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Electrochemical lithium storage kinetics of self-organized nanochannel niobium oxide electrodes

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ABSTRACT

Oriented nanochannel niobium pentoxide (Nb_2O_5) films with different geometries were prepared via the anodization of Nb foils, and the electrochemical lithium storage kinetics for batteries and hybrid supercapacitors were investigated using cyclic voltammetry. The morphology and crystal structure of the nanoporous Nb_2O_5 films were examined by X-ray diffraction analysis and scanning and transmission electron microscopies. Analyses of the cyclic voltammograms indicated that the film morphology, including the pore size and film thickness, significantly affects the Li insertion and extraction kinetics. Furthermore, electronic transport through the nanochannel film appears to become a major limiting factor for reversible lithium storage as both the potential sweep speed and film thickness increase. To enhance the electrochemical lithium storage kinetics in the ordered nanochannel Nb_2O_5 films, the use of a conductive material coating and phase transformation are suggested.

1. Introduction

With the ever-increasing worldwide energy demand, electrochemical energy storage devices have attracted much attention, and their applications are expanding from portable electronics to electric vehicles and large-scale energy storage such as power grids. Among electrochemical devices, the development of rechargeable batteries and electrochemical capacitors (supercapacitors) is the most focused on because of their energy density, power, and cycle life characteristics. Batteries exhibit relatively high energy density, whereas supercapacitors exhibit superior power (rate performance) and cycle life owing to the charge storage mechanism [1]. Recently, interest in hybrid capacitors, such as Li-ion capacitors, has been increasing because they can be constructed using a battery electrode, which has good rate performance, and a supercapacitor electrode, to achieve both high power and increased energy density [2–5].

Among the various candidate materials for hybrid capacitors, niobium pentoxide shows promise as an electrode material. Approximately 30 years ago, it was found that lithium storage was possible in Nb_2O_5 materials via electrochemical reaction in an aprotic solution [6,7]. Since then, Nb_2O_5 has been studied extensively for application as cathode material in 2 V lithium rechargeable batteries [8–14]. Recently, Dunn et al. published several research papers on Nb_2O_5 materials that exhibit very good rate capability [15–18]. In these reports, Nb_2O_5 materials with a specific crystal structure exhibited advantages for fast lithium intercalation and deintercalation reactions, and thus, suitability for supercapacitor or hybrid capacitor electrodes. These results triggered further investigation on Nb_2O_5 materials with different morphologies.

One-dimensional (1D) nanostructured materials such as nanotubes and nanowires have received great attention because of their unique physical and chemical properties [19–22]. Particularly, in battery and supercapacitor electrodes, the 1D structure can be beneficial for enabling fast electronic and ionic transport [23–25]. Self-ordered oxide nanostructures can be formed by the anodization process of a range of metals under optimized experimental conditions. Representatively, nanoporous aluminum oxide (Al_2O_3) and titanium oxide (TiO_2) nanotubes can be easily prepared by anodizing pure metal substrates [26,27]. Until recently, Nb could only be transformed to a nanotube or nanochannel structure by anodization with a limited thickness of a few hundred nanometers to a few micrometers [28–31]. Recently, it was reported that ordered nanochannel niobium oxide with a thickness of more than a few micrometers can be successfully grown on a Nb substrate [32]. However, the niobium oxide layer had mixed phases of NbO_2 and Nb_2O_5, and the electrochemical properties for lithium storage were only tested with a 1.5 μm-thick niobium oxide film.

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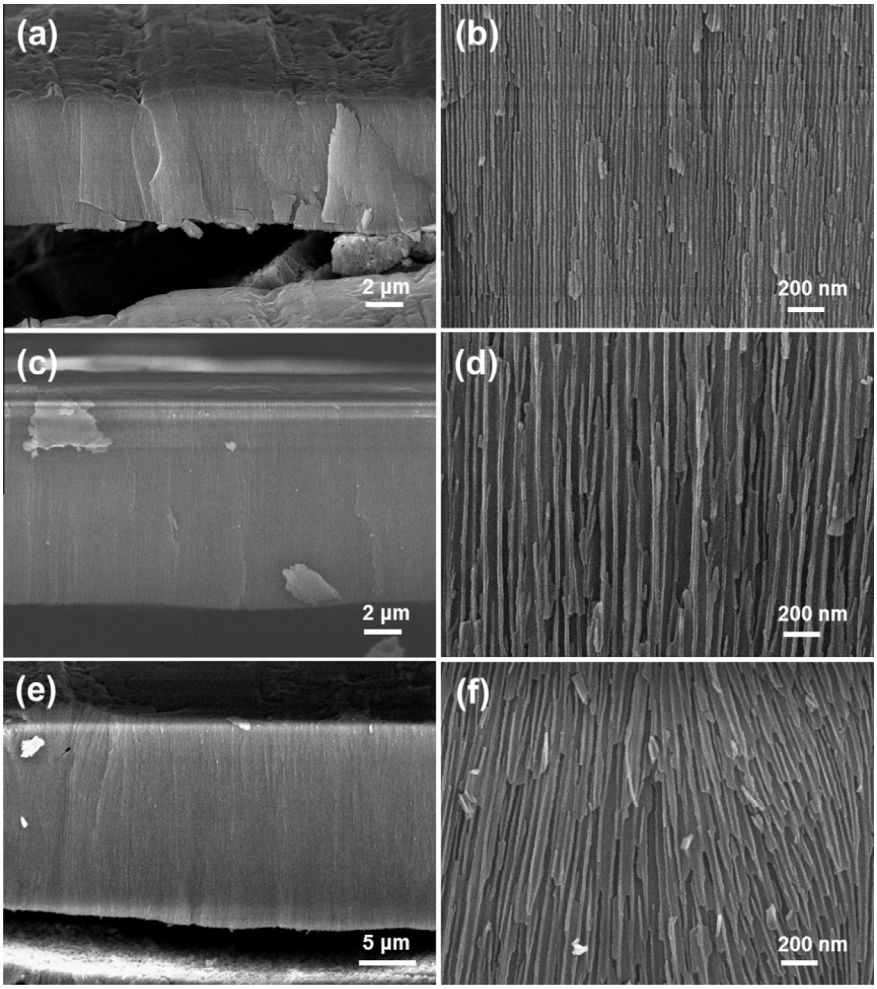

Fig. 1. Cross-sectional FE-SEM images of oriented nanochannel Nb_2O_5 films with different thicknesses: (a, b) 7, (c, d) 12, and (e, f) 18 μm.

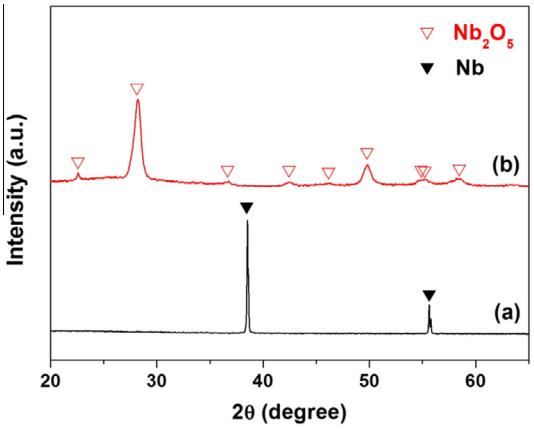

Fig. 2. XRD patterns of (a) as-grown and (b) annealed Nb_2O_5 films.

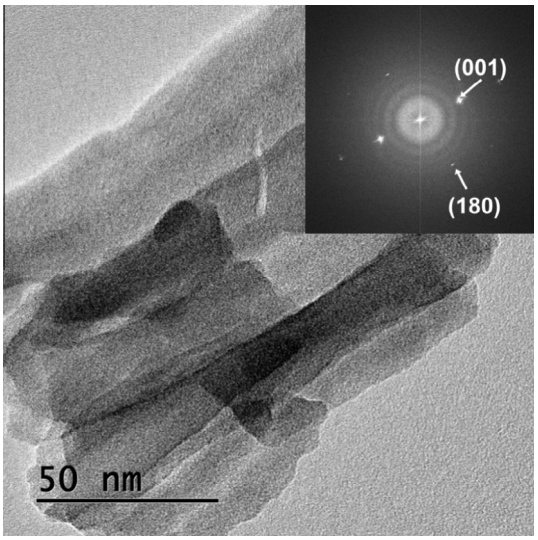

Fig. 3. TEM image of the Nb_2O_5 film (inset: SAED pattern).

In this study, we successfully fabricated the oriented nanoporous niobium pentoxide (Nb_2O_5) films aligned perpendicular to a Nb substrate with thicknesses varying from 7 to 18 μm using the electrochemical anodization process. The aligned nanochannel Nb_2O_5 films have enough thickness to be incorporated as electrodes in lithium storage devices. Furthermore, the nanochannel electrode is not mixed with any binder and conducting agent such as carbon black materials. These are very good features to investigate the intrinsic lithium storage properties in niobium oxide. Using these thick-film electrodes, the electrochemical lithium insertion and extraction kinetics into/from the oriented Nb_2O_5 nanochannel film were investigated in non-aqueous