ALD of ZnO-SnO_2 composite thin-film for lithium ion battery applications

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To increase energy density in lithium-ion batteries (LIBs), novel anode materials are considered based on conversion- and alloying mechanisms, as these typically possess far higher storage capacity than graphite (theoretical capacity of 372 mAh g^{-1}). Unfortunately, the cyclability of these compounds is typically poor due to the large volume change during the charge and discharge processes.[1, 2] To overcome these issues, ternary or ‘mixed’ compounds are considered.[3, 4] However, the degree of mixing of these compounds is often overlooked. Atomic layer deposition (ALD) is a method for thin film deposition that can precisely control the film thickness, composition and degree of intermixing at the atomic level.[5]

Here, we use the ALD method for generating precisely controlled layers of ZnO-SnO_2 as model systems for anode materials. Firstly, we control two different nanostructures of thin-film ZnO–SnO_2 electrodes: an atomically intermixed structure for which the Zn, Sn and O are intermixed at the atomic scale in a single amorphous layer, versus a nanolaminated structure where the ZnO layer and SnO_2 layers form a multilayered structure.[6] Secondly, we control two different compositions in a ZnO-SnO_2 composite film by tuning the ratio of ZnO and SnO_2. In addition, we annealed the intermixed ZnO–SnO_2 composite film, crystallizing it into spinel Zn_2SnO_4.

The electrochemical performance of these different variations of ternary ZnO-SnO_2 composites was investigated as anode materials in LIBs. The results demonstrated that the exact composition and crystalline nature exert a relatively modest influence on the electrochemical performance, while the degree of intermixing proved more critical for the electrochemical performance of these anodes. Atomically intermixed films (either amorphous or crystalline) show good reversibility, while nanolaminated films performed more poorly, indicating the importance intermixing at atomic length-scales for these composite materials. The results demonstrate the potential of ALD as a research tool in LIBs applications, and the major impact of atomic scale intermixing in these ternary oxides as anodes.

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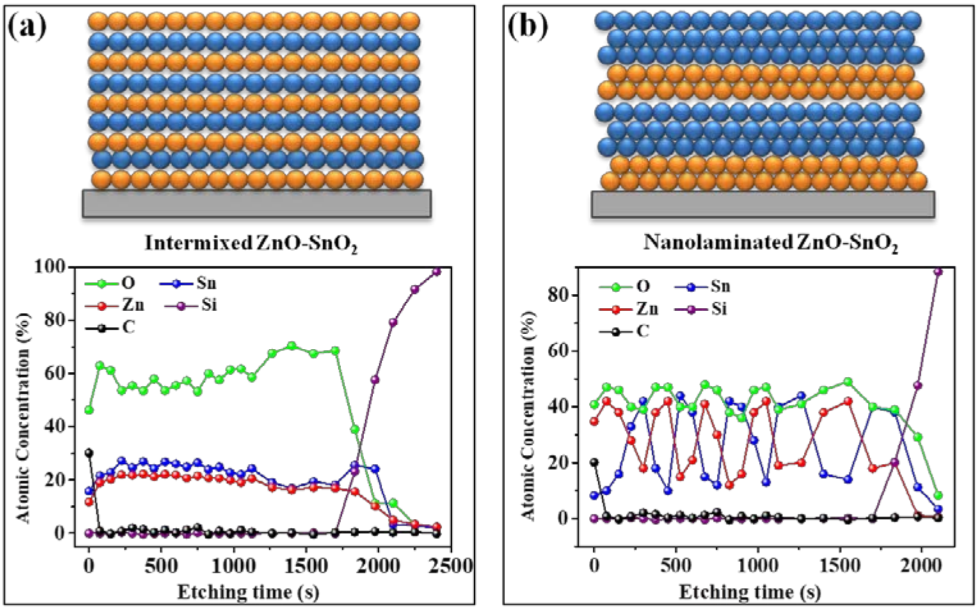

Figure 1. Schematic illustration and the atomic concentration of Sn, Zn, O, C and Si element from XPS depth profile for the (a) intermixed and (b) nanolaminated ZnO-SnO_2 composite film.

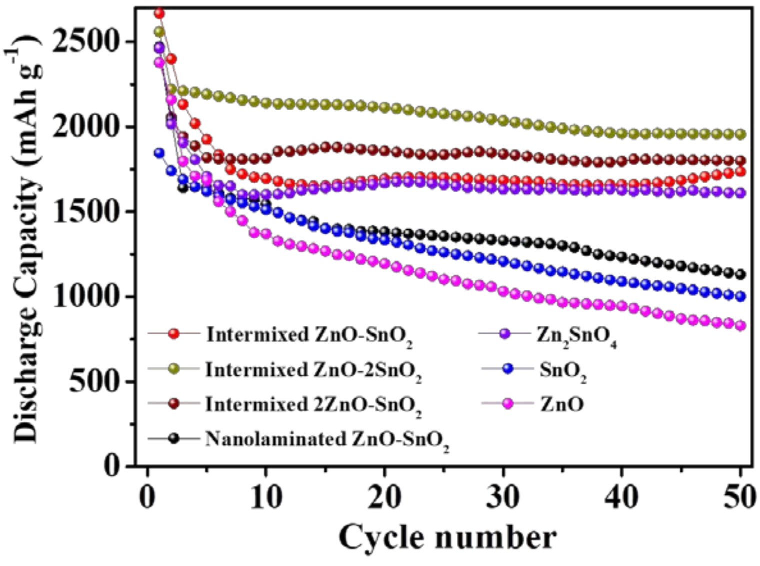

Figure 2. The discharge capacity of pure ZnO, pure SnO_2, spinel Zn_2SnO_4, nanolaminated ZnO-SnO_2, intermixed ZnO/SnO_2 with ratio 1/2, 1/1 and 2/1.