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Robust Free-standing Electrodes for Flexible Lithium-ion Batteries Prepared by a Conventional Electrode Fabrication Process

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ABSTRACT

Highly flexible free-standing electrodes for flexible lithium-ion batteries (LIBs) are prepared by casting slurry on a glass substrate and detaching the film after drying. The slurry is composed of lithium cobalt oxide ($LiCoO_2$) as a cathode material and Super-P as a conductive agent. These are currently used in conventional electrode fabricating. The flexible electrode contains the similar constituents and composition to the electrodes in commercial LIBs, but does not include metal foil as a current collector as that limits the flexibility of the LIB. Polyvinylidene fluoride (PVDF) with hexafluoropropylene (HFP) is used as a binder instead of PVDF alone due to its better mechanical properties (tensile stress, strain, and peel-off strength). In order to compensate for the low electronic conductivity of flexible electrodes without metal foil, a carbon nanotube (CNT) is incorporated into the electrode. The flexible electrodes offer great flexibility with the ability to be bent and folded without deforming. The flexible electrode exhibits high overpotential during charging/discharging process and inferior electrochemical performance (rate capability, energy density and cycling stability) to conventional electrodes with metal foil due to the low electronic conductivity but it delivers reasonable performance in a punch cell with an aluminum-deposited PET substrate as a current collector. Using CNT enhances the electrochemical properties of flexible electrodes, but weakens its mechanical strength at the same time. Therefore, the optimum amount of CNT needs to be determined.

1. Introduction

Since 1990s, lithium-ion batteries (LIBs) have replaced conventional rechargeable batteries, such as NiCd or NiMH batteries, as electronic power sources due to their high volumetric/specific energy density, low memory effect and long cycle life [1–8]. Recently, applications for LIBs have grown to include electric vehicles (xEVs) and electric energy storage systems (ESSs), going beyond power sources for portable electronic devices. At the same time, the demand for flexible LIBs has grown meet the demand for new products like wearable and flexible IT devices (smart watches, flexible displays, etc.). Conventional LIBs have several rigid, or at least 'not so flexible', components that limit their flexibility [9–11]. To resolve these problems, extensive studies have been carried out. Cellulose, carbon felt and metal mesh have been used to impart flexibility to the electrodes as a backbone to accommodate the active material, binder and conductive agent [12–18]. The electrode with a novel structure has been suggested to enhance the flexibility and demonstrated promising performance for flexible LIBs [19–22]. Especially, Li et al. have reported that the flexible electrode composed of $Li_4Ti_5O_{12}$ with graphene foam could retain 55% of capacity at 1 C-rate increasing the current density up to 20 C-rate [23]. The graphene foam provides a high electronic conductivity, large surface area and highly porous structure to the electrode. Liu et al. have reported that TiO_2(B) and activated carbon fiber derived from poly-acrylonitrile (PAN) composite showed an ultra-long life property up to 2000 cycles at 20 C-rate [24]. The intrinsic open channel structure and large surface area of the ultra-thin TiO_2(B) nano-sheets were pointed out as the reasons for the fast charge and discharge. They also suggested that the carbon fiber could also impart high electronic conductivity to the electrode. Koo et al. suggested the flexible all-solid-state system fabricated by using PDMS and LiPON and they demonstrated that PDMS substrate could efficiently reduce compressive force applied to the cell during bending process.

However, these approaches has some drawbacks such as much higher resistance of the electrodes and lower loading level of the active material than the conventional electrodes and low robustness and mechanical strength in repeated bending or folding

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process. Moreover, these approaches require employment of complicated fabrication process and extensive investigation of the reliability prior to use. In some of those studies, physical stability of the electrodes could be secured against external forces due to the flexibility of polymer [25–28]. If we can borrow the fabrication method of the conventional electrode for LIBs in preparing the flexible electrodes, it would save much time and efforts to verify the reliability of the flexible electrode. Conceptually, it would be possible to prepare the free-standing flexible electrodes only by removing the current collector (metal foil) from the conventional electrodes. To our best knowledge, the studies to investigate the feasibility of applying conventional type of electrodes for LIBs to free-standing flexible electrodes are seldom.

In this study, we prepared free-standing flexible electrodes for LIBs employing the conventional materials/parts and fabricating process of the LIBs currently in use to maximize the reliability of the flexible battery. At the same time, we compared PVDF and PVDF-HFP as a binder in the flexible electrode and investigated the effects of CNT added to the flexible electrode on the mechanical and electrochemical properties. PVDF-HFP is one of the polymers safe to use for LIBs as it has been widely used in gel-polymer coating on the separator for LIBs due to its chemical, physical and electrochemical stability [29–34]. Moreover, PVDF-HFP forms a sticky foam with an electrolyte that can manage the volumetric change of the electrode during cycling [31,33,35–37]. The mechanical and electrochemical properties of the free-standing flexible electrodes were investigated and described in this study.

2. Experimental

2.1. Preparation of the electrodes

We prepared the free-standing flexible electrodes by casting slurry on a glass substrate and detaching the electrode after drying at 100 °C. (Scheme 1) The slurry was composed of lithium cobalt oxide (LCO, POSCO ESM) as a cathode material and Super P (Timcal@Li) as a conductive agent. Two kinds of binders (PVDF (KF1300, Korea) and PVDF-HFP (Sigma-Aldrich)) were used to examine the effect of the binder on the flexible electrode's properties. The formulation of the electrode (LCO as conductive agent and binder) was adjusted to identify the effect of the binder composition on the properties of flexible electrodes. CNT was added to the flexible electrodes by replacing a part of the Super-P, maintaining the total carbon content, to examine the effect of adding CNT. We also cast the slurry on aluminum foil and glass plate to examine the ease of peeling off the flexible electrodes depending on the type of casting substrate.

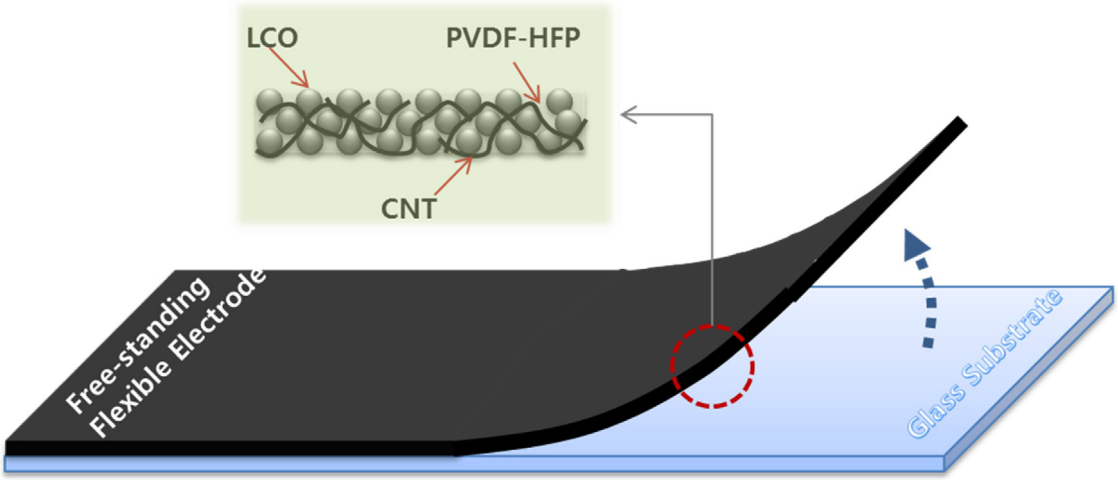
For comparison, a conventional electrode which had an Al-foil current collector and normal slurry formulation (LCO:PVDF:Super-P = 90:5:5 wt%) was prepared. The conventional electrode is denoted as 'Electrode_AL'. Polymer films containing no additives (LCO and Super P) were prepared by casting a polymer solution of PVDF (Film 1) and PVDF-HFP (Film 2) to examine the mechanical and optical properties of the polymer films. The sample name and the information on the fabrication method for the electrodes and polymer films are summarized in Table 1.

2.2. Electrode characterization

The surface and internal structure of the electrodes were studied by scanning with electron microscopy (SEM, HITACHI S4300). To examine the adhesive force and detachability of the electrodes, an adhesive and peel testing system (INSTRON, 5960) was used. The mechanical strength and flexibility were evaluated with the same testing system as used for measuring adhesive force. The electrode for evaluation has a dimension of 20 mm (W) x 60 mm (L) and a thickness of 35 μm. The measurement started when the electrode became flat and ended at the point when the electrode broke. The distance rate imposed on the sample was 10 mm/min. The electric conductivity of the electrodes was measured with 4-point probe system. The samples were prepared in a rectangular shape of 40 mm (W) x 40 mm (L) and a thickness of 45 μm.

2.3. Fabrication of the cell and electrochemical test

The electrochemical properties were evaluated using coin-type half cells (CR2032) and punch cells at 25 °C. A 1.0 M solution of $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DEC) (1:1 v/v) was used as an electrolyte. The free-standing flexible electrodes, or Al-electrode, was cut into a disk or rectangular shape and used as a working electrode. A porous polyethylene film was used as a separator and lithium metal foil was used as a counter electrode. All of the cells were assembled in an Ar-filled glove box with the contents of moisture and oxygen below 1.0 ppm. The punch cells consist of aluminum-coated PET film as a current collector and the free-standing flexible electrodes (Electrode-G). Aluminum was deposited on a PET film with an evaporator [38]. The electrochemical performances were evaluated by using a cycler (PNE Solution, PESC). The coin cells were cycled between 0.01 and 2.5 V (vs. Li^+/Li)



Scheme 1. Schematic diagram of the fabrication process of the free-standing flexible electrodes.