Investigation of Ion Irradiation Effect for Improving Electrochemical Performance of Niobium Oxide Electrodes

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1. Introduction

Hybrid Supercapacitors employ battery-type electrodes on one side and capacitor-type electrodes on the other to enhance power density while addressing lower energy density. However, due to slow electrode kinetics on the negative side, an imbalance arises with the fast electrode kinetics of the capacitor-type electrode, compromising device performance [1].

Currently, the prevailing method for electrode fabrication involves slurry casting. This approach entails mixing active material, binder, conducting agent, and solvent to create a slurry, which is then spread onto a current collector to form the electrode. The use of binders in this process, being electrically insulating, increases electrode resistance and diminishes its kinetics. Consequently, research has extensively explored the direct deposition of active material onto the current collector as a solution. Among various techniques, anodization offers a simple means to form oxide layers with nanostructures on metals. Oxide layers produced through anodization are often recognized for their amorphous nature, preferred due to their higher defect density compared to crystalline counterparts, contributing to improved performance [2].

To further introduce enhancing defects for electrochemical performance, methods such as hydrogen annealing and plasma treatment exist. However, these methods typically require high temperatures and pressure and are time-consuming, rendering them highly inefficient. Ion beam irradiation emerges as an alternative, capable of inducing substantial defects in materials at room temperature and within a short timeframe.

In this study, we focus on the fabrication of niobium oxide, a material with fast electrode kinetics. Utilizing anodization without binders, we created the electrode. Subsequently, we employed the Stopping Range of Ions in Matter (SRIM) code to calculate ion irradiation damage within the fabricated electrode, aiming to generate defects. Nitrogen ion beams, known for enhancing electrical conductivity upon doping, were adopted. Our goal is to derive optimal conditions for generating significant vacancies in niobium oxide through computational analysis.

2. Method

2.1 Anodization

The Nb foil was cut into rectangular shapes of 15 mm * 20 mm dimensions. To prevent the backside of the Nb foil from oxidation during anodization, Kapton tape and silicone adhesive were used. The fabrication of Nb2O5 was carried out using an anodization system with a cathode and anode. The Nb electrode was cleaned with ethanol prior to anodization. The Nb electrode was used as the anode, while a Pt foil (10 mm * 12 mm * 2 mm) served as the counter electrode (cathode). The distance between the two electrodes was set at 2 cm in molten ortho-phosphoric acid. The anodization was performed voltage of 30 V, with the electrolyte temperature at 160°C during the experiment. The anodization time varied from 5 minutes to 60 minutes.

2.2 Characteriaztion

Surface morphologies of the sample were examined with a field emission scanning electron microscope (FESEM, Magellan400, FEI Company, Oregon, USA). Cross-sectional data for the Nb2O5 electrode was obtained by employing a focused ion beam (FIB). The crystal structures of the electrode were investigated by X-ray diffraction (XRD, SmartLab, RIGAKU, Tokyo, Japan) and high-resolution Raman/PL system (LabRAM HR Evolution Visible NIR, HORIBA, Kyoto, Japan).

2.3 Electrochemical measurements

Typical CR2032 coin cells were adopted to evaluate the electrochemical performance of the Nb2O5 as anode active materials. The coin cell consisted of the prepared electrode as a working electrode with a diameter of 15 mm, and Li meatal (300 μm in thickness) with diameter of 16 mm as counter and reference electrode. Both electrode were separated by a Polypropylene(Celgard PP2075) with a diameter of 19

mm. the coin cells were filled with the $LiPF_6$ in EC/DMC/EMC solution. The coin cell fabricaition was carried out in an argon atmosphere (Fig.2.2). Cyclic voltammetry (CV) and rate capability of the electrodes in the potential range of 1.0–3.0 V (vs. Li/Li+) were measured with an electrochemical system (WBCS3000Le32, WonATech, Seoul, Korea).

2.4 SRIM Simulation

The SRIM-2008 code developed by James F. Ziegler was employed to conduct the simulation. Nitrogen ion beams were adopted for the ion irradiation. The target sample used in this study is Nb_2O_5, with a sample density of 2.829 g/cm^3, considering the porous structure of the oxide layer. The oxide layer's length was set to 10 µm. The depths of the two layers were designated as 10 and 100 µm, respectively. To approximate the distribution, a total of 10,000 ions were input.

For the simulation settings, "Ion Distribution and Quick Calculation of Damage" and "Ion Distribution with Recoils projected on Y-Plane" were selected as the damage type and basic plots, respectively. The angle of incidence was set to 0 degrees. The output files included ion ranges, backscattered ions, and transmitted ions/recoils. The damage, expressed as damage per atom (dpa) per unit fluence, was calculated using Equation 1 [3].

$$dpa = \frac{total\ vacancies}{atom\ density} \times fluence \tag{1}$$

3. Result and Discussion

The anodization process was carried out with the samples maintained at 160°C and 30 V, while the durations of the experiments varied between 5 to 60 minutes. Visualizing the samples through high-magnification SEM images (Fig. 1), it became apparent that the pore sizes were influenced by the anodization time. Specifically, samples subjected to 20 to 60 minutes of anodization displayed comparable pore sizes. However, as the time decreased from 10 minutes, a reduction in pore size was observed. Detailed measurements revealed the specific pore sizes for each 10-60 minute sample: 36.4 ± 10.4 nm, 87.1 ± 16.1 nm, 102.1 ± 16.7 nm, 100.1 ± 16.1 nm, and 106.9 ± 17.7 nm, respectively.

A comprehensive analysis of the oxide layer's thickness was achieved by obtaining cross-sectional images through Focused Ion Beam (FIB) imaging (Fig. 2). The results revealed a direct correlation between the thickness of the oxide layer and the anodization time. As anodization time increased, so did the thickness of the oxide layer. Precisely, the oxide layer thicknesses

were measured for each 10-60 minute sample: 4.5 µm, 10 µm, 24 µm, 31 µm, and 47 µm, respectively.
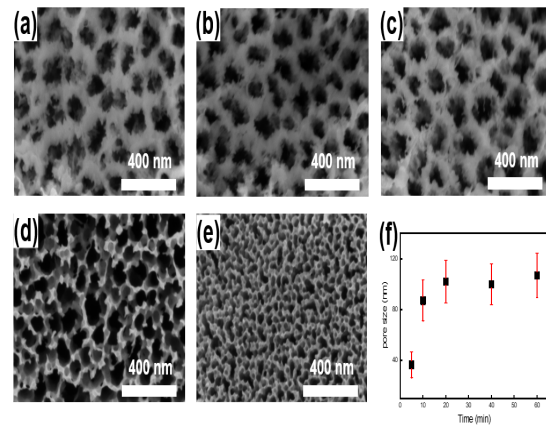

Fig. 1. FE-SEM images of the top-view morphology of Nb_2O_5 electrode anodized for: (a) 60 min, (b) 40 min, (c) 20 min, (d) 10 min, (e) 5 min at 30 V and 160℃. (f) Variation of pore size with anodization time for the Nb_2O_5 electrode.
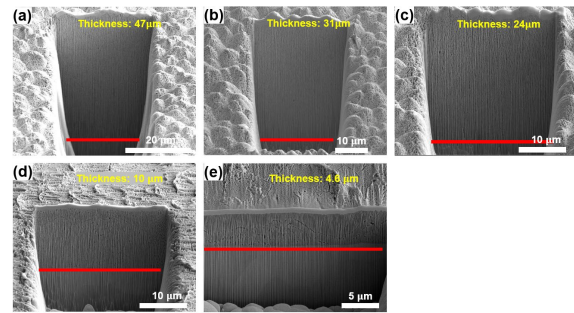

Fig. 2. FIB images of the Cross section-view morphology of Nb_2O_5 electrode anodized for: (a) 60 min, (b) 40 min, (c) 20 min, (d) 10 min, (e) 5 min at 30 V.

The comparison between amorphous samples obtained post-anodization and annealed samples was performed through annealing at various temperatures (500 to 800°C) for an hour. Crystal structure analysis was conducted using X-ray Diffraction (XRD). The annealed samples exhibited distinct crystal structures based on the temperature range. Specifically, samples annealed at 500-600°C exhibited the crystal structure of $TT-Nb_2O_5$ (Pseudohexagonal, JCPDS no. 00-028-0317), while samples annealed at 700-800°C exhibited the crystal structure of $T-Nb_2O_5$ (orthorhombic, JCPDS no. 00-030-0873). Among these, the 800°C annealed sample displayed a well-defined crystalline structure, notably with the (0 0 1) peak. This plane is recognized for its capacity to enhance ion diffusion through the reduction of Li-ion transport distance. Additionally, Raman spectra of the 800°C annealed sample confirmed its crystal structure (Fig.3).
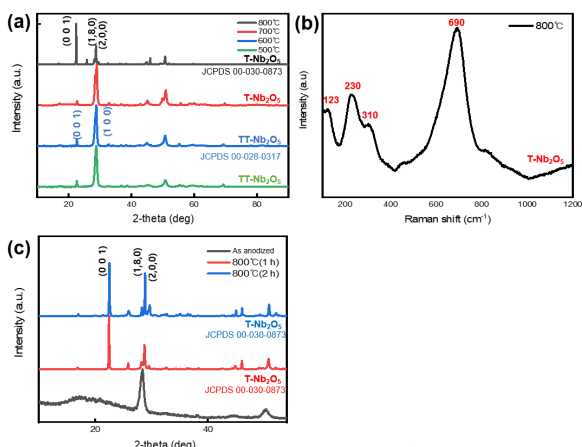
Fig. 3. (a) XRD patterns of the annealing Nb2O5 electrode. (b) Raman Spectra of the 800℃ Annealed Nb2O5 Electrode. (c) XRD patterns of the 800℃ Annealed Nb2O5 electrode and as anodized Nb2O5 electrode.

Electrochemical investigation was undertaken to analyze the effects of varying anodization times on the supercapacitor performance. Based on CV curve analysis, areal capacitance and specific capacitance were calculated. The specific capacitance values ranged as follows: 307.9 F/g, 469.8 F/g, 258.4 F/g, 263.4 F/g, and 266.4 F/g, corresponding to anodization times of 5 to 60 minutes, respectively. Remarkably, the sample anodized for 10 minutes at 160°C displayed the highest specific capacitance of 469.8 F/g, indicating an optimal oxide layer thickness and pore size (Fig. 4).
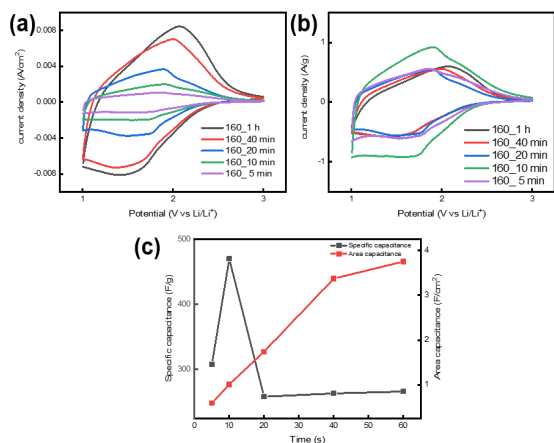

Fig. 4. CV curves of the samples at different anodization time (5 – 60 min): (a) CV curve of current density per unit area, (b) CV curve of current density per unit weight. (c) Variation of capacitance with anodization time for the Nb_2O_5 electrode

To further investigate defect induction, SRIM simulations were employed on the most effective 10-minute sample. The simulations utilized nitrogen ion beams with a fluence of $1.00 * 10^{17}$ ions/cm^2. Due to the porous nature of the current sample, adjustments were necessary to account for the discrepancy between porous and flat-film irradiation. Adjustments were made based on the density ratio derived from the original Nb_2O_5 sample and the oxide layer weight and volume of the anodized sample. The simulation results suggested that the ion energy leading to a specific end point was 6 MeV. However, achieving a uniform defect distribution with this energy proved challenging. Subsequent investigation indicated that ion energies of 2 MeV and 500 keV were necessary for a consistent defect distribution. Consequently, this study determined that utilizing ion energies of 6 MeV, 2 MeV, and 500 keV could yield uniform and substantial defect creation within the sample's oxide layer.
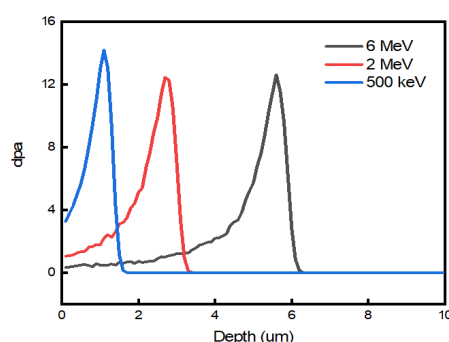

Fig. 5. Damage distribution calculated using SRIM code for Nb_2O_5 electrode irradiated by N ions

4. Conclusion

The samples produced through anodization exhibited a nano-porous structure, which was confirmed by XRD to be amorphous in nature. electrochemical analysis revealed that the highest specific capacitance of 469.8 F/g was achieved at 160°C, 30 V, and 10 minutes. Additionally, SRIM simulations indicated that for uniform defect creation within the oxide layer, nitrogen ion beam energies of 500 keV, 2 MeV, and 6 MeV should be selected.

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