



Niobium oxide nanoparticle core–amorphous carbon shell structure for fast reversible lithium storage



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ABSTRACT

The hybrid supercapacitor concept involving a battery electrode and a supercapacitor electrode was recently introduced to meet the demand for high energy and power electrochemical energy storage devices. To successfully apply this device, high-capacity and rate electrode materials for Li storage should be developed. Niobium pentoxide (Nb₂O₅) has recently attracted considerable attention owing to its reasonable capacity, excellent rate capability, and cycling stability. However, the low electronic conductivity of the material is a major limitation. To address this issue, carbon incorporation is usually performed. Herein, we report Nb₂O₅ nanoparticle core-amorphous carbon shell materials prepared by hydrothermal reaction and one-step carbon formation with annealing. During the one-step process, it was found that pyrolysis of a carbon precursor could significantly influence the structural evolution of Nb₂O₅ with increasing temperature. In addition, Nb₂O₅ is reduced to NbO₂ in Ar atmosphere with further increase in temperature. The niobium oxide-carbon core-shell structure was thoroughly examined by using transmission electron microscopy. It was demonstrated that the proposed carbon-coated materials exhibited excellent electrochemical properties in terms of rate and cycle performances.

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1. Introduction

In the times of ever-growing energy demands, electrochemical energy storage has become a core technology in various applications [1–3]. Among energy storage devices, rechargeable batteries and electrochemical capacitors (supercapacitors) are the major ones that store electrical energy via electrochemical reactions at the electrodes. The two systems are contrary to each other in terms of their energy storage mechanisms and electrochemical performance. Batteries have the advantage of relatively high energy density because ions can be stored in the bulk of electrode materials by diffusion-limited insertion. Conversely, supercapacitors exhibit the superior characteristics of high power (rate) and cycle life, resulting from the surface charge storage mechanisms involving Faradaic electrochemical reactions or formation of electrical double layers. Owing to the difference in the charge storage methods of two devices, better energy density and power/cycling stability characteristics are difficult to achieve simultaneously.

To overcome the gap between batteries and supercapacitors, the hybrid supercapacitor (HSC) concept has been introduced by adopting a battery electrode and a supercapacitor electrode [4–8]. In this device, the battery-type electrode materials such as Li₄Ti₅O₁₂ and TiO₂ are used for anodes by using Li insertion chemistry and the capacitor-type electrode materials such as activated carbon are employed as cathodes by adopting surface charge storage mechanism. To narrow the kinetic gap between two different type electrodes, the anode should have high-rate capability with moderate capacities. As a result, hybrid supercapacitors can exhibit high power with considerable energy densities by combining the advantages of Li-ion batteries and non-aqueous supercapacitors.

In this context, niobium pentoxide (Nb₂O₅) materials have recently attracted considerable interest as anode materials for HSCs because they can provide (1) relatively high theoretical capacity (~200 mAh g⁻¹ = 720 C g⁻¹) compared to conventional pseudocapacitor materials such as RuO₂ and MnO₂, (2) excellent rate capability induced by pseudocapacitive intercalation reactions, and (3) relative abundance in nature. Actually, Nb₂O₅ has great potential for use in various applications because of its unique performance characteristics resulting from its energy band structure and the existence of several crystal structures and

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morphologies [9,10]. This material has mainly been used in specific applications, such as gas sensors, electrochromics, and catalysts [11,12]. In recent years, however, its applications have expanded to rechargeable batteries and supercapacitors based on its ability to store alkali ions [12–17]. Recently, Nb_2O_5 materials with a specific crystal structure were reported to have the advantage of fast Li intercalation reactions [18–30]. However, to use this material in HSCs, two prerequisites must be satisfied. One is crystal structure and morphology, as mentioned above. Dunn et al. reported interesting results on this issue [20,21]. According to the papers, nanostructured orthorhombic Nb_2O_5 is beneficial for relatively high-capacity and high-rate lithium storage owing to its ability to rapidly transport Li^+ ions through its open and layered crystallographic structure [31]. The other issue is the low electronic conductivity of the materials [32,33]. Stoichiometric Nb_2O_5 is known to be an insulator with an electrical conductivity (σ) of $\sim 3 \times 10^{-6} \text{ S cm}^{-1}$ [34]. To address this issue, carbon and conducting polymer incorporation have been performed [22–27,35].

In this study, we introduce a one-step annealing and carbon coating process after simple hydrothermal synthesis of Nb_2O_5 nanoparticles. The as-synthesized niobium oxide particles showed a less-crystalline phase, and the particles were annealed to obtain an orthorhombic structure, which is favorable for fast Li^+ storage. During this annealing process, carbon coating by chemical vapor deposition (CVD) through sublimation of a solid precursor can be performed simultaneously. Here, we report the effect of the carbon coating process on the crystal structure transition of niobium oxide for the first time. A simple annealing process without carbon sources only leads to structural evolution from less-crystalline to orthorhombic and tetragonal Nb_2O_5 sequentially with increasing temperature, as reported in the literature [9–12]. By contrast, one-step annealing and carbon coating with a carbon precursor causes the crystal structure change of the as-prepared niobium oxide into pseudohexagonal and orthorhombic Nb_2O_5 , and tetragonal NbO_2 at different temperatures. The material characterization of the prepared carbon-coated Nb_2O_5 was carried out by several analytical tools. The electrochemical characterization demonstrated that the Nb_2O_5 nanoparticles with amorphous carbon shell layer had excellent rate and cycle performances.

2. Experimental

Materials synthesis: First, niobium oxide nanoparticles were synthesized according to the following hydrothermal synthesis procedure. 4.56 g of ammonium niobate oxalate hydrate ($\text{C}_4\text{H}_4\text{NNbO}_9 \cdot x\text{H}_2\text{O}$, Sigma Aldrich) and 0.8 g of Pluronic F-127 (Sigma Aldrich) were dissolved in individual de-ionized (DI) water solutions (80 ml) under stirring for 20 min. Then, the ammonium niobate solutions and HCl (2 M, 1 ml) were added to the F-127 solution under stirring. The solutions were transferred into a Teflon-lined steel autoclave. The sealed autoclave was heated to 200°C and maintained at the temperature for 24 h to facilitate hydrothermal reaction. The resulting suspension was centrifuged to separate the white precipitates. After thorough washing with DI water and ethyl alcohol several times, the precipitates were dried at 80°C . For annealing and carbon-coating, the precipitates were placed in a quartz tube within a vertical furnace, as reported elsewhere [36]. The furnace was heated to each temperature (800 , 850 , 900 , and 1000°C) with/without the carbon precursor of naphthalene in Ar atmosphere. After maintaining at each target temperature for 3 h, the furnace was cooled to room temperature.

Materials characterization: The crystal structures of the synthesized materials were identified by X-ray diffraction (XRD, Rigaku D/MAX-2500 V with $\text{Cu K}\alpha$ radiation). X-ray photoelectron spectroscopy (XPS, Thermo Scientific $\text{K}\alpha$) was used to analyze the chemical state of the materials after carbon coating. The morphology and microstructures of the samples were observed using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7401F) and a high-resolution transmission electron microscope (HR-TEM, JEOL ARM-200F) with a probe C_s aberration corrector (CEOS GmbH) and an energy dispersive spectroscope (EDS). Raman spectroscopy (Raman Microscope, Renishaw) was employed to characterize the phase transition of Nb_2O_5 and the carbon shell layer. Thermogravimetric analysis (TGA, TA Instruments Q600 V20.9 Build 20) was performed to determine the carbon content of the carbon-coated Nb_2O_5 nanoparticles.

Electrochemical characterization: For the half-cell test, carbon-coated Nb_2O_5 material (80 wt%), a conducting agent (Super P, 10 wt%), and polyvinylidene fluoride binder (PVDF, 10

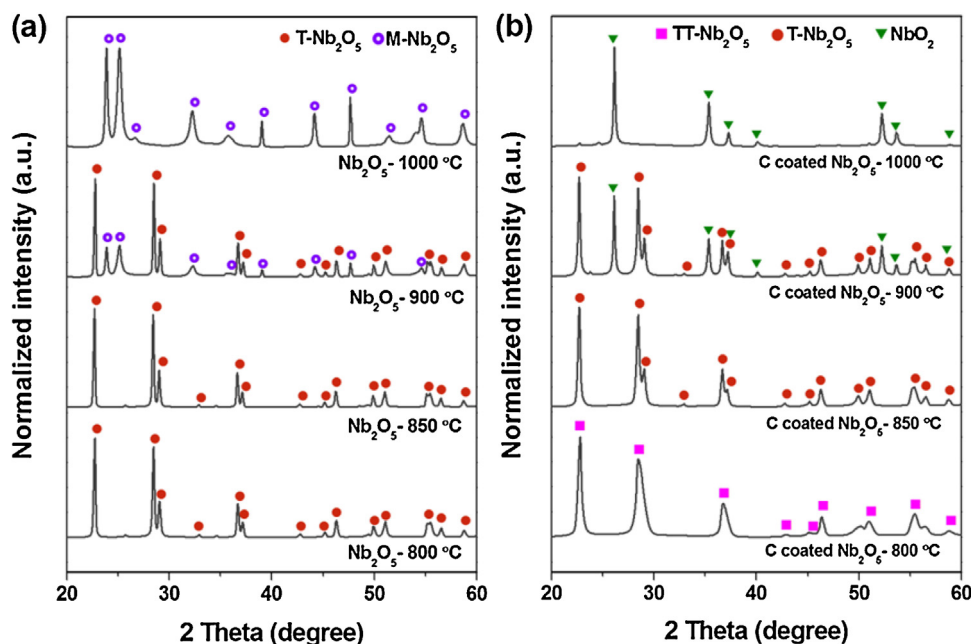


Fig. 1. XRD patterns of Nb_2O_5 samples annealed in Ar atmosphere for 3 h at various temperatures: (a) without and (b) with carbon precursor.

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