



Silicon composite thick film electrodeposited on a nickel micro-nanocones hierarchical structured current collector for lithium batteries

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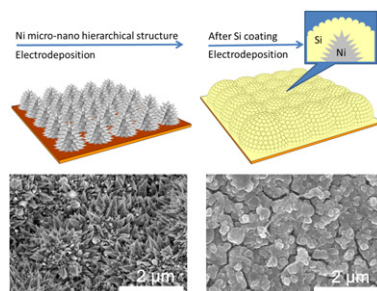
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HIGHLIGHTS

- ▶ Micro-nanocones hierarchical structure (MHS) was fabricated by electrodeposition.
- ▶ Si composite thick film was electrodeposited on MHS current collector.
- ▶ The MHS supported Si anode demonstrated outstanding Li⁺ storage properties.
- ▶ The unique architecture of MHS and porous Si film favor a stable cycling behavior.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 26 May 2012

Received in revised form

31 August 2012

Accepted 3 September 2012

Available online 11 September 2012

Keywords:

Si anode

Thick film

Electrodeposition

Micro-nanocones hierarchical structure

Current collector

Lithium battery

ABSTRACT

Electrodeposition methods were developed for the fabrication of Si composite anodes with nickel micro-nanocones hierarchical structure (MHS) current collectors for Li secondary batteries. This unique structured nickel current collector is electrodeposited in a simple process to create a complex high surface area conductive substrate, as well as to enhance the interfacial strength between active materials and substrate during cyclic lithiation/delithiation. The MHS supported Si composite anode demonstrated outstanding Li⁺ storage properties with reversible capacity over 800 mAh g⁻¹ (600 μAh cm⁻²) after 100th cycle with superior retention of 99.6% per cycle. The improved performance of nickel MHS supported Si thick films indicate the potential for their application as electrode materials for high performance energy storage.

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1. Introduction

It is essential to develop Li-ion batteries with higher storage capacity, greater cycling stability, higher power and faster charging rate for next-generation electrical vehicles [1–5]. Silicon has been targeted to replace carbon as one of the most promising anode

materials owing to its high theoretical specific capacity (4200 mAh g⁻¹, 10 times that of commercial graphite anodes), high volumetric capacity (9786 mAh cm⁻³), and low charge/discharge voltage [6–10]. However, silicon experiences a large volume change due to the lithiation/delithiation process during charge–discharge cycles, which leads to severe silicon particle pulverization and loss of contact with the current collector [11,12]. This mechanical disintegration and electronic degradation thereby triggered drastic capacity fading and have hindered the practical implementation of Si anodes.

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In our previous study, a novel Si composite film was developed for Li battery anodes by electrodeposition from an organic solvent [13,14]. The electrodeposition method was introduced based on the assumption that, to form a Si containing anode from an organic solution, the composite of Si with an organic/inorganic compound withstands the stress during the anode operation. This film, several microns thick, performed as a Li battery anode with a discharge capacity of ca. 1000 mAh g⁻¹ of Si at 2000 cycle and ca. 800 mAh g⁻¹ even at 7000 cycle, which substantially improved electrochemical performance both in specific capacity and cycle ability.

Despite the excellent performance of the proposed Si composite anode, a much thicker film is required to provide sufficient capacity for matching the cathode material of commercialized Li batteries. However, increasing the thickness of the Si composite films seriously affected its electrochemical behavior, because of the poor electron conductivity of the active material and the weak adhesion strength between the thick film and the current collector.

To circumvent these issues, one way is to use a gas deposition method to form a thick film with very strong adhesion between the particles as well as between the active materials and the substrate [15]. Another efficient way is to design a specific structured substrate with high roughness to improve adhesive properties between active materials and current collector [16]. Kim et al. demonstrated that a Cu current collector with a properly modified surface morphology efficiently enhanced the electrochemical performance of a Si-based anode [17]. Uehara et al. introduced a 1.1 μm thick silicon film deposited on a well-etched substrate maintained specific capacity over 1500 mAh g⁻¹ even after 400 cycles [18]. However, these methods have some disadvantages such as comparatively complicated procedures, and high synthesis costs.

Recently, we have developed a unique nickel micro-nanocones hierarchical structure (MHS) fabricated by a simple and economical electrodeposition method with a crystallization modifying agent. This unique structure has been once reported for its super-hydrophobic performance [19]. In this paper, we introduce this Ni MHS as the current collector to support the electrodeposited Si composite thick film anode for Li battery, and demonstrate that this MHS substrate plays an important role in maintaining high performance in the thick film anode.

Fig. 1 illustrates a typical architecture and preparation procedure of this MHS supported Si composite electrode. The design includes large surface area Ni MHS as the inactive confining buffer to accommodate the volume variation as well as the structural support to enhance the adhesion strength between the active materials and current collectors. Subsequently, an Si composite thick film is electrodeposited from an organic solvent on the Ni

MHS substrate as the electrochemically active material for lithium-ion storage. The Ni MHS supported Si composite anodes exhibit a relatively high reversible capacity of around 800 μAh cm⁻² (1000 mAh g⁻¹) with 88% capacity retention over 300 cycles.

2. Experimental

The nickel MHS films were electroplated onto commercial pure Cu foils. The Cu foils were anodized at 0.25 A cm⁻² in a solution containing 10 g l⁻¹ KOH, 10 g l⁻¹ santomerse, and 70 g l⁻¹ deoil powder for 30 s and acid-cleaned with 10% HCl for another 10 s before electroplating. The electrodeposition solution was composed of analytical pure NiCl₂·6H₂O (providing Ni ions) 1 mol L⁻¹, H₃BO₃ (pH buffer) 0.5 mol L⁻¹, and crystal modifier (ethylenediamine dihydrochloride) 1.5 mol L⁻¹ dissolved in deionized water. The temperature of the deposition solution was kept at 60 °C and pH value was 4.0. The deposition current density was varied from 0.5 A dm⁻² to 5.0 A dm⁻². The deposition time was also controlled to obtain micro-nanocones of different size. The hierarchical structure Ni film was produced by two steps. First, a layer of microcones array was deposited at a relatively lower current density of 0.5 A cm⁻² for 20 min. After that, nanocones were deposited onto the surface of the microcones at a higher current density of 5.0 A cm⁻² for 1 min to form an MHS. This two-step process provides flexibility in the fabrication of a variety of hierarchical structures. The MHS substrate was then rinsed with distilled water, dried in vacuum overnight, and transferred into an Ar atmosphere.

For electrodeposition of the Si composite, the electrolytic solution containing 0.5 mol dm⁻³ SiCl₄ (Sigma–Aldrich) and 0.5 mol dm⁻³ tetrabutylammonium perchlorate in propylene carbonate (TBAP, Kanto Chemical/PC, Kishida, H₂O content less than 30 ppm) was prepared in dry air with dew point below -50 °C. The electrochemical cell equipped with a Li/Li⁺ reference electrode, 1.0 cm² MHS on the Cu foil as a working electrode, and Pt counter electrode was set up in Ar atmosphere with dew point lower than -100 °C. A constant cathodic current of 1.0 mA cm⁻² was applied to pass a charge of 2–20 C cm⁻² for the deposition. The deposit on the MHS substrate was then transferred into an electrochemical cell containing 1.0 mol dm⁻³ lithium perchlorate (LiClO₄) in PC – ethylenecarbonate (EC) (1:1 v/v) electrolyte solution (Kishida, H₂O content less than 20 ppm), and reduced by constant-current–constant-voltage mode with 500 μA cm⁻² and 0.01 V vs. Li/Li⁺ for 10 h.

Electrochemical performance of the resultant composite as an anode of a Li battery was characterized by a constant current charge–discharge test with 500 μA cm⁻² in the potential range

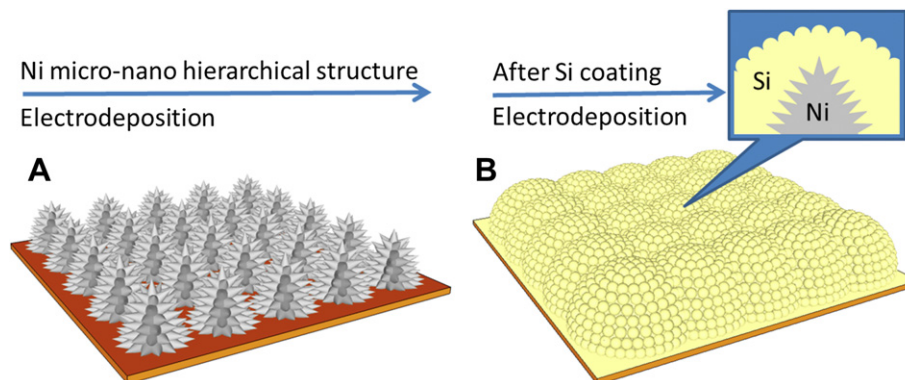


Fig. 1. Schematic diagram illustrating the fabrication of a nickel nanocone-array supported silicon anode architecture: (A) nickel micro-nanocones hierarchical structure; (B) after silicon composite electrodeposition.

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