Journal of Industrial and Engineering Chemistry 96 (2021) 364–370

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

10 μm-thick MoO_3-coated TiO_2 nanotubes as a volume expansion regulated binder-free anode for lithium ion batteries

Bumgi Heo, Jaeyun Ha, Yong-Tae Kim*, Jinsub Choi*

Department of Chemistry and Chemical Engineering, Inha University, 22212, Incheon, South Korea

ARTICLE INFO

Article history:
Received 5 November 2020
Received in revised form 29 December 2020
Accepted 31 January 2021
Available online 5 February 2021

Keywords:
Anodization
TiO_2 nanotube
Cyclic voltammetry
MoO_3
Lithium ion battery

ABSTRACT

In this study, 10 μm-thick TiO_2 nanotube arrays (TNAs) coated with a MoO_3 layer were prepared by electrochemical oxidation on titanium foil followed by successive cyclic voltammetric deposition, aiming at the fabrication of a thick binder-free anode with high capacity and good cycling stability for lithium ion batteries (LIBs). Through the evaluation of the electrochemical performance of electrodes prepared under various conditions, the electrode obtained at a precursor concentration of 5 mM showed the best electrochemical performance, exhibiting high reversible capacity and enhanced cycling stability. With the structural advantage and intrinsic characteristics of TNAs, the large volume expansion of MoO_3 is successfully accommodated, resulting in 97% retention at a rate of 5 C over 500 cycles and 91% retention even at a high rate of 25 C.

Introduction

Lithium ion batteries (LIBs) have been widely used in our daily lives, and the demand for higher power, energy density, longer cycle life, and lighter weight in LIBs are increasing with the rapid development of electric vehicles and portable electronic devices [1,2]. As an important component of LIBs, anodes are crucial for practical battery performance, such as working output voltage and fast charge/discharge property. However, commercial graphite electrodes currently used with low theoretical capacities (375 mAh g^{-1}) are limited in their ability to satisfy the growing demand for advanced LIBs [3,4]. Therefore, numerous studies have been conducted on anode materials with excellent properties, including modified carbon-based nanomaterials [5–7], transition metal oxides [8–10], lithium metals [11,12], and metal alloys [13,14]. Among them, TiO_2 has attracted considerable interest because of its high abundance, chemical stability, safe working voltage (1.7 V vs. Li/Li^+), and extremely low volume expansion during the charge/discharge cycle [15–17]. However, the low theoretical capacity (175 mAh g^{-1}) with poor electronic and ionic conductivities has been a challenge for its application [18,19]. Various approaches to overcome such limitations have been reported, such as combining foreign active materials with TiO_2 using coating or atomic layered deposition (ALD) methods [20–22]. Anodically prepared TiO_2 nanotube arrays (TNAs) directly grown from the Ti metal substrate can allow the formation of binder-free and conductive-agent-free electrodes, which have the advantage of battery capacity in terms of specific or areal capacity. However, TNAs length is generally restricted to approximately 1 μm because of the difficulty in forming a uniform coating layer in a 1D nanotube structure with a high aspect ratio [8,23–25].

In this work, we designed and constructed 10 μm-thick TNAs decorated with MoO_3 using facile anodization and subsequent cyclic voltammetry (CV) deposition. As a foreign active material, MoO_3 is adopted herein. MoO_3, which has high chemical stability and a superior theoretical capacity of approximately 1117 mAh g^{-1} is known to have a problem of significant capacity fading due to its large volume expansion during the charge/discharge, resulting in severe electrode loss and poor cycling performance [26–28]. With simple CV electrodeposition, MoO_3 was successfully coated uniformly throughout the whole nanotube area even for a length of 10 μm, which can provide increased space for MoO_3 deposition and volume expansion buffering during the subsequent battery cycles. Based on the prepared composite electrode, we demonstrate its superior performance as an anode for LIBs in terms of its high gravimetric capacity, excellent rate capability, long-term cycling stability, and fast charging ability.

Experimental

Preparation of MOA@TNAs

Titanium foil (0.127 mm thick, 99.7%, Sigma-Aldrich; USA) was cut into 1.5 × 1.5 cm^2 and cleaned by ultrasonication in acetone, ethanol, and deionized (DI) water for 20 min each. Subsequently, the Ti foil was anodized in 0.3 wt.% ammonium fluoride (NH_4F) and 13 wt.% DI water containing ethylene glycol at 60 V for 8 h. The as-prepared TNAs was

* Corresponding authors.
E-mail addresses: yongtaekim@inha.ac.kr (Y.-T. Kim), jinsub@inha.ac.kr (J. Choi).

https://doi.org/10.1016/j.jiec.2021.01.048
1226-086X/