Fabrication of Nanoporous Cu-Ti Alloy and Its Supercapacitor Performance Postprint

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Abstract

Nanoporous copper-titanium alloy was prepared using a combined method of magnetron sputtering and dealloying. A copper-titanium alloy thin film (Cu35Ti65) with a thickness of 720 nm was fabricated by magnetron sputtering using a Cu-Ti alloy target with an atomic ratio of 40:60 as the raw material. This film was then placed in a 0.13 mol/L hydrofluoric acid solution and etched via the dealloying method to obtain a nanoporous copper-titanium alloy thin film. The prepared copper-titanium alloy thin film was employed as the negative electrode material in a three-electrode test system to evaluate its capacitive performance. This study measured and calculated the specific capacitance of this nanoporous copper-titanium thin film electrode in a 1 mol/L Na2SO4 electrolyte. The results demonstrate that the electrode exhibits good electrochemical performance in this neutral solution, with a specific capacitance of 8.96 $mF \cdot cm^{-2}$, representing a significant improvement over existing nanoporous copper electrodes. The cyclic charge-discharge performance tests of the NPCu/Ti electrode indicate that it possesses excellent cycling stability, showing marked improvement compared to existing nanoporous copper electrodes. This improvement is attributed to the porous structure of the electrode material.

Full Text

Fabrication of a Three-dimensional Nanoporous Cu-Ti Alloy with Excellent Electrochemical Capacitance Performance

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Abstract

A thin film of nanoporous Cu-Ti alloy was prepared as a promising electrode material for electrochemical capacitors using a two-step process. First, a $Cu_{35}Ti_{65}$ thin film with a thickness of 720 nm was deposited on a silicon substrate by magnetron sputtering using a $Cu_{40}Ti_{60}$ alloy target. The sputtered film was then dealloyed in 0.13 mol/L HF solution for 12 h to prepare the freestanding nanoporous Cu-Ti alloy thin film. Electrodes fabricated from the nanoporous Cu-Ti alloy exhibited excellent electrochemical capacitance performance, achieving a specific capacitance of 8.96 $mF \cdot cm^{-2}$ in 1 mol/L Na_2SO_4 solution. Furthermore, the nanoporous Cu-Ti alloy electrode demonstrated remarkable chemical stability under cyclic charging and discharging conditions. The superior electrochemical performance can be attributed to the high specific surface area of the nanoporous structure.

Keywords: metal materials, nanoporous Cu-Ti, magnetron sputtering, dealloying, electrochemical capacitance, electrochemical capacitor

Introduction

The increasing scarcity of traditional energy resources and growing environmental concerns associated with fossil fuels have intensified research interest in energy storage and conversion devices. Electrochemical capacitors (ECs), also known as supercapacitors (SCs), offer advantages including high energy density, excellent cycling performance, and low material costs. Electrode materials are a critical factor determining the specific capacitance of supercapacitors. Current electrode materials for new energy applications fall into three categories: novel carbon materials, conductive polymers, and metallic materials [1-5]. Metallic electrodes facilitate rapid electron transfer and reversible redox reactions at the electrode surface, enabling efficient energy conversion, which makes them promising candidates for energy storage applications [6-11].

In recent years, nanoporous metallic materials have attracted significant attention in the field of new energy materials due to their high specific surface area, high energy density, and excellent cycling performance. These materials possess both structural and functional characteristics that bulk metals lack, offering broad development prospects. Nanoporous metals have found applications primarily in industrial, defense, and environmental protection fields, demonstrating tremendous potential for scientific and engineering applications [12-17]. This study employs the established dealloying method to fabricate a

novel nanoporous Cu-Ti alloy thin film and systematically evaluates its electrochemical performance.

Conventional dealloying methods for preparing nanoporous metals utilize bulk alloys obtained through wire cutting or melt spinning [18-20], which often result in non-uniform microstructures and poor control over precursor alloy thickness. To overcome these limitations, we employed magnetron sputtering to prepare Cu-Ti alloy thin films with uniform thickness and composition, followed by dealloying to create the nanoporous Cu-Ti alloy. The microstructure, composition, and electrochemical performance of the resulting material were comprehensively characterized and evaluated.

Experimental Methods

1.1 Preparation of Cu-Ti Alloy Thin Films by Magnetron Sputtering

Cu-Ti alloy thin films were prepared using a $Cu_{40}Ti_{60}$ alloy target (50.8 mm diameter, 5 mm thickness) and a pure Ti target. Silicon substrates (35 mm × 25 mm × 1 mm) served as the base material. The sputtering process was conducted in two stages: first, a Ti base layer was deposited for 15 min at 50 W DC power, followed by deposition of the Cu-Ti alloy layer for 40 min at 100 W RF power, resulting in a final film thickness of 720 nm.

1.2 Fabrication of Nanoporous Cu-Ti Electrodes

Dealloying is a process where the more active component of an alloy is selectively dissolved under controlled corrosion conditions, while the more stable component enriches and reorganizes to form a nanoporous metal structure [18]. In this study, the magnetron-sputtered Cu-Ti alloy thin films were immersed in 0.13 mol/L HF solution at a controlled temperature. Due to the higher dissolution tendency of Ti in HF solution, Ti atoms were selectively corroded. After a specified duration, the samples were retrieved using glass slides and rinsed with deionized water three times at 10-minute intervals, yielding nanoporous Cu-Ti alloy thin films.

1.3 Sample Characterization

The microstructure and morphology were analyzed using a FEI SIRON 200/INCA field emission scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Phase composition was determined by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer operating at 40 kV with a scanning rate of 5°/min over a 2 range of 20°-80°. Conductive glass was used as the sample holder for XRD measurements.

Electrochemical testing was performed using a PARSTAT 2273 workstation in a three-electrode configuration, with a saturated calomel electrode (SCE) as the reference electrode and a platinum plate (15 mm × 15 mm × 0.2 mm) as the counter electrode. The working electrode was prepared by transferring

the nanoporous Cu-Ti alloy film onto a glassy carbon electrode, followed by deposition of 2 L of 0.05% Nafion solution onto the film surface and drying at room temperature for 40 min. The electrolyte was 1 mol/L Na_2SO_4 solution.

Cyclic voltammetry (CV) was conducted over a potential window of 0–0.4 V at scan rates ranging from 100 to 600 $mV \cdot s^{-1}$. The specific capacitance (C, in $F \cdot cm^{-2}$) was calculated using the formula [21], where I is the response current, V is the potential window, v is the scan rate, and S is the effective area of the active material.

Galvanostatic charge-discharge tests were performed over the same potential window (0–0.4 V) at current densities of 50–300 $A \cdot cm^{-2}$. The specific capacitance was calculated from the discharge curves using formula [21], where I is the constant current, t is the discharge time, and S is the effective area.

Electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range of 1 MHz–10 Hz with an AC amplitude of 10 mV, with all tests conducted immediately after open-circuit potential stabilization.

Results and Discussion

Figure 1a [Figure 1: see original paper] shows a cross-sectional SEM image of the magnetron-sputtered Cu-Ti alloy thin film, revealing a 160 nm-thick Ti interlayer beneath the 720 nm-thick Cu-Ti alloy layer. This Ti interlayer facilitates delamination of the film from the silicon substrate during dealloying, as it reacts with HF to release the Cu-Ti layer, which then floats on the solution surface. The surface morphology (Figure 1b [Figure 1: see original paper]) exhibits a striated structure. Energy-dispersive X-ray spectroscopy (EDAX) analysis indicates that the white boundaries (marked by arrows) correspond to Cu_3Ti phase, while the dark regions (circled) represent Cu-Ti phase, with both phases distributed uniformly and alternately throughout the film.

EDAX elemental analysis of the Cu-Ti layer (Figure 2a [Figure 2: see original paper]) confirms a Cu:Ti atomic ratio of 35:65 (Table 1), indicating the precursor alloy composition is $Cu_{35}Ti_{65}$. XRD analysis (Figure 3a [Figure 3: see original paper]) reveals that the major binary alloy phases in the sputtered film are Cu_3Ti(020) and CuTi(211). However, the Cu-Ti binary phase diagram (Figure 3d [Figure 3: see original paper]) shows that at a Cu:Ti atomic ratio of 35:65, the expected phases should be $CuTi_2$ and CuTi. This discrepancy indicates a phase transformation from $CuTi_2$ to Cu_3Ti occurred during magnetron sputtering. This transformation results from the combined effects of clustering and ordering in the supersaturated solid solution [22-24], where copper enrichment during sputtering drives the conversion of $CuTi_2$ to the copper-rich Cu_3Ti phase (also known as β-Cu_4Ti) [23].

Figures 1c and 1d [Figure 1: see original paper] present SEM surface morphologies after dealloying in 0.13 mol/L HF solution for 8 h and 12 h, respectively. The nanoporous Cu-Ti alloy exhibits a uniform distribution of pores and liga-

ments, forming a complete three-dimensional continuous porous structure. The pore size distribution (inset) shows that after 8 h of corrosion, the pore diameters are primarily around 30 nm, while after 12 h they increase to approximately 80 nm. This demonstrates that with extended corrosion time, copper atoms undergo diffusion and reorganization, leading to gradual pore coarsening. A higher-magnification image of the 12 h sample (Figure 1e [Figure 1: see original paper]) reveals nanoscale cracks that expose the cross-section, confirming the uniform nanoporous structure throughout the film thickness and verifying the three-dimensional interconnected nature of the nanoporous Cu-Ti alloy.

EDAX analysis of samples dealloyed for 8 h and 12 h (Figures 2b and 2c [Figure 2: see original paper]) shows residual Ti remains after dealloying, with Ti content decreasing only slightly with extended corrosion time. Based on the original film' s microstructure (Figure 1b [Figure 1: see original paper]) and XRD phase analysis (Figure 3a [Figure 3: see original paper]), the precursor $Cu_{35}Ti_{65}$ film consists of Cu_3Ti and CuTi phases. The formation of a homogeneous nanoporous structure after corrosion occurs through selective dissolution of Ti atoms from both phases [25,26]. During this process, most copper atoms agglomerate to form pure copper phase, while a small fraction reorganizes with residual Ti to form Cu_3Ti phase, resulting in a uniformly distributed, structurally homogeneous three-dimensional bicontinuous nanoporous Cu-Ti alloy.

Figure 4a [Figure 4: see original paper] compares CV curves for nanoporous Cu-Ti electrodes prepared with different dealloying times, measured at a scan rate of 400 $mV \cdot s^{-1}$ within a 0–0.4 V potential window (where the CV curves exhibit optimal rectangular performance). The sample dealloyed for 12 h shows a larger CV curve area, indicating greater specific capacitance associated with higher porosity and specific surface area. Figures 4b and 4c [Figure 4: see original paper] present CV curves at various scan rates, which maintain their rectangular shape even at high scan rates. This behavior demonstrates ideal capacitive characteristics [27,28] and excellent electrochemical stability. Two mechanisms can explain charge storage in the nanoporous Cu-Ti electrode: (1) intercalation/deintercalation of alkali metal ions (such as Na^+) or protons during reduction/oxidation processes [29], and (2) adsorption of cations from the electrolyte onto the electrode surface [30].

Figure 4d [Figure 4: see original paper] illustrates the effect of scan rate on specific capacitance, with calculated values summarized in Table 2 . The specific capacitance decreases with increasing scan rate, consistent with literature reports [31,32]. In the electrochemical behavior of nanoporous Cu-Ti films, the redox process is primarily governed by intercalation/deintercalation of Na^+ and H^+ ions from the Na_2SO_4 electrolyte within the nanoporous structure. At higher scan rates, these ions can only access the surface rather than the interior pores, resulting in reduced specific capacitance. The capacity retention is 82.4% for the 8 h sample (decreasing from 8.47 to 6.98 $mF \cdot cm^{-2}$) and 84.6% for the 12 h sample (decreasing from 8.96 to 7.85 $mF \cdot cm^{-2}$) as scan rate increases. The 12 h sample thus exhibits more stable rated capacitance [21] with a specific

capacitance of 8.96 $mF \cdot cm^{-2}$ at 400 $mV \cdot s^{-1}$, corresponding to 813 $F \cdot g^{-1}$—significantly higher than existing nanoporous metal supercapacitors (Table 3).

Galvanostatic charge-discharge curves (Figure 5a [Figure 5: see original paper]) for electrodes tested at 50 $A \cdot cm^{-2}$ in 1 mol/L Na_2SO_4 solution show linear voltage-time relationships, indicating excellent pseudocapacitive performance [33]. The 12 h sample exhibits longer discharge times and higher specific capacitance, consistent with CV results. Figures 5b and 5c [Figure 5: see original paper] demonstrate that the linear relationship is maintained at various current densities, confirming good rate capability—a critical parameter for electrode and battery applications [30]. The specific capacitance values calculated from these curves at different current densities are listed in Table 4 .

Cycling stability was evaluated by galvanostatic charge-discharge testing at 50 $A \cdot cm^{-2}$ for 1000 cycles (Figure 5d [Figure 5: see original paper]). The electrode retained over 85% of its initial capacitance after 1000 cycles, demonstrating excellent stability. Figure 6 [Figure 6: see original paper] presents the electrochemical impedance spectrum and equivalent circuit model. The fitted parameters (Table 5) reveal that the three-electrode system can be modeled as a solution resistance (R), interfacial resistance between the nanoporous Cu-Ti electrode and electrolyte (R), and a constant phase element (CPE). These results confirm that the fabricated nanoporous Cu-Ti alloy thin film exhibits superior electrochemical performance and cycling stability, making it a promising supercapacitor material.

Conclusion

Magnetron sputtering enables fabrication of homogeneous Cu-Ti alloy thin films, which can be converted into structurally intact, three-dimensionally continuous nanoporous Cu-Ti films through dealloying. When assembled as supercapacitor electrodes, these films achieve a specific capacitance of 8.96 $mF \cdot cm^{-2}$ at a scan rate of 400 $mV \cdot s^{-1}$ and retain over 85% of their initial capacitance after 1000 charge-discharge cycles at 50 $A \cdot cm^{-2}$. The nanoporous Cu-Ti electrodes prepared by this method exhibit excellent rate capability and cycling stability, demonstrating significant potential for supercapacitor applications.

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