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Gold-coated silicon nanowire–graphene core–shell composite film as a polymer binder-free anode for rechargeable lithium-ion batteries

Han-Jung Kim [a], Sang Eon Lee [a], Jihye Lee [a], Joo-Yun Jung [a], Eung-Sug Lee [a], Jun-Hyuk Choi [a], Jun-Ho Jung [a], Minsub Oh [b], Seungmin Hyun [b], Dae-Geun Choi [a,*]

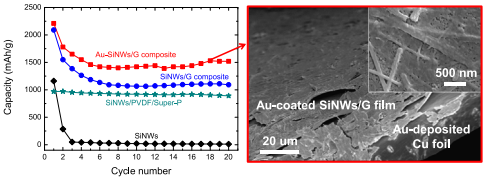
[a] Department of Nano Manufacturing Technology, Nano-Mechanical System Research Division, Korea Institute of Machinery & Materials, 104, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

[b] Department of Nano Mechanics, Nano-Mechanical System Research Division, Korea Institute of Machinery & Materials, 104, Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

HIGHLIGHTS

- Gold-coated silicon nanowires/graphene hybrid composite as a polymer binder-free anode for rechargeable lithium-ion batteries.
- Strong adhesion comes from the bonding process between Au, SiNWs and G, which prevents fast capacity fading during cycling.
- Simple, wafer-scale, and low-cost process for the fabrication of high energy density anodes for rechargeable lithium-ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

We designed and fabricated a gold (Au)-coated silicon nanowires/graphene (Au–SiNWs/G) hybrid composite as a polymer binder-free anode for rechargeable lithium-ion batteries (LIBs). A large amount of SiNWs for LIB anode materials can be prepared by metal-assisted chemical etching (MaCE) process. The Au–SiNWs/G composite film on current collector was obtained by vacuum filtration using an anodic aluminum oxide (AAO) membrane and hot pressing method. Our experimental results show that the Au–SiNWs/G composite has a stable reversible capacity of about 1520 mA h/g which was maintained for 20 cycles. The Au–SiNWs/G composite anode showed much better cycling performance than SiNWs/polyvinylidene fluoride (PVDF)/Super-P, SiNWs/G composite, and pure SiNWs anodes. The improved electrochemical properties of the Au–SiNWs/G composite anode material is mainly ascribed to the composite's porous network structure.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have now become an inseparable part of modern society as the power source for portable electronics such as cellular phones, laptops and digital cameras [1–5]. The most widely used anode material for rechargeable LIBs is graphite. However, the theoretical capacity of graphite is limited to 372 mA h/g [3–5]. To increase the specific energy of rechargeable LIBs, alternative anode materials with higher capacity are needed.

In the past decade, silicon (Si)-based anodes such as Si films and Si composites have been widely studied because of their high theoretical specific capacity of 4200 mA h/g, which is far larger than that of graphite [2,4–7]. However, the volume of Si changes by about 400% during repeated insertion and extraction of lithium-ions (Li). The stresses generated by the huge volume

* Corresponding author.
E-mail address: lamcdg@kimm.re.kr (D.-G. Choi).

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change cause the anode to crack or pulverize [4–6]. Consequently, much of the active material loses contact with the current collector, resulting in poor transport of electrons [7]. In light of this, a new strategy for fabricating high-performance Si-based anode materials has focused on designing a unique structural architecture, as well as employing a highly conductive matrix, to alleviate the volume change during cycling and to improve the electrical conductivity of the electrode. Recently, silicon nanowires (SiNWs) and their one-dimensional (1D) properties have been studied as an anode material to accommodate the large volume change and to avoid rapid capacity fading during Li charge/discharge cycling [4–6]. Actually, many research groups have successfully demonstrated that a SiNW battery electrode can be realized, using the vapor–liquid–solid (VLS) or vapor–solid (VS) growth methods to produce SiNWs directly onto stainless steel current collectors [6,8–10]. However, VLS or VS synthesis methods have major commercialization drawbacks. Since they rely on the use of toxic precursors such as SiH_4, the costs of the overall processes are too expensive for mass-production [11,12].

In contrast, a simple, low-cost and mass producible process via metal-assisted chemical etching (MaCE) process has been suggested for fabrication of SiNWs [12–16]. MaCE is a direct electroless Si wafer etching process resulting in high crystalline quality and good conductivity [12–16]. To date, most of the SiNWs prepared by MaCE process for the anode materials of LIBs have been in one of two forms: the as-prepared state on Si wafer, or a solution-processable composite type. The composite type includes conventional polymer binders such as polyacrylonitrile (PAN), Polyvinylidene fluoride (PVDF), or a conductive carbon additive like Super-P [16–20].

Commercial batteries and most of the research efforts have used polymeric binders in the anodes, adding redundant weight, and ultimately reducing the specific capacity of the electrode. Moreover, the most widely used polymeric binder, PVDF, is known to react with graphitic materials. Since metallic Li produces 7180 J/g [21], the presence of a reactive binder could lead to thermal runaway, thus necessitating incorporation of additional safety features in the LIB. Advanced LIBs, hence, need a binder-free electrode, to avoid that type of capacity loss and the additional safety features [22,23].

A single layer of graphite, referred to as graphene (G), might be a potential alterative anode material for rechargeable LIBs. The extraordinary mechanical and chemical properties of graphene have already been exploited for possible energy storage and microelectronics [22]. Moreover, the high surface area and excellent electronic properties of graphene suggest that it may be incorporated as an electrode component into stable, high-capacity LIBs [22].

In recent years, noble metals such as Au and Ag have also been among the many candidate elements (or components) for LIB anode materials. Since Au and Ag have superior conductivity, and good solubility for Si, it is expected that as anodes Si–Au (or Si–Ag) composites will offer improved conductivity and strong binding to the Cu current collectors for sustainable cycling. Because of these merits, metal has been investigated for use in LIBs as a conducting agent, as a composite with carbon (C), as a thin film, as a nanostructure, and as a component in anodes [23–26]. However, because the specific capacity of Ag is lower than that of Si, the contribution of Ag may result in a decrease of the specific capacity of the Si-based anodes [27].

To address all these issues, we propose here a unique Au-coated SiNWs/G hybrid composite anode for LIBs without the polymer binder. Strong adhesion comes from the bonding process between Au, SiNWs and G, which prevents fast capacity fading during cycling. For use as high capacity anode materials for rechargeable LIBs, the SiNWs can be prepared by the MaCE processing of Si wafers based on the top-down method. In this study, an Au–SiNWs/G composite film was obtained by vacuum filtration using an anodic aluminum oxide (AAO) membrane and Au evaporation.

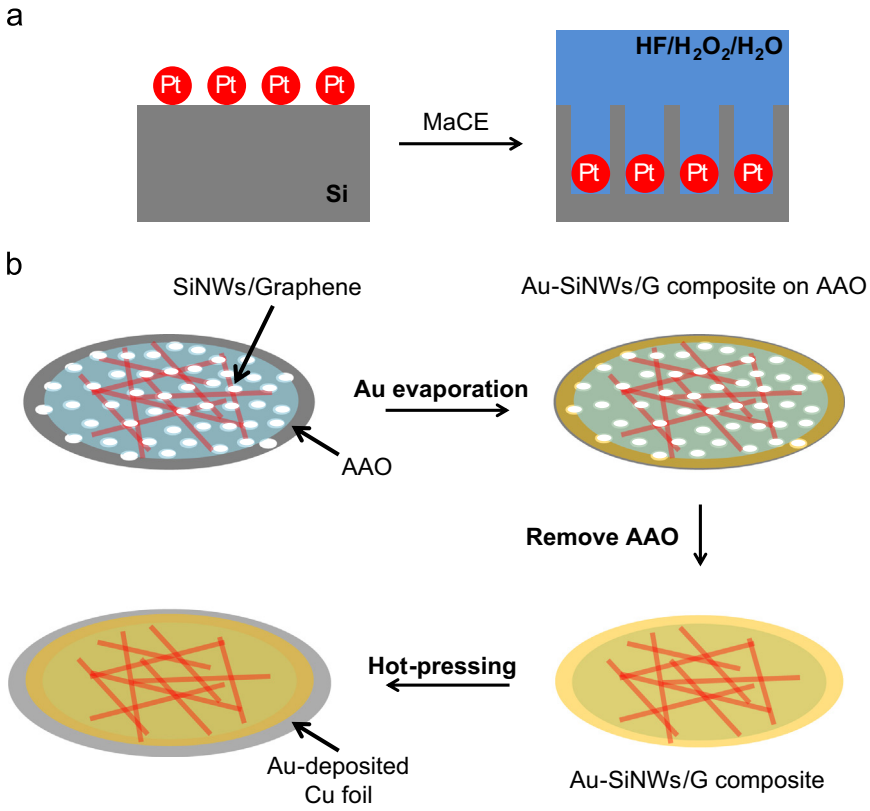

Fig. 1. (a) Schematic formation of SiNWs via Pt-induced etching process. (b) Fabrication process of the Au–SiNWs/G composite anode.