Composites Science and Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Lithium iron phosphate coated carbon fiber electrodes for structural lithium ion batteries

Johan Hagberg[a,*], Henry A. Maples[d], Kayne S.P. Alvim[d], Johanna Xu[b], Wilhelm Johannisson[c], Alexander Bismarck[d,e], Dan Zenkert[c], Göran Lindbergh[a]

[a] Applied Electrochemistry, Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[b] Polymeric Composite Materials, Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-97187, Luleå, Sweden
[c] Lightweight Structures, Department of Aeronautical and Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden
[d] Polymer and Composite Engineering (PaCE) Group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, A-1090 Vienna, Austria
[e] Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

ARTICLE INFO

Keywords:
Electrophoretic deposition
Structural positive electrode
Carbon fibers
Lithium-ion battery
Multifunctional battery

ABSTRACT

A structural lithium ion battery is a material that can carry load and simultaneously be used to store electrical energy. We describe a path to manufacture structural positive electrodes via electrophoretic deposition (EPD) of $LiFePO_4$ (LFP), carbon black and polyvinylidene fluoride (PVDF) onto carbon fibers. The carbon fibers act as load-bearers as well as current collectors. The quality of the coating was studied using scanning electron microscopy and energy dispersive X-ray spectroscopy. The active electrode material (LFP particles), conductive additive (carbon black) and binder (PVDF) were found to be well dispersed on the surface of the carbon fibers. Electrochemical characterization revealed a specific capacity of around 60–110 mAh g^{-1} with good rate performance and high coulombic efficiency. The cell was stable during cycling, with a capacity retention of around 0.5 after 1000 cycles, which indicates that the coating remained well adhered to the fibers. To investigate the adhesion of the coating, the carbon fibers were made into composite laminae in epoxy resin, and then tested using 3-point bending and double cantilever beam (DCB) tests. The former showed a small difference between coated and uncoated carbon fibers, suggesting good adhesion. The latter showed a critical strain energy release rate of ~200–600 J m^{-2} for coated carbon fibers and ~500 J m^{-2} for uncoated fibers, which also indicates good adhesion. This study shows that EPD can be used to produce viable structural positive electrodes.

1. Introduction

Lithium-ion batteries (LIB) are the dominant battery technology for electric and hybrid electric vehicles. One of the major challenges when transitioning from internal combustion engines to battery powered drive lines, in vehicles, is the much lower energy density of batteries compared to petrol and diesel. A lot of research is therefore focused on increasing the gravimetric and volumetric energy density of lithium ion batteries [1].

A possible route to reduce the weight of electrical vehicles is to replace heavy battery packs with structural batteries. These are materials that can carry load, while storing and delivering electrical energy [2]. Integrating a structural battery can lower the weight of a vehicle by allowing the structure to become part of the energy storage system. In recent years there has been considerable effort to realize this concept. There are three main component in a structural battery: The positive electrode/current collector, negative electrode/current collector and a solid electrolyte/separator. Many studies have focused on using carbon fibers as negative electrodes, because of their mechanical properties and their ability to intercalate lithium [2–7]. Several other studies have investigated replacing the composite matrix with a solid polymer electrolyte. These multifunctional materials have the added functionality of ion conductivity [2,8,9]. However, there have been few studies investigating potential positive electrodes for use in structural batteries. Liu et al. [10] manufactured a structural battery using carbon nanofibers and lithium cobalt oxide dispersed in polyvinylidene fluoride (PVDF) as a positive electrode. However, the carbon nanofibers were not used as current collectors and they were mixed in the electrolyte in chopped form, an additional aluminum current collector was used. Wang et al. [11] demonstrated a structural positive electrode based on carbon nanotubes and cobalt fluoride. They achieved fairly stable cycling performance and mechanical properties, however, a large

* Corresponding author.
E-mail address: johagb@kth.se (J. Hagberg).

https://doi.org/10.1016/j.compscitech.2018.04.041
Received 24 January 2018; Received in revised form 27 March 2018; Accepted 30 April 2018
0266-3538/ © 2018 Published by Elsevier Ltd.

disadvantage is the price of carbon nanotubes. Both Liu et al. [10] and Wang et al. [11] used nanocomposites in some form but the mechanical performance of these materials does not match those of continuous carbon fiber reinforced polymers (both the ultimate tensile strength and the modulus is several orders of magnitude lower). This study aims at bridging this gap, by manufacturing coated positive structural carbon fiber electrodes.

In addition to using carbon fibers as negative electrodes in structural batteries, some studies have investigated replacing metallic current collectors with carbon fibers [12–15]. In addition to the mechanical properties, carbon fibers have been shown to be more electrochemically stable than aluminum [13]. One technique that has been used to coat carbon fibers and other substrates is electrophoretic deposition (EPD). EPD has been used to deposit nanofibers or nanotubes onto carbon fibers, which resulted in improved interfacial properties (adhesion, shear strength and fracture toughness) between coated carbon fibers and a matrix [16,17]. EPD has also been used to deposit electrode materials onto other substrates such as graphite, titanium, aluminum, copper, carbon cloths or nickel [18–20].

There are numerous other deposition techniques to deposit thin or thick films on various surfaces, planar or more complicated porous 3D substrates. Some examples are chemical vapor deposition [21], pulsed laser deposition [22], atomic layer deposition [21,23], or sputtering [24]. EPD was chosen due to its low cost, low environmental impact, scalability, controllability, high deposition rate and relative simplicity [25], combined with the possibility to coat individual carbon fibers.

In this study we present a structural positive electrode consisting of lithium iron phosphate (LFP) coated carbon fibers. The carbon fibers are continuous, self-standing tows acting as current collectors and will provide mechanical stiffness and strength. Under optimal conditions, the fibers are coated individually. The morphology and composition of the electrodes have been characterized as well as the adhesion of the coating to the carbon fibers and a composite matrix. Electrochemical characterization was carried out to test capacity, rate performance, cycle life and the presence of side reactions.

The results show that the electrochemical properties are good with a reasonable capacity of around 60–110 mAh g^{-1}, good rate performance (0.7 retention at 2C compared to 0.1C) and high coulombic efficiency (99.8%). The mechanical tests reveal that the adhesion of the coating is sufficient for the electrodes to be used in a load carrying composite material.

2. Materials and methods

2.1. Materials

$LiFePO_4$ (LFP, Life Power P2) with a particle size of 100–300 nm was supplied by Phosphate Lithium. LFP was carbon coated (2–3 wt.%) and had a specific capacity of 150 mAh g^{-1}. Carbon black (CB, Super-P) was provided by Imerys Graphite & Carbon and had a particle size of 10–100 nm. PVDF (Kynar® 711) used as binder was kindly supplied by ARKEMA Innovative Chemistry (Serquigny, France). Different mixtures of LFP, CB and PVDF were coated onto carbon fibers (see Table 1). The compositions are henceforth given as weight ratios of LFP:CB:PVDF. Note that the compositions used throughout the manuscript refers to the bath compositions which might differ from the composition in the coating itself, rigorous stirring by ultrasonication is used to minimize the difference. Unsized polyacrylonitrile-based carbon fibers (Hexcel Hextow AS4, Hexcel Cambridge UK) having a nominal diameter of 7.1 μm were used as substrate for fabrication of the structural electrodes. The coating bath contained I_2 (purity ≥ 99.8%, Sigma-Aldrich Co.) and the non-ionic surfactant polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (Triton X-100, Sigma-Aldrich Co.) dissolved in acetone (purity ≥ 99%, Sigma-Aldrich Co.). The composition of the impregnation bath used for EPD is given in Table 1.

Table 1
Coating and bath compositions.

Coating			EPD Bath		
LFP (wt. %)	CB (wt. %)	PVDF (wt. %)	I_2 (mg)	Triton X-100 (ml)	Acetone (ml)
92	4	4	182	1.2	300
90	6	4	182	1.2	300
88	8	4	182	1.2	300
88	6	6	182	1.2	300
86	6	8	182	1.2	300

2.2. Electrophoretic deposition

The different ratios of LFP, CB and PVDF (Table 1) were coated onto carbon fibers via EPD. A schematic of the EPD setup is shown in Fig. 1. The working electrode (WE) consisted of a 25 cm long bundle of about 3000 carbon fibers, separated from a spread 12k tow, which was pulled over a glass tube framework. Two platinum rods (length 10 cm, diameter 0.2 cm), serving as counter electrodes (CE), were fixed parallel to the carbon fibers at a distance of 3.5 cm. The electrodes were submerged in to an EPD bath containing an excess of the coating materials listed in Table 1. It has been shown that when adding I_2 to acetone, protons form through the following chemical reaction: [26,27].

$$CH_3COCH_3 \leftrightharpoons CH_3C(OH)CH_2$$

$$CH_3C(OH)CH_2 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

These protons adsorb on the surface of the particles dispersed in the bath, causing them to be positively charged. The charged particles are accelerated in the electric field produced between the electrodes causing them to move towards the negative carbon fiber electrode (CF). The surfactant (Triton X-100) was added to aid the dispersion of the particles and avoid the formation of aggregates. The carbon fiber tow working electrode (WE) was connected to the negative output and the counter electrode (CE) to the positive output of an adjustable bench power supply delivering 61–65 V (EA-PS 3065-05 B, Elektro-Automatik, Germany). Before EPD the bath was ultrasonicated for at least 20 min using an ultrasonic processor (UP100H, Hielscher Ultrasonics GmbH). EPD was performed for 300 s. The same EPD procedure was used for all samples.

2.3. Material characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) was used to investigate the quality and composition of the EPD coating deposited onto the carbon fibers. SEM images of the samples before and after cycling were collected using a Zeiss Supra 55 VP FESEM at an acceleration voltage of 5 kV. EDX with elemental mapping was performed using the same instrument operating at an acceleration voltage of 20 kV. The cross-section and high magnification SEM images were collected using a Hitachi S-4800 SEM operated at an acceleration voltage of 2 kV.

2.4. Electrochemical characterization

For electrochemical cycling experiments, a pouch cell design was used. The EPD coated carbon fibers were dried in a vacuum oven overnight at 60 °C prior to cell assembly in a glove box with argon atmosphere (< 1 ppm H_2O and O_2). To ensure electrical contact an aluminum current collector was attached to the end of the carbon fiber tows on an uncoated part with silver glue, and then sealed inside the pouch outside of the active cell volume to ensure the electrolyte was not contaminated. A schematic of the pouch cell design is presented in Fig. S1. A half-cell setup was used with lithium foil as the common counter

Download English Version:

https://daneshyari.com/en/article/7214419

Download Persian Version:

https://daneshyari.com/article/7214419

Daneshyari.com