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# Thermo-luminescent optical fibre sensor for Li-ion cell internal temperature monitoring

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## Abstract

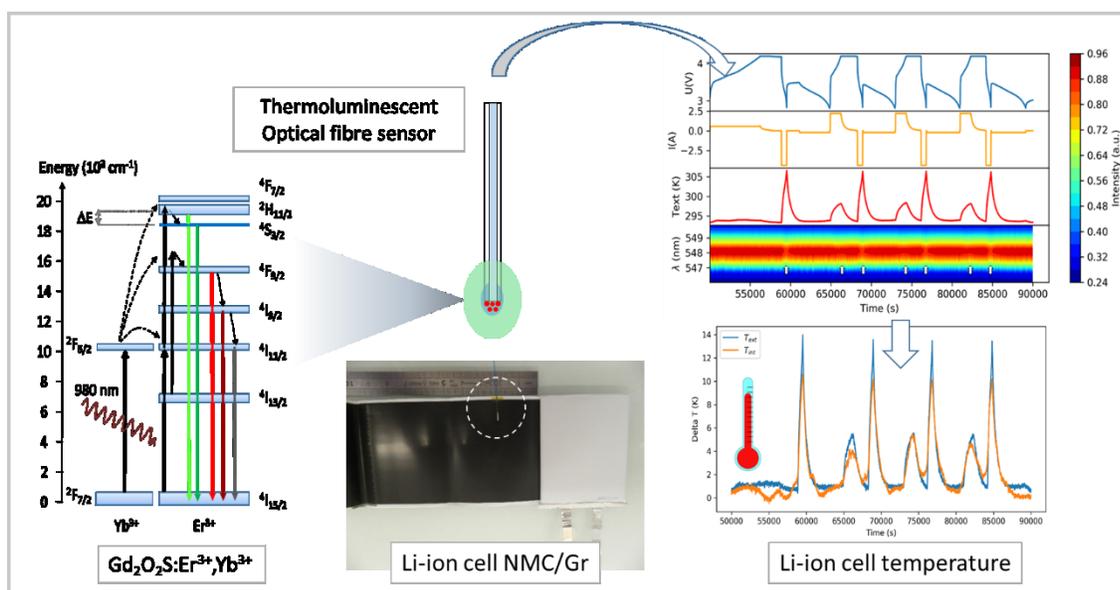
The internal temperature of a Li-ion battery is one of the critical parameters for monitoring cell performance, ageing and safety. The development of new sensor technologies to control the internal temperature of cells without compromising performance and safety remains a challenge. It is one of the objectives of the European INSTABAT project in the framework of the Battery2030+ initiative. The objective of this paper is to describe the development of a new optical fibre sensor based on a thermoluminescent material to monitor internal cell temperature. The development of the sensor, its thermal characterisation and its calibration are presented here. This sensor was inserted into a commercial Li-ion cell and its response during cycling at high charge and discharge rates (2C in charge and 4C in discharge) was investigated. The comparison between external and internal temperature measurements shows good agreement. These results demonstrate the ability of this type of sensor to monitor the internal temperature of a Li-ion battery without affecting its performance at high loading.

**Keywords:** Li-ion batteries; Optical Fibre; Temperature Sensors; Fast-charging; *operando* analysis, Smart-cell

## Abbreviations

$B_l$ : The Biot number, B: Constant in expression of FIR, CCD: Charge-Coupled Device,  $\delta T$ : Temperature uncertainty (K),  $\Delta E$ : Energy difference between two barycentre of the coupled level (radiative transition) using for calculation of FIR, F:  $^2F_{9/2}$  to  $^4I_{15/2}$  radiative transition, FIR: Fluorescence Intensity Ratio,  $h$ : Global thermal transfer coefficient (0.5 W/m/K), H:  $^2H_{11/2}$  to  $^4I_{15/2}$  radiative transition,  $I_{cell}$ : Cell current (I),  $I_i$  ( $i=1$  or  $2$ ): Luminescence intensity of the two peaks 1 and 2 use for FIR calculation, IR: Infrared,  $k_B$ : Boltzmann constant,  $\lambda_b$ : Thermal conductivity (0.5W/m/K),  $L_c$ : Characteristic length in our case the half of cell thickness (1 mm), LED: Light Emissive Diode, NIR: Near Infrared, PMMA: Poly Methyl Methacrylate, S:  $^4S_{3/2}$  to  $^4I_{15/2}$  radiative transition,  $S_a$ : Absolute sensitivity,  $S_r$ : Relative Sensitivity, SOC: State of Charge, T: Temperature (K),  $T_{ext}$ : External temperature of the cell (K),  $T_{int}$ : Internal temperature of the cell (K),  $U_{cell}$ : Cell potential (V), UV: Ultraviolet, VIS: Visible light, QY= Quantum Yield

## 40 Graphical abstract



41

42

### 43 1. Introduction

44 Improving battery safety and performance requires developing battery management systems with  
45 accurate estimators (state of charge, state of health, state of safety, etc.) based on monitoring critical cell  
46 parameters in real-time [1]. The measurement of internal cell parameters should provide better  
47 understanding of degradation mechanisms, failure prevention and ageing anticipation. To achieve these  
48 goals, the development of new sensor technologies is required and their integration inside Li-ion batteries  
49 without affecting cell performance and safety remains challenging [2,3]. These goals are clearly identified  
50 in the roadmap of the Battery2030+ initiative [4] and are currently pursued by three European projects on  
51 smart batteries: INSTABAT, SENSIBAT and SPARTACUS [5]. Among the important physical parameters, the  
52 internal temperature of the cell is one of the most critical since the temperature determines performance,  
53 ageing and safety [6]. Much effort must be devoted to cell and pack design to limit temperature increases  
54 and to develop accurate and non-invasive techniques to measure the internal temperature of the cell [7].  
55 Measuring the internal temperature of the cell raises problems. Thermal sensors must be compatible with  
56 the chemistry of the cell and small in size. In addition, the insertion of thermal sensors must not affect the  
57 performance, ageing or safety of the cell. Among the different sensor technologies, optical fibre sensors  
58 have been developed [8,9] due to their fast response, their compact size, which allows their integration in  
59 multiple environments, and their immunity to electromagnetic fields. This kind of sensor has already  
60 proved its worth in monitoring the internal parameters of Li-ion cells [10–22].

61 Fibre Bragg Gratings (FBG) sensors are widely used to monitor the internal and external temperature of  
62 the cell. This technique has several advantages such as the possibility of having several sensors in the same  
63 fibre, high sensitivity and good accuracy. However, the signal response of FBG sensors is dependent on  
64 temperature and strain, and it is difficult to properly decouple these two contributions [23–27]. One  
65 solution is the use of two optical fibres to decouple temperature and strain. However, sensor integration  
66 increases the complexity and size of the sensor, which can affect the correct operation of the cell. Recent

67 work by J. Pinto *et al.* [28] reported a new strategy to decouple temperature and strain measurement  
68 with the same optical fibre by using panda fibre with FBG sensors. Another publication from J.M.  
69 Tarascon's team [27] obtained results from the comparison of two types of optical fibres with FBG sensors  
70 to decouple strain and temperature. However, this kind of FBG sensor requires an expensive interrogator  
71 which makes it difficult to integrate this sensor into a BMS while managing performance, cost and size.

72 Using thermoluminescent probes is another way of measuring temperature using optical fibre. This  
73 technique was developed a long time ago for various applications [29–32]. Phosphor co-doped with  
74 trivalent lanthanide ions has been selected from the thermoluminophore family due to its long-term  
75 thermoluminescence properties (no or low photobleaching and fast and reproducible response) and its  
76 chemical and thermic stability over time [29,32]. Some examples present temperature sensors based on  
77 optical fibres incorporating phosphor doped with trivalent cations. However, these temperature sensors  
78 are either limited for their temperature range and not really designed for specific applications [33–37]  
79 (development of materials and the corresponding temperature sensors as proofs of concept), or they are  
80 compatible only with a specific environment such as in photonic applications [36,38]. The luminescence of  
81 inorganic materials used for thermoluminescent probe depends only on temperature and is completely  
82 independent of the surrounding chemical environment and strain [29,32]. The measurement can be  
83 performed by using low-cost light sources and a portable spectrophotometer [32,39]. This detection  
84 system is cheaper than commercial FBG interrogators and can be easily used for *in-situ* measurements  
85 (*e.g.*, in vehicle battery packs). There are many techniques for measuring temperature with luminescence  
86 [39]. The ratiometry technique is based on the relative intensity variation of two radiative transitions. This  
87 technique presents a few advantages from the others such as relative independence from the excitation  
88 sources and easier detection with cheaper components compared to the lifetime based method [40]. A  
89 temperature sensor dedicated to *in situ* temperature monitoring requires a temperature range between  
90 253 K to 423 K corresponding to the operating range of Li-ion battery temperature (with optimal use in  
91 the restricted temperature zone of 293 to 313 K). This particular temperature range differs from the  
92 classical ranges used in the development of temperature sensors for other applications (such as biological  
93 applications with the temperature range around the physiological temperature [41] and industrial  
94 applications with high temperature ranges [29]). Furthermore, the development of sensors for Li-ion  
95 batteries must meet additional prerequisites: such as a mechanical resistance due to their integration  
96 inside the battery (for *in-situ* temperature monitoring) as well as a chemical resistance to the battery  
97 environment and particularly to the by-products resulting from the lithium salts formed during the  
98 electrochemical cycling of the battery [42]. Despite the fact that this type of sensor has been used in many  
99 fields for several years, to our knowledge only one article mentions its application for measuring the  
100 internal temperature of a battery [43]. In this paper, H. Li *et al.* used  $\beta\text{-NaYF}_4\text{:Er}^{3+}/\text{Yb}^{3+}@ \text{NaYF}_4$   
101 nanoparticles embedded in a PMMA matrix deposit at the end of an optical fibre to monitor the internal  
102 temperature of a pouch cell (NMC111/Graphite, 3.7V, 1200 mAh. They demonstrated the capability of a  
103 thermoluminescent optical fibre sensor to monitor the internal temperature of the cell. However, these  
104 thermoluminescent nanoparticles have low efficiency (*i.e.* quantum yield in upconversion) and  
105 consequently require the use of a high-power laser source for excitation. However, for industrial  
106 applications, such as battery management systems, it is crucial to reduce the cost and size of the sensor.

107 In this study, we demonstrate the possibility of using a more efficient thermoluminescent optical fibre  
108 sensor, based on one of the most efficient commercial upconverter materials, and associated with a low-  
109 cost excitation source such as a Light Emissive Diode (LED). The choice of excitation wavelength and its

110 potential negative effect on the cell components is another parameter to consider. Some  
111 thermoluminophores require UV excitation. However, UV light could damage the organic materials inside  
112 the cell such as the separator and the electrode binder. Moreover, UV light requires more expensive optics  
113 than visible (VIS) and near-infrared (NIR) light. For these reasons, we focus our work on an inorganic  
114 material excited by near-infrared (NIR) light (980 nm) with luminescence emission in the visible wavelength  
115 range (between 400 to 700 nm). Herein, we present the performance and the potential of a new  
116 temperature sensor based on optical fibre dedicated to Li-ion battery internal temperature *operando*  
117 monitoring. First, the temperature dependency of the luminescence of powder was calibrated. Then we  
118 calibrated the thermoluminescent optical fibre sensor alone and inserted it inside a commercial Li-ion cell  
119 (1 Ah). We demonstrate that internal and external temperatures can be monitored during cell cycling at  
120 high charge and discharge rates opening the way for the low cost, ease-of-use smart sensing of Li-ion  
121 batteries.

122

## 123 2. Materials and Methods

### 124 2.1. Characterisation of thermoluminescent particles

125  $\text{Gd}_2\text{O}_2\text{S}(\text{Er}^{3+}, \text{Yb}^{3+})$  (PTIR545UF) and  $\text{NaYF}_4(\text{Er}^{3+}, \text{Yb}^{3+})$  (PTIR550F) microparticles were purchased from  
126 Phosphor Technology (<http://phosphor-technology.com/>). The size and morphology of the particles were  
127 analysed by Scanning Electron Microscopy (SEM, Hitachi, model S- 5500; 5KV at 15 $\mu$ A). SEM images  
128 confirmed the micron size of the commercial particles (*Figure S1* for PTIR545UF and *Figure S2* for PTIR550F,  
129 Supporting information). Composition and crystallinity were analysed with a Bruker D8 Advance X-ray  
130 powder diffractometer (Cu/K $\alpha$  radiation source and LynxEye detector). Chemical composition was in good  
131 agreement with the supplier's data according to the X-ray diffraction analysis (*Figure S3* for PTIR 545/UF  
132 and *Figure S4* for PTIR550F, Supporting information). The luminescence of the powders was measured as  
133 received and compared in the same conditions of excitation power and integration time.

134

### 135 2.2. Optical Sensor preparation

136 To prepare the optical fibre sensor, we used FT200EMT optical fibre from Thorlabs (0.39 NA,  $\varnothing$ 200  $\mu$ m  
137 Core Multimode Optical Fibre, low hydroxyl content for 400 - 2200 nm, TECS Clad). The Tefzel<sup>®</sup> buffer was  
138 stripped with mechanical tools and the optical fibre was cloven perpendicularly prior to the coating with  
139 particles.

140 The protocol for particle insertion in silica sol-gel coating at the fibre tip was performed according to the  
141 following procedure. To prepare the sol-gel coating, (3-Aminopropyl)triethoxysilane, tetraethoxysilane  
142 and poly(methacrylic acid methyl ester), PMMA, average Mw = 350,000, were supplied by Merck Inc. and  
143 used without any purification. Optical fibres were cleaned with acetone and placed for 10 minutes in an  
144 ultrasound bath in acetone at 303 K before use. Then the optical fibres were dipped in a mixture of 80/20  
145 wt% of tetraethoxysilane/(3-aminopropyl)triethoxysilane under argon atmosphere and stored for 5  
146 minutes at room temperature at 50% relative humidity). The optical fibre with sol coating was put in  
147 contact with the phosphor powders, which had previously been finely ground in an agate mortar. The  
148 grinding operation served to de-agglomerate the particles to ensure homogeneous insertion in the  
149 coating. The modified optical fibres were stored for 1 hour under ammonia vapour to complete the sol-

150 gel polymerisation at room temperature. Then sample was dried at ambient temperature for 1h. Finally,  
151 the modified optical fibres were dipped in a 5 wt% methylene chloride solution of PMMA and dried at  
152 room temperature for 1h.

153 The PMMA is deposited as a protective layer to improve the mechanical properties of the modified optical  
154 fibres, we carried out both a coating of high molecular weight PMMA (MW 350,000) in DCM and/or an in  
155 situ growth of a highly reticulated PMMA type coating (the outer part of the fibres was previously treated  
156 with an isocyanate methacrylate monomer to create a strong urethane bond between the binder and the  
157 fibre surface). We did not observe any difference between these two routes in terms of thermal sensing.  
158 We therefore concentrated our efforts on the simplest route. We chose PMMA-type materials because  
159 we had carried out a screening of polymer stability in new and aged electrolytes by monitoring the swelling  
160 of polymer particles (3 mm diameter; molecular weight in the range 35,000 to 450,000) in carbonate  
161 electrolytes. By far, the high molecular weight PMMAs showed the best behaviour and were able to survive  
162 in the electrolyte for more than 12 months. Some previous studies show the degradation of PMMA by  
163 carbonates <sup>[44,45]</sup>. However, these results concern PMMA with a low molecular weight of around 35,000.  
164 In this work we increase the molecular weight up to 350,000 to increase the stability of the PMMA against  
165 the carbonate. The stability of the materials used to prepare the sensor has also been demonstrated by  
166 the ageing tests presented in this article (see Results section).

167  
168 *Figure S5* (Supporting Information) illustrates the optical microscope (Keyence VHX-500F/VH-Z20R) image  
169 of the sensor (optical fibre with thermoluminescent particle coating). We can see in this figure that the  
170 coating is located at the end of the fibre with the majority of the particles located on the tip surface. The  
171 thickness of the coating is relatively small compared to the diameter of the fibre (less than 10% of the fibre  
172 diameter).

### 173 174 2.3. Cell preparation

175 A non-activated cell (without electrolyte) from Li-FUN Technology Corporation was used for the insertion  
176 of the optical fibre sensor. The cell's characteristics are listed in the Table S1. Supporting Information. The  
177 active material is  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC622) as a positive electrode in combination with graphite as a  
178 negative electrode. It was a wound pouch cell with a capacity of 1101 mAh measured at a rate of C/20.  
179 The instrumentation operations were carried out in the dried room. *Figure S6* (Supporting Information)  
180 illustrates the main steps of instrumenting the cell with the thermal sensor. The cell was taken out of the  
181 laminated aluminium bag and unrolled over 2 turns. The optical fibre was then placed between the positive  
182 electrode and the separator. The foils of the components were then rewound. Additional tabs were  
183 welded on the existing tabs and the cell was repackaged in a bag. Two sides of the bag were then sealed  
184 with a sealing machine at 453 K. After drying at 328 K under vacuum overnight, the cell was inserted in the  
185 glove box and then activated. The electrolyte used was a commercial mixture of ethylene carbonate (EC)  
186 and ethyl methyl carbonate (EMC) in a weight ratio of 1:2 with 1M  $\text{LiPF}_6$  conductive lithium salt and 2 % of  
187 vinyl carbonate (VC) additive. Finally, the bag was closed under vacuum. Following the recommendations  
188 of the equipment supplier, a degassing step was performed after the formation cycles.

189

#### 190 2.4. *Optical setup*

191 The luminescent material used for the thermal probe required a light source to excite the Yb<sup>3+</sup> cations at  
192 980 nm and a spectrophotometer to measure the luminescence peaks of *H*, *S* and *F* transitions in the visible  
193 range (between 500 nm and 750 nm). We used an optical fibre coupled with M970F3 LED (970 nm, 5.9  
194 mW, Thorlabs) as the excitation source. The excitation light was transferred through a RP20 (Thorlabs)  
195 multimode optical fibre to the sample. It collected the light from the sample and sent it to  
196 spectrophotometer. The spectrometer was a compact CCD spectrometer (CCS200, Thorlabs). Multimode  
197 optical fibre with a core diameter of 200 μm was used to transport the light between the collimator  
198 coupling box and the sample (FT200EMT optical fibre from Thorlabs). An achromatic collimator for  
199 multimode fibres (F950SMA-A Thorlabs) was used to measure the powder luminescence in the collimator  
200 coupling box. *Figure S7* (Supporting Information) shows a schematic view of the optical test bench for dual  
201 luminescence and electrochemistry measurements.

202

#### 203 2.5. *Sensor calibration*

204 Two different configurations were selected for calibration, depending on the step of the sensor's  
205 development and its integration inside the cell (see *Figure S6*, Supporting Information). For the powder  
206 calibration, thermoluminescent particles were inserted in a quartz tube and placed in a programmable  
207 climatic chamber (Weiss). A thermocouple was fixed inside the tube to measure the temperature of the  
208 powder and another one in the centre of the climatic chamber. The luminescence was measured through  
209 the quartz by using a collimating lens at the end of the optical fibre. The rest of the optical bench was the  
210 same as for the other experiment (optical source, optical fibre, optical element and spectrometer). The  
211 climatic chamber was programmed at different temperatures, from 260 to 320 K every 5 K. Each  
212 temperature was kept constant for 50 min for thermal stabilisation. During the calibration, the  
213 luminescence from the sensor and the temperature from the thermocouple were acquired every 10 s.  
214 Luminescence was recorded in a full spectrum range between 200 to 1000 nm.

215 We proceeded with the same methodology for the optical fibre sensor calibration (alone and inside the  
216 cell) except for the optical connection. The optical fibre sensor was directly connected to the test bench  
217 *via* the collimator coupling box (see *Figure S7*, Supporting Information). The optical fibre used for the  
218 powder calibration was the same type as RP20 fibre (FT-200EMT). The only difference was the collimating  
219 lenses between the end of the fibre and the powder sample. This optical component had no significant  
220 impact on the luminescent signal.

221

#### 222 2.6. *Data processing*

223 Post-processing python 3 script was developed for the data post processing. Pandas (v2.4.2), Numpy  
224 (1.16.4), Scipy (1.2.1), and Pywavelets (1.0.3) libraries are used for data denoising, analysis and Matplotlib  
225 (3.1.0) for data visualisation. The optical signal from the spectrometer was noisy due to the CCD  
226 characteristics<sup>[46,47]</sup> and required the use of denoising techniques. For the data treatment two methods  
227 were tested, the first based on the Savitzky-Golay filter (savgol\_filter algorithm from Scipy<sup>[48]</sup>). The second  
228 one used the continuous wavelet transform method<sup>[49]</sup> with the "*coiflets 5*" function<sup>[50,51]</sup>. *Figure S8*  
229 (Supporting Information) shows the results of the noise reduction by these two methods. The grey curve

230 represents the luminescence intensity ratio between the H and S transitions. The orange curve gives the  
231 result after Savitzky-Golay filtering and the red one the result after wavelet filtering. The second method  
232 proved to be more powerful and was applied to all the luminescence data.

233

## 234 2.7. *Electrochemical cycling.*

235 The pouch cell was placed on a holder and connected to a cycling battery test bench (Bio-logic, VMP3  
236 series). Its effective capacity after formation was 1.017 Ah (C/10, 298 K). To monitor the external  
237 temperature, a thermocouple was fixed on the centre of the cell before applying mechanical compression.  
238 Constant mechanical stress was applied by a rigid polymer plate and clamps. Two polymer foams were  
239 placed between the cell and polymer plate to homogenise the mechanical stress. The cell was tested in  
240 the laboratory at constant ambient temperature (298 K). The ambient and surface cell temperatures were  
241 measured by thermocouples connected to a data acquisition system (Keysight 34972A + 34910A). The  
242 current and cell voltage were measured with the Biologic VMP3 electrochemical bench.

243 *Figure S9* (Supporting Information) shows the current and potential of the cell during cycling. The  
244 experiment started with a full charge (State of Charge SOC=100%).

245 The sequence consisted of:

- 246 1- An initial discharge at a constant current of C/5 up to 2.8 V, and a relaxation at  $I = 0$  A for 30 min.
- 247 2- A cycle consisting to :
  - 248 – a charge at a constant current of C/5 up to 4.2 V that is followed by a second step at  
249 constant voltage (4.2V) up to  $I \leq C/20$  or 1h (SOC reached = 100%)
  - 250 – a discharge at C/5 down to 2.8 V (SOC reached = 0%).
- 251 3- A cycle consisting to :
  - 252 – a charge at a constant current of C/2 up to 4.2 V that is followed by a second step at  
253 constant voltage (4.2V) up to  $I \leq C/20$  or 1h (SOC reached = 100%)
  - 254 – a discharge at a constant current of 4C down to 2.8 V that is followed by another discharge  
255 step at a lower current rate of C/2 down to 2.8 V (SOC reached = 0%). This second step  
256 allows the cell to be completely discharged before starting the next charge.
- 257 4- A cycle consisting to :
  - 258 – a charge at a constant current of 1C up to 4.2 V that is followed by a second step at  
259 constant voltage (4.2V) up to  $I \leq C/20$  or 1h (SOC reached = 100%)
  - 260 – a discharge at a constant current of 4C down to 2.8 V that is followed by another discharge  
261 step at a lower current rate of C/2 down to 2.8 V (SOC reached = 0%). This last sequence  
262 was repeated 3 times. Discharge at 4C and charge at 2C are the maximum rates for this  
263 type of cell. It is well known that cell heating increases with discharge current rate,

264 especially. Therefore, in order to maximize the temperature increase, we used the  
265 maximum discharge rate.

266 For the ageing test, the cell was submitted to calendar ageing and cycling ageing with protocol of:

267 1- Calendar ageing:

268 After the cycling test, the cell was stored for 18 months at SOC 30% in a fridge at  $T=5^{\circ}\text{C}$ . The luminescence  
269 of the sensor was tested before and after calendar ageing.

270 2- Cycling ageing:

271 For the ageing test, the cell was tested in the laboratory at constant ambient temperature (298 K) with the  
272 same experimental setup and configuration as in the previous test. The cell was tested with a 2C charge  
273 and 4C discharge cycle with the following protocol:

274 2-1 A low current cycle to evaluate the SOH of the cell, consisting of :

- 275 – a charge at a constant current of  $C/10$  up to 4.2 V that is followed by a second step at constant  
276 voltage (4.2V) up to  $I \leq C/20$  or 1h (SOC reached = 100%)
- 277 – a discharge at  $C/10$  down to 2.8 V (SOC reached = 0%).

278 2-2 150 successive cycles composed of :

- 279 – a charge at a constant current of 2C up to 4.2 V that is followed by a second step at constant  
280 voltage (4.2V) up to  $I \leq C/20$  or 1h (SOC reached = 100%)
- 281 – a discharge at 4C down to 2.8 V

282 Between each charge/discharge, there is a rest period of 30 min.

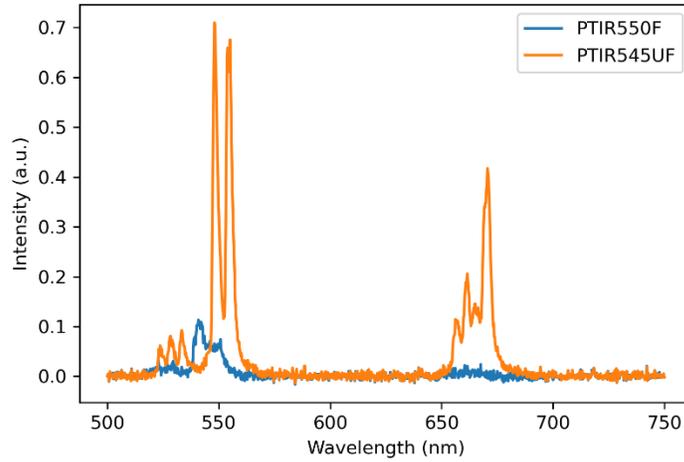
283 2-3 A final cycle in the same conditions as sequence 1

284

### 285 3. Results and discussion

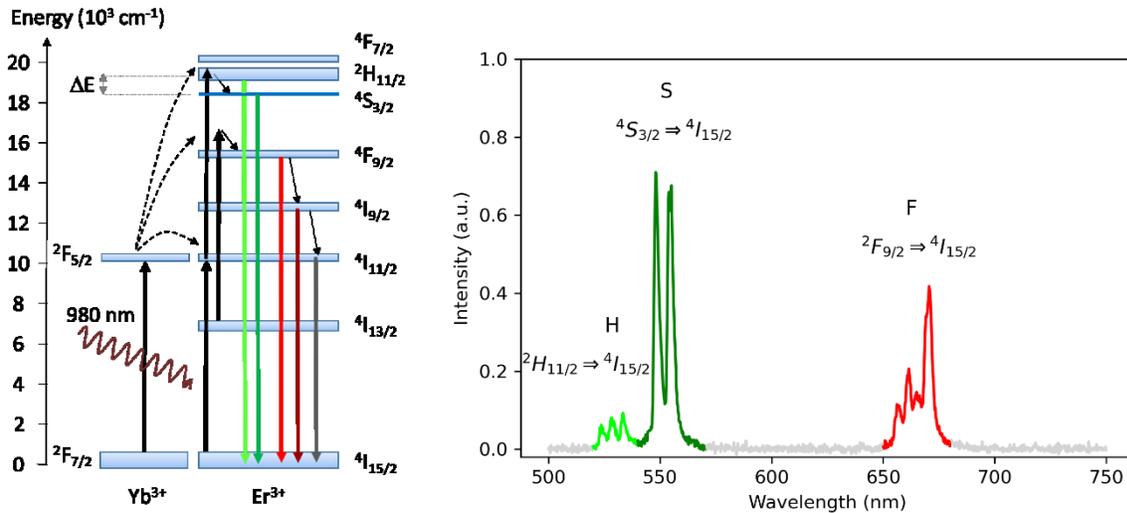
286  $\text{Gd}_2\text{O}_2\text{S} (\text{Er}^{3+}, \text{Yb}^{3+})$  (PTIR545UF) was selected as luminescent material for the temperature measurement.  
287 This micron sized particle material is an upconverter with a high quantum yield (4.2%) close to the micron-  
288 sized  $\text{NaYF}_4 (\text{Er}^{3+}, \text{Yb}^{3+})$  (7.8%)<sup>[52,53]</sup>. The thermoluminescence of this material was studied previously by D.  
289 Avram *et al* [51] under excitation at 980 nm and 1550 nm with high pulsed power and continuous laser  
290 sources. This material exhibits a higher luminescence under 980 nm excitation with high thermal  
291 sensitivity. *Figure 1* compares the luminescence spectra for PTIR545UF ( $\text{Gd}_2\text{O}_2\text{S} (\text{Er}^{3+}, \text{Yb}^{3+})$ ) and PTIR550F  
292 ( $\text{NaYF}_4 (\text{Er}^{3+}, \text{Yb}^{3+})$ ) at 298K excited at 980 nm (5.9 mW LED). It can be seen that the luminescence of  
293 PTIR545UF is seven times higher than PTIR550F. This difference is not due to the quantum yield (QY) but  
294 the higher absorption coefficient of  $\text{Gd}_2\text{O}_2\text{S} (\text{Er}^{3+}, \text{Yb}^{3+})$  compared to  $\text{NaYF}_4 (\text{Er}^{3+}, \text{Yb}^{3+})$ . QY is not the only  
295 parameter for luminescence intensity, the absorption efficiency also play a role. The best comparison  
296 between two materials is to compare the luminescence in the same environmental condition with same  
297 optical system. In our case we observe that the PTIR545/UF ( $\text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+}, \text{Yb}^{3+}$ ) is more luminescent than  
298 (PTIR550/F,  $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ ), see **Figure 1**. In our experiment, the luminescence of PTIR545/UF is 7 times  
299 more intense than the PTIR550/F. The article by T. Soukka *et al*<sup>[54]</sup> shows similar results with the intensity  
300 of the peak at 550 nm is 4.71 times more intense for the PTIR545/UF compared to the PTIR550/F.

301 Due to its higher luminescence intensity, we decided to select PTIR545UF microparticles for the  
 302 preparation of a thermoluminescent optical fibre sensor.



303  
 304 **Figure 1.** Comparison of luminescence spectra of  $Gd_2O_2S$  ( $Er^{3+}$ ,  $Yb^{3+}$ ) PTIR545UF and  $NaYF_4$  ( $Er^{3+}$ ,  $Yb^{3+}$ ) PTIR550F, under 980 nm  
 305 LED excitation at 298K with the same excitation power and integration time.

306  
 307 *Figure 2* shows the up-conversion of  $Gd_2O_2S$  ( $Er^{3+}$ ,  $Yb^{3+}$ ) (PTIR545UF) under excitation at 980 nm and the  
 308 associated emission spectra in the visible wavelength range (between 500 to 750 nm). Electrons from  $^4I_{15/2}$   
 309 level of  $Er^{3+}$  and  $Yb^{3+}$  are excited to a higher energy level by multiple absorptions of infrared photons at  
 310 980 nm (bold black arrow). Then electrons return to the lower energy levels by non-radiative transition  
 311 (dashed arrows) or radiative transition (colored arrows).



313  
 314 **Figure 2.** Up-conversion of  $Gd_2O_2S$  ( $Er^{3+}$ ,  $Yb^{3+}$ ) PTIR545UF under excitation at 980 nm, (left) Energy diagram of  $Yb^{3+}$  and  $Er^{3+}$  with  
 315 schematic representation of absorption and radiative transition, (right) up-conversion spectra between 500 to 700 nm at 298 K.

316

317 The transitions between excited states ( $^2H_{11/2}$ ,  $^4S_{3/2}$  and  $^2F_{9/2}$ ) to the ground state ( $^4I_{15/2}$ ) produce two green  
318 and one red emission (labelled H, S and F respectively). The luminescence intensity of these three  
319 transitions (H, S and F) depends on the temperature which is why we can use this material as a  
320 thermometer. The common approach is to use radiometry between two peaks of intensity  $I_1$  and  $I_2$ , named  
321 *FIR* (Fluorescence Intensity Ratio), where the intensity ( $I$ ) of transition is equal to the area under the peak  
322 in luminescence spectra. If we assume the validity of the Boltzmann distribution [32], the intensity ratio  
323 between two peaks can be expressed as:

324

$$325 \quad FIR = \frac{I_1}{I_2} = B e^{\left(-\frac{\Delta E}{k_B T}\right)} \quad (1)$$

326

327 where  $k_B$  is the Boltzmann constant,  $T$  the temperature,  $\Delta E$  the energy difference between the barycentre  
328 of the two coupled electronic levels ( $^2H_{11/2}$ ,  $^4S_{3/2}$ ), and  $B$  is a constant. For the  $Gd_2O_2S (Er^{3+}, Yb^{3+})$ , transitions  
329 H and S are separated by a small energy gap  $\Delta E \sim 800 \text{ cm}^{-1}$  [52,53] and are used for the temperature  
330 measurement by radiometry. In this case  $I_1$  corresponds to the intensity of the H transition and  $I_2$  the  
331 intensity of the S transition. From equation (1),  $\ln(FIR)$  presents a linear variation as a function of  $\frac{1}{T}$ .

332

$$333 \quad \ln(FIR) = \ln\left(\frac{H}{S}\right) = -\frac{\Delta E}{k_B} \left(\frac{1}{T}\right) + \ln(B) \quad (2)$$

334

335 Temperature can be estimated by the following equation:

336

$$337 \quad T = \frac{\Delta E}{k_B} \frac{1}{\ln(B/FIR)} = \frac{\Delta E}{k_B} \left[ \frac{1}{\ln(B) - \ln(FIR)} \right] \quad (3)$$

338

339 The uncertainty on temperature can be estimated by [32]:

340

$$341 \quad \delta T = \frac{1}{S_r} \frac{\delta FIR}{FIR} \quad (4)$$

342

343 Absolute ( $S_a$ ) and relative ( $S_r$ ) sensitivities are defined by the following expression. These two parameters  
344 were introduced by Collins *et al.* [55] and have been used extensively for comparisons between  
345 thermometer performances.

346

347 
$$S_a = \frac{\partial FIR}{\partial T} \quad (5)$$

348 
$$S_r = \frac{1}{FIR} \left| \frac{\partial FIR}{\partial T} \right| \quad (6)$$

349

350 Using  $\frac{\partial e^{u(x)}}{\partial x} = \frac{\partial u(x)}{\partial x} e^{u(x)}$ , we simplify the expression of absolute sensitivity  $S_a$  by:

351

352 
$$S_a = \frac{\Delta E}{k_B T^2} FIR \quad (7)$$

353

354 and the expression of the relative sensibility  $S_r$  becomes:

355

356 
$$S_r = \left| \frac{\Delta E}{k_B T^2} \right| \quad (8)$$

357

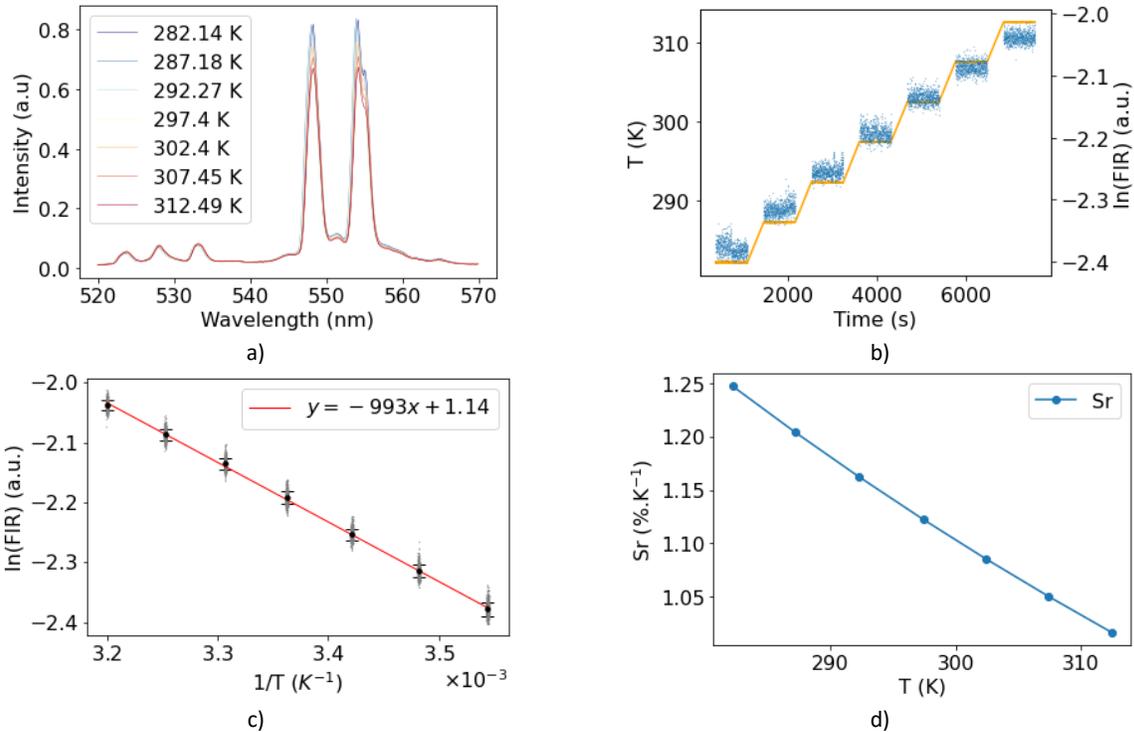
358  $S_a$  depends on the measurement apparatus.  $S_r$  is more appropriate for comparing the performances of  
359 different thermoluminophores.

360 The luminescence of PTIR545UF powder has been measured between 283 to 313K; this temperature range  
361 is compatible with the expected internal temperature of the 1A.h cell during a cycling test at 298 K. *Figure*  
362 *3a* shows the variation of luminescence spectra of Gd<sub>2</sub>O<sub>2</sub>S (Er<sup>3+</sup>, Yb<sup>3+</sup>) PTIR545UF as a function of  
363 temperature. Each spectrum was normalized on the maximum intensity of the peak corresponding to the  
364 *H* transition. A decrease of the peak corresponding to the *S* transition is observed when the temperature  
365 increases. The variation of  $\ln(FIR)$  as a function of  $1/T$  (blue point) and the linear regression (redline) are  
366 shown on *Figure 3b*. The linear regression coefficient is close to  $1.10^3$  (K<sup>-1</sup>) and corresponds to a  $\Delta E =$   
367  $695 \text{ cm}^{-1}$ . This value is very close to the value of  $\sim 700 \text{ cm}^{-1}$  found by D. Avram et al. [52] and also close  
368 to the theoretical energy gap between the H and S transition  $\Delta E = 800 \text{ cm}^{-1}$ . The relative sensitivity ( $S_r$ )  
369 is between 1.25 and 1.00 % . K<sup>-1</sup> in the range of temperature between 280 to 315 K, which is in agreement  
370 with the values reported in the literature [29,31].

371

372

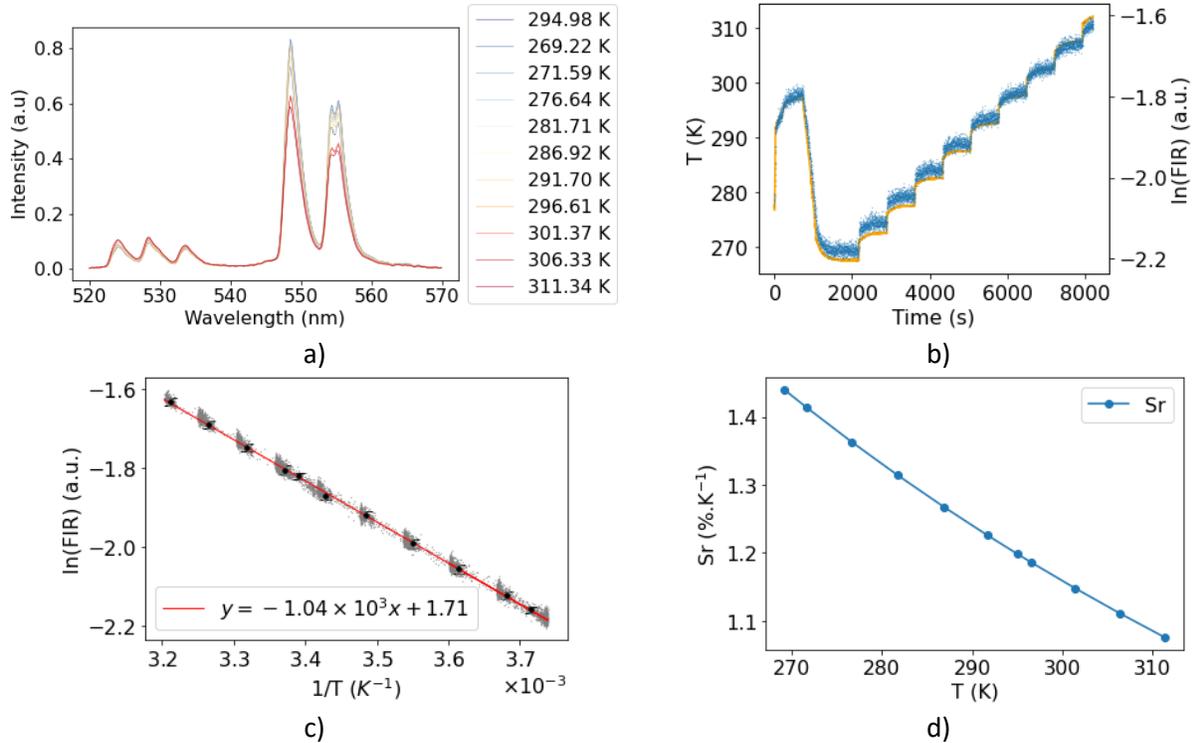
373



374 **Figure 3.** Thermoluminescence of Gd<sub>2</sub>O<sub>2</sub>S (Er<sup>3+</sup>, Yb<sup>3+</sup>) PTIR545UF powder: a) Evolution of luminescence spectra between 282 to  
 375 312 K, (b) Ln(FIR) (blue point) and Temperature (orange line) variation as a function of time during calibration, (c) Linear variation  
 376 of Ln(FIR)=f(1/T): measure (grey), mean and error bar correspond to the root mean square RMS (dark) and linear regression (red).  
 377 (d) Relative sensitivity ( $S_r$ ) as a function of temperature calculated from linear regression coefficients (Ln(FIR)=f(1/T)).

378

379 The temperature dependence of luminescence was tested with the same protocol for both the optical  
 380 fibre sensor and for optical fibre sensors embedded inside of the cell. The results obtained for the optical  
 381 fibre sensor are shown in *Figure 4*. The variation of Ln(FIR) as a function of 1/T has a slope of 1044 (K<sup>-1</sup>),  
 382 which is close to the slope calculated for the Gd<sub>2</sub>O<sub>2</sub>S (Er<sup>3+</sup>, Yb<sup>3+</sup>) PTIR545UF powder. This comparison  
 383 indicates that the insertion of the luminescent particles into the silica matrix covered by a PMMA layer (as  
 384 a protective layer) at the end of optical fibre does not affect the performances of the thermoluminescent  
 385 particles. A small intensity difference is observed in the two luminescence peaks of the S transition  
 386 between the powder and the optical fibre sensor. The intensity of the second peak of the S transition is  
 387 smaller than the first one for optical fibre sensor (*Figure 4a*). This variation is due to the absorption of the  
 388 optical fibre itself and does not affect the performances of the thermal probe (*Figure 4*). Furthermore, the  
 389 same linear variation of Ln(FIR) as function of 1/T in *Figures 3a* and *4a* confirms that the introduction of  
 390 thermoluminescent particles in the sol matrix surrounded with a protective layer does not affect their  
 391 thermoluminescence properties. The relative sensitivity ( $S_r$ ) of the optical fibre is slightly higher than that  
 392 of the thermoluminescent particles, with a range of 1.10 to 1.45 %·K<sup>-1</sup> for temperature in the same  
 393 temperature range (from 312 to 272 K).

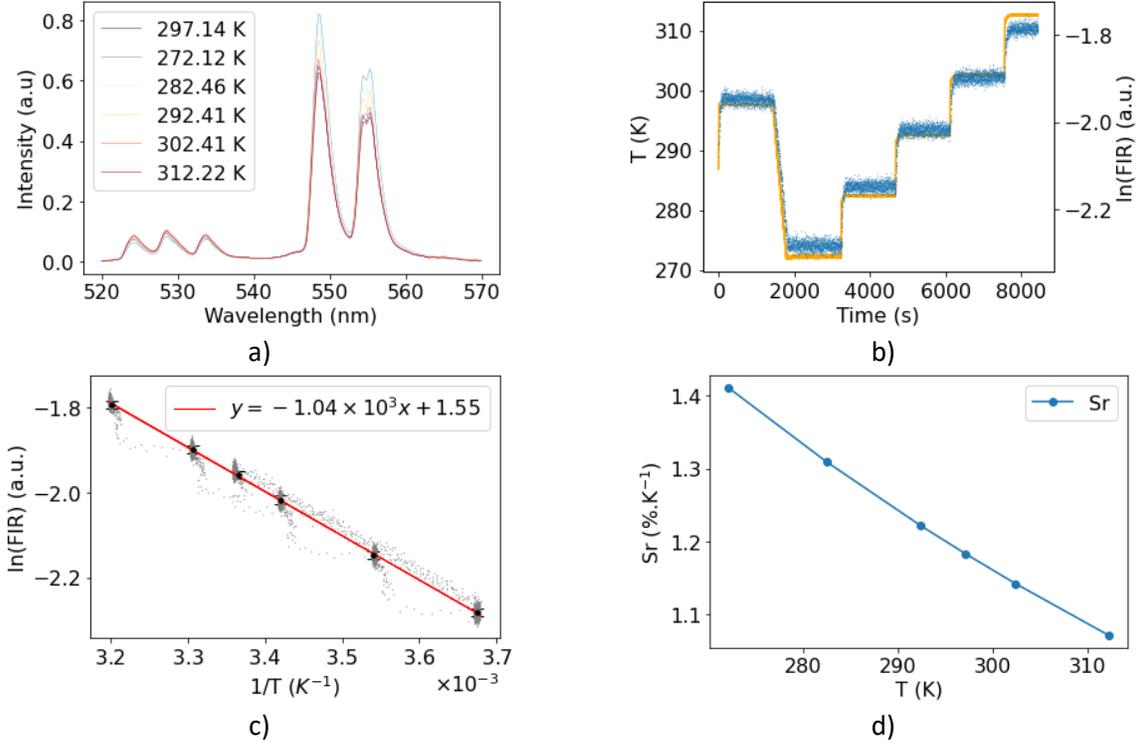


394 **Figure 4.** Thermoluminescence of optical fibre with Gd<sub>2</sub>O<sub>2</sub>S (Er<sup>3+</sup>, Yb<sup>3+</sup>) PTIR545UF powder (in the silica matrix) and PMMA  
 395 coating: a) Luminescence spectra evolution between 272 to 312 K, (b) Ln(*FIR*) (blue point) and Temperature (orange line) variation  
 396 as a function of time during calibration, (c) Linear variation of Ln(*FIR*)=f(1/*T*): measure (grey), mean and error bar error bar  
 397 correspond to the root mean square RMS (dark) and linear regression (red) . (d) Relative sensitivity (*S<sub>r</sub>*) as a function of  
 398 temperature calculated from the linear regression coefficients (Ln(*FIR*)=f(1/*T*)).

399

400 The same results were obtained for the calibration of the optical fibre inserted inside the Li-ion cell (*Figure*  
 401 5). There is no observable modification of the emission spectrum due to the insertion of the sensor inside  
 402 the cell. The slope of the Ln(*FIR*) as a function of (1/*T*) is equal to the slope before the insertion (1044 (K<sup>-1</sup>)). The *S<sub>r</sub>*  
 403 value is very similar to the value obtained with the optical fibre before insertion inside the cell.  
 404 A small variation of the shape of the second peak of the *S* transition is observed due to the difference of  
 405 the length of the optical fibre between the thermal probe and the spectrophotometer. However, the slope  
 406 of the linear regression in Ln(*FIR*) as a function of (1/*T*) is close to the previous value, around 1000 (K<sup>-1</sup>).  
 407 The relative sensitivity *S<sub>r</sub>* varied between 1.1 and 1.4 between 308 and 270 K. All these measurements  
 408 show several small variations in the calibration of sensors depending on the environment and the  
 409 measurement system. Although the variations are small, it is necessary to calibrate the sensor inside the  
 410 cell to obtain optimum accuracy. When calibrating of the sensor inside the cell we decide to add a  
 411 temperature step at 300K at the beginning of the calibration protocol (see *Figure 5*). The aim is to evaluate  
 412 if the sensor is sensitive to the order of the temperature during calibration. In the results (*Figure 5*) all the  
 413 points are well aligned and we conclude that there is no memory effect when there is a sudden  
 414 temperature change related to the cooling or heating.

415



416 **Figure 5.** Thermoluminescence of optical fibre with Gd<sub>2</sub>O<sub>2</sub>S (Er<sup>3+</sup>, Yb<sup>3+</sup>) PTIR545UF powder in silica matrix and PMMA coating  
 417 inside the Li-ion cell: a) Luminescence spectra evolution between 272 to 312 K, (b) Ln(*FIR*) (blue point) and Temperature (orange line)  
 418 variation as a function of time during calibration, (c) Linear variation of Ln(*FIR*)=f(1/*T*): measure (grey), mean and error bar  
 419 correspond to the root mean square RMS (dark) and linear regression (red). (d) Relative sensitivity (*S<sub>r</sub>*) as a function of temperature  
 420 calculated from the linear regression coefficient (Ln(*FIR*)=f(1/*T*)).

421 The accuracy of the optical probe (powder) and the sensor was calculated from the calibration data. The  
 422 variance ( $\delta FIR$ ) of the *FIR* from the theoretical value ( $FIR_{th}$ ) for each temperature was calculate from the  
 423 equation (9) below:

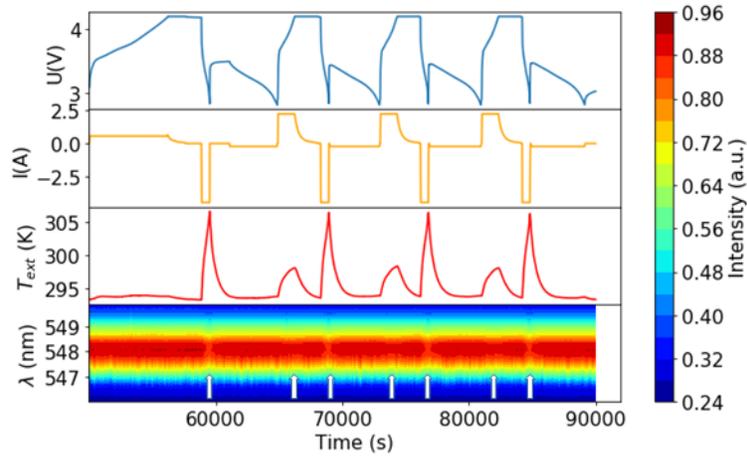
$$424 \quad \delta FIR = \frac{FIR}{FIR_{th}} \quad (9)$$

425 Where  $FIR_{th}$  is calculated from equation (2) with the linear coefficients  $-\frac{\Delta E}{k_B}$  and  $B$  determined by  
 426 calibration data (**Figure 4** for optical probe and **Figure 5** for sensor). The temperature measurement error  
 427  $\delta T$  is calculated from the equation (4). The Figure S10 and S11 show the  $\delta FIR$  and  $\delta T$  as a function of *T*  
 428 for the sensor alone and inserted in the cell. The uncertainty of the temperature  $\delta T$  is about +/- 1°C over  
 429 the range tested. A higher value for the error between two constant temperature plateaus is shown in  
 430 Figure S11 for the sensor inside the cell. This error is not related to the sensor but to the thermal gradient  
 431 between the sensor temperature inside the cell and the reference temperature measured in the climate  
 432 chamber during the temperature transition. These points are outliers. They are not taken into account  
 433 when evaluating the accuracy of the sensor.

434 **Figure 6** shows the variation of the maximum luminescence for the peak at 548 nm (*S* transition) over time  
 435 with the cell potential *U*(V), cell current *I*(A) and cell surface temperature  $T_{ext}$  (K). The correlation between  
 436 the external temperature and the *S* transition peak variation is shown clearly. The *S* peak intensity  
 437 decreases when the temperature increases during the cell charge at a rate of 1C and discharge at a rate of

438 4C. The variation of luminescence during discharge at a rate of 4C is greater than the charge at a rate of  
 439 1C due to a higher rise in temperature.

440

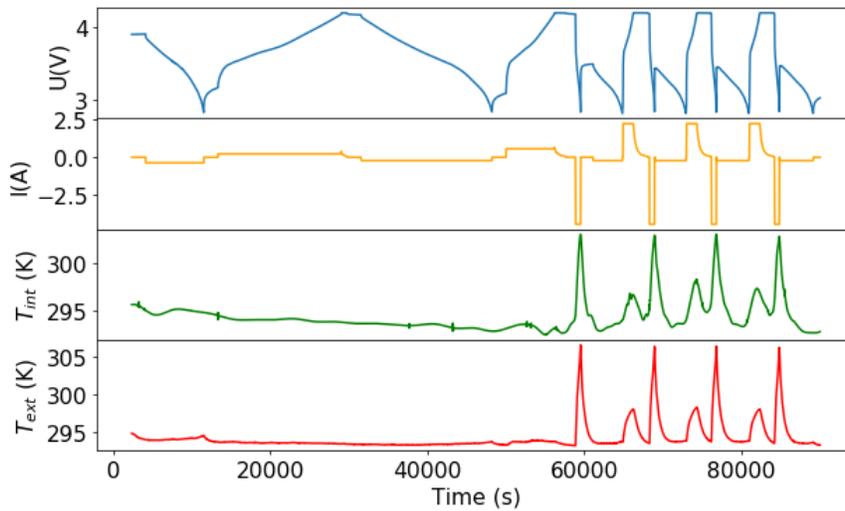


441

442 **Figure 6.** Variation of the cell potential  $U(V)$ , cell current  $I(A)$ , external cell temperature  $T_{ext}$  and luminescence variation of the S  
 443 transition (maximum peak at 548 nm). The arrow highlights the signal variation in the spectrum when the temperature increases.

444

445 *Figure 7* represents the measurement of cell potential ( $U$ ), cell current ( $I$ ), external temperature ( $T_{ext}$ ) from  
 446 a thermocouple sensor and internal temperature ( $T_{int}$ ) from our luminescent sensor. During the first charge  
 447 and discharge steps at low C-rates, the temperature of the cell does not change. The surface temperature  
 448 increases during the discharge at 4C up to 14 K and charge at 1C up to 5 K in comparison with the ambient  
 449 temperature (see *Figure 8*).



450

451

**Figure 7.** Internal and external cell temperature variations during cell cycling

452

453 The temperature variation is clearly correlated with the charge and discharge profiles. The shape and the  
 454 intensity of the temperature variations are similar to those in the literature for this type of Li-ion cell [56].  
 455 The signal from the thermoluminescent sensor shows the same variation over time with good correlation  
 456 with the surface temperature measurement. The cell used for this experiment was a pouch cell with a  
 457 small capacity (1A.h). The Biot number ( $B_i$ ) can be calculated to evaluate if there is a difference between  
 458 the internal and external temperatures. The Biot number is defined as:

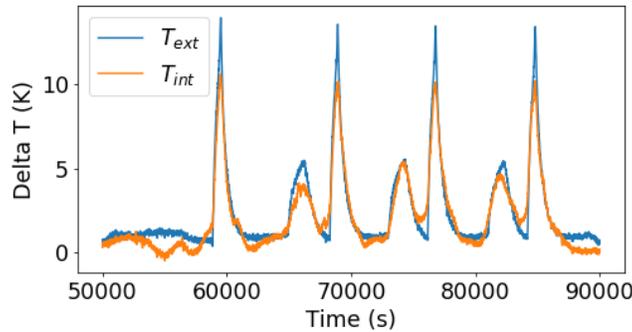
459

$$460 \quad B_i = \frac{hL_c}{\lambda_b} \quad (10)$$

461

462 where  $h$  is the global thermal transfer coefficient (0.5 W/m/K),  $L_c$  the characteristic length, in our case  
 463 half of the cell thickness (1 mm),  $\lambda_b$  the thermal conductivity (0.5W/m/K).

464 In our case the Biot number is very small (0.04) and much lower than 0.1. Thus, it can be considered that  
 465 the gradient between the centre and the surface is less than 1K [57,58]. We can conclude that the internal  
 466 temperature measurement should be close to the external temperature measured at the surface of the  
 467 cell, which is in agreement with the measurements performed with the optical sensor.

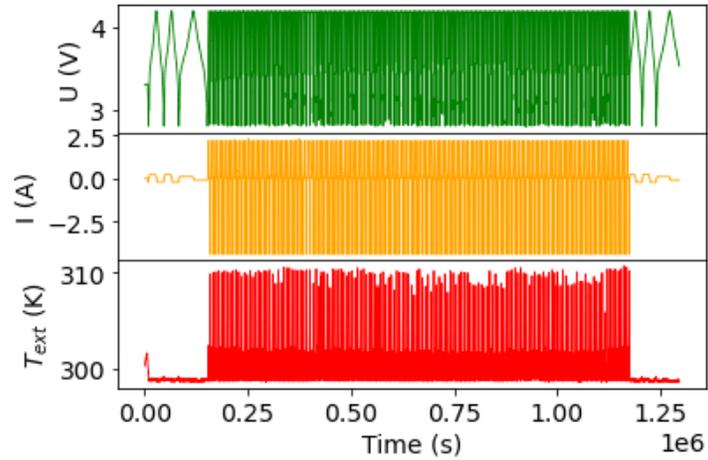


468

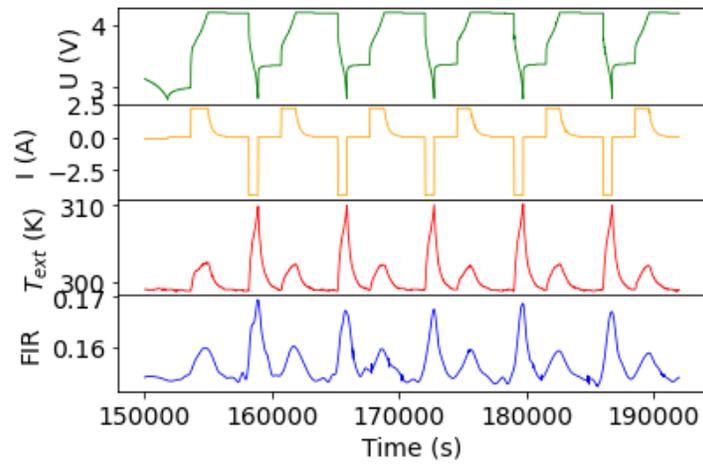
469 **Figure 8.** Temperature variation from ambient: comparison between external and internal measurement during cell cycling.

470 The variation of the signal during the first step at a low C-rate is probably due to the stability of the light  
 471 source. *Figure 8* displays variations of the baseline for the luminescence sensor and a lower value for the  
 472 four peaks during 4C discharge. This difference is attributed to the loss of accuracy during signal denoising  
 473 (*Figure S8*, Supporting Information). To limit this effect and increase the accuracy of the sensor, optical  
 474 optimisation is required to limit the noise and increase the luminescence signal.

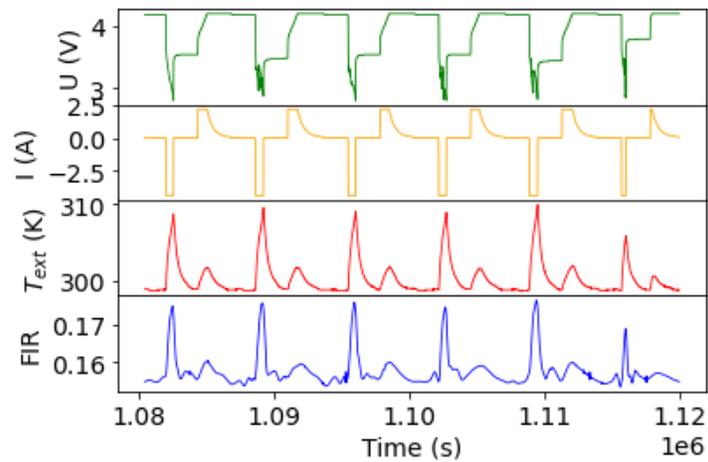
475



a)



b)



c)

476 Figure 9: Aging result during cycling test. a) Full view of the cycling test with the variation of the cell potential ( $U$ ), the cell current  
 477 ( $I$ ) and the external temperature of the cell  $T_{ext}$  measured by thermocouple. Zoom of the 5 first cycles (b) and the 6 last cycles (c)  
 478 with the luminescence ratio correlate to the  $T_{ext}$ ,  $I$  and  $U$  cell.

479 The results of the ageing test are shown in the Figure 9. The external cell temperature ( $T_{ext}$ ), current ( $I$ ) and  
 480 potential ( $V$ ) are shown in the Figure 9. a). A zoom of the 5 first and 6 last cycles are shown in the Figure

481 9. b) and Figure 9. c) represent the chronogram of the variation of the optical signal from the sensor (FIR)  
482 compared to the  $T_{\text{ext}}$  measurement, cell current and cell potential. The variation of the  $\text{SOH}_{2\text{C}}$  and  $\text{SOH}_{4\text{D}}$   
483 variation during ageing is shown in the Figure S13 (Supplementary data).  $\text{SOH}_{2\text{C}}$  is defined as the ratio of  
484 the capacity charged at 2C during the cycle  $n$  divided by the capacity charged at 2C during the first cycle.  
485  $\text{SOH}_{4\text{D}}$  is calculated in the same way with the discharge capacity during the discharge at 4D. The maximum  
486 temperature reached during the charge phase at 2C and the discharge phase at 4D are plotted in figure  
487 S14. In both figures we can see the degradation rate of the cell. After 150 cycles, about 15% of the capacity  
488 is lost in the charge (2C) and discharge (4D) phases. The maximum temperature of the cell (text) during  
489 the 2C charge decreases by less than  $0.25^\circ\text{C}$ . The mean value of the maximum temperature during the  
490 discharge phase at 4D remains constant during ageing. However, we observe a greater dispersion of the  
491 maximum temperature during discharge at 4C. This dispersion is related to the dispersion of the discharge  
492 capacity during ageing. This dispersion becomes more important as the number of cycles increases. It's a  
493 sign of the degradation of the cell's performance. This degradation is visible in the cell potential during  
494 discharge at 4C (see green curve in Figure 9).

495 For the optical sensor, we can see in Figure 9 b) and c) that the FIR signal is correlated with the cell  
496 temperature during all the ageing test. These results demonstrate the good stability of the sensor in the  
497 high C-rate condition over 150 cycles. After 150 cycles, we can see that the intensity of the signal from the  
498 sensor has not been affected by the ageing of the cells.

499

#### 500 **4. Conclusions and perspectives**

501 We demonstrated the interest of using thermoluminescent material as a thermal probe to monitor the  
502 internal temperature of a lithium ion cell during fast charging. For the first time,  $\text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+}$  was used  
503 as a thermal probe in combination with an optical fibre sensor to monitor internal cell temperature during  
504 cycling at high current in charges and discharges with a low cost and compact excitation and detection  
505 system. This material has a higher luminescence than  $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$  previously described by H. Li et al.  
506 [43], and has a high relative sensitivity ( $1.25\% \cdot \text{K}^{-1}$  at 280 K). We demonstrated that the  
507 thermoluminescence performances of  $\text{Gd}_2\text{O}_2\text{S}:\text{Er}^{3+},\text{Yb}^{3+}$  are not affected by the preparation of the optical  
508 fibre sensor, even after the insertion of the sensor inside the Li-ion cell. We showed that insertion inside  
509 the cell does not affect the performance of the cell and that measurement is possible at high  
510 corresponding C-rates (fast charging and high power loading of the cell). These results validate the interest  
511 of this kind of sensor for use in battery management systems. The use of LEDs as optical sources reduces  
512 the cost of this type of sensor compared with other optical fibre sensors used previously for temperature  
513 monitoring in Li-ion batteries. The instrumented cell with sensor was tested in ageing (calendar during 18  
514 months) and over 150 cycling at high c-rate. The optical signal of the sensor shows no major degradation  
515 after the ageing test. These results show the stability of the sensor in the environment and justify the  
516 choice of materials. In the future, it will be interesting to carry out tests over a longer period of time and  
517 under different conditions in order to characterise the durability of the sensor more fully. Furthermore,  
518 the results published on the use of internal cell temperature sensors with fibre optics only concern a few  
519 cycles<sup>[59]</sup>. To the best of our knowledge, the results presented here of 150 cycles at high C-rate in charge  
520 and discharge presented here are new.

521 In terms of accuracy, this sensor is less sensitive than FBG type sensors (1°C versus 0.1°C). However, this  
522 accuracy is sufficient to characterise high capacity cells for fast charge and discharge. This accuracy can be  
523 improved by increasing the power of the optical source and the sensitivity of the detection system. In  
524 addition, other work on thermoluminescence shows that it is possible to use this technique to achieve a  
525 resolution comparable to the FBG of 0.1°C [29,32]. However, this comes at an increased cost. The advantage  
526 of this solution over an FBG-type sensor is precisely its lower cost. For example, the cost of the  
527 spectrophotometer for this sensor is 15 times lower than for an FBG interrogator with a resolution of 0.1°C.

528 We conclude that this new thermal sensor based on functionalised optical fibre is a good candidate for  
529 achieving the goals of the BATTERY2030+ roadmap and for the development of smart batteries [4].

530 The outlook for this work is to further increase sensor sensitivity by improving the optical component and  
531 signal post-treatment to reduce signal noise. The long-term stability of this type of sensor still needs to be  
532 studied; likewise for its integration into an industrial cell manufacturing process. These results open the  
533 way to a producing a new sensitive thermal sensor for monitoring the internal temperature of Lion cells.

534

#### 535 **Credit authorship contribution statement**

536 Olivier Raccurt: Conceptualization, Writing - Original draft, Visualization, Project administration &  
537 supervision, funding acquisition. Elise Villemin, Sylvie Genies, Cédric Septet and Pierre Balfet: Cell  
538 fabrication and instrumentation, Experiment preparation, Electrochemistry tests and Results analysis,  
539 Writing, review & editing. Olivier Poncelet & Sonia Desousa-Nobre: Optical fibre sensor preparation and  
540 Optical characterisation, Writing, review & editing. Romain Franchi: Development of the platform for data  
541 acquisition and visualisation. Jérôme Houny & Martin Guillon: Calibration of the sensor, data treatment,  
542 Writing, review & editing.

543

#### 544 **Declaration of competition interest**

545 The authors declare that they have no known competing financial interests or personal relationships that  
546 could have appeared to influence the work reported in this paper. There are no conflicts to declare.

#### 547 **Data availability**

548 The data that support the findings of this study are available from the corresponding author upon  
549 reasonable request.

#### 550 **Supplementary materials**

551 Supplementary material associated with this article can be found at the end of these file.

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562

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## Supplementary Information

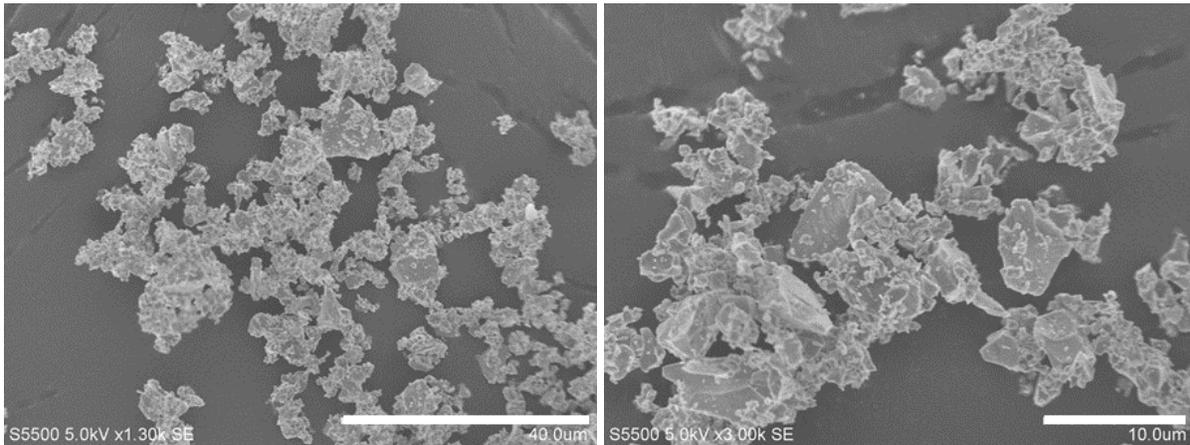
### Thermo-luminescent optical fibre sensor for Li-ion cell internal temperature monitoring

Elise Villemin<sup>1</sup>, Sylvie Genies<sup>1</sup>, Olivier Poncelet<sup>2</sup>, Pierre Balfet<sup>1</sup>, Cédric Septet<sup>1</sup>, Romain Franchi<sup>1</sup>, Martin Guillon<sup>1</sup>, Jérôme Houny<sup>1</sup>, Sonia Sousa-Nobre<sup>2</sup>, Olivier Raccurt<sup>1\*</sup>

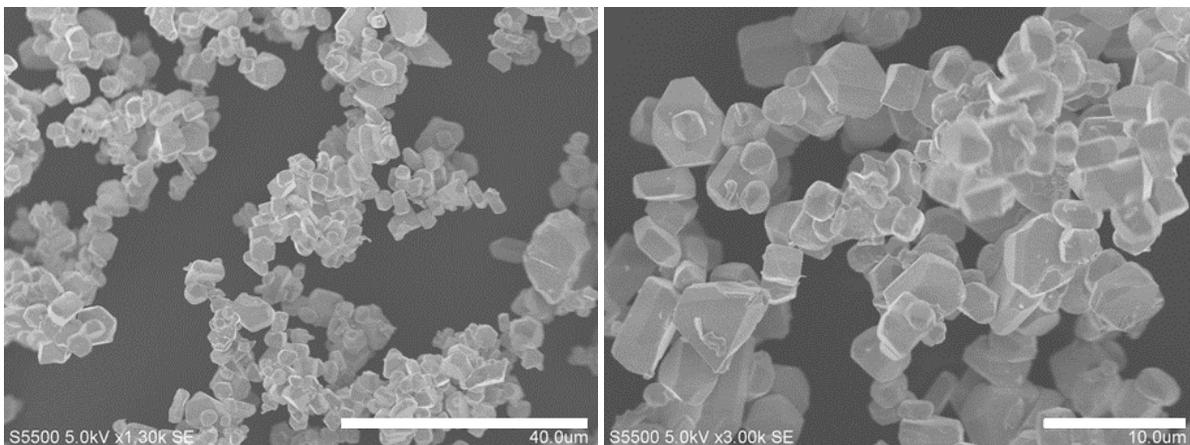
<sup>1</sup> Univ. Grenoble Alpes, CEA, LITEN, DEHT, F-38000 Grenoble, France

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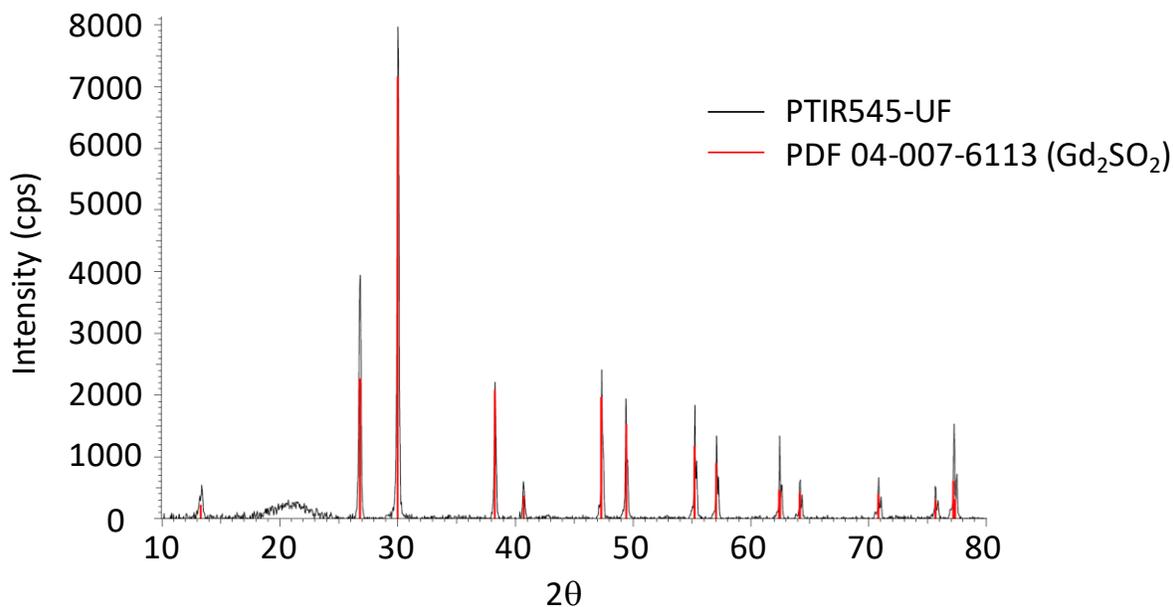
**Figure S10:** Scanning Electronic Microscope image of PTIR545UF  $Gd_2O_2S:Er^{3+}, Yb^{3+}$  Powder. Left: scaling x1300, scaling bare: 40  $\mu m$ . Right: scaling x3000, scaling bare: 10  $\mu m$ .



677 **Figure S11:** Scanning Electronic Microscope image of PTIR550F NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> powder. Left:  
678 scaling x1300, scaling bare: 40 μm. Right: scaling x3000, scaling bare: 10 μm.

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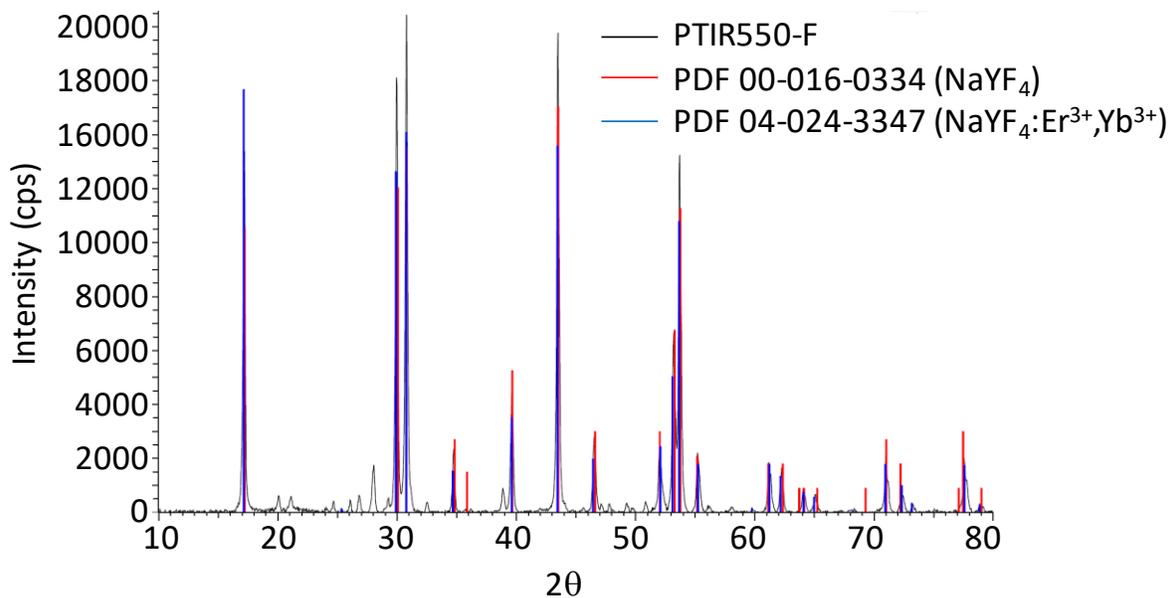
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682 **Figure S12:** X-ray diffraction analysis (XRD) of PTIR545-UF powder compared to the reference  
683 PDF 04-007-6113 (ICCD) for Gd<sub>2</sub>SO<sub>2</sub> material.

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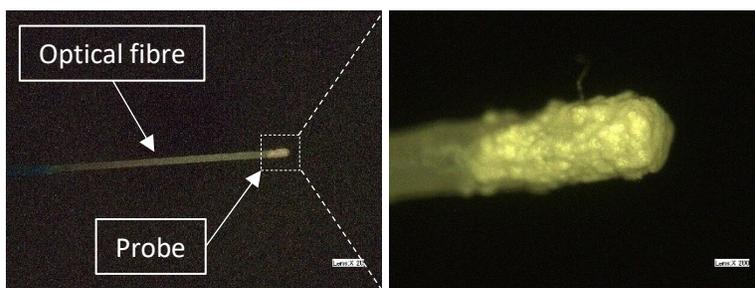


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686 **Figure S13:** X-ray diffraction analysis (XRD) of PTIR550-F powder compared to the reference  
 687 PDF 00-016-0334 (ICCD) for NaYF<sub>4</sub> material and the reference PDF 04-024-3347 (ICCD) for  
 688 NaYF<sub>4</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> material.

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692 **Figure S14:** Optical microscope image of the sensor. (Left): Optical fibre with the  
 693 thermoluminescent particles on the tip (x20), (right) close-up of the end of the tip (x200).

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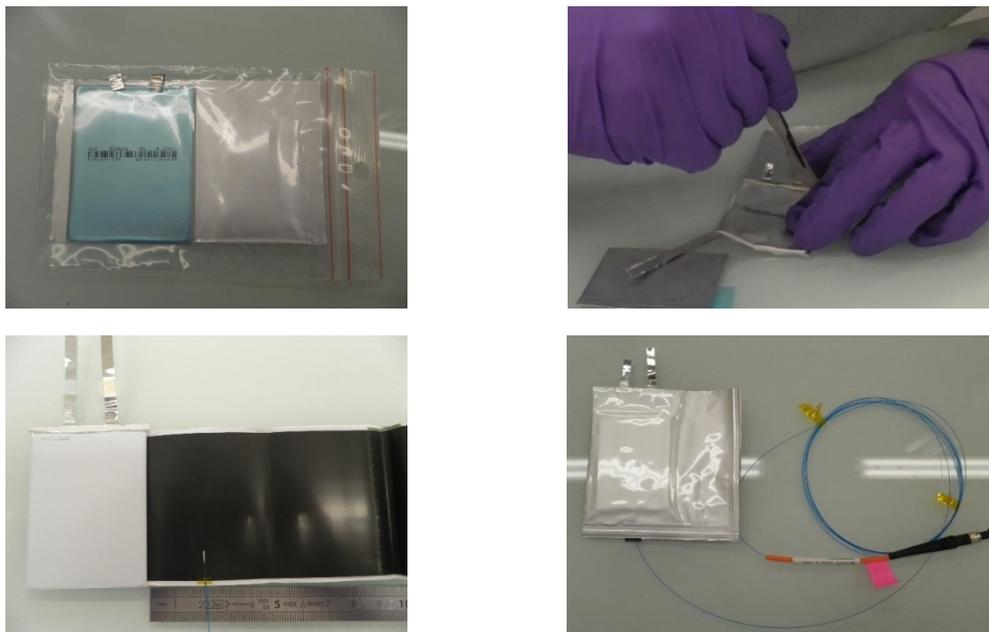
**Table S1:** Cell characteristics.

Electrochemical characteristics	
Voltage range (V)	3.0 - 4.2
Average voltage (V)	3.7 at room temperature and 0.2 C
Optimal capacity (mAh)	1100 mAh at room temperature and 0.2 C
Positive real capacity (mAh/cm <sup>2</sup> )	1100 mAh at room temperature and 0.2 C
Negative real capacity (mAh/cm <sup>2</sup> )	2.8
Energy density (Wh/kg)	214
Energy density (Wh/L)	425
Cathode	
Material	NMC622
Active material loading (%)	96.4
press density (g/cc)	3.30
Coating Weight (mg/cm <sup>2</sup> )	16.7
Anode	
Material	Graphite
Active material loading (%)	94.8
press density (g/cc)	1.8
Coating Weight (mg/cm <sup>2</sup> )	10
Separator	
Material	PE with Al <sub>2</sub> O <sub>3</sub> coating on NMC side
Thickness	15 μm

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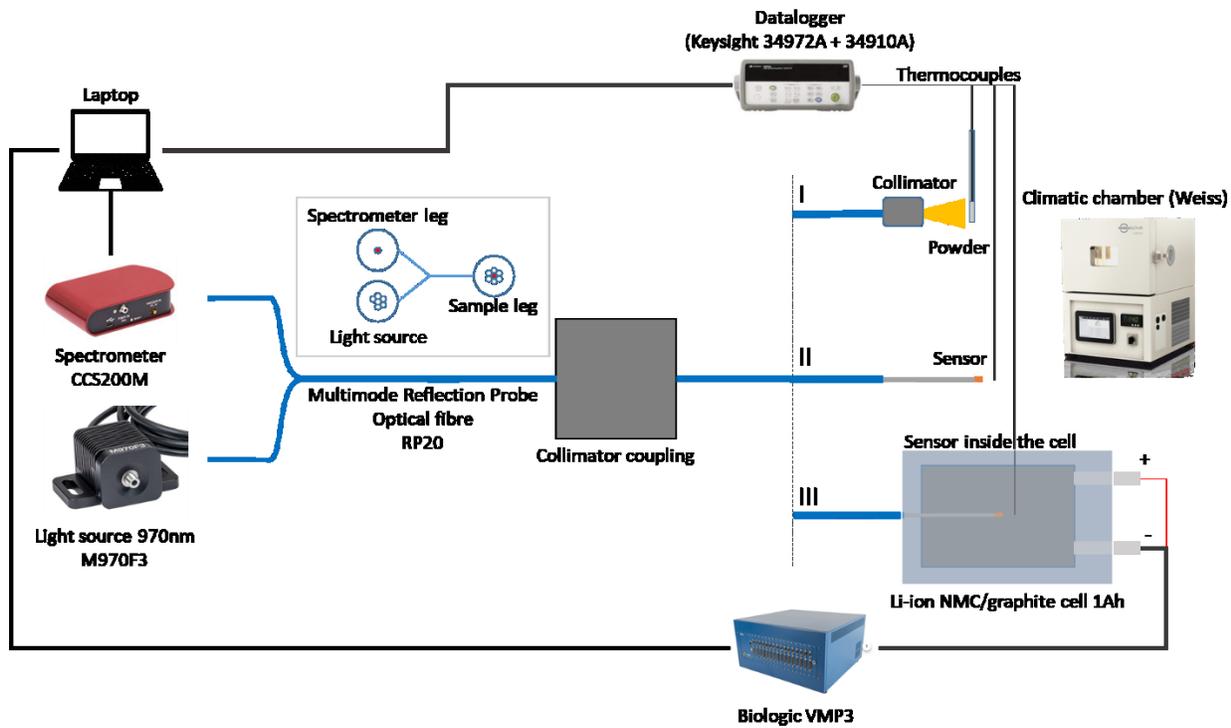
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700 **Figure S15:** Cell instrumentation: Non-activated commercial cell (top, left), Cell opening (top,  
701 right), optical fibre sensor insertion (bottom, left), instrumented cell (bottom).

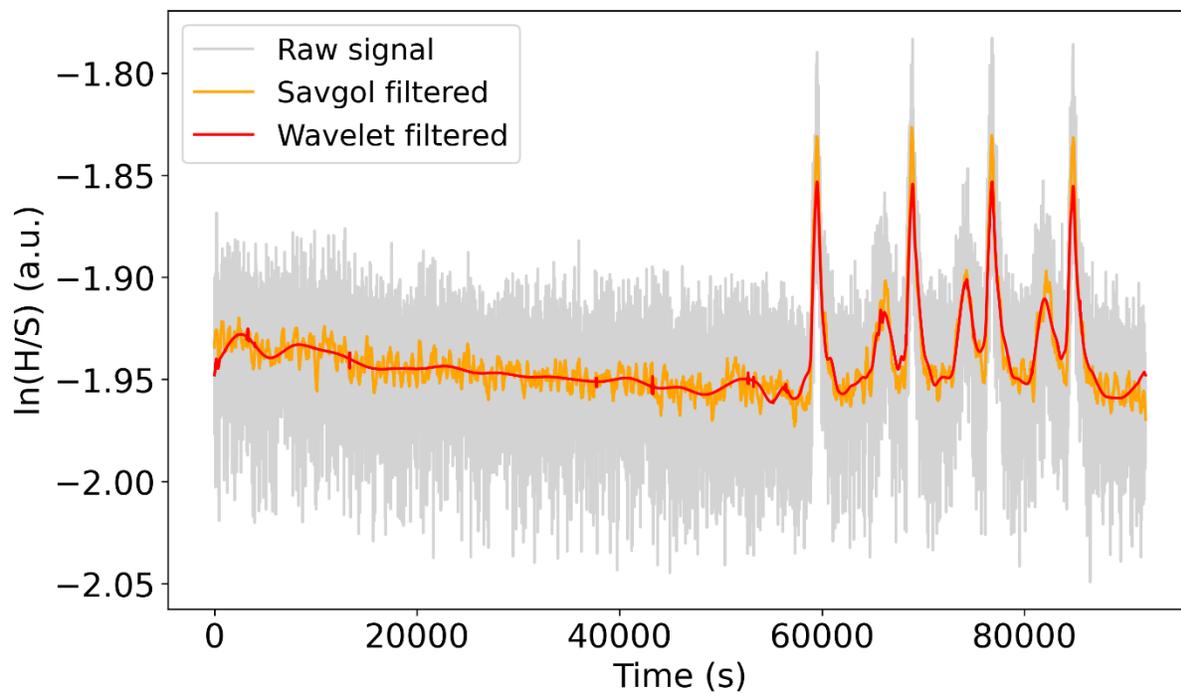
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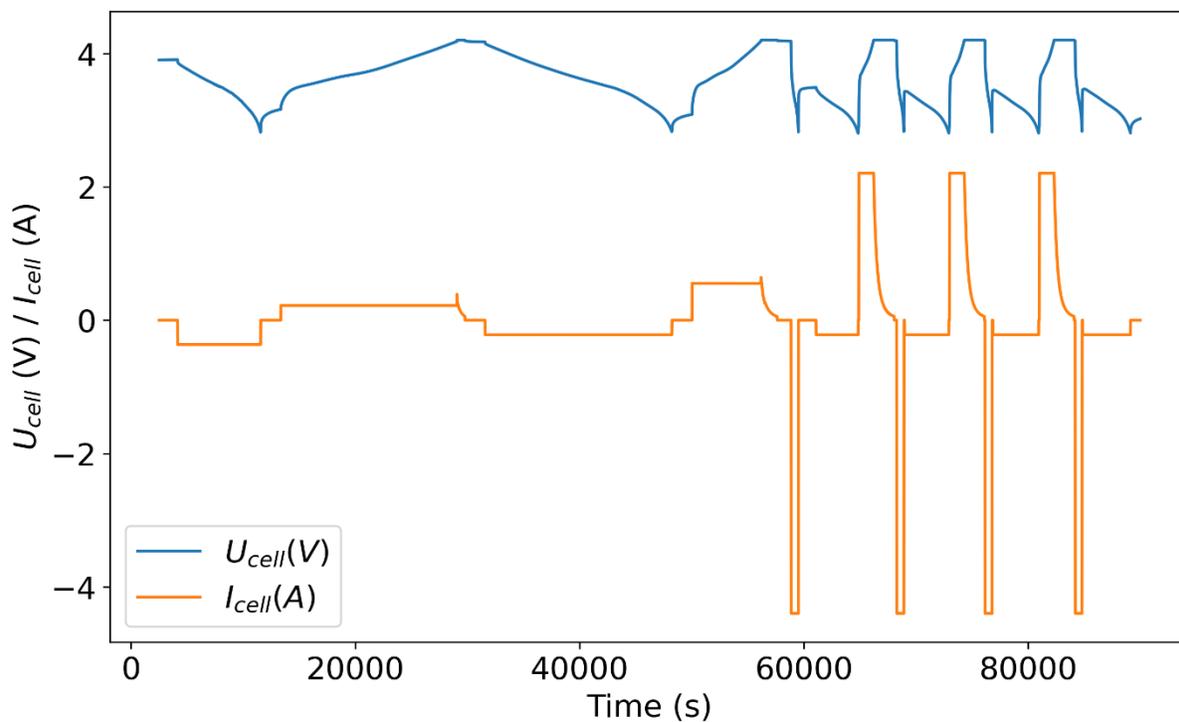


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 705 **Figure S16:** Schematic view of the experimental setup for powder calibration (I), optical fibre  
 706 sensor calibration (II), calibration and cycling test of the instrumented cell (III).

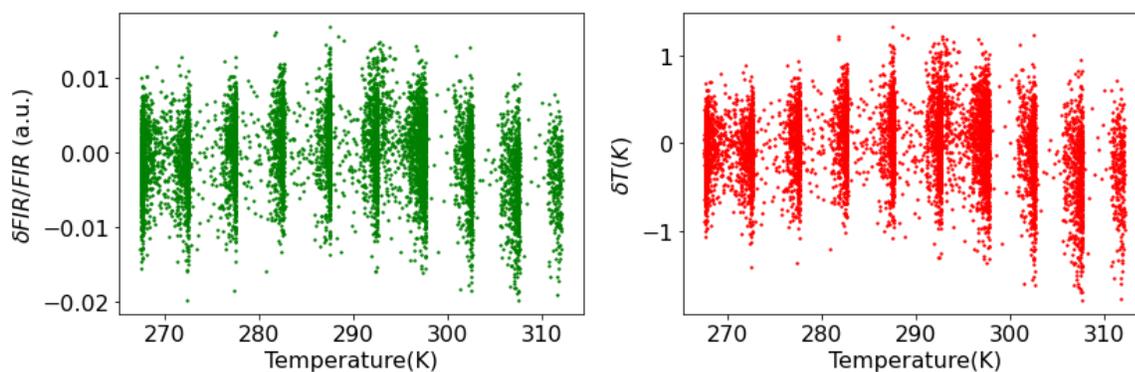
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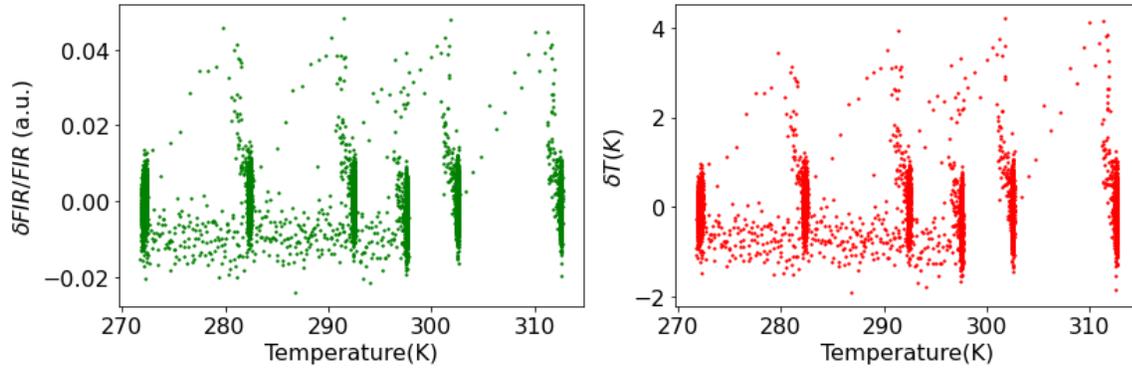
708  
709 **Figure S17:** Luminescence signal denoising. Variation of  $\ln(H/S)$  as a function of time raw signal  
710 (gray), savgol filtered (orange), wavelet filtered (red).  
711



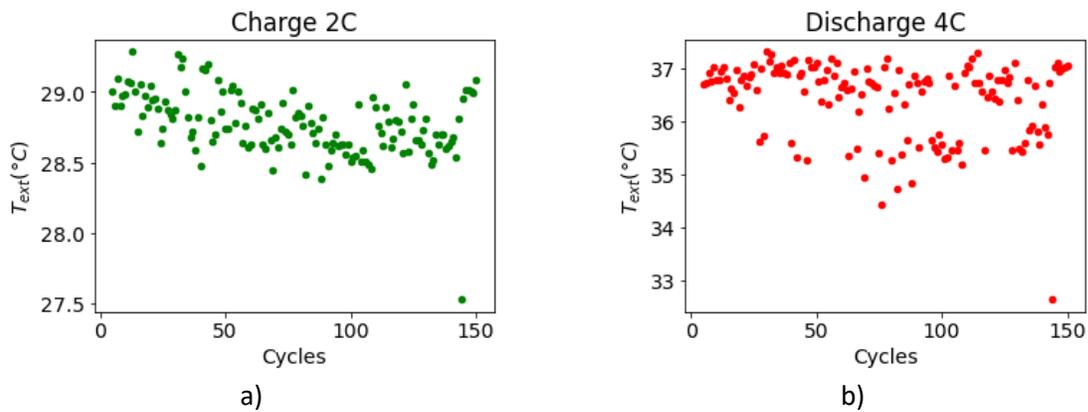
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 713 **Figure S18:** Cycling protocol during the experiment: cell potential (blue), cell current (orange)  
 714 over time.  
 715



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 717 **Figure S19:** Error  $\delta\text{FIR}$  (left) and  $\delta T$  (right) as function of temperature for sensor calculate from  
 718 calibration curves.

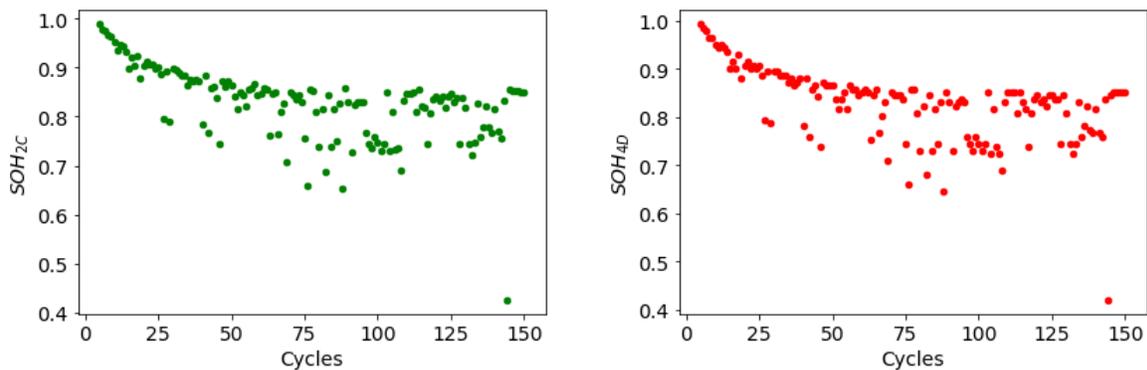


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 720 **Figure S20:** Error  $\delta\text{FIR}$  (left) and  $\delta T$  (right) as function of temperature for sensor inside the cell  
 721 form calibration curves.



722 **Figure S21:** Evolution of the maximum of the external cell temperature  $T_{\text{ext}}$  during the charge at  
 723 2C and discharge at 4C over ageing.

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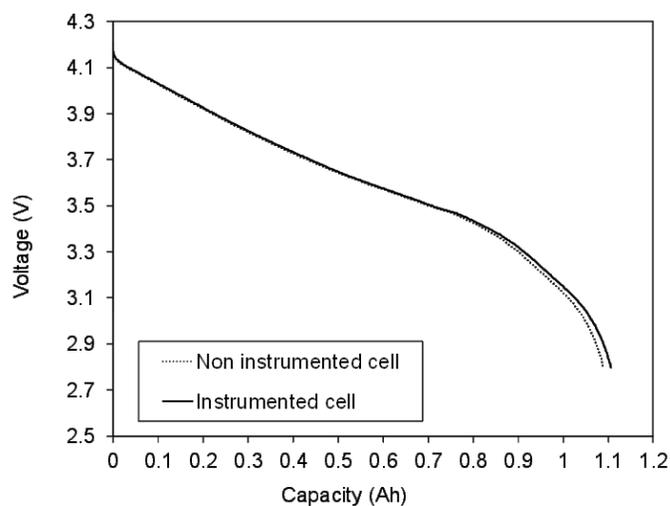
726 **Figure S22:** Evolution of the State of Health (SOH) the charge at 2C and discharge at 4C over  
 727 ageing.

728

729 **Table S2:** Irreversible capacity (1<sup>st</sup> Cycle) in % and initial capacity (measured at C/5) in Ah of  
 730 instrumented and non-instrumented cell

	Irreversible capacity (1st cycle) [%]	Capacity (at C/5) [Ah]
Non instrumented cell	16.4%	1.089
Instrumented cell	16.2%	1.192

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733 **Figure S23:** Comparison of cell potential curve of instrumented cell and non-instrumented cell  
 734 measured at in discharge at C/5 just after formation protocol (initial capacity).

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