



Corrosion protection of aluminum in LiPF_6 by poly(3,4-ethylenedioxythiophene) nanosphere-coated multiwalled carbon nanotube

S.J. Richard Prabakar, Myoung-ho Pyo*

Department of Printed Electronics and Engineering in World Class University (WCU) Program, Suncheon National University, Suncheon, Chonnam 540-742, Republic of Korea

ARTICLE INFO

Article history:

Received 25 September 2011

Accepted 27 December 2011

Available online 3 January 2012

Keywords:

A. Polymer

A. Aluminum

B. Polarization

C. Pitting corrosion

ABSTRACT

We propose the synthesis and characterization of poly(ethylenedioxythiophene) nanospheres (PEDOT-NSP) coated onto a multi-walled carbon nanotube (MWNT) (PEDOT-NSP/MWNT) and the application of the resultant materials as a corrosion inhibitor for aluminum in LiPF_6 . Doping PEDOT-NSP with negatively charged MWNT minimized the anion exchange property of PEDOT, impeding the penetration of pit-causing PF_6^- anions. The COOH groups of MWNT, which remained intact in PEDOT-NSP/MWNT, also blocked the access of anions to the aluminum by electrostatic repulsion. This synergistic effect allowed PEDOT-NSP/MWNT to protect the aluminum more effectively compared with PEDOT and PEDOT-wrapped MWNT with a coaxial structure (PEDOT-COX/MWNT).

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

To develop lithium ion batteries (LIB) with high nominal charging–discharging voltage and, therefore, high energy density, it is necessary to improve the electrochemical stability of the various components comprising LIBs. For example, the advent of 5 V-class LIB may require the reconsideration of a commonly used electrolyte system. Corrosion inhibition of the current collector for the positive electrodes in commercial LIB also needs further improvement. Aluminum is currently the first choice in most applications due to its outstanding characteristics such as high mechanical strength, excellent ductility, low density, and good electrical and thermal conductivity. In addition, native Al_2O_3 film formed on the aluminum surface, which can effectively reduce the corrosion rate, makes the aluminum more attractive as a current collector [1–3]. Such a thin film, however, can be easily susceptible to localized corrosion (pitting) [4–6] at high potentials or when exposed to, reducing the cycling performance of LIB. There are two popular strategies which studied to improve the compactness of the oxide layer on the surface, such as annealing at a high temperature (ca. 400 °C) or electrochemical anodization [7,8].

The electrolyte used in LIB generally consists of mixed alkyl carbonates with lithium salts. The most commonly used salt, LiPF_6 , produces a stable passivation layer during charging that prevents aggressive aluminum corrosion. This salt also exhibits very good conductivity and electrochemical stability. Therefore, LiPF_6 is preferred to other electrolytes in LIB, but it is sometimes unstable

in organic solutions under certain conditions [9]. The corrosion of aluminum reportedly occurs to a considerable extent during cycling until a passive film (AlF_3) is formed [10]. The continuous corrosion during cycling can severely shorten the lifespan and decrease the safety of LIB. Moreover, even after film formation, AlF_3 can be susceptible to localized corrosion that causes the passivation film to degrade at high oxidizing potentials, thereby accelerating the dissolution of the underlying metal [6,11].

To date, only a limited number of studies have focused on the problem of aluminum corrosion in high-voltage LIB, compared to the number of anticorrosion studies on other metal substrates. Gores et al. demonstrated that room-temperature ionic liquids as additives to electrolytes could suppress aluminum corrosion effectively and improve the performance of LIB [12]. Li and Fedkiw [6] and Armand et al. [13] also reported that high-purity lithium bis(fluorosulfonyl)imide as a conducting salt for nonaqueous liquid electrolytes can outperform LiPF_6 , exhibiting superior stability towards hydrolysis and ultimately improve the safety of LIB by inhibiting aluminum corrosion.

Conducting polymers [14,15] reportedly behave as corrosion protection layers for various metals [16–18]. Conducting polymers deposited on a metal surface have been used to stabilize the stationary potential within a passive range (i.e., the open circuit potential created at the metal-passive layer–electrolyte interface) [19]. The undoping process of conducting polymers functions as a cathodic reaction, whereas metal oxidation works as an anodic reaction. This process eventually results in the corrosion potential being shifted to a positive potential by stabilizing the passive film at the metal–polymer interface [20]. Another judicious tactic was to coat conducting polymer composites, which possess cation-exchange properties, by incorporating a negatively charged

* Corresponding author. Tel.: +82 61 750 3638; fax: +82 61 750 3608.

E-mail address: mho@suncheon.ac.kr (M. Pyo).

immobile dopant into a matrix [18,21]. COOH-functionalized MWNT is a promising candidate for this, because it can function as a dopant of a conducting polymer to change the ion transport mechanism to cation-specific. Moreover, COOH-functionalized MWNT itself can behave as the negatively charged species when exposed to the electrolyte. The electrostatic repulsion between the negative charges on the MWNT surface and PF_6^- can impede the access of the anions to the metal surface. This type of electrostatic repulsion is dependent upon the hybrid pattern that the conducting polymer forms on the MWNT surface. At this point, it should be pointed out that there have been numerous works on the hybrid of conducting polymers and MWNT for various purposes [22–25]. This includes the utilization of the hybrid as a corrosion inhibiting material on stainless steel or iron [26,27]. However, to the best of our knowledge, no previous literature has been published relating to the use of PEDOT-NSP-coated MWNT with a synergistic effect (the cation-specific property of PEDOT and electrostatic repulsion of MWNT) as a corrosion inhibitor.

Herein, we report a strategy that uses PEDOT-NSP/MWNT as a corrosion inhibiting material via a synergistic effect. We synthesized PEDOT-NSP with an average size of about 20–50 nm on MWNT, using ammonium persulfate (APS) as an oxidant in the presence of sodium dodecyl sulfate (SDS) and cuprous oxide (Cu_2O). We chose PEDOT because it exhibits excellent stability, low oxidation potential, and high conductivity relative to other conducting polymers [28–31]. PEDOT-NSP/MWNT is demonstrated to effectively inhibit the corrosion of aluminum at high potentials. The performance of a hybrid synthesized without using surfactant (PEDOT-COX/MWNT) is also compared. In PEDOT-NSP/MWNT, both PEDOT-NSP and the uncovered surface of MWNT can effectively repel pit-causing anions by electrostatic repulsion. This is in contrast to PEDOT-COX/MWNT with a coaxial structure. PEDOT-COX/MWNT shows similar corrosion inhibition to PEDOT, the corrosion inhibition of which is not so effective as PEDOT-NSP/MWNT.

2. Experimental methods

All chemicals used in this study were analytical grade and were obtained from Sigma–Aldrich, unless otherwise specified. Aluminum foil (thickness 20 μm , Wellcos, Korea) was cleaned with anhydrous ethanol and dried under a nitrogen stream before use. SDS, APS, and 3,4-ethylenedioxythiophene (EDOT) monomer were used as received. MWNT (10–20 nm diameter, 10–30 μm length, 2 wt.% COOH content, Nanostructured and Amorphous Materials, Inc., USA) was used without further purification. For the preparation of PEDOT-NSP/MWNT, the polymerization of EDOT on MWNT was performed in a microemulsion medium prepared by dissolving EDOT and SDS in 40 mL triply distilled water under ultrasonic stirring for 10 min. Cu_2O was then added to the EDOT mixture and stirred for 30 min. Various amounts of MWNT were dispersed in the above mixture by ultrasonic stirring for 30 min (10, 20, and 30 wt.% relative to EDOT were added). Thermogravimetric analysis of the final products revealed that the MWNT contents relative to PEDOT were 19.2, 36.4, and 51.3 wt.% respectively. However, these three composites will be hereafter designated by their loading amounts of MWNT, i.e., 10, 20, and 30 wt.%. APS dissolved in 10 mL of water was added (therefore, the resulting concentrations of EDOT, SDS, Cu_2O , and APS were 0.01, 0.01, 0.005 and 0.01 M, respectively) and polymerization was allowed to proceed for 24 h at 40 °C. Dark blue precipitates were obtained by filtering. After washing with water and methanol successively, the precipitates were dried at 50 °C for 24 h. For comparison, pristine PEDOT was synthesized under identical experimental conditions without MWNT and a PEDOT-COX/MWNT composite was synthesized in the absence of surfactant.

During polymerization, MWNT was first dispersed in aqueous solutions containing SDS to limit aggregation and produce an MWNT–SDS template. When EDOT monomer was added to the MWNT–SDS solution, the hydrophobic monomer diffused into the interior of the micelles to form EDOT filled spherical micelles. Since the APS oxidant was hydrophilic, the polymerization took place at the water/micelle interface. At this step, the Cu_2O served as a hard template for the preparation of PEDOT nanospheres in the presence of APS [32,33]. Cu^+ or Cu^{2+} ions were produced by the reaction of Cu_2O with APS. These Cu ions formed coordination bonds with the sulfur of EDOT and functioned as a micelle stabilizer for the formation of regular-shaped PEDOT nanospheres with better homogeneous distribution [33].

A 2-electrode custom-built Teflon cell was used for cyclic voltammetry measurements, in which a Li foil was used as a reference and counter electrode. PEDOT-NSP/MWNT dispersed in CHCl_3 (1.0 mg/mL) was drop-coated onto an aluminum working electrode (area of 1.0 cm^2). The thin-layer-coated aluminum foil was dried at 60 °C for 1 h and fitted in an electrochemical cell. The electrochemical cell was placed inside an Ar-filled glove box for at least for 1 h before testing. Coin cells (CR 2032) of a Li/electrolyte/hybrid-coated aluminum configuration, in which the separator was sandwiched between two electrodes, were assembled in a glove box. Li metal (foil of 1 mm thickness) was punched into a 1.63 cm diameter disc and used as the anode/reference electrode in contact with a Li^+ ion electrolyte [34]. The LiPF_6 was dissolved in a mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) (50:50 by vol.%) to make a 1.0 M concentration. The oxygen and water content was maintained below 1 ppm. Hybrid-coated aluminum foil was punched to be a disc of 1.6 cm diameter and then welded to the stainless steel case. The separator was a Celgard 2400 microporous polypropylene membrane wetted in the electrolyte. A stainless steel spacer and a spring were used to maintain good contact between the cell components. The impedance measurements were normalized to an electrode area of 1.0 cm^2 .

UV–Vis–NIR spectra of the composites were recorded using a JASCO V-670 spectrophotometer. The morphology of the nanocomposites was examined using field emission transmission electron microscopy (FE-TEM, JEOL JEM 2100F). X-ray diffraction (XRD) patterns of the nanocomposites were also compared (X'pert Pro, Philips, Netherlands). Electrochemical measurements were performed on a WBCS3000 battery cycler (WonATech, Korea). For electrochemical impedance spectroscopy (EIS) measurements, a Princeton Applied Research PARSTAT 2273 potentiostat was used and measurements were made by applying a 10 mV AC signal at 4.3 V vs. Li/Li^+ over the frequency range of 10^{-1} – 10^5 Hz. The obtained EIS was analyzed using Z-View software (Scribner and Associates Inc.).

3. Results and discussion

3.1. TEM characterization and formation of the hybrid composites

The morphology of the PEDOT-modified MWNT was examined by TEM to investigate the formation of PEDOT nanospheres on the MWNT surface. A distinct difference in morphology between PEDOT-NSP/MWNT and PEDOT-COX/MWNT can be confirmed from the TEM images shown in Fig. 1A and B. Those figures demonstrate that, while the surface of PEDOT-COX/MWNT is relatively smooth, the PEDOT-NSP/MWNT prepared with 30% MWNT had a rough surface. From Fig. 1A and inset, it is obvious that the nanospheres of PEDOT were produced on the MWNT with a diameter ranging from 20 to 50 nm. The formation of the nanospheres was due to the self-organization of PEDOT induced by the SDS with the assistance of Cu_2O . However, TEM results also revealed that

Download English Version:

<https://daneshyari.com/en/article/1469617>

Download Persian Version:

<https://daneshyari.com/article/1469617>

[Daneshyari.com](https://daneshyari.com)