



Electrochemical performance of Li-ion batteries assembled with water-processable electrodes



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ABSTRACT

This paper describes the preparation and electrochemical characterization of Li-ion batteries prepared with electrodes containing non-fluorinated water dispersible polymers as electrode binders. Two commercial adhesives based on polyvinyl acetate and polystyrene acrylate, were used as the positive and negative electrode binders, respectively. The main advantages to using these polymers are related to their low cost, large diffusion, and negligible toxicity. Furthermore, since the polymers are water dispersible their use allows replacing the organic solvent, employed to dissolve the fluorinated polymer normally used as the binder in lithium battery technology, with water. In such a way it is possible to decrease the hazardousness of the preparation process as well as the production costs of both the electrodes. In the paper the preparation, characterization and the electrochemical performance of the Li-ion batteries obtained by coupling the two electrodes are described.

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1. Introduction

Lithium-ion batteries are generally assembled by sandwiching a thin sheet of porous separator between two composite electrodes. The negative electrode contains graphite or other carbonaceous materials as the active material while lithiated oxides or phosphates of transition metals are used for the cathode. The composite electrodes also contain carbon to enhance the electric conductivity. The electrode active materials and the carbon are held together by a binder which primarily ensures the mechanical stability of the electrodes. The traditional polymer used for producing electrode for Li-ion batteries is the polyvinylidene fluoride (PVdF), both in the cathode and in the anode. The production process (solvent-based) for the electrode manufacturing involves the following steps: mixing the powder of the active material with carbon, dissolving the PVdF with the solvent, mixing the powders with the solution to form a slurry, spreading the slurry on a current collector and drying the electrode while recovering the solvents [1]. The solvent commonly used to dissolve the fluorinate polymer is N-methyl pyrrolidone (NMP). NMP is a toxic substance that can provoke cell mutagenicity, carcinogenicity and reproductive toxicity. For these reasons the NMP cannot be left free in the environment and it must be recovered in the drying phase. For environmental consistency and

cost considerations, the replacement of organic solvent base process with an aqueous based process is gaining favor and has attracted significant interest [2]. In literature it is possible to find several papers dealing with the preparation of negative electrodes for Li-ion battery based on water soluble or water dispersible polymers. Among the various polymers compatible with water, the aqueous emulsion of styrene-butadiene rubber (SBR) mixed with sodium carboxymethyl cellulose (CMC) is the most commonly used binder for anodes and cathodes of Li-ion batteries [3]. The effects of SBR/CMC and polyvinylidene difluoride (PVDF) binders on the electrochemical characteristics of a type of micro-sized mesocarbon microbead (MCMB) anode were investigated by Yen et al. [4]. They found that the use of SBR/CMC binder reduces the first-cycle irreversible capacity loss and, most surprisingly, enhances the high-temperature (55 °C) cycle-life of the battery [5]. Besides the use of SBR/CMC it is possible to find in the literature other water-compatible polymers used as binders for the preparation of graphite-based electrodes for lithium ion batteries. Nguyen and Oh used poly(acrylonitrile-butyl acrylate) (P(AN-BA)) as a binder [6]. The electrochemical performance of these electrodes was found superior when compared to electrodes prepared with SBR binder. Ling et al. proposed the Eastman AQTM55S polymer (EAQ) as an alternative to the conventional PVDF, CMC and SBR binders [7]. Lithium and sodium salts of carboxymethyl cellulose (LiCMC and NaCMC) and Xanthan Gum (XG) or the conjugated polymer poly(3,4-ethylenedioxythiophene) (PEDOT) were investigated as binders for MCMB carbon anodes [8]. In order to improve the negative electrode characteristics of a graphite electrode in a

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propylene carbonate (PC)-containing electrolyte, Koichi et al. [9] have prepared a graphite negative electrode coated with a water-soluble polyacrylic acid (PAA) as a binder. Park et al. [10] have investigated the use of polyacrylic acid (PAA) as a binder for silicon-based anode finding that the electrode containing the PAA as a binder has a low irreversible capacity at the first cycle compared to other electrodes. On the other hand, the publication of papers dealing with the use of water-dispersible polymers for the preparation of cathode electrodes is more recent. Porcher et al. [11] investigated the use of polyvinyl alcohol and polyethylene glycol or of a butadiene–acrylonitrile copolymer rubber latex as cathode electrode binders. Guerfi et al. [12] reported on the characterization of LiFePO_4 cathodes obtained by using an elastomer based on saturated organic compounds. Aqueous-based pastes to fabricate the cathode of lithium-ion battery were investigated by Lee et al. using carboxymethyl cellulose and poly(acrylic acid) as a binder [13]. The effects of additions of dispersants, poly(4-styrene sulfonic acid), poly(ammonium acrylate) and poly(acrylic acid-co-maleic acid) on the dispersion and electrochemical properties of carbon-coated lithium iron phosphate cathodes were studied by Li et al. [14,15]. Carboxymethyl chitosan was recently reported as a water soluble binder for the positive electrode of Li-ion batteries by Sun et al. [16] while Zhon et al. [17] used a mixture of carboxymethyl chitosan and chitosan lactate.

In previous works [18,19] we reported on the preparation of electrodes for Li-ion batteries based on polyvinyl acetate (PVAc) and polystyrene acrylate (PSA) used as binders in the cathode and in the anode, respectively. In this work we used the previously described electrodes to assemble Li-ion batteries. The batteries were tested and in this paper we are reporting their electrochemical behavior as a function of discharge rate and cycle number.

2. Experimental

2.1. Preparation of the composite cathode

1.5 g of lithium iron phosphate (Gelion lib Group, ShanDong, PR China) and 0.25 g of carbon black (Super P, MMM Carbon) were weighed and then transferred to a mechanical mill. The mixture of powders was mixed by operating the device for a few minutes. 0.5 g of 50 wt.% PVAc (Vinavil SpA, via Valtellina, 63-20159 Milano–Italia) was dispersed in 5 g of water. The suspension of PVAc was subsequently added to the powder mixture and the components were mixed by operating the mill for a few minutes. The suspension that was thus obtained was used to paint an aluminum sheet covering a surface area of 100 cm^2 . After drying in air at $130\text{--}150 \text{ }^\circ\text{C}$, the procedure was repeated as many times as was necessary to use up the entire suspension. A typical positive electrode composition was 75 wt.% LiFePO_4 , 12.5 wt.% PVAc, and 12.5 wt.% Super P.

2.2. Preparation of the composite anode

A procedure quite similar to that reported for the preparation of the cathode was used for the preparation of the negative electrode. 0.7 g of graphite (Gelion lib Group, ShanDong, P.R. China) and 0.04 g of carbon black (Super P, MMM Carbon) were weighed and then transferred to the mill for the mixing. 0.10 g of Pattex PL50 (Henkel Loctite Adesivi S.r.l., Milano) with a solid mass fraction of 90% was dispersed in 3 g of water. The suspension was subsequently added to the powder mixture and the components were mixed by operating the mill for a few minutes. The suspension that was thus obtained was used to paint a copper sheet covering a surface area of 100 cm^2 . After drying in air at $130\text{--}150 \text{ }^\circ\text{C}$, the procedure was repeated as many times as was necessary to use up the entire suspension. A typical negative electrode composition was 84.4 wt.% graphite, 10.8 wt.% Pattex PL50, and 4.8 wt.% Super P. Prior of the electrochemical characterization the electrodes were dried overnight by heating under vacuum at $110 \text{ }^\circ\text{C}$.

2.3. SEM characterization

The morphology of the tapes was evaluated by scanning electron microscopy (SEM). High magnification microphotographs were obtained by means of Jeol JSM-5510LV. The specimens were directly mounted onto a conductive carbon double face tape, which was previously mounted on a slab.

2.4. Electrochemical characterization

For the electrochemical characterization, circular electrodes with a diameter of 12 mm were punched from the electrode tapes. The electrochemical properties of the electrodes were tested in a two electrode lithium cell in which lithium acted both as counter and reference electrode. Lithium-ion batteries were assembled by sandwiching a glass fiber, used as the separator, between the positive and the negative electrodes. The cycling performance and cycle life of the cells were evaluated in 2032-type coin cells. Coin cells were filled with a 1.0 M solution of LiPF_6 dissolved in ethylene carbonate/diethyl carbonate (1:1). The cycling tests were automatically carried out with a battery cycler (Maccor 4000). Material handling, composite cathode preparation, cell assembly, test and storage were performed at $20 \text{ }^\circ\text{C}$ in a dry room (R.H. < 0.1% at $20 \text{ }^\circ\text{C}$).

3. Results

3.1. SEM characterization

The morphology of the positive and negative electrode was investigated by scanning electron microscopy. Fig. 1 left shows a cross section of the cathode electrode. The electrode appears very uniform and from

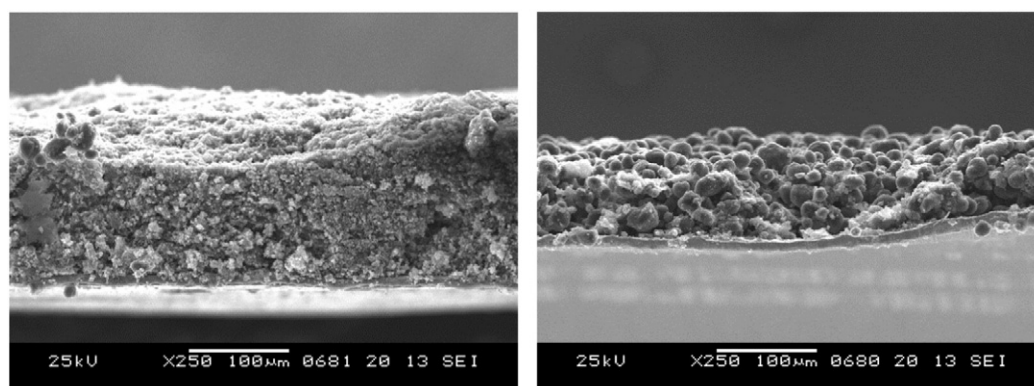


Fig. 1. Scanning electron micrographs of the cross section of the cathode tape (left) and anode tape (right) at high magnification.

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