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Additive-free electrode fabrication with reduced graphene oxide using supersonic kinetic spray for flexible lithium-ion batteries

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ABSTRACT

Thin, lightweight, and flexible lithium-ion batteries (LIBs) are emerging as a promising power source for high-performance flexible electronics. However, their technological drawbacks have hindered the development of fully flexible electronics because of a lack of reliable electrode materials that combine superior electrochemical properties with mechanical flexibility. As a solution to this problem, we herein demonstrate an additive-free electrode fabrication process, where reduced graphene oxide (rGO) is coated onto a current collector using a supersonic kinetic spray technique (spray-rGO). The spray-rGO demonstrates outstanding mechanical and electrochemical properties compared to those of rGO electrodes fabricated using the conventional process. Moreover, despite being fabricated without any binders, spray-rGO exhibits high adhesion energy, which enables the fabrication of highly flexible electrodes with no structural deterioration or capacity degradation. This approach to fabricate additive-free flexible electrodes, which results in electrodes that satisfy other important criteria such as high rate capability, long-term cyclability, and facile and fast fabrication, is a prospective method for developing high-performance flexible LIBs.

1. Introduction

Flexible, stretchable, and wearable electronic devices are being actively investigated as emergent and promising next-generation technologies [1–6]. However, several issues facing the development of flexible energy storage devices for powering electronics in a flex/bent state are yet to be overcome [7,8]. Flexible energy storage devices must demonstrate essential electrochemical and mechanical characteristics such as high capacity, high rate capability, long cycle life, low cost, and high flexibility.

Currently, lithium-ion batteries (LIBs) dominate the market because of their properties such as high rate capability, high energy density, and long cycle life [9,10]. The fabrication processes of LIB electrodes involve coating slurry onto a metal current collector, where the slurry comprises a mixture of an active material, a conductive agent, and a binder. However, the application of such devices as flexible batteries in flexible electronic devices has been limited because of unreliable or improper electrode materials and fabrication processes. Various issues with conventional LIB electrodes need to be resolved for them to be used in flexible batteries. The first problem is weak adhesion at the interface between the electrode materials and the current collector because of the point contact formed by only binder particles [11,12]. Electrodes with weak adhesion can develop cracks and delamination at the interface because of deformation in the bent/flex state and volumetric expansion during repeated charge and discharge, resulting in capacity loss and performance deterioration. Among the other constraints, the additives, which are approximately 5–10% of the total weight of the electrodes, are not electrochemically active, and thus, do not store Li^+ ions, thereby reducing the overall gravimetric

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capacity. Furthermore, additives can result in degradation of electrochemical performance. The irreversible capacity increases with increasing additive content in the electrode materials [13,14]. Such issues with additives have been a main constraint in developing fully flexible LIBs. Therefore, a novel process that ensures high adhesion energy and compensates for the capacity loss due to additives would enable the fabrication of flexible electrodes for flexible LIBs.

In this regard, several approaches for solving the aforementioned issues related to additives and adhesion-energy problems for flexible LIBs have been reported. In some approaches, the surface of a current collector was roughened by a surface treatment such as a porous Cu foil or nanostructure growth over the surface to increase the adhesion energy at the interface [15–18]. Other approaches include use of nonmetallic current collectors with higher adhesion energy, such as graphite sheets, carbon fibers, or carbon paper [19–27]. Even though these approaches improve the adhesion energy at the interface, the fundamental problems of detachment and additive content have not been resolved. On the other hand, additive-free electrode fabrication such as vacuum filtration, chemical vapor deposition (CVD), and hydrothermal synthesis methods have been investigated [28–33]. However, these approaches have complicated processing steps and do not result in electrodes that simultaneously satisfy all necessary characteristics for use in flexible LIBs (e.g., high rate capability, long lifetime, and mechanical flexibility). Hence, a facile electrode fabrication process that yields electrodes that fulfil all requirements for flexible LIBs is urgently needed.

Herein, we describe a novel method for the fabrication of an additive-free reduced graphene oxide (rGO) electrode using the supersonic kinetic spray technique (spray-rGO) [34] and successfully demonstrate its incorporation into a flexible LIB. Because the supersonic kinetic spray imparts high energy to the particles, the coated rGO film enables direct coating and exhibits a self-healing effect. However, the most widely used anode material, graphite, is not suitable for use in the spray process because its large particles size results in a poor coating efficiency. By contrast, rGO particles, which are produced through a chemical exfoliation process from graphite, are much smaller than graphite particles, making them suitable for use in the supersonic kinetic spray process. Moreover, rGO possesses various outstanding properties, including excellent conductivity, large surface area, and high lithium-ion diffusivity ($\sim 10^{-7}$ to 10^{-6} cm^2 s^{-1}), indicating suitable characteristics for use in high-power LIBs [35]. Therefore, using supersonic kinetic spray technique and rGO particles, we have fabricated an additive-free rGO electrode. Among the various improved properties of the spray-rGO electrode, it exhibits better adhesion energy than an rGO electrode fabricated by the conventional slurry method (slurry-rGO) because of the large contact area at the interface between the electrode and the current collector; thus, its properties render it suitable for use in flexible LIBs. Moreover, the spray-rGO electrode shows better electrochemical performance, including better rate capability and long-term cyclability than slurry-rGO. The mechanical flexibility of spray-rGO is successfully demonstrated via improved adhesion energy in flexible LIBs when the batteries are bent and twisted severely. Because this proposed method increases the adhesion energy without using any binders, this novel electrode fabrication process will facilitate the future development of flexible LIBs with broad potential application.

2. Experimental section

2.1. Fabrication of spray-rGO and slurry-rGO

The precursor suspension for the spray-rGO coating process was prepared by mixing 0.8 g of rGO (product name: N002-PDR; size < 10 μm; Angstrom Company) in a 40 mL solution of isopropyl alcohol (Samjeon Chem.) and dimethylformamide (Sigma-Aldrich) (3:1 ratio in v/v). The dispersive solution was sonicated for 2 h to form a uniform rGO suspension. After confirming by visual inspection that the rGO suspension was free of precipitates, we fabricated the rGO electrode (without using a binder) on the Cu current collector by injecting the solution using a supersonic kinetic spray [34]. The detailed parameters used for the spray-coating process were as follows: pressure of 4 bar, nozzle temperature of 300 °C, flow rate of 3.0 mL min^{-1} using a 50 mL syringe, and 10 sweeps per syringe to produce a thick and uniform coating for use as an LIB electrode. The thickness of the coating after the spraying process was approximately 15 μm. This coated electrode was directly used as an anode for LIBs in coin cells and in flexible LIBs without any additional treatment such as a cleaning, aging, or thermal treatment.

The slurry-rGO was prepared by mixing of rGO with the carbon black super-P (Timcal Ltd.,) as a conducting agent, and poly(-vinylidone difluoride) (PVDF) in N-methyl-2-pyrrolidone (NMP) solvent with the weight ratio of 90:7:3. The mixing of the materials was carried out for almost 1 h in order to form uniform distribution of active materials with additives. The mixed slurry was then coated on the Cu current collector uniformly. After coating, the slurry-rGO on Cu-current collector was dried at 80 °C in a vacuum oven for more than 12 h to evaporate solvent.

The loaded mass for both slurry-rGO and spray-rGO was about 100 g/m^2; however, the exact loaded mass of rGO materials in slurry-rGO was 90% of total slurry weight (i.e. 90 g/m^2) and the other portion (~10%) was additives. Due to additive-free fabrication process, the gravimetric capacity of spray-rGO shows about 10% more than that of slurry-rGO.

2.2. Adhesion energy measurements

A force station (Physionics Co., Ltd.)-based adhesion test system was used to measure and compare the adhesion energy of spray-rGO and slurry-rGO on Cu current collectors. The structural configuration for adhesion measurements was as follows: From bottom to top, the lower part for sustaining the electrode on the stage consisted of stage/double-sided tape/supporting and handling glass substrate/double-sided tape/target electrode of spray-rGO or slurry-rGO on a Cu current collector. The upper part for measuring adhesion energy consisted of double-sided tape/supporting and handling glass substrate/double-sided tape/driving unit of the force station. The area of the upper double-sided tape, which directly contacted the electrode surface, was limited to 1 cm × 1 cm to ensure that each electrode had the same exposed area. The measurement sequence involved two steps of pressing and pulling. Initially, after a force of 20 N was applied to make fine contact between the upper tape and the electrode surface, various parameters such as displacement, force, and time were simultaneously measured by the force station as the pulling force was increased.

2.3. Material characterization

Raman spectroscopy (Horiba, Lab Ram ARAMIS) was used to characterize the self-healing effect of the supersonic kinetic spray on spray-rGO. Field-emission scanning electron microscopy (JEOL, JSM-7001F) was used to observe the morphology of the surface and the thickness of spray-rGO. For the cross-section observations, the edges were cleanly cut using a cross-section polisher (CP, JEOL, IB-19510CP). Electrochemical measurements such as cyclic voltammogram, charge/discharge profiles, cycle performance, rate