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Flexible catholyte@carbon nanotube film electrode for high-performance lithium sulfur battery

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ABSTRACT

A lithium sulfur (Li-S) battery is attracting considerable attention as a next-generation, high-performing battery. In response to the great demand for lightweight, high-capacity batteries, persistent efforts have been made to solve Li-S battery problems such as polysulfide shuttling. In particular, it has become important to develop a flexible battery in portable electronics. In this study, a Li-S battery is made by a catholyte (Li_2S_6) solution-impregnated carbon nanotube (CNT) film (catholyte@CNT film) with a conductive 3D network structure. The flexibility and electrochemical properties of the prepared Li-S battery are analyzed. The Li-S battery made of the catholyte@CNT film yields an initial discharge capacity of 975 mAh/g and is stable after charge/discharge of 500 cycles. The battery retains more than 95% of its initial capacity even after 1000 cycles of a limited depth of charge/discharge. A pouch cell battery is fabricated to evaluate performance under several bending tests. As a result, it is observed that the battery maintains good open circuit voltage (OCV) despite 1000 repeated deformation tests and exhibits a stable cycling performance both in the folded and unfolded states. These findings suggest that the CNT film is highly suitable for use as an electrode in flexible Li-S batteries.

1. Introduction

The interest and demand for electric vehicles and portable electronics is increasing the need for high-capacity and lightweight batteries. Lithium sulfur (Li-S) batteries are the most likely to satisfy such high demands because they have a high energy density of 2600 Wh/kg and a capacity of 1675 mAh/g, which is approximately seven times higher than lithium ion (Li-ion) batteries made of metal oxide cathodes [1–3]. The practical energy density of the Li-S battery was reported to be 400 Wh/Kg by Sion Power, the highest available for a rechargeable battery. The reduction of energy density at cell level is mainly due to the light weight of sulfur which causes inactive cell components dominate the mass of cell. In addition, Li-S batteries are more eco-friendly and economical compared to the Li-ion batteries due to the low price and nonpoisonous property of sulfur [1]. Unlike Li-ion batteries which are charged and discharged through an intercalation mechanism of Li ion, Li-S batteries are operated by forming a polysulfide (Li_2S_x, $1 \le x \le 8$) as the S_8 ring undergoes a chemical reaction with Li [4].

In general, a cathode electrode of Li-S is prepared by mixing the sulfur with a polymer binder and a conducting agent, then coating a metal current collector with the resulting slurry. The cathode electrode made in this way offsets its advantage in lightness because the polymer binder, conducting agent, and current collector add weight without contributing to the capacity. However, the biggest problem of Li-S batteries is the shuttling phenomenon that occurs as polysulfides dissolved in electrolyte migrate to the Li metal anode during the charge/discharge process. The dissolved polysulfides diffuse toward the anode and react with the Li metal, and the high-order polysulfides are reduced to low-order polysulfides such as Li_2S and Li_2S_2, which do not dissolve in the electrolyte. These low-order polysulfides form an insulation layer on the surface of the Li metal, which reduces the capacity and lifespan of a Li-S battery [5,6]. A number of studies have attempted to resolve this shuttling phenomenon, and a typical solution is to prepare a composite electrode by confining sulfur in a porous carbon material [7–11]. However, the methods are difficult to apply to flexible batteries because the composite electrodes usually cannot stand alone. Thus, the composite electrodes are usually mixed with

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a polymeric binder and a conductive agent, after which an Al foil is coated with the mixture for use in the battery. However, the electrodes made in this way are quite vulnerable to bending deformation [12]. To solve this problem, G. Zhou et al. used the graphene coated poly(dimethyl siloxane) (PDMS) electrode to demonstrate the flexible electrode [13]. The graphene was synthesized on a nickel (Ni) foam, followed by coating with PDMS. Finally, the Ni template was removed via an etching process. However, this complicated process may limit the practical applications of such a concept. Also, there were many attempts to demonstrate the free-standing flexible electrode with CNT sheets which were prepared via vacuum filtration process [14–17]. However, these are not suitable for flexible electrodes because they are merely agglomeration of CNT powders and cannot stand up to mechanical deformation such as bending [18,19].

In this study, we studied on a flexible cathode electrode for a Li-S battery fabricated with carbon nanotube (CNT) film only. The CNT film has an entangled structure of conductive CNT bundles, so it contains numerous pores inside the film where sulfur can be confined. Due to these characteristics, a free-standing cathode which has long electron pathways and easy accessibility of electrolyte could be prepared. The electrochemical performance and flexibility of a Li-S battery prepared with the CNT film are analyzed in this study.

2. Experimental

2.1. Fabrication of a catholyte@CNT film electrode

An electrolyte was prepared by dissolving 1 M lithium trifluoromethanesulfonate ($LiCF_3SO_3$, 98%, TCI) in a 1:1 (v/v) mixture of 1,3-Dioxolane (DOL, 99.5%, Acros) and ethylene glycol dimethyl ether (DME, 99.5%, Acros) with a 0.1 M lithium nitrate ($LiNO_3$, 99%, Acros) additive. In an Ar-filled glove box, catholyte (Li_2S_6) was synthesized by reacting sulfur with Li_2S (5:1 in molarity ratio) in the electrolyte at 55 °C for 24 h. The CNT film, which acted as a support of the catholyte and the current collector, was synthesized via a direct spinning method [20] using a solution of acetone (carbon source, 99.7%, Samchum chemical [Korea]), ferrocene (catalyst precursor, 98%, Sigma Aldrich), thiophene (promotor, $\geq$99%, Sigma Aldrich) and polysorbate_20 (surfactant, Sigma Aldrich). The synthesis solution was injected at a rate of 11 ml/h with a carrier gas (H_2) at the flow rate of 1100 sccm into a vertical reactor heated to 1200 °C [20]. The catholyte@CNT film electrode was prepared by dropping an appropriate amount of catholyte onto the CNT film.

2.2. Electrochemical measurements

CR2032-type coin cells were used to assemble test cells. The catholyte@CNT film and Li metal were used as a working electrode and a counter electrode, respectively. PP/PE film (Celgard 2325) was used as a separator, and all cells were assembled in an Ar-filled glove box. Galvanostaic charge/discharge tests were carried out at various current densities over the voltage range 1.7 V–2.6 V (vs. Li/LI^+) using a charge/discharge cycler (Shin Corporation, TOSAT-3100U). Cyclic voltammetry (CV) tests and electrochemical impedance spectroscopy (EIS) measurements were performed using a PGSTAT 320 N (Auto lab). The CV was recorded at a scan rate of 0.1 mVs^{-1}, and the EIS measurement was recorded from 10 kHz to 10 mHz with an AC voltage amplitude of 10 mV. A repeated bending test of an assembled pouch cell was conducted using a bending machine (Science Town) whose bending radius was 5 mm. The open circuit voltage (OCV) was measured via a multimeter at every 200th bending deformation.

2.3. Characterization methods

The catholyte diluted to 0.1 M in the glovebox was used for the UV–Vis experiments. UV–visible absorption spectroscopic data were collected in the range of 200–800 nm on a UV-3600, SHIMADZU UV–Vis spectrophotometer. Morphology of the catholyte@CNT film was measured with a FE-SEM (JSM-6700F, JEOL), and the catholyte@CNT film taken from the cycled coin cell was washed with DME/DOL (1:1 v/v) several times before the measurement. The XRD samples were prepared by washing the electrode with DME/DOL (1:1 v/v), and the XRD holder was sealed with Kapton tape in a glove box. The measurement was carried out with X-ray diffraction (2D PHSER, BRUKER). The surface area and pore size distribution of the CNT film was measured with Micromeritics ASAP 2020, and the pore size was calculated by the Barett-Joyner-Halenda method.

3. Results and discussion

3.1. Characterization of free-standing, flexible catholyte@CNT film

The synthesized catholyte was analyzed with UV–Vis spectroscopy, and the result was presented in Fig. 1(a). The peak appearing in the 400–500 nm (I) indicates the possibility of the co-existence of several polysulfides such as S_6^{2-}, S_4^{2-}, which means that the dissociated Li_2S_6 exists in an equilibrium state as shown in reaction (1). The peak at near 620 nm (II) is also attributable to S_3^-, which results from the dissociation of S_6^{2-} as shown in reaction (2) [21–23]. These results reveal that Li_2S_6 was successfully synthesized.

$$2S_6^{2-} \leftrightarrow S_4^{2-} + S_8^{2-} \quad (1)$$

$$S_6^{2-} \leftrightarrow 2S_3^- \quad (2)$$

A catholyte@CNT film electrode was prepared by dropping the prepared catholyte onto a CNT film of porous structure as shown in Fig. 1(b) and (c). As can be seen from the energy dispersive spectroscopy (EDS) of Fig. 1(c), sulfur is uniformly dispersed inside the CNT film. Since the catholyte was absorbed into the internal space of the CNT film, its structure was analyzed with BET (Fig. 2). As shown on the plots, the CNT film has a high specific surface area of 195 m^2/g, and most pores are less than 10 nm, which indicates that the film is a mesoporous material. Since the sulfur is confined by such an internal space in pores formed with the conductive CNT bundles, the CNT film is suitable as a free-standing electrode. In addition, its electrical conductivity is very high as much as 10^5 S/m as reported in our previous paper [13], and it is highly flexible as shown in Fig. S1.

3.2. Electrochemical properties of catholyte@CNT film electrodes

Fig. 3(a) shows the voltage profiles of the catholyte@CNT film electrode. Two voltage plateaus appear at 2.4 V and 2.0 V, as commonly observed in Li-S batteries [4]. These plateaus are also reflected on the CV curves of Fig. 3(b) where cathodic peaks at 2.35 V and 2.0 V and anodic peaks at 2.35 V and 2.4 V appear. The first cathodic peak on the CV curve is very small because the cell was discharged in the state in which high-order polysulfide of Li_2S_6 was formed. A broad cathodic peak was observed around at 1.6 V in the first cycle, and disappeared in the second cycle. This peak originates from irreversible reduction of $LiNO_3$, which is an addictive of liquid electrolyte [24]. The $LiNO_3$ undergoes irreversible reduction on the carbon surface at potential around 1.6 V in the first discharge process. It is similar to formation of solid electrolyte