



Poly(isobutylene-*alt*-maleic anhydride) binders containing lithium for high-performance Li-ion batteries



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HIGHLIGHTS

- A new binder is obtained by using a Li containing PIMA polymer.
- An artificial pre-SEI can enhance the Coulombic efficiency and cyclability of LIBs.
- Li-PIMA film prevents the formation of an additional SEI and facilitates the Li diffusion.

ARTICLE INFO

Article history:

Received 30 December 2014
Received in revised form
27 February 2015
Accepted 3 April 2015
Available online 9 April 2015

Keywords:

Lithium ion battery
Binder
Artificial SEI
Coulombic efficiency

ABSTRACT

Anode materials including graphite are known to be thermodynamically unstable toward organic solvents and salts and become covered by a passivating film (Solid electrolyte interphase, SEI) which retards the kinetics because of the high electronic resistivity. To achieve high performance in lithium ion batteries (LIBs), the SEIs are required to be mechanically stable during repeated cycling and possess highly ion-conductive. In this work, we have investigated an artificial pre-SEI on graphite electrode using a polymer binder containing lithium (i.e., a Li-copolymer of isobutylene and maleic anhydride, Li-PIMA) and its effect on the anode performances. During charging, the polymer binder with the functional group (–COOLi) acts as a SEI component, reducing the electrolyte decomposition and providing a stable passivating layer for the favorable penetration of lithium ions. Hence, by using the binder containing lithium, we have been able to obtain the first Coulombic efficiency of 84.2% (compared to 77.2% obtained using polyvinylidene fluoride as the binder) and a capacity retention of 99% after 100 cycles. The results of our study demonstrate that binder containing lithium we have used is a favorable candidate for the development of high-performance LIBs.

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1. Introduction

Lithium-ion batteries (LIBs) occupy a large and an increasing share of the energy storage device market on account of their excellent performance in terms of long-life, energy density, and high safety. Among various electrode materials used for LIBs, graphitic materials, which are representative of carbon materials, have been the most commonly used anode materials because of their low working potential, which is close to the metallic lithium anode, and remarkable cycling performances. LIBs typically operate

beyond the thermodynamic stability of organic electrolytes; hence, reduction products of chemical reactions occurring during the first few cycles form passivating films on the carbon anode, which are termed as the ‘solid electrolyte interphase (SEI)’ [1–3]. The SEI, comprising of an electrochemically insulating layer, plays an important role of in preventing further electrochemical reactions taking place between the electrode surface and the electrolyte, enabling only lithium ions to tunnel through the layer [4]. The formation of SEI layers is known to be detrimental factor to the performance of LIBs, affecting their cycle-life, life-time, power capability, and even safety. While the SEI plays an essential part in delivering the best performance, the development of SEI layers is caused by an irreversible reaction accompanying electrolyte decomposition, which decreases the Coulombic efficiency during

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the first few cycles. When a stable SEI is not formed, any accidental misuse, such as overcharge, exposure to high temperature, and mechanical impact might damage the formed SEI, resulting in a more irreversible reaction during charging [5,6]. The new anode surface immediately reacts when exposed to the electrolyte to form a fresh thin protective film, which eventually leads to a poor cyclability and other undesirable properties in LIBs. Thus, to improve the performance of LIBs, in addition to minimizing electrolyte degradation, a thinner SEI film with excellent passivating properties is required because a thick and resistive SEI film is unfavorable for battery operation [7,8].

Many research studies are thus focused on the improvement of the chemical nature and morphology of SEIs [3,8–13]. Typically, the use of electrolyte additives is an efficient method to improve the SEI properties. The most common and commercially used electrolyte additive is vinylene carbonate (VC). It is well-known that the vinyl group undergoes electrochemical polymerization with the SEI material on the graphite surface during SEI formation, which can improve the cycle-life and the reversible capacity of LIBs [10,14,15]. In addition, to modify SEI films to achieve superior properties, several previous studies have reported the use of a polymer binder in the SEI and the resulting electrochemical effects on the LIBs [16–20]. The effects of modifying the graphite electrode surface with a functional polymer binder, such as polyacrylic acid, are reported in widely in literature [21–24]. Polyion complex layers with oxygen-containing functional groups have been reported to play the role of an artificial SEI to assist facile penetration of lithium ions [22,23]. The stable and efficient operation of LIBs is clearly closely connected to the composition of the surface films, their morphology, and coverage features.

In this paper, we report that an artificial pre-SEI, composed of a polymer binder containing lithium and a functional group (such as $-\text{COOLi}$), can enhance the Coulombic efficiency and cyclability of LIBs. Furthermore, the electrochemical performance is compared with SEI films produced from different binders, with various quantities of lithium included in the copolymer of isobutylene and maleic anhydride (PIMA). X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) were used to analyze the surface film composition and morphology of the graphite anode. The resistivity of the surface films and their relationship to the electrochemical performances were also analyzed by using electrochemical impedance spectroscopy (EIS) and charge–discharge cycling tests.

2. Experimental methods

2.1. Materials

SFG6 (Timcal) graphite with an average size of 6 μm was selected as the active material. Three types of polymer binders, polyvinylidene fluoride (PVdF, Solvay), polyisobutylene and maleic anhydride (PIMA, Mw: 300,000, Kuraray), and Li70, 100-PIMA (PIMA binder substituted with 0.7 and 1.0 mol of lithium), were used. Li-PIMA was prepared by the neutralization of the carboxyl groups using lithium hydroxide. In contrast to water soluble polymers, such as polyacrylic acid (PAA) and carboxymethyl cellulose (CMC), PIMA is used by reacting with alkali. Stoichiometric amount of PIMA was added to the LiOH solution to prepare binders with 6 wt% concentration. The mixture was stirred overnight. For the preparation of Li70-PIMA, it is desirable to dissolve PIMA at 90–100 $^{\circ}\text{C}$ with stirring. As a result, the polymer becomes solvated by the base ring-opening the anhydride functionality to form a metal ester salt.

2.2. Characterization of materials

For proton nuclear magnetic resonance (^1H NMR) analysis the PIMA polymers containing lithium were dissolved in a concentration of 2 wt% in D_2O and then the dissolved solution analyzed on a 300 MHz NMR (DPX300 spectrometer, Bruker). For field-emission SEM (FE-SEM, SU-8030, Hitachi) and X-ray photoelectron spectroscopy (XPS) analyses, the cells were dismantled in a dry room and the cycled electrodes were washed with dimethyl carbonate (DMC). A hermetic holder was used to transfer the electrode samples from the dry room to the instrument chamber. The XPS profiles were obtained (Quantera II spectrometer, Physical Electronics, USA) using $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV) under ultrahigh vacuum. The C 1s and Li 1s spectra were calibrated on the basis of the C 1s graphite peak binding energy at 284.5 eV. High-resolution measurements of the target elements were carried out with a pass energy of 55 eV (energy step 0.1 eV). Depth profiling was performed by using 1 kV argon-ion sputtering.

2.3. Electrochemical measurements

To prepare the composite electrodes, a mixture of the SFG6 graphite powder and binders was dispersed in *N*-methyl pyrrolidone (NMP) and water by using C-Mixer (Dae Wha Tech, PDM-300V). PVdF and PIMA were dissolved in NMP, while Li70, 100-PIMA were dissolved in water. The resulting slurry was coated on a piece of copper foil. After drying in a vacuum oven at 120 $^{\circ}\text{C}$ for 2 h, the electrode was pressed to so that the density of the graphite sample is about 3.5 mg cm^{-2} . A coin-type two electrode 2032 cell was fabricated with lithium foil as the counter electrode. The electrolyte used was 1.3 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (in a volume ratio 3:5:2). Galvanostatic charge/discharge cycling was performed at a current density of 35 mA g^{-1} (during the first cycle) and at 175 mA g^{-1} (after the first cycle) in the voltage range 0.01–1.5 V (vs. Li/Li^+). For a complete charging, additional constant voltage step was included at 0.01 V until the current decayed to 3.5 mA g^{-1} (during the first cycle) and to 17.5 mA g^{-1} (after the first cycle). Differential capacity analysis was carried out to determine the voltage window of the electrolyte decomposition in the SFG6, binder/Li coin cells. EIS (Solartron) was carried out in which the alternating current (AC) impedance measurement was recorded using a signal with an amplitude of 10 mV and frequency ranging from 1 MHz to 10 mHz. After the cells were charged or discharged to the target voltage (vs. Li/Li^+) with a current density of 35 mA g^{-1} and stabilized by resting for 1 h, the AC impedance spectra were recorded at the open-circuit voltage (OCV).

3. Results and discussion

Fig. 1 shows the ^1H NMR spectra of substituted PIMA with 0.2, 0.5, 0.7, and 1.0 mol of lithium. In particular, the proton on the four positions (marked by a, b, c, and d on the spectra and structural formula) of the copolymer of isobutylene and maleic anhydride in Fig. 1a (inset) can be used to determine the degree of substitution. In Fig. 1a, signals from both a and b (2.67 and 2.22 ppm corresponding to Li100-PIMA) associated with the anhydride structure are significantly down shifted and the split peaks are merged according to the degree of substitution of lithium ions, whereas, signals from the c and d (1.92 and 1.52 ppm corresponding to Li100-PIMA) are shifted in accordance with the polymer chain type. As shown in Fig. 1b, and c, compared to signal a, signal b substantially down shifted in the fully substituted spectrum. The change in the peak from proton b strongly involved in the anhydride structure,

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