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Short communication

Performance of various rosin-derivatives as binder additives for lithium titanium oxide anodes



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ABSTRACT

In our recent work, we demonstrated that the use of bio-derived rosin as a binder additive could improve the electrochemical performance of lithium titanium oxide (LTO) anodes. As a sequential study, four representative modified rosin-derivatives are used as additives for polyvinylidene difluoride (PVdF) binders in order to further improve the cell performance of LTO electrodes. The rosin derivative modified via simple hydrogenation retains carboxylic acids and is favorable to lithium ion transport when compared to the modified rosins, which loose these functional groups via esterification. The hydrogenated rosin additive increases cyclic capacities, initially by 10 mAh g^{-1} and more so at high current charge/discharge rates.

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1. Introduction

The applications of medium- and large-sized lithium ion batteries (LIBs) have recently increased due to the expansion of electric vehicles (EVs) and energy storage system (ESS) markets, which require high power as well as high energy. With increases in size, LIBs now require extremely stable cyclic performance compared to the small LIB used for mobile devices. In this sense, spinel-structured lithium titanium oxide (Li₄Ti₅O₁₂, LTO) is one of the most suitable anode materials for large LIBs due to its structural stability and high-rate capability during the charge/discharge process [1–4]. In addition, LTO reacts with lithium ions at a high operating voltage of 1.55 V (vs. Li⁺/Li) before electrolyte decomposition occurs on the surface of the active materials [3–5].

While many studies in this area have been recently performed, the appropriate binder for the LTO active material has not yet been thoroughly studied. Most binder studies have focused on improving the electrochemical performance of graphite and silicon anode materials, and only a few researchers focused on enhancing LTO performance through the polymer binder [5–9]. These works were reviewed in our previous publications [10–12]. Very recently, we showed that bio-derived rosin improved the dispersion of the super-P conducting agent and PVdF binder in LTO electrodes, ultimately leading to enhanced electrochemical performance when used as an additive for PVdF binder [13].

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The focus of this study is to determine the optimal binder additives for improved LTO performance. Four types of modified rosins (MR) are applied as binder additives and their performance is compared through representative electrochemical characterization techniques.

2. Experimental

Four commercial MRs were used as additives of the PVdF (Solef 5130, Solvay Plastics) binder for LTO (Posco ESM Co., $d_{avg} = 10 \ \mu m$) electrodes, and their performance was compared using various physical and electrochemical tests. The four MR materials were purchased from Eastman Chemical Company and the commercial names of the products are Staybelite-E, Poly-pale, Foral 85-E, and Foral 105-E.

Some of the MRs were first dissolved in *N*-methyl-2-pyrrolidine (NMP), an organic solvent, and PVdF powder was then added to the solution. Here, the weight ratios of the PVdF rosin additives are fixed at 1:4 due to adhesion limitations. An excess amount of the additives significantly reduced the adhesion strength of the binder system. The electrode, made of 85 wt.% LTO as active material, 10 wt.% binder including MR additives and 5 wt.% super-P as a conducting agent, was coated onto copper foil and dried in a convection oven at 130 °C for 30 min. Before being assembled to 2016 types of coin-half cells, the LTO electrodes were completely dried in a vacuum oven at 70 °C for 24 h to remove all remaining solvent, moisture, and dust. The cells were assembled in an argon-filled glove box using the LTO electrode as the working electrode and lithium metal as the counter- and reference electrode; commercial electrolyte (Panaxetec Co., 1:1:1 ethylene

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carbonate, ethylmethyl carbonate and dimethyl carbonate with 1 M LiPF_6) was used.

A video-connected device (Theta Lite 100, KSV Instrument Ltd.) and a texture analyzer (TA-PLUS, Lloyd Instruments Ltd.) were used to measure the contact angles of the binder films and 180° peel strength of the LTO electrodes. The surface elements of the LTO electrode were observed via X-ray photoelectron spectroscopy (ESCALAB 250, Thermo Fisher Sci.) using an Al Ka X-ray source. The electrochemical performance of the 2016 coin-half cells was measured using galvanostatic charge/discharge tests between 1 and 2.6 V at a rate of 0.1C for the first 2 cycles and a rate of 1 C for the 48 subsequent cycles. The rate capability was tested at various rates between 1 C and 10 C using a battery cycler (PNE solution Co., Korea). The electrochemical impedance spectroscopy (EIS, VSP, BioLogic Science Instruments) of the LTO electrodes was measured at a frequency range between 0.01 Hz and 100 kHz after 2 cycles at a rate of 1 C.

3. Results and discussion

The MRs used here are widely used for tackifiers in various adhesive and coating components. They possess outstanding resistance to oxidation and discoloration. The Staybelite-E and Poly-pale samples are pure rosin derivatives, and are produced via the partial hydrogenation and dimerization of rosin acids; the Foral samples are rosin esters derived from rosin esterification with two types of alcohols, glycerol (Foral 85-E), and pentaerythritol (Foral 105-E). These are all illustrated in Scheme 1, including a representative abietic rosin acid. In what follows, Staybelite-E, Poly-pale, Foral 85-E, and Foral 105-E are noted as MR1, MR2, MR3, and MR4, respectively, for convenience.

As expected from Scheme 1, the pure rosin derivatives, MR1 and MR2, maintain high acid numbers of 162 and 155, respectively, due to the carboxyl groups in the samples [14]. On the contrary, MR3 and MR4 had acid numbers of 9 and 14, respectively, because carboxylic acids were converted to esters through reactions with the alcohols [14].

The electrochemical characteristics of the MRs were first compared through cyclic and rate capability tests of the LTO electrodes containing PVdF binder and MR additives. The results are shown in Fig. 1. As expected from our previous results [13], all of the MR binder additives improved the electrochemical performance of the LTO electrodes, when compared to the LTO containing PVdF binder only with no additive. Of the MRs, MR1 and MR2 increased the initial discharge capacity of the LTO electrode by approximately 10 mAh g^{-1} , whereas the values of MR3- and MR4-containing LTO electrodes are very close to 176 mAh g^{-1} , which is the initial discharge capacity of the LTO containing no additive. This difference may be attributed to the existence of carboxyl groups in the binder additives. It was reported that the COOH groups in polyacrylic acid and carboxymethyl cellulose binder irreversibly reacted with lithium ions during the charge/discharge process and formed -COOLi, leading to an increase in the initial discharge capacity [15,16]. They also proposed that the carboxylic functional groups were ionically conductive via hopping of lithium ions between them [15-17]. While MR3 and MR4 lose functional groups via esterification, MR1 and MR2 remain the acid groups even after modification, as illustrated in Scheme 1 (b, c). It is plausible that the MR1- and MR2-containing electrodes have relatively large capacity loss at the second cycle when compared to the MR3- and MR4-containing ones, because the acid groups were already occupied by lithium ions at the first cycle.

As shown in Fig. 1, the MR binder additives evidently contribute to the cyclic performance and rate capability of LTO/PVdF electrode systems. In particular, the cyclic capacity of the MR1-containing LTO electrode is 169 mAh g⁻¹ at the 50th cycle of 1 C, which is significantly larger than that of the LTO electrode with no MR additive (159 mAh g⁻¹). MR1, a simply-modified rosin via partial hydrogenation, is therefore a more efficient additive for PVdF binder when compared to the somewhat complicated rosin derivatives produced by either dimerization or esterification.

Several physical and electrochemical characterizations were performed to analyze the electrochemical performance of the MR-added LTO electrodes. The essential property of polymer binder is an ability to adhere all electrode components to the current collector. This is generally estimated via a 180° peel strength test performed on the electrode. As shown in Fig. 2, use of the MR additives significantly reduced the adhesion strength of the binder system, even though only 20 wt.% of PVdF was replaced by MR additives, the results were expected



Scheme 1. Schematic illustrations of (a) abietic acid, (b) Staybelite-E (partially-hydrogenated rosin, MR1), (c) Poly-pale (partially-dimerized rosin, MR2), (d) Foral 85-E (rosin tri-ester, MR3), and (e) Foral 105-E (rosin tetra-ester, MR4).

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