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Highly reversible conversion reactions in lithiated SnO_2 based thin film anode materials

Tin dioxide (SnO_2) has been considered one of the most promising alternative anode materials for lithium batteries. In the past two decades, extensive studies have been directed to gaining a fundamental understanding of the lithiation/delithiation reactions to improve the performance of SnO_2-based electrodes. However, the conversion reaction in lithiated SnO_2 that produces Li_2O has long been believed irreversible and considered the main cause of large capacity loss and low initial Coulombic efficiency of SnO_2 and other oxide electrodes. Accordingly, a key question highlighted in Chiang's Perspectives (Building a better Battery, Science, 2010, 330, 1485) is how to overcome the irreversibility of Li_2O in SnO_2 anode to fully exploiting the limit of the capacity of the electrode materials.

Here we demonstrated that Li_2O can indeed be highly reversible in a SnO_2 thin film electrode with controlled nanostructure and achieved an initial Coulombic efficiency of ~95.5%, much higher than that previously believed possible (52.4%). Insitu spectroscopic and diffraction analyses corroborate the highly reversible electrochemical cycling, suggesting that the interfaces and grain boundaries of nano-sized SnO_2 may suppress the coarsening of Sn and enable the conversion between Li_2O and Sn to amorphous SnO_2 when de-lithiated. Furthermore, we have found that the application of super-elastic films of NiTi alloy could accommodate the internal stress and volume change of lithiated nano-SnO2 layer and thus effectively suppress Sn coarsening, to retain the high reversibility of the SnO_2 layer with reversible capacity more than 800mAh/g (based on SnO_2) for over 300 cycles, demonstrating stable charge capacities of ~400mAh/g in the potential ranges of 0.01-1.0V and 1.0-2.0V(vs. Li/Li+), respectively.

Furthermore, we designed a double-layer electrode of a SnO_2 film coated with an ALD Al_2O_3 Layer. The Al_2O_3 coating (~2 nm in thick) on the surface helps to maintain the structural stability of SnO_2 layer (~20 nm), while the inside filling Al_2O_3 increases the boundary integrity of SnO_2 naocrystals, and acts as barriers to prevent the lithiation induced Sn coarsening during cycling. In particular, the Al_2O_3 layer stabilizing the solid electrolyte interphase formed on the surface of electrode, enabling enhanced roundtrip efficiency. Thus this SnO_2/Al_2O_3 electrode contributes superior electrochemical performance with a high ICE (88.1%), better reversible capacity retention (88.9% after 200 cycles) than that of the pure SnO2 anode (30.6%), demonstrating that surface modification on nanograins of conversion type anode materials could be helpful for enhancing the reversibility and cyclability of the electrode, enabling high stable reversible capacity.

References

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Figures

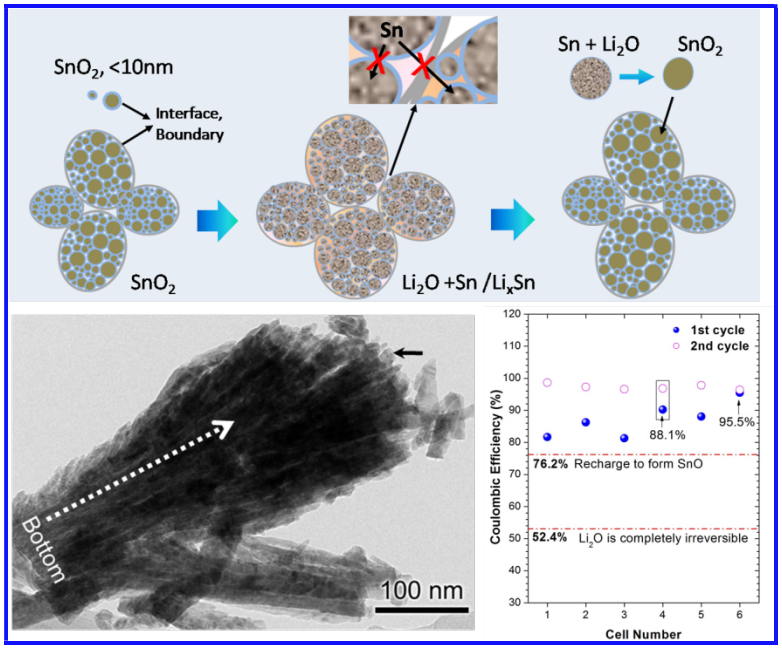

Figure 1: The high density interfaces and grain boundaries of nano-sized SnO2 suppress the coarsening of Sn and enable the conversion between Li2O and Sn to amorphous SnO2 when de-lithiated, resulting in a high initial Coulombic efficiency of ~95.5% in pure SnO2 film anodes.

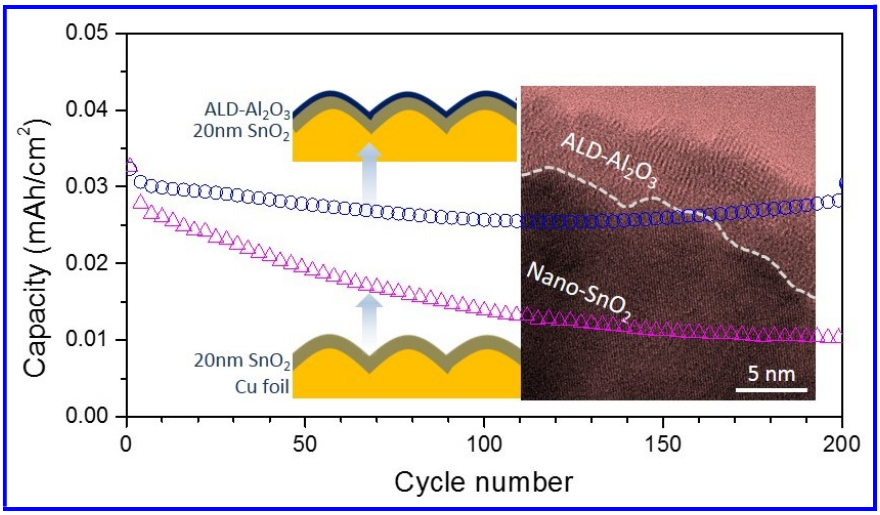

Figure 2: SnO_2/Al_2O_3 film electrode contributes superior electrochemical performance with a high ICE (88.1%), better reversible capacity retention (88.9% after 200 cycles) than that of the pure SnO_2 film anode (30.6%).