

## **Tin Oxide Nanoporous Structure for Lithium-ion Battery Anode Applications**

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### **Extended Abstract**

Tin oxide is promising as a potential substitute for graphite as an anode in lithium ion batteries (LIB) due to its high theoretical capacity (782 mAh/g), low cost, abundance, and environmentally friendly properties. Thus, its theoretical capacity is much higher than that of graphite (~372 mAh/g). However, metal oxide anodes typically have poor cycling performance due to large volume change upon lithium insertion and extraction. Among various morphologies, porous structures are usually preferred due to their high capacity and good ion exchange features.

Nanoporous structures can be prepared by a variety of methods. Common method for preparing titania nanotube arrays is anodization. This method can be used for other metal oxide materials, although it typically results in less ordered structures. In the case of tin, anodization will result in a non-periodic porous structure (Zaraska et al., 2013). We have deposited a tin film on top of copper foil, so that after anodization of tin the samples could directly be used as anodes in LIB (standard CR2032 coin cell with pure Li as counter electrode, with electrolyte consisting of 1 M LiPF<sub>6</sub> in an equal volume mixture of ethylene and diethyl carbonates). This preparation method has an advantage compared to the conventional anode preparation that it is free of additives and binders, and likely to retain good conductivity due to being directly grown on copper foil.

We investigated the influence of anodization conditions (bias voltage, anodization time and oxalic acid concentration) on the morphology of tin oxide layer obtained. Several nanostructured morphologies were prepared with different electrolyte concentration of oxalic acid (from 0.05 M to 0.3 M), bias voltages (from 4 V to 7 V), and reaction time (from 3 to 20 minutes). The optimized anodization condition resulted in a nanoporous tin oxide layer suitable for LIB anode application. After drying in vacuum oven for 24 hours at 120°C, the anode prepared can be used to assemble LIB. LIBs are assembled in glove box in argon atmosphere. Batteries were tested using a LAND Tester with discharging/charging rate at 32.5  $\mu\text{Ah}/\text{cm}^2$  (Gregorio et al., 2014).

Figure 1 shows the SEM images of the tin layer on copper foil formed at room temperature by electrodeposition. The electrolyte was 7 g/L SnCl<sub>2</sub> and 25 g/L sodium citrate. Figure 1a shows the tin film after 25 minutes of electrodeposition, while Figure 1b shows the tin film after 15 minutes of electrodeposition. It can be observed that with large deposition time, the grain size of the film increases. Thus, 15 minutes deposition, which results in a flat tin film, was selected to prepare samples for anodization.

Anodization result is shown in figure 2a. Porous structures can be clearly seen in the images. The sample was prepared by 5 minutes anodization at a bias of 7 V. The battery performance with prepared nanoporous SnO<sub>2</sub> is shown in figure 2b. The cutoff voltage window ranges from 0.01 to 2.7 V. The initial capacity (first cycle) was 214  $\mu\text{Ah}/\text{cm}^2$ . Typical initial drop in capacity common for metal oxide is observed after the first cycle, so that the obtained capacity for the second cycle was 135  $\mu\text{Ah}/\text{cm}^2$ . After

55 cycles the capacity was still remains at about  $120 \mu\text{Ah}/\text{cm}^2$ , demonstrating excellent cycling performance of nanoporous tin oxide. The stable capacity can be attributed to its porous structure feature which not only enhances the diffusion of liquid electrolyte, but also gives more space for the volume change in charging and discharging reactions. The coulombic efficiency is 76.36 % in the first cycle and increases to 94.20 % in the second cycle. And the efficiency remains higher than 97 % from the third to fifty-fifth cycle.

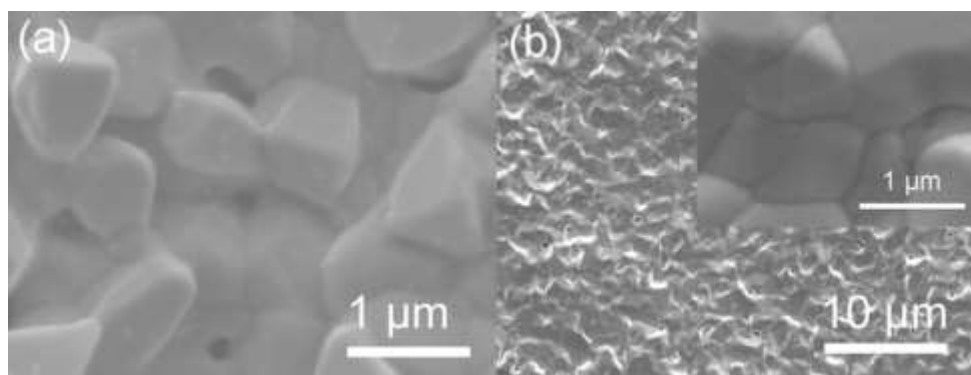


Fig. 1. Tin layer on copper foil formed by electrodeposition with constant current  $1.2 \text{ mA}/\text{cm}^2$  (a) for 25 minutes (b) for 15 minutes.

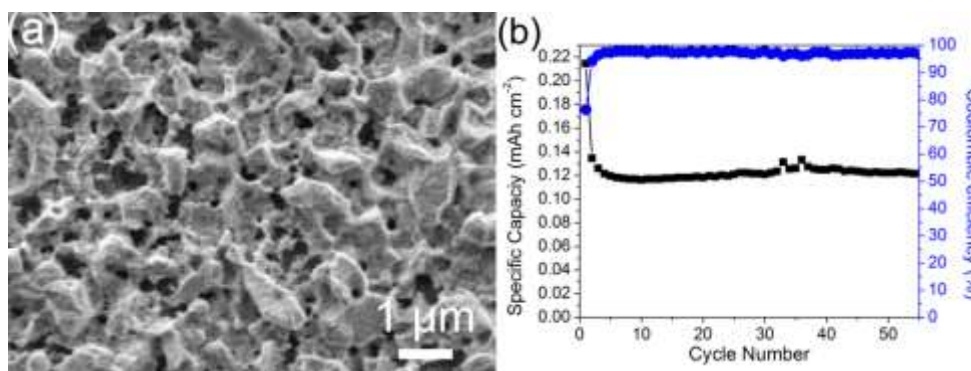


Fig. 2. (a) Porous structure of  $\text{SnO}_2$  after anodization, the condition was 7 V for 5 minutes and the electrolyte was 0.05 M Oxalic Acid. (b) Cyclic performance of the prepared nanoporous  $\text{SnO}_2$  anode material.

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