Electrochimica Acta 237 (2017) 119–126

Contents lists available at ScienceDirect

Electrochimica Acta

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

Ultra-flexible lithium ion batteries fabricated by electrodeposition and solvothermal synthesis

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ARTICLE INFO

Article history:
Received 7 November 2016
Received in revised form 21 March 2017
Accepted 27 March 2017
Available online 30 March 2017

Keywords:
Flexible battery
Lithium-ion battery
Conformal electrodeposition
Bending

ABSTRACT

Cathodes have been one of the major challenges of flexible batteries. The traditional slurry-based technologies lead to loose interparticle connection, which is vulnerable upon bending. The direct fabrication of cathode materials requires high temperatures, which may destroy flexible substrates. Here we developed an electrodepostion and solvothermal route to conformally coat cathode material on a flexible scaffold. The monolithic electrode enables an ultra-flexible lithium ion battery because of the close attachment of active materials to flexible scaffolds and the interlock effect between the hard shell and soft core. This ultra-flexible battery retains 58.8% of initial capacity even after bending 4000 cycles.

1. Introduction

Flexible batteries have been long expected for many decades [1–5]. Until recently, the growing market of flexible electronics such as wearable sensors, roll-up display, touch screen, flexible medical devices stimulates more research on flexible lithium ion (Li-ion) batteries [6,7]. A flexible battery has to be able to provide electrochemical energy storage and meanwhile accept a certain degree of mechanical deformation (such as bending and folding). Traditional Li-ion battery electrodes are usually fabricated by slurry-casting the mixture of active material particles, binders, and conductive agents on metal foils [8–10]. After drying, active material particles are held together by polymer binders. Although the slurry-based technologies have achieved tremendous commercial successes, they fall short of satisfying emerging needs for flexible electronics because of their intrinsically inflexible electrode structures, which are basically agglomerates of rigid particulate components [11,12]. The mechanical strain caused by repeated deformation inevitably leads to electrical discontinuities [13–15]. An alternative approach is to cast or infiltrate active material slurries into flexible scaffolds such as carbon nanotube (CNT)/nanofiber network, graphene foam, cellulose paper, textile, and so on [16–19]. By using the good flexibility of scaffolds, the resulting composite electrodes are able to accept the strains caused by mechanical deformation. Although modest strides have been made, these approaches do not change the intrinsic nature of the loose interparticle connections and thus still fail after extended bending tests due to electrical discontinuities caused by mechanical deformation.

The direct fabrication of active materials on flexible scaffolds is highly desired because of the following advantages: 1) the close attachment of active materials to scaffolds is enabled by the direct deposition; 2) the flexible conductive scaffold, as the continuous electron conducting pathway, is able to keep wiring active materials during bending; 3) the strains of active materials coating could be transferred to flexible scaffold and the detachment of active materials is, to some degree, avoided. However, most flexible scaffolds (metallic or carbonaceous materials) degrade at the synthetic temperatures (>700 °C) of cathode materials such as $LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$ [20–22] and lead to failure if conventional solid-state routes are employed [23,24]. Flexible cathodes have been one of the major challenges in the research and development of flexible batteries [1,25–27].

Atomic layer deposition (ALD), chemical vapour deposition, hydrothermal syntheses, and sol-gel routes have been developed to coat cathode materials on scaffolds or substrates. For example, Chen et al fabricated $LiFePO_4$ nanoparticles on graphene foam by in situ hydrothermal deposition [16]. Sun et al developed the new ALD procedure of depositing amorphous $LiFePO_4$ at 300 °C [28]. Although many reports have demonstrated that the direct fabrication of cathode materials on scaffolds have the potentials

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http://dx.doi.org/10.1016/j.electacta.2017.03.202
0013-4686/

to improve the bendability of flexible batteries, the maximum bendable cycles are still limited to a few hundred times (see the summary list of Table 1). The low bendable cycle numbers have severely hindered the development of flexible batteries.

Here we present a CNT@$LiMn_2O_4$ flexible cathode by an electrodeposition and solvothermal lithiation route. The batteries using CNT@$LiMn_2O_4$ demonstrate ultra-flexible properties. The fabrication procedure is illustrated in Fig. 1. Manganese dioxide (MnO_2) is conformally electrodeposited on CNT paper and then converted to spinel $LiMn_2O_4$ by solvothermal lithiation. Due to the conformal deposition, the lithiated MnO_2 closely attaches to the flexible CNT scaffold and enables an ultra-flexible Li-ion cathode. The resulting electrode is then assembled with graphitized carbon fiber (GCF) into a flexible Li-ion battery (Fig. 1d). The obtained battery could deliver about 58.8% of its initial capacity after bending for 4000 cycles. The good flexibility is attributed to the close adhesion of active materials to the flexible scaffold and the interlock effect between them, which are enabled by the monolithic structure and the conformal fabrication technologies.

2. Experimental

2.1. Preparation of flexible cathodes

A piece of commercial CNT paper (Time nano Corp.) was pre-treated in Ar gas at 1000 °C for 3 h. The annealed CNT sample was

Table 1
Summary of flexible Li-ion battery properties in literatures.

Cathode and Anode Materials	Electrode Structures or Fabrication Methods	Capacity Retention	Bending Cycles	Ref
$LiFePO_4$@graphene foam// $Li_4Ti_5O_{12}$@graphene foam	Hydrothermal synthesis on 3D graphene foam	98	20	[16]
$LiCoO_2$//$ZnCo_2O_4$ nanowire arrays@carbon cloth	Hydrothermal synthesis of nanowire arrays on carbon cloth	98.2	120	[17]
V_2O_5/CNT//Lithiated SnO_2/CNT	Electrospun nanocables	93.5	1	[18]
$LiCoO_2$//$Li_4Ti_5O_{12}$	Blade coating	92.3	1	[19]
$LiCoO_2$//V_2O_5/PPY	Hydrothermal synthesis of V_2O_5 NW, Vacuum filtration	93.3	10	[27]
Activated cotton textile/NiS_2-graphene//Li foil	Chemical synthesis on 3D porous structure	83.3	1	[29]
$LiCoO_2$//Si/rGO films	Vacuum filtration and blade coating cathode	87.5	1	[30]
$LiCoO_2$//Nitridated-Fe_2O_3@carbon cloth	Hydrothermal synthesized anode on carbon cloth and slurry-coated cathode	92.9	1	[31]
$LiCoO_2$//TiN@carbon fabric	Hydrothermal synthesis and annealing in NH_3 gas with blade coating cathode	97.5	1	[32]
$LiMn_2O_4$ nanowire//Mn_2O_3@Ti	Hydrothermal synthesis, annealing at high temperatures and blade coating cathode	~100	1	[33]
$LiMn_2O_4$//$Li_4Ti_5O_{12}$	Hydrothermal synthesis and blade coating	90.8	1	[34]
$LiCoO_2$/CNT//$Li_4Ti_5O_{12}$/CNT	Dip coating CNT	92	400	[35]
$LiCoO_2$//Graphene	Blade coating and CVD	90.9	1	[36]
$LiMn_2O_4$//In_2O_3@CNFs	Electrospinning and blade coating cathode	91.7	120	[37]
$LiMn_2O_4$/Carbon cloth//$Li_4Ti_5O_{12}$/ Carbon cloth	Hydrothermal synthesis and electrodeposition with slurry coated cathode	97.9	60	[38]
$LiFePO_4$//MnO_2 nanowire/MWCNT	Hydrothermal synthesis of MnO_2 nanowires and slurry coating	80.3	100	[39]
$LiCoO_2$/CNT//$Li_4Ti_5O_{12}$/CNT	Coating on CNT	–	50	[40]
$LiCoO_2$//Si nanowire arrays@carbon	3D Si nanowires by CVD	Voltage	160	[41]
Zn-Air battery	Fibrous electrodes with Zn spring	Voltage	100	[42]
MnO_2//Zn	Ink-print to mesh electrodes	85.2	1	[43]
CNT/SnO_2//Li	Vacuum filtration and Polyol method	84.6	1	[44]
$LiCoO_2$//Li	Sputtering thin film	Voltage	20000	[45]
3D Graphene/$LiFePO_4$//Li	Solvent evaporation	86.3	100	[46]
$LiCoO_2$//TiO_2@TiN	Hydrothermal synthesis of anode materials on 3D carbon cloth and slurry coated cathode	97	1	[47]
Twisted CNT@Si//Li	CVD coating and twisted fibrous shape	94.3	100	[48]
$LiCoO_2$//PDMS-CNT	Porous nanocomposites	–	Folding	[49]
$LiCoO_2$//MoS_2@Carbon cloth	Hydrothermal synthesis of MoS_2 nanoflake array on carbon cloth and slurry coated cathode	–	50	[50]
V_2O_5 nanowire//Li	Hydrothermal synthesis of V_2O_5 nanowire, vacuum filtration and slurry coated cathode	–	–	[51]
$LiCoO_2$//$ZnCo_2O_4$@Carbon fibers	Hydrothermal synthesis of urchins on carbon fiber and slurry coated cathode	91.7	250	[52]
TiO_2/CNT//Li	Hydrothermal, synthesis of TiO_2 nanofiber vacuum filtration and slurry coated cathode	–	–	[53]
$LiCoO_2$//Fe_2N@Carbon textile	Hydrothermal synthesis of Fe_2N nanoparticles on textile, high temperature anneal in NH_3 gas and slurry coated cathode	98.1	1	[54]
$LiNi_{0.5}Mn_{1.5}O_4$/CNT//Li	Solid state reaction and vacuum filtration	Voltage	1	[55]
$LiCoO_2$//$Li_4Ti_5O_{12}$	Polymer electrolyte and slurry coating	Voltage	15	[56]
$LiCoO_2$//Ge nanowire/ Carbon nanofibers	Electrospun nanowires, in-situ growth of Ge NW	–	–	[57]
$LiCoO_2$//NiO@Carbon cloth	Hydrothermal and calcined	–	1	[58]
$LiFePO_4$//$Li_4Ti_5O_{12}$	Spray painting	–	1	[59]
$LiCoO_2$//Graphene nanoplatelets	Vacuum filtration, annealed in air	–	1	[60]
$LiCoO_2$//Porous nanofibers	Electrospun fibers, carbonized in high temperature	–	1	[61]
$LiFePO_4$//$CoMoO_4$/PPY	Hydrothermal synthesis of nanoarrays on carbon cloth	–	–	[62]
3D CNT//Li	CVD	Voltage	1	[63]
$LiCoO_2$//MnO_2@Carbon foam	Hydrothermal synthesis of MnO_2 fabric foam, CVD carbon coating	–	1	[64]
SWCNTs//Li	Vacuum filtration	81.3	1000	[65]
$LiFePO_4$//Zn_3P_2 nanowire/ Carbon cloth	CVD synthesis of nanowires and slurry coated cathode	97.2	100	[66]
TiO_2/carbon fiber//Li	Hydrothermal synthesis of nanocrystals and annealing	–	–	[67]

CNT: Carbon nanotube, CNFs: carbon nanofibers, PDMS: Polydimethylsiloxane, PPY: Polypyrrole, MWCNT: Multiwall carbon nanotubes, SWCNT: Singlewall nanotube, CVD: chemical vapor deposition.
Cathodes and anodes are separated by a double slash.