

Durability evaluation of hexagonal WO₃ electrode for lithium ion secondary batteries



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ABSTRACT

We evaluated the durability of a hexagonal tungsten oxide (h-WO₃) electrode for use as the negative electrode in lithium ion secondary batteries (LIBs). H-WO₃ has attracted attention as an electrode for LIBs owing to its large hexagonal tunnels, in which Li ions can be inserted. However, when a charge-discharge cycling test was carried out in the voltage range 2.5–1.0 V (vs LiCoO₂) for 500 cycles, its discharge capacity decreased by 73% compared with the initial value. To clarify the reasons for the degradation, various types of analysis were performed. The deposited layer on the electrode and changes in both the crystalline structure and the electrolyte composition are considered to be the main reasons for the degradation. The observed changes in the valence of W also affected the degradation. We also report that the voltage range plays an important role in increasing the durability.

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1. Introduction

The use of lithium ion secondary batteries (LIBs) as storage batteries for portable electronic devices and electric cars and as stationary storage batteries for solar cells and wind power generation is increasing yearly. However, their properties, such as energy density, power density, safety and durability, require further improvement to increase their use. Although graphite electrodes have been used as the negative electrode in LIBs, the durability is not long enough. Therefore, new materials for use as the negative electrode that can replace graphite have attracted interest. Transition-metal oxides are actively studied due to their good durability, high energy density and high power density [1–4]. Among the transition-metal oxide materials, WO₃ is known to possess interesting properties that make it a promising candidate for a wide range of applications such as photocatalysis, gas sensors, electrochromic devices and secondary batteries [5–14]. WO₃ is also well known to exhibit various crystalline structures such as monoclinic, triclinic, cubic and hexagonal structures. All these structures can be described as deformations of the perfect ReO₃ cubic model. Among these crystalline structures, hexagonal crystalline WO₃ is of great interest as an intercalation host owing to its tunnel structure, and it is converted to tungsten bronzes M_xWO₃ (M = Li⁺, Na⁺, K⁺, etc.) upon intercalation [15–19]. Furthermore, other studies have reported that the effective diffusion coefficient of lithium intercalation for h-WO₃ is 1–2 orders of magnitude higher than that for monoclinic crystalline WO₃ [15]. For these reasons, h-

WO₃ has the potential to achieve high energy density and power density in LIBs.

However, LIBs fabricated with h-WO₃ exhibit poor durability. Therefore, their improvement is strongly desired. The reason for the capacity decrease of LIBs using h-WO₃ in charge-discharge cycling tests has not been well studied. In this work, we carried out a charge-discharge cycling test in the voltage range 2.5–1.0 V (vs LiCoO₂) for 500 cycles and attempted to clarify the degradation mechanism of h-WO₃ when used as the negative electrode of LIBs. To our knowledge, this is the first detailed study on the degradation mechanism of h-WO₃ in rechargeable batteries.

2. Experimental procedure

First, h-WO₃ powder was prepared by the following process. Ammonium paratungstate (APT) solution was used as the tungsten source. Hydrochloric acid was added to the APT solution, the pH was adjusted to 7.3 and the mixture was left to stand at 2 °C for 48 h. Next, the mixture was stirred for 24 h at room temperature to induce the formation of the h-WO₃ precursor. The obtained powder was filtered, then washed with deionized (DI) water, and dried at 120 °C for 2 h. Finally, the powder was annealed in air at 390 °C for 30 min to remove the hydrate W. The h-WO₃ powder was mixed with acetylene black (AB) and a polyvinylidene fluoride (PVDF) binder in *N*-methylpyrrolidone (NMP) solvent in the weight ratio 100:5:5. The obtained paste was coated on an Al film (thickness: 15 μm) using a film applicator and annealed in air at 120 °C for 10 min to remove the NMP solvent. The thickness of the electrode was adjusted to 50 μm (weight per unit area: 10 mg/cm²). The LIBs in this study were composed of an h-WO₃

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Fig. 1. SEM images of the fabricated h-WO₃ powder.

negative electrode and a LiCoO₂ positive electrode, which were separated by a 25 μm thickness polypropylene separator. The electrolyte was a 1 M solution of LiPF₆ dissolved in a 50:50 vol% mixture of ethylene carbonate (EC) and diethylene carbonate (DEC). The assembly of the LIBs was carried out in Ar in a dry glove box.

The performance of the LIBs was evaluated by performing a charge-discharge test for 500 cycles in the voltage range 2.5–1.0 V (vs LiCoO₂) at 25 °C. To investigate the changes in the crystalline structure of h-WO₃ during the first charge-discharge cycle, we performed in situ X-ray diffraction (XRD) measurements with a Be X-ray window at various states of charge (SOCs). Cu Kα radiation was used in all X-ray measurements. After 500 charge-discharge cycles, we analyzed the structural changes in the h-WO₃ by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Furthermore, atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrophotometry (ICP-AES) were performed to investigate the changes in the electrolyte composition.

3. Results and discussion

SEM images of the fabricated h-WO₃ powder samples are shown in Fig. 1. Rodlike structures with a diameter of 5–50 μm and a length of 20–200 μm were observed.

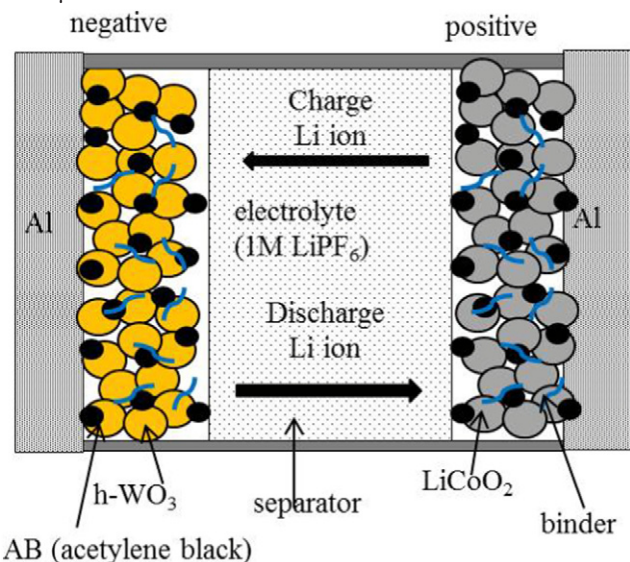


Fig. 2. Structure of the LIBs used in this study.

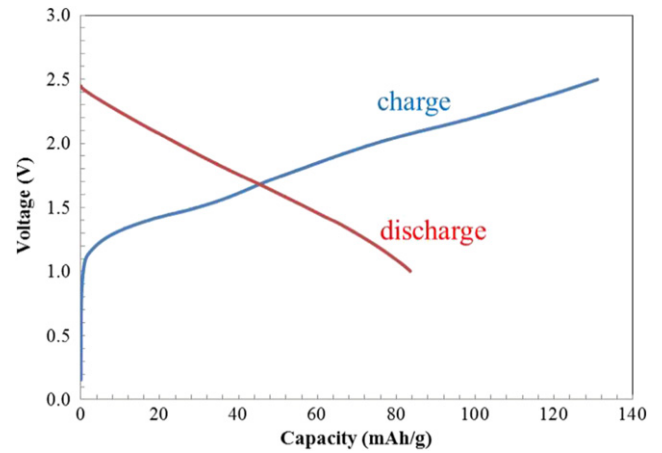
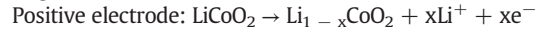
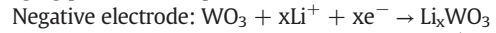


Fig. 3. Curves of first charge-discharge between 2.5 and 1.0 V.

Fig. 2 shows the structure of the LIBs used in this study. h-WO₃ was used as the negative electrode and LiCoO₂ was used as the positive electrode. The reactions of the negative and positive electrodes during the charging process are expressed as follows.



Typical first charge-discharge curves between 2.5 and 1.0 V measured at a constant current density of 0.22 mA/cm² at 25 °C are shown in Fig. 3. The initial charge capacity was 131.0 mAh/g and the discharge

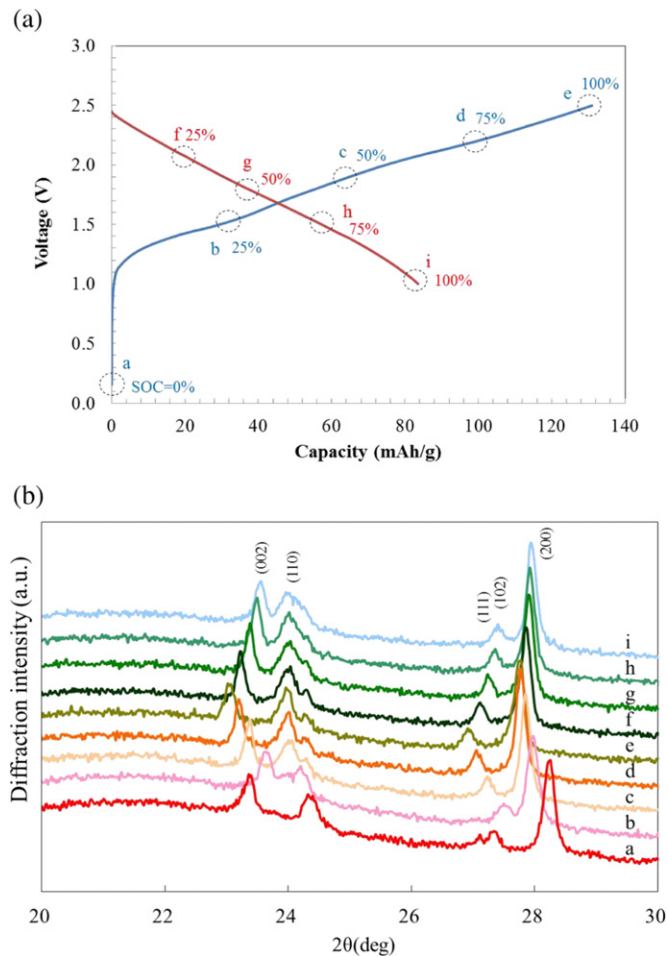


Fig. 4. (a) In situ XRD measurement points for various SOC levels. (b) XRD patterns measured at points a–i.

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