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1 **Kinetic insight into the electrochemical lithium insertion process**
2 **in the puckered-layer γ' -V₂O₅ polymorph**

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6 **Abstract**

7 Cycling properties, rate capability performance and kinetic parameters for Li insertion in the
8 puckered γ' -V₂O₅ host lattice are reported here in the 4.0 V- 2.5 V voltage window
9 corresponding to $0 \leq x \leq 1$ in γ -Li_xV₂O₅. Whereas a high reversible behaviour and good
10 cycling performance are achieved (135 mAh g⁻¹ after 50 cycles at C/10), the rate capability
11 study shows a rapid increase in the discharge-charge hysteresis with the current density,
12 impeding the recovering of high capacity values even at C/2 rate. The kinetics of the
13 electrochemical lithium insertion reaction in γ' -V₂O₅ has been investigated by ac impedance
14 spectroscopy and discussed in the light of the structural mechanism. The chemical diffusion
15 coefficient D_{Li} is found constant in the $0 \leq x < 0.4$ biphasic region while lithium ions more
16 rapidly diffuse in the solid solution domain $0.4 \leq x \leq 1$ with greater D_{Li} values by one or two
17 orders of magnitude (around 10⁻⁹ cm² s⁻¹). An increase in charge transfer resistance and
18 cathode impedance characterizes nevertheless the second part of the discharge. These findings
19 explain the limitations in the reaction kinetics in the micrometric γ' -V₂O₅ cathode material
20 and give directions toward improved performance.

21
22 **Keywords:** γ' -V₂O₅, cathode material, kinetics, Li diffusion, AC impedance spectroscopy

23

24 **Introduction**

25 The α - V_2O_5 polymorph was among the first transition metal oxide identified as Li
26 intercalation compounds [1]. Its interest stems from a layered structure made of V_2O_5 sheets
27 with Van der Waals interactions between oxide planes promoting facile insertion reactions. In
28 addition, the presence of 2 V^{5+} ions allows a high capacity to be reached, i. e. $\approx 150 \text{ mAh g}^{-1}$
29 and 300 mAh g^{-1} obtained for $0 < x \leq 1$ (3.5 V - 2.5 V potential window) and $0 < x \leq 2$ (3.5 V
30 - 2.3 V potential window), respectively. Quite logically its possible application as cathode
31 material in secondary Li batteries and Li-ion batteries prompted many researchers to work on
32 the electrochemical properties of α - V_2O_5 [1-10] with a special focus on the associate
33 structural behaviour [4, 6-18]. Some results emerging from these works have allowed to
34 establish the $Li_xV_2O_5$ phase diagram with $0 < x < 2$ in which the successive emergence of
35 more or less distorted lithiated phases is described [2, 4, 7-9, 18]. In addition, the Li transport
36 kinetics in this canonical intercalation host lattice has been deeply investigated as a function
37 of x in $Li_xV_2O_5$ [19-25].

38 Recent studies based on DFT calculations have outlined the interest of metastable phases
39 obtained from topochemical removal of cations from the appropriate $M_xV_2O_5$ bronzes ($M =$
40 Li, Cu, Ag) [26, 27]. A higher open circuit voltage combined with lower diffusion barriers are
41 predicted as specific features of such cation-free metastable phases. Among the V_2O_5
42 polymorphs, the γ' - V_2O_5 has been firstly mentioned to coexist with α - V_2O_5 after a discharge-
43 charge cycle in the 3.8 V-2.15 V potential range [8, 28, 29]. This γ' - V_2O_5 polymorph is
44 indeed the charge product of the highly puckered γ - LiV_2O_5 phase irreversibly produced upon
45 discharge at 2.3 V. Its formation is responsible for a voltage enhancement of ≈ 0.2 V related
46 to the presence of two additional voltage plateaus at 3.6 V and 3.5 V upon cycling [8].
47 However, even when the chemical synthesis of γ' - V_2O_5 was early proposed [28], only its
48 lithiated γ - LiV_2O_5 has been investigated as positive electrode material for Li-ion batteries [29-
49 35]. Various synthesis ways of γ - LiV_2O_5 were used such as carbothermal reduction at 600°C
50 [30], precipitation reaction [31], hydrothermal or solvothermal routes [32-34], sol-gel
51 templating route [35] leading to controversial and scattered results especially in the large 4 V-
52 2 V window.

53 Surprisingly, the interest in the γ' - V_2O_5 polymorph toward insertion reactions has been firstly
54 illustrated in the case of sodium insertion [36-39]. Indeed, sodium is reversibly
55 accommodated in γ' - V_2O_5 at a high working voltage of 3.3 V vs Na^+/Na , remarkably at the

56 same energy level as lithium insertion [36]. The strong puckering of the oxide layers in γ' -
57 V_2O_5 probably promotes insertion reactions compared to the α - V_2O_5 form. It is one of the
58 reasons for considering the γ' -polymorph as an interesting candidate as cathode material for
59 Li batteries.

60 The electrochemical and structural study of γ' - V_2O_5 toward Li insertion has been very recently
61 reported [40]. A detailed XRD and Raman spectroscopy study allowed to establish the
62 complete phase diagram of the Li/ γ' - V_2O_5 system in the widest 4.00 V- 2.15 V voltage
63 window. This pioneering work unveiled the interest of the corrugated γ' - V_2O_5 framework to
64 accommodate a large amount of Li ions (up to 2 Li/mole of oxide). The typical discharge
65 exhibits two pairs of well-defined reversible steps at 3.58/3.47 V and 2.42/2.36 V separated
66 by a sharp potential drop of about 1 V. A strong influence of the depth of discharge on the
67 cycling performance was outlined [40]. In the widest 4.00 V- 2.15 V voltage window ($0 < x \leq$
68 1.94), a high capacity of 285 mAh g^{-1} was reported. However, severe capacity fading upon
69 cycling was observed in this voltage range due to the emergence of the fully lithiated ζ -
70 $Li_{\approx 2}V_2O_5$ phase at 2.36 V. By reducing the voltage limits to 4.0 V- 2.4 V region ($0 < x \leq 1.3$),
71 an attractive capacity of 185 mAh g^{-1} was reached, but still associated to a continuous
72 capacity fading. Furthermore, the sharp potential drop of 1 V around $x = 1$ constitutes another
73 important drawback in the 4.0 V- 2.4 V voltage range.

74 The present paper focuses on the electrochemical properties of γ' - V_2O_5 in the high voltage
75 window corresponding to the exchange of 1 Li^+ /mole of oxide (147 mAh g^{-1}). Cycling
76 properties, rate capability behaviour and kinetics parameters for Li insertion in γ' - V_2O_5 are
77 reported here in the 4.0 V - 2.5 V voltage window. The kinetic data are discussed at the light
78 of the structural mechanism recently evidenced for γ' - V_2O_5 .

79

80 **Experimental**

81 γ' - V_2O_5 is obtained by chemical oxidation of γ - LiV_2O_5 synthesized by the carbothermal
82 reduction method [30]. A solution of NO_2BF_4 (solid Alfa Aesar 96%) in acetonitrile, molar
83 ratio 1:4, allows the complete Li removal from the γ - LiV_2O_5 host structure. The solution is
84 maintained under stirring at room temperature for 24h. After reaction and decantation, the
85 supernatant liquid is removed by pipetting. After three successive washing steps with

86 acetonitrile, the powder is then vacuum dried at 70°C for 24h. The powder color changing
87 from black to orange confirms the complete lithium deintercalation. Electrochemical titration
88 and chemical redox titration confirmed the 5+ oxidation state of vanadium in γ' -V₂O₅.
89 Two-electrode coin cells (CR 2032) with lithium disk as reference and auxiliary electrodes
90 were used to perform electrochemical studies. γ' -V₂O₅ positive electrode was prepared by
91 mixing 80 wt % of active material, 7.5 wt% of acetylene black, 7.5 wt% of graphite and
92 5wt% of teflon as binder agent. About 10 mg of this mixture was pressed on a stainless steel
93 grid (14 mm diam., 0.35 mm thick) under a pressure of 5 tons per cm². The separator consists
94 of three glass Whatman microfiber filters soaked by a solution of 1M LiClO₄ in propylene
95 carbonate (PC) as electrolyte. All the coin cells were assembled in an argon-filled glove box
96 where water and oxygen concentrations were kept less than 1 ppm. Electrochemical
97 experiments were performed at ambient temperature using a VMP3 Biologic apparatus.
98 Impedance measurements were carried out in conventional three electrode cells under argon
99 atmosphere. The cell was filled with 1M LiClO₄ in propylene carbonate (PC). The positive
100 electrode was made of the active material in the same manner as the composite electrode used
101 in coin cell for cycling and rate capability experiments. Reference and counter electrodes
102 were made of Li wires in separate compartments filled up with electrolyte. The working
103 electrode composition was changed by coulometric titration using a low current density
104 corresponding to a C/20 rate. Equilibrium was considered as reached when the open circuit
105 voltage remained stable (< 0.2 mV for 1h). A discharge curve performed at very low rate
106 (C/100) is considered as the OCV curve. Impedance measurements were performed in the
107 frequency range 4×10^4 to 0.5×10^{-3} Hz with a VMP3 Biologic Multipotentiostat-Galvanostat
108 apparatus. The excitation signal was 10 mV peak to peak. All these electrochemical
109 measurements were performed in an argon-filled glove box.
110 XRD measurements were performed using a Panalytical X'pert pro diffractometer equipped
111 with an X'celerator detector and a Co K α radiation (wavelength $\lambda = 1.7889$ Å).

112

113

114

115 **Results and discussion**

116 The X-ray diffraction pattern of the γ' -V₂O₅ powder is shown in **Figure 1**. All the diffraction
117 lines can be indexed on the basis of an orthorhombic symmetry (space group *Pnma*) with the
118 following unit cell parameters: $a = 9.95 \text{ \AA}$; $b = 3.59 \text{ \AA}$; $c = 10.04 \text{ \AA}$. These values are in good
119 accord with those previously reported [28, 36-38]. The γ' -V₂O₅ powder is characterized by a
120 high *00l* preferred orientation corresponding to the stacking of platelets along the *c* axis. SEM
121 micrograph (see inset in **Figure 1**) indicates big aggregates made of platelets of a few μm .
122 The corresponding layered structure is composed of infinite ribbons parallel to the *b* axis
123 made of VO₅ edges-sharing distorted pyramids alternatively up and down, as illustrated in
124 **Figure 2**. These ribbons are linked to each other along the *a*- direction by one corner's
125 oxygen, leading to folded layers laying in the (*ab*) plane and stacked along the *c*- axis.

126
127 A typical discharge curve performed at very low current density (C/100) allows to get a quasi-
128 equilibrium voltage-composition curve E vs x in γ -Li_xV₂O₅ (**Figure 3**). From the very first
129 lithium ions, the potential rapidly decreases from 4 V to 3.62 V and remains stable near 3.6 V
130 in the $0.02 < x < 0.4$ lithium composition range. Then, a potential decline from 3.6 to 3.55 V
131 is observed for $0.4 < x < 0.5$ followed by a less sloping decrease from 3.55 V to 3.45 V in the
132 $0.5 < x < 0.92$ composition range. For higher Li contents, a sharp potential drop up to 2.5 V
133 leads to the full lithiation of γ' -V₂O₅ into γ -LiV₂O₅. The maximum specific capacity delivered
134 by γ' -V₂O₅ in this voltage window reaches the value of 147 mAh g⁻¹.

135
136 The discharge-charge curves of γ' -V₂O₅ performed at C/10 exhibit a similar profile,
137 consisting in two steps located at 3.58 V and 3.47 V (**Figure 4**). The first discharge process
138 involves a specific capacity of 145 mAh g⁻¹. Then, a quantitative charge process allows the
139 extraction of 1 lithium ion from γ -LiV₂O₅ in two steps located at 3.65 V and 3.52 V, leading
140 to a symmetric charge-discharge profile. The cycling experiments (see inset in **Figure 4**)
141 indicate a high reversible behaviour and a slow capacity decline limited to 6% with still 135
142 mAh g⁻¹ recovered after 50 cycles. This behaviour competes well with the value of 125 mAh
143 g⁻¹ reported at C/5 for γ -LiV₂O₅ prepared by the carbothermal reduction method [30] and
144 outperforms the capacities of 100-110 mAh g⁻¹ and 57 mAh g⁻¹ reported for γ -LiV₂O₅
145 prepared respectively by a precipitation technique [31] and a direct sol-gel soft templating
146 method [35].

147

148 The influence of the C rate on the discharge-charge profile of γ' -V₂O₅ is reported in **Figure 5**.
149 At C/5 and C/10, similar capacities are achieved, i.e. 145 and 140 mAh g⁻¹ respectively, and a
150 value of still 130 mAh g⁻¹ can be recovered at C/2. However, increasing the current density in
151 the C/2-5C range leads an increase in the polarization (**Figure 5a**). The hysteresis value of
152 200 mV at C/2 greatly increases with higher current densities, which impedes the recovering
153 of high efficiency when the C rate exceeds 1C: discharge capacities of 100, 80 and 40 mAh g⁻¹
154 are obtained at C, 2C and 5C respectively (**Figure 5b**). These findings suggest some kinetic
155 limitations occur and prompted us to examine in details the electrochemical kinetics of Li
156 insertion into γ' -V₂O₅.

157
158 The typical AC impedance diagrams obtained for γ -Li_xV₂O₅ electrodes are reported in **Figure**
159 **6**. The conventional equivalent circuit developed for intercalation compounds was used
160 [41]. Two kinds of Nyquist diagrams can be observed. For $0 < x \leq 0.6$ (**Figure 6a**), all the
161 spectra practically superimpose, showing a well-defined charge transfer semi-circle centered
162 at 130-160 Hz followed by a straight line with a phase angle of 45° up to 0.5 mHz
163 corresponding to the Warburg region (when $\omega \gg 2D_{Li}/L^2$, L being the maximum length of
164 the diffusion pathway) [41]. For higher Li contents, i.e. $0.6 < x \leq 1$, all the diagrams
165 superimpose again but no reliable Warburg region can be defined (**Figure 6b**). Instead, the
166 well-defined high frequency semi-circle is followed by a quasi-vertical line corresponding to
167 the finite diffusion ($\omega \ll 2D_{Li}/L^2$). This behaviour reveals a faster Li diffusion in the richest
168 Li composition range. Another discrepancy concerns the lower value of the characteristic
169 frequency of charge transfer, of 100 Hz in the $0.6 < x \leq 1$ composition range vs. 160-130 Hz
170 for $0 < x \leq 0.6$. Finally, the cathode impedance is significantly larger in the second half of the
171 discharge.

172
173 The main kinetic parameters of the Li insertion reaction into γ' -V₂O₅ like the cathode
174 impedance $|Z|$, the charge transfer resistance R_{ct} and the double layer capacitance C_{dl} are
175 reported in **Figure 7** as a function of the Li content x. A crucial difference is seen between the
176 two composition ranges for the cathode impedance : $|Z|$ slightly decreases with x between
177 180 and 140 Ω for $x \leq 0.6$ but then strongly increases by a factor 2 for $x > 0.6$ and more to
178 reach 475 Ω for γ -LiV₂O₅ (**Figure 7a**). As seen from **Figure 7b**, the charge transfer resistance
179 R_{ct} remains constant around $\approx 55 \Omega$ in the first half of the Li insertion process ($0 < x \leq 0.4$)
180 with an exchange current density of 0.46 mA cm⁻², in line with usual j^0 values found for other

181 transition metal oxides [20, 25, 41, 42]. This constant R_{ct} value corresponds to a biphasic
182 region where γ' - V_2O_5 and γ - $Li_{0.4}V_2O_5$ coexist [40]. For $x > 0.5$, the kinetics of charge transfer
183 is however progressively slowed with further lithiation, as indicated by the continuous R_{ct}
184 increase to reach 75Ω for γ - LiV_2O_5 ($j^\circ = 0.34 \text{ mA/cm}^2$). The double layer capacitance C_{dl}
185 remains stable, around $18 \mu\text{F cm}^{-2}$ in the first part of the discharge, to reach $24 \mu\text{F cm}^{-2}$ in the
186 second half (**Figure 7c**).

187

188 These electrochemical results have been interpreted in the light of the structural data recently
189 reported during the electrochemical Li insertion in γ' - V_2O_5 [40]. It was shown that the
190 discharge-charge profile in the $0 < x \leq 1$ composition range corresponds to a two phase
191 behaviour for $0 < x < 0.4$ followed by a wide single phase γ - $Li_xV_2O_5$ domain for $0.4 \leq x \leq 1$.
192 These structural changes are associated to a weak unit cell volume expansion of only 4%.
193 Clearly, the present study evidences a change in the cathode impedance $|Z|$, the charge
194 transfer resistance R_{ct} and the double layer capacitance C_{dl} in the second half of the discharge,
195 i.e. from $x \approx 0.5$. This change in the kinetic parameters characterizes the Li enrichment of the
196 γ - $Li_{0.4}V_2O_5$ phase according to a solid solution behaviour to progressively reach the γ - LiV_2O_5
197 phase [40]. The C_{dl} increase can be explained by the slight volume expansion of the active
198 material of a few percent, leading to a moderate increase in the electrochemical surface area.
199 The significant increase in both the charge transfer resistance and electrode impedance
200 suggests that the growing V^{4+}/V^{5+} ratio disadvantages the rate of charge transfer, because of a
201 decrease in the electronic conduction. Such an assumption is supported by the
202 crystallographic data reported for the two types of vanadium environment available in the Li-
203 free γ' - V_2O_5 phase and the lithiated γ - LiV_2O_5 phase [39, 40]. Indeed, V_aO_5 and V_bO_5
204 pyramids volumes are similar in γ' - V_2O_5 (4.461 \AA^3 and 4.531 \AA^3 , respectively), due to the
205 presence of V^{5+} ions in both polyhedra. Conversely, in γ - LiV_2O_5 , different values of
206 respectively 4.675 \AA^3 and 5.114 \AA^3 account for the existence of V^{5+} ions in V_aO_5 pyramids
207 and V^{4+} ions in V_bO_5 pyramids. This highly localized electron character highlighted in γ -
208 LiV_2O_5 is well correlated with the highest cathode impedance and charge transfer resistance
209 values observed for the $x = 1$ composition. Then, the upward trend of both parameters with x
210 suggests a progressive increase in the electron localization with the V^{4+}/V^{5+} ratio.

211 A reliable evaluation of the apparent lithium diffusion coefficient D_{Li} has been achieved over
212 the whole $0 < x \leq 1$ lithium composition range. In the first part of the discharge ($0 < x \leq 0.6$),

213 a Warburg domain can be reliably defined (see inset in **Figure 6a**). The numerical values of
 214 D_{Li} have been calculated from the analysis of the Warburg impedance plotted in the complex
 215 plane:

216 $-\text{Im } Z$ or $\text{Re } Z = A_w \omega^{-1/2}$, using equation (1) [41]:

$$217 \quad A_w = V_M \cdot (dE/dx)_x / F \sqrt{2} S D_{Li}^{1/2} \quad \omega \gg 2D_{Li}/L^2 \quad (\text{eq 1})$$

218 A_w is the Warburg prefactor, V_M is the molar volume of the compound ($V_M = 53.9 \text{ cm}^3 \cdot \text{mol}^{-1}$),
 219 S is the geometric surface area of the electrode (1 cm^2), $(dE/dx)_x$ is the slope, at fixed x , of the
 220 equilibrium potential composition curve (**Figure 3**).

221 For $0.6 < x \leq 1$, D_{Li} has been calculated from the limiting low frequency resistance R_L , using
 222 equation (2) [41]:

$$223 \quad R_L = (V_m/nFS) (dE/dx) (L/3D_{Li}) \quad \omega \ll 2D_{Li}/L^2 \quad (\text{eq 2})$$

224 L is the maximum length of the diffusion pathway, estimated to a few μm from SEM images,
 225 i.e., $L \approx 1.5 \cdot 10^{-4} \text{ cm}$. R_L is graphically determined from the intersection of the low frequency
 226 asymptote with the real axis after subtraction of electrolyte and charge transfer resistances
 227 (see inset in **Figure 6b**). R_L values of 24, 12, 13 and 8Ω are found for respectively $x = 0.7$,
 228 0.8, 0.9 and 1.

229

230 The resulting D_{Li} values in the $0 < x \leq 1$ composition range are plotted in **Figure 8**. The
 231 lowest D_{Li} values are found at the beginning of the reaction for $0 < x \leq 0.3$ around $10^{-12} \text{ cm}^2 \text{ s}^{-1}$
 232 ¹, i.e. practically in the $\gamma^{\prime}\text{-V}_2\text{O}_5/\gamma\text{-Li}_{0.4}\text{V}_2\text{O}_5$ biphasic region. Then, as soon as the first member
 233 of the monophasic region is formed ($x = 0.4$), Li transport is significantly promoted with
 234 values in the range 10^{-10} - $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ in spite of higher Li contents ($x = 0.4, 0.5$ and 0.6). In the
 235 second half of the discharge, the disappearance of the Warburg region at the benefit of the
 236 quasi-vertical line of the finite diffusion highlights a much faster diffusion kinetics. Assuming
 237 a L value of $\approx 1.5 \mu\text{m}$, D_{Li} is found to still increase from $2.4 \cdot 10^{-10}$ to $4.3 \cdot 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ from $x =$
 238 0.7 to $x = 1$. The order of magnitude between the two sets of data should be at least of one
 239 decade given the comparison of extrapolated limiting frequencies: in the order of 10^3 Hz
 240 when $0.1 \leq x \leq 0.6$ against a few dozen of mHz when $0.7 \leq x \leq 1$.

241 D_{Li} appears as constant in the biphasic region, i.e. when $x < 0.4$ while lithium ions more
 242 rapidly diffuse in the single-phase region $0.4 \leq x \leq 1$. It is worth noticing the present D_{Li}
 243 evolution evidenced for the puckered $\gamma^{\prime}\text{-V}_2\text{O}_5$ host lattice contrasts with the more complex
 244 variations of lithium diffusivity reported for the parent $\alpha\text{-V}_2\text{O}_5$ oxide [6, 19-21, 23, 24]. This

245 discrepancy can be related to the emergence of successive distorted phases during Li insertion
246 in α -V₂O₅ in the same $0 < x \leq 1$ composition range.

247

248 The higher Li diffusivity evidenced in the second part of the discharge indicates that the
249 capacity decline observed at higher C rate (**Figure 4**) could not be ascribed to diffusional
250 limitations but mainly to large cathode impedance and slowdown in the charge transfer
251 kinetics. Improvement of the rate capability must therefore comprise the optimization of these
252 two parameters. Substitutional or interstitial cation incorporation in γ' -V₂O₅ could be
253 envisioned to enhance the electronic conductivity. Combined with appropriate mastering of
254 the particle size and morphology, such strategies should allow optimizing the charge transfer
255 rate and taking advantage of the high Li mobility highlighted in γ' -V₂O₅.

256

257 **Conclusion**

258 The electrochemical properties of the puckered γ' -V₂O₅ polymorph toward Li insertion are
259 reported here in the high voltage window corresponding to the exchange of 1 Li⁺/mole of
260 oxide (4.0 V - 2.5 V). The corresponding specific capacity of 147 mAh g⁻¹ is interestingly
261 available at a higher working voltage than α -V₂O₅ (+ 0.2 V). Two well-defined steps at 3.6 V
262 and 3.5 V account for the formation of the lithiated γ -LiV₂O₅ phase. A good cycle life is
263 achieved at C/10 rate with still 130 mAh g⁻¹ recovered after 50 cycles. In addition, the rate
264 capability is satisfactory with specific capacities of 100 mAh g⁻¹ and 80 mAh g⁻¹ at C and 2C
265 rates, respectively. The kinetic parameters for the electrochemical Li insertion reaction have
266 been investigated using AC impedance measurements. A reliable determination of the
267 chemical diffusion coefficient is made over the whole $0 \leq x \leq 1$ lithium composition range,
268 using either the Warburg domain or the limiting resistance. This study highlights the diffusion
269 rate is slower in the first half of the discharge ($x < 0.4$) corresponding to a diphasic region
270 while the solid solution domain ($0.4 < x \leq 1$) is characterized by higher D_{Li} values by one or
271 two orders of magnitude (around 10⁻⁹ cm² s⁻¹). In the second part of the discharge, the kinetics
272 of the reaction is however impeded by a slowdown in the electron transfer kinetics, as
273 illustrated by the increase in charge transfer resistance R_{ct} and cathode impedance. The highly
274 localized electron character in γ -LiV₂O₅ accounts probably for the highest cathode impedance
275 and charge transfer resistance values observed for the $x = 1$ composition. The kinetic
276 behaviour revealed in this work for γ' -V₂O₅ differs from that of the unfolded parent α -V₂O₅

277 oxide showing large and complex D_{Li} variations. Such discrepancy originates probably from
278 different structural mechanisms upon lithiation of the two polymorphs, i.e. minimal structural
279 changes involving a large solid solution domain for the puckered-layered V_2O_5 polymorph vs.
280 successive phase transitions toward distorted ϵ - and δ - $Li_xV_2O_5$ for α - V_2O_5 . Further efforts
281 made in direction of particle size mastering and morphology have already allowed a great
282 enhancement in the rate capability performance. These results will be published very soon.

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Figure captions

- Figure 1.** X-ray diffraction pattern of γ' - V_2O_5 . Inset: SEM micrograph of the γ' - V_2O_5 powder
- Figure 2.** Crystal structure of γ' - V_2O_5
- Figure 3.** Discharge curve of γ' - V_2O_5 at low current density (C/100 rate)
- Figure 4.** Discharge-charge curves of γ' - V_2O_5 in the 4.00 V- 2.50 V potential range. C/10 rate
- Figure 5.** Influence of the C rate on the discharge-charge profiles of γ' - V_2O_5 (a) Discharge capacity as a function of the C-rate (b). C/10-5C range
- Figure 6.** AC impedance diagrams for γ - $Li_xV_2O_5$ electrodes (a) $0 \leq x \leq 0.6$; (b) $0.7 \leq x \leq 1$
- Figure 7.** Evolution of the cathode impedance $|Z|$ (a), the charge transfer resistance R_{ct} (b) and the double layer capacitance C_{dl} (c) in γ - $Li_xV_2O_5$ ($0 < x \leq 1$).
- Figure 8.** Evolution of the apparent chemical diffusion coefficient of lithium D_{Li} as a function of x in γ - $Li_xV_2O_5$. The double dashed line separates the composition domain in which D_{Li} has been determined using either eq (1) or eq (2).

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Figures

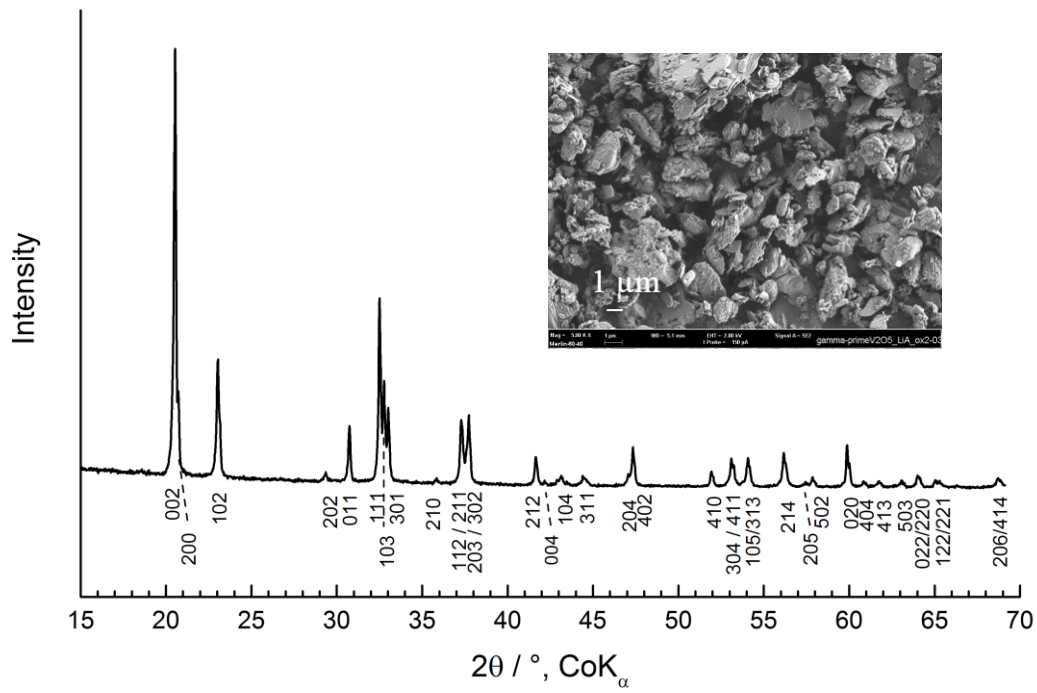


Figure 1. X-ray diffraction pattern of γ' - V_2O_5 . Inset: SEM micrograph of the γ' - V_2O_5 powder

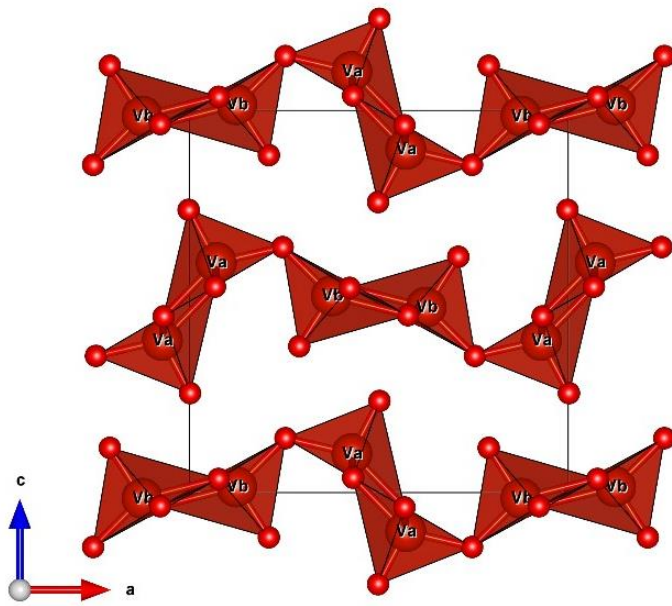


Figure 2. Crystal structure of γ' -V₂O₅

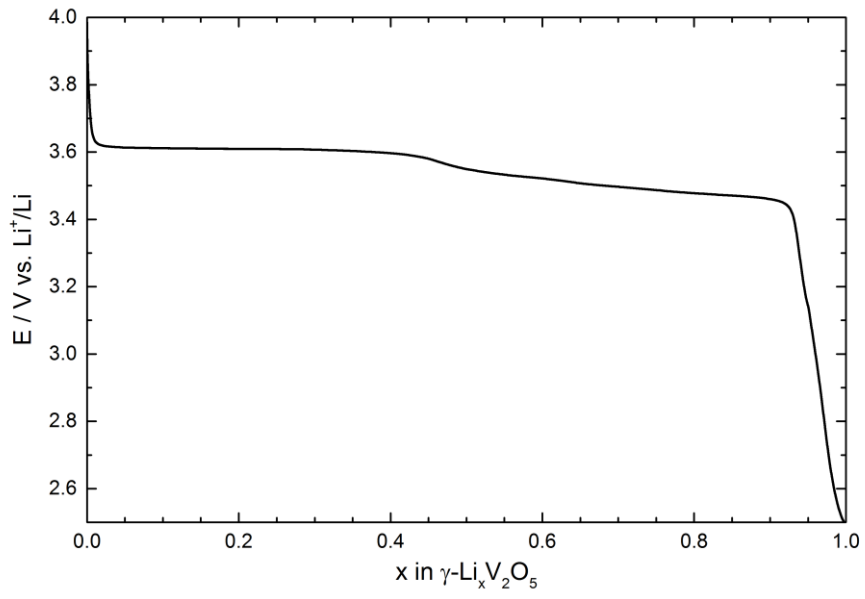


Figure 3. Discharge curve of γ' - V_2O_5 at low current density (C/100 rate)

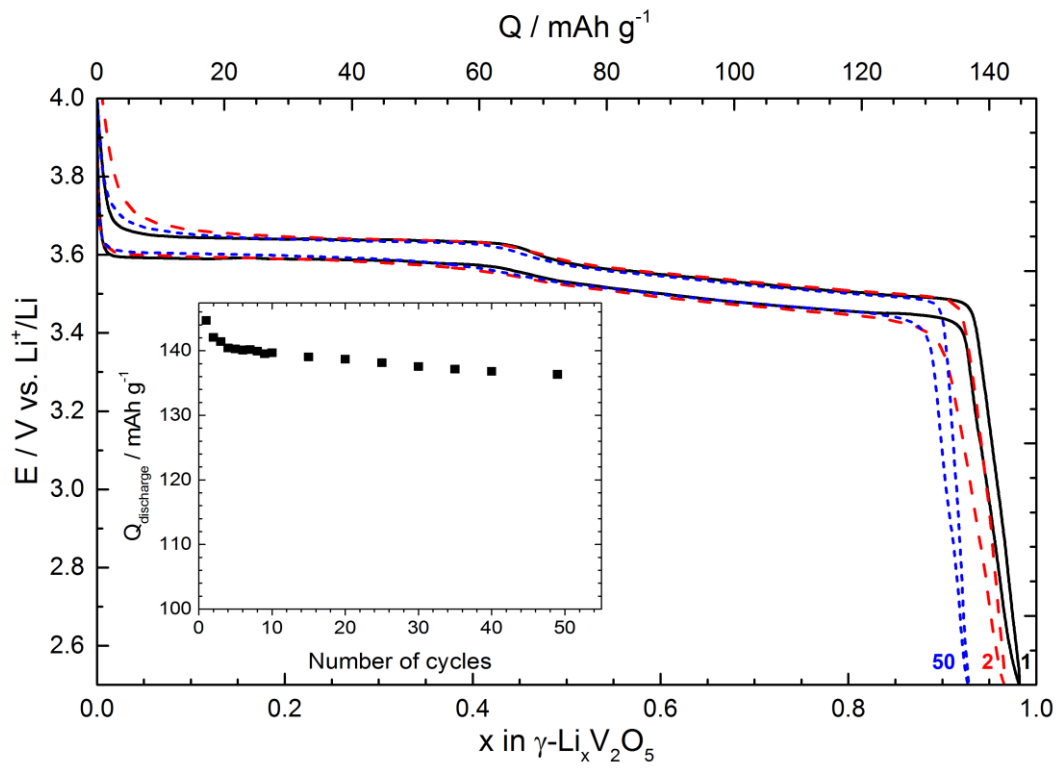


Figure 4. Discharge-charge curves of γ' - V_2O_5 in the 4.00 V- 2.50 V potential range. C/10 rate

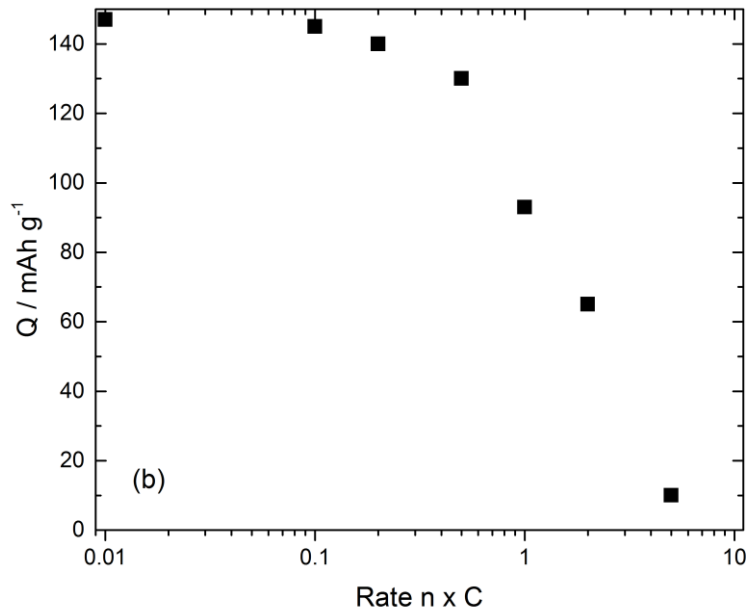
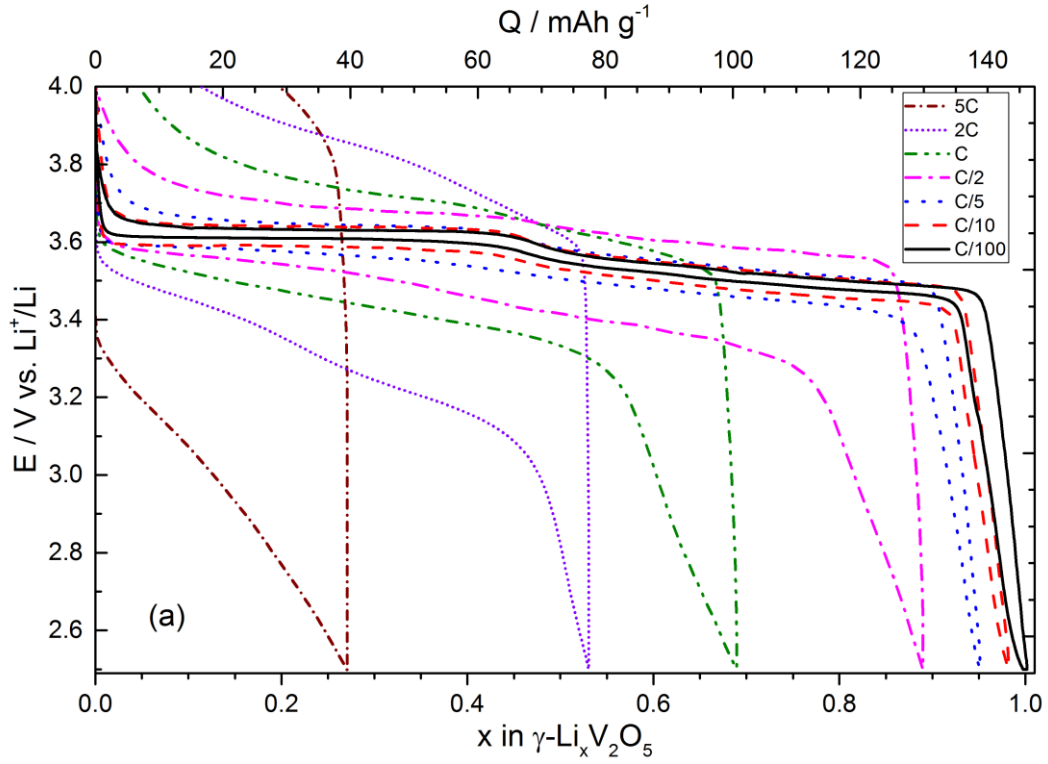


Figure 5. Influence of the C rate on the discharge-charge profiles of γ' - V_2O_5 (a) Discharge capacity as a function of the C-rate (b). C/10-5C range

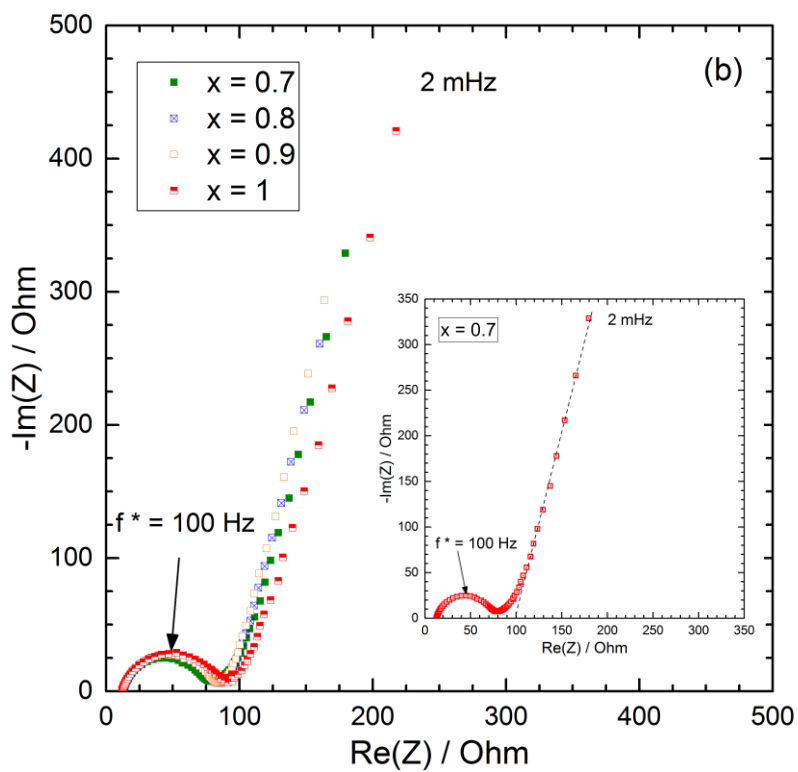
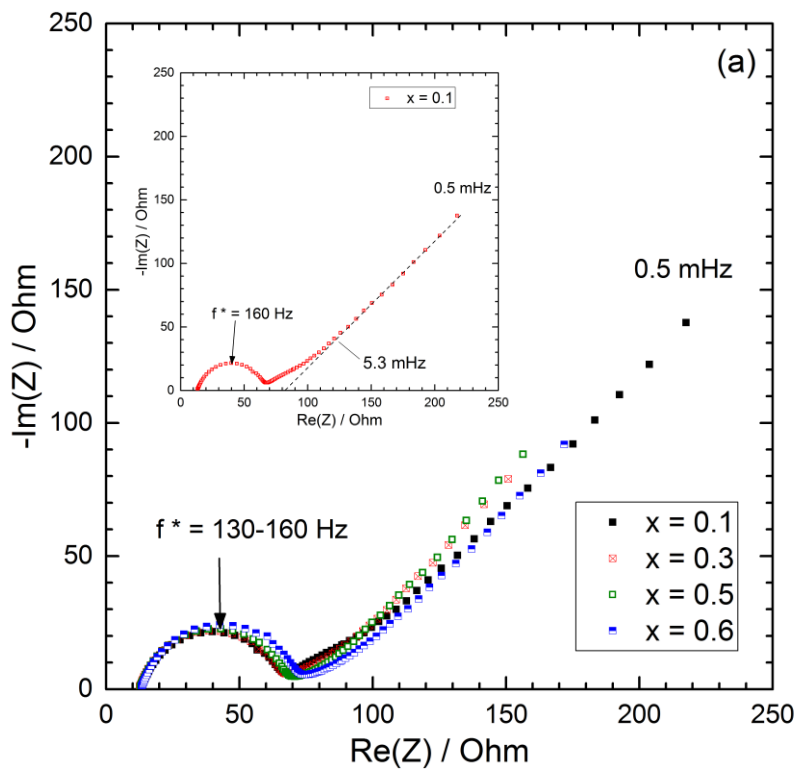


Figure 6. AC impedance diagrams for γ - $\text{Li}_x\text{V}_2\text{O}_5$ electrodes (a) $0 \leq x \leq 0.6$; (b) $0.7 \leq x \leq 1$

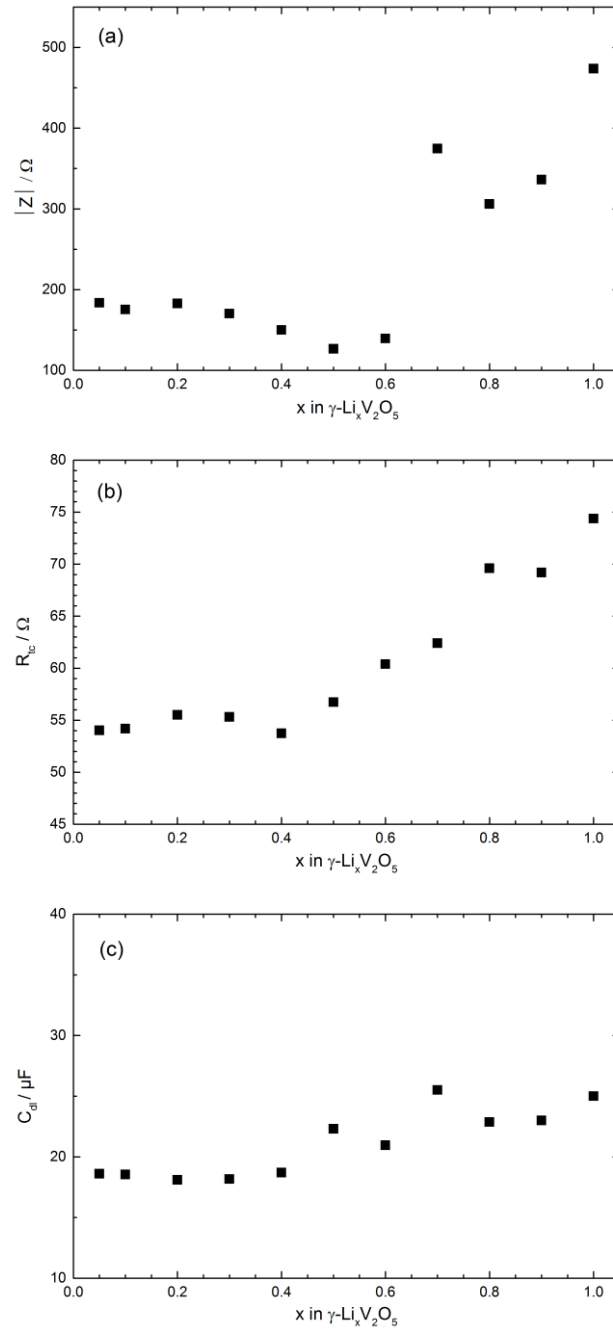


Figure 7. Evolution of the cathode impedance $|Z|$ (a), the charge transfer resistance R_{ct} (b) and the double layer capacitance C_{dl} (c) in $\gamma\text{-Li}_x\text{V}_2\text{O}_5$ ($0 < x \leq 1$).

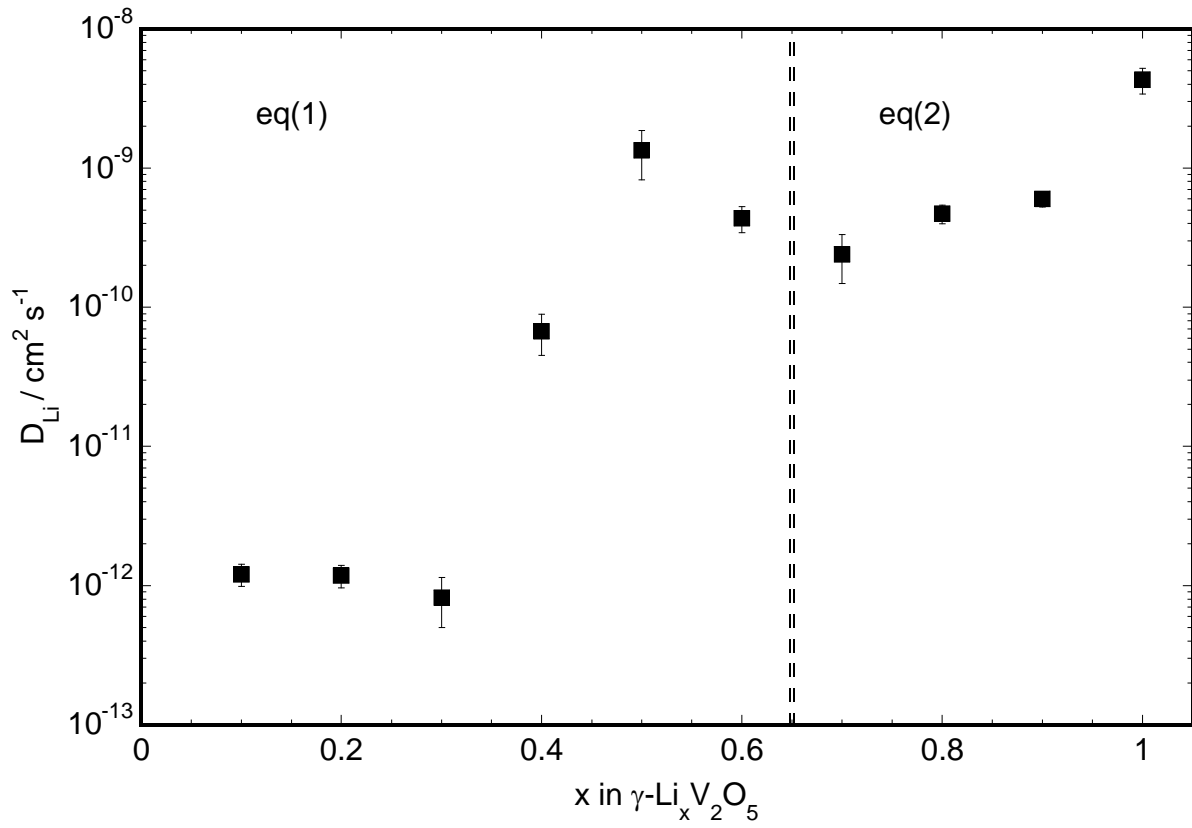


Figure 8. Evolution of the apparent chemical diffusion coefficient of lithium D_{Li} as a function of x in $\gamma\text{-Li}_x\text{V}_2\text{O}_5$. The double dashed line separates the composition domain in which D_{Li} has been determined using either eq (1) or eq (2).