Supporting Information

Ultrahigh Performance Cu_2ZnSnS_4 Thin Film and Its Application in Microscale Thin Film Lithium-Ion Battery: Comparison with SnO_2

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1. Surface and cross section morphologies of thin SnO_2, thick CZTS and $LiCoO_2$ films.

The substrate is uniformly covered by the dense SnO_2 film without any aggregations or pores (**Figure S1a**). Some large aggregations of CZTS particles can be observed in the thick CZTS film (**Figure S1b**), leading to the severe stress accumulation related to the drastic capacity decay. Some little cracks of the layer-structured $LiCoO_2$ film can be seen in the surface image (**Figure S1c**), but the film is fabricated without any heat treatments in case of generating more defects. As measured in the pictures, the thicknesses of thin SnO_2, thick CZTS and $LiCoO_2$ films on Si substrates are ~300, 1000 and 230 nm, respectively.

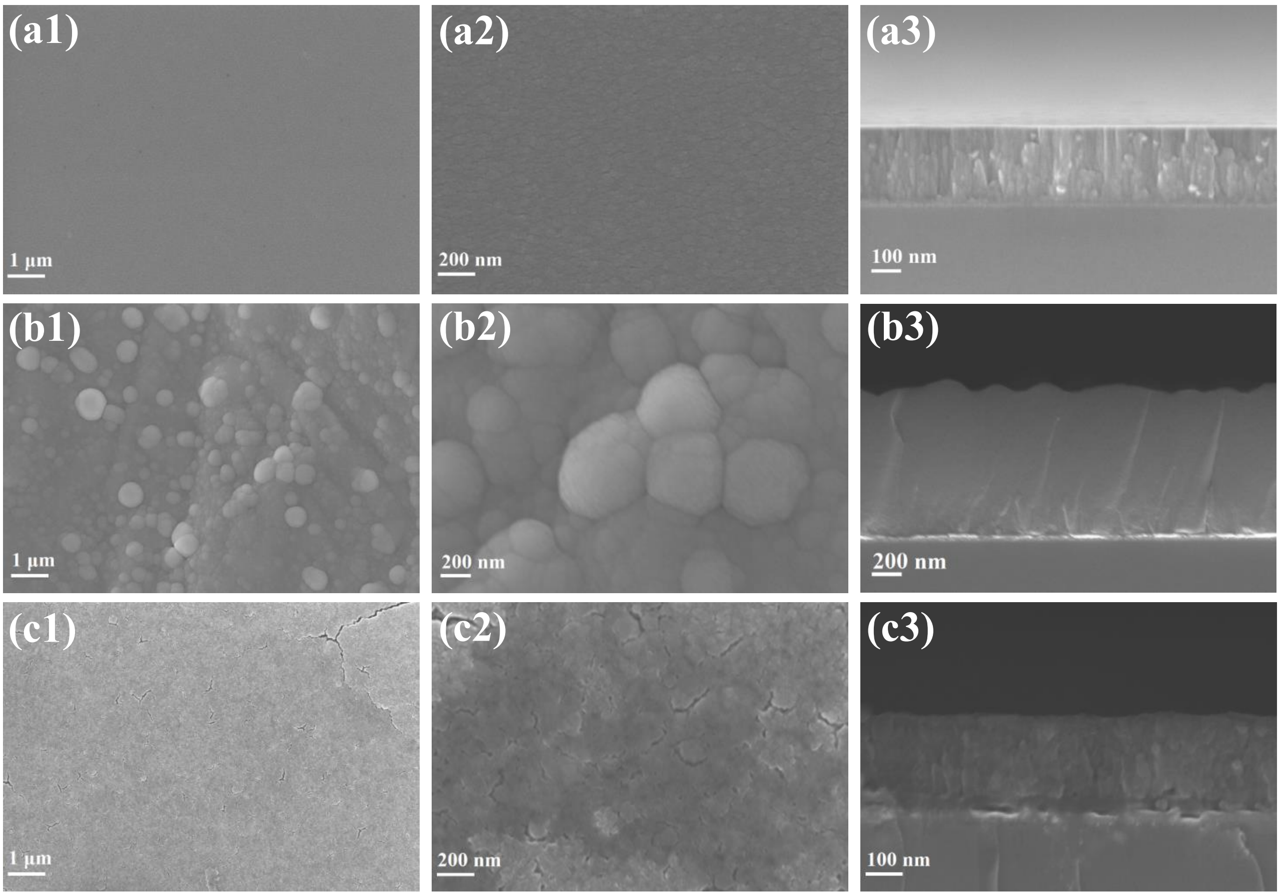

Figure S1. Surface and cross section SEM images of (a1-a3) thin SnO_2, (b1-b3) thick CZTS and (c1-c3) $LiCoO_2$ films.

2. Comparison of cyclability between thin (300 nm) and thick (1 μm) SnO_2 films.

The capacity decaying is more serious in the thick film than in the thin film, but due to the low capacity, the coulombic efficiency (CE) of the thick film is very stable after 50 cycles.

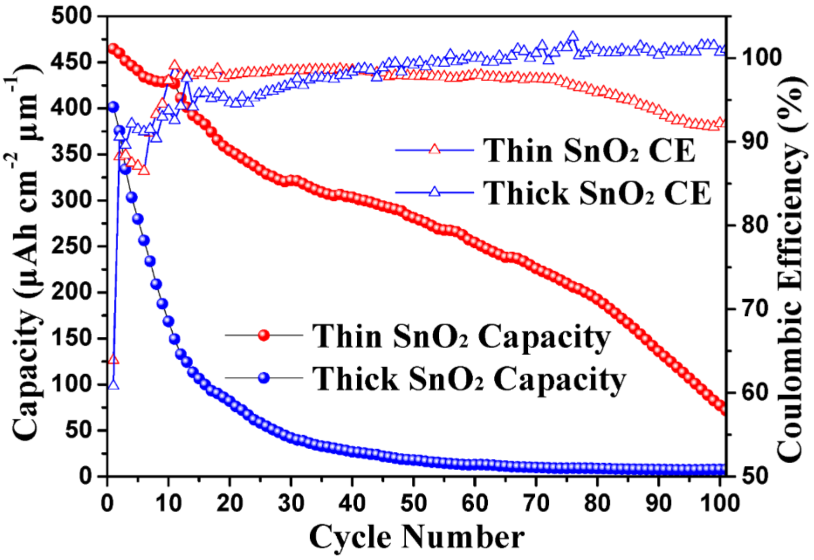

Figure S2. Cycle performance of thin and thick SnO_2 films in half-cells based on charge capacity.

3. Differential charge plots of CZTS thin film before, in and after capacity increasing steps.

The peaks at ~2.5 V corresponding to the reversible "conversion reaction" apparently increase after 150 cycles, and the related reactions contribute to the gradually increasing capacity values.

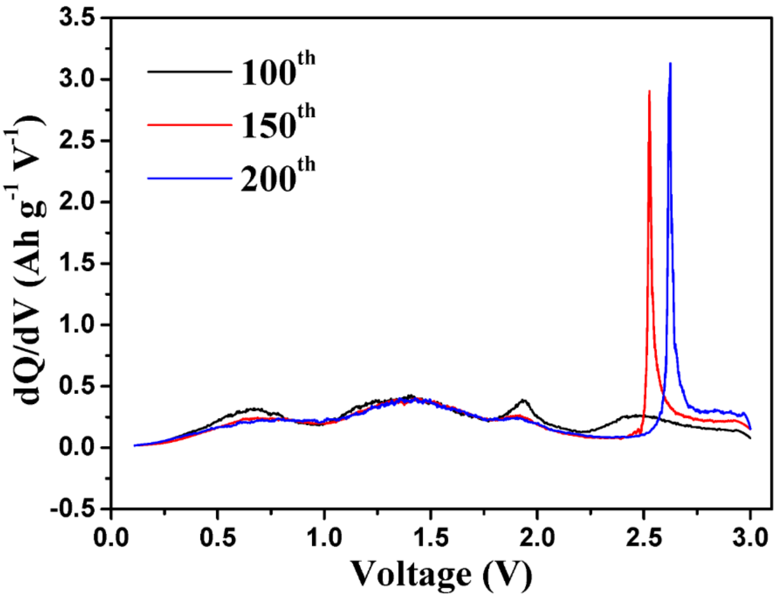

Figure S3. Differential charge plots of CZTS thin film (300 nm) in 100th, 150th and 200th cycles.

4. Comparison of rate performance with other reports.

Basically, the capacity values presented in **Figure S4b** are the last charge capacity obtained in each current density. Apparently, the CZTS thin film in this work exhibits the best rate performance. The references listed in **Figure S4b** are corresponding to the ones in main text.

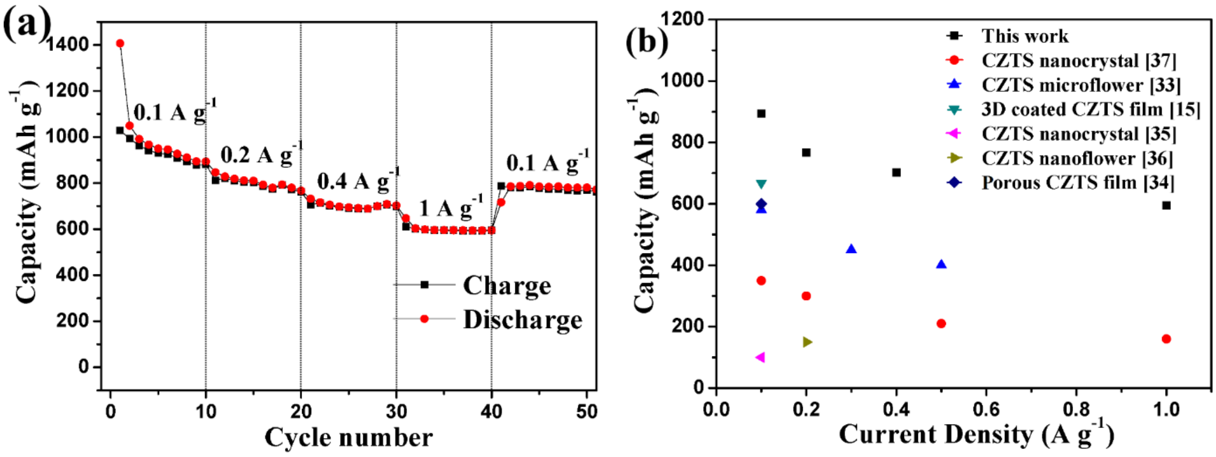

Figure S4. (a) Rate capability of CZTS thin film (300 nm) and (b) comparison with other reports.

5. Bode plots of EIS tests.

Since two peaks can be seen in **Figure S5b** indicating the two interface resistances of the SEI film and charge transfer resistances, the rational equivalent circuit model can be determined.

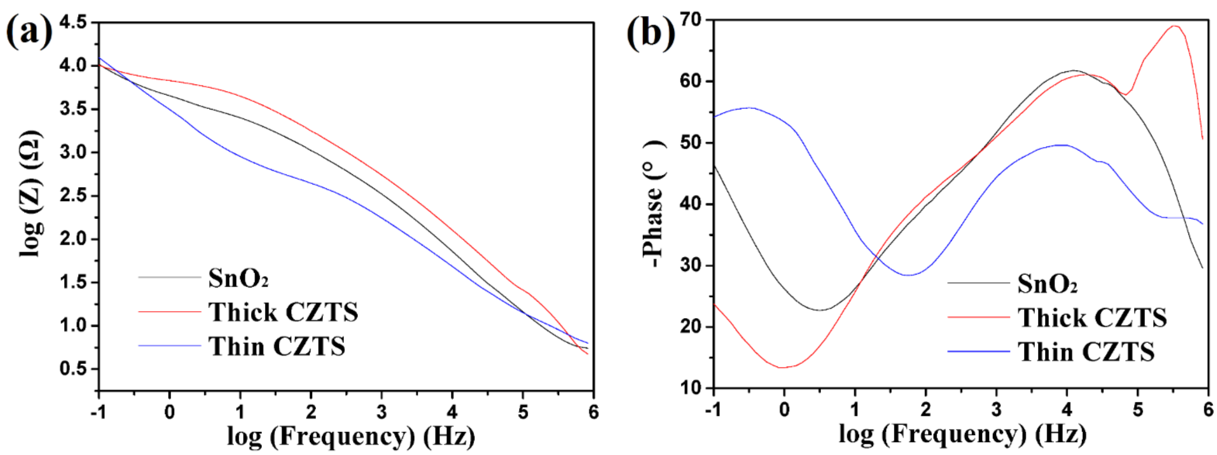

Figure S5. Bode plots of (a) Z-Frequency and (b) Phase-Frequency curves.