Journal of Power Sources 324 (2016) 150–157

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

A new strategy to mitigate the initial capacity loss of lithium ion batteries

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HIGHLIGHTS

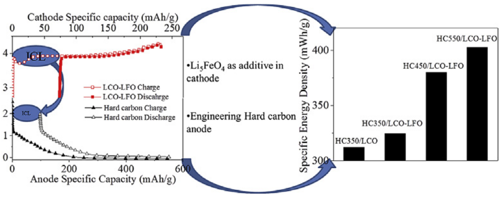
- Added Li_5FeO_4 in the cathode to mitigate the initial capacity loss of the anode.
- Promoted the specific capacity and capacity retention of cathode simultaneously.
- Improved the power and energy density of LIB simultaneously.

ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
10 May 2016
Accepted 16 May 2016

Keywords:
Hard carbon
Initial capacity loss
Li_5FeO_4 (LFO)
Lithium source additive
Lithium ion battery

GRAPHICAL ABSTRACT



ABSTRACT

Hard carbon (non-graphitizable) and related materials, like tin, tin oxide, silicon, and silicon oxide, have a high theoretical lithium delivery capacity (>550 mAh/g depending on their structural and chemical properties) but unfortunately they also exhibit a large initial capacity loss (ICL) that overrides the true reversible capacity in a full cell. Overcoming the large ICL of hard carbon in a full-cell lithium-ion battery (LIB) necessitates a new strategy wherein a sacrificial lithium source additive, such as, Li_5FeO_4 (LFO), is inserted on the cathode side. Full batteries using hard carbon coupled with LFO-$LiCoO_2$ (LCO) are currently under development at our laboratory. We find that the reversible capacity of a cathode containing LFO can be increased by 14%. Furthermore, the cycle performance of full cells with LFO additive is improved from <90% to >95%. We show that the LFO additive not only can address the irreversible capacity loss of the anode, but can also provide the additional lithium ion source required to mitigate the lithium loss caused by side reactions. In addition, we have explored the possibility to achieve higher capacity with hard carbon, whereby the energy density of full cells can be increased from ca. 300 Wh/kg to >400 Wh/kg.

1. Introduction

Electrode materials and electrolyte choices largely dictate the design parameters and the type of lithium-ion battery (LIB) that can be optimized and eventually utilized. All three components (anode, electrolyte, and cathode) must work in harmony to produce the highest possible energy density achievable for an LIB-based energy storage device. Balancing the electrochemical performance characteristics of the cathode and anode active materials is critical for maximizing the power/energy density of an LIB [1–4]. Many anode materials, including hard carbon, tin, tin oxide, silicon, and silicon oxide, have high theoretical capacities (>550 mAh/g) but tend to exhibit a large initial capacity loss (ICL) [3,5–12]. This is an

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http://dx.doi.org/10.1016/j.jpowsour.2016.05.063
0378-7753/

important issue for the commercial application of some types of high capacity anodes in full LIBs that overrides the true reversible capacity of the anode itself [12–18].

Whereas extensive research has been conducted to address capacity loss during extended cycling of lithium ion batteries [5,6,8–10,12,19–22], the initial large capacity loss of the anodes of LIBs has been studied to a lesser extent. Furthermore, the existing strategies employed to address this issue usually involve adding different lithium sources to the anode, such as, lithium powder or lithiated transition metal nitrides [23–27]. Unfortunately, these strategies are not facile and may create safety issues in the practical application of LIBs. In order to overcome the large ICL of next generation LIB anodes, a new strategy is needed wherein a sacrificial lithium source additive, such as Li_5FeO_4 (LFO) with theoretical capacity equal to 867 mAh/g is used on the cathode side, i.e., an additive that in theory could release up to 5 lithium cations per mole to the cell upon first charge [28,29]. As such, small amounts of LFO co-blended with the active cathode powder particles in conventional electrode laminate coatings could provide exactly what is needed to mitigate the ICL issues of hard carbon and related anode materials with high theoretical energy density.

In this work, we selected the commonly used $LiCoO_2$ (LCO) phase as the cathode, because of its high (97%) coulombic efficiency. For the anode we chose hard carbon (which has only ca. 80% coulombic efficiency but relatively high capacity) to fabricate full cells with which to demonstrate the feasibility of the LFO-based cathode additive concept. The capacity usage of the hard carbon anode was controlled by varying the loading of the hard carbon laminate. We present here are a series of results that demonstrate how specific capacity, capacity retention, operating voltage, and energy density of full cells are all simultaneously improved. All of these factors work in harmony to demonstrate an effective approach that facilitates the implementation of hard carbons in LIBs for commercial applications. This work also points to a novel strategy for the utilization of other high capacity anode materials, like tin, tin oxide, silicon, and silicon oxide, which have been precluded from commercial applications due to their large initial capacity loss issues [6,10–12].

2. Experimental section

2.1. Synthesis of Li_5FeO_4 (LFO)

LFO was synthesized by solid state synthesis in an Ar-filled glovebox. Firstly, LiOH-H_2O (Sigma-Aldrich) and Fe_2O_3 (<50 nm, Sigma Aldrich) were mixed at a 10 to 1 M ratio followed by co-grinding. The mixture was calcined according to the following procedure. (1) The mixture was calcined at 450 °C overnight and then furnace cooled. (2) The product from (1) was ground, calcined at 600 °C overnight, and furnace cooled. (3) The product from (2) was ground and calcined at 800 °C for 70 h, then furnace cooled. Finally, the product from (3) was ground to a fine powder and stored in an Ar-filled glove box prior to electrode fabrication.

2.2. Electrode preparation

The preparation of the hard carbon (HC) anode electrode was as follows: Firstly, the HC powder (Kureha Battery Materials Japan) was placed in a solution of polyvinylidene difluoride (PVDF, Solvay 5310) dissolved in N-methy-2-pyrrolidone (NMP). After the slurry was stirred at 2000 RPM for 3 min using a Thinky mixer ARE-310, it was coated onto Cu foil. Differently dimensioned doctor blades were used to tune the thickness of the coating on the Cu foil. Then the electrode was dried at 75 °C for 4 h, followed by drying at 75 °C in vacuum overnight. The final thicknesses of the HC anode electrodes ranged from 20 μm to 39 μm. To remove any residual moisture, the electrodes were dried at 120 °C under vacuum for over 4 h before being assembled into 2032 type coin cells. The preparation of the $LiCoO_2$ (LCO, American Elements)/Li_5FeO_4 (LFO) cathodes was performed in an Ar-filled glove box using the following procedure: LFO was mixed with LCO by mortar and pestle co-grinding. Carbon black (14 wt%) was added followed by further grinding. Anhydrous NMP was added with thorough stirring to fully wet the powders. Next PVDF (8%, Solvay 5130) solution was added together with more anhydrous NMP to obtain the proper viscosity for the slurry. The slurry was cast on pre-cleaned Al foil (20 μm) using a 225 μm doctor blade. The laminate was dried at 75 °C on a hot plate and calendered with a hand-roller. The cathode electrodes were handled and stored in an Ar box before assembly into coin cells. The pure LFO and LCO electrodes for the control experiments were prepared using the same procedures described above.

2.3. Electrode characterization

The surface morphologies and compositions of the HC electrodes and LCO-LFO electrodes were characterized using a scanning electron microscope (SEM, Hitachi S-4700 at 20 KV) in conjunction with energy dispersive spectroscopy (EDS). To confirm the compositions and morphologies of the HC electrodes, Raman measurements on the HC were carried out using an inVia Raman microscope (Renishaw) with 785 nm laser excitation. The methodology used to perform the Raman spectroscopy has been described elsewhere [30]. The high-energy synchrotron XRD measurements on the LCO-LFO electrode were carried out at Beamline 11-ID-C at the Advance Photon Source at Argonne National Laboratory ($\lambda = 0.11798$ Å) to confirm the composition and crystal structure of the electrode.

2.4. Electrochemical characterization of half cells

The galvanostatic cycling tests on the HC electrodes in half cells were conducted using a Maccor series 4000 potentiostat at a rate of 0.1 C under room temperature conditions. The HC electrodes were forced to a series of specific capacities of 250 mAh/g, 350 mAh/g, 450 mAh/g, and 550 mAh/g to investigate their discharging voltage and initial capacity loss characteristics. Galvanostatic cycling tests of pure LFO, pure LCO, and blended LCO-LFO electrodes in half cells were also conducted under the same conditions to determine the initial capacity loss and the reversible capacities of these electrodes. Lithium metal was used as the counter electrode and a solution of 1.2 M $LiPF_6$ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (3/7 wt ratio) was used as the electrolyte in all half cells.

2.5. Electrochemical testing of full cells

HC electrodes with different thicknesses ranging from 20 μm to 39 μm were coupled with LCO-LFO electrodes in the full cells used for performance testing. The initial 3 formation cycles of the full cells were carried out from 2.0 to ~4.3 V under a constant current of ~0.05 C at room temperature to obtained their capacities and operating voltage profiles. After that, the full cells were tested at rates of C/5, C/3, C/2, 1C, and 2 C from 2.0 to ~4.3 V. Finally, the cycling tests of the full cells were carried out using a rate of C/3 at room temperature. A solution of 1.2 M $LiPF_6$ in EC/EMC (3/7 wt ratio) was used as the electrolyte in all full cells. Testing of the full cells using HC anodes coupled with LCO and LCO-LFO cathodes was performed under the same conditions as the control experiments.