POLITECNICO DI TORINO
Repository ISTITUZIONALE

Ultrasmall SnO2 directly grown on commercial C45 carbon as lithium-ion battery anodes for long cycling performance

Original
Ultrasmall SnO2 directly grown on commercial C45 carbon as lithium-ion battery anodes for long cycling performance / Versaci, Daniele; Costanzo, Alberto; Ronchetti, Silvia Maria; Onida, Barbara; Amici, Julia; Francia, Carlotta; Bodoardo, Silvia. - In: ELECTROCHIMICA ACTA. - ISSN 0013-4686. - 367:(2021), p. 137489. [10.1016/j.electacta.2020.137489]

Availability:
This version is available at: 11583/2856112 since: 2020-12-10T15:41:09Z

Publisher:
Elsevier

Published
DOI:10.1016/j.electacta.2020.137489

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright
Elsevier postprint/Author's Accepted Manuscript

© 2021. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/.The final authenticated version is available online at: http://dx.doi.org/10.1016/j.electacta.2020.137489

(Article begins on next page)

12 October 2024

Ultrasmall SnO_2 directly grown on commercial C45 carbon as Lithium-ion battery anodes for long cycling performance.

Daniele Versaci[a], Alberto Costanzo[b], Silvia Maria Ronchetti[b], Barbara Onida[b], Julia Amici[a], Carlotta Francia [a] and Silvia Bodoardo[a]**

[a] Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino (Italy)

[b] Supercritical fluids and materials chemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino (Italy)

*Corresponding authors:

Daniele Versaci, Tel.: +39 011 090 4789; E-mail address: daniele.versaci@polito.it;

Silvia Bodoardo, Tel.: +39 011 090 4641; E-mail address: silvia.bodoardo@polito.it;

KEYWORDS: Li-Ion Battery, SnO_2 nanoparticle, energy storage, TIMCAL C-NERGY™ SUPER C45 carbon black, Lithium-Ion Battery anode, electrochemistry.

ABSTRACT

Development of high-performance SnO_2 anodes is hampered by its peculiar electrochemical behavior, characterized by two processes: conversion and alloying reactions. The conversion reaction being irreversible leads to specific capacities lower than theoretical, however rational design of nanosized SnO_2 can mitigate this issue, though SnO_2 low conductivity and electrode pulverization justify the need of carbon matrices. Some carbon structures proved to be strongly effective at laboratory-scale, but most are too expensive or complicated to obtain for scaling-up. Herein, we exploit the high concentration of oxide and carboxylic surface functional groups of C-NERGY™ Super C45 carbon black for one-pot synthesis of ultrafine SnO_2 nanoparticles over the carbon surface. These functional groups accomplish the hydrolysis/oxidation of $SnCl_2$, resulting in finely dispersed SnO_2 nanoparticles (5 nm in average size) growth over C45. Presence of oxygen species on C45 surface, accessible to tin, prevent fast formation of Li_2O, allowing to achieve high capacity and extreme electrode stability. The assembled cells with SnO_2/C45 exhibit for more than 400 cycles the reversible capacity of 560 mA h g^{-1} per pure SnO_2 (after subtracting C45 contribution) at 1C, demonstrating prolonged cycling operation thus providing an interesting opportunity for scalable production of stable and high-capacity battery anodes alternatively to graphite.

1. INTRODUCTION

Lithium-ion batteries (LIBs) are well established energy storage devices for electronic, transportation and renewable-energy applications [1]. To meet the rapid growth of lithium storage energy density and safety requirements [2], high voltage cathode materials [3] non-flammable solid electrolytes [4] and polymer electrolytes [5] as well as high capacity anode materials [6] are currently under development. As concerns LIB anodes, those based on graphite can surely satisfy long lifespan and low-cost manufacture but have the disadvantages of low theoretical specific capacity (372 mA h g^{-1}) [7] and safety issues related to lithium deposition. A key challenge for high capacity and safer anodes is the replacement of graphite with active materials that can store more Li ions, such as tin dioxide. The peculiarity of SnO_2 reaction mechanism includes both conversion and alloying reactions, which explains the high theoretical specific capacity, which is four folds higher than that of graphite (782 mA h g^{-1} cycled in the voltage range of V = 0.005−1.0 V; and 1493 mA h g^{-1} cycled in the voltage range of V = 0.005−2.0 V) [8]. This feature, combined with SnO_2 intrinsic non toxicity, high chemical stability and low cost, could allow to achieve sustainable high energy density batteries.

During lithiation, the reactions at the SnO_2 electrode involve both conversion and alloying processes according to the following [7]:

$$4Li^+ + 4e^- + SnO_2 \rightarrow 2\,Li_2O + Sn \quad (1)$$

$$xLi^+ + xe^- + Sn \rightleftharpoons Li_xSn\ (0 < x < 4.4) \quad (2)$$

The electrochemical conversion of SnO_2 to metallic Sn and Li_2O (reaction (1)) occurs at 1.2 V *vs.* Li^+/Li, while reaction (2) defines the reversible alloying/dealloying of Sn, which forms a series of Li_xSn-type alloys with lithium below 0.5 V *vs.* Li^+/Li [8]. One of the main issues of tin dioxide anodes

is the rapid capacity loss seen upon cycling, with typical 50 % capacity loss at the first cycle and Coulombic efficiencies lower than 52 % [9]. Reaction (1) was initially believed to be the critical step to achieve the high capacity due to the irreversible conversion of Li_2O to SnO_2, driving the large capacity loss (about 50 %) and the low Coulombic efficiency of SnO_2 anodes [10]. Subsequent findings suggested that the conversion reaction is partially reversible using SnO_2 nanoparticles as the active material [11]. Photoelectron spectroscopy XPS studies underlined the overlap of the conversion, alloy, and electrolyte decomposition reactions in the 1.2−0.4 V *vs.* Li^+/Li range that concur to incomplete SnO_2 conversion and to the inability in regenerating the reduced SnO_2 on the subsequent oxidative process [9]. Recent studies on thin-film electrodes emphasized the presence of partially reversible intermediates during lithiation, while during de-lithiation, decomposition/dissolution of Li_2O is found to occur in parallel to the de-alloying reaction [12]. Although the experimental identification of those intermediate species is still not fully understood, to date, research has proven that substantial improvements of the electrochemical performance are mostly achieved by downsizing SnO_2 particles to nano-scale [10,13-14].

The other drawback that hampers SnO_2 application in LIBs, so that no commercial cell is actually exploiting this anode, is the enormous volume expansion and contraction on lithiation/delithiation during alloying (reaction (2)). This results in relevant stresses, loss of contact among particles and pulverization of active material. Reducing particle size limits the stresses arising from the lithiation/delithiation process and it is recognized that most appropriate particle dimensions should be lower than 10 nm [15]. To overcome this issue, the strategy is to achieve a good distribution of nanoparticles in a light matrix that restrains volume expansion and provides electronic conductivity. Well-designed nanostructured composites of SnO_2 and carbon with graphene [16,17], carbon nanotubes (CNTs) [18,19], ordered mesoporous carbon nanospheres (OMCS) [20] and others carbonaceous materials [21] were developed [22] to buffer SnO_2 volume expansion and prevent aggregation and pulverization of particles. However, the synthesis of composites generally involves

two steps: preparation and/or surface activation of the carbon matrix followed by the growth of tin dioxide particles directly on the carbon support by hydrothermal [23-25], microwave-assisted hydrothermal [20] sono-chemical [26] or electrospinning [27] methods. Some of these approaches are expensive, require the use of solvents or complex techniques that make their scale-up extremely difficult and such complexity is not in line with requirements of cost affordable batteries [28,29]. To date, newly developed commercial conductive carbon blacks are available [30] that enable water based slurries for electrode manufacture. The easy C45 dispersion in water or in other polar solvents is due to the its particular surface group chemistry. The presence of surface oxide and carboxylic functional groups gather the possibility to tailor the nature of interaction with the metal oxide (SnO_2) especially when the wet impregnation technique is used in the preparation of the composite material. The surface oxygen functional groups on the carbon provide anchorage sites for metal oxide precursor and act as active centers for nucleation. Moreover, such surface groups decrease the hydrophobicity of the carbon and this eases the access of metal precursor solutions [31]. Such conductive carbons are widely and commercially available since they are currently used as additives in lithium batteries in combination with water soluble binders.

Herein, we propose a hassle-free approach to prepare SnO_2/C composite using a simple, fully sustainable and economic synthesis process, in which tin oxide is in situ nucleated on commercial carbon black C-NERGY^{TM} Super C45 (Imerys Graphite & Carbon) in form of homogenously distributed nanoparticles. The synthesis is carried out by wet impregnation without any acid treatment or high temperature process. We focused on the presence of the existing oxygen species on the carbon surface that are accessible for tin and promote Sn-O-C interactions, suggesting synergies between the two components, with an active role of the carbon support in the SnO_2 conversion reaction.

2. EXPERIMENTAL SECTION

2.1. Material preparation

The synthesis of SnO_2/C45 consists in two simple steps: in situ deposition of SnO_2 on C45 followed by elimination of the impurities. In situ deposition of SnO_2 was achieved by pouring an aqueous solution of $SnCl_2 \cdot 2H_2O$ (purity > 98 %, Sigma-Aldrich) on commercial carbon black (TIMCAL C-NERGY™ Super C45- Imerys) to obtain a semi-solid sludge with Sn/C = 2/3 (mass ratio). Typically, $SnCl_2 \cdot 2H_2O$ (1.2 g) was dissolved into Milli-Q® water (12 g) to obtain a milky suspension (9.0 % w/w, pH = 1.74). Then C45 (2.0 g) was added to the suspension under stirring at room temperature. Finally, the sludge was dried in oven (80 °C) overnight, to obtain the raw SnO_2/C45 material. In the second step, the removal of impurities was carried out by washing the sample with water and centrifuging (10000 rpm for 15 minutes) several times until pH raised 4.0. The so obtained product was dried in oven (80 °C) overnight and labelled SnO_2/C45.

2.2. Material characterization

The thermal stability and the amount SnO_2 were detected by TGA in air from room temperature to 850 °C, at the heating rate of 10 °C min^{-1} using a SETARAM 92. XRD analysis was carried out by a PANalytical X'Pert (Cu Ka radiation) diffractometer. Data were collected with a 2D solid state detector (PIXcel) from 10 to 80° 2θ with a step size of 0.026 2θ and a wavelength of 1.54187 Å. Crystallites size was determined according to Scherrer equation by comparing the profile width of a standard profile with the sample profile. The Scherrer equation relates the width of a powder diffraction peak to the average dimensions of crystallites in a polycrystalline powder:

$$D = K \lambda / \beta_{(2\theta)hkl} \cos\theta$$

where β is the crystallite size contribution to the peak width (full width at half maximum) in radians, K (shape factor) is a constant near unit and D is the average thickness of the crystal in a

direction normal to the diffracting plane *hkl*. Profile fits were performed using X'Pert High Score Plus, using Pseudo-Voigt peak function with Ka_1 and Ka_2 fitting on a background stripped pattern. The sample-induced peak broadening β was determined by subtracting the instrumental peak width from the measured peak width. The instrumental broadening was determined using LaB_6 powder (NIST SRM®660a, size of crystallites in the 2 μm -5 μm range).

FESEM analysis was carried out by Zeiss SUPRA™ 40 with Gemini column and Schottky field emission tip (tungsten at 1800 K). Acquisitions were made at acceleration voltage of 3 kV and working distance (WD) between 2.1–8.5 mm, with magnification up to 1000 KX. The scanning/transmission electron microscope (S/TEM) analysis was carried out using a Thermo Scientific™ Talos F200X. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a PHI Model 5000 electron spectrometer equipped with an aluminium anode (1486 eV) monochromatic source, with a power of 25.0 W, and high-resolution scan with 11.75 eV pass energy. The instrument typically operates at pressures below 5×10^{-8} mbar.

The Brunauer-Emmett-Teller specific surface area (SSA) was determined by nitrogen physisorption at 77 K using a Micrometrics ASAP 2020 instrument. The specific surface area was calculated with the BET model in the relative pressure range of 0.07–0.30 by assuming 0.162 nm^2/molecule as the molecular area of nitrogen.

2.3. Electrochemical measurements

The working electrodes were prepared by solvent tape casting method. An aqueous based slurry of the as-prepared SnO_2/C45 sample was mixed with sodium-carboxymethilcellulose binder (Na-CMC, Deicel), in the weight ratio of 90:10. In the slurry preparation sodium carboxymethyl cellulose was chosen as aqueous binder, assuming that carboxyl groups and the other functional

groups of this polysaccharide can form strong covalent bond with the surface groups of SnO_2/C45, giving major stability to the electrode. The mixture was mechanically deposited on the copper current collector by Doctor Blade technique. The blade was adjusted for 200 µm deposition using an automatic film applicator (Sheen 1133N) with a speed of 50 mm/s. After solvent evaporation in air, disks of 2.54 cm^2 were punched out, vacuum dried at 120 °C (Büchi Glass Oven B-585) for 4 h, then transferred into an Argon filled dry glove-box (MBraum Labstar, H_2O and O_2 content < 1 ppm) for cell assembly. The active material loading of the SnO_2/C45 was ~ 0.7 mg cm^{-2}. For comparison electrodes of pure C45 and, commercial SnO_2 (Sigma Aldrich, product number 549657, SnO_2 nanopowder, ⩽100 nm avg. part. size) mechanically mixed with C45 (29:71) by ball milling at 20 Hz for 20 minutes (named commercial SnO_2 + C45), were prepared following the same procedure. The electrodes were assembled either in T-cells (for CV) or in 2032 coin-type cells (for GC); with lithium foil (Chemetall Foote Corporation) as counter and reference electrode and two glass-wool disks (Whatmann GF/A; 0.63 mm thickness) each as the separator. The electrolyte was a solution 1.0 M of lithium hexafluorophosphate ($LiPF_6$) in 1:1 mix of Ethylene Carbonate (EC) and Diethyl Carbonate (DEC) + 1.0% Vinyl Carbonate (VC) (battery grade, Solvionic). The cycling performance was investigated by means of galvanostatic discharge-charge cycling (GC) using an Arbin BT-2000 battery tester at room temperature. GCs were carried out in the potential interval 0.01-2.0 V vs. Li^+/Li at different current rates. For cyclic voltammetry (CV), the electrode potential was reversibly scanned between 0.01 and 2.0 V vs. Li^+/Li at 0.5 mV /s. The scan started from open circuit potential (OCV) towards the cathodic branch of the potential scan. In the tests, discharge refers to the lithium insertion process, while charge refers to the lithium de-insertion process.

3. RESULTS AND DISCUSSION

3.1. Morphological characterization of SnO_2/C45

The steps involved in the synthesis of sub-5 nm SnO_2 nanoparticles spatially distributed on carbon black C-NERGY™ Super C45 are schematically illustrated in Fig. S1. The strategy allows one-shot production of SnO_2/C composite exploiting the ease of the hydrolysis and the advantage of surface chemistry of C45, which contains high concentration of oxygen functional groups [30]. The chemical behavior of $SnCl_2$ in excess of water depends on many factors such as the solution concentration, the pH and the presence of aerial oxygen. $SnCl_2$ is readily soluble in water where the following reaction (Equation (3)) occurs [32-34]:

$$2SnCl_2 + O_2 + 2H_2O \rightarrow 2SnO_2 + 4HCl \quad (3)$$

However, if the pH ranges in the interval of 1.24 - 4.13, $Sn_4(OH)_2Cl_6$ colloidal particles are formed as a result of the hydrolysis reaction (4) [32]:

$$4SnCl_2 + 2H_2O \rightleftarrows Sn_4(OH)_2Cl_6 + 2HCl \quad (4)$$

The $Sn_4(OH)_2Cl_6$ phase converts into SnO thus, hydrolysis of $SnCl_2$ requires HCl acid environment at pH down below 1.24 to obtain SnO_2 [32,35]. However, by wet impregnation, $SnCl_2$ undergoes direct hydrolysis/oxidation and acidification is not needed [36]. For the purpose, the easy dispersion of C45 in aqueous environment allows the use of a concentrated $SnCl_2$ solution to form a semi-solid slurry instead of a liquid mixture. First, a milky-white colloidal suspension is produced by solubilizing $SnCl_2 \bullet 2H_2O$ in distilled water, after addition of C45 to the colloidal suspension, the positively charged $Sn(OH)^+$ species [37] can be easily loaded on the carbon surface, by electrostatic interactions with the negatively charged surface groups of C45, where they experience hydrolysis:

$$Sn(OH)^+Cl^-(aq) + H_2O(l) \rightarrow Sn(OH)_2(aq) + HCl \quad (5)$$

Owing to oxygen in air, tin (II) is oxidized to tin (IV) [38] so that $Sn(OH)_2(aq)$ self-evolves into ultra-small SnO_2 nanoparticles on the surface of C45 (reaction (6)); the latter supplies nucleation sites for the deposition:

$$Sn(OH)_2(aq) + ½\ O_2(g) \rightarrow SnO_2 + H_2O \qquad (6)$$

It is worth noting that C45 is essential to obtain SnO_2 nanoparticles. C45 presents oxide and carboxylic acid surface functional groups and lower degree of graphitization (sp^2 carbon concentration) in comparison to other commercial carbons. For instance, SnO_2 nanoparticles are not formed with commercial graphite (TIMREX® SLS30 TIMCAL graphite, CAS number: 7782-42-5), although such type of graphite is typically suitable for aqueous based slurries [39]. In this respect, C45 does not act as a mere carbon support but directs the homogeneous nucleation of SnO_2 nanoparticles. This is consistent with previous thermodynamic studies [34] demonstrating the tendency of tin ions to form complexes on activated carbon (AC) sites [40]. Particularly, oxygen containing groups on the carbon surface are responsible for the chemical attraction of positively charged tin species [20] and this stems from the fact that Lewis basicity associated to the aromatic rings in the activated carbons is weak [41] and the main basicity results from the oxygen containing groups [36]. Fig. 1 depicts the XRD, TGA analyses and N_2 adsorption/desorption measurements for sample SnO_2/C45. In Fig. 1a, the XRD pattern of C45 clearly shows two peaks at 25° and 44°, which are assigned to (002) and (101) graphitic planes, respectively [42]. In the XRD pattern of SnO_2/C45, three main broad peaks at 26.5°, 33.9° and 51.8° correspond to the (110), (101) and (211) planes of rutile-tetragonal SnO_2 phase (JCPDS card No. 41-1445). The peak broadening is attributed to the small particle size of SnO_2, which average size is calculated to be about 5.0 nm according to Scherrer's equation [43].

Please insert here Figure 1

Here the particle size is comparable to that of SnO_2 prepared via hydrothermal method and encapsulated in graphene 2D layers [44,45], which achieved high reversible capacities of 800-1350 mA h g^{-1} over 500-1000 cycles. Thermogravimetric analysis (TGA) was performed on SnO_2/C45 under air atmosphere between 25°C and 800 °C in order to estimate the ratio of SnO_2 and C45 from the residual SnO_2 weight, after oxidative decomposition of C45 (Fig. 1b). The TGA analysis was also carried out in the same experimental conditions, on the mixture consisting of commercial SnO_2 (Aldrich) and C45, mechanically mixed in the ratio 29:71 w/w for comparison.

The TGA curve of SnO_2/C45 points out two stages of weight loss. The initial weight loss in the temperature range of 25–200°C is due water and gases absorbed from the ambient atmosphere. Next, the decomposition of the surface functional groups on the C45 is observed at 200°- 450°C [46]. The TGA of SnO_2/C45 also shows a small inflection after 500 °C due to the oxidation of residual stannous compounds. The significant weight loss observed between 500 and 600 °C is ascribed to the carbon combustion. Above 600 °C, the residual weight is attributed to SnO_2. The mass percentage of SnO_2 in the composite is around 29 wt %. It's worth noting that combustion of SnO_2/C45 starts at lower temperature (about 500 °C) than that of the mechanically mixed commercial SnO_2-C45 powders, which is about 650 °C. According to the catalytic effect known as Mars–van Krevelen mechanism [47], oxygen does not oxidize carbon directly, but is activated by transformation into lattice oxygen on the surface of SnO_2[48], which presents defects ensuring the high mobility of such lattice oxygen [49]. The resultant shift of the oxidation temperature requires the close proximity of tin dioxide to carbon and explains the metal oxide/carbon composite formation, confirming the strong chemical interaction between SnO_2 and C45 in SnO_2/C45[46]. The BET specific surface area (SSA) is evaluated by means of N_2 adsorption/desorption isotherms (Figure 1 c,d). The BET values of C45

and SnO_2/C45 are 52 m^2 g^{-1} and 65 m^2 g^{-1}, respectively. The slight increase in the SSA of SnO_2/C45 can be due to the SnO_2 nanoparticles piled on the outer sphere of C45. The N_2 adsorption/desorption isotherms of pure C45 and SnO_2/C45 composite are compared in Fig. 1c. The curves show type II isotherms with a small hysteresis at low p/p_0 range. The hysteresis loop is classified as H3 type, typical for non-rigid aggregates with a pore network consisting of both mesopores and macropores (Fig. 1d). The SnO_2/C45 composite displays the same inhomogeneous micro-meso porosity of the parental carbon (Fig. 1d inset) and no relevant change of porosity is observed, as the geometrical area of C45 primary particles mostly contributes to the surface area of the material [31].

The fine dispersion of sub-5 nm SnO_2 nanoparticles is confirmed both by TEM and by FESEM analyses. C45 consists of slightly large primary particles, with average particle diameter ascribed between 40 – 60 nm [31], as shown in Fig. 2e-f. FESEM micrographs of SnO_2/C45 highlight the presence of SnO_2 nanoparticles homogeneously dispersed on the C45 surface (Fig. 2 b-d). Specifically, at high magnification (100000 KX), the surface of pure C45 appears smooth (Fig. 2 f), while the surface of SnO_2/C45 is rough due to anchoring of SnO_2 nanoparticles (Fig. 2 c). As it is observed, SnO_2 nanoparticles evenly cover the entire C45 surface. Some areas are seen in which particles are less gathered, enlighten in Fig. 2d. As clearly seen, SnO_2 average particle dimension is about 5.0 nm or even less. Previous investigations on ultrasmall Si quantum dots (3.0±0.5 nm in size) anchored on graphene sheets showed extraordinary rate capability and remarkable cycling stability. These features were attributed to the ultrafine SiQDs that promoted fast surface controlled lithium storage behavior rather than slow diffusion-controlled mechanisms, highlighting the importance of approaching the downsizing limit of anode active materials in lithium storage [50]. Moreover, nanometer-sized quasi-spherical SnO_2 on C45 ~~are expected to provide a high packing density and allow high volumetric energy density~~ could have less tendency to fragment during cycling than coarse SnO_2 particles. As a result, the electrode capacity should be more stable due to less volume variations

[51]. At low magnification, SnO_2/C45 shows a good interconnection among carbon particles to form a continuous network, ensuring the necessary electronic conductivity. The space among SnO_2 nanoparticles is desired to accommodate the large volume expansion during the alloying process, avoiding pulverization of the active material, so that the electrode can afford long cycling performances [52].

Please insert here Figure 2

TEM micrographs of SnO_2/C45 (Fig. 3 a-f) show that the particle size is less than 10 nm, in the average the diameter of SnO_2 nanoparticles is 5.0 nm, which is consistent to XRD (Fig. 1a) and FESEM analysis previously discussed. The lattice fringes (Fig. 3f inset) of randomly arranged nanoparticles highlight inter-planar distances of 3.34 and 2.64 Å ~~which~~ are assigned to (110) and (101) planes of rutile-tetragonal SnO_2, ~~corroborating the idea of the high crystallinity of tin dioxide~~ [53]. It is important to note that C45 makes significant contribution to restrict the crystal growth and prevent SnO_2 nanoparticle agglomeration during synthesis.

Please insert here Figure 3

EDS elemental analysis was performed on SnO_2/C45 composite (Fig. S2 in Supporting Information). After washing the sample, chlorides are almost absent: the weight ratio C:Sn is about 1:3, indicating that successful sample purification is achieved. Increasing SnO_2 amount resulted in the increase of particle size (Fig. S3 a, b Supporting Information). The optimized SnO_2/C45 composite with ~ 30 wt. % SnO_2 showed the best electrochemical performances with lower degradation issues, due to the small particle size (Fig. S3 c Supporting Information).

X-ray photoelectron spectroscopy (XPS) analysis was carried out to understand the SnO_2 – carbon interaction (Fig. 4). The XPS survey of SnO_2/C45 shows the presence of Sn, C and O and again, no chloride is detected, in agreement with the previous observations (Fig. S4 in Supporting Information).

Please insert here Figure 4

Deconvolution of the C1s peak for C45 results in two main contributions (Fig. 4a): the peak at 284.8 eV is attributed to C=C (72 %) and the peak at 285.6 eV is assigned either to C−OH or C−O−C (28 %). In SnO_2/C45 (Fig. 4b), the C1s peak is de-convoluted in four main components at 284.8, 285.9, 287.3 and 289.8 eV, which are associated to C=C (51 %), C−O and possible Sn−O−C interaction (33%), C=O (13 %), -COOH (3%), respectively [26,54]. In both C45 and SnO_2/C45 samples, the major contribution is due to sp^2 bonded carbon, which is smaller in SnO_2/C45 (51 % at.) than in C45 (72 % at.). Through FTIR analysis, Bogeat *et al.* [36] enlighten that C−O−C reducing structures in carbons are oxidized (entirely or partially) into –COOH groups during the composite synthesis. More precisely, the oxidation of surface groups of the carbon into –COOH entails the involvement of strong oxidizing species that originate from O_2 (air) and catalyzed by SnO_2 during the oven-drying step at 80°C. This explains the 3.0 % at. contribution of –COOH in the C1s of SnO_2/C45. Moreover, in such spectra, ~~the presence of~~ the peak at 285.9 eV corroborates the idea that some SnO_2 nanoparticles are anchored to the C45 surface due to the possible establishment of the Sn-O-C interaction as suggested by Sun et. al [23]. This could be beneficial to preserve both stability and integrity of the composite during cycling. The high-resolution spectrum of O1s of SnO_2/C45 (Fig. 4c) is de-convoluted in two peaks that are centered at 531.8 eV and 533.2 eV and attributed to Sn−O and C−O/C=O, respectively [55]. In the XPS Sn3d spectrum (Fig. 4d), two main peaks at 496.3 and 487.9 eV are assigned to Sn $3d_{3/2}$ (~40% at.) and Sn $3d_{5/2}$ (~60% at.) of Sn^{4+} (Sn bonded to O). The

binding energy separation of 8.4 eV well agrees with the values reported in literature for SnO_2-based materials [56] moreover, no Sn (0) or Sn^{2+} are present [54]. Particularly, Sn directly bonded to C atoms should result in additional peaks Sn−C on the left-hand side of Sn $3d_{3/2}$ and Sn $3d_{5/2}$ peaks [57]. Those peaks are absent in SnO_2/C45 spectrum suggesting that SnO_2 could interact preferentially ~~interacts~~ with C−O. This interaction should contribute to modify the properties of pure tin dioxide and enhance lithium storage performance.

3.3. Electrochemical characterization

To date, the alloying/de-alloying has been considered the highly reversible process, which mostly contributes to the reversible lithium storage capacity, while the conversion reaction is generally thought to be irreversible. However, the conversion reaction becomes partially reversible when the Li_2O exists in form of nanosized structure [58,59]. To assess the electrochemical processes of SnO_2/C45, cyclic voltammetry (CV) was carried out at a scan rate of 0.5 mVs^{-1} in a voltage range from 2.0 to 0.01 V *vs.* Li^+/Li (Fig. 5a). The first five consecutive cycles are representative of the initial stages of the electrochemical processes since pulverization associated with large volumetric changes of active material is typically seen after 100 galvanostatic charge/discharge cycles. It must be remarked that the first cathodic cycle shows higher current values through the whole potential range, which is due to SEI formation involving irreversible reactions at the electrode-electrolyte interface. At the 1st CV cycle, the cathodic branch shows a peak at 1.0 V related to the reduction of SnO_2 to Sn (0) with the simultaneous formation of Li_2O. This is followed by multistage lithium alloying process to form Li_xSn at 0.4V and 0.15 V, respectively. Similarly, in the anodic branch, the peak at 1.25 V corresponds to the reversed conversion reaction, indicating excellent reversibility of SnO_2/C45. The oxidation peak at 0.5 V is due to the phase transition of the alloying, the process being diffusion-controlled as manifests a single-phase transformation [60].

Please insert here Figure 5

In the anodic branch, the peak at 0.05 V is ascribed to lithium ion intercalation in C45, as it clearly appears in the CV of C45 alone (at around 0.0-0.3 V; Fig. 5c). The process of Li insertion into C45 contributes to a small fraction of the total capacity delivered by SnO_2/C45 and partially accounts to the large irreversible capacity at the first cycle (Fig. S5 Supporting Information). What is noteworthy here is the anodic peak at 1.24 V, which is relatively more obvious and stable than expected. Since this peak is related to the backward reaction of equation (1), it means that Sn produced from SnO_2 is oxidized back to SnO_2 and Li_2O is almost entirely decomposed. This implies that the conversion reaction is favored by the small particle size of SnO_2 firmly anchored to C45 and to the high fraction of Sn/Li_2O interfaces during SnO_2 reduction. The good overlap of the anodic peaks from the 1st to 5th cycle and those cathodic peaks from the 2nd to 5th cycle, indicate excellent cycling stability. The results highlight the importance of an interconnected structure of SnO_2/C45 that controls preponderant Li_2O formation and maintains ultrafine Sn particles in the Li_2O matrix, resulting in the better reversibility of the conversion reaction. To analyze the relationships between structural features and electrochemical performance with a focus on the integrated structure of SnO_2/C45, the electrode consisting of commercial SnO_2 and C45 mechanically mixed in the ratio 29:71 w/w is used as comparison. Fig. 5b shows five consecutives CV cycles of the electrode. The main difference is seen at the 1st cathodic branch of the CV curve. The performance marks a noticeable peak at 0.85 V that indicates extended presence of metallic Sn and Li_2O along with SEI formation. ~~The process therefore appears fast and not limited by diffusion of Li^+, which is typical of an interface reaction taking place at the SnO_2 surface rather than in the bulk of the material~~. After the first cycle the process appears irreversible as the anodic peak at 1.25 V is almost inconspicuous and fast decreases upon cycling,

which means that both SnO_x regeneration and Li_2O consumption are almost negligible [10]. During the subsequent cycles, in the cathodic branch, the peak shifts to 0.95 V due to the limited reduction of SnO_2 to Sn. In the first CV cycle of commercial SnO_2 + C45, one single peak at 0.25 V refers to the alloying process which has its reverse reaction at 0.47 V in the anodic branch. At the 3rd cycle, two small peaks at 0.57 V (cathodic) and 0.65 V (anodic) due to different alloying phases are visible. The anodic branch of the CV plot (Fig. 5b) shows that the peak near 0 V, ascribed to lithium ions intercalation in C45 increases upon cycling, similar to what was previously observed with SnO_2 nanorod-planted graphite electrodes [58]. This result suggests that the contribution of C45 to the overall capacity is higher in the simple mixed commercial SnO_2 + C45, and the discharge/charge process is based on two steps: in the first step Li alloys with Sn, in the second step Li is intercalated in C45. In the backward reaction, Li de-intercalation from C45 occurs before de-alloying of Li_xSn. To compare the real performance of the two composite materials SnO_2/C45 (29:71), the reversible capacity has been calculated from following equation [46]:

$$Cap._{SnO2} = (Cap._{SnO2/C45} * 1.00 – Cap._{C45} * 0.71) / 0.29 \quad (7)$$

where $Cap._{SnO2}$ represents the capacity purely ascribable to the SnO_2 particles, $Cap._{SnO2/C45}$ is the capacity attributed to SnO_2/C45 (29:71) and $Cap._{C45}$ is the capacity of C45. The reversible capacity $Cap._{C45}$ was determined independently, through galvanostatic cycling tests, on a pristine C45 electrode (Fig. S5 Supporting Information), which was subjected to the same current density applied to SnO_2/C45 (0.31 mA cm^{-2}). The first galvanostatic charge/discharge voltage profiles vs. specific capacity are depicted in Fig. 6, cycling tests were carried out at 0.1C rate (assuming 1C = 1494 mA g^{-1}).

Please insert here Figure 6

The results show that the specific capacity of the electrodes upon cycling is sensitive to the structure and synergies between SnO_2 and C45. During the 1st lithiation most of the processes are irreversible and only a small percentage of the initial capacity is recovered in the following de-lithiation. At 0.1C, the commercial SnO_2 + C45 anode displays low (Fig. 6a) charge capacities ranging from 815 to 741 mA h g^{-1}. A strong change in the voltage profile is observed from the 1st to the 2nd cycle since the flat plateau at 0.9 V *vs.* Li^+/Li disappears at the 2nd cycle. This is consistent with CV results and mostly suggests incomplete Li_2O conversion from the 1st cycle. ~~Further contribution to the capacity loss is due to irreversible Li^+ storage in C45~~. In the same experimental conditions, SnO_2/C45 electrode (Fig. 6b) exhibited higher charge capacities ranging from 1486 to 1409 mA h g^{-1}. Since the observed capacities are totally ascribable to the SnO_2 particles, these values are very close to the theoretical one (1494 mA h g^{-1}) that includes both the alloying and conversion processes. Thus, SnO_2/C45 showed improved reversibility of the electrochemical reaction benefitting of the synergic effect between SnO_2 and C45. Improvements are more significant through long cycling tests (Fig. 7).

Please insert here Figure 7

At higher current density (1C; 0.31 mA cm^{-2}) the electrode prepared by mixing commercial SnO_2 and C45 suffered severe capacity fading (Fig. 7a). In this case, lithiation of SnO_2 delivers 792 mAhg^{-1}, which decreases to 255 mA h g^{-1} after 100 cycles with ~ 67 % loss. At the 400th cycle the specific capacity is 50 mA h g^{-1}, which means no SnO_2 is electrochemically active. In contrast, the SnO_2/C45 anode (Fig. S6 in Supporting Information) exhibited almost steady-state and reversible capacity through long cycling operation (Fig. 7b). For example, in the first 100 cycles the Coulombic

efficiency is almost 98.8 %. The specific capacity is ~750 mA h g^{-1} relative to SnO_2 particles (eq. (7)). The capacity retention is excellent, with only 11.1 % loss from 10th to 100th cycles. After 100 cycles the discharge capacity is still stable at 616 mA h g^{-1} until ~400th cycle, in which it reaches the value of 560 mA h g^{-1} resulting in CE of 99.8 %. After 1000 cycles the specific capacity is almost 300 mA h g^{-1} with CE of 99.9 %, but when the current returns to 0.1C the recovered capacity is still 670 mA h g^{-1} demonstrating the good stability of SnO_2/C45 composite. Considering the fast and inexpensive method used to prepare SnO_2/C45, the results presented here in terms of reversible capacities and long cycling stability are competitive among recent results for SnO_2-based materials obtained by hydrothermal [24, 61, 62], sonochemical [26], solvothermal [63] and molten salts methods [52] and make this composite particularly interesting for scale-up. The rate performance of SnO_2/C45 was also evaluated (Fig. 7c). The specific capacities of SnO_2/C45 are 580, 430, 370, 315 mA h g^{-1} at 2C, 5C, 10C, 20C respectively. When the current density reverts to 2C after 85 cycles, the specific capacity is still 520 mA h g^{-1} equivalent to 89.7 % of the initial value, confirming the stable electrochemical behavior at high current regimes. Post cycling FESEM analysis was carried out to evaluate the morphology of SnO_2/C45 material after 1000 galvanostatic charge/discharge cycles (Fig. S7b) in comparison with the pristine material (Fig. S7a). After cycling, the electrode shows particles ascribable to tin species, which confirm that C45 provides sufficient anchoring to SnO_2 nanoparticles. After long cycling the average particle size is around 10 nm suggesting that, although particle agglomeration occurred as a consequence of lithiation and de-lithiation reactions, the material still retains its original morphology, which reflects the ability of our anode to mitigate any large morphological change.

Fig. 8 shows the dQ/dV curves obtained from the capacity of de-lithiation in the range of 0.01–2.00 V, at different cycles for both commercial SnO_2 + C45 (Fig. 8a) and SnO_2/C45 (Fig. 8b) electrodes at 1C.

Please insert here Figure 8

At the 5th cycle, no obvious peak is visible in the potential range of 1.0-2.0 V for commercial SnO_2 + C45 suggesting that the activity of the conversion reaction declined dramatically at the very first cycles. There are three sharp peaks in the range of 0.5 - 0.7 V, responsible for de-alloying ($Li_xSn \rightarrow Sn$). These peaks decrease in intensity and shift to higher potentials as the number of cycles increases. This result has an explanation in the coarsening/agglomeration of Sn and Li_xSn phases in the Li_2O matrix, which affects the reaction kinetics and increase the polarization of the de-alloying process. Such lithiation-induced Sn coarsening has been observed in pure SnO_2 film electrodes [64] and is explained as the gradual diffusion of Sn from one Sn/Li_2O zone to the others nearby, due to the tendency of nanosized Sn grains to reduce their surface/interface energy in the lithiated SnO_2. At the 5th cycle, the differential capacity (dQ/dV) curves of SnO_2/C45 (Fig. 8b), show that the peaks due to de-alloying process are not as sharp as in commercial SnO_2 + C45. The curves corresponding to the 10th and 5th cycle almost overlap without showing any shrinkage of the peaks, indicating very good cyclability of SnO_2/C45. No shift to higher potentials is seen for the peaks related to the de-alloying process, which results in less polarization of the electrode upon cycling. The dQ/dV curves still reveal the high activity of the reversed conversion in the initial cycles due to the large intensity of the peak at 1.3 V, which still accounts 29.6 % of the charge integral intensity at the 100th cycle. According to Cheng et al [54] the chemical bond between SnO_2 and carbon affects the reversibility of the conversion reaction, due to fast electron transport and facilitates the reaction of Sn and other oxygenated species (like Li_2O) to reform SnO_2. After lithiation, in highly dispersed SnO_2 nanodots formed on Ketijen Black (KB) carbon, a blended amorphous structure like a solid-solution of three element Sn, O and Li, such as -$Li_xSnO_{1.45}$ was identified as responsible of the high capacity retention

of the electrode [46]. Such multiple phases of Sn, Li, O, and C (KB) species enabled to achieve reversible conversion reactions. The proposed new species were found to be confined within the structure of carbon and partially inhibited the irreversible Li_2O formation by the maintenance of Sn-Li and Sn-O bonds, providing reversible reaction mechanisms. Here, the evolution of the peaks in dQ/dV *vs* V curves suggests the possibility for the conversion of SnO_2 to Sn(0) to proceed through different intermediate species instead of separated Sn and Li_2O [12]. Unfortunately, the intermediate reaction steps are mostly overlapped, confirming the difficulty to discriminate the various contributions. The good dispersion of SnO_2 nanoparticles on C45 and the chemical interaction among Sn, O an C, observed by XPS analysis, can reasonably affect the reversible conversion reaction and most of the re-formed SnO_x phases could result from the reaction of Sn with neighboring oxygen and not from direct decomposition of Li_2O [65], conclusively showing a stable material system where most of the initial capacity is retained after prolonged cycling at reasonably high C rates.

4. CONCLUSIONS

In summary, we have demonstrated a facile, low cost, production strategy to synthesize tin dioxide material with average size 5.0 nm SnO_2 nanoparticles (NPs) immobilized across the surface of commercial C-NERGY super C45 carbon black, as an efficient and stable, high capacity anode for Li-ion batteries. The C45 supplies nucleation sites for the deposition of SnO_2 and assists in chemically anchoring SnO_2 NPs over its surface. SnO_2 NPs are finely dispersed within the carbon host, which offers enough space among SnO_2 nanoparticles to accommodate the large volume expansion during the alloying process. This reflects the ability of the material to mitigate any large morphological change. The remarkable stability we observe from this anode is two-fold: the material is morphologically stable with no obvious structural modification after 1000 cycles. It is also electrochemically active, where the consistency in charge-discharge processes ensures efficient cell

operation, with both high specific capacity and Coulombic efficiency. The novel architecture of the composite offers for more than 100 cycles the high specific capacity of 750 $mAhg^{-1}$ per pure SnO_2 particles, after subtracting the capacity attributed to C45 in the composite and retains 560 $mAhg^{-1}$ after 400 cycles with CE of 99.8 % at 1C. Such long cycle life along with excellent capacity retention were achieved owing to the peculiar nanostructure of the composite that enables the possibility to maintain reversible SnO_2 conversion reaction for many cycles. This strategy is a simple and scalable manufacturing process to design efficient electrodes for high performance Li-ion batteries, by integrating conductive functionalized carbon blacks directly in the active material. The latter are cost affordable, commercially available and widely used in battery manufacture in combination with water soluble binders.

Acknowledgments

The authors grateful thank Dr. Melina Cozzarìn for her help and support regarding TEM analysis carried out at Y-TEC (YPF Tecnologia), Berisso, (Buenos Aires (1923)).

Captions to Figures

Fig. 1. (a) XRD analysis of C45 (black line) and SnO_2/C45 (red line), (b) TGA analysis of C45, SnO_2/C45 and of commercial SnO_2 + C45 mixed in weight ratio 29:71. (c) N_2 adsorption/desorption measurements of SnO_2/C45 and C45 (inset), (d) pore distribution of SnO_2/C45 and C45 (inset).

Fig. 2. FESEM micrographs of SnO_2/C45 at low (a, b) and high (c,d) magnifications. FESEM micrographs of C45 at low (e) and high (f) magnifications.

Fig. 3. TEM analyses of SnO_2/C45 at different magnifications (a-f).

Fig. 4. (a) High resolution C1s spectrum of C45 from XPS analysis. (b) High resolution C1s spectrum of SnO_2/C45. (c) High resolution XPS spectrum O1s of SnO_2/C45. (d) High resolution XPS spectrum Sn2p of SnO_2/C45.

Fig. 5. Cyclic voltammetry at 0.5 mVs^{-1} between 2.0-0.01 V *vs* Li^+/Li of: a) SnO_2/C45, b) commercial SnO_2 + C45 (in the ratio 29:71 w/w), c) C45.

Fig. 6. Galvanostatic charge/discharge voltage profiles of the electrodes in the initial cycles at 0.1C: a) commercial SnO_2 + C45, b) SnO_2/C45.

Fig. 7. Galvanostatic charge/discharge profiles of the electrodes at 1C: a) commercial SnO_2 + C45, b) SnO_2/C45; c) Cycling performance of SnO_2/C45 galvanostatically tested at different current regimes.

Fig. 8. Derivative curves dQ/dV *vs.* cell voltage and specific capacity *vs.* cell voltage of: a) commercial SnO_2 + C45; b) SnO_2/C45. Note that the specific capacity associated to the de-lithiation process is relative to the mass of SnO_2 in the electrode (no conversion of the capacity *via eq. (7)*).

References:

[1] D. Larcher, S. Beattie, M. Morcrette, K. Edström, J-C Jumas, J-M. Tarascon, Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries, J. Mater. Chem. 17 (2007) 3759-3772, https://doi.org/10.1039/B705421C

[2] M.M. Thackeray, C. Wolverton, E. D. Isaacs, Electrical energy storage for transportation approaching the limits of, and going beyond, lithium-ion batteries, Energy Environ. Sci. 5 (2012) 7854-7863., https://doi.org/10.1039/C2EE21892E

[3] P. K. Nayak, E. M. Erickson, F. Schipper, T. R. Penki, N. Munichandraiah, P. Adelhelm, H. Sclar, F. Amalraj, B. Markovsky, D. Aurbach, Review on Challenges and Recent Advances in the Electrochemical Performance of High Capacity Li- and Mn-Rich Cathode Materials for Li-Ion Batteries, Adv. Energy Mater. 8 (2018) 1702397, https://doi.org/10.1002/aenm.201702397

[4] X. Fan, L. Chen, O. Borodin, X. Ji, J. Chen, S. Hou, T. Deng, J. Zheng, C. Yang, S-C. Liou, K. Amine, K. Xu, C. Wang, Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries, Nature Nanotechnology 13 (2018) 715-722, https://doi.org/10.1038/s41565-018-0183-2

[5] J. Amici, S. Romanin, M. Alidoost, D. Versaci, C. Francia, F. Smeacetto, S. Bodoardo, UV-cured methacrylate-based polymer composite electrolyte for metallic lithium batteries, J. Electroanal. Chem. 837 (2019) 103-107, https://doi.org/10.1016/j.jelechem.2019.02.027

[6] S-H. Yu, S. H. Lee, D. J. Lee, Y-E. Sung, T. Hyeon, Conversion Reaction-Based Oxide Nanomaterials for Lithium Ion Battery Anodes, Small 12 (2016) 2146-2172, https://doi.org/10.1002/smll.201502299

[7] I. Sandu, T. Brousse, D.M. Schleich, M. Danot, SnO_2 negative electrode for lithium ion cell: in situ Mössbauer investigation of chemical changes upon discharge, J. Solid State Chem. 177 (2004) 4332-4340, https://doi.org/10.1016/j.jssc.2004.06.032

[8] M. V. Reddy, T. T. Linh, D. T. Hien, B. V. R. Chowdari, SnO_2 Based Materials and Their Energy Storage Studies, ACS Sustainable Chem. Eng. 4 (2016) 6268-6276, https://doi.org/10.1021/acssuschemeng.6b00445

[9] S. Böhme, B. Philippe, K. Edström, L. Nyholm, Photoelectron Spectroscopic Evidence for Overlapping Redox Reactions for SnO_2 Electrodes in Lithium-Ion Batteries, Phys. Chem. C 121 (2017) 4924-4936, https://doi.org/10.1021/acs.jpcc.7b01529

[10] R. Hu, D. Chen, G. Waller, Y. Ouyang, Y. Chen, B. Zhao, B. Rainwater, C. Yang, M. Zhu, M. Liu, Dramatically enhanced reversibility of Li_2O in SnO_2-based electrodes: the effect of nanostructure on high initial reversible capacity, Energy Environ. Sci. 9 (2016) 595-603, https://doi.org/10.1039/C5EE03367E

[11] K. Ui, S. Kawamura, N. Kumagai, Fabrication of binder-free SnO_2 nanoparticle electrode for lithium secondary batteries by electrophoretic deposition method, Electrochim. Acta 76 (2012) 383-388, https://doi.org/10.1016/j.electacta.2012.05.048

[12] G. Ferraresi, C. Villevieille, I. Czekaj, M. Horisberger, P. Novák, M. El Kazzi, SnO_2 Model Electrode Cycled in Li-Ion Battery Reveals the Formation of Li_2SnO_3 and Li_8SnO_6 Phases through Conversion Reactions, ACS Appl. Mater. Interfaces 10 (2018) 8712-8720, https://doi.org/10.1021/acsami.7b19481

[13] X. Zhou, Z. H. Dai, S. H. Liu, J. C. Bao, Y. G. Guo, Ultra-Uniform SnO_x/Carbon Nanohybrids toward Advanced Lithium-Ion Battery Anodes, Adv. Mater. 26 (2014) 3943, https://doi.org/10.1002/adma.201400173

[14] Z. P. Guo, G. D. Du, Y. Nuli, M. F. Hassan, H. K. Liu, Ultra-fine porous SnO_2 nanopowder prepared *via* a molten salt process: a highly efficient anode material for lithium-ion batteries, J. Mater. Chem. 19 (2009) 3253-3257, https://doi.org/10.1039/B821519G

[15] C. Kim, M. Noh, M. Choi, J. Cho, B. Park, Critical Size of a Nano SnO_2 Electrode for Li-Secondary Battery, Chem. Mater. 17 (2005) 3297-3301, https://doi.org/10.1021/cm048003o

[16] W. Yao, S. Wu, L. Zhan, Y. Wang, Two-dimensional porous carbon-coated sandwich-like mesoporous SnO_2/graphene/mesoporous SnO_2 nanosheets towards high-rate and long cycle life lithium-ion batteries, Chem. Engineering J. 361 (2019) 329-341, https://doi.org/10.1016/j.cej.2018.08.217

[17] Y. Deng, C. Fang, G. Chen, The developments of SnO_2/graphene nanocomposites as anode materials for high performance lithium ion batteries: A review, J. Power Sources 304 (2016) 81-101, https://doi.org/10.1016/j.jpowsour.2015.11.017

[18] M. Liu, S. Zhang, H. Dong, X. Chen, S. Gao, Y. Sun, W. Li, J. Xu, L. Chen, A. Yuan, W. Lu, Nano-SnO_2/Carbon Nanotube Hairball Composite as a High-Capacity Anode Material for Lithium Ion Batteries, ACS Sust. Chem. & Engin. 7 (4) (2019) 4195-4203, https://doi.org/10.1021/acssuschemeng.8b05869

[19] X. Zhou, L. Y. Xiong, W. Lou, Nanowire-templated formation of SnO_2/carbon nanotubes with enhanced lithium storage properties, Nanoscale 8 (2016) 8384-8389, https://doi.org/10.1039/C6NR01272H

[20] P-Y Chang, R. Doong, Microwave-assisted synthesis of SnO_2/mesoporous carbon core-satellite microspheres as anode material for high-rate lithium ion batteries, J. Alloys and Compounds 775 (2019) 214-224, https://doi.org/10.1016/j.jallcom.2018.10.038

[21] J. S. Chen, X. W. (D.) Lou, SnO_2-Based Nanomaterials: Synthesis and Application in Lithium-Ion Batteries, Small 9 (2013) 1877-1893, https://doi.org/10.1002/smll.201202601

[22] S. M. Paek, E. J. Yoo, I. Honma, Enhanced Cyclic Performance and Lithium Storage Capacity of SnO_2/Graphene Nanoporous Electrodes with Three-Dimensionally Delaminated Flexible Structure, Nano Lett. 9 (1) (2009) 72-75, https://doi.org/10.1021/nl802484w

[23] L. Sun, H. Si, Y. Zhang, Y. Shi, K. Wang, J. Liu, Y. Zhang, Sn-SnO_2 hybrid nanoclusters embedded in carbon nanotubes with enhanced electrochemical performance for advanced lithium ion batteries, J. Power Sources 415 (2019) 126-135, https://doi.org/10.1016/j.jpowsour.2019.01.063

[24] D. Song, S. Wang, R. Liu, J. Jiang, Y. Jiang, S. Huang, W. Li, Z. Chen, B. Zhao, Ultra-small SnO_2 nanoparticles decorated on three-dimensional nitrogen-doped graphene aerogel for high-performance bind-free anode material, Appl. Surf. Sci. 478 (2019) 290-298, https://doi.org/10.1016/j.apsusc.2019.01.143

[25] H. Li, B. Zhang, Q. Zhou, J. Zhang, W. Yu, Z. Ding, M. A. Tsiamtsouri, J. Zheng, H. Tong, Dual-carbon confined SnO_2 as ultralong-life anode for Li-ion batteries, Ceram. Int. 45 (2019) 7830-7838, https://doi.org/10.1016/j.ceramint.2019.01.090

[26] X. Han, R. Li, S. Qiu, X. Zhang, Q. Zhang, Y. Yang, Sonochemistry-enabled uniform coupling of SnO_2 nanocrystals with graphene sheets as anode materials for lithium-ion batteries, RSC Adv. 9 (2019) 5942, https://doi.org/10.1039/C9RA00554D

[27] H. Ji, C. Ma, J. Ding, J. Yang, G. Yang, Y. Chao, Y. Yang, Complementary stabilization by core/sheath carbon nanofibers/spongy carbon on submicron tin oxide particles as anode for lithium-ion batteries, J. Power Sources 413 (2019) 42-49, https://doi.org/10.1016/j.jpowsour.2018.12.022

[28] L. Ding, S. He, S. Miao, M.R. Jorgensen, S. Leubner, C. Yan, S.G. Hickey, A. Eychmüller, J. Xu, O.G. Schmidt, Ultrasmall SnO_2 Nanocrystals: Hot-bubbling Synthesis, Encapsulation in Carbon Layers and Applications in High Capacity Li-Ion Storage, Sci. Rep. 4 (2014) 4647, https://doi.org/10.1038/srep04647

[29] J.S. Cho, Y.C. Kang, Nanofibers Comprising Yolk–Shell Sn@void@SnO/SnO2 and Hollow SnO/SnO_2 and SnO_2 Nanospheres via the Kirkendall Diffusion Effect and Their Electrochemical Properties, Small 11 (2015) 4673-4681, https://doi.org/10.1002/smll.201500940

[30] M.E. Spahr, D. Goers, A. Leone, S. Stallone, E. Grivei, Development of carbon conductive additives for advanced lithium ion batteries, J. Power Sources 196 (2011) 3404-3413, https://doi.org/10.1016/j.jpowsour.2010.07.002

[31] A. Barroso-Bogeat, M. Alexandre-Franco, C. Fernández-González, V. Gómez-Serrano, Preparation of activated carbon-metal oxide hybrid catalysts: textural characterization, Fuel Processing Technology 126 (2014) 95-103, https://doi.org/10.1016/j.fuproc.2014.04.022

[32] H. T. Fang, X. Sun, L. H. Qian, D. W. Wang, F. Li, Y. Chu, F. P. Wang, H. M. Cheng, Synthesis of Tin (II or IV) Oxide Coated Multiwall Carbon Nanotubes with Controlled Morphology, J. Phys. Chem. C 112 (2008) 5790-5794, https://doi.org/10.1021/jp077261g

[33] W. Q. Han, A. Zettl, Coating Single-Walled Carbon Nanotubes with Tin Oxide, Nano Lett. 3 (2003) 681-683, https://doi.org/10.1023/A:1020381722804 10.1021/nl034142d

[34] K. Ke, Y. Yamazaki, K. Waki, A Simple Method to Controllably Coat Crystalline SnO2 Nanoparticles on Multiwalled Carbon Nanotubes, J. Nanosci. and Nanotech. 9 (2009) 366-370, https://doi.org/10.1166/jnn.2009.J083

[35] O. V. Reva, T. N. Vorobeva, Oxidation, Hydrolysis and Colloid Formation in Storage of $SnCl_2$ Aqueous Solutions Russ. J. Appl. Chem. 75 (2002) 700 https://doi.org/10.1023/A:1020381722804

[36] A. B. Bogeat, M.A. Franco, C. F. González, A. M. García, V. G. Serrano, Preparation of Activated Carbon-SnO_2, TiO_2, and WO_3 Catalysts. Study by FT-IR Spectroscopy, Ind. Eng. Chem. Res. 55 (18) (2016) 5200-5206, https://doi.org/10.1021/acs.iecr.5b04563

[37] C.A. Ibarguen, A. Mosquera, R. Parra, M.S. Castro, J.E. Rodríguez-Páez, Synthesis of SnO_2 nanoparticles through the controlled precipitation route, Materials Chemistry and Physics 101 (2007) 433-440, https://doi.org/10.1016/j.matchemphys.2006.08.003

[38] J. Przyluski, M. Kasprzak, J. Bielinski, Investigations of SnCl2-sensitizing solutions for electroless plating, Surf. Coat. Technol. 31 (1987) 203-211, https://doi.org/10.1016/0257-8972(87)90073-9

[39] N. P. Wagner, K. Asheim, F. Vullum-Bruer, A. M. Svensson, Performance and failure analysis of full cell lithium ion battery with LiNi0.8Co0.15Al0.05O2 and silicon electrodes, J. Power Sources 437 (2019) 226884, https://doi.org/10.1016/j.jpowsour.2019.226884

[40] M. F. Al-Khatib, S. E. Iyuke, A. B. Mohamad, W. R. W. Daud, A. A. H. Kadhum, A. M. Shariff, M. A. Yarmo, The effect of impregnation of activated carbon with SnCl2.2H2O on its porosity, surface composition and CO gas adsorption, Carbon 40 (2002) 1929-1936, https://doi.org/10.1016/S0008-6223(02)00026-X

[41] M. A. Montes-Morán, J. A. Menéndez, E. Fuente, D. Suárez, Contribution of the Basal Planes to Carbon Basicity: An Ab Initio Study of the H3O+−π Interaction in Cluster Models, J. Phys. Chem. B 102 (1998) 5595-5601, https://doi.org/10.1021/jp972656t

[42] T. Jiang, S. Whittingham, A Comparative Study of Carbon Anodes Produced by Ball Milling for Lithium-Ion Batteries, JOJ Material Sci. 1(3) (2017) 555561. https://doi.org/10.19080/JOJMS.2017.01.555562

[43] P. Scherrer, Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels Röntgenstrahlen, Göttinger Nachrichten Math. Phys. 2 (1918) 98. https://doi.org/10.1007/978-3-662-33915-2_7

[44] X. Zhou, L-J. Wan, Y-G. Guo, Binding SnO_2 Nanocrystals in Nitrogen-Doped Graphene Sheets as Anode Materials for Lithium-Ion Batteries, Adv. Mater. 25 (2013) 2152, https://doi.org/10.1002/adma.201300071

[45] H. Song, N. Li, H. Cui, C. Wang, Enhanced capability and cyclability of SnO_2–graphene oxide hybrid anode by firmly anchored SnO_2 quantum dots, J. Mater. Chem. A 1 (2013) 7558-7562, https://doi.org/10.1039/C3TA11442B

[46] K. Kisu, M. Iijima, E. Iwama, M. Saito, Y. Orikasa, W. Naoi, K. Naoi, The origin of anomalous large reversible capacity for SnO_2 conversion reaction, J. Mater. Chem. A 2 (2014) 13058-13068, https://doi.org/10.1039/C4TA01994F

[47] P. Mars, D. W. V. Krevelen, Oxidations carried out by means of vanadium oxide catalysts, Chem. Eng. Sci. 3 (1954) 41-59 (special issue), https://doi.org/10.1016/S0009-2509(54)80005-4

[48] S. Aksel, D. Eder, Catalytic effect of metal oxides on the oxidation resistance in carbon nanotube–inorganic hybrids, J. Mater. Chem. 20 (2010) 9149-9154, https://doi.org/10.1039/C0JM01129K

[49] M. Dimitrov, T. Tsoncheva, S. Shao, R. Ko¨hn, Novel preparation of nanosized mesoporous SnO_2 powders: Physicochemical and catalytic properties, Applied Catalysis B: Environmental 94 (2010) 158-165, https://doi.org/10.1016/j.apcatb.2009.11.004

[50] B. Wang, X. Li, B. Luo, L. Hao, M. Zhou, X. Zhang, Z. Fan, L. Zhi, Approaching the Downsizing Limit of Silicon for Surface-Controlled Lithium Storage, Adv. Mater. 27 (2015) 1526-1532, https://doi.org/10.1002/adma.201405031

[51] G. Cui, Y-S. Hu, L. Zhi, D. Wu, I. Lieberwirth, J. Maier, K. Müllen, A One-Step Approach Towards Carbon-Encapsulated Hollow Tin Nanoparticles and Their Application in Lithium Batteries, Small 3 (2007) 2066-2069, https://doi.org/10.1002/smll.200700350

[52] L. Ren, Y. Yao, K. Wang, S. Li, K. Zhu, J. Liu, Novel one-step in situ growth of SnO_2 quantum dots on reduced graphene oxide and its application for lithium ion batteries, J. Solid State Chem. 273 (2019) 128-131, https://doi.org/10.1016/j.jssc.2019.01.028

[53] R. Liu, D. Li, C. Wang, N. Li, Q. Li, X. Lü, J. S. Spendelow, G. Wu, Core–shell structured hollow SnO_2–polypyrrole nanocomposite anodes with enhanced cyclic performance for lithium-ion batteries, Nano Energy 6 (2014) 73-81, https://doi.org/10.1016/j.nanoen.2014.03.010

[54] Y. Cheng, J. Huang, H. Qi, L. Cao, J. Yang, Q. Xi, X. Luo, K. Yanagisawa, J. Li, Adjusting the Chemical Bonding of SnO_2@CNT Composite for Enhanced Conversion Reaction Kinetics, Small 13 (2017) 1700656, https://doi.org/10.1002/smll.201700656

[55] Y. Yang, X-A Yang, D. Leng, S-B Wang, W-B. Zhang, Fabrication of g-C_3N_4/SnS_2/SnO_2 nanocomposites for promoting photocatalytic reduction of aqueous Cr(VI) under visible light, Chemical Engineering Journal 335 (2018) 491-500, https://doi.org/10.1016/j.cej.2017.10.173

[56] Y. Hong, W. Mao, Q. Hu, S. Chang, D. Li, J. Zhang, G. Liu, G. Ai, Nitrogen-doped carbon coated SnO_2 nanoparticles embedded in a hierarchical porous carbon framework for high-performance lithium-ion battery anodes, J. Power Sources 428 (2019) 44-52, https://doi.org/10.1016/j.jpowsour.2019.04.093

[57] Y. Lee, M. R. Jo, K. Song, K. M. Nam, J. T. Park, Y. M. Kang, Hollow Sn–SnO_2 Nanocrystal/Graphite Composites and Their Lithium Storage Properties, ACS Appl. Mater. Interfaces 4 (2012) 3459-3464, https://doi.org/10.1021/am3005237

[58] J. G. Kim, S. H. Nam, S. H. Lee, S. M. Choi, W. B. Kim, SnO_2 Nanorod-Planted Graphite: An Effective Nanostructure Configuration for Reversible Lithium Ion Storage, ACS Appl. Mater. Interfaces 3 (2011) 828-835, https://doi.org/10.1021/am101169k

[59] B. Huang, X. Li, Y. Pei, S. Li, X. Cao, R. C. Massé, G. Cao, Novel Carbon-Encapsulated Porous SnO_2 Anode for Lithium-Ion Batteries with Much Improved Cyclic Stability, Small 12 (2016) 1945-1955, https://doi.org/10.1002/smll.201503419

[60] A. Sivashanmugam, T. Prem Kumar, N.G. Renganathan, S. Gopukumar, M. Wohlfahrt-Mehrens, J. Garche, Electrochemical behavior of Sn/SnO_2 mixtures for use as anode in lithium rechargeable batteries, J. Power Sources 144 (2005) 197-203, https://doi.org/10.1016/j.jpowsour.2004.12.047

[61] T. Shi, X. Kuai, W. Zhu, K. Tian, H. Lu, X. Huang, L. Gao, J. Zhao, *In-situ* high loading of SnO_2 monocrystals in a tridimensional carbon network via chemical bonding for enhanced lithium storage performance, J. Alloys Compound. 775 (2019) 790-799, https://doi.org/10.1016/j.jallcom.2018.10.205

[62] Z. Xu, W. Yue, R. Lin, C. Y. Chiang, W. Zhou, Direct growth of SnO_2 nanocrystallites on electrochemically exfoliated graphene for lithium storage, J. Energy Storage 21 (2019) 647-656, https://doi.org/10.1016/j.est.2019.01.001

[63] Y. Zhao, Q. Lin, Y. Li, C. Ma, An ordered mesoporous network consisting of carbon-coated ultrasmall SnO_2 nanoparticles with enhanced Lithium storage, Int. J. Appl. Ceram. Technol. 2019, 16, 304-314, https://doi.org/10.1111/ijac.13066

[64] R. Hu, H. Zhang, Z. Lu, J. Liu, M. Zeng, L. Yang, B. Yuan, M. Zhu, Unveiling critical size of coarsened Sn nanograins for achieving high round-trip efficiency of reversible conversion reaction in lithiated SnO_2 nanocrystals, Nano Energy Volume 45 (2018) 255-265, https://doi.org/10.1016/j.nanoen.2018.01.007

[65] S. Y. Lee, K. Y. Park, W. S. Kim, S. Yoon, S. H. Hong, K. Kang, M. Kim, Unveiling origin of additional capacity of SnO_2 anode in lithium-ion batteries by realistic *ex situ* TEM analysis, Nano Energy 19 (2016) 234-245, https://doi.org/10.1016/j.nanoen.2015.10.026