Electrochimica Acta 216 (2016) 1–7

Contents lists available at ScienceDirect

Electrochimica Acta

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

Polyimide binder by combining with polyimide separator for enhancing the electrochemical performance of lithium ion batteries

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ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 29 July 2016
Accepted 15 August 2016
Available online 17 August 2016

Keywords:
Lithium ion battery
Polyimide
Separator
Binder
Rate Performance

ABSTRACT

Lithium ion battery (LIB) has been assembled by a polyimide (PI) binder, which is prepared by one-pot solution polycondensation, and PI non-woven separator. Compared to the cell using the traditional PVDF binder and polyethylene (PE) separator, the cell with PI binder and PI separator (PI-PI) not only has a better thermal stability but also displays significantly improved electrochemical performance, especially rate performance and cycling behavior. The thermogravimetric analysis (TGA) shows that the temperature of the weight loss of 10% of PVDF and PI is 464.6 °C and 525.9 °C, respectively. The properties of the separator, including wettability, electrolyte uptake and mechanical performance are tested. Owing to the hydrophilic imide group and the rigid aromatic nucleus. These properties make a possibility of a battery to meet higher requirements. In the terms of electrochemistry, when the current density over 1C, the cell with PVDF binder and PE separator (PVDF-PE) only retains no more than 61% of its capacity at a rate of 0.05C. However the cell that based on PI-PI still maintains 72.6%. Besides, the cycle performance of PI-PI gains a significant improvement. It can stay over 85% capacitance retention ratio after 200 cycles at a rate of 1C, while the PVDF-PE is only 57.68%. The outstanding improvement of the rate capability is due to the reduction of internal resistance of the battery.

1. Introduction

Lithium ion battery (LIB) has succeeded in attracting more and more attention as one of a potential power source, which owes to their high energy density and outstanding cycle life. As is much more widely applied to large-scale battery including electric vehicle (EV) as well as hybrid electric vehicles (HEV), cycle retention, energy density, the safety issue and power capability of the lithium ion battery have to achieve higher standards, compared to the small electronic such as the cellular phone, laptop and digital cameras [1–5].

As an important part of the battery, the binder has great influence on the electrochemical performance of the whole battery. And the most commonly used binder is Poly(vinylbenzene fluoride) (PVDF) on account of its excellent binding capability, ability to absorb electrolyte, chemical and electrochemical stability [4,6–12]. However, its low melting point results in its poor thermal stability, which will have the adverse impact on security [13]. Besides, when PVDF dissolved in nonaqueous liquid electrolytes, it will gain a viscous fluid or gel polymer electrolyte, which will lead to desquamation of electrode particles. The rate performance and cycle life will be shortened [14–16].

Considering addressing these problem, various researchers began to turn their attention to seek the binder with good thermal stability and insolubility in electrolytes. Polyimide, which is widely known as a polymer with high temperature resistance, remarkable mechanical strength, good chemical resistance and low dielectric constant, has been widely used in many fields [17–19]. And based on these considerations, many researcher began to apply polyimide as binder in LIB. Ohta, et al. found that PI can improve the reversible capacity of rechargeable LIB effectively and the capacity became larger with the carbonyl oxygen in the monomer unit increasing [20]. Choi, et al. reported that introducing the PI as the cathode binder can significantly improve the cycle performance of LIB under 60 °C conditions [21]. Kim, et al. compared the electrochemical performances of the Si cells with PVDF and PI. They showed that the Si-PI electrode could suppress the physical stress caused by induced phase transition in the alloy reaction of Li^+[22]. Yuan, et al. combined PI with the graphite-Si/SiOx/C composite anode and found the retention of cycle stability is much higher after 30 cycles. In addition, the composite anode showed

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http://dx.doi.org/10.1016/j.electacta.2016.08.065
0013-4686/

outstanding mechanism[23]. However, They all use the polyolefin membrane, such as polyethylene (PE), polypropylene (PP) [20–23]. The difference of the molecular structure of binder and separator leads to the poor coordination. In addition, the polyolefin membrane has the low wettability of the electrolyte, which would raise the internal resistance of the batteries [24,25]. Both of the two factors will cause the terrible performance of rate and cycle, especially at the high current density.

In this paper, we report a simple method to gain a LIB with high temperature resistance and rate performance where polyimide materials act both as binder and separator. The coordination of PI binder and PI separator can enhance the affinity of the electrode and minimize the internal resistance efficiently, which makes it operate much better in the LIB than the conventional ones. And the polyimide materials with high molecular weight are synthesized by a simple one-pot method which is gained by polycondensation of dianhydride and diamine at high temperature. The heterocyclic imide rings on the backbone and aromatic rings on the backbone and/or side groups of the polyimide materials greatly contribute to its high temperature resistance. The difference of PVDF and PI on thermal stability has been investigated. And the existence of imide group of PI separator makes the possibility of improving the surface polarity and leaves it wetted with the electrolyte sufficiently. Besides, the electrolyte wettability of the PE and PI has also been tested. Except for those, we measure the electrochemical performances of the cells with different binders and separators. In the end, we gain a coin cell, which has the wonderful thermal stability and rate performance.

2. Experimental

2.1. Sample preparations

3,3′4,4′-Diphenylsulfonetetracarboxylic dianhydride (DSDA) is purchased from Tokyo Chemical Industry Co., Ltd. 1,4-bis (4-amino-2-trifluoromethylphenoxy) benzene (6FAPB), 4,4′- Oxydianline (ODA) and isoquinoline are gained from Beijing POME Sci-tech Co., Ltd., Sinopharm Chemical Reagent Co., Ltd. and Beijing jkchemical, cn., respectively. Other chemicals, including N-methyl-2-pyrrolidinone (NMP), toluene and ethanol, are bought from Shanghai Lingfeng Chemical Reagents Company. All of the powders are dried in a vacuum oven beforehand for use. Toluene is refluxed at its boiling point.

2.2. Synthesis of Polyimide

The PI is prepared from DSDA, ODA and 6FAPB by the following steps as the method of Wang, et al. A completely dried 500 mL four-necked flask is equipped with a mechanical stirrer, a nitrogen inlet, a thermometer, and a Dean-Stark trap. The mixture, which is consisted of 6FAPB (8.0300 g, 18.75 mmol), ODA (3.7550 g, 18.75 mmol) and NMP is added into the flask at room temperature in nitrogen atmosphere. When the mixture is completely dissolved and forms a homogeneous solution, DSDA (13.435 g, 37.5 mmol), isoquinoline (0.2 g) and toluene (22.5 mL) are added. The solution is stirred for 10 h at ambient temperature, then heats it to 180 °C and maintained for 10 h (the reaction equation is shown in Fig. 1). The water formed in the reaction of imidization is removed simultaneously by azeotropic distillation. After the solution is cooled down to 90 °C, the viscous solution is poured slowly into excess ethanol and washed thoroughly with ethanol. The PI is gained after dried in vacuum at 120 °C for 8 h [26]. The PI which will be used as the binder in coin-type half cell is reserved in the dryer.

2.3. Assembly of LIB

The slurry consisting of graphite as the active material, Denka black (DB) as the conducting agent, and PI as the binder dissolved in NMP is coated on the copper foil, playing the role of the working

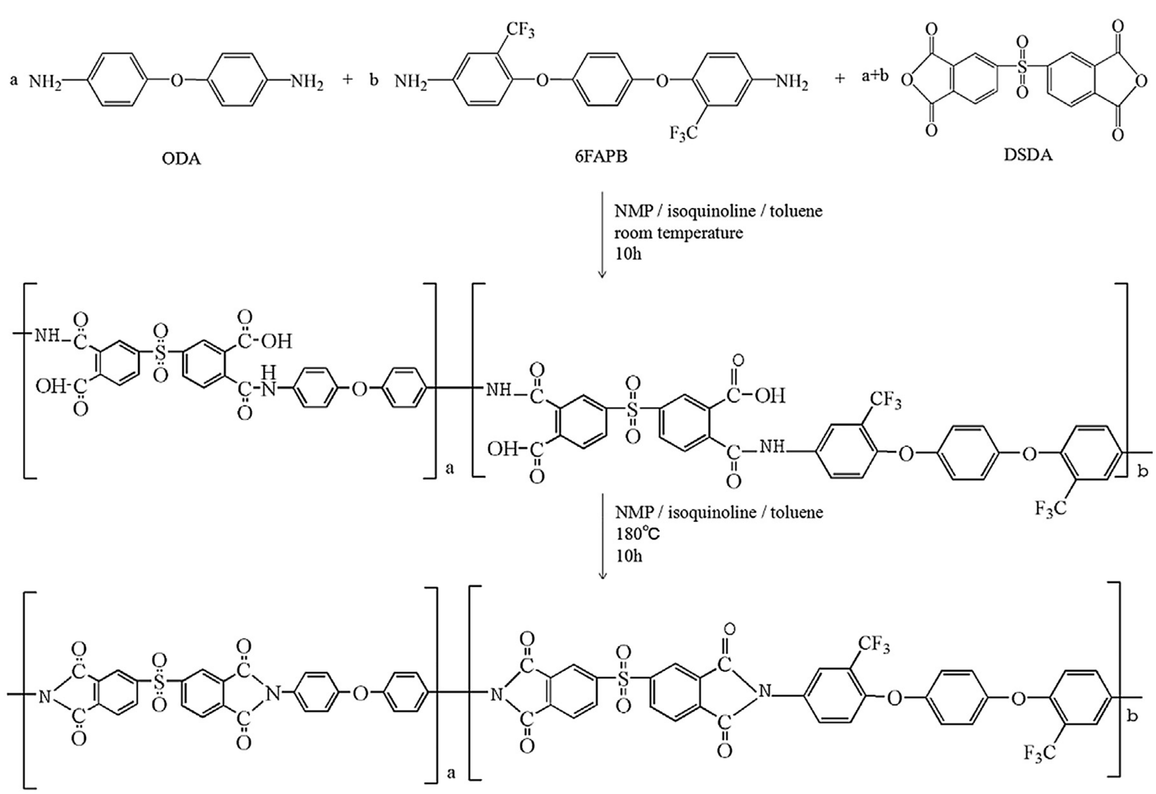

Fig. 1. Synthesis of PI.