

## Ultrasmall SnO<sub>2</sub> directly grown on commercial carbon black: a versatile composite material for Li-based energy storage

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Among metal oxides, tin dioxide (SnO<sub>2</sub>) is a very versatile low-cost raw material for energy storage, for example in lithium-ion batteries, exhibiting a high lithium storage capacity and an excellent cycling performance. Recently, SnO<sub>2</sub> has also been reported as a promoter catalyst for oxygen reduction reaction (ORR) for Li-O<sub>2</sub> batteries. Therefore, this work reports a simple, fully sustainable, and economic synthesis process to obtain SnO<sub>2</sub> nanoparticles (in average 5 nm diameter) finely dispersed on a commercial carbon black and tested both as anode material in Li-ion cells and ORR catalyst at the cathode of Li-O<sub>2</sub> cells.

Herein, we propose a hassle-free approach to prepare SnO<sub>2</sub>/C composite using a simple, fully sustainable, and economic synthesis process, in which tin oxide is *in situ* nucleated on commercial carbon black C-ENERGY™ Super C45 (Imerys Graphite & Carbon) in form of homogeneously 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<sub>2</sub> conversion reaction.

On one hand, in Li-ion technology, development of high-performance SnO<sub>2</sub> anodes is hampered by its peculiar electrochemical behavior, characterized by two processes: conversion and alloying reactions. The conversion reaction being irreversible leads to specific capacities lower than theoretical, however rational design of nanosized SnO<sub>2</sub> can mitigate this issue, though SnO<sub>2</sub> 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. Presence of oxygen species on C45 surface, accessible to tin, prevent fast formation of Li<sub>2</sub>O, allowing to achieve high capacity and extreme electrode stability. The assembled cells with SnO<sub>2</sub>/C45 exhibit for more than 400 cycles the reversible capacity of 560 mA h g<sup>-1</sup> per pure SnO<sub>2</sub> (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].

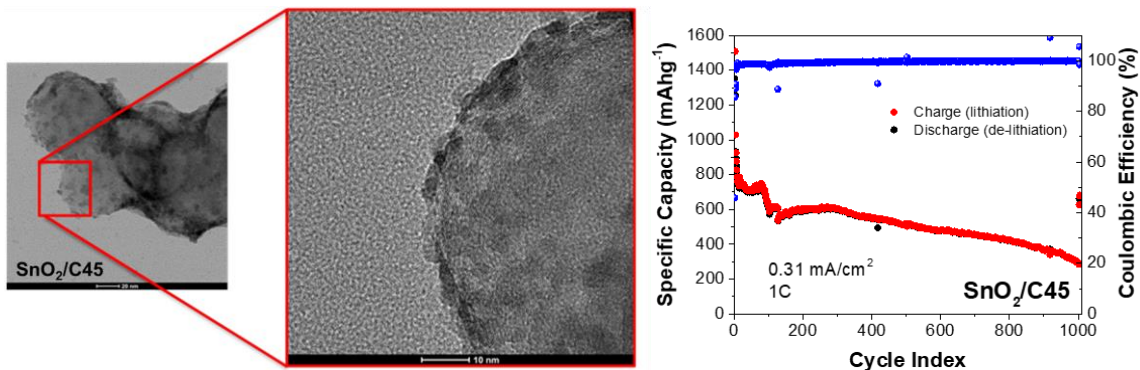


Figure 1. TEM micrograph of SnO<sub>2</sub>/C45 (on the left), galvanostatic charge/discharge capacities of the SnO<sub>2</sub>/C45 electrode at 1C (on the right)

On the other hand, developing efficient and low cost electrocatalysts for ORR is fundamental to bring the Li-O<sub>2</sub> technology closer to practical applications. The obtained composite material shows an optimal ORR activity with a final reduction mechanism following the 4 electrons pathway. This is confirmed in Li-O<sub>2</sub> cells, indeed compared to pure C45 air-cathodes, the composite cathodes lead to the formation of much more reversible film-like discharge products, allowing for reduced overvoltage and therefore improved cycling performances both at the high current density of 0.5 mA cm<sup>-2</sup> with more than 70 cycles and in prolonged discharge/charge conditions with over 1250 h of operation at the fixed capacity of 2.5 mAh cm<sup>-2</sup> [2].

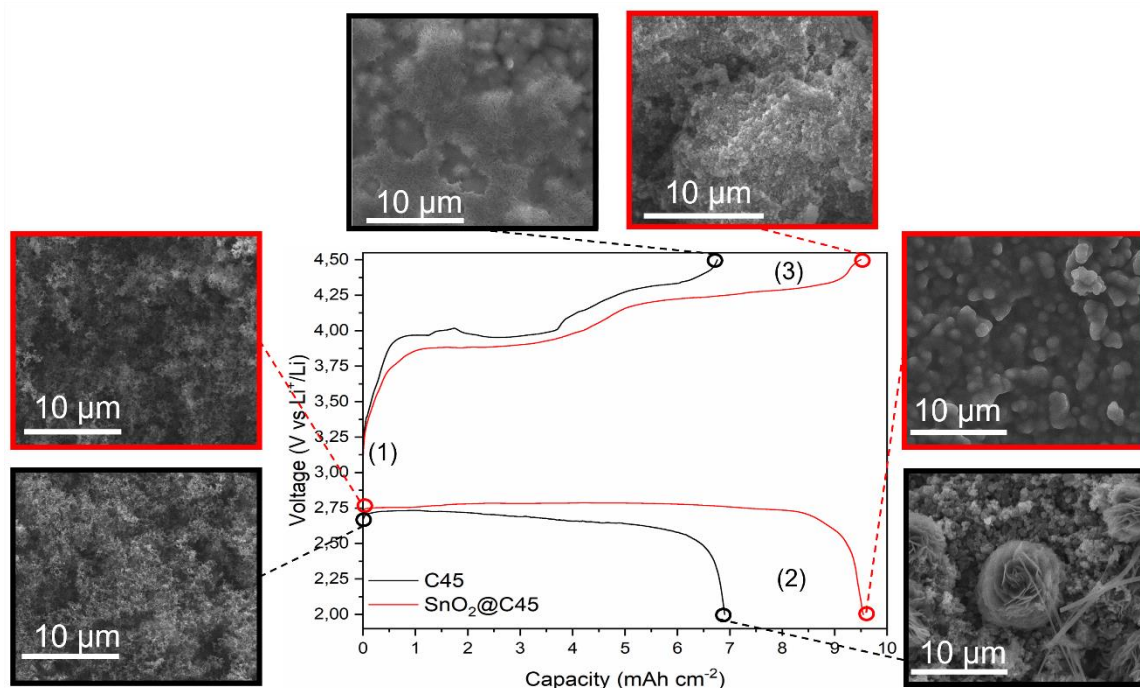


Figure 2. FESEM micrographs of C45 (black border) and SnO<sub>2</sub>@C45 (red border) cathodes surface in different steps: pristine (1), after full discharge at current density of 0.1 mA cm<sup>-2</sup> (2), after full recharge at the same current density (3).

Considering the fast and inexpensive method used to prepare SnO<sub>2</sub>/C45, these results, in terms of reversible capacities and long cycling stability, are competitive among others

obtained for SnO<sub>2</sub>-based materials synthesized by other methods such as hydrothermal, sonochemical, solvothermal, etc. All these considerations make the synthetic route reported a suitable and interesting approach for large scale production.

### References

1. D. Versaci et al., *Electrochim. Acta*, **367**, 137489 (2020).
2. J. Amici et al.. *J. Power. Sources*, in press (2022).