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

Xin Su^{1a}, Chikai Lin^{1b}, Xiaoping Wang^{1c}, Victor A. Maroni^{1d}, Yang Ren^{2e}, Christopher S. Johnson^{1f}, Wenquan Lu^{1g}*

¹ Chemical Science and Engineering Division and ²Advanced Photon Source, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439-4837, United States

^a suxin81@gmail.com ^b chikai.moses.lin@gmail.com ^c xiaoping.wang@anl.gov ^d maroni@anl.gov ^e ren@aps.anl.gov ^f cjohnson@anl.gov ^g luw@anl.gov

*Corresponding author: Wenquan Lu

Address: 9700 South Cass Avenue, Argonne, Illinois 60439-4837, United States

Phone: +1(630)-252-3704; Fax: 630-972-4414

E-mail: luw@anl.gov

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.

Keywords: hard carbon, initial capacity loss, Li_5FeO_4 (LFO), lithium source additive, lithium ion battery

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 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, $\text{LiOH} \cdot \text{H}_2\text{O}$ (Sigma-Aldrich) and Fe_2O_3 (<50 nm, Sigma Aldrich) were mixed at a 10 to 1 molar 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 hours, 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 minutes 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 4h, 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 weight 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 obtain 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 weight 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.

3. Results and Discussion

The HC anode employed in this research was firstly characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy, and Raman spectroscopy to determine the surface morphology and composition as shown in Figure 1(a) and 1(b). The particle size

of the HC (as shown by SEM) was several micrometers. From the Raman spectrum in Figure 1(b), the intensity of the D band at 1308 cm^{-1} , which is attributable to the graphitic grain boundary phonon, is stronger than that of the graphite G band at 1590 cm^{-1} , which is a vibrational band involving symmetric bond stretching within the graphite plane. This indicates the HC is much more disordered than well crystallized graphite due to its nanoporous nature and disarranged layered structure. The HC electrode was firstly assembled into a lithium half-cell to evaluate its electrochemical properties. As shown in Figure 2(a), the HC anode exhibits a large ICL (22%) when the initial capacity of the anode is 350 mAh/g . This large ICL is what precludes HC from conventional use in lithium ion batteries even though it provides excellent rate performance.

Figure 1. (a) SEM/EDS results and (b) Raman spectrum of the HC anode; (c) SEM and (d) XRD of the as-prepared LFO; (e) SEM/EDS and (f) XRD of the blended LCO-LFO cathode.

The LFO powder used in this work was synthesized through the procedure developed in our laboratory as described above in the experimental section and also in reference [29]. This LFO powder was examined by XRD (see Figure 1(d)) and was found to have a pattern totally consistent with that of pure LFO as reported in JCPDS#75-1253. The morphology of the synthesized LFO powder can be seen from the SEM image in Figure 1(c). Its secondary particle size was determined to range from a few μm to 30 μm . From prior work in our laboratory we know that LFO is capable of releasing at least 4 lithium cations per mole of LFO to the cell upon first charge according to Equation 1, which theoretically equates to ca. 700 mAh/g of anode capacity.[29]

In the above reaction, the lithium removed from the LFO is not reversible but it can be used to compensate for the ICL of the anode. As such, only a relatively small amount of LFO is needed to blend with the cathode material.

In this work, 7 wt.% LFO powder was blended with LCO powder and fabricated into a conventional electrode laminate. The as prepared LCO-LFO cathode was examined by SEM

and X-ray diffraction (XRD) as shown in Figure 1(e) and 1(f). The XRD indicated that the laminate contains the active cathode material LCO (JCPDS#50-0653) together with the LFO additive. The SEM image in Figure 1(e) gives evidence that the LFO is uniformly mixed with LCO in the cathode. As shown in Figure 2(b), 2(c) and 2(d), the pure LFO electrode in the half cell can offer over 700 mAh/g during the initial charge to 4.3V, but the de-lithiation of the LFO is almost completely irreversible during the first discharge. On the otherhand, the pure LCO electrode provides a reversible capacity of 160 mAh/g with less than 3% ICL during the 1st cycle in a half cell embodiment using the same cut-off voltage. In the case of the LCO-LFO cathode (7 wt % LFO), the first charge to 4.3 V yielded a specific capacity of 233 mAh/g and 160 mAh/g was obtained during the first discharge, resulting in a 31% ICL. All the ICL of the LCO-LFO electrode can be attributed to LFO due to its almost 100% ICL. It is worthy of note that the 31% ICL of the LCO-LFO (7% wt.% LFO) cathode is more than enough to compensate for the characteristic 22% ICL of the HC anode and the LFO amount in LCO-LFO electrode can be further reduced.

Figure 2. Voltage profiles of half cells using (a) HC, (b) pure LFO, (c) pure LCO, and (d) blended LCO-LFO (7 wt.% LFO) during the formation tests.

Figure 3(a) and 3(b) illustrate how the LFO additive affects the capacity usage of LCO in full cells with HC as the anode. The first lithiation capacity of the HC used in the full cells (without and with LFO additive) was set at 350 mAh/g. Figure 3(a) shows first charge/discharge voltage profiles of Li/HC (bottom curve) and Li/LCO half cells (top curve) which are same as in Figure 2(a) and 2(c). Assuming that the capacity ratio of the negative (HC) electrode to the positive electrode (LCO) is equal to 1 ($n/p = 1$, determined by the first charge capacity), the HC/LCO full cell voltage profile, shown in Figure 3a (middle curve), was calculated from the Li/HC and Li/LCO half cells. The useable capacity of the LCO

cathode is determined to be 121 mAh/g due to the large ICL of HC, which is much smaller than that of LCO in a half cell (160 mAh/g). However, for the HC/LCO-LFO full cell, shown in Figure 3b, is calculated from Li/HC and Li/LCO-LFO half cells. The reversible capacity of LCO-LFO cathode is determined to be 159 mAh/g (middle curve), since the extra lithium from the LFO can compensate the large ICL of the HC anode and all the capacity of the LCO can thereby be utilized.

Figure 3. Voltage profiles for (a) the Li/HC half cell, the Li/LCO half cell, and the HC/LCO full cell, (b) the Li/HC half cell, the Li/LCO-LFO half cell, and the HC/LCO-LFO full cell, and (c) cycling performance of the full cells using LCO-LFO (square ($\square$) normalized to the total mass of LFO and LCO; dash line (---) normalized to the mass of LCO), LCO as the cathode and HC as the anode with the initial capacity of 350 mAh/g.

The respective electrochemical performances of the full cells using the LCO-only cathode and the LCO-LFO cathode shown in Figure 3(c) are exactly the same in accord with the predictions spelled out above. The reversible specific capacities of the LCO and LCO-LFO electrodes are 126 mAh/g and 144 mAh/g (which is actually equivalent to 156 mAh/g when normalized to the mass of LCO only), respectively, which are consistent with the calculation according to Figure 3(a) and 3(b). Therefore, the reversible specific capacity of the LCO-LFO cathode in the full cell can be increased by 14%, which is equivalent to a 10% increase in energy density. The energy density can be further improved by reducing the LFO content in the LCO-LFO electrode, since the 7 wt% LFO in LCO electrode results in a 31% ICL, which is more than enough to address the 22% ICL of HC electrode. Furthermore, the capacity retentions of the full cells during the 50 cycles of testing are also improved from <90% for LCO alone to $\geq 95\%$ when the LFO is added. It is well accepted that one of the factors causing capacity fading in LIBs is the side reaction between electrolyte and anode, which tends to consume lithium ions leading to less available lithium. The extra lithium from LFO can behave as a lithium reservoir that provides lithium ions continuously during cycling to compensate for the lithium loss. Therefore, the LFO cathode additive not only mitigates ICL, but also improves cycle performance.

In this work, we also investigated the capacity limit of HC. First, the HC electrodes were discharged (lithiated) to a series of specific capacities ranging from 250 mAh/g to 550 mAh/g in half cells. As shown in the corresponding voltage profiles of Figure 4(a), 4(b), 4(c) and 4(d), increasing the specific capacity of HC from 250 mAh/g to 550 mAh/g reduces the average voltage for charging/discharging. This indicates that when HC is used as the anode in a full cell, increasing the capacity of the HC anode can simultaneously increase the output voltage of the full cell. This means that the energy and power density of full cells with HC anodes can be simultaneously increased. Meanwhile, based on the voltage profiles in Figure

4(e), we see that the end-of-discharge-voltage does not start to increase until the capacity of the HC anode reaches 550 mAh/g, which indicates that lithium plating does not occur for anode capacities ≤ 550 mAh/g. This observation provides a basis for the development of LCO-LFO full cells with HC anodes of varying thickness (i.e., varying capacity) depending on performance requirements.

Figure 4. Voltage profiles for HC electrodes in half cells lithiated to a series of specific capacities: (a) 250mAh/g, (b) 350mAh/g, (c) 450mAh/g, and (d) 550 mAh/g; (e) the enlarged image of the voltage profiles at the end of discharging.

The voltage profiles during the formation tests of full cells using the same LCO-LFO electrodes (5.8 mg/cm^2) coupled with various HC electrodes with thicknesses of 20 μm , 24 μm , 31 μm , and 39 μm , are shown in Figure 5(a). The mass loading of HC in the anode is proportional to the electrode thickness, which is shown in Figure 5(c). As we expected, when

reducing the thickness of the HC from 39 μm to 20 μm , the average output voltage of the full cells increases from 3.5 V to 3.8 V. Furthermore, the reversible capacity of HC can be increased from 206 mAh/g to 401 mAh/g at the same time as seen in Figure 5(b). Therefore, the average energy densities of full cells are increased from ca. 300 Wh/kg to >400 Wh/kg (normalized to the total weight of both the cathode and the anode) as seen in Figure 5(c), when reducing the thickness of the HC from 39 μm to 20 μm . In addition, the capacity retention of full cells can be maintained at the similar value of ~95%, when reducing the thickness of HC from 39 μm to 24 μm . However, when reducing the thickness of HC to 20 μm , the capacity retention of the full cell drops to <90%. This is probably due to lithium plating on the HC when its initial capacity is close to 550 mAh/g. This is supported by the SEM images for the 20 μm and 24 μm HCs after cycling as shown in Figure 6(a) and 6(c), where we observe some tiny lithium dendrites on the 20 μm HC anode that do not appear on the 24 μm HC anode.

Figure 5. (a) Voltage profiles of the full cells using LCO-LFO as cathodes and HCs with different thicknesses as anodes during the initial formation tests; (Note: the cathode specific capacities are normalized to the total mass of LCO and LFO.) (b) The corresponding specific capacities of the HC anodes; (c) the coating mass of HCs with different thicknesses as anodes and corresponding LCO-LFO cathodes in the full cells; (d) the corresponding average output voltages and specific energy densities of the full cells. (Note: The specific energy densities are normalized to the total mass of HC, LCO and LFO.) (e) Cycling performance of the full cells using the HC with different thicknesses as the anode and LCO-LFO as the cathode.

According to the electrochemical reaction for LFO in Equation 1, LiFeO_2 will be generated in the cathode after the first discharge. Since Fe (in the form of LiFeO_2) is introduced into the cathode, there is concern about Fe dissolution and subsequent deposition on the anode. The HC anodes and LCO-LFO cathodes from cycled cells were characterized by SEM, EDS, and Raman spectroscopy. As shown in the EDS of the anodes and the cathodes after cycling (see Figure 6(a), 6(b), 6(c) and 6(d)), the iron is retained in the cathode rather than being transported to the anode during the series of full cell tests. The surface morphologies of the cathodes are similar before and after cell testing. We also used Raman spectroscopy to study the HC before and after tests. The Raman spectra and the corresponding $I(\text{G})/I(\text{D})$ ratios for the HCs in Figure 7(a) and 7(b) demonstrate that the crystalline percentage of the HCs is same after the series of cell tests as it was before. All of the results

demonstrate an effective strategy that not only mitigates the ICL issues plaguing HC anodes (and by implication, tin, tin oxide, silicon, and silicon oxide anodes as well) in a full cell embodiment, but also improves the specific capacity, capacity retention, operating voltage, and energy density of full cell LIBs.

Figure 6. SEM images of (a) the 24 μm HC anode, (b) the LCO-LFO cathode employed with the 24 μm HC anode, (c) the 20 μm HC anode, and (d) the LCO-LFO cathode employed with the 20 μm HC anode; all of which were extracted after the full cell cycling tests.

Figure 7. (a) Raman spectra and (b) the corresponding I(G)/I(D) band intensity ratios for the HC electrodes of different thicknesses after the full cell cycling tests.

4. Conclusions

A new strategy has been developed to overcome the large ICL confronting HC type anodes in full cell LIB embodiments, wherein a sacrificial lithium source additive, e.g., Li_5FeO_4 (LFO), is used on the cathode side. Full cells using HC anodes and LCO cathodes without and with LFO additive were fabricated and subjected to detailed electrochemical testing. Comparison of full cells with LCO cathodes (without and with LFO additive) and HC anodes showed that with LFO additive the reversible specific capacity of the cathode increased by 14% and the corresponding capacity retention increased from <90% to >95% during 50 cycle charge/discharge testing. The extra lithium introduced to the full cells by adding only a small amount of LFO not only compensates for the ICL of HC, but also serves as a lithium reservoir that provides lithium ions continuously during cycling to compensate for lithium loss due to, e.g., side reactions.

In addition, we explored the possibility of achieving high capacity levels using HC. We found that the capacity, output voltage, and energy density of full cell LIBs can be simultaneously increased from 206 mAh/g to 401 mAh/g, from 3.5 V to 3.8 V, and from ca. 300 mWh/g to >400 mWh/g, respectively, by tuning the loading of HC in cells using LCO-LFO as the cathode and HC as the anode. All of the results demonstrate an effective strategy for overcoming the large initial capacity loss of anodes, like HC and also by implication tin, tin oxide, silicon, and silicon oxide as well; a problem that has hindered their commercial application.

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Graphical abstract