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

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ABSTRACT

Development of high-performance SnO₂ 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 SnO₂ can mitigate this issue, though SnO₂ 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-ENERGY™ Super C45 carbon black for one-pot synthesis of ultrafine SnO₂ nanoparticles over the carbon surface. These functional groups accomplish the hydrolysis/oxidation of SnCl₂, resulting in finely dispersed SnO₂ nanoparticles (5 nm in average size) growth over C45. Presence of oxygen species on C45 surface, accessible to tin, prevent fast formation of Li₂O, allowing to achieve high capacity and extreme electrode stability. The assembled cells with SnO₂/C45 exhibit for more than 400 cycles the reversible capacity of 560 mA h g⁻¹ per pure SnO₂ (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 $V = 0.005\text{--}1.0 \text{ V}$; and 1493 mA h g^{-1} cycled in the voltage range of $V = 0.005\text{--}2.0 \text{ V}$) [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]:



The electrochemical conversion of SnO_2 to metallic Sn and Li_2O (reaction (1)) occurs at $1.2 \text{ V vs. Li}^+/\text{Li}$, while reaction (2) defines the reversible alloying/dealloying of Sn, which forms a series of Li_xSn -type alloys with lithium below $0.5 \text{ V vs. Li}^+/\text{Li}$ [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-ENERGYTM 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 SnO₂/C45 consists in two simple steps: in situ deposition of SnO₂ on C45 followed by elimination of the impurities. In situ deposition of SnO₂ was achieved by pouring an aqueous solution of SnCl₂·2H₂O (purity > 98 %, Sigma-Aldrich) on commercial carbon black (TIMCAL C-ENERGY™ Super C45- Imerys) to obtain a semi-solid sludge with Sn/C = 2/3 (mass ratio). Typically, SnCl₂·2H₂O (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 SnO₂/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 SnO₂/C45.

2.2. Material characterization

The thermal stability and the amount SnO₂ 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 K α radiation) diffractometer. Data were collected with a 2D solid state detector (PIXcel) from 10 to 80° 2 θ with a step size of 0.026 2 θ 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-carboxymethylcellulose 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 SnO₂/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 cm² 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 (MBraun Labstar, H₂O and O₂ content < 1 ppm) for cell assembly. The active material loading of the SnO₂/C45 was ~ 0.7 mg cm⁻². For comparison electrodes of pure C45 and, commercial SnO₂ (Sigma Aldrich, product number 549657, SnO₂ nanopowder, ≤100 nm avg. part. size) mechanically mixed with C45 (29:71) by ball milling at 20 Hz for 20 minutes (named commercial SnO₂ + 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 (LiPF₆) 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 SnO₂/C45

The steps involved in the synthesis of sub-5 nm SnO₂ nanoparticles spatially distributed on carbon black C-ENERGY™ Super C45 are schematically illustrated in Fig. S1. The strategy allows one-shot production of SnO₂/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 SnCl₂ in excess of water depends on many factors such as the solution concentration, the pH and the presence of aerial oxygen. SnCl₂ is readily soluble in water where the following reaction (Equation (3)) occurs [32-34]:



However, if the pH ranges in the interval of 1.24 - 4.13, Sn₄(OH)₂Cl₆ colloidal particles are formed as a result of the hydrolysis reaction (4) [32]:



The Sn₄(OH)₂Cl₆ phase converts into SnO thus, hydrolysis of SnCl₂ requires HCl acid environment at pH down below 1.24 to obtain SnO₂ [32,35]. However, by wet impregnation, SnCl₂ 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 SnCl₂ solution to form a semi-solid slurry instead of a liquid mixture. First, a milky-white colloidal suspension is produced by solubilizing SnCl₂•2H₂O 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:



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



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 $\text{SnO}_2/\text{C45}$. 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 $\text{SnO}_2/\text{C45}$, 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 SnO₂ 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 SnO₂/C45 under air atmosphere between 25°C and 800 °C in order to estimate the ratio of SnO₂ and C45 from the residual SnO₂ 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 SnO₂ (Aldrich) and C45, mechanically mixed in the ratio 29:71 w/w for comparison.

The TGA curve of SnO₂/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 SnO₂/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 SnO₂. The mass percentage of SnO₂ in the composite is around 29 wt %. It's worth noting that combustion of SnO₂/C45 starts at lower temperature (about 500 °C) than that of the mechanically mixed commercial SnO₂-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 SnO₂[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 SnO₂ and C45 in SnO₂/C45[46]. The BET specific surface area (SSA) is evaluated by means of N₂ adsorption/desorption isotherms (Figure 1 c,d). The BET values of C45

and SnO₂/C45 are 52 m² g⁻¹ and 65 m² g⁻¹, respectively. The slight increase in the SSA of SnO₂/C45 can be due to the SnO₂ nanoparticles piled on the outer sphere of C45. The N₂ adsorption/desorption isotherms of pure C45 and SnO₂/C45 composite are compared in Fig. 1c. The curves show type II isotherms with a small hysteresis at low p/p₀ 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 SnO₂/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 SnO₂ 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 SnO₂/C45 highlight the presence of SnO₂ 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 SnO₂/C45 is rough due to anchoring of SnO₂ nanoparticles (Fig. 2 c). As it is observed, SnO₂ nanoparticles evenly cover the entire C45 surface. Some areas are seen in which particles are less gathered, enlighten in Fig. 2d. As clearly seen, SnO₂ average particle dimension is about 5.0 nm or even less.

Previous investigations on ultras-small 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 SnO₂ 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 SnO₂ particles. As a result, the electrode capacity should be more stable due to less volume variations

[51]. At low magnification, SnO₂/C45 shows a good interconnection among carbon particles to form a continuous network, ensuring the necessary electronic conductivity. The space among SnO₂ 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 SnO₂/C45 (Fig. 3 a-f) show that the particle size is less than 10 nm, in the average the diameter of SnO₂ 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 SnO₂, ~~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 SnO₂ nanoparticle agglomeration during synthesis.

Please insert here Figure 3

EDS elemental analysis was performed on SnO₂/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 SnO₂ amount resulted in the increase of particle size (Fig. S3 ~~a, b~~ Supporting Information). The optimized SnO₂/C45 composite with ~ 30 wt. % SnO₂ 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 SnO₂ – carbon interaction (Fig. 4). The XPS survey of SnO₂/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 SnO₂/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 SnO₂/C45 samples, the major contribution is due to sp² bonded carbon, which is smaller in SnO₂/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 O₂ (air) and catalyzed by SnO₂ during the oven-drying step at 80°C. This explains the 3.0 % at. contribution of –COOH in the C1s of SnO₂/C45. **Moreover, in such spectra, the presence of the peak at 285.9 eV corroborates the idea that some SnO₂ 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 SnO₂/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 Sn⁴⁺ (Sn bonded to O). The

binding energy separation of 8.4 eV well agrees with the values reported in literature for SnO₂-based materials [56] moreover, no Sn (0) or Sn²⁺ 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 SnO₂/C45 spectrum suggesting that SnO₂ could interact preferentially 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 Li₂O exists in form of nanosized structure [58,59]. To assess the electrochemical processes of SnO₂/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 SnO₂ to Sn (0) with the simultaneous formation of Li₂O. 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 SnO₂/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 SnO₂/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 SnO₂ is oxidized back to SnO₂ and Li₂O is almost entirely decomposed. This implies that the conversion reaction is favored by the small particle size of SnO₂ firmly anchored to C45 and to the high fraction of Sn/Li₂O interfaces during SnO₂ 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 SnO₂/C45 that controls preponderant Li₂O formation and maintains ultrafine Sn particles in the Li₂O 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 SnO₂/C45, the electrode consisting of commercial SnO₂ and C45 mechanically mixed in the ratio 29:71 w/w is used as comparison. Fig. 5b shows five consecutive 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 Li₂O 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 SnO₂ 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 Li₂O 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 SnO₂ to Sn. In the first CV cycle of commercial SnO₂ + 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 SnO₂ nanorod-planted graphite electrodes [58]. This result suggests that the contribution of C45 to the overall capacity is higher in the **simple mixed commercial SnO₂ + 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 SnO₂/C45 (29:71), the reversible capacity has been calculated from following equation [46]:

$$\text{Cap.}_{\text{SnO}_2} = (\text{Cap.}_{\text{SnO}_2/\text{C45}} * 1.00 - \text{Cap.}_{\text{C45}} * 0.71) / 0.29 \quad (7)$$

where Cap._{SnO₂} represents the capacity purely ascribable to the SnO₂ particles, Cap._{SnO₂/C45} is the capacity attributed to SnO₂/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 SnO₂/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 SnO₂ 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 delithiation. At 0.1C, the commercial SnO₂ + 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 Li₂O conversion from the 1st cycle. **Further contribution to the capacity loss is due to irreversible Li⁺ storage in C45.** In the same experimental conditions, SnO₂/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 SnO₂ particles, these values are very close to the theoretical one (1494 mA h g⁻¹) that includes both the alloying and conversion processes. Thus, SnO₂/C45 showed improved reversibility of the electrochemical reaction benefitting of the synergic effect between SnO₂ 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 SnO₂ and C45 suffered severe capacity fading (Fig. 7a). In this case, lithiation of SnO₂ delivers 792 mA h g⁻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 SnO₂ is electrochemically active. In contrast, the SnO₂/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 $\sim 750 \text{ mA h g}^{-1}$ 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 $\sim 400^{\text{th}}$ 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 $\text{SnO}_2/\text{C45}$ composite. Considering the fast and inexpensive method used to prepare $\text{SnO}_2/\text{C45}$, 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 $\text{SnO}_2/\text{C45}$ was also evaluated (Fig. 7c). The specific capacities of $\text{SnO}_2/\text{C45}$ 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 $\text{SnO}_2/\text{C45}$ 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 $\text{SnO}_2 + \text{C45}$ (Fig. 8a) and $\text{SnO}_2/\text{C45}$ (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 SnO₂ + 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→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 Li₂O 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 SnO₂ film electrodes [64] and is explained as the gradual diffusion of Sn from one Sn/Li₂O zone to the others nearby, due to the tendency of nanosized Sn grains to reduce their surface/interface energy in the lithiated SnO₂. At the 5th cycle, the differential capacity (dQ/dV) curves of SnO₂/C45 (Fig. 8b), show that the peaks due to de-alloying process are not as sharp as in commercial SnO₂ + C45. The curves corresponding to the 10th and 5th cycle almost overlap without showing any shrinkage of the peaks, indicating very good cyclability of SnO₂/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 SnO₂ 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 Li₂O) to reform SnO₂. After lithiation, in highly dispersed SnO₂ 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 $\text{Sn}(0)$ 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 and 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-ENERGY 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.

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Captions to Figures

Fig. 1. (a) XRD analysis of C45 (black line) and SnO₂/C45 (red line), (b) TGA analysis of C45, SnO₂/C45 and of commercial SnO₂ + C45 mixed in weight ratio 29:71. (c) N₂ adsorption/desorption measurements of SnO₂/C45 and C45 (inset), (d) pore distribution of SnO₂/C45 and C45 (inset).

Fig. 2. FESEM micrographs of SnO₂/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 SnO₂/C45 at different magnifications (a-f).

Fig. 4. (a) High resolution C1s spectrum of C45 from XPS analysis. (b) High resolution C1s spectrum of SnO₂/C45. (c) High resolution XPS spectrum O1s of SnO₂/C45. (d) High resolution XPS spectrum Sn2p of SnO₂/C45.

Fig. 5. Cyclic voltammetry at 0.5 mVs⁻¹ between 2.0-0.01 V vs Li⁺/Li of: a) SnO₂/C45, b) commercial SnO₂ + 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 SnO₂ + C45, b) SnO₂/C45.

Fig. 7. Galvanostatic charge/discharge profiles of the electrodes at 1C: a) commercial SnO₂ + C45, b) SnO₂/C45; c) Cycling performance of SnO₂/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 SnO₂ + C45; b) SnO₂/C45. Note that the specific capacity associated to the de-lithiation process is relative to the mass of SnO₂ 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/sml.201502299>
- [7] I. Sandu, T. Brousse, D.M. Schleich, M. Danot, SnO₂ 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, SnO₂ 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 SnO₂ 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 Li₂O in SnO₂-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 SnO₂ 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, SnO₂ Model Electrode Cycled in Li-Ion Battery Reveals the Formation of Li₂SnO₃ and Li₈SnO₆ 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 SnO₂ 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 SnO₂ 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 SnO₂/graphene/mesoporous SnO₂ 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 SnO₂/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-SnO₂/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 SnO₂/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 SnO₂/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, SnO₂-Based Nanomaterials: Synthesis and Application in Lithium-Ion Batteries, *Small* 9 (2013) 1877-1893, <https://doi.org/10.1002/sml.201202601>
- [22] S. M. Paek, E. J. Yoo, I. Honma, Enhanced Cyclic Performance and Lithium Storage Capacity of SnO₂/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-SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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/SnO₂ and SnO₂ Nanospheres via the Kirkendall Diffusion Effect and Their Electrochemical Properties, *Small* 11 (2015) 4673-4681, <https://doi.org/10.1002/sml.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 SnCl₂ 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-SnO₂, TiO₂, and WO₃ 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 SnO₂ 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](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 LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ 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](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 SnO₂ 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 SnO₂–graphene oxide hybrid anode by firmly anchored SnO₂ 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 SnO₂ 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](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. Köhn, Novel preparation of nanosized mesoporous SnO₂ 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 SnO₂ 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 SnO₂–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 SnO₂@CNT Composite for Enhanced Conversion Reaction Kinetics, *Small* 13 (2017) 1700656, <https://doi.org/10.1002/sml.201700656>
- [55] Y. Yang, X-A Yang, D. Leng, S-B Wang, W-B. Zhang, Fabrication of g-C₃N₄/SnS₂/SnO₂ 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 SnO₂ 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-SnO₂ 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, SnO₂ 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 SnO₂ Anode for Lithium-Ion Batteries with Much Improved Cyclic Stability, *Small* 12 (2016) 1945-1955, <https://doi.org/10.1002/sml.201503419>
- [60] A. Sivashanmugam, T. Prem Kumar, N.G. Renganathan, S. Gopukumar, M. Wohlfahrt-Mehrens, J. Garche, Electrochemical behavior of Sn/SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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 SnO₂ 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>