The electrochemical reactions of SnO₂ with Li and Na: a study using thin films and mesoporous carbons

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Abstract

In this work we have determined the room temperature electrochemical reactivity of SnO_2 thin films and mesoporous carbons filled with SnO_2 anodes with Na, and compare the results with those obtained during the reaction with Li. We show that SnO_2 can reversibly deliver up to 6.2 Li/ SnO_2 whereas the reaction with Na is significantly limited. The initial discharge capacity is equivalent to less than 4 Na/ SnO_2 , which is expected to correspond to the formation of 2 Na_2O and Sn. This limited discharge capacity suggests the negative role of the formed Na_2O matrix upon the reversible reaction of Sn clusters. Moreover, the reversible cycling of less than 1 Na/ SnO_2 , despite the utilization of 6-7 nm SnO_2 particles, is indicative of sluggish reaction kinetics. The origin of this significant capacity reduction is likely due to the formation of a diffusion limiting interface. Furthermore, there is a larger apparent hysteresis compared to Li. These results point to the need to design composite structures of SnO_2 nanoparticles with suitable morphological and conductivity components.

1. Introduction

While lithium-ion batteries are widely applied in consumer electronics, cheaper alternative electrochemical systems will need to be developed for large scale storage applications, like the electrical grid. For this purpose, the sodium ion battery system is of significant interest since the cathode could be based on earth abundant elements such as Fe, Mn and Na [1,2]. Moreover, since Na and Al do not alloy, a current collector made of the cheaper and lighter Al can be used on the anode in place of the Cu used in lithium ion batteries. Furthermore, the energy density reported for Na-ion electrode materials is relatively high with storage capacities and operating voltages similar to those of materials obtained with lithium ion batteries [1,2]. To this date, research on sodium ion battery electrodes is primarily academic or scoping in nature and building off our knowledge of Li-ion electrodes.

One of the major challenges has been identifying suitable anode materials as Na does not intercalate in between the planes of the classic graphite electrode. Jache and Adelhelm [3] have recently circumvented the absence of Na-intercalation into graphite by employing a diglyme solvent that allows reversible co-intercalation into the structure. This novel electrode/electrolyte system can sustain a moderate storage capacity (100 mAh g^{-1}) over 1000 cycles with high coulomb efficiency. Alternative compounds with somewhat higher storage capacities such as $\text{Na}_2\text{Ti}_3\text{O}_7$ [4] and hard carbons [5,6] were identified as potential Na-ion anodes but suffer from relatively small storage capacities and slow reaction kinetics [4-6]. Several groups have focused efforts on the study of metals and intermetallics, which have high theoretical capacities and excellent rates [7-31]. Their works are pioneering the study and understanding of the reaction mechanisms of a wide array of Sn-, Sb-, Ge-, and In-based materials such as Sn [7-12], Cu_6Sn_5 [13,14], pure Sb [15-18], Cu_2Sb [19-21], Mo_3Sb_7 [22], AlSb [23], SnSb [16,24-26], FeSb_2 [27],

Co-Sn alloys [28,29], Ge [30-33] and In [34]. Tin [7-12] and antimony [15-18] are particularly interesting since they can store up to 3.75 and 3 Na/M (M=Sn, Sb), corresponding to large expected storage capacities of 847 and 660 mAh g⁻¹, respectively. One main drawback of the alloying systems, however, is the large volume expansion coupled with the electrode surface passivation due to electrolyte decomposition, which can lead to quick capacity fade.

Another class of materials of potential interest for rechargeable battery anodes are conversion electrodes which also offer large storage capacities and better cycle life than the parent alloying elements [35]. In these systems the second element of the electrode composition, such as O, N, P, etc, is expected to convert into an inert buffering matrix, e.g. Li₂O or Na₂O, and could provide a more robust and durable electrode structure to cope with the large volume changes of the active electrode clusters [35]. One such case is antimony oxide, Sb₂O₄, which exhibits a high reversible capacity around 900 mAh g⁻¹ as an anode material [36]. Furthermore, a few recent reports highlighted that the conversion anode SnO₂ mixed with graphene [37], reduced graphene oxide [38] or carbon nanotubes [39] may be potential Na-ion anode materials. These studies employed either very fine (2-10 nm) SnO₂ nanoparticles [37,38] or relatively larger crystals of about 60 nm [39], and reported storage capacities around 400-700 mAh g⁻¹. However, these capacities were only achievable at very low rates and dropped rapidly at higher currents, with for instance a capacity of 700 mAh g⁻¹ at 20 mA g⁻¹ current for the graphene composite [37], 400 mAh g⁻¹ at 100 mA g⁻¹ for the reduced graphene oxide composite [38] and 500 mAh g⁻¹ at 0.05 C-rate for the carbon nanotubes composite [39].

An *in situ* transmission electron microscopy (TEM) study has recently reported the reaction and failure mechanism of SnO₂ nanowires during the reaction with Na [40], and observed a conversion reaction taking place at the nanoscale according to the conversion of SnO₂ into Na₂O

and Na_xSn compounds, with x up to 3.75 in $\text{Na}_{15}\text{Sn}_4$. This reaction would lead to a maximum storage capacity of 1378 mAh g^{-1} (7.75 Na/SnO_2) assuming the complete reversibility of the reaction. However, it is unknown how the electron beam influences the single nanowire reaction and whether it may promote the extent of the reaction. Another work discussed the reaction of SnO thin film during the reaction with Na and presented storage capacities around 600 mAh g^{-1} [41]. In that case the expected maximum storage capacity is 1144 mAh g^{-1} (5.75 Na/SnO). It is important to note that the reaction of a regular electrochemical cell based on SnO_2 nanowires or other SnO_2 -based nanomaterials matching the theoretical capacity of the proposed reaction mechanism (1378 mAh g^{-1}) has not been reported to this date.

In order to understand why SnO_2 has limited storage capacity, if the effect is intrinsic to SnO_2 , due to carbon additives or the interplay between the carbon matrix and SnO_2 [37-39], and whether practical reaction rates can be obtained in cells not utilizing nanowires or complicated single particle sodiation setup [40], we have conducted a basic study utilizing both pure SnO_2 thin films and soft-templated mesoporous carbons filled with SnO_2 nanoparticles ($\text{SnO}_2@\text{C}$) as anode model systems. Thin films are an ideal model system consisting of the pure material well anchored onto a current collector enabling short electronic and diffusion pathways. Soft-templated mesoporous carbons filled with SnO_2 are an attractive anode material for rechargeable batteries, as has been recently reported for Li-ion batteries [42]. In this architecture, the active electrode material SnO_2 is primarily confined into the nanochannels of the mesoporous carbons, which is expected to provide a robust backbone to cope with the volume changes associated with the reaction of SnO_2 with Na . Our present work is the first study investigating the properties of SnO_2 thin films and of $\text{SnO}_2@\text{C}$ mesoporous carbons prepared with and without microporosity for Na-ion battery applications. Moreover, the reaction with Na has been compared to that taking

place with Li in order to assess if the prepared materials are suitable for electrochemical reactions. The starting materials were thoroughly characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), TEM, gas adsorption measurements, thermal gravimetric analysis (TGA) and electrochemical cycling measurements. Moreover, post-mortem characterization using XRD was conducted on selected electrodes to understand the origins of the low capacity observed during the reaction with Na.

2. Experimental

2.1. Samples preparation

Ordered mesoporous carbons (OMCs) were synthesized according to Wang *et al.* [43]. In a typical synthesis, 0.625 g of resorcinol and 0.625 g of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic F127) were dissolved in 4.62 g of ethanol-water (10:7 wt. ratio) solution and stirred vigorously at room temperature. After complete copolymer dissolution HCl acid was added as a catalyst. The resulting solution was stirred for additional 30 min. Subsequently, 0.625 mL of 37% formaldehyde was added to the synthesis mixture. The resulting mixture turned cloudy after 1 h of stirring then eventually separated into two layers. The polymer-rich bottom layer obtained after separation was transferred to a Petri dish and treated at 100 °C for 24 h. Carbonization of the resulting film was performed in a tube furnace under N₂ flow using a heating rate of 2 °C min⁻¹ up to 180 °C, keeping the sample at this temperature for 5 h, resuming heating with 2 °C min⁻¹ up to 400 °C and with 5 °C min⁻¹ up to 850 °C, and finally keeping the sample at 850 °C for 2 h. Natural cooling was then applied.

In order to study the effect of an increased surface area of the OMCs, some OMC materials were subjected to a base (KOH) activation, in which the carbon-KOH mixture (1:3 ratio) was heated under flowing N_2 at $5\text{ }^{\circ}\text{C min}^{-1}$ to $850\text{ }^{\circ}\text{C}$ for 2 hrs. The resulting activated ordered mesoporous carbon (a-OMC) was washed with DI water followed by dilute hydrochloric acid then dried at $80\text{ }^{\circ}\text{C}$ for 24 hrs.

Filling of pores of the carbons with SnO_2 was conducted on both activated OMC ($\text{SnO}_2\text{@C}$ #1 and #2) and non-activated OMC ($\text{SnO}_2\text{@C}$ #3), as follows: 0.3 g of mesoporous carbon was impregnated with aqueous $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ solution and allowed to dry in the vacuum oven at $60\text{ }^{\circ}\text{C}$. Next, samples were transferred to a container containing 14% ammonia solution (without the direct contact between the carbon and ammonia solution). The container was sealed and heated in an oven for 3hrs at $80\text{ }^{\circ}\text{C}$. The entire procedure was repeated once (two impregnations) for a batch of activated OMC ($\text{SnO}_2\text{@C}$ #1) to increase the Sn loading whereas a single impregnation was carried out for activated OMC ($\text{SnO}_2\text{@C}$ #2) and non-activated OMC ($\text{SnO}_2\text{@C}$ #3). The final product was washed several times with DI water and ethanol. The final thermal treatment was performed in a tube furnace under flowing Ar using a heating rate of $2\text{ }^{\circ}\text{C min}^{-1}$ up to $300\text{ }^{\circ}\text{C}$, keeping the sample at this temperature for 1 h, resuming heating with $2\text{ }^{\circ}\text{C min}^{-1}$ up to $550\text{ }^{\circ}\text{C}$ and finally keeping the sample at $550\text{ }^{\circ}\text{C}$ for 3hrs. Natural cooling was then applied.

Electrodes were prepared by gently mixing for a few minutes a mixture of 1:9 wt ratio of PVDF (Sigmal-Aldrich) and $\text{SnO}_2\text{@C}$ powders, respectively. The mixture was then dissolved in anhydrous 1-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) and milled with YSZ balls for several minutes. The homogeneous slurry was cast onto as-provided rough Cu foils (OAK-MITSUI, Figure S1) with a blade and dried under vacuum at $90\text{ }^{\circ}\text{C}$ overnight. The active material loading

was typically between 1.5-2 mg cm⁻² by multiple weighting using a Sartorius microbalance with 10 µg precision.

SnO₂ thin film preparation was carried out onto rough Cu foils by means of DC magnetron sputtering in an Ar/O₂ (20:10 vol/vol) plasma using high purity Sn (99.99%, Lesker) as target and Ar and O₂ (99.99%, Air Liquide) as sputtering gases. The chamber was evacuated below 10⁻⁶ Torr after which sputtering was performed at 20 W power and 20 mTorr pressure. Thickness was estimated using a quartz microbalance installed inside the vacuum chamber. Samples weight was determined by multiple weighting using a Sartorius microbalance with 10 µg precision. Reported thickness values were estimated based on the weight of the films and the expected density of 7.0 g cm⁻³ for SnO₂ (PDF 01-088-0287).

2.2. Characterization

XRD measurements were conducted using a PANalytical X'Pert Pro MPD with a Cu-K_α source operated at 45 kV / 40 mA, Ni filter and X'Celerator solid-state detector. The starting mesoporous carbons were measured with an automatic divergence slit (ADS) to fix the beam length over the sample to a constant value (3 mm) at all angles. The spectra were converted to a fixed divergence slit configuration to fulfill the constant volume approximation. The SnO₂ thin film was measured with an ADS to ensure the measurement of a constant volume. Cycled electrodes were sealed with Kapton tape (25 µm) onto a glass slide inside an Ar glovebox to protect the electrode material from air exposure during the XRD collection. Transmission electron microscopy (TEM) imaging was performed on a Hitachi HD-2000 scanning transmission electron microscope (STEM) with an accelerating voltage of 200 kV. SEM images were collected on thin film samples using a Hitachi S4800 field emission microscope.

Surface chemistry was probed with a PHI 3056 XPS spectrometer using a Al K_{α} source (1486.6 eV). High resolution scans were acquired at 350 W, 23.5 eV constant pass energy, and 0.05 eV energy step, and survey scans were measured at 350 W, 93.9 eV constant pass energy, and 0.3 eV energy step. The binding energies were adjusted by setting the O1s signals from the O^{2-} lattice of SnO_2 to 530.5 eV to prevent incommensurate charging effects resulting from the C- SnO_2 interactions. This energy was selected as this is the binding energy measured for the SnO_2 thin films after adjusting the C1s signal related to adventitious carbon to 284.8 eV.

TGA was performed on TGA 2950 Thermogravimetric analyzer (TA Instruments) in the temperature range of 30-1000 °C under flowing air. Nitrogen adsorption isotherms were measured at -196 °C using TriStar 3000 volumetric adsorption analyzer (Micromeritics Instrument Corp., Norcross, GA). Before adsorption measurements, the carbon powders were degassed under flowing nitrogen for 2 hrs at 200 °C. The specific surface area of the samples was calculated using the Brunauer-Emmett-Teller (BET) method within the relative pressure range of 0.05–0.20. Pore size distributions (PSD) were calculated using the BJH algorithm for cylindrical pores according to the improved KJS method calibrated for pores up to 12 nm [44].

Electrochemical characterization was conducted at 25°C in a thermostatic incubator using 2-electrode 2032 coin cells (Hohsen, Japan) prepared inside an Ar-purified glovebox (O_2 , H_2O < 1 ppm). The cells consisted of pure Na (Sigma-Aldrich) or Li (Alfa Aesar) as counter electrodes, glass fiber separators (Whatman) impregnated with 1M $NaClO_4$ in PC (Sigma-Aldrich) or Cellgard 2500 separators impregnated with 1.2 M $LiPF_6$ in dimethyl carbonate (DMC) and EC (Novolyte) electrolyte solutions, and SnO_2 samples as working electrodes. Galvanostatic cycling was performed on a Maccor 4000 series. The C-rate current values are based on the practical storage capacities.

3. Results and Discussion

The XRD patterns of the thin film and mesoporous carbon materials filled with SnO₂ nanoparticles are presented in Figure 1. In all cases, the patterns display broad peaks at the positions expected for pure SnO₂ (tetragonal rutile) with no noticeable impurity being present. The patterns of the mesoporous carbons show relative intensities close to the reference pattern, which supports the presence of randomly oriented nanocrystallites in the X-ray beam, whereas the thin film pattern clearly show some preferred orientation of the nanocrystallites with stronger than predicted (121) and (031) peaks at about 52 and 66°, respectively. Such preferred orientation is widely observed for sputtered thin films [9,19,27]. Based on the Scherrer's equation taking into account the instrumental line broadening and using the width of the strongest peaks ((110) and (011) near 26.5 and 33.8°, respectively), the samples have estimated nanocrystallite sizes of 5.1, 6.7, 5.8, and 6.1 nm for the SnO₂@C #1, #2 and #3, and thin film samples, respectively.

The surface composition and chemistry of the materials was further analyzed using XPS. Both Sn3d and Sn4d spectra show the response for Sn⁴⁺ cations inside an O²⁻ framework, as evidenced by peaks at about 486.6 eV, 495.0 eV and 26.4 eV for Sn3d5/2, Sn3d3/2 and the unresolved Sn4d5/2-Sn4d3/2 signals [9]. No evidence for the formation of metallic Sn or Sn²⁺-O species were found, and no Cl (Figure S2) leftovers from the precursor solution were detected. Hence, the XPS results further support the formation of pure SnO₂ materials.

The nitrogen adsorption isotherms, pore size distributions and thermal decomposition curves for mesoporous carbon-based materials are presented in Figure 3. Physicochemical properties of these materials derived from the adsorption isotherms are listed in Table 1. As one can see from

Figure 3a and Figure S3, both activated mesoporous carbons filled with SnO₂ (SnO₂@C #1 and SnO₂@C #2) possess lower surface area and lower pore volume than the parent material. Indeed, rather moderate BET surface area (487 m² g⁻¹ and 580 m² g⁻¹) compared to the parent activated carbon (around 1600 m² g⁻¹) are calculated (Table 1). The same trend is also observed for the meso- and micropore volumes, which decrease significantly after pore filling (Table 1). The important decrease in surface area and pore volume suggests not only constriction of the channel cross-section due to wall coverage by SnO₂ but also the complete filling of some micro- and mesopores. The filling of some channels is further suggested by the agreement between the size of the SnO₂ nanocrystallites estimated from the analysis of the XRD patterns (see above) and the average size of the mesopore size distribution around 7 nm (Table 1). The analysis of the high quality pore size distribution curves (Figure 3b, Figure S3) highlights that in the case of SnO₂@C #1, the pore width is smaller by almost 1 nm compared to SnO₂@C #2 (Table 1). Since SnO₂@C #1 and SnO₂@C #2 originate from the same activated OMC material, this lower pore size value further supports thicker SnO₂ film formation inside the mesopores as well as the channel constriction discussed above for SnO₂@C #1, as expected from its larger SnO₂ loading (see later). SnO₂@C #3 was prepared by the impregnation of the non-activated mesoporous carbon. The latter possessed a surface area of about 790 m² g⁻¹, which after the formation on SnO₂ nanoparticles inside the pores reduced importantly to about 170 m² g⁻¹ (Table 1).

TGA results (Figure 3c) show substantial differences in SnO₂ nanoparticle loadings in both SnO₂@C #1 and SnO₂@C #2 samples (76 vs. 31 wt% for the former and the latter, respectively), as expected from the double impregnation step applied to sample SnO₂@C #1. The more than doubled loading for SnO₂@C #1 (76 vs 31%), combined with relatively similar structural properties obtained from nitrogen adsorption isotherms suggest that some of the SnO₂

nanoparticles were also formed on the external surface of the SnO₂@C #1 carbon. The structure of the SnO₂@C #1 and #2 composite materials was imaged using TEM (Figure 4). Both materials are composed of fine SnO₂ particles of 10 nm or less incorporated inside the mesoporous carbon channels. There is also evidence for the formation of a small proportion of SnO₂ particles outside of the mesoporous carbon materials (not presented), as discussed above. The thin films morphology over long scales is dependent on the rough Cu substrate (Figure 4c, Figure S1 and Figure S4), as was also observed for other thin films systems deposited onto these Cu foils [13,19]. At the local scale, the thin films are composed of secondary particles agglomerates of sizes from about 20 to 100 nm (Figure 4d, Figure S4 and Figure S5) with primary nanoparticles with a size typically below 10 nm (Figure 4d, Figure S5).

The electrochemical profiles of SnO₂ thin films during the reactions with Li and Na are presented in Figure 5. The reaction with Li is very extensive, and exhibits an initial discharge (lithiation) capacity of about 1600 mAh g⁻¹ (9.0 Li/SnO₂) and a reversible capacity around 1100 mAh g⁻¹ (6.2 Li/Sn). The discharge capacity corresponds to the conversion of SnO₂ according to:

The global reaction corresponds to a total discharge capacity of 1469 mAh g⁻¹ when assuming the formation of Li_{21+5/16}Sn₅, the end-member of the Li-Sn system [45]. The difference between this capacity and the discharge capacity of 1600 mAh g⁻¹ measured here can be related to the electrolyte decomposition, which leads to the formation of a so-called solid electrolyte interphase (SEI) film. A discharge capacity larger than 1469 mAh g⁻¹ has also been observed in works studying the reaction mechanism of SnO₂ electrode [46-48]. The charge (delithiation) reaction

was related to the formation of Sn, Sn²⁺ and Sn⁴⁺ species [48]. For simplicity, it is, however, often written as [46]:

Alternatively, the charge reaction could involve the back conversion of Li₂O to form SnO, as suggested in [48], according to:

Further reaction could lead to the full conversion back into SnO₂, however, this was not observed experimentally [46-48]. Reaction (3) corresponds to the exchange of 6.26 Li and a capacity of 1113 mAh g⁻¹, which is in very good agreement with our experimental data during the first and second cycles. This indicates good reaction reversibility and shows that the present thin films are a very good model system for the reaction of SnO₂ with Li. Moreover, the results also suggest that the irreversible conversion of SnO₂ into a compound with a composition of 2 Li/SnO₂, such as SnO + Li₂O, or a ternary mixture [46-48], occurs on the plateau observed at 1 V during the first cycle.

During the reaction of the SnO₂ thin films with Na (Figure 5), the initial discharge capacity for all samples average about 700-750 mAh g⁻¹ (~4 Na/SnO₂), which is significantly reduced compared to Li. This capacity accounts for the electrode bulk conversion reaction as well as the electrode surface passivation due to the SEI formation. At most, the value of 4 Na/SnO₂ represents the conversion of SnO₂ into 2 Na₂O + Sn. However, as evidenced by *ex situ* XRD on a thin film electrode short-circuited for 48 h (Figure S6), the conversion of SnO₂, which is expected to react with 4 Na to yield 2 Na₂O + Sn, *i.e.* 4 Na/SnO₂, is not complete after such long period of time. This is clearly observed by the persistence of the two strongest diffraction lines of

SnO₂ thin films near 52 and 66°, which suggests the incomplete bulk conversion. Since less than 4 Na are inserted into the electrode for all film thicknesses, we suspect that the reaction proceeds with the formation of a phase or a mixture of phases in which Na-ion diffusion is strongly impeded, perhaps due to the formation of Na₂O. This hypothesis should be further investigated by employing techniques such as the electrochemical impedance spectroscopy of 3 electrode cells, in order to probe the changes in diffusion and charge transfer kinetic parameters. Furthermore, characterization tools capable of probing the local order in amorphous materials, such as nuclear magnetic resonance, X-ray absorption spectroscopy and ¹¹⁹Sn Mössbauer spectroscopy, would be very useful to help in the elucidation of the reaction limitations, a topic of future study. Compared to Li, there is also a much larger apparent hysteresis between discharge and charge during the reaction with Na. The apparent hysteresis observed here is likely due to both the thermodynamic and kinetic, and demonstrates that the reaction of SnO₂ with Na is significantly more difficult than with Li. This could be attributed to the more difficult formation of Na₂O compared to Li₂O during bond breaking/formation (thermodynamic), and possibly lower electronic and ionic conductivities (kinetic) of the Na₂O/Sn composite.

The reversible capacity, which corresponds to the amount of Na removed from the electrode during charge, is substantially smaller as well, with values from 70 to 120 mAh g⁻¹, depending on the film thickness (Figure 5a). The data is consistent with the thicker films exhibiting lower reversible capacities and larger overpotentials during the initial discharge compared to thinner films. Given that the reversible capacity amounts to, at most, less than 1 Na/SnO₂, this could indicate a significant reaction barrier that forms during sodiation. Li₂O has a unit cell volume of 24.51 Å³ (PDF 00-012-0254) versus 42.97 Å³ for the almost two times larger Na₂O (PDF 00-023-0528). The conversion of the unit cell of SnO₂ of 35.76 Å³ (PDF 01-088-0287) would lead,

according to (1') or its equivalent reaction for Li, to the formation of 27.05 Å³ of Sn (PDF 00-004-0673) and 49.02 Å³ for 2 Li₂O or 85.94 Å³ for 2 Na₂O. This represents a volume fraction occupation of about 64.4% for Li₂O against 76.0% for Na₂O, and a volume expansion of 113% and 216% for Li and Na, respectively.

The reaction of SnO₂@C mesoporous carbons is discussed next. The potential profiles of the three carbon materials studied during the reactions with Li and Na are presented in Figure 6. During the reaction with Li, SnO₂@C #1 and #3 display similar profiles that compare well with the shapes of those measured for the thin films and those obtained for the similar mesoporous carbon system reported in [42]. Compared to the profiles of the thin films, the main difference is the larger discharge capacities (about 1900 mAh g⁻¹ for SnO₂@C #1 and about 2100 mAh g⁻¹ for SnO₂@C #3). These larger initial discharge capacities are likely due to the large surface area of carbons compared to thin films, hence favoring electrolyte decomposition. For SnO₂@C #2, the profile has a different shape than for the thin film sample. Moreover, the discharge capacity is much larger, at about 4500 mAh g⁻¹. The features can be explained by the much larger proportion of carbon material in SnO₂@C #2 with 69 wt% vs. 24 wt% in SnO₂@C #1 (Table 1) resulting in more surface for the decomposition reaction to proceed. Although the BET surface areas of the starting materials SnO₂@C #1 and SnO₂@C #2 are similar, we expect that given the lower SnO₂ loading in SnO₂@C #2, more channels can open in this material during the lithiation reaction, thus exposing a significant amount of formerly-inaccessible micro- and mesopores to the electrolyte and lead to a larger irreversible capacity. For all mesoporous carbons, the reversible capacities are comparable (about 900 mAh g⁻¹), which is smaller but comparable to the capacity obtained with the thin films. This shows that SnO₂ incorporated within the mesoporous carbons can be accessed to a large extent. In the case of SnO₂@C #2, based on the shape of the potential

profiles, we suspect that part of the reversible capacity, similar to the initial discharge, results from the carbon material.

Similar to the thin films, the reaction of SnO₂@C mesoporous carbons with Na is importantly limited (Figure 6). SnO₂@C #1, SnO₂@C #2 and SnO₂@C #3 show discharge capacities of about 700, 2400 and 1000 mAh g⁻¹, respectively, and reversible capacities of about 100, 300 and 200 mAh g⁻¹, respectively. Although the capacity of SnO₂@C #2 is large, it also shows the largest initial irreversible capacity (Figure 6 and S7), which is related to its larger amount of C and further supports that SnO₂ has a limited reactivity with Na. The origins of the low reversible capacity were studied using *ex situ* XRD (Figure S6). A SnO₂@C #1 electrode short-circuited for 48 h still possesses a substantial fraction of unreacted SnO₂ clusters, as has also been evidenced for thin films. The limited sodiation reaction (less than 4 Na/SnO₂) is clearly observed for thin films as thin as 190 nm and composed of very fine primary nanoparticles (~6 nm), as well as for SnO₂ nanoparticles (5-7 nm) embedded in mesoporous carbons. Upon desodiation, we estimate that less than 1 Na/SnO₂ is extracted from the SnO₂ material. The large capacity values observed for other SnO₂@C systems described earlier [37-39] suggests a synergistic coupling of certain kinds of carbon materials, such as carbon nanotubes and graphene layers with very fine SnO₂ particles. It could also be that these carbon surfaces become more active towards Na during the synthesis steps with SnO₂. More work should be devoted to study the actual extent of the reaction of SnO₂ clusters in these other carbon composite electrodes [37-39]. The ionic conduction of Na ions is also a critical aspect to consider during the electrode formulation if SnO₂ is used as an active anode material, and open or conductive framework structures are more likely to promote the electrochemical reaction.

The retained capacity retention and coulombic efficiency of the electrode materials are presented in Figure 7 and Figure S7, respectively. During the cycling with Li, the capacity retention is the highest for SnO₂@C #2, then for SnO₂@C #1 and SnO₂@C #3 with initial reversible capacities around 900 mAh g⁻¹, and about 600, 200 and 100 mAh g⁻¹ retained after 100 cycles, respectively. With Na, the initial reversible capacities are about 300, 200 and 100 mAh g⁻¹ for SnO₂@C #2, SnO₂@C #1 and SnO₂@C #3, respectively. The capacities slowly increase upon cycling, likely due to some activation of the incorporated SnO₂ clusters, similarly to what is happening for the thin film material (Figure 7). After 100 cycles, the retained capacities are about 200, 70 and 50 mAh g⁻¹ for SnO₂@C #2, SnO₂@C #1 and SnO₂@C #3, respectively. Although SnO₂@C #2, an activated OMC with low SnO₂ filling, presents the best reversible capacity value and retention, the very large irreversible initial capacities discard it from practical applications. In fact, its higher C loading compared to SnO₂@C #1 increases the Na and Li storage capacities and capacity retention, and support that C participates significantly during the reaction. The fade in capacity retention is probably related to the partial filling of the pores with SEI products, as has been observed for micron-sized pores [49] as well as for similar pore sizes of mesoporous carbon materials filled with SnO₂ [42]. A solution to reduce the SEI partial filling of the pores is through tuning the electrolyte composition by using additives to promote the formation of a thinner and stable SEI film. It could also be that the volume expansion of the SnO₂ clusters during the reaction block the access of deeper pores and isolate ionically certain parts of the electrode material. A trade-off needs to be found between the sizes of the mesopores and of the nanoparticles to allow for ionic diffusion throughout the channels framework.

4. Conclusions

The electrochemical properties of SnO₂ thin films and SnO₂@C mesoporous carbon electrode materials were studied for the first time during the reaction with Na and Li. The results show that the starting SnO₂ nanomaterials undergo a very extensive reaction with Li, with high reversible storage capacities corresponding to about 6.2 Li/SnO₂ exchanged for thin films and about 5.1 Li/SnO₂ for mesoporous carbons filled with SnO₂. With a stark contrast, the reaction with Na is importantly limited with storage capacities of only 120 mAh g⁻¹ for thin films and between 100 and 300 mAh g⁻¹ for mesoporous carbons filled with SnO₂. For the latter, part of the reversible capacity is related to the carbonaceous material. *Ex situ* XRD results demonstrate that not all SnO₂ has reacted over the course of a 48h reaction in short-circuited cells, hinting for important reaction kinetic limitations (Na-ion diffusion and/or electronic conductivity of the intermediate reaction products). Overall, we estimate that at room temperature less than 4 Na/SnO₂ can be inserted into SnO₂ nanoparticles and less than 1 Na/SnO₂ can be extracted from the electrode material. The role of the carbon framework openness, ionic conduction, surface modification leading to enhanced electrochemical reaction with Na and synergistic coupling with SnO₂ particles should be investigated further.

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Figures captions

Figure 1. X-ray diffraction patterns for a pure SnO_2 thin film deposited onto Cu foil, and for the $\text{SnO}_2@\text{C}$ studied materials. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Figure 2. $\text{Sn}3\text{d}$ and $\text{Sn}4\text{d}$ high resolution XPS spectra for the $\text{SnO}_2@\text{C}$ mesoporous carbons and SnO_2 thin film materials. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Figure 3. (a) Nitrogen adsorption isotherm, (b) pore size distribution, and (c) thermogravimetric decomposition curves recorded in air for the $\text{SnO}_2@\text{C}$ mesoporous carbon materials. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Figure 4. Bright Field TEM images for (a) $\text{SnO}_2@\text{C}$ #1 and (b) $\text{SnO}_2@\text{C}$ #2 (B) samples. SEM images for SnO_2 thin films are shown in (c) and (d) at different magnifications. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Figure 5. Electrochemical potential profiles during the first two cycles for SnO_2 thin films during the reaction with Li and Na. Different film thicknesses were studied with Na. The current densities are indicated on the figures.

Figure 6. Electrochemical potential profiles at C/10 during the first two cycles for $\text{SnO}_2@\text{C}$ mesoporous carbon samples during the reaction with Li and Na. The reaction with Li is shown in the left column whereas the reaction for Na is presented in the right column. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Figure 7. Capacity retention of the $\text{SnO}_2@\text{C}$ mesoporous carbon materials during the reaction with Li and Na. The capacity of SnO_2 thin films with Na is included as reference. Cycling was

performed at about $C/10$, based on the reversible (charge) capacity. See the Experimental section for the $\text{SnO}_2@\text{C}$ samples characteristics.

Table 1. Surface area (S_{BET}), pore volumes (V_{total} , V_{micro} and V_{meso}) and mesopore size distribution (W_{KJS}) obtained from the N_2 gas adsorption experiments. The gravimetric filling of the mesoporous carbons obtained from the TGA measurements (RTGA) are also given. Notation: S_{BET} —BET specific surface area; V_{total} —single-point pore volume; V_{micro} —volume of fine pores (mainly micropores) obtained by integration of PSD up to 3.5 nm; V_{meso} —volume of mesopores obtained by integration of PSD from 4 nm to 20 nm; W_{KJS} — mesopore diameter at the maximum of the PSD curve obtained by the modified KJS method; RTGA- remaining weight (%) obtained from the TGA curve recorded in air in the temperature range 100-800°C.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	W_{KJS} (nm)	RTGA (%)
OMC	787	0.67	0.17	0.37	7.2	-
ac-OMC	1604	1.07	0.36	0.48	7.5	-
$\text{SnO}_2@\text{C}$ #1	580	0.35	0.15	0.12	6.3	76.3
$\text{SnO}_2@\text{C}$ #2	487	0.32	0.11	0.14	7.2	31.1
$\text{SnO}_2@\text{C}$ #3	167	0.14	0.03	0.08	6.7	51.1

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.