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Influence of electrode fabrication process on nanocrystalline tin oxide electrochemical behaviour for high voltage SnO₂/LNMO full cell Li-ion battery / Versaci, Daniele; Kastrinaki, Georgia; Ganas, George; Zarvalis, Dimitrios; Karagiannakis, George; Amici, Julia; Francia, Carlotta; Bodoardo, Silvia. - In: JOURNAL OF ENERGY STORAGE. - ISSN 2352-152X. - 65:(2023), pp. 1-11. [10.1016/j.est.2023.107357]

Availability:

This version is available at: 11583/2978108 since: 2023-04-23T07:18:47Z

Publisher:

Elsevier

Published

DOI:10.1016/j.est.2023.107357

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<http://dx.doi.org/10.1016/j.est.2023.107357>

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1 Influence of electrode fabrication process on
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13
14 KEYWORDS: SnO₂ nanoparticles, sol-gel synthesis, anodes, LNMO, Full cell, Li-ion
15 battery

16
17 **ABSTRACT**

18 Tin oxide is one of the most promising anode materials to replace graphite in the next
19 generation lithium-ion batteries thanks to its high theoretical specific capacity, low cost
20 and large availability. Unfortunately, its large-scale application is still limited, due to
21 marked capacity loss and poor cyclability. Recent findings demonstrated improved
22 reversibility of the electrochemical reactions through the optimization of SnO₂ particles
23 size. In this frame, the sol-gel method has proved to be one of the most interesting
24 synthesis processes to obtain mono and polycrystalline SnO₂ particles, which guarantee
25 higher reversibility of the conversion reaction. In this work, SnO₂ nanoparticles was

26 synthesized by sol-gel method, with an average size of 5 - 50 nm, depending on the post
27 calcination temperature. Subsequently, the optimization of the electrode composition in
28 terms of mass loading and binder allowed to achieve a specific capacity of 350 mAh g⁻¹,
29 with a coulombic efficiency of 99.9 % after 100 cycles at high current rate of 0.75 A g⁻¹.
30 Finally, the optimized and pre-lithiated SnO₂ anode was coupled with the high voltage
31 LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cathode in full-cell configuration, and the contribution of the
32 voltage window and formation step to the final cell capacity was studied to determine the
33 optimum conditions at which high cycling stability can be obtained.

34

35 **1. Introduction**

36 Nowadays, it is generally accepted that Li-ion battery technology can play a crucial
37 role in the energy transition, facilitating decarbonization of the transportation sector and
38 providing a pivotal contribution in the energy storage from intermittent solar and wind
39 sources [1].

40 At the same time, for all these applications a battery system able to guarantee fast and
41 safe charge is fundamental and strategic for the mass adoption and diffusion of these
42 technologies [2][3][4].

43 However, it is generally accepted that the lithium-ion intercalation in graphite-based
44 electrodes is one of the bottlenecks for the fast charging, limiting the performance of the
45 battery and strongly affecting the safety of the system [5][6]. In addition, graphite has a
46 theoretical specific capacity of 372 mAh g⁻¹, which cannot meet the future generations
47 battery requirements [7][8].

48 In the last decades, different materials have been studied as alternative anodes for Li-
49 ion battery such as alloys, conversion materials and metal oxides. However, many of these
50 materials show some issues and drawbacks, such as poor cyclability, reduced operational
51 potential, poor electronic conductivity, or high production cost, which have inevitably
52 limited their diffusion and commercialization [8][9].

53 More recently, the use of hybrid materials such as silicon and graphite blends are
54 among the most attractive options to increase energy density and achieve the targets set
55 for next generation batteries. Electrodes with a variable percentage of silicon and graphite
56 have been developed and are currently used in commercial lithium-ion batteries with the
57 aim of increasing the specific capacity of the system [10][11]. However, the percentage
58 of silicon is still low compared to that of graphite, and the limits associated with fast
59 charging are not addressed yet. Furthermore, silicon is within the materials that are
60 recognized as critical in the “Report on critical raw materials” by EU in 2020 [12]. For
61 these reasons, there is a clear need to study and develop alternative anodic materials able
62 to guarantee higher energy densities and good rate capabilities while being widely
63 available.

64 In this frame tin dioxide (SnO_2) is one of the most valued materials for Li-ion battery
65 (LIBs) anodes and has gained particular interest due to its low cost, high availability and
66 above all, excellent electrochemical properties. It is indeed characterized by a high
67 theoretical specific capacity (for alloying/de-alloying reaction $\sim 782 \text{ mAh g}^{-1}$ and for
68 alloying/de-alloying and conversion reactions, $\sim 1494 \text{ mAh g}^{-1}$) as well as an average
69 charge and discharge potential of 0.5 V and 0.3 V vs. Li^+/Li [13][14][15]. Unfortunately,
70 the widespread use of SnO_2 as anode has been strongly limited by its intrinsic low
71 electronic conductivity, by the limited reversibility of the conversion reaction and the
72 marked volume expansion during the alloying reaction. These drawbacks have been

73 partially overcome through material engineering, such as miniaturization of the particles
74 and creation of hybrid materials, in which a carbonaceous material or carbon-based matrix
75 limits the volumetric expansion and, at the same time, guarantees good electronic
76 conductivity [16][17][18]. Therefore, many different nanostructured SnO₂ and
77 composites have been reported in literature, such as SnO₂ and Sn/SnO₂ hybrids [19] with
78 hollow structures, able to provide extra void space alleviating the stresses of Li de-
79 /intercalation processes [20], thin carbon layer applied to the exterior surface of SnO₂
80 hollow spheres [21] as well as well-designed surface engineering of porous carbon
81 coatings on CNT@SnO₂ composites that increased the Li ion diffusion through an open
82 tunnel-like architecture [22]. The embedding of either Sn [23] or SnO₂ nanoparticles into
83 porous carbon or carbon nano/micro spheres provided materials with high surface area
84 allowing more surface lithium storage sites [24], while the fabrication of SnO₂ quantum
85 dots on N-doped carbons significantly decreased the diffusion distance for ion/electrons
86 improving the rate capability of the cell [25].

87 More recent researches intensively explored the complex reaction mechanism of Li
88 storage in SnO₂ by in situ/in operando techniques in both liquid [26] and solid electrolytes
89 [27] and validated that SnO₂ conversion/alloying reaction is a five step mechanism
90 involving several different phases such as SnO_x, Li₈SnO₆, Li₂SnO₃, Li_xSn, Sn and Li₂O,
91 depending on the lithiation potential. At the same time, it has been observed that the
92 irreversible capacity during the first cycles and the poor cycling stability are ascribable to
93 the aggregation of Sn particles into inactive clusters during charge/discharge processes.
94 Such Sn coarsening-induced volume shrinkage is one of the main reasons for capacity
95 fading thus, the repeated formation of very small Sn particles starting from nanosized and
96 robust SnO₂ is still the most feasible way to obtain high capacity and stable cycling
97 performances [28].

98 As a consequence, the SnO₂ anode performance in LiBs are strictly related to the
99 variety of morphologies in which the material can be prepared, *i.e.* 1D [29], 2D [30], 3D
100 [31], along with its particle size [32] and their distribution in confining matrices that limit
101 their coalescence and improve their conductivity [33]. Unfortunately, such matrices
102 usually lead to increase the content of the inert mass, which lowers the volumetric and
103 gravimetric energy density of the final battery. It is almost certain that the breakthrough
104 for SnO₂ as anode will require the design of nanocomposite electrode [34] materials, but
105 currently most of the production processes appear complicated for scale-up.

106 Taking into account all these considerations, SnO₂ nanoparticles have been prepared
107 by cost-effective and highly scalable sol-gel approach, followed by calcination at
108 different temperatures. Sol-gel method has been chosen for its ability to provide fine
109 dispersion of tin precursors limiting coarsening of nanoparticles [35], and resulting in
110 narrow dispersion of SnO₂ NPs with an average size between 5-10 nm, (which can
111 increase to 20 nm by post treatment). Besides, nanosizing of SnO₂ particles allows to
112 maintain a high fraction of Sn/Li₂O interfaces, which strongly improves the reversible
113 dis-/charge reactions [36].

114 Then, through the chemical-physical and morphological study of the particles obtained
115 by sol-gel approach, the optimal post-treatment process has been identified in order to
116 obtain finely dispersed SnO₂ nanoparticles with high surface area.

117 In a second step, the material with the best morphological properties has been studied
118 from an electrochemical point of view as suitable anode material for LIBs. Particular
119 attention is given to the engineering of the electrode by studying different slurry
120 compositions, different mass loading and different binder/solvent couples. In fact, the
121 impressive electrochemical performances of highly nanostructured SnO₂ electrodes are

122 often achieved at very low mass loadings (*i.e.* 1.0 mg cm⁻² or less), where the mass of the
123 inert components (current collectors and separators) highly exceeds the one of the active
124 material [37][38][39][40].

125 Finally, the electrochemical performances of the optimized SnO₂ electrode have been
126 evaluated in a full cell configuration, coupling the tin oxide-based anode with a cobalt-
127 free LiNi_{0.5}Mn_{1.5}O₄ (LNMO) cathode. LNMO is chosen because it is considered a good
128 candidate for the next generation cobalt-free positive AMs, but its commercial application
129 is still hindered by some drawbacks such as the dissolution of transition metals (*i.e.* Mn)
130 and the electrolyte decomposition occurring at high operating potential [41], in particular
131 if coupled with the graphite anode.

132 Hence the evaluation of the electrochemical performance of SnO₂ in a full cell
133 configuration with high voltage cathode materials, is promising but has not fully been
134 characterized yet.

135

136 **2 Material and methods**

137 **2.1 Preparation of SnO₂ through sol-gel synthesis**

138 SnO₂ nanoparticles were synthesized by a sol-gel method. Typically, 9 gr of
139 SnCl₄·2H₂O (Sigma-Aldrich) were dissolved in 100 ml deionized water under stirring,
140 NH₄OH (25%) was added up to pH 8 dropwise. The resulting solution was stirred for 2
141 hours and left in a closed flask for 24 hours before calcination. The calcination
142 temperatures were 400, 700, 900 and 1000 °C for 2 hours (samples respectively named
143 SnO₂-400, SnO₂-700, SnO₂-900 and SnO₂-1000). Commercial SnO₂ nanoparticles
144 purchased from Sigma-Aldrich were used as comparison (Sigma Aldrich, SnO₂
145 nanopowder, ≤ 100 nm avg. part. size).

146 **2.2 Characterization of SnO₂ nanoparticles**

147 The synthesized nanoparticles were characterized on a carbon holey grid by TEM
148 (JEOL, JEM-2010, Japan) for their morphology, and their size distribution was measured
149 on the TEM images by ImageJ software on 50 particles per sample. The surface area was
150 characterized by nitrogen adsorption and desorption isotherms at 150 °C (Autosorb-1,
151 Quantachrome Instruments, US). The X-Ray diffraction was performed by an XRD
152 D500/501 apparatus (Siemens, Berlin, Germany), equipped with Cu K α radiation source
153 from 10–80 2 θ angle with 0.04 step. The crystallites size was determined according to
154 Scherrer equation that relates the width of a powder diffraction peak to the average
155 dimensions of crystallites in a polycrystalline powder:

$$156 \quad D = K\lambda/\beta (2\theta)_{hkl} \cos\theta,$$

157 where β is the crystallite size contribution to the peak width (full width at half
158 maximum) in radians, K (shape factor) is a constant near unit and D is the average
159 thickness of the crystal, in a direction normal to the diffracting plane hkl. The Raman
160 analysis was carried out by an in Via Renishaw instrument with a laser of 514.5 nm at 5
161 mW.

162 SnO₂ particles morphology was also assessed by FESEM on a Zeiss SUPRA TM 40
163 with Gemini column and Schottky field emission tip (tungsten at 1800 K). Acquisitions
164 were made at acceleration voltage of 3 kV and working distance (WD) between 2.1 and
165 8.5 mm, with magnification up to 150 KX.

166

167 **2.3 SnO₂ anode preparation and half-cell assembling**

168 All the electrodes were prepared by solvent tape casting method. Different slurries
169 composed of SnO₂, conductive carbon additive (TIMCAL C-ENERGY™ Super C65,
170 Imerys Carb.) and a polymeric binder (poly(vinylidenedifluoride) PVdF-HSV900
171 dispersion at 10 wt.% in N-methyl-2-pyrrolidinone solution), in different weight ratio: (i)
172 40:50:10, (ii) 50:40:10, (iii) 60:30:10 and (iv) 70:20:10 were prepared in order to evaluate
173 the effect of the mass-loading, and electrode composition. All the different mixtures were
174 mechanically deposited on a copper current collector by Doctor Blade technique. The
175 blade was adjusted for a 200 μm deposition using an automatic film applicator (Sheen
176 1133N) with a speed of 50 mm s⁻¹. Successively to the slurry deposition, the coated
177 copper foil was dried at 60 °C for 1.5 hours in air. After solvent evaporation, disks of
178 0.785 and 1.766 cm² were punched out, vacuum dried at 120 °C (in a Büchi Glass Oven
179 B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraun Labstar, H₂O
180 and O₂ content < 1 ppm) for the half-cell and full-cell assembly. The final active material
181 loading of the anode electrodes was respectively 1.1, 1.6, 2.5 and 3.5 mg cm⁻² for (i), (ii),
182 (iii) and (iv) respectively.

183 To evaluate the effect of the binder, slurries of SnO₂-400 (SnO₂ nanoparticles obtained
184 from the 400 °C calcination), C65 and CMC in water, with weight ratio 70:20:10 (mass
185 loading of 3.6 mg cm⁻²) were prepared by the same procedure.

186 The as prepared electrodes were tested in 2032 coin cells (for galvanostatic cycling
187 test), using lithium disks (Ø 16 mm, thickness 0.6 mm, Tobmachine) as counter and
188 reference electrodes, while a glass-wool (glass fiber separator, thickness 0.65 mm, EL-
189 Cell) was used as separator. The electrolyte adopted was a solution of 1.0 M LiPF₆
190 dissolved in a mixture 1:1 v/v of Ethylene Carbonate (EC) and Diethyl Carbonate (DEC)
191 (battery grade, Solvionic).

192 The cycling performances were investigated by means of galvanostatic discharge-
193 charge cycling (GC) using an Arbin BT-2000 battery tester at room temperature. GCs are
194 carried out in the potential range of 0.01 – 2.0 V vs. Li/Li⁺ at different C-rates (1495 mAh
195 g⁻¹ is the theoretical capacity of SnO₂). Here, the potential is referred versus Li/Li⁺, and
196 the specific charge is presented per mass of SnO₂ material.

197 To better evaluate the overall resistance inside the cells Potentiostatic Electrochemical
198 Impedance Spectroscopy (PEIS) measurements were carried out by a versatile
199 multichannel potentiostat (VMP-3 Biologic). Impedance measurements were performed
200 using an amplitude of 10 mV in the frequency range of 500 kHz to 50 mHz.

201 Two-probe plane electronic conductivity measurement was used to evaluate the out-of-
202 plane conductivity of the electrodes. Circular electrode discs with a diameter of 18 mm
203 were inserted into EL cells ECC-Ref according to the following configuration: bottom
204 cell – electrodes – current collector – pistons – spring – top cell. Galvanostatic
205 Electrochemical Impedance Spectroscopy (GEIS) measurements were carried out by the
206 multichannel potentiostat (VMP-3 Biologic). Impedance measurements were performed
207 repeatedly on three different electrodes for each samples using an amplitude of 0.5 mA
208 in the frequency range of 100 kHz to 100 mHz. During the GEIS measurements the
209 working and counter electrodes were separated for the respective references in order to
210 avoid the contribution of cable resistance.

211

212 **2.4 LNMO cathode preparation and SnO₂/LNMO full cell assembly and**
213 **characterization**

214 The cathode slurry was prepared mixing 90 wt% of active material LNMO
215 ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, NANOMYTE-SP10, NEI corp.), 5 wt% of conducting Carbon Black
216 (TIMCAL C-ENERGYTM Super C65, ImerysCarb.) and 5 wt% of binder PVdF (HSV900,
217 10 wt.% in NMP solution) in N-methyl pyrrolidone. The as prepared slurry was casted
218 on aluminium foil by a solvent tape casting method, using a doctor blade (adjusted for
219 300 μm deposition) and an automatic film applicator (Sheen 1133N) with a speed of 50
220 mm s^{-1} . After evaporating the solvent at 60 °C for 1.5 hours, electrode disks with an area
221 of 1.766 cm^2 were punched out and vacuum dried at 120 °C (Büchi Glass Oven B-585)
222 for 4 h, then transferred into an Argon filled dry glove-box (MBraum Labstar, H_2O and
223 O_2 content < 1 ppm). The final mass loading of the LNMO dried electrodes was in the
224 range of 6 mg cm^{-2} .

225 Before the full-cell assembly, the anode was charged and discharged ten times at C/10
226 with a final step of pre-lithiaion (at C/20) to 0.01 V in half-cell, in order to address the
227 initial irreversible capacity loss and form a certain lithium reservoir. Subsequently, the
228 anode electrode was coupled with LNMO electrode and tested either in T-cells (for three-
229 electrodes test) or in coin cells 2032 (for two-electrodes test). The three-electrodes cell
230 configuration was used to control and deconvolute the voltage profiles of the anode and
231 cathode during charge and discharge process, using lithium metal as reference electrode.
232 All electrochemical studies were performed at room temperature. The full cell
233 electrochemical behaviour was investigated in two operational potential windows, from
234 3.5 - 4.9 V and 2.5 - 4.9 V vs. Li/Li^+ . While the charge/discharge rate was based on
235 the LNMO theoretical specific capacity of 147 mAh g^{-1} .

236

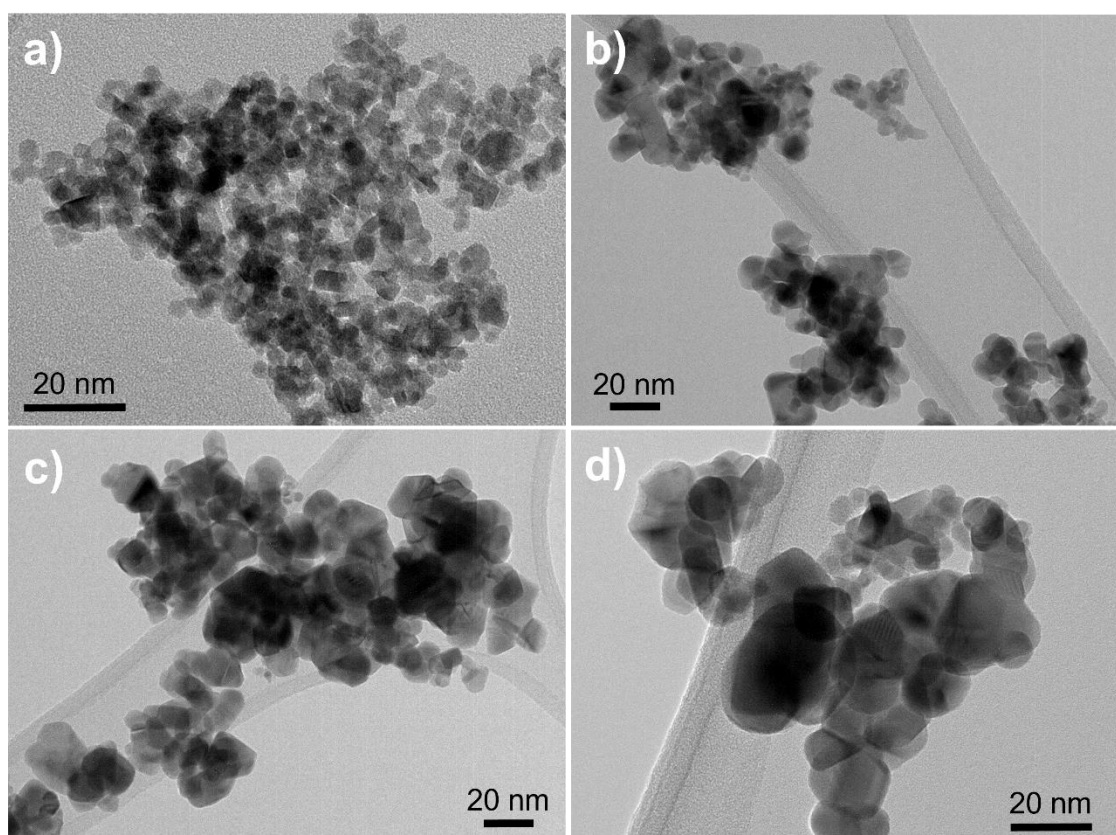
237 **3 Results and Discussion**

238 3.1 SnO₂ structural and morphological characterization

239 The first step of this study is aimed to screen the morphological and chemical-physical
240 characteristics of the synthesized materials. In particular, the effect of the calcination
241 treatment on the tin dioxide particles is evaluated.

242 **Figure 1a-d** shows the TEM and **Figure S1** the FESEM images of the sol-gel
243 synthesized SnO₂ nanoparticles calcined at the different temperatures of 400°C, 700°C,
244 900°C, 1000°C respectively, and that of commercial SnO₂ is shown in **Figure S2b** as
245 comparison. Both TEM and FESEM images indicate that SnO₂ is composed of
246 nanoparticles that are in the order of five to fifty nanometres in size, depending on the
247 calcination temperature. As can be seen in **Figure 1a**, **Figure S1a-b** and in **Figure S2a**,
248 sample SnO₂-400 shows a homogeneous, uniform distribution of SnO₂ nanoparticles
249 agglomerates. Moreover, SnO₂-400 nanoparticles appear ultra-fine, with a mean particle
250 size of about 5.8 nm, which is very similar to the size of particles determined by XRD
251 analysis using the Scherrer's equation, as shown in **Table S1**. For samples calcined above
252 400°C, the mean particle size of the nanoparticles, obtained by TEM analysis, increases
253 with the calcination temperature (**Table S1**). This effect has been reported by Aziz *et al.*
254 [42] who observed the same trend between the average particle size of SnO₂ and the
255 calcination temperature. The structural coarsening of SnO₂ driven by temperature is
256 attributed to the growth of nanometer-scale SnO₂ crystallites [35]. In fact, the
257 microstructure at 700 °C and 1000 °C is similar but SnO₂-1000 has larger grain size and
258 larger size distribution (**Figure 1b,c** and **Figure S1g-h**). Moreover, for samples SnO₂-
259 700, SnO₂-900 and SnO₂-1000 a discrepancy is also observed between the mean particle

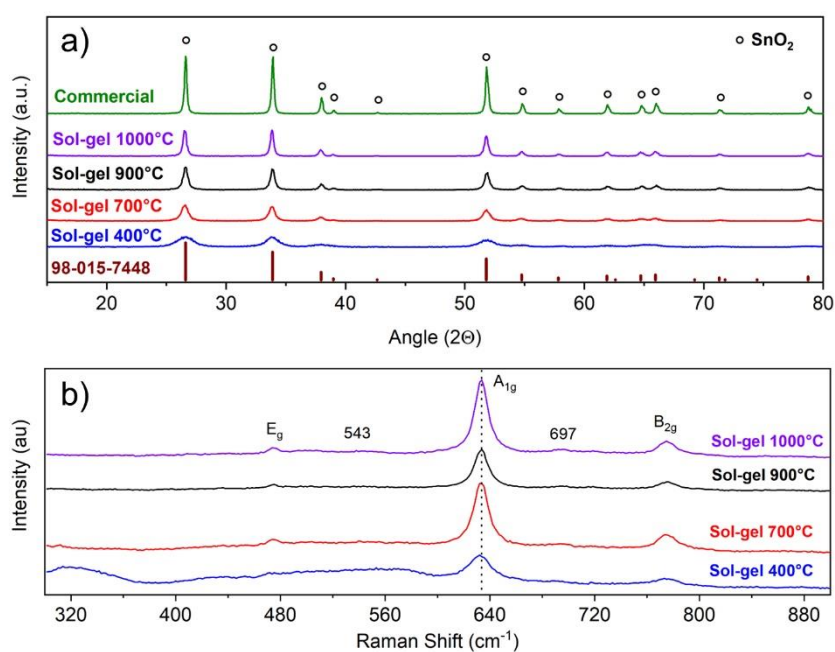
260 size obtained from TEM micrographs and the values calculated by the Scherrer's
261 equation, indicating polycrystalline SnO₂ (**Table S1**).



262

263 To evaluate the phase purity and the crystallite size of the synthesized SnO₂, XRD
264 analysis is carried out and reported in **Figure 2a** with the XRD pattern of the commercial
265 sample as comparison. The XRD analyses show the characteristic peaks of SnO₂
266 corresponding to the tetragonal rutile structure with a P4₂/mm space group (reference
267 code 98-015-7448) and these results confirm a single phase. Among all the samples,
268 SnO₂-400 exhibits broader peaks consistent to the smaller particle size and less degree of
269 crystallinity. The XRD peaks of SnO₂ become sharp and narrow with the increase of the
270 calcination temperature, this means that the phase does not change with temperature but
271 the crystallinity degree increases as well as the nanoparticle size [43], as observed by
272 TEM analysis. **Figure 2b** shows the Raman spectra of the synthesized SnO₂
273 nanoparticles. From Raman analysis the peaks at 633, 475 and 774 cm⁻¹, correspond to

274 the A_{1g} , E_g and B_{2g} vibrational modes, respectively. These are the typical modes of the
 275 tetragonal rutile structure of SnO_2 consistent to a pure phase sample [44]. In particular,
 276 A_{1g} and B_{2g} are attributed to the symmetric stretching modes of the Sn-O bond, while E_g
 277 is attributed to the vibration of oxygen in the oxygen plane. Additionally, two modes at
 278 697 cm^{-1} and 543 cm^{-1} are exhibited in the Raman spectrum of SnO_2 -1000 in **Figure 2b**,
 279 that are usually referred to local lattice disorder. In **Figure 2b**, the intensities of the A_{1g} ,
 280 E_g and B_{2g} vibrational modes of SnO_2 -400 are lower than those of the other SnO_2 samples
 281 and this can be related to the lower crystallinity degree and higher surface disorder of
 282 SnO_2 -400. Finally, the blue shift of the A_{1g} mode further confirms the increase in particle
 283 size with the calcination temperature [44]. It is evident that the material calcined at the
 284 lower temperature $400\text{ }^\circ\text{C}$ exhibits the highest surface area ($88.6\text{ m}^2\text{ g}^{-1}$), and the lowest
 285 crystallite size and particle size (5 nm), possibly due to monocrystalline nanoparticles;
 286 while further calcination increases particle and crystalline size and decreases surface
 287 areas, to values of 55 nm, 24 nm and $13\text{ m}^2\text{ g}^{-1}$ respectively. The commercial material
 288 exhibits values in the range of 43 nm particle size, 36 nm crystallite size and $8\text{ m}^2\text{ g}^{-1}$
 289 surface area.



291

292 In relation to previous studies [45] it is expected that nanosized SnO₂ shows advantages
293 in cycling behaviour with characteristics related to strong resistance to fragmentation, less
294 volumetric changes during conversion/alloying reactions and enhanced diffusion of Li-
295 ions in the bulk phase. Thus, the attention has been focused on the sol-gel monocrystalline
296 SnO₂-400 material with the smallest particle size (5 nm) and larger BET surface area
297 which is expected to show enhanced electrochemical performance.

298

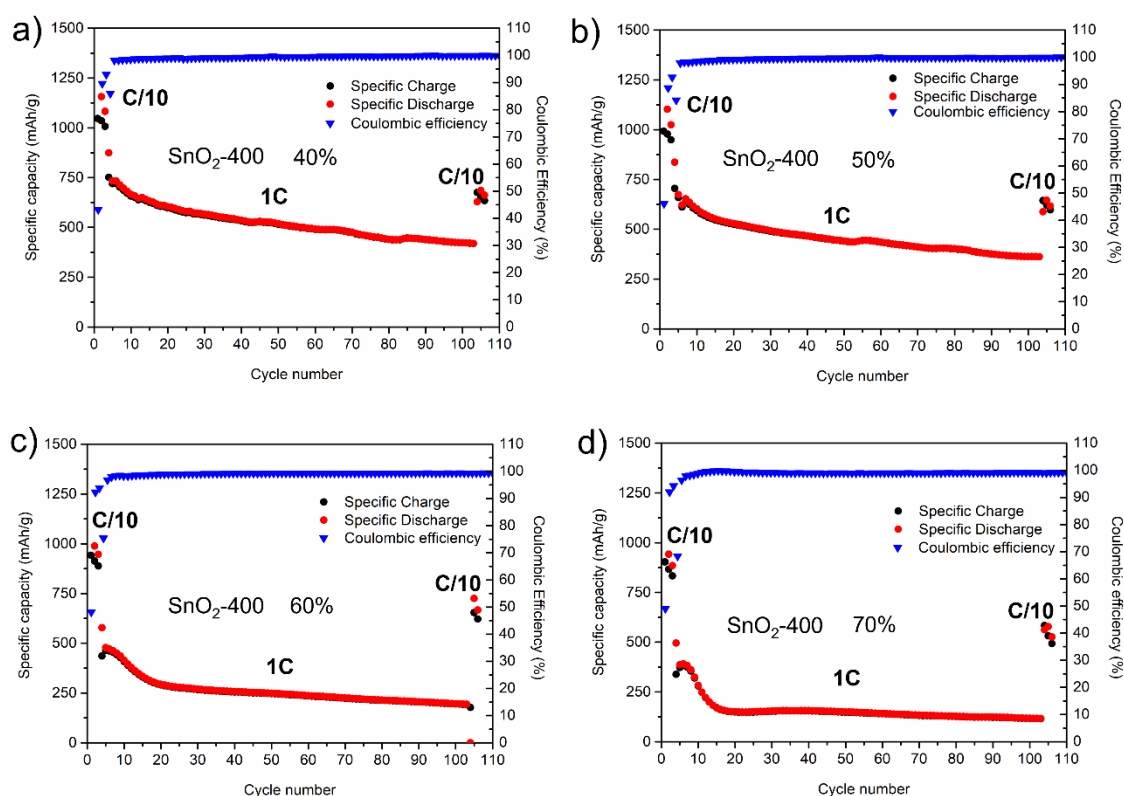
299 **3.2 Electrochemical characterization**

300

301 *3.2.2 Characterization of SnO₂-400 half cell tests: the effect of the mass loading.*

302 As mentioned before, in addition to morphology, the electrochemical performance of
303 SnO₂ is highly sensible to the electrode composition [46]. In this section, SnO₂-400
304 sample is selected and the effect of electrode engineering, such as the mass loading, is
305 analysed. For this reason, four electrodes are prepared with different weight ratio of active
306 and inactive components (named: SnO₂-400-40%, SnO₂-400-50%, SnO₂-400-60%,
307 SnO₂-400-70%), corresponding to active material loadings of 1.15, 1.61, 2.55 and 3.65
308 mg cm⁻², respectively. Galvanostatic cycling is performed in half cells to assess the
309 electrochemical performances of the different electrodes. After three cycles at C/10, the
310 cells are galvanostatically lithiated at 1C for 100 cycles and then at C/10 for the last three
311 cycles, within the potential range of 0.01 – 2.0 V. Delithiation is performed at 1C. **Figure**
312 **3a-d** show the specific capacity vs cycle number for SnO₂-400 cells with different SnO₂
313 mass loadings. As can be seen at the 2nd cycle at C/10, all cells experience similar
314 lithiation capacity, which ranges between 984 and 1154 mAh g⁻¹ depending on the SnO₂

315 mass loading, reaching 66 – 77% of the total theoretical capacity of the material. **Figure**
 316 **3a** shows that SnO₂-400-40% cell delivers stable capacity of 550 mAh g⁻¹ at 1C and
 317 retains 660 mAh g⁻¹ at C/10 after 100 cycles. Similarly, the electrode containing 50% of
 318 SnO₂ shows a capacity retention higher than 50% at 1C and a specific capacity close to
 319 650 mAh g⁻¹ at C/10 after 100 cycles. On the contrary, the electrodes with higher mass
 320 loadings experience lower capacity retention at 1C, which is 33% for SnO₂-400-60% and
 321 23% for SnO₂-400-70%, calculated from the 4th to the 103rd cycle. From these results,
 322 there is a clear evidence of the benefit of carbon black addition to SnO₂-400 in the
 323 electrode preparation, which improves the electrochemical performances at higher C-
 324 rates (1C).



325

326 In **Figure S4a-g** the specific capacity vs voltage plots at the 1st, 2nd and 105th cycle at
 327 C/10 of SnO₂-400 are reported, along with the corresponding differential capacity vs
 328 voltage curves. The differential capacity plots are smooth and display fewer sharp peaks.

329 This trend is typical of small grain and less crystalline SnO₂ material [47]. The overall
330 voltage profile at the 1st cycle at C/10 (**Figure S4a**) leads to high irreversible capacity
331 (2500 mAh g⁻¹) during initial lithiation, consistent with more severe electrolyte
332 decomposition and higher solid electrolyte interface (SEI) formation, due to the high
333 specific surface area of SnO₂-400 [48]. The differential capacity profiles (**Figure S4d, e**)
334 show additional peaks at 0.03V (in reduction) and at 0.07 V (in oxidation). These peaks
335 disappear in the dQ/dV plots when the weight percentage of C in the electrode is
336 decreased, and can be related to the intercalation of Li ions into carbon black. This
337 accounts for a small fraction of the total capacity delivered by SnO₂-400 (SnO₂ 40% and
338 SnO₂ 50%) along with the larger irreversible capacity observed at the 1st cycle.
339 Differential capacity profiles at the 105th cycle (green line in **Figure S4d-f**) show the role
340 of carbon black in limiting aggregation of Sn during cycling. In fact, the peaks related to
341 the conversion and alloying reactions of SnO₂ are clearly visible in the dQ/dV curves of
342 the electrodes with higher C content (SnO₂ 40% and SnO₂ 50%). At the 105th cycle, large
343 and smooth peaks appear in the dQ/dV curves of SnO₂ 70%, this shape is associated with
344 the aggregation of Sn into larger regions during cycling [45]. These results highlight that
345 at least 40% of C in the electrode composition is necessary, both to increase the
346 conductivity and prevent coalescence of tin particles.

347 In order to understand the role of carbon black in the electrode formulation, two-probe
348 plane measurements have been carried out to study the conductivity of electrodes, in
349 particular the out-of-plane conductivity, which controls the charge transport from the
350 current collector to the active sites [49]. The experimental set-up is reported in **Figure**
351 **S4**. Basically, Galvanostatic Electrochemical Impedance Spectroscopy (GEIS) is used to
352 measure the resistance (R) that is the sum of the resistance of the composite material
353 (SnO₂/Carbon black/binder) and the contact resistance. This resistance can be used to

354 calculate the resistivity (ρ) of the system and the conductivity (σ), according to equation
355 (1) and (2) reported in the SI.

356 As can be seen in **Table S2**, similar values of conductivity are obtained for the
357 electrodes containing 40 and 50 wt.% of SnO₂, respectively. The electronic conductivity
358 increases for the electrode with 60 wt.% of SnO₂ and decreases again by increasing SnO₂
359 content to 70 wt.%. These values highlight that the electronic conductivity is not simply
360 related to content of carbon black in the electrode but is the result the complex distribution
361 of the materials inside the electrode along with the formation of conductive networks with
362 different porosity and tortuosity. In fact, the higher electronic conductivity does not
363 directly correspond to the higher capacity values, since also the ionic conductivity plays
364 a fundamental role both at high and low C-rates [50].

365 To better evaluate the overall cell resistance, Potentiostatic Electrochemical Impedance
366 Spectroscopy (PEIS) analysis was performed during the forming cycles for all the
367 electrodes more precisely, at the end of the first and the third cycle at C/10. As reported
368 in **Figure S5a,b**, the Nyquist plots show two semicircles: one at high frequencies referring
369 to SEI layer resistance (R_{SEI}) and the second at mid-frequencies related to charge transfer
370 resistance (R_{CT}). The initial resistance at the highest frequencies is due to the electrolyte
371 resistance and/or contact resistance (R_{EL}), while the straight line at low frequencies
372 represents the lithium-ion diffusion in the bulk material [51]. All Nyquist plots are fitted
373 according to the equivalent circuit reported in **Figure S5c** and the fitted values are listed
374 in **Table S3**. From the Nyquist plot, the cells show very low resistance, which is lower
375 than 20 Ω . From fitting the Nyquist profiles, it is possible to identify and discriminate the
376 various contributions of the resistance. The initial resistance (R_{EL}) is between 4 and 6 Ω
377 and lower for the electrodes with higher amounts of carbon black. This could be related

378 to the higher permeation of the electrolyte in the porosity of the electrode and to the lower
379 contact resistance. However, at the third cycle, R_{EL} remains roughly constant for SnO₂-
380 400-50, SnO₂-400-60 and SnO₂-400-70, while it increases for SnO₂-400-40. This is
381 probably due to a greater reactivity of the carbon black with the electrolyte. The greater
382 tendency to form SEI layer at the electrolyte/electrode interface with higher amount of
383 carbon black is confirmed by the R_{SEI} observed after the first cycle, which turns out to be
384 higher for SnO₂-400-40 than for the others. The charge transfer resistance (R_{CT}) decreases
385 as the amount of SnO₂ increases. This should be due to the better distribution of the
386 components within the electrode, which facilitates the charge transfer from one particle
387 to another. However, all R_{CT} values are very similar and in the range of 5.5 to 8.9 Ω . After
388 three cycles, both the R_{SEI} and the R_{CT} decrease, confirming that more stable SEI layer is
389 achieved. To sum up, the internal resistance of the different electrodes is similar.
390 However, after several cycles, the cell capacity is strongly influenced by the initial
391 distribution of both SnO₂ and carbon particles inside the electrode, since such distribution
392 allows the carbon particles to better buffer the volume changes of SnO₂.

393

394 3.2.2 Characterization of SnO₂-400 half cell tests: the effect of binder.

395

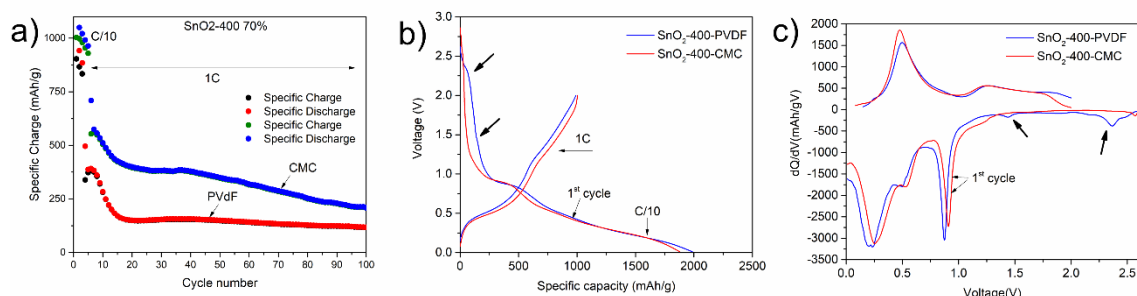
396 Equally to the mass loading optimization, the use of less expensive binders and eco-
397 sustainable processes turns out to be one of the most important challenges of future
398 electrode manufacturing process [52]. In this frame, commercial sodium carboxymethyl
399 cellulose (Na-CMC), containing carboxylic groups acting as dispersing agents during
400 slurry preparation [46], should feature many advantages over PVdF binder, especially
401 with ultra-fine SnO₂ nanoparticles [53]. To verify such hypothesis, the composition

402 70:20:10 (SnO₂-400:C45:CMC), corresponding to the highest mass loading obtained in
403 the previous part, has been selected.

404 This formulation was selected because it is the most extreme condition, in terms of
405 amount of SnO₂, reported in this study. In fact, As can be seen in the previous paragraph,
406 the higher amount of SnO₂ in the electrode corresponds to the lower specific capacity and
407 capacity retention. At the same time, high SnO₂ mass loadings allow to better appreciate
408 the role of the binder and its influence on the electrochemical properties of the electrode.

409 The galvanostatic charge/discharge performance with CMC are shown in **Figure 4a**
410 against those of SnO₂-400 electrode with similar mass loading (3.65 mg cm⁻²) and PVDF
411 binder. With water-based binder SnO₂-400 has twice the capacity, with the same number
412 of cycles, and affords better capacity retention compared to PVDF. These results highlight
413 that CMC offers better connectivity between SnO₂-400 and carbon black particles,
414 allowing higher SnO₂ utilization than PVDF, at comparable mass loading. **Figure 4b-c**
415 shows the voltage profile and dQ/dV plots of SnO₂ anodes with the different binders at
416 the 1st cycle. The shape of the dQ/dV plot at the 1st cycle is different for the two binders,
417 suggesting different interfacial reactions. Two peaks at 2.35 and 1.4 V (highlighted with
418 black arrows in **Figure 4c**) can be seen with SnO₂-PVDF electrode, which are mostly
419 ascribable to the reduction of the electrolyte [54]. These peaks are not present in the
420 dQ/dV of SnO₂-CMC, which exhibits only a small peak at 1.2 V. A similar behaviour
421 was observed on Si anodes by Lucht and co-workers [55], who reported the formation of
422 a thick SEI layer after 5 charge/discharge cycles with PVDF binder. They claimed that
423 the SEI isolated the Si NPs and was responsible for a rapid capacity decay. On the
424 contrary, a thinner SEI was observed around Si NPs when using CMC, which resulted in
425 better cyclability. This might explain the higher specific capacity (349 mAh g⁻¹ for
426 SnO₂/CMC vs 149 mAh g⁻¹ for SnO₂/PVDF at 50th cycle, 1C) and the better capacity

427 retention (36.24% for SnO₂/CMC vs 31.2% for SnO₂/PVdF after 100 cycles at 1C)
428 observed for SnO₂-400 with CMC binder.



429

430 To sum up, the CMC binder, which is rich of acidic functionalities, can better interact
431 with tin oxide nanoparticles, by hydrogen and/or covalent bonding, allowing an
432 enhancement of electrode performances even at the highest SnO₂ mass loadings that can
433 be achieved with the coin cell design.

434

435 3.2.3 Characterization of the SnO₂-400/LNMO Li-ion full cell.

436

437 In order to study the behaviour of SnO₂-400 as alternative anode to graphite in a full
438 Li-ion cell, the SnO₂ anode is tested against a commercial LNMO cathode.

439 Starting from the observations of the previous paragraphs, an anode composition of 50
440 %wt of SnO₂-400 is selected, as good compromise in terms of mass loading and
441 electrochemical performances. At the same time, CMC is chosen as aqueous binder for
442 its higher electrochemical stability, eco-sustainability and reduced cost. While for the
443 cathode composition, the selected ratio is 90:5:5 (LNMO:C65:PVdF).

444 For the electrochemical characterization, two different cell designs are used: three-
445 electrodes T-cell and 2-electrodes coin-cell configuration. In fact, T-cell configuration

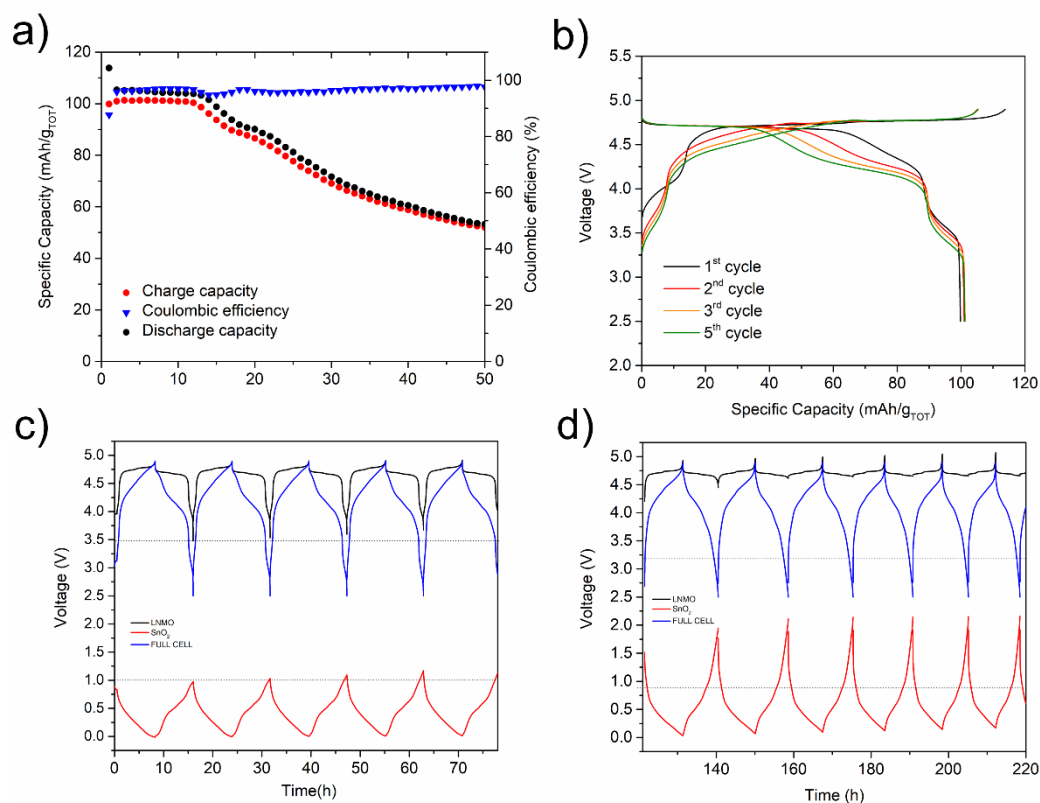
446 enables the use of a Li reference electrode for monitoring the potential of individual
447 electrodes, while the coin cell design enables longer cycling tests at C/10.

448 Prior to cell assembly, both SnO₂ and LNMO are individually cycled vs. Li anode in
449 the half coin cell configuration, mainly to limit the large irreversibility of SnO₂ anode and
450 build up a certain Li reservoir. Specifically, the procedure for SnO₂ involves 10 cycles at
451 C/10 followed by one lithiation at C/20 until the cut-off potential of 0.01 V is reached.
452 The N:P ratio, was calculated on the basis of the practical capacities of both electrodes,
453 obtained at C/10 in half-cell configuration, and it has been set to a value of ~1.1/1.2. In
454 the full-cell the dis-/charge rate is based on the LNMO cathode at C/10, which
455 corresponds to a specific current of 14.5 mA g⁻¹ LNMO. Two operational potential
456 windows of 2.5 – 4.9 V and 3.5 – 4.9 V are selected for cycling the full cell, in order to
457 better understand and exploit the electrochemical behaviour of the electrodes. As
458 depicted in **Figure S6a,c** the full cell with SnO₂/LNMO cycled in the potential range of
459 2.5 – 4.9 V shows an initial discharge capacity of 100 mAh g⁻¹ based on the sum of the
460 masses of the negative and positive active materials, which corresponds to 118 mAh g⁻¹
461 based on the LNMO active mass only. The initial Coulombic efficiency is around 89% at
462 the 1st cycle and then settles to 97% until the 50th cycle is reached. Considering and
463 average voltage of 4.2 V, the specific energy (based on the anode and cathode active
464 material) is higher than 400 Wh kg⁻¹ for more than 15 cycles. As can be seen in **Figure**
465 **S6a**, after the first cycles the cell experiences a slight but steady capacity fading. This
466 observation can be clarified by considering the voltage characteristics of both electrodes
467 in **Figure S6c**, which depicts the trend of the potential vs time of the full cell, the anode
468 and the cathode, respectively. In fact, cycling the full cell in the potential range 2.5 – 4.9
469 V, the anode reaches the upper cut-off voltage of 1.06 V while the lower cut-off voltage

470 is 0.2 V, which means that, in this regime of potential, both the conversion and the
471 alloying reactions of SnO₂ are not fully exploited. At the same time, for LNMO the lower
472 cut-off voltage is 4.7 V, which implies that only the two-nickel redox couple are involved
473 in the reaction while the manganese couple remains unutilized. This results in 55%
474 capacity retention from the 1st to the 50th cycle. On the other hand, when decreasing the
475 potentials in the range 3.5 – 4.9 V, the SnO₂/LNMO full cell shows a very stable specific
476 capacity for the first 12 cycles (**Figure 5a**). Also in this case, the initial Coulombic
477 efficiency is rather low, around 87%, which indicates a certain fraction of side reactions
478 due to SEI formation, but then it stabilizes at 97% until the 50th cycle. Concerning the
479 specific capacity, at the 2nd cycle, it is 105 mAh g⁻¹ based on the total mass of active
480 material, corresponding to 127 mAh g⁻¹ considering only LNMO mass, which means that
481 the full capacity of the cathode is used.

482 As depicted in **Figure 5c**, within this cell cut-off potentials (between 3.5 and 4.9 V) the
483 LNMO cathode experiences stable dis-/charge cycles, and both the manganese (at 4.1 V
484 vs Li/Li⁺) and the nickel (at 4.7 V vs Li/Li⁺) redox couples are clearly visible, in particular
485 in the early cycles. In addition, at the 1st cycle, SnO₂ operates within the range of potential
486 of 0.96 – 0.01 V vs Li/Li⁺, which means that the anode does not reach its upper cut-off
487 voltage and the conversion reaction does not take place at full capacity. However, a slight
488 increase of the upper cut-off voltage of the anode is observed in the following cycles
489 (**Figure 5c**), which becomes more and more important as the number of cycles increases
490 until the upper cut-off voltage of 2.0 V is reached (**Figure 5d**). The mentioned shift of
491 the anode potential is accompanied with the capacity loss of the full cell during the first
492 20 cycles (**Figure 5a**), and the fading of the redox plateau of the manganese couple of the
493 LNMO cathode, which disappears at around the 7th cycle (**Figure 5d**). This phenomenon
494 has been explained as a loss of electrochemically available lithium [56], which is

495 consumed in continuous SEI formation. It is important to note that, apart from the
 496 electrolyte, lithium mainly comes from the LNMO material, which continuously
 497 experiences Li^+ losses in the full cell during cycling, compared to its behaviour in the
 498 half-cell (*i.e.* vs lithium) [57][58].



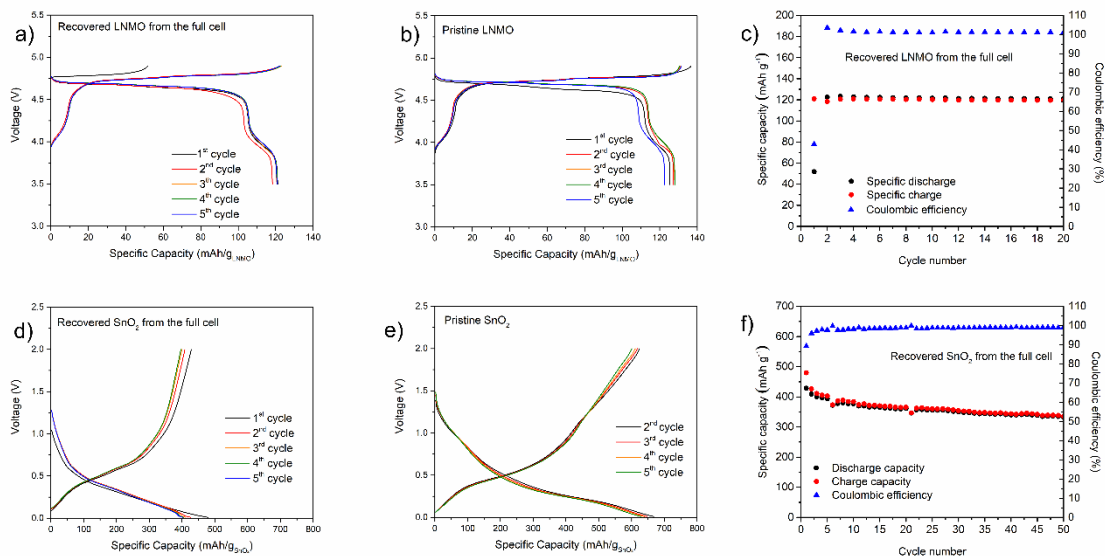
499

500 To better highlight the single electrode behaviour in 2-electrodes full cell, the
 501 differential capacity vs voltage plots (dQ/dV) of the LNMO cathode, vs Li reference
 502 electrode at the 1st and 15th cycle, are shown in **Figure S7**. At the 1st cycle, the peaks of
 503 $\text{Ni}^{\text{II/III}}$ oxidation at the potential of 4.70 V and the $\text{Ni}^{\text{III/IV}}$ oxidation at 4.74 V are clearly
 504 seen, meaning that the lithium amount is enough for the complete lithiation of the LNMO
 505 material. After 15 cycles, there is a shift of the oxidation peaks of nickel towards lower
 506 potentials, which is accompanied by the decreasing of $\text{Ni}^{\text{II/III}}$ peak and by the increasing
 507 of the $\text{Ni}^{\text{III/IV}}$ peak. As cycling proceeds, the fraction of fully lithiated phase, which
 508 corresponds to the $\text{Ni}^{\text{III/IV}}$ couple, also decreases because the electrochemically available

509 lithium in the cell is bound at the electrode [56], this explains the observed capacity fading
510 from the 15th to the 50th cycle in the full cell, observed in **Figure 5a**.

511 In order to verify that the loss of electrochemically available lithium is mainly
512 responsible for the degradation of the capacity in the full cell, both the cathode and the
513 anode were retrieved from the full cell and two half-cells were assembled with Li as
514 counter electrode. **Figure 6a** shows the capacity voltage curves of the LNMO cathode
515 after cycling in the full cell compared to those of pristine LNMO (**Figure 6b**). Except for
516 the 1st cycle, in which the capacity of the cathode is still affected by the incomplete
517 lithiation of LNMO experienced in the full cell (which corresponds to a charge capacity
518 of 51 mAh g⁻¹), then the capacity settles down to the value of 120 mAh g⁻¹, which is
519 comparable to the one obtained with the pristine LNMO cathode (128 mAh g⁻¹). This
520 behaviour is maintained in the following cycles (**Figure 6c**) indicating no substantial
521 modifications in the LNMO material after cycling in the full cell. A similar behaviour is
522 observed for SnO₂-400 (**Figure 6d**), except for a capacity loss of 23% with respect to the
523 pristine material (**Figure 6e**). The trend of capacity of the recovered SnO₂ anode in the
524 half cell is fully consistent with its capacity retention with cycling, which is depicted in
525 **Figure 3**.

526



527

528

529 In general, the obtained performances are in line with similar systems based on
 530 conversion/alloying anodes and LNMO cathodes [59],[60]. The cycling stability of the
 531 cell is comparable to full cells based on TiO₂ coated-SnO₂ anodes and LFP cathodes [61],
 532 and only slightly lower than that of chemically pre-lithiated nanocomposite SnO₂/C
 533 electrodes [62] and TM co-doped SnO₂ with N/P ratio of 2 [60]. Nevertheless, a direct
 534 comparison is not simple, because most of the works use different cathode materials in
 535 combination with the SnO₂ anode, which imply that different potential ranges, SnO₂ mass
 536 loadings and electrolytes are used. In this work, the capacity of the full cell, in the
 537 potential range of 3.5 – 4.9 V, is greater than 350 mAh g⁻¹ at the 50th cycle, which is
 538 consistent with the values reported in literature, where SnO₂ is combined with other
 539 cathode materials (NMC, LFP, etc) [63–70]. In addition, it is worth noting that, in the
 540 present work, except for the SnO₂ particles size optimization, no further strategies have
 541 been adopted (*i.e.* electrolyte optimization, carbon coating, chemical pre-lithiation or

542 other complex approaches [71]), which would have been useful to improve the cycling
543 stability.

544

545 **4 Conclusions**

546 A scalable sol-gel method was proved to be suitable to synthesise phase-pure and
547 crystalline SnO₂ and finely dispersed nanoparticles with an average size of about 5 nm,
548 which can be controlled by optimizing the calcination temperature at 400 °C. The
549 additional optimization of the electrode composition further improved the cycling
550 stability and SnO₂-400 exhibited a reversible specific capacity higher than 350 mAh g⁻¹,
551 with a coulombic efficiency close to 99.9 % after 100 cycles, adopting a higher current
552 regime of 0.75 A g⁻¹. The optimized SnO₂ electrode was then pre-lithiated and coupled
553 with a LNMO-based cathode showing high energy density of about 400 Wh kg⁻¹,
554 corresponding to a reversible specific capacity higher than 350 mAh g⁻¹ (based on the
555 SnO₂ mass) which makes the combination of these two electrodes an interesting option
556 for the next generation Li-ion batteries. Overall, this study has revealed that the
557 investigation of the electrode formulation, beneficial to increase both the electrochemical
558 characteristics (electronic conductivity, reversibility of processes, coulombic efficiency,
559 etc.), and the mechanical properties (particle distribution, adhesion between components,
560 cycling stability) along with the identification of the best conditions for electrochemical
561 testing, have a dramatic impact on the performance of full cells, and it is expected to
562 provide some guidelines for the development of future tin oxide-based advanced anodes.

563

564

565 **References**

- 566 [1] M. Fichtner, K. Edström, E. Ayerbe, M. Berecibar, A. Bhowmik, I.E. Castelli, S. Clark, R.
567 Dominko, M. Erakca, A.A. Franco, A. Grimaud, B. Horstmann, A. Latz, H. Lorrmann, M.
568 Meeus, R. Narayan, F. Pammer, J. Ruhland, H. Stein, T. Vegge, M. Weil, Rechargeable
569 Batteries of the Future—The State of the Art from a BATTERY 2030+ Perspective, *Adv*
570 *Energy Mater.* 12 (2022). <https://doi.org/10.1002/aenm.202102904>.
- 571 [2] J. Amici, P. Asinari, E. Ayerbe, P. Barboux, P. Bayle-Guillemaud, R.J. Behm, M. Berecibar,
572 E. Berg, A. Bhowmik, S. Bodoardo, I.E. Castelli, I. Cekic-Laskovic, R. Christensen, S. Clark,
573 R. Diehm, R. Dominko, M. Fichtner, A.A. Franco, A. Grimaud, N. Guillet, M. Hahlin, S.
574 Hartmann, V. Heiries, K. Hermansson, A. Heuer, S. Jana, L. Jabbour, J. Kallo, A. Latz, H.
575 Lorrmann, O.M. Løvvik, S. Lyonnard, M. Meeus, E. Paillard, S. Perraud, T. Placke, C.
576 Punckt, O. Raccurt, J. Ruhland, E. Sheridan, H. Stein, J.-M. Tarascon, V. Trapp, T. Vegge,
577 M. Weil, W. Wenzel, M. Winter, A. Wolf, K. Edström, A Roadmap for Transforming
578 Research to Invent the Batteries of the Future Designed within the European Large Scale
579 Research Initiative BATTERY 2030+, *Adv Energy Mater.* 12 (2022).
580 <https://doi.org/10.1002/aenm.202102785>.
- 581 [3] B. Babu, P. Simon, A. Balducci, Fast Charging Materials for High Power Applications, *Adv*
582 *Energy Mater.* 10 (2020). <https://doi.org/10.1002/aenm.202001128>.
- 583 [4] M. Weiss, R. Ruess, J. Kasnatscheew, Y. Levartovsky, N.R. Levy, P. Minnmann, L. Stolz, T.
584 Waldmann, M. Wohlfahrt-Mehrens, D. Aurbach, M. Winter, Y. Ein-Eli, J. Janek, Fast
585 Charging of Lithium-Ion Batteries: A Review of Materials Aspects, *Adv Energy Mater.* 11
586 (2021). <https://doi.org/10.1002/aenm.202101126>.
- 587 [5] J. Asenbauer, T. Eisenmann, M. Kuenzel, A. Kazzazi, Z. Chen, D. Bresser, The success story
588 of graphite as a lithium-ion anode material-fundamentals, remaining challenges, and
589 recent developments including silicon (oxide) composites, *Sustain Energy Fuels.* 4 (2020)
590 5387–5416. <https://doi.org/10.1039/d0se00175a>.
- 591 [6] H. Zhang, Y. Yang, D. Ren, L. Wang, X. He, Graphite as anode materials: Fundamental
592 mechanism, recent progress and advances, *Energy Storage Mater.* 36 (2021) 147–170.
593 <https://doi.org/10.1016/j.ensm.2020.12.027>.
- 594 [7] M. Armand, P. Axmann, D. Bresser, M. Copley, K. Edström, C. Ekberg, D. Guyomard, B.
595 Lestriez, P. Novák, M. Petranikova, W. Porcher, S. Trabesinger, M. Wohlfahrt-Mehrens,
596 H. Zhang, Lithium-ion batteries – Current state of the art and anticipated developments,
597 *J Power Sources.* 479 (2020). <https://doi.org/10.1016/j.jpowsour.2020.228708>.
- 598 [8] H. Cheng, J.G. Shapter, Y. Li, G. Gao, Recent progress of advanced anode materials of
599 lithium-ion batteries, *Journal of Energy Chemistry.* 57 (2021) 451–468.
600 <https://doi.org/10.1016/j.jechem.2020.08.056>.
- 601 [9] M.A. Azam, N.E. Safie, A.S. Ahmad, N.A. Yuza, N.S.A. Zulkifli, Recent advances of silicon,
602 carbon composites and tin oxide as new anode materials for lithium-ion battery: A

- 603 comprehensive review, *J Energy Storage*. 33 (2021).
604 <https://doi.org/10.1016/j.est.2020.102096>.
- 605 [10] L. Sun, Y. Liu, R. Shao, J. Wu, R. Jiang, Z. Jin, Recent progress and future perspective on
606 practical silicon anode-based lithium ion batteries, *Energy Storage Mater.* 46 (2022) 482–
607 502. <https://doi.org/10.1016/j.ensm.2022.01.042>.
- 608 [11] M. Ge, C. Cao, G.M. Biesold, C.D. Sewell, S.-M. Hao, J. Huang, W. Zhang, Y. Lai, Z. Lin,
609 Recent Advances in Silicon-Based Electrodes: From Fundamental Research toward
610 Practical Applications, *Advanced Materials*. 33 (2021).
611 <https://doi.org/10.1002/adma.202004577>.
- 612 [12] S. Bobba, S. Carrara, J. Huisman, F. Mathieux, C. Pavel, Critical Raw Materials for Strategic
613 Technologies and Sectors in the EU - a Foresight Study, 2020.
614 <https://doi.org/10.2873/58081>.
- 615 [13] P. Meister, H. Jia, J. Li, R. Kloepsch, M. Winter, T. Placke, Best Practice: Performance and
616 Cost Evaluation of Lithium Ion Battery Active Materials with Special Emphasis on Energy
617 Efficiency, *Chemistry of Materials*. 28 (2016) 7203–7217.
618 <https://doi.org/10.1021/acs.chemmater.6b02895>.
- 619 [14] X. Lan, X. Xiong, J. Liu, B. Yuan, R. Hu, M. Zhu, Insight into Reversible Conversion Reactions
620 in SnO₂-Based Anodes for Lithium Storage: A Review, *Small*. 18 (2022).
621 <https://doi.org/10.1002/smll.202201110>.
- 622 [15] F. Zoller, D. Böhm, T. Bein, D. Fattakhova-Rohlfing, Tin Oxide Based Nanomaterials and
623 Their Application as Anodes in Lithium-Ion Batteries and Beyond, *ChemSusChem*. 12
624 (2019) 4140–4159. <https://doi.org/10.1002/cssc.201901487>.
- 625 [16] S. Wang, G. Xu, K. Wang, B. Han, Y. Wang, L. Li, D. Ju, M. Chai, D. Zhang, W. Zhou,
626 Fabrication and electrochemical performances of SnO₂@C composite materials, *Current*
627 *Research in Green and Sustainable Chemistry*. 4 (2021).
628 <https://doi.org/10.1016/j.crgsc.2021.100099>.
- 629 [17] D. Versaci, A. Costanzo, S.M. Ronchetti, B. Onida, J. Amici, C. Francia, S. Bodoardo,
630 Ultrasmall SnO₂ directly grown on commercial C45 carbon as lithium-ion battery anodes
631 for long cycling performance, *Electrochim Acta*. 367 (2021).
632 <https://doi.org/10.1016/j.electacta.2020.137489>.
- 633 [18] D. Versaci, J. Amici, C. Francia, S. Bodoardo, Simple approach using g-C₃N₄ to enable
634 SnO₂ anode high rate performance for Li ion battery, *Solid State Ion*. 346 (2020).
635 <https://doi.org/10.1016/j.ssi.2019.115210>.
- 636 [19] R. Liu, W. Su, P. He, C. Shen, C. Zhang, F. Su, C.-A. Wang, Synthesis of SnO₂/Sn hybrid
637 hollow spheres as high performance anode materials for lithium ion battery, *J Alloys*
638 *Compd.* 688 (2016) 908–913. <https://doi.org/10.1016/j.jallcom.2016.07.194>.

- 639 [20] J.S. Chen, L.A. Archer, X. Wen Lou, SnO₂ hollow structures and TiO₂ nanosheets for
640 lithium-ion batteries, *J Mater Chem.* 21 (2011) 9912–9924.
641 <https://doi.org/10.1039/c0jm04163g>.
- 642 [21] R. Liu, W. Su, C. Shen, J. Iocozzia, S. Zhao, K. Yuan, N. Zhang, C.-A. Wang, Z. Lin,
643 Hydrothermal synthesis of hollow SnO₂ spheres with excellent electrochemical
644 performance for anodes in lithium ion batteries, *Mater Res Bull.* 96 (2017) 443–448.
645 <https://doi.org/10.1016/j.materresbull.2017.03.004>.
- 646 [22] Y. Li, J. Song, X. Hong, Q. Tian, Z. Sui, L. Yang, Boosting the lithium storage performance
647 of tin dioxide by carbon nanotubes supporting and surface engineering, *J Colloid*
648 *Interface Sci.* 602 (2021) 789–798. <https://doi.org/10.1016/j.jcis.2021.06.076>.
- 649 [23] G.-L. Xu, Y.-D. Gong, C. Miao, Q. Wang, S.-Q. Nie, Y. Xin, M.-Y. Wen, J. Liu, W. Xiao, Sn
650 nanoparticles embedded into porous hydrogel-derived pyrolytic carbon as composite
651 anode materials for lithium-ion batteries, *Rare Metals.* 41 (2022) 3421–3431.
652 <https://doi.org/10.1007/s12598-022-02073-3>.
- 653 [24] Q. Tian, Y. Chen, Z. Sui, J. Chen, L. Yang, The sandwiched buffer zone enables porous
654 SnO₂@C micro-/nanospheres to toward high-performance lithium-ion battery anodes,
655 *Electrochim Acta.* 354 (2020). <https://doi.org/10.1016/j.electacta.2020.136699>.
- 656 [25] C.-P. Wu, K.-X. Xie, J.-P. He, Q.-P. Wang, J.-M. Ma, S. Yang, Q.-H. Wang, SnO₂ quantum
657 dots modified N-doped carbon as high-performance anode for lithium ion batteries by
658 enhanced pseudocapacitance, *Rare Metals.* 40 (2021) 48–56.
659 <https://doi.org/10.1007/s12598-020-01623-x>.
- 660 [26] J.Y. Huang, L. Zhong, C.M. Wang, J.P. Sullivan, W. Xu, L.Q. Zhang, S.X. Mao, N.S. Hudak,
661 X.H. Liu, A. Subramanian, H. Fan, L. Qi, A. Kushima, J. Li, In situ observation of the
662 electrochemical lithiation of a single SnO₂ nanowire electrode, *Science* (1979). 330
663 (2010) 1515–1520. <https://doi.org/10.1126/science.1195628>.
- 664 [27] M. Mirolo, X. Wu, C. A. F. Vaz, P. Novák, M. El Kazzi, Elucidation of the Complex (De-
665)Lithiation Reactions of SnO₂ in All Solid-State Battery Using Operando X-Ray
666 Photoelectron Spectroscopy, *ECS Meeting Abstracts.* MA2019-02 (2019) 708–708.
667 <https://doi.org/10.1149/MA2019-02/7/708>.
- 668 [28] S. Zhao, C.D. Sewell, R. Liu, S. Jia, Z. Wang, Y. He, K. Yuan, H. Jin, S. Wang, X. Liu, Z. Lin,
669 SnO₂ as Advanced Anode of Alkali-Ion Batteries: Inhibiting Sn Coarsening by Crafting
670 Robust Physical Barriers, Void Boundaries, and Heterophase Interfaces for Superior
671 Electrochemical Reaction Reversibility, *Adv Energy Mater.* 10 (2020).
672 <https://doi.org/10.1002/aenm.201902657>.
- 673 [29] D. Zhou, W.L. Song, L.Z. Fan, Hollow Core-Shell SnO₂/C Fibers as Highly Stable Anodes for
674 Lithium-Ion Batteries, *ACS Appl Mater Interfaces.* 7 (2015) 21472–21478.
675 <https://doi.org/10.1021/acsami.5b06512>.

- 676 [30] Q. Tan, Z. Kong, X. Chen, L. Zhang, X. Hu, M. Mu, H. Sun, X. Shao, X. Guan, M. Gao, B. Xu,
677 Synthesis of SnO₂/graphene composite anode materials for lithium-ion batteries, *Appl*
678 *Surf Sci.* 485 (2019) 314–322. <https://doi.org/10.1016/j.apsusc.2019.04.225>.
- 679 [31] R. Tian, Y. Zhang, Z. Chen, H. Duan, B. Xu, Y. Guo, H. Kang, H. Li, H. Liu, The effect of
680 annealing on a 3D SnO₂/graphene foam as an advanced lithium-ion battery anode, *Sci*
681 *Rep.* 6 (2016) 1–9. <https://doi.org/10.1038/srep19195>.
- 682 [32] K. Zhao, L. Zhang, R. Xia, Y. Dong, W. Xu, C. Niu, L. He, M. Yan, L. Qu, L. Mai, SnO₂
683 Quantum Dots@Graphene Oxide as a High-Rate and Long-Life Anode Material for
684 Lithium-Ion Batteries, *Small.* 12 (2016) 588–594.
685 <https://doi.org/10.1002/smll.201502183>.
- 686 [33] A. Jahel, C.M. Ghimbeu, L. Monconduit, C. Vix-Guterl, Confined ultrasmall SnO₂ particles
687 in micro/mesoporous carbon as an extremely long cycle-life anode material for Li-ion
688 batteries, *Adv Energy Mater.* 4 (2014). <https://doi.org/10.1002/aenm.201400025>.
- 689 [34] J.S. Chen, X.W. Lou, SnO₂-based nanomaterials: Synthesis and application in lithium-ion
690 batteries, *Small.* 9 (2013) 1877–1893. <https://doi.org/10.1002/smll.201202601>.
- 691 [35] J.H. Harreld, J. Sakamoto, B. Dunn, Non-hydrolytic sol-gel synthesis and electrochemical
692 characterization of tin-based oxide aerogels, *J Power Sources.* 115 (2003) 19–26.
693 [https://doi.org/10.1016/S0378-7753\(02\)00626-2](https://doi.org/10.1016/S0378-7753(02)00626-2).
- 694 [36] R. Hu, D. Chen, G. Waller, Y. Ouyang, Y. Chen, B. Zhao, B. Rainwater, C. Yang, M. Zhu, M.
695 Liu, Dramatically enhanced reversibility of Li₂O in SnO₂-based electrodes: The effect of
696 nanostructure on high initial reversible capacity, *Energy Environ Sci.* 9 (2016) 595–603.
697 <https://doi.org/10.1039/c5ee03367e>.
- 698 [37] X. Chen, H. Lu, Y. Lei, J. Zhang, F. Xiao, R. Wang, P. Xie, J. Xu, Expanded graphite confined
699 SnO₂ as anode for lithium ion batteries with low average working potential and enhanced
700 rate capability, *J Mater Sci Technol.* 107 (2022) 165–171.
701 <https://doi.org/10.1016/j.jmst.2021.06.087>.
- 702 [38] N. Yesibolati, M. Shahid, W. Chen, M.N. Hedhili, M.C. Reuter, F.M. Ross, H.N. Alshareef,
703 SnO₂ anode surface passivation by atomic layer deposited HfO₂ improves li-ion battery
704 performance, *Small.* 10 (2014) 2849–2858. <https://doi.org/10.1002/smll.201303898>.
- 705 [39] K. Zhao, L. Zhang, R. Xia, Y. Dong, W. Xu, C. Niu, L. He, M. Yan, L. Qu, L. Mai, SnO₂
706 Quantum Dots@Graphene Oxide as a High-Rate and Long-Life Anode Material for
707 Lithium-Ion Batteries, *Small.* 12 (2016) 588–594.
708 <https://doi.org/10.1002/smll.201502183>.
- 709 [40] S. Wang, G. Xu, K. Wang, B. Han, Y. Wang, L. Li, D. Ju, M. Chai, D. Zhang, W.M. Zhou,
710 Fabrication and electrochemical performances of SnO₂@C composite materials, *Current*
711 *Research in Green and Sustainable Chemistry.* 4 (2021) 100099.
712 <https://doi.org/10.1016/j.crgsc.2021.100099>.

- 713 [41] I. Dienwiebel, M. Diehl, B. Heidrich, X. Yang, M. Winter, M. Börner, Enabling Aqueous
714 Processing for LiNi 0.5 Mn 1.5 O 4 -Based Positive Electrodes in Lithium-Ion Batteries by
715 Applying Lithium-Based Processing Additives, *Advanced Energy and Sustainability*
716 *Research*. 2 (2021) 2100075. <https://doi.org/10.1002/aesr.202100075>.
- 717 [42] M. Aziz, S. Saber Abbas, W.R. Wan Baharom, Size-controlled synthesis of SnO₂
718 nanoparticles by sol-gel method, *Mater Lett*. 91 (2013) 31–34.
719 <https://doi.org/10.1016/j.matlet.2012.09.079>.
- 720 [43] C. Gervillié, A. Boisard, J. Labbé, K. Guérin, S. Berthon-Fabry, Relationship between tin
721 environment of SnO₂ nanoparticles and their electrochemical behaviour in a lithium ion
722 battery, *Mater Chem Phys*. 257 (2021).
723 <https://doi.org/10.1016/j.matchemphys.2020.123461>.
- 724 [44] P. Sangeetha, V. Sasirekha, V. Ramakrishnan, Micro-Raman investigation of tin dioxide
725 nanostructured material based on annealing effect, *Journal of Raman Spectroscopy*. 42
726 (2011) 1634–1639. <https://doi.org/10.1002/jrs.2919>.
- 727 [45] I.A. Courtney, Electrochemical and In Situ X-Ray Diffraction Studies of the Reaction of
728 Lithium with Tin Oxide Composites, *J Electrochem Soc*. 144 (1997) 2045.
729 <https://doi.org/10.1149/1.1837740>.
- 730 [46] Y. Surace, F. Jeschull, T. Schott, S. Zürcher, M.E. Spahr, S. Trabesinger, Improving the
731 Cycling Stability of SnO₂-Graphite Electrodes, *ACS Appl Energy Mater*. 2 (2019) 7364–
732 7374. <https://doi.org/10.1021/acsaem.9b01344>.
- 733 [47] J. Wang, H. Zhao, X. Liu, J. Wang, C. Wang, Electrochemical properties of SnO₂/carbon
734 composite materials as anode material for lithium-ion batteries, *Electrochim Acta*. 56
735 (2011) 6441–6447. <https://doi.org/10.1016/j.electacta.2011.04.134>.
- 736 [48] C. Kim, M. Noh, M. Choi, J. Cho, B. Park, Critical size of a nano SnO₂ electrode for Li-
737 secondary battery, *Chemistry of Materials*. 17 (2005) 3297–3301.
738 <https://doi.org/10.1021/cm048003o>.
- 739 [49] R. Tian, N. Alcala, S.J.K. O’Neill, D. V. Horvath, J. Coelho, A.J. Griffin, Y. Zhang, V. Nicolosi,
740 C. O’Dwyer, J.N. Coleman, Quantifying the Effect of Electronic Conductivity on the Rate
741 Performance of Nanocomposite Battery Electrodes, *ACS Appl Energy Mater*. 3 (2020)
742 2966–2974. <https://doi.org/10.1021/acsaem.0c00034>.
- 743 [50] J. Entwistle, R. Ge, K. Pardikar, R. Smith, D. Cumming, Carbon binder domain networks
744 and electrical conductivity in lithium-ion battery electrodes: A critical review, *Renewable*
745 *and Sustainable Energy Reviews*. 166 (2022) 112624.
746 <https://doi.org/10.1016/j.rser.2022.112624>.
- 747 [51] B. Lee, S.C. Han, M. Oh, M.S. Lah, K.-S. Sohn, M. Pyo, Tin dioxide nanoparticles
748 impregnated in graphite oxide for improved lithium storage and cyclability in secondary
749 ion batteries, *Electrochim Acta*. 113 (2013) 149–155.
750 <https://doi.org/10.1016/j.electacta.2013.09.093>.

- 751 [52] S. Dühnen, J. Betz, M. Kolek, R. Schmuch, M. Winter, T. Placke, Toward Green Battery
752 Cells: Perspective on Materials and Technologies, *Small Methods*. 4 (2020).
753 <https://doi.org/10.1002/smt.202000039>.
- 754 [53] S.L. Chou, J.Z. Wang, C. Zhong, M.M. Rahman, H.K. Liu, S.X. Dou, A facile route to carbon-
755 coated SnO₂ nanoparticles combined with a new binder for enhanced cyclability of Li-ion
756 rechargeable batteries, *Electrochim Acta*. 54 (2009) 7519–7524.
757 <https://doi.org/10.1016/j.electacta.2009.08.006>.
- 758 [54] X. Zhang, R. Kostecki, T.J. Richardson, J.K. Pugh, P.N. Ross, Electrochemical and Infrared
759 Studies of the Reduction of Organic Carbonates, *J Electrochem Soc*. 148 (2001) A1341.
760 <https://doi.org/10.1149/1.1415547>.
- 761 [55] C.C. Nguyen, T. Yoon, D.M. Seo, P. Guduru, B.L. Lucht, Systematic Investigation of Binders
762 for Silicon Anodes: Interactions of Binder with Silicon Particles and Electrolytes and
763 Effects of Binders on Solid Electrolyte Interphase Formation, *ACS Appl Mater Interfaces*.
764 8 (2016) 12211–12220. <https://doi.org/10.1021/acsami.6b03357>.
- 765 [56] P. Jehnichen, K. Wedlich, C. Korte, Degradation of high-voltage cathodes for advanced
766 lithium-ion batteries—differential capacity study on differently balanced cells, *Sci Technol*
767 *Adv Mater*. 20 (2019) 1–9. <https://doi.org/10.1080/14686996.2018.1550625>.
- 768 [57] J.H. Kim, N.P.W. Pieczonka, Z. Li, Y. Wu, S. Harris, B.R. Powell, Understanding the capacity
769 fading mechanism in LiNi_{0.5}Mn_{1.5}O₄/graphite Li-ion batteries, *Electrochim Acta*. 90
770 (2013) 556–562. <https://doi.org/10.1016/j.electacta.2012.12.069>.
- 771 [58] J. Kasnatscheew, T. Placke, B. Streipert, S. Rothermel, R. Wagner, P. Meister, I.C. Laskovic,
772 M. Winter, A Tutorial into Practical Capacity and Mass Balancing of Lithium Ion Batteries,
773 *J Electrochem Soc*. 164 (2017) A2479–A2486. <https://doi.org/10.1149/2.0961712jes>.
- 774 [59] J. Asenbauer, J.R. Binder, F. Mueller, M. Kuenzel, D. Geiger, U. Kaiser, S. Passerini, D.
775 Bresser, Scalable Synthesis of Microsized, Nanocrystalline Zn_{0.9}Fe_{0.1}O-C Secondary
776 Particles and Their Use in Zn_{0.9}Fe_{0.1}O-C/LiNi_{0.5}Mn_{1.5}O₄ Lithium-Ion Full Cells,
777 *ChemSusChem*. 13 (2020) 3504–3513. <https://doi.org/10.1002/cssc.202000559>.
- 778 [60] A. Birrozzi, J. Asenbauer, T.E. Ashton, A.R. Groves, D. Geiger, U. Kaiser, J.A. Darr, D.
779 Bresser, Tailoring the Charge/Discharge Potentials and Electrochemical Performance of
780 SnO₂ Lithium-Ion Anodes by Transition Metal Co-Doping, *Batter Supercaps*. 3 (2020)
781 284–292. <https://doi.org/10.1002/batt.201900154>.
- 782 [61] D. Wei, S. Zhong, H. Zhang, X. Zhang, C. Zhu, J. Duan, L. Li, Z. Chen, P. Liu, G. Zhang, H.
783 Duan, In situ construction of interconnected SnO₂/nitrogen-doped Carbon@TiO₂
784 networks for lithium-ion half/full cells, *Electrochim Acta*. 290 (2018) 312–321.
785 <https://doi.org/10.1016/j.electacta.2018.08.094>.
- 786 [62] F. Li, G. Wang, D. Zheng, X. Zhang, C.J. Abegglen, H. Qu, D. Qu, Controlled prelithiation of
787 SnO₂/C nanocomposite anodes for building full lithium-ion batteries, *ACS Appl Mater*
788 *Interfaces*. 12 (2020) 19423–19430. <https://doi.org/10.1021/acsami.0c00729>.

- 789 [63] N. Kamboj, B. Debnath, S. Bhardwaj, T. Paul, N. Kumar, S. Ogale, K. Roy, R.S. Dey, Ultrafine
790 Mix-Phase SnO-SnO₂ Nanoparticles Anchored on Reduced Graphene Oxide Boost
791 Reversible Li-Ion Storage Capacity beyond Theoretical Limit, ACS Nano. 16 (2022) 15358–
792 15368. <https://doi.org/10.1021/acsnano.2c07008>.
- 793 [64] Y. Wang, N. Jiang, D. Pan, H. Jiang, Y. Hu, C. Li, Controllable oxygen vacancy SnO₂-x
794 anodes for lithium-ion batteries with high stability, Chemical Engineering Journal. 437
795 (2022) 135422. <https://doi.org/10.1016/j.cej.2022.135422>.
- 796 [65] J. Long, T. Han, Y. Ding, C. Hu, J. Liu, Co-coating ZnCo₂O₄ and carbon on a biomimetic sea
797 anemone-shaped SnO₂ mesostructure for high-performance lithium-ion batteries and
798 semi-solid lithium slurry batteries, Appl Surf Sci. 591 (2022) 153220.
799 <https://doi.org/10.1016/j.apsusc.2022.153220>.
- 800 [66] M. Tu, L. Yu Ruixin Jia, X. Kong, R. Zhang, B. Xu, Chitosan modulated engineer tin dioxide
801 nanoparticles well dispersed by reduced graphene oxide for high and stable lithium-ion
802 storage, J Colloid Interface Sci. 635 (2023) 105–116.
803 <https://doi.org/10.1016/j.jcis.2022.12.126>.
- 804 [67] H. Song, K. Tian, Z. Fang, C. Guan, H. Jiang, M. Lu, M. Zhang, S. Zhuang, H. Wei, D. Wei, X.
805 Li, Steric-hindrance effect and self-sacrificing template behavior induced PDA@SnO₂-
806 QDs/N-doped carbon hollow nanospheres: Enhanced structural stability and reaction
807 kinetics for long-cyclic Li-ion half/full batteries, J Colloid Interface Sci. 631 (2023) 214–
808 223. <https://doi.org/10.1016/j.jcis.2022.11.035>.
- 809 [68] G. Wen, H. Liu, T. Liang, Y. Ouyang, L. Tan, R. Hu, J. Liu, Y. Zhang, M. Zhu, Good cycling
810 stability and high initial efficiency demonstrated in full cells with limited lithium source
811 for an advanced SnO₂-Co-C composite anode, Electrochim Acta. 334 (2020) 135640.
812 <https://doi.org/10.1016/j.electacta.2020.135640>.
- 813 [69] D. Wei, S. Zhong, H. Zhang, X. Zhang, C. Zhu, J. Duan, L. Li, Z. Chen, P. Liu, G. Zhang, H.
814 Duan, In situ construction of interconnected SnO₂/nitrogen-doped Carbon@TiO₂
815 networks for lithium-ion half/full cells, Electrochim Acta. 290 (2018) 312–321.
816 <https://doi.org/10.1016/j.electacta.2018.08.094>.
- 817 [70] X. Yang, Y. Huang, M. Wang, Z. Miao, H. Liu, Z. Chen, Z. Yang, J. Yu, Double hollow
818 Zn₂SnO₄/SnO₂@N-doped carbon nanocubes as anode material for High-performance Li-
819 ion batteries, Chem Phys Lett. 813 (2023) 140285.
820 <https://doi.org/10.1016/j.cplett.2022.140285>.
- 821 [71] Z. Cui, F. Zou, H. Celio, A. Manthiram, Paving Pathways Toward Long-Life Graphite/LiNi
822 0.5 Mn 1.5 O₄ Full Cells: Electrochemical and Interphasial Points of View, Adv Funct
823 Mater. 32 (2022) 2203779. <https://doi.org/10.1002/adfm.202203779>.

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827 **Figures Captions**

828 **Figure 1:** TEM micrographs of SnO₂-400 a), SnO₂-700 b), SnO₂-900 c) and SnO₂-1000
829 d).

830 **Figure 2:** a) XRD analysis of SnO₂-400, SnO₂-700, SnO₂-900, SnO₂-1000, commercial
831 SnO₂ and the reference pattern of SnO₂ (code: 98-015-7448); b) Raman analysis of SnO₂-
832 400, SnO₂-700, SnO₂-900, SnO₂-1000.

833 **Figure 3:** Specific capacity vs cycle number plot of SnO₂-400 cells. Lithiation testing
834 protocol: first three cycles at C/10 followed by cycling at 1C and last three cycles at C/10.
835 De-lithiation at 1C. Electrodes are prepared with different weight ratio of the components
836 SnO₂-400: carbon black: PVdF: (a) 40:50:10, (b) 50:40:10, (c) 60:30:10 and (d) 70:20:10.

837 **Figure 4:** Specific capacity vs cycle number plot of a) SnO₂-400 with different binders
838 (aqueous slurry with CMC and NMP slurry with PVdF). Galvanostatic cycling comprises
839 formation at C/10 followed by 100 cycles at 1C (lithiation process). De-lithiation is
840 carried out at 1C. SnO₂: carbon black: binder ratio is 70:20:10; b) voltage profiles and c)
841 dQ/dV plots of the 1st and 2nd cycles.

842 **Figure 5:** Specific capacity vs cycle number plot of a) SnO₂/LNMO full cell in the
843 potential range of 2.5 - 4.9V vs. Li⁺/Li and b) correspondent voltage vs capacity plots.
844 Voltage vs time plots of the full cell, cathode and anode measured towards Li reference
845 electrode.

846 **Figure 6:** Voltage vs capacity plots of a) recovered LNMO in the half cell, b) pristine
847 LNMO in the half cell, c) specific capacity vs cycle number of recovered LNMO in the
848 half cell. Voltage vs capacity plots of d) recovered SnO₂ in the half cell, e) pristine SnO₂
849 in the half cell, f) specific capacity vs cycle number of recovered SnO₂ in the half cell.