

Enhanced electrochemical properties of SnO₂ anode by AlPO₄ coating

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Abstract

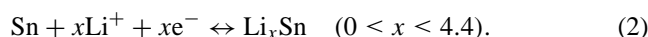
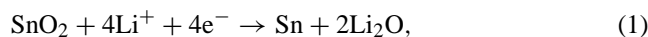
A SnO₂ anode material undergoes severe capacity loss, which is mainly associated with cracking/crumbling of the material by the large volume change between the Li_xSn and Sn phases, and the intensive reactions with the electrolyte solution. However, AlPO₄ nanoparticle coating showed drastically improved electrochemical properties with decreased surface cracks. The AlPO₄-coated SnO₂ exhibited a capacity of 781 mAh/g, approaching its theoretical capacity at the first cycle, with 44% capacity retention after 15 cycles between 2.5 and 0 V at a relatively high C rate of 105 mA/g. In contrast, the bare SnO₂ showed an initial capacity of 680 mAh/g, with only 8% capacity retention after 15 cycles. © 2004 Elsevier Ltd. All rights reserved.

Keywords: SnO₂ anode; Aluminum phosphate; Nanoparticle; Coating

1. Introduction

Since amorphous tin-based composite oxides were first reported, exhibiting a capacity approximately twice that of carbon (372 mAh/g), researches on anodes have been focused on the tin-based materials for high-capacity Li-ion batteries [1]. Similarly, oxide compounds consisting of 3d transition-metal oxides (CoO, FeO and CuO) have also been actively studied due to their high initial capacity over 800 mAh/g [2–4]. However, these two kinds of materials have different Li reaction mechanisms, depending on the nature of the metal.

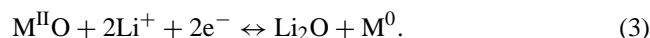
The reaction mechanisms of SnO₂ with lithium have been reported as [5]:



On the first discharge, the lithium bonds to the oxygen in SnO₂, forming the tin metal and Li₂O. Then, the Sn

alloys/dealloys up to the theoretical limit of Li_{4.4}Sn (capacity of 783 mAh/g) [5,6]. However, SnO₂ has some critical problems: (i) the irreversible capacity is very large (~700 mAh/g), and the capacity fading is very severe, (ii) its cyclability depends strongly on the grain size, cutoff voltage, and charge rate [6]. For example, the capacity retention on cycling was significantly affected by the cutoff voltage: a higher cutoff voltage caused deterioration in capacity retention due to the larger volume change and destruction of the Li₂O matrix holding the Sn particles [6,7]. Consequently, fracturing and a loss of contact among the grains lead to the destruction of the electrode conduction, which increases the internal resistance of the cell. The large irreversible capacity of the SnO₂ electrode is associated with both the bulk formation of Li₂O, and intense surface reactions with the Li–Sn compounds and the electrolyte solution [5–15].

On the other hand, non-alloy metal oxides, such as 3d transition-metal oxides (CoO, FeO and CuO), can be reversibly reduced and oxidized, coupled with the formation and destruction of lithium oxide, respectively [2–4]:



At the first discharge, the reduction reaction is similar to that of SnO₂, but it is reversible. These materials were observed to react reversibly with a large amount of Li, leading to sustained capacities as high as ~700 mAh/g of CoO upon

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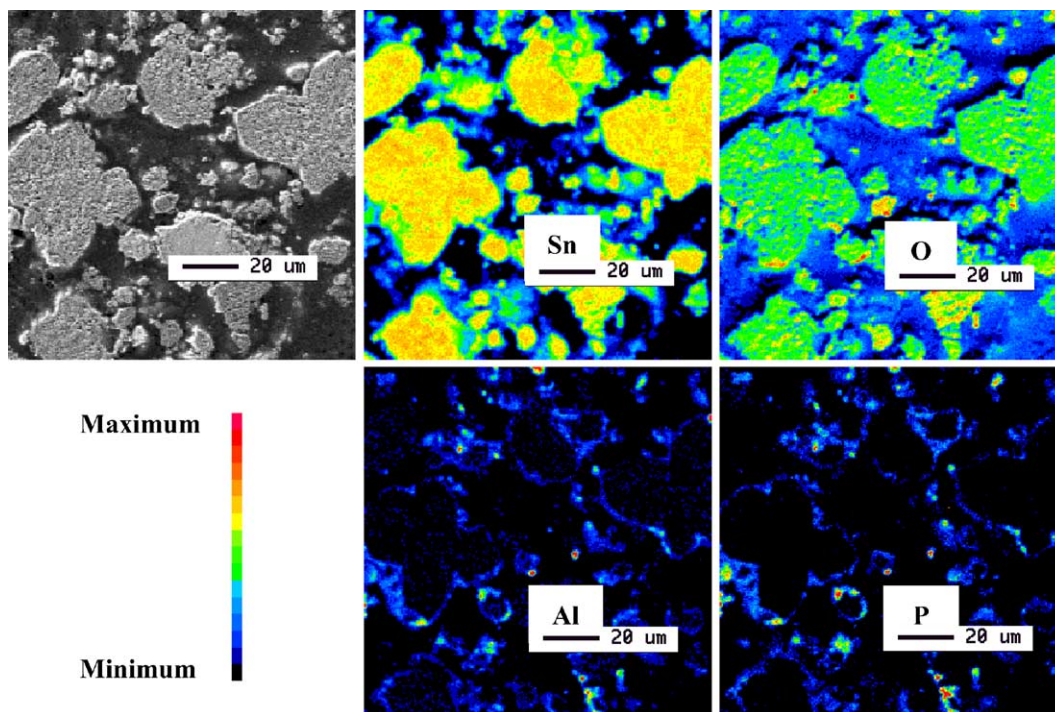


Fig. 1. EPMA mapping of AlPO_4 -coated SnO_2 , with Sn, O, Al, and P distributions across the cross-sectioned powders.

cycling between 3 and 0.02 V, and capacity fading is also less than that of SnO_2 . However, a major limiting factor of CoO is the increased cell voltage on the subsequent cycling (showing over 1.5 V), which is approximately 0.5 V higher than SnO_2 . Even though the irreversible capacity of CoO (over 320 mAh/g) is smaller than SnO_2 , it still needs to be improved [3].

Recently, Cho et al. reported that a metal-oxide coating (Al_2O_3 , ZrO_2 , TiO_2 , etc.) on the cathode materials can improve the cycle life and rate capability of the cathodes, and the coating layer can reduce the degradation in Li diffusivity [16–19]. In addition, a nanoparticle AlPO_4 coating exhibited a much better thermal stability at higher voltages than the metal-oxide coating [20,21].

Here, the AlPO_4 nanoparticle coating on SnO_2 was explored for the first time to reduce the irreversible capacity and improve the cycle life of SnO_2 with a potential window of 2.5–0 V at a relatively high C rate.

2. Experimental

SnO_2 was prepared from the direct oxidation of SnO in a strong acid solution with $\text{pH} \approx 2$ for 30 min, which was followed by firing at 500 °C for 2 h. The X-ray diffraction (XRD) pattern of the powder confirmed the sole presence of tetragonal SnO_2 phase. AlPO_4 -coated SnO_2 was prepared by the following process: Al-nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (6.0 g) and $(\text{NH}_4)_2\text{HPO}_4$ (2.2 g) were dissolved in a distilled water (30 g) until a light white-suspension solution (AlPO_4 nanoparticle solution) was observed. (The pH of the coat-

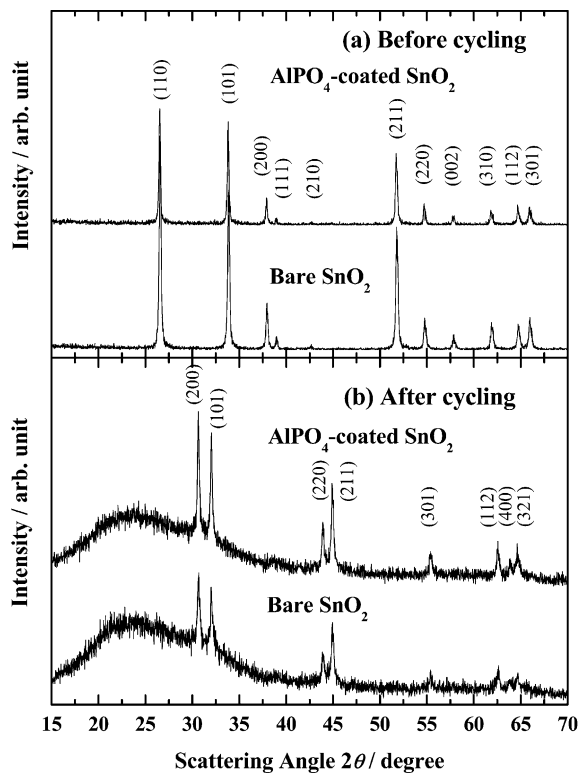


Fig. 2. XRD patterns of the bare and AlPO_4 -coated SnO_2 : (a) before cycling and (b) after cycling. The (hkl) diffraction indices are from tetragonal SnO_2 phase in (a), and from tetragonal Sn phase in (b).

ing solution was ~ 2 .) One hundred grams of SnO powder (with an average particle size of $\sim 10 \mu\text{m}$) were then slowly added to the coating solution and mixed for 10 min, which was followed by drying in an oven for 6 h at 100°C . Subsequently, the dried powders were annealed at 700°C under an air-stream for 5 h in a furnace. The weight percentage by the AlPO_4 coating is $\sim 1.7 \text{ wt.}\%$ of the SnO_2 used.

The electrode composition was SnO_2 : binder: carbon black in a weight ratio of 8:1:1. The electrolyte used was 1 M LiPF_6 with ethylene carbonate/diethylene carbonate/ethyl-methyl carbonate (EC/DEC/EMC), and the anode was lithium metal. The cycle life of the cells was tested at a rate of 0.045C ($=35 \text{ mA/g}$) or 0.134C ($=105 \text{ mA/g}$) between a fixed voltage window of 2.5–0 V or 1.2–0 V. More binder and carbon conductor are required to overcome the disadvantage of our relatively large $\sim 10 \mu\text{m}$ SnO_2 powders. Supplementary cycling experiments were performed for the better cyclability and rate capability ($375 \text{ mA/g} = 0.48\text{C}$), in a weight ratio of 4:3:3 in SnO_2 : binder: carbon black. For the *ex situ* XRD measurements of cycled electrodes, the cells charged to 2.5 or 1.2 V after cycling were disassembled in a glove box (H_2O level $< 50 \text{ ppm}$) and the SnO_2 powders were rinsed thoroughly with a DMC solution to remove the LiPF_6 salts.

3. Results and discussion

Fig. 1 shows electron-probe micro analysis (EPMA) mapping of the AlPO_4 -coated SnO_2 powders. To examine the distribution of Al and P elements near the particle surface, an EPMA was carried from a cross section of the AlPO_4 -coated SnO_2 powders. The result indicates that large amount of Al and P elements are observed in the vicinity of the surface, clearly confirming the AlPO_4 coating on the particle surface. The calculated coating thickness is $\sim 100 \text{ nm}$ (with $\sim 10 \mu\text{m}$ powder), while the measured thickness is $\sim 1 \mu\text{m}$ (in Fig. 1), with the convolution of EPMA beam size of $\sim 1 \mu\text{m}$.

Fig. 2(a) shows the XRD patterns (with $\text{Cu K}\alpha$) of the SnO_2 samples before cycling. The bare and AlPO_4 -coated SnO_2 phases are tetragonal (with a space group of $P4_2/mnm$), while the phase of nanoscale AlPO_4 coating layer does not show clear diffraction peaks. The AlPO_4 coating did not cause a particular change in the lattice constants, a and c , of SnO_2 . The bare and AlPO_4 -coated SnO_2 , respectively, exhibit $a = (4.739 \pm 0.002) \text{ \AA}$ and $c = (3.182 \pm 0.004) \text{ \AA}$ and $a = (4.747 \pm 0.003) \text{ \AA}$ and $c = (3.183 \pm 0.007) \text{ \AA}$.

The scanning electron microscopy (SEM) images of the bare and AlPO_4 -coated SnO_2 are shown in Fig. 3(a). The bare particle consists of aggregated nano-sized grains, but

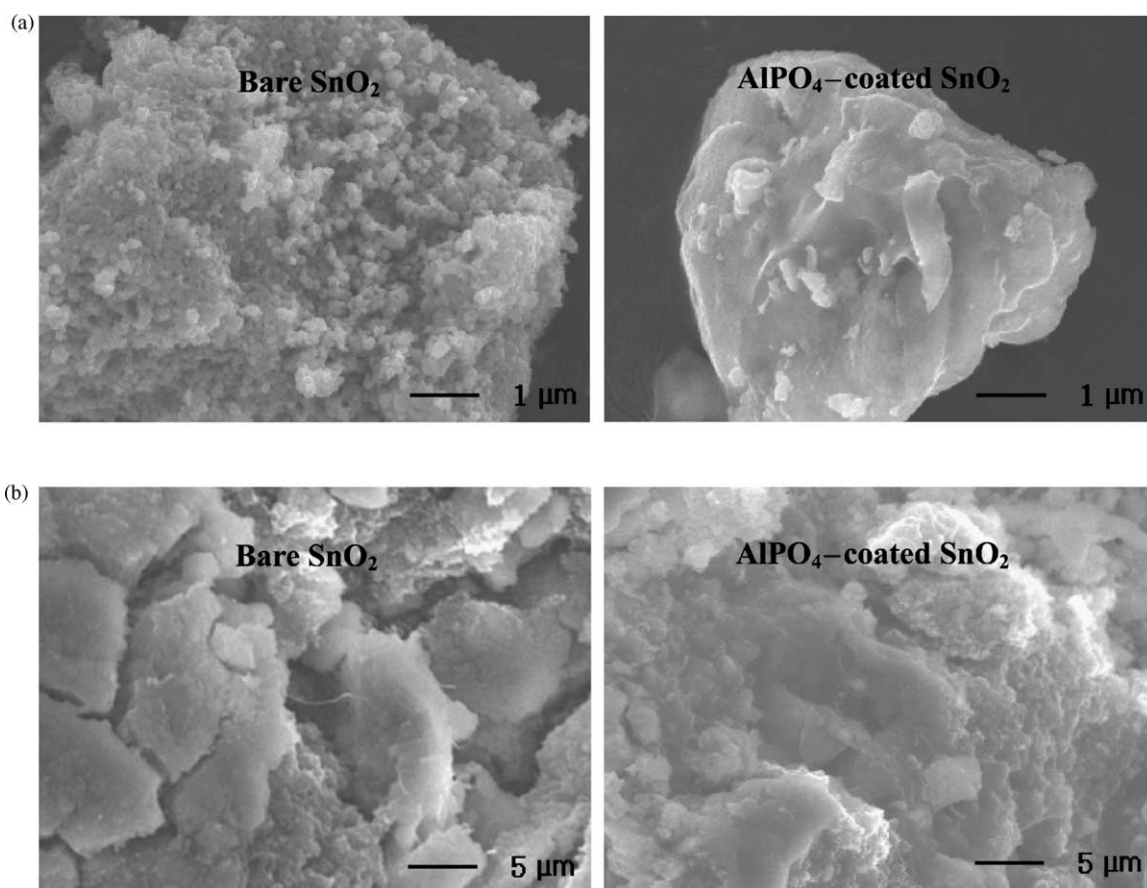


Fig. 3. SEM micrographs of the bare and AlPO_4 -coated SnO_2 particles: (a) before cycling and (b) after cycling.

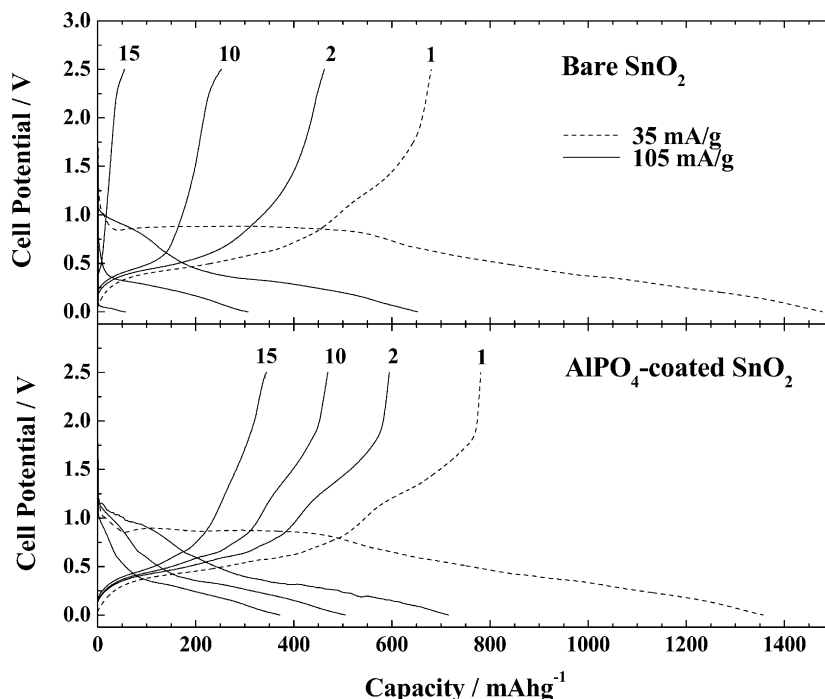


Fig. 4. Voltage profiles of the bare and AlPO_4 -coated SnO_2 between 2.5 and 0 V. The cells were cycled at 35 mA/g ($=0.045C$) for the first discharge/charge, followed by 105 mA/g ($=0.134C$) afterwards.

the AlPO_4 coating led to a smooth surface morphology before cycling. Fig. 4 shows the voltage profiles of the bare and AlPO_4 -coated electrodes at 35 mA/g (for the first cycle) and 105 mA/g (for subsequent cycles) between 2.5 and 0 V in the half-cells (Li/SnO_2). The AlPO_4 -coated SnO_2 exhibited a capacity of 781 mAh/g, approaching its theoretical capacity at the first cycle, with 44% capacity retention (344 mAh/g) after 15 cycles. In contrast, the bare SnO_2 showed an initial capacity of 680 mAh/g, with only 8% capacity retention (54 mAh/g) after 15 cycles. The AlPO_4 layer is an electronic insulator, so oxidation/reduction reactions with Li ion and electron occur mainly at the interface of Sn alloy and AlPO_4 coating layer, not at the interface of AlPO_4 layer and electrolyte. The AlPO_4 coating layer plays as a solid electrolyte, and the initial uniformly-coated layer can prevent additional formation of non-conducting passivation layer. Therefore, the AlPO_4 -coated powders with decreased solid-electrolyte interface (SEI) formation showed smaller discharge capacity than the uncoated samples at the first Li-intercalation cycle, and the former exhibited larger charge capacity than the bare one at the first Li-deintercalation cycle. The reduced SEI formation may lead to higher coulombic efficiency in the coated sample.

The AlPO_4 -coated SnO_2 electrode cycled between 2.5 and 0 V with 105 mA/g C rate exhibited better capacity retention than the previously-reported results of Dahn's group with a nano-sized (~ 5 nm) SnO_2 electrode cycled between 1.3 and 0.2 V with 37 mA/g C rate [5]. It should be noted that the nature of the lithium-insertion reaction and the stability of Li–Sn alloy phases formed depend strongly on the

particle size, potential window, and charge rate. Scrosati's group used SnO_2 powders in gel-type polymer electrolyte cells. The capacity retention was good because of the plastic nature of electrolyte medium, accommodating the volume changes of the contacting electrodes. However, the initial charge capacity was low (~ 450 mAh/g) regardless of the low C rate and small particle size (~ 1 μm) [7]. Aurbach's group reported that nanoparticle SnO_2 anode material showed relatively high charge capacity. However, these results were from the small particle size (~ 5 nm) and low charge current (~ 14 mA/g) [8].

The initial charge capacity (781 mAh/g) of the AlPO_4 -coated SnO_2 increased by ~ 100 mAh/g compared to the bare electrode (680 mAh/g). Also, the irreversible capacity of AlPO_4 -coated one is relatively small compared to the bare SnO_2 . Aurbach et al. reported that the irreversible capacity in SnO_2 is closely related to the intensive side reactions between the $\text{Sn}/\text{Li}_2\text{O}$ and electrolyte species (especially LiPF_6), generating a non-conducting passivation layer [12]. Hence, it causes a rapid increase of the impedance at the interface.

The voltage profiles of the bare and AlPO_4 -coated electrodes at the rate of 105 mA/g between 1.2 and 0 V are shown in Fig. 5. The AlPO_4 -coated electrode exhibited a capacity of 561 mAh/g at the first cycle, with 67% capacity retention (376 mAh/g) after 30 cycles. On the other hand, the bare electrode showed an initial capacity of 462 mAh/g, with 13% capacity retention (58 mAh/g) after 30 cycles. As expected, the limited potential window led to an improved capacity retention on cycling, compared to the voltage win-

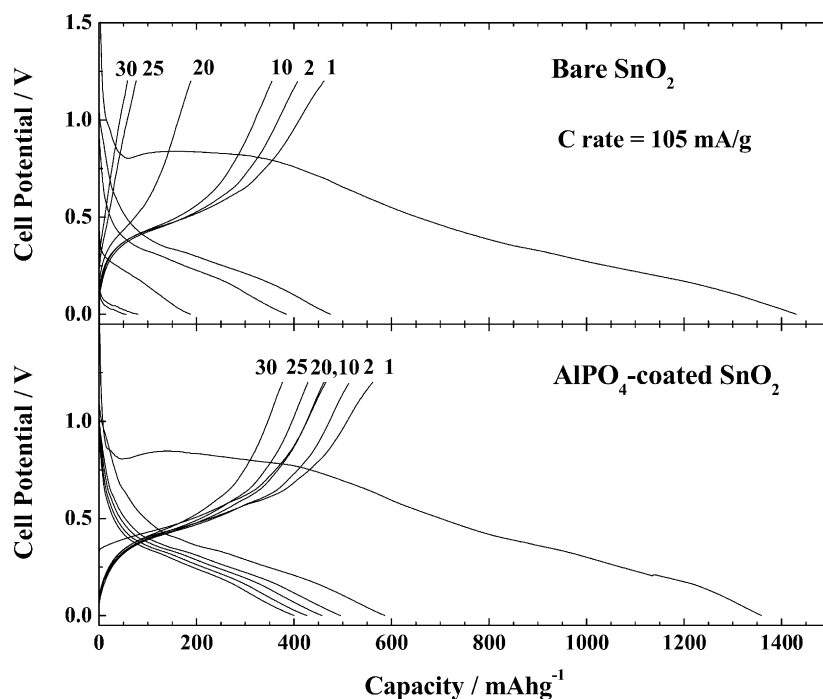


Fig. 5. Voltage profiles of the bare and AlPO_4 -coated SnO_2 at a rate of 105 mA/g (between 1.2 and 0 V).

dow of 2.5–0 V. However, the initial irreversibility of both the bare and AlPO_4 -coated electrodes increased compared to the 2.5–0 V window case (Fig. 4), because of the higher C rate (105 mA/g) at the first cycle. Considering that the capacity retention of SnO_2 anode strongly depends on the C rate, the results of Figs. 4 and 5 obtained from $\sim 10 \mu\text{m}$ -sized

particles with AlPO_4 coating are clearly improved compared to the previous works from nano-sized particles [5,7,8].

Fig. 2(b) shows the XRD data of the bare and AlPO_4 -coated samples after 15 cycles between 2.5 and 0 V. The XRD pattern of the AlPO_4 -coated sample is similar to that of the bare one, showing a tetragonal Sn phase. (The broad

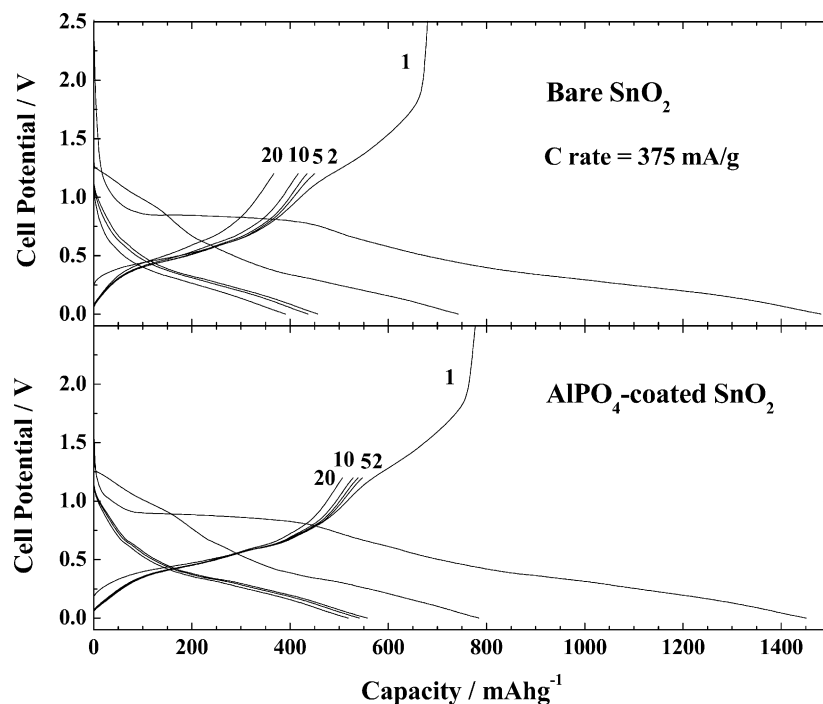


Fig. 6. Voltage profiles of the bare and AlPO_4 -coated SnO_2 , with more binder and carbon conductor, at a rate of 375 mA/g ($=0.48C$). The first cycle was performed between 2.5 and 0 V, followed by cycles between 1.2 and 0 V afterwards.

peak at $\sim 25^\circ$ is associated with a glass holder.) The bare SnO_2 continues to crack and crumble as a result of the large volume change on cycling, according to the reaction shown in Eq. (2). These cracking and crumbling during cycling keep generating new active surfaces that were previously passivated by the stable surface films. Hence, the repeated reaction between the electrolyte and $\text{Sn}/\text{Li}_2\text{O}$ induces capacity fading, as shown in Fig. 4. SEM micrographs of 15-cycled bare SnO_2 particles demonstrate that the grains are destroyed and covered with large cracks (Fig. 3(b)). However, such cracks are not observed in the AlPO_4 -coated SnO_2 particles after cycling. It is quite likely that the AlPO_4 coating significantly reduces the formation of surface cracks induced from the volume change in the Li_xSn phase, and therefore diminishes the repetitive formation of electrode/electrolyte interfaces affecting the capacity fading. More detailed experiments are currently underway to elaborate the surface microstructures of the bare and AlPO_4 -coated materials after cycling.

Our electrochemical cycling tests were under severe and extreme conditions, such as larger particle size, extended voltage window, and higher C rate, compared to other reports. The improvements on the cyclability of AlPO_4 -coated SnO_2 are clearly observed compared to bare SnO_2 anode in the extreme experimental conditions.

For the better cyclability and rate capability, the electrode composition was optimized to SnO_2 : binder: carbon black in a weight ratio of 4:3:3. Additional cycling tests with these electrodes were performed at a high C rate of 375 mA/g ($=0.48C$). The voltage profiles and cycle properties of the bare and AlPO_4 -coated SnO_2 by these electrodes are shown in Fig. 6. The AlPO_4 -coated SnO_2 showed the initial capacity of 778 mAh/g, close to the theoretical capacity, while the bare SnO_2 had the initial capacity of 680 mAh/g for 2.5–0 V at the first cycle (similar results to Fig. 4). AlPO_4 coating on the SnO_2 anode led to larger initial capacity and also improved capacity retention (up to the 20th cycle) even at a high C rate, with the improved electrode composition.

In conclusion, the AlPO_4 -coated SnO_2 anode showed superior electrochemical properties, such as capacity fading and irreversible capacity. However, the mechanisms involved with the AlPO_4 coating need to be identified. The improved electrochemical properties of the AlPO_4 -coated SnO_2 may be applicable to Li-ion cells.

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