



Polyethylene separator: stretched and coated with porous nickel oxide nanoparticles for enhancement of its efficiency in Li-ion batteries



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ARTICLE INFO

Article history:

Received 14 April 2014

Received in revised form 3 June 2014

Accepted 4 June 2014

Available online 11 June 2014

Keywords:

Separator

Nickel oxide

Coating

Safety

Capacity retention

ABSTRACT

Polyethylene separator of 300% uni-axial stretching ratio is dip-coated with sol-gel synthesized NiO nanoparticles. The crystalline structure and the porous nature of the synthesized NiO nano particles are confirmed using X-Ray diffractometer (XRD) and field emission scanning electron microscope (FE-SEM). The dip-coated stretched PE separator is to be observed with high ionic conductivity of 2.12 mS cm^{-1} and lower MacMullin number of 3.9 compared to the uncoated stretched PE separator. With regard to the thermal behavior coated separator has around six times lower enthalpy value, lower weight loss, and lower thermal shrinkage behavior as proven by differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA) and even when exposed to high temperature, respectively. The above characteristics of coated separator enhance the safety of Li-ion batteries. The electrochemical property is tested using electrochemical cyler and Li-ion cells with coated separator possess a similar initial discharge capacity but with enhanced capacity retention ratio of 95.73%. The obtained cycling behavior is well scrutinized by plotting the discharge profile and also by measuring its interfacial stability i.e., charge transfer resistance (R_{ct}) based on cycle numbers using electrochemical impedance spectroscopy (EIS). Improved rate capability behavior of Li-ion cells with coated separator is also demonstrated.

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1. Introduction

Several synthesis procedures, composites, alloys, different doping and coating elements had been studied by the researchers for the anode and cathode electrodes used in Li-ion batteries to improve the energy density, safety and to reduce the cost [1], whereas the separators received very less attention. Very few ceramic compounds such as SiO_2 [2–4], Al_2O_3 [5], and TiO_2 [6] had been examined by the researchers for improving the efficiency of separators. Also not much interest had been shown on the structural modifications of those ceramic compounds. Ceramic compounds are generally coated over the polymer separator or doped into the polymer matrix to enhance the mechanical strength, wettability, ionic conductivity, and thermal behavior.

Separators used in Li-ion battery plays major role in preventing the electronic contact between the cathode and anode electrodes to avoid short circuit and also it enables the ionic transport between electrodes. Polyethylene (PE), polypropylene

(PP) and trilayer PP/PE/PP are the most commonly used separators [7]. Factors such as mechanical and dimensional stability, physical strength, wettability, electrolyte (ionic) resistance, degradation by electrolyte, migration of particles or colloidal or soluble species between electrodes, and thickness [8] can be concentrated for the better performance of the separator in Li-ion batteries. In specific the shutdown (SD) behavior of the separator have to be improved largely, because greater the mechanical integrity at high temperature is the greater margin of safety, the separator can provide. The loss of mechanical integrity would allow direct contact between the electrodes, which results in thermal runaway. Various efforts such as stretched separators [9,10], nanocomposite-coated PE separators [11], nonwoven-ceramic composite separators [12], nanofiber-based separators [13], and plasma treated separators [14] have been taken to improve the efficiency of the separator in Li-ion batteries.

The stretched separators had been reported earlier by us for its improved electrochemical behavior by determining its pore size, porosity, Gurley value, MacMullin number, and tortuosity [15]. Further in an effort to improve the properties of stretched separators, in this research we have focused on the synthesis of nickel oxide (NiO) nano particles for coating on the 300% stretched PE

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separator to improve its efficiency in Li-ion batteries. Apart from other predominantly used ceramic materials such as SiO_2 , Al_2O_3 , etc., NiO is chosen due to its low cost, easy to process using variety of methods, and environmental benign nature. We have chosen 300% stretched PE separator with regard to its affirmative behavior, which we reported in our previous research works [15,16]. Porous nature of the synthesized NiO nanoparticle and its structure is characterized using FE-SEM and XRD respectively. Physical properties, thermal properties, and electrochemical behavior of the coated and uncoated samples are clearly demonstrated in view for its application in Li-ion batteries.

2. Experimental

2.1. NiO synthesis and characterization

Well known sol-gel method is employed for preparation of NiO nanoparticles, where $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid monohydrate were accurately weighed and dissolved in deionized water by continuous stirring for 24 h at 50°C . After this process green gel is obtained and it is heated at 100°C for 12 hours. Such prepared precursor is cooled for a while and it is calcined in a programmable furnace at the rate of $1^\circ\text{C}/\text{min}$ to attain 600°C and allowed to stay at that temperature for 6 h. The prepared NiO nanoparticles are characterized by XRD and FE-SEM for its structural and surface morphological behavior.

2.2. Dip-coating process

For the dip-coating process, NiO and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) nanoparticles in the weight ratio of 9:1 were taken. PVDF-HFP is completely dissolved in acetone by vigorous stirring and then NiO nanoparticles are added with continued stirring for 5 h. The prepared solution is sonicated for 2 minutes before dip-coating process. The PE separator, with stretching ratio of 300%, thickness of $20\ \mu\text{m}$, mean pore size of $0.08\ \mu\text{m}$ and porosity of 45% provided by CS Tech Co. Ltd, South Korea is coated on both sides by dipping it into the sonicated solution for a minute. Then the coated PE separator is dried using vacuum dryer at the temperature of 50°C for 4 h. The weight ratio of materials used and dip-coating time is optimized after several trials to avoid drastic increase in thickness. The final thickness was observed to be around $24 \pm 1\ \mu\text{m}$.

2.3. Physical characterization

The structure of the synthesized NiO nanoparticles, the coated and uncoated separator is examined through XRD and the surface morphology of the synthesized NiO nanoparticles, the coated and uncoated separator is characterized using FE-SEM (Leo Supra 55, Genesis 2000, Carl Zeiss) analyzer. For FE-SEM analysis of the coated and uncoated separator samples were dipped into liquid nitrogen for 5 min. Then the sample is attached to the holder with carbon tape, and platinum coating is applied to enhance electronic conductivity.

The wettability of the coated and uncoated PE separator is tested for the electrolyte 1 M LiPF_6 in EC:DEC (1:1, vol%) used in Li-ion battery fabrication, by contact angle method. Contact angle is carried out using sessile drop method with a KSV Sigma 701 Tensiometer. Surface energies were calculated by measuring the contact angle of the testing liquid on the sample surfaces at room temperature.

The ionic conductivity (σ , mS cm^{-1}) measurement is carried out using CR 2032 coin cell assembled with the separator immersed in the 1 M LiPF_6 in EC:DEC (1:1, vol%) electrolyte and placed between two stainless steel (SS) electrodes ($16\ \text{mm}$ diameter). Cell assembling is performed in argon atmosphere. Assembled cell is kept with

no run for 24 h, so that the separator gets well saturated with the electrolyte. Measurements were carried out at ambient temperature using EIS (IVIUM technologies instruments) over the frequency range from 0.1 Hz to 100 kHz at 10 mV scan rate. The ionic conductivity of separator σ_s is calculated using the Eq. (1).

$$\sigma_s = \frac{l}{R_b r^2 \pi} \quad (1)$$

Where l is the thickness and r is the radius of the separator used, R_b is the bulk resistance obtained from AC impedance measurements.

MacMullin number (N_m) is also calculated using conductivity measurements. MacMullin number describes the relative contribution of a separator to cell resistance. It is calculated from the following Eq. (2)

$$N_m = \frac{\sigma_e}{\sigma_s} \quad (2)$$

Where σ_e is the conductivity of the used electrolyte, which is $8.3\ \text{mS cm}^{-1}$ and it is commonly used for both separators [10]. σ_s is the conductivity of separator.

2.4. Thermal characterization

The thermal property of the coated and uncoated separator is characterized using DSC analysis. DSC experiment is carried out using TA Instruments, Model 2920 where the samples are placed in sample pan made of aluminum. DSC measures the difference of energy required to heat a reference pan and a sample pan at a fixed temperature sweep rate. Here the sample is scanned between 50°C to 200°C by heating at a rate of $20^\circ\text{C min}^{-1}$. DSC provides information regarding the melting point and the SD behavior of the coated and uncoated separator. From the DSC curve degree of crystallinity (X_c) is also calculated using the following Eq. (3)

$$X_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\% \quad (3)$$

Where ΔH_f and ΔH_f^* are melting enthalpies of the present sample and of perfectly crystalline PE, respectively. In this study $288.0\ \text{J g}^{-1}$ is used for ΔH_f^* [17]. TGA is then used to evaluate the weight loss of the coated and uncoated separators. During TGA, separators were heated from 25°C to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 atmosphere. The mandatory thermal shrinkage property is determined by measuring the dimensional change of coated and uncoated separators, before and after being exposed to temperatures of 150°C for 0.5 h.

2.5. Electrochemical characterization

The cycling performance during charge and discharge is carried out using the 2032 coin cell assembled by sandwiching the separator between the $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode prepared by doctor blade method and lithium metal anode along with the 1 M LiPF_6 in EC:DEC (1/1, vol%) electrolyte. The above mentioned cathode is prepared by mixing the active material $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$, the conductive agent super p black, and the binder PVDF in the weight ratio of 90:5:5, respectively. This test is conducted for both the coated and uncoated separators. The cell is cycled between the cut-off voltage of 2.7 V and 4.2 V at constant 0.2 C-rate at room temperature using BT2000 Arbin cyler. From this, the specific discharge capacity, discharge profiles of 1st, 25th, and 50th cycles, and capacity retention ratio for 50 cycles are observed and interpreted.

EIS measurements were carried out for half cell, which consists of $\text{Li}[\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ as cathode, lithium metal as anode, coated and uncoated separators, and 1 M LiPF_6 in EC:DEC (1/1 vol%) electrolyte at specific intervals of charge-discharge cycle, namely after

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