



Micro-length anodic porous niobium oxide for lithium-ion thin film battery applications

Jeong Eun Yoo, Jiyoung Park, Gihoon Cha, Jinsub Choi *

Department of Chemical Engineering, Inha University, Incheon, 402-751, Republic of Korea

ARTICLE INFO

Article history:

Received 3 February 2012
Received in revised form 4 January 2013
Accepted 7 January 2013
Available online 31 January 2013

Keywords:

Anodic films
Niobium oxide
Nanoporous
Thin film battery

ABSTRACT

The anodization of niobium in an aqueous mixture of H_3PO_4 and HF in the potential range from 2.5 to 30 V for 2 h at 5 °C was performed, demonstrating that anodic porous niobium oxide film with a thickness of up to 2000 nm, including a surface dissolution layer, can be obtained by controlling the applied potential and composition of the electrolytes. Specifically, surface dissolution-free porous niobium oxide film with a thickness of 800 nm can be prepared in a low electrolyte concentration. The surface dissolution is observed when the concentration ratio of HF (wt.%): H_3PO_4 (M) was more than 2:1. The discontinuous layers in the niobium oxide film were observed when the thickness was higher than 500 nm, which was ascribed to the large volume expansion of the niobium oxide grown from the niobium metal. The anodic porous niobium oxide film was used as the cathode for lithium-ion batteries in the potential range from 1.2 to 3.0 V at a current density of $7.28 \times 10^{-6} \text{ A cm}^{-2}$. The first discharge capacity of ca. $53 \mu\text{A h cm}^{-2}$ was obtained in 800 nm thick niobium oxide without a surface dissolution layer.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Niobium pentoxide (Nb_2O_5) is a white n-type transition metal oxide semiconductor with a wide bandgap (3.2–4 eV) and a large dielectric constant (~ 40) [1,2]. Due to its attractive physical properties, Nb_2O_5 has been considered for use in fiber optics, gas sensors, catalysts, biocompatible materials, electrolytic capacitors, and dye sensitized solar cells [1–8]. Kodama et al. suggested that niobium oxide is one of the few cathode candidates for 2 V rechargeable lithium-ion batteries [9]. Le Viet et al. investigated the charge/discharge behavior of lithium-ion batteries based on niobium oxide with different crystal structures and found that the tetragonal and monoclinic structural niobium oxide demonstrated a high discharge capacity and good cycling stability [2]. Wei et al. reported that niobium oxide nanobelts demonstrate a high reversible charge/discharge capacity, high rate capability, and excellent cycling stability for lithium-ion batteries [10].

The niobium oxide was primarily prepared using sol–gel, hydrothermal synthesis and anodization [11–16]. Because anodization is a simple method of controlling the thickness and pore density, there have been many studies that have focused on the production of various niobium oxide films via anodization [14–17]. As reported in previous articles, anodic niobium oxide films with a thickness of 200 nm and a pore diameter of 20 nm can be routinely prepared [14,17]. However, the preparation of thicker porous niobium oxide in aqueous electrolytes has not been achieved because the surface of the porous

niobium oxide is easily dissolved as a result of the attack of F^- during long anodization times. In order to avoid the surface dissolution, pre-annealing or adding surfactant to the electrolyte were undertaken [18,19]. Even though the anodization of niobium in a non-aqueous electrolyte at high temperature produced 28 μm thick porous niobium oxide, the water content in the electrolyte should be controlled [15].

To date, anodic porous niobium oxide film has not been studied for the electrode of lithium-ion batteries. In this article, the electrochemical conditions required to produce a niobium oxide film with a thickness of up to 2000 nm, which until now has not been achieved in an aqueous electrolyte, will be discussed. In addition, the prepared niobium oxides with different thicknesses with or without the surface dissolution are studied for electrodes in lithium-ion batteries. Note that porous type oxide should be produced in order to obtain thicker anodic film by anodization. Because the anodic nanoporous niobium oxide films prepared in this work do not require binding and conductive agents for application in lithium-ion batteries, it is expected that it will provide a simple and routine process to prepare 2 V rechargeable thin film lithium-ion batteries.

2. Experimental details

2.1. Synthesis and characterization of niobium oxide

High purity Nb foils with a thickness of 0.25 mm (99.9%; Goodfellow, England) were used as a starting material for fabricating the porous niobium oxide film. The Nb foils were washed in acetone, ethanol and deionized water ($\geq 18 \text{ M}\Omega$) with an ultrasonicator and were subsequently

* Corresponding author. Tel.: +82 32 860 7476; fax: +82 32 866 0587.
E-mail address: jinsub@inha.ac.kr (J. Choi).

Table 1
The thickness of the nanoporous niobium oxide with/without surface dissolution and discontinuous layers in terms of anodizing conditions.

Electrolyte		Temp./°C	Voltage/V	Time/h	Thickness/nm	Dissolution (D)/dissolution free (F)	Discontinuous (D)/continuous (C) layer
H ₃ PO ₄ /M	HF/wt.%						
0.1	1	5	5	2	550	D	D
0.25	0.5		5		180	F	C
0.5	1	8	250	F	C		
		5	800	F	D		
		8	630	F	D		
		5	680	D	D		
1	1	8	1060	D	D		
		10	1040	D	D		
		2.5	110	F	C		
		2.5	240	F	C		
		5	650	F	D		
	2	8	420	F	C		
		10	450	F	C		
		20	360	F	C		
		5	800	D	D		
		8	1100	D	D		
2	1	10	1260	D	D		
		15	1880	D	D		
		20	2000	D	D		
		30	1600	D	D		
		5	290	F	C		

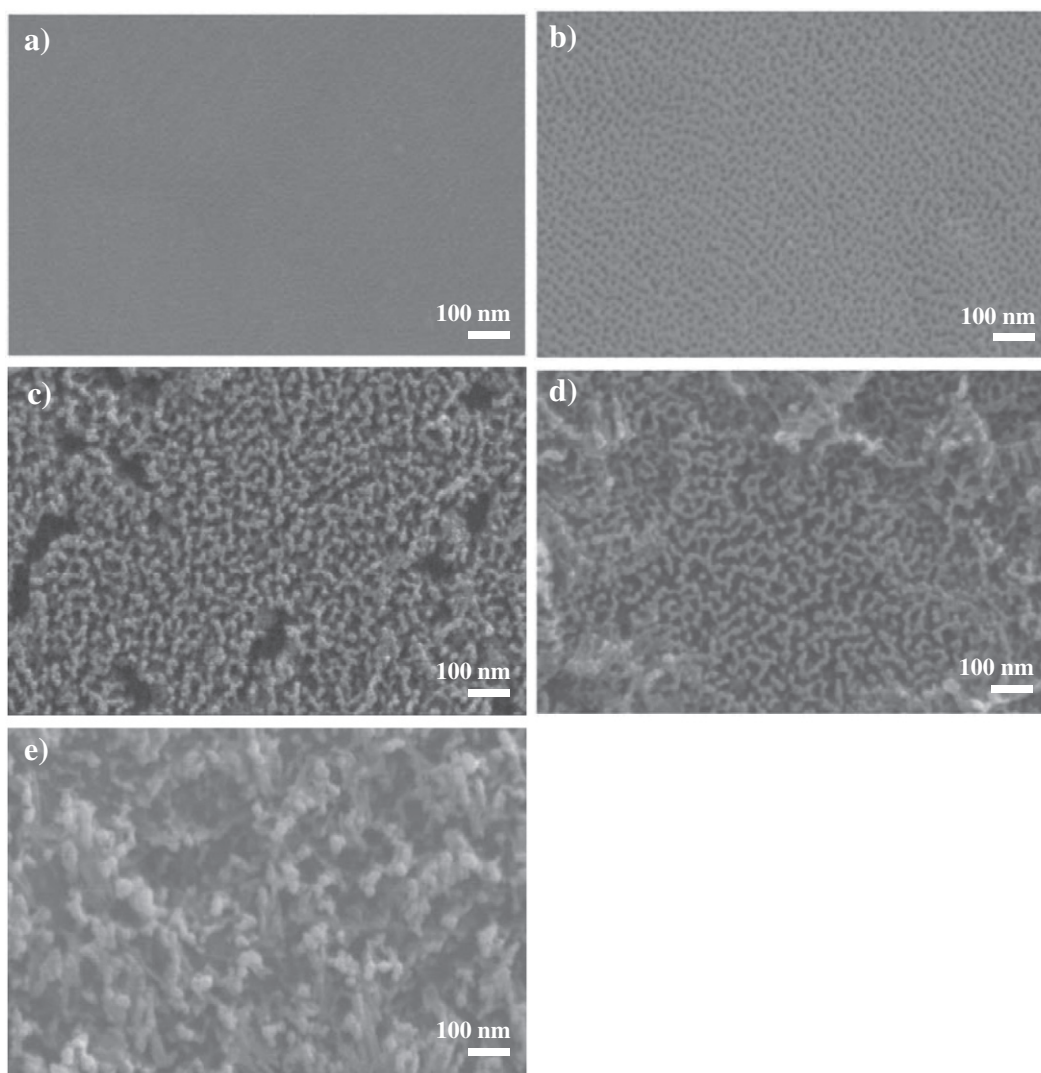


Fig. 1. FE-SEM images of top view of the niobium oxide formed via anodization of a Nb foil for 2 h at 5 °C in a mixture of (a) 1 M H₃PO₄ and 1 wt.% HF at 2.5 V, (b) 0.5 M H₃PO₄ and 1 wt.% HF at 5 V, (c) 1 M H₃PO₄ and 2 wt.% HF at 5 V, (d) 1 M H₃PO₄ and 2 wt.% HF at 8 V and (e) 1 M H₃PO₄ and 2 wt.% HF at 20 V.

Download English Version:

<https://daneshyari.com/en/article/8037217>

Download Persian Version:

<https://daneshyari.com/article/8037217>

[Daneshyari.com](https://daneshyari.com)