

A high voltage cathode prepared by using polyvinyl acetate as a binder



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ARTICLE INFO

Article history:

Received 7 November 2014

Received in revised form 25 February 2015

Accepted 6 March 2015

Available online 21 March 2015

Keywords:

Poly vinyl acetate

Composite cathode

Lithium battery

LiNi_{0.5}Mn_{1.5}O₄

ABSTRACT

This paper describes the preparation and characterization of a high voltage composite cathode for lithium ion-batteries based on LiNi_{0.5}Mn_{1.5}O₄ as the active material and poly vinyl acetate (PVAc) as the binder. To assess the effect of the PVAc binder on the electrode properties, the PVAc-based electrode is compared with a traditional one prepared by using Teflon as the binder. The electrode morphologies are investigated by scanning electron microscopy and the thermal behavior of the PVAc-based electrode evaluated by thermo gravimetry and differential thermal analysis. The distribution of oxygen, manganese, and nickel on the electrode is investigated by X-ray electron diffraction spectroscopy. The electrodes are used as cathodes to prepare lithium metal cells and their electrochemical properties are investigated through galvanostatic charge/discharge cycles conducted at various discharge currents.

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1. Introduction

The research activity on high voltage cathode materials represents one of the key challenges for developing new advanced batteries with higher specific energies. Among the various high voltage cathode, LiNi_{0.5}Mn_{1.5}O₄ (LNMO) spinel is emerging as one of the most promising active materials for the construction of high energy Li-ion batteries [1–7]. This is mainly due to its high theoretical gravimetric specific capacity of 146.7 mAh g⁻¹ coupled with a high working voltage (about 4.7 V below the Fermi energy of a lithium metal anode) leading to a theoretical gravimetric specific energy as high as 650 Wh kg⁻¹ [7]. Due to the reduced nickel content in the material the use of LNMO is also attractive from an economical point of view [8]. One of the main problems encountered in working with high voltage cathode materials is related to their low stability against the electrolyte [8]. The poor stability can cause unwanted side reactions that can reduce the efficiency and the cycle life of the battery. These reactions can occur during overcharge or overdischarge and cause electrolyte decomposition, passive film formation, active material dissolution, and other phenomena [9]. For this reason the research activities on high voltage batteries should mainly be addressed to study the interactions between the electrolyte and the cathode active material in order to significantly improve the energy of the battery without sacrificing its safety. Furthermore, when introducing a new binder, its stability towards the active

material has to be accurately investigated. Among the binders currently used in lithium-ion battery technology, poly(vinylidene fluoride) (PVdF) is the most popular one and it has been widely adopted in both the anode [10] and the cathode [11]. The reasons for its success are mainly due to its good electrochemical stability and high adhesion both to the electrode active material and the current collector. Usual PVdF-based electrodes processing relies on the use of an organic solvent (eg. N-methyl-2-pyrrolidone, NMP) to dissolve the fluorinate polymer. For cost, safety and environmental considerations, in these last years the NMP tends to be replaced by other solvents more compatible with the environment. Currently, water-based processes are intensively investigated in order to replace the machining employing organic solvent with more affordable and environmentally benign aqueous fabrication processes [12–14]. These processes require the use of alternative binders to PVdF that must necessarily be soluble or dispersible in water. Wang et al. prepared high voltage cathodes based on LiNi_{0.4}Mn_{1.6}O₄ as the active material by using carboxymethyl cellulose (CMC) as a binder finding that CMC can make LiNi_{0.4}Mn_{1.6}O₄ deliver better electrochemical performance [15]. In order to reduce both the process costs and the environmental impact, in a previous paper we proposed the use of PVAc as a binder for the fabrication of cathodes for lithium-ion battery [16]. PVAc is a not toxic thermoplastic resin produced by the polymerization of vinyl acetate monomer [CH₃COOCHCH₂]. PVAc is stable, non-flammable and not hazardous health-wise product and, furthermore, its cost is very competitive when compared to other polymers. PVAc is water dispersible and it is commercialized as a water emulsion, with a solid content of 50–55%. Since its discovery in 1915 by Klatte [17], PVAc has found many industrial applications and new areas are still being added. The aim of the present work is to demonstrate the possibility to use PVAc as a

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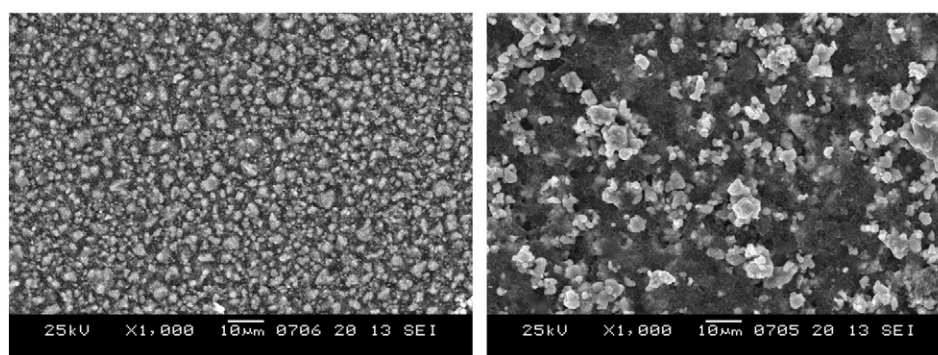


Fig. 1. High magnification micrographs of the Teflon-based (left) and PVAc-based (right) electrode surface.

binder in combination with high voltage cathode materials. For this purpose we prepared and characterized electrodes using PVAc as the binder and spinel LNMO as the cathode active material.

2. Materials and methods

2.1. Preparation of PVAc-based cathode

The preparation described herein refers to a 50 cm² of cathode. 0.75 g of LiNi_{0.5}Mn_{1.5}O₄ (Nanomyte SP-10, NEI Corporation Somerset, NJ, United States) and 0.10 g of carbon black (Super P, MMM Carbon, Belgium) were weighed and transferred to a mechanic mill. The powder was mixed by operating the device for a few minutes. A water dispersion of PVAc with a solid mass fraction of 50% was used (Vinavil SpA via Valtellina, 63-20159 Milano - Italia). 0.30 g of the PVAc dispersion was diluted with 8 g of water. The suspension of PVAc was added to the powder mixture and mixed by operating the mill for a few minutes. The so obtained suspension was used to paint a thin aluminum sheet covering a surface area of 50 cm². After drying in air at 130–150 °C, the procedure was repeated as many times it was necessary to use up the entire suspension. The electrode composition was 75 wt.% LiNi_{0.5}Mn_{1.5}O₄, 15 wt.% PVAc, and 10 wt.% SuperP. Electrodes were punched in the form of disks, typically with a diameter of 12 mm and a thickness of 70–94 µm. The electrode weight ranged from 18.4 to 20.6 mg, which corresponds to a specific mass loading of 16.2–18.2 mg cm⁻². Prior of the electrochemical characterization the electrodes were dried by heating under vacuum at 110 °C for 12 h.

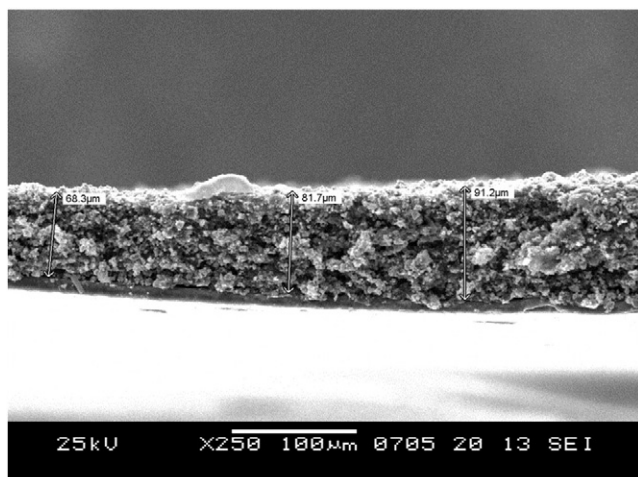


Fig. 2. Low magnification image ($\times 250$) of the PVAc-based electrode cross section.

2.2. Preparation of Teflon-based cathode

A dry mixing procedure was used to prepare the Teflon-based cathode. The electrodes were prepared without any current collector. 0.5 g of the active material and 0.1 g of carbon were weighted and mixed in a mortar for 5 min. 0.07 g of the binder (Teflon, DuPont) was weighted and added to the mixture. The blend was intimately mixed to obtain a plastic-like material. Composite electrode tapes were made by roll milling the plastic-like material. The quantities of active material, binder and carbon in the tape were 75 wt.% LiNi_{0.5}Mn_{1.5}O₄, 10 wt.% Teflon, and 15 wt.% SuperP. Electrodes were punched in the form of disks, typically with a diameter of 12 mm and a thickness of 80–92 µm. The electrode weight ranged from 21.0 to 24.0 mg. The specific mass loading was 18.6–21.2 mg cm⁻².

2.3. Chemical–physical characterization of the electrodes

The morphology and composition of the tapes were evaluated by a scanning electron microscopy (SEM). High magnification microphotographs were obtained by means of a Jeol JSM-5510LV. The surface chemistry was mapped by energy dispersive X-ray spectroscopy (EDS) with an IXRF EDS-2000 system. The specimens were directly mounted onto a conductive carbon double face tape, which was previously mounted on a slab. The density of the materials was determined by using a helium pycnometer (Accupyc Micromeritics).

2.4. Thermal characterization

Thermal stabilities were verified in nitrogen using a simultaneous TG-DTA (Q600 SDT, TA Instruments) equipped with the Thermal Solution Software (version 1.4). The temperature was calibrated using the nickel Curie point as the reference. The mass was calibrated using ceramic standards provided with the instrument. High purity aluminum oxide was used as the reference material. Open platinum crucibles (cross-section = 0.32 cm²) were used to contain the samples. The experiments were performed on 10–12 mg samples that were stored, handled, and weighed in a dry-room. The thermal stability was investigated by heating the samples from room temperature up to 550 °C at a rate of 10 °C min⁻¹. The onset temperature was calculated by thermal analysis software (Universal Analysis version 2.5) as the intersection between the extrapolated baseline weight and the tangent through the inflection point of the weight vs. temperature curve.

2.5. Electrochemical characterization

The electrochemical performance and cycle life of the electrodes were examined in 2032-type coin cells. Two electrodes lithium cells, in which lithium acted both as counter and reference electrode, were prepared. A glass fiber was used as the separator. Coin cells were filled with a 1.0 M solution of LiPF₆ in ethylene carbonate/diethyl carbonate

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