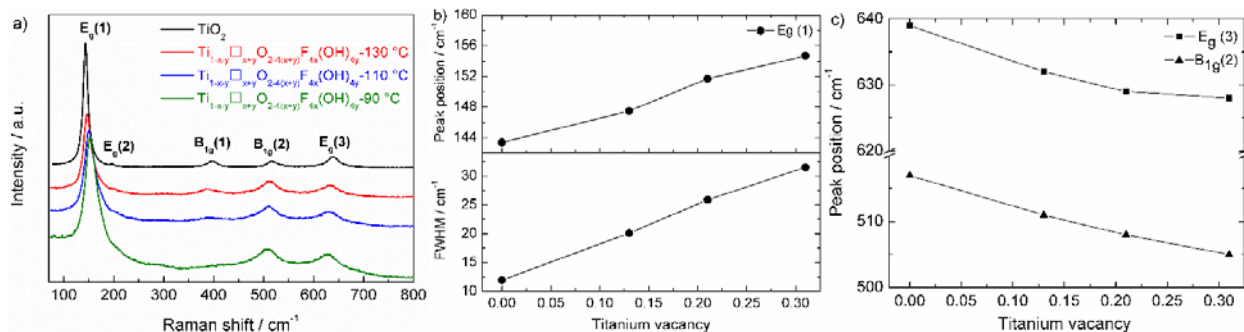
269 It is not straightforward to distinguish the influence of a single effect among the others because
270 they are often simultaneously present in the investigated sample. However, according to the
271 phonon band structure of anatase³¹, a shift toward higher wavenumbers is expected for the $E_g(1)$
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 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= O^{2-} , F^- , 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 cm^{-1}) and $\text{E}_g(3)$ (639 to 628
279 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.

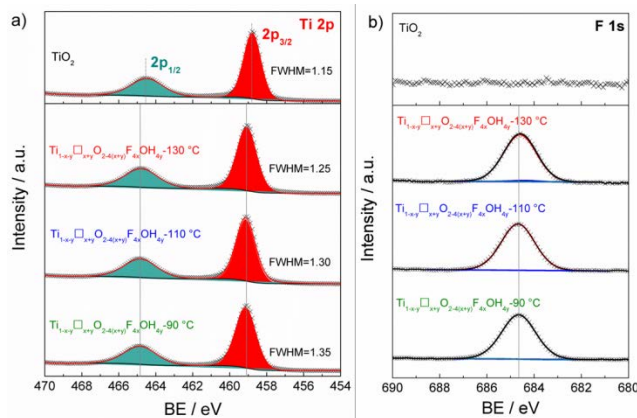
286 X-ray photoelectron spectroscopy was performed on anatase TiO_2 and $\text{Ti}_{1-x-y}\square_{x+y}\text{O}_{2-4(x+y)}\text{F}_{4x}(\text{OH})_{4y}$
287 samples (**Figure 4**). On one hand, the spectrum of TiO_2 displays a Ti $2p_{3/2}$ peak that can be fitted
288 with a single component centered at 458.8 eV characteristic of the binding energy for
289 stoichiometric TiO_2 .³⁸ 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.*, F^- anion. Furthermore, upon increasing the monovalent doping (F^- and 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.³⁹⁻⁴¹ 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 TiO₂ (reference nanocrystalline anatase powder) and Ti₁₋
 299 _{x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} 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 TiO₂ and Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y}
 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 TiO₂ and Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y}
 305 anatase samples prepared at 90 °C, 110 °C and 130 °C.

306 Electrochemical properties.

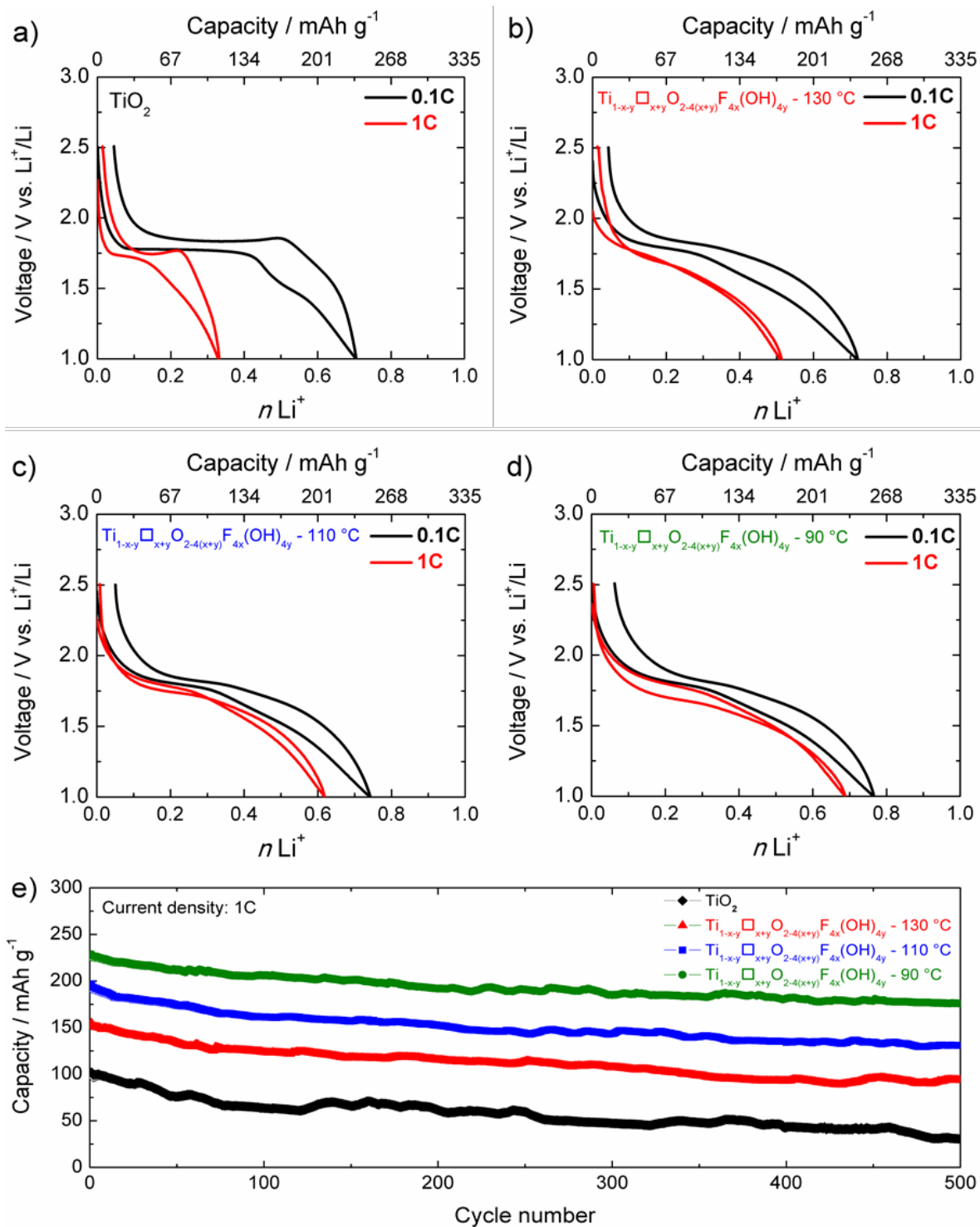
307 The electrochemical properties of anatase Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} were evaluated and
 308 compared with the stoichiometric anatase TiO₂ using galvanostatic discharge/charge

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⁻¹).
311 Under 0.1 C rate, the samples Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} prepared at 90 °C, 110 °C and 130 °C
312 show slightly higher discharge capacities with 255 mAh g⁻¹, 248 mAh g⁻¹ and 241 mAh g⁻¹,
313 respectively (corresponding to 0.76, 0.74 and 0.72 Li⁺ per formula unit), in comparison with 234
314 mAh g⁻¹ (corresponding to 0.70 Li⁺ per formula unit) for TiO₂. Under 1C rate, the samples Ti_{1-x-}
315 y□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} prepared at 90 °C, 110 °C and 130 °C maintain high discharge capacities of
316 229 mAh g⁻¹, 208 mAh g⁻¹ and 174 mAh g⁻¹, respectively (corresponding to 0.68, 0.62 and 0.52
317 Li⁺ per formula unit). In contrast, a capacity decreases down to 110 mAh g⁻¹ (corresponding to
318 0.33 Li⁺ per formula unit) is observed for TiO₂. 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_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} 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 TiO₂ anatase after 500 cycles.

323 **Intercalation mechanism.**

324 The lithium intercalation mechanism that takes place in anatase Ti_{1-x-y}□_{x+y}O_{2-4(x+y)}F_{4x}(OH)_{4y} and
325 TiO₂ 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 TiO₂ corresponding to the phase transition from
328 tetragonal to orthorhombic Li-rich phase.⁴²⁻⁴⁴ 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 vacancies⁷ acting as additional sites for lithium ions that can minimize the formation of the
332 edge-shared LiO_6 octahedra driving the phase transition.²² In this study, anatase TiO_2 and 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.⁴⁵

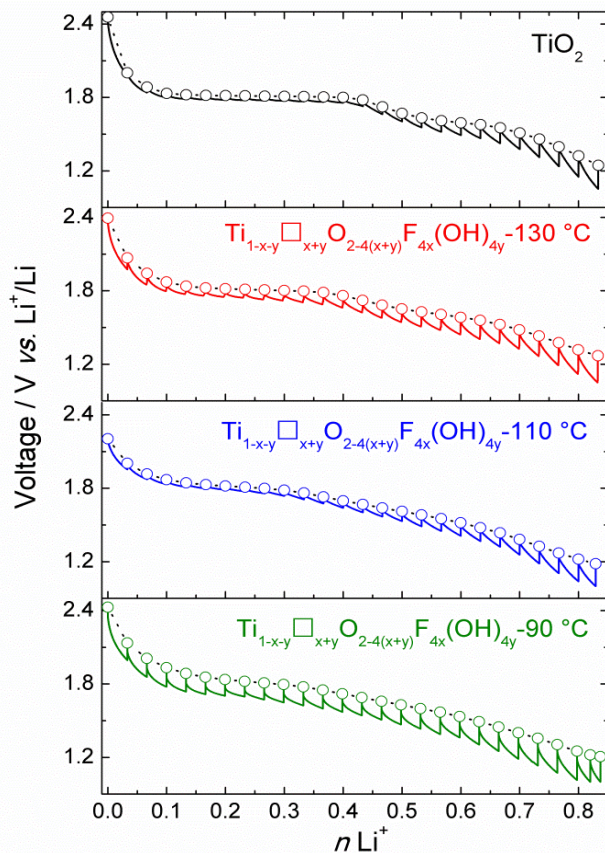


336

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

338 (e) long cycling performance at 1C rate for anatase TiO₂ and Ti_{1-x-y}O_{2-4(x+y)}F_{4x}(OH)_{4y} 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 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}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

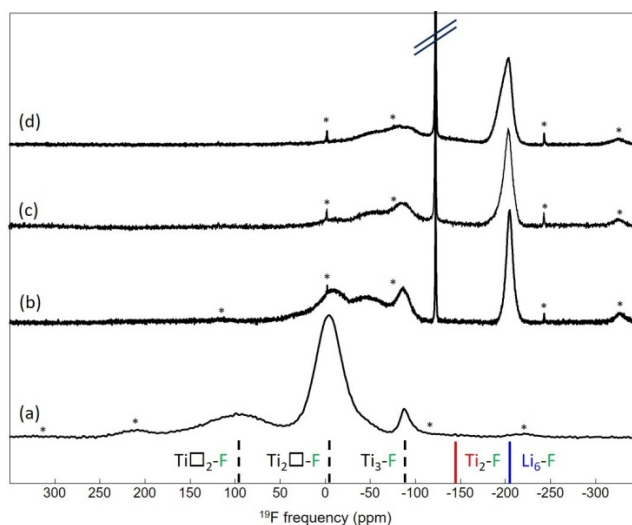
347 chemical composition from $\text{Ti}_{0.69}\square_{0.31}\text{O}_{0.76}\text{F}_{0.48}(\text{OH})_{0.76}$ to $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$.² **Figure 7**

348 shows the ^{19}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 Li^+ per

350 formula unit (**Figures 7b-d**). ^7Li solid state MAS NMR spectra of the chemically lithiated samples

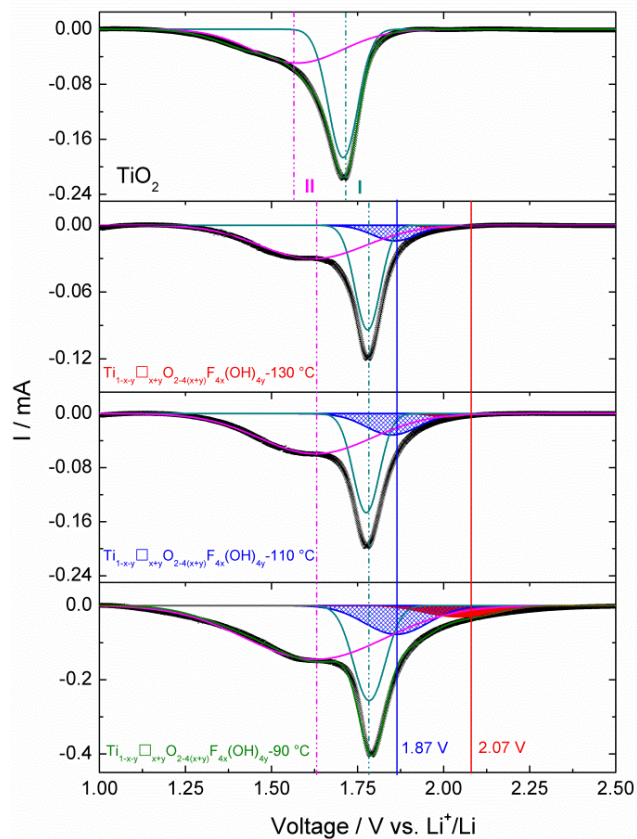
351 showed that the signal increases when the concentration of n-butyl lithium increases
352 confirming the increasing insertion of lithium (**Figure S5, Supporting Information**). Moreover,
353 we note the presence of LiF upon lithiation as revealed by X-ray diffraction analysis (**Figure S10,**
354 **Supporting Information**). The ^{19}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 F^- ions which suggest that chemical lithiation damages
357 the material. Based on the ^{19}F isotropic chemical shift (δ_{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)⁴⁶ and in TiF_3 (-144.8
359 ppm, $\text{Ti}^{\text{III}}_2\text{-F}$)⁴⁷ and on the decrease of the δ_{iso} value of fluoride anions when the number of
360 surrounding cations increases, the insertion of Li^+ ion in a titanium vacancy and/or in an
361 interstitial site and the reduction of a Ti^{4+} ion into a Ti^{3+} ion are both expected to induce a
362 decrease of the δ_{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 Li^+ per
365 formula unit and from 0.5 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}F NMR spectra, the
368 assignment of the NMR lines is complex and could not be achieved.



369
 370 **Figure 7.** ^{19}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 Li^+ per formula unit samples) (34 kHz). The
 372 asterisks indicate the main spinning sidebands. The dashed lines indicate the ^{19}F d_{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}F d_{iso} values of the $\text{Ti}^{\text{III}}_2\text{-F}$ environment in TiF_3 and the $\text{Li}_6\text{-F}$ environment in LiF . Ti^{IV} are in
 375 black and Ti^{III} are in red. The narrow lines observed on the spectra of the lithiated samples are
 376 assigned to adsorbed 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 TiO_2 . A slow-scan rate of 0.05 mV s^{-1} at the condition approaching equilibrium was applied,
 380 which allows excluding the capacitive contribution.⁴⁸ **Figure 8** shows the anodic part of the Li
 381 insertion process obtained after one activating cycle. For anatase TiO_2 , the cyclic
 382 voltammogram was reconstructed using two signals (signal I and II) at 1.71 and 1.56 V vs. Li^+/Li .
 383 The higher redox potential corresponds to the lithium insertion reaction in the interstitial sites
 384 of anatase.⁴⁹ 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 $\text{Li}_{0.5}\text{TiO}_2$.⁵⁰
 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.

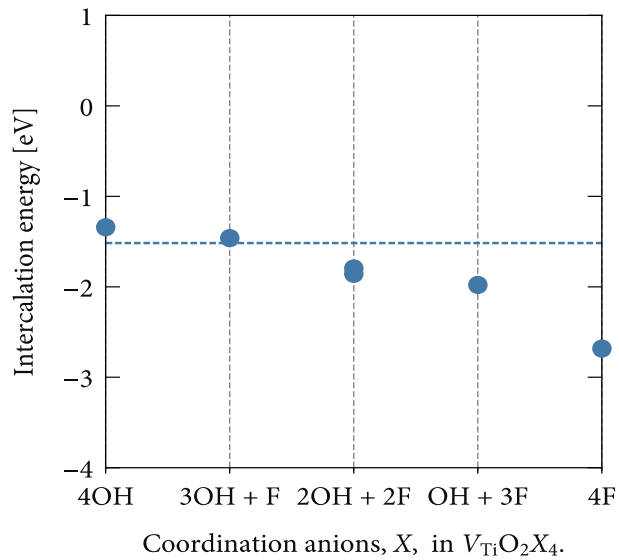


394

395 **Figure 8.** Slow scanning liner sweep voltammetries of 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 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 TiO_2 , and at titanium vacancies in fluorine-substituted anatase TiO_2 .^{7, 24}
402 For Li insertion into stoichiometric anatase, we found intercalation energy of -1.23 eV. For the
403 cation-deficient anatase 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 [²⁷]).
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.⁵¹

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 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}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 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 Li^+ in both 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.⁵²⁻⁵³ The
 429 variation of the diffusion coefficients as a function of the Li^+ concentration was plotted in **Figures**
 430 **10b** and **e**.

431 At the early stage of lithiation of anatase TiO_2 , the diffusion coefficient decreases from $8.3 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ 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
432 the reduction of Ti^{4+} causing the progressive shortening of the O-O pairs through which Li^+
433 diffuses, further increasing the site migration barriers.⁵⁴ Upon increasing x to 0.5 Li^+ , the diffusion
434 coefficient increases back to $2.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ which is caused by the structural transition toward
435 the ordered lithiated orthorhombic phase. Thereafter, it further decreases during the solid
436 solution lithiation in the orthorhombic phase. Finally, we observed a subsequent increase of the
437 diffusion coefficient to $9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ which can be related to a second phase transition toward
438 the Li-rich tetragonal phase. We note that the diffusion coefficients obtained in this study differ
439 from the literature values due to the different thickness of the electrode films. In the case of
440 $\text{Ti}_{0.78}\square_{0.22}\text{O}_{1.12}\text{F}_{0.40}(\text{OH})_{0.48}$, the evolution of the lithium diffusion coefficient showed less
441 pronounced variation. At the early stage of lithiation, the diffusion coefficient decreases from 8.0
442 $\times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ 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
443 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 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 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 TiO₂ 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.⁵⁵ 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 TiO₂Li _{n} ; 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 (ΔG_{Li}^E) of formation of the lithium insertion in the substrate, which is the heart of the battery
471 operation. For a compound TiO₂Li _{n} , the insertion of one mole of Li, i.e. formation of (TiO₂) _{z} Li (with
472 $z = \frac{1}{n}$) is

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

474 the more negative ΔG_{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,⁵⁶ 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,⁵⁷ and φ is a damping factor introduced to take

481 account of the thermodynamic properties of the system.^{55, 58}

482 In previous papers⁵⁹⁻⁶⁰, 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. ψ_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 ψ_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-TiO₂ system, (**Figure**
495 **10a**) correspond to the composition TiO₂Li_{0.65} and TiO₂Li_{0.3}.

496 In order to consider the implementation of one mole of lithium, the compounds can be written
497 as Li(TiO₂)_{1.54} and Li(TiO₂)_{3.33}. 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 curves⁵²⁻⁵³ (**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

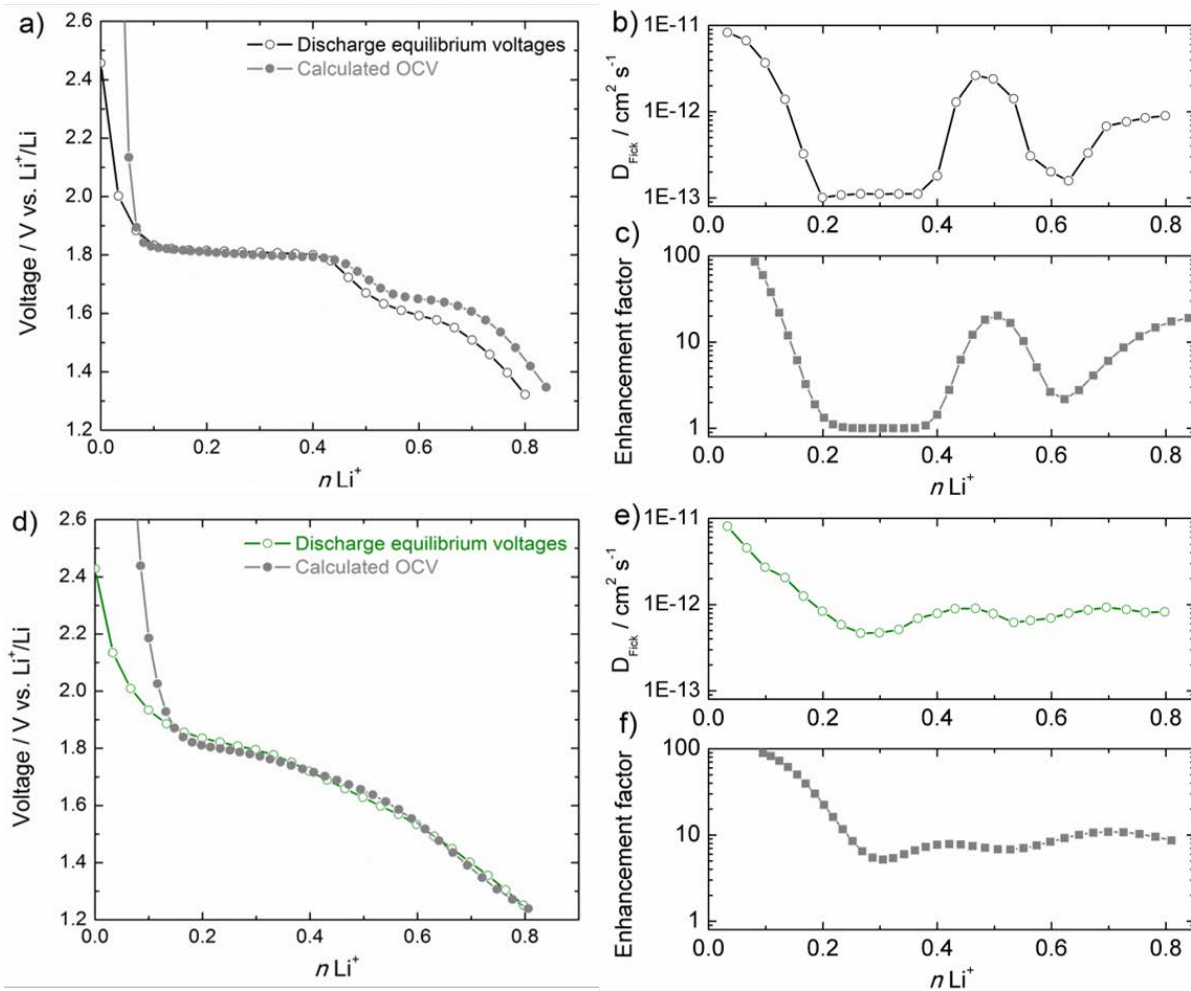
$$510 \quad D_{Fick} = \zeta D \quad (8)$$

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-TiO₂ 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 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}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 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.⁴⁷

545 ASSOCIATED CONTENT

546 **Supporting Information.** Additional information such as XRD patterns and fits of ^{19}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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560 **Notes**

561 The authors declare no competing financial interests.

562 **ACKNOWLEDGMENT**

563 The research leading to these results has received funding from the French National Research
564 Agency under Idex@Sorbonne University for the Future Investments program (No. ANR-11-
565 IDEX-0004-02). Region Ile-de-France is acknowledged for partial funding of the XPS equipment.

566 This research used resources of the Advanced Photon Source, a U.S. Department of Energy
567 (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne
568 National Laboratory under Contract No. DE-AC02-06CH11357. B. J. M. acknowledges support
569 from the Royal Society (UF130329). DFT calculations were performed using the Balena High

570 Performance Computing Service at the University of Bath, and using the ARCHER
571 supercomputer, with access through membership of the UK's HPC Materials Chemistry
572 Consortium, funded by EPSRC grant EP/L000202.

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