Short communication

Application of Stabilized Lithium Metal Powder (SLMP®) in graphite anode – A high efficient prelithiation method for lithium-ion batteries

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HIGHLIGHTS

- Develop a method to apply SLMP in graphite anode.
- The prelithiated graphite anode can compensate first cycle capacity loss and maintain capacity.
- No low external current driven formation is required with SLMP-prelithiated graphite anode.
- Manufacturing cost for cell formation can be significantly reduced with additional of SLMP.
- Potential application of high capacity non-lithiated cathode.

ARTICLE INFO

ABSTRACT

Stabilized Lithium Metal Powder (SLMP®) was applied in graphite anode and the effects of this pre-lithiation method to cell performance were investigated. Performance of prelithiated cells was compared with that of regular graphite based cells. The first cycle capacity loss of SLMP prelithiated cell was largely reduced and the corresponding first cycle Coulombic efficiency was significantly improved. The graphite/NMC cell with SLMP prelithiation but without any standard cell formation process showed better cycle performance than that of none SLMP containing cell with standard formation process. Prelithiation of graphite electrode with SLMP promote stable solid electrolyte interface (SEI) formation on the surface of graphite anode. Application of SLMP in lithium-ion battery thus provides an effective method to enhance capacity, and promises a low cost SEI formation process. This also implies the potential use of other promising anode materials, such as Si and Sn that have large first cycle capacity loss, in commercial lithium-ion batteries.

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1. Introduction

With increasing demanding of energy, it becomes more and more important to find alternative energy sources beyond fossil fuels. To utilize other "clean" and sustainable energy sources, such as solar and wind, it is necessary to develop effective energy storage systems (ESS) to ensure around-the-clock energy delivery and mediate power fluctuations. As the most widely used ESS, batteries, especially lithium-ion batteries (LIB), have drawn significant research attention due to their unique advantages of high energy densities (up to 150 Whkg^{-1}) [1]. Application of LIBs has been extended from consumer electronics to large-scale energy storage. To meet the requirement for applications in electric vehicles (EV) and hybrid electric vehicles (HEV), it is desirable to develop high energy density and low cost materials [2]. With current Li-ion technology, lithium source in the cell is limited from cathode material, e.g. $LiCoO_2$, and electrolyte. Solid-Electrolyte Interphase (SEI) formation on the surface of anode during initial cycles consumes lithium and results partial capacity loss irreversibly. The incorporation of Stabilized Lithium Metal Powder (SLMP), developed by FMC corporation, into graphite anode has been suggested to help overcome the irreversible capacity loss, and increase the capacity by 5–10% in lithium-ion batteries [3–5]. A recent study on pre-lithiation of silicone-carbon nanotube (Si-CNT) anodes in lithium-ion batteries by using SLMP showed that the 20–40% first cycle irreversible capacity loss could be eliminated [6]. This implies that

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anode materials inside commercial lithium ion cells can be chosen from other promising anode materials such as Si and Sn, which have very high capacity but large first cycle capacity loss and thus cannot be used in current commercial lithium-ion batteries. Moreover, some non-lithiated materials with high specific capacities such as Reduced Graphene Oxide/Fe_2O_3 composite and [7] and V_6O_{13} [8] can be used as cathode materials if coupled with pre-lithiated anodes [3]. Using this prelithiation strategy, the full cell energy density can be significantly improved and meet requirements for EV batteries in the future [2].

Although application of SLMP in anode such graphite [3–5] or Si-CNT [6] has been found to improve cell performance, these studies only compared performance of the studied cells after regular formation processes (e.g., a few initial cycles with small current charge/discharge). These formation processes are long and tedious, and are inevitable in current LIB industry. To our knowledge, there has no report so far on the possibility to skip the formation steps, and reduce the manufacturing cost, with prelithiation by SLMP. In this study, we have demonstrated the application of SLMP in graphite anode and investigated its impact on the formation of SEI and cycle performance of the cells. Based on our results, we discussed the feasibility of skipping the external current driven formation steps in LIB manufacturing, instead of using the spontaneous SEI formation induced by the SLMP additives in the anode electrode.

To apply SLMP into the anode electrodes, two different methods have been applied: SLMP was either added into electrode slurry for film casting [3,9], or loaded directly on top of dried anode laminate [6]. In this study, we used the latter method to incorporate SLMP into graphite anode since this is a relatively simple way to apply SLMP. To investigate the impact of SLMP on the SEI formation, cells assembled with SLMP prelithiated graphite anodes were allowed to rest for a period of time at open circuit before cycling. Impact of SLMP on graphite performance was first studied based on lithium metal counter electrode cells (half cells). Upon prelithiation with SLMP, changes of the voltage profile and first cycle Coulombic efficiency were examined. After that, performance of the cells containing prelithiated graphite anode and $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) cathode (full cell) was studied. Our results showed improvement on both first cycle Coulombic efficiency and following cycle performance of the cell with SLMP, indicating that the formation of an effective SEI layer on prelithiated graphite anode surface. This implies that the battery formation process could be simplified and the manufacturing cost for cell formation could be significantly reduced with additional of SLMP. The effect of SLMP to the cell formation has not been discussed in the literature so far. This study is the first to demonstrate the benefit of formation by the SLMP addition.

2. Experimental

2.1. Materials and electrode fabrication

The anode mixture consists of graphite (CGP-G8, Conoco Phillips), carbon black (Denka), and polyvinylidene fluoride (PVDF, Kureha America, Inc.). SLMP was provided by FMC-Lithium Co. N-Methyl-2-pyrrolidone (NMP) is from Sigma–Aldrich (anhydrous, 99.5%). $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) cathode material is from Umicore N. V. The electrolyte is composed of a 1 M $LiPF_6$ solution in ethyl carbonate (EC) and diethyl carbonate (DEC) with volume ratio of 1:1 purchased from BASF.

CGP-G8 graphite powder was mixed with PVDF and acetylene black (AB) with the weight ratio of: 82% graphite, 15% PVDF, and 3% AB in NMP to make slurry. For NMC cathode, NMC powder was mixed with PVDF and AB in NMP with weight ratio of 92.8% NMC,

4.2% PVDF, and 3.0% AB. Both mixtures were homogenized using Polytron PT10-3 homogenizer. The formed graphite or NMC slurry was then coated on 18 μm thick battery grade copper or aluminum sheet respectively using a Mitutoyo doctor blade and a Yoshimitsu Seiki vacuum coater. Typical mass loading of active material was ∼6 mg/cm² for graphite anode and ∼10 mg/cm² for NMC cathode. After NMP dried off, both electrodes were further dried in vacuum oven at 130 °C for 16 h. SLMP was then loaded on top of the graphite electrode or copper foil disk (9/16″ OD) evenly by spreading out method [10]. In the case of loading SLMP on electrode, the electrode with SLMP was then calendared with rolling press (EQ-MR 100A from MTI Corporation) to activate SLMP. In the case of loading SLMP on copper foil disk, the copper foil with SLMP was first compressed with the rolling press and then placed under the electrode for cell assembling.

2.2. Cell assembling and testing

2325-type coin cells (parts from National Research Council Canada) were assembled in an argon-filled glove box with oxygen mixing ratio of 0.1 ppm and dew point of −70 °C. For graphite half cells, the counter electrode was lithium metal disk of 11/16″ OD (Li foil from FMC-Lithium Co.). For full cells, graphite electrode and NMC electrode were 9/16″ OD and 1/2″ OD, respectively. The separator used was polypropylene film (Celgard® 2400). Prelithiated graphite anode was prepared by placing a piece of copper foil with activated SLMP beneath it. Galvanostatic cyling tests were performed on a Maccor series 4000 cell tester. For half cells, the voltage window was 0.01–1.0 V, and for full cells, the voltage window was 2.8–4.3 V. The cells containing SLMP were rested for certain period of time (1–4 days) at open circuit before cycling.

3. Results and discussion

Graphite half cells with and without SLMP were cycled at C/10 rate and the first cycle voltage profiles are shown in Fig. 1(a) for comparison. SLMP content in the electrode is about 5 wt.%. The SLMP cell was rested for two days at open circuit before cycling. Compare the initial OCV of both cells, it is clear that SLMP prelithiated graphite half cell has a much lower voltage, e.g., ∼0.1 V, than that of the regular graphite cell (∼3.0 V, not shown here). Since the 1st lithiation process of graphite normally occurs at around 0.2 V vs. Li/Li⁺ ($0.083Li^+ + C_6 + 0.083e^- \rightarrow Li_{0.083}C_6$) [11], this ∼0.1 V cell potential very likely indicates graphite inside the cell is already partially lithiated. After assembled in the cell, SLMP at graphite side releases lithium ions when in contact with electrolyte. These lithium ions spontaneously migrate to graphite surface and some interclate into graphene layers since Li+ in graphene layers possess a lower chemical potential than with Li metal. As a result, graphite is partially lithiated during the rest time. The 1st lithiation (discharge) capacity of this SLMP contained cell only reaches ∼200 mAh/g, significantly less than the ∼340 mAh/g capacity achieved in the regular graphite cell, confirming the partial lithiation behavior. Furthermore, the small plateau at 0.6–0.7 V during the first discharge of the regular graphite half cell, which has been ascribed to the decomposition of electrolyte and formation of SEI on graphite surface [12], is not observed in the voltage profile for the SLMP contained cell, suggesting absence of SEI formation process during its 1st discharge. Formation or development of the SEI layer in this cell therefore very likely happened during its rest period. The first cycle capacity loss for the regular graphite half cell (without SLMP) is around 20 mAh/g, which accounts for ∼7% of its total capacity. The 1st delithiation (charge) capacity of the SLMP cell, however, is higher than its 1st discharge capacity, and reaches ∼340 mAh/g, even slightly higher than that of the regular graphite
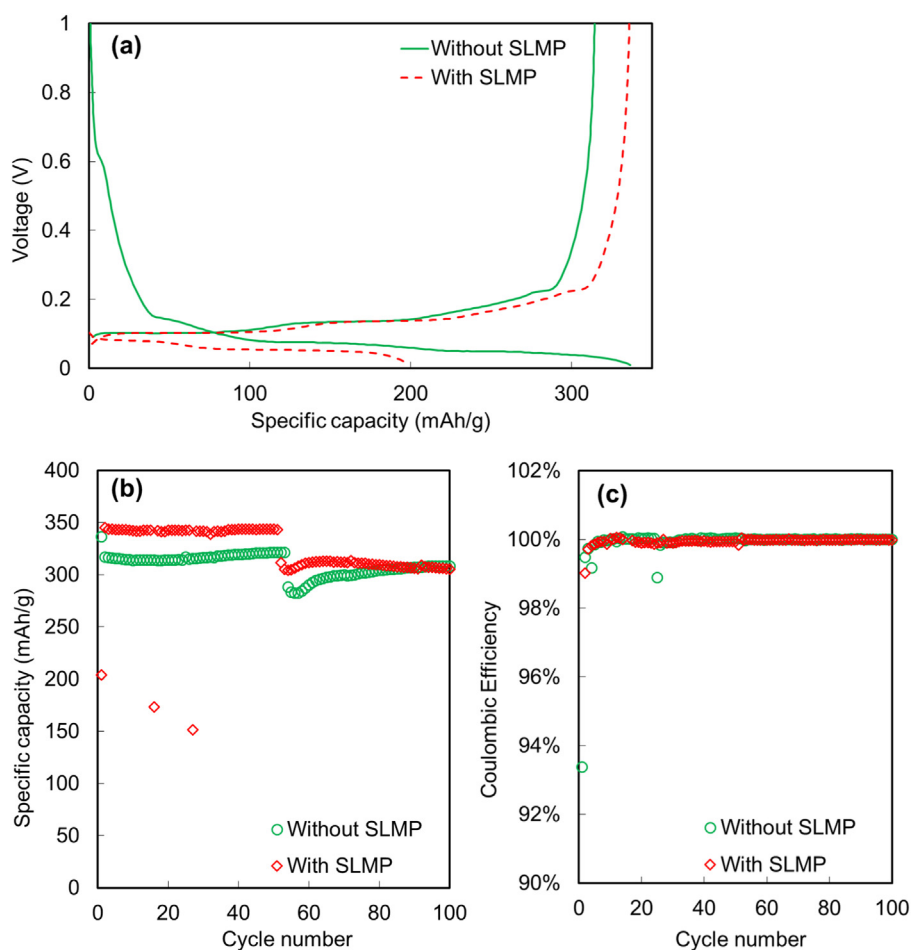
Fig. 1. (a) The first cycle voltage profiles for graphite half cells without SLMP (green solid line) and with 5 wt.% SLMP (red dashed line) at C/10 rate. (b) The cycle performance for graphite half cells without (circles) and with SLMP (diamonds). The rate for the first 50 cycles was C/10, and that for cycle 51 to 100 was C/3. (c) Coulombic efficiency of the half cells without (circles) and with SLMP (diamonds). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

cell, indicating the prelithiation does not compromise the delithiation process. Cycle performance of these two cells under C/10 (cycle 1–50) and C/3 (cycle 51–100) cycling conditions is then compared. The delithiation capacity of the SLMP cell maintains ∼5% higher than that of the regular graphite cell for the first 50 cycles. The delithiation capacities of both cells are comparable at current density of C/3. Fig. 1(c) indicates that there is no significant difference for the Coulombic efficiencies after the first several cycles. As shown in Fig. 1(b) and (c), SLMP contained cell displays similar, if not better, steady cycle behavior to the regular graphite cell at both current rates. Overall, these results indicate the full development of SEI on SLMP-lithiated graphite during the resting time, and such developed SEI (using SLMP method) is equivalent effective to that formed using slow electrical charged formation protocols in the regular cell.

To further understand how SLMP impact the SEI formation process, a comparison study has been conducted on another group of graphite half cells. Particularly, three cells were assembled, one with about 1.2 wt.% of SLMP and two without. The cell with SLMP was cycled at C/3 rate after resting for four days, one of the two regular cells was cycled at C/3 rate right after assembling, and the other regular cell was cycled at C/3 after a formation process (2 cycles at C/25 and 5 cycles at C/10). The first cycle voltage profiles of the two cells starting with C/3 cycle rate are shown in Fig. 2(a). The open circuit voltage of the cell with 1.2 wt.% SLMP is 0.4 V, higher than that of the above cell with 5 wt.% SLMP, indicating a less extent

of prelithiation. Nonetheless, plateau at 0.6–0.7 V is still absent, suggesting development of SEI is already completed with presence of SLMP during rest period. The first cycle Coulombic efficiency of this cell is about 100%, showing that 1.2% of SLMP is enough to provide a full compensation to the capacity loss in this system, and therefore its charge capacity was not sacrificed. For the first regular cell without SLMP (no formation), its 1st discharge and charge capacities at C/3 current rate reach 297 and 276 mAh/g, respectively (Fig. 2(a)), both are lower than those obtained at C/10 (shown in Fig. 1(a)), but the Coloumbic efficiency does not vary much (about 93%). Cycle performance and Coulombic efficiency of all three cells are compared and results are shown in Fig. 2(b). Specific capacity of the cell without SLMP and without formation reaches only around 280 mAh/g, while both the cell with SLMP and the one without SLMP but with formation process reach capacity of around 320 mAh/g when the cells cycling capacities are stabilized (Fig. 2(b)). The cell with SLMP has an even better cycle performance than the cell without SLMP but with formation (Fig. 2(b)), indicating SEI formed in the cell with SLMP is as effective as, or better than that formed in the regular cell during low current (e.g., C/25 or C/10) formation process. The Coulombic efficiencies of all the three cells are comparable. These results confirm the effective prelithiation of anode by SLMP, and SLMP induced SEI formation on graphite electrode surface.

After the prelithiated graphite anode with SLMP was successfully applied in half cell, the next step is to investigate its impact in
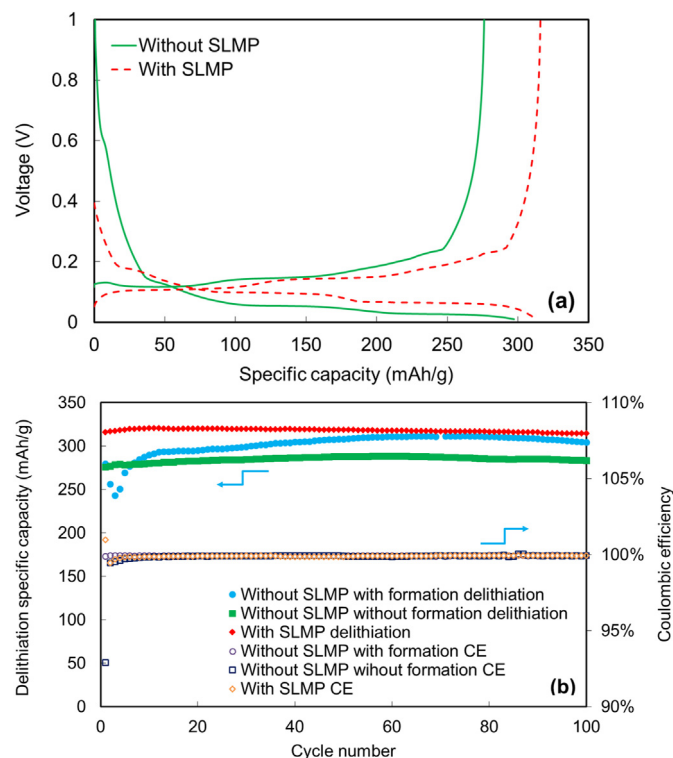
Fig. 2. (a) The first cycle voltage profiles for graphite half cells without SLMP (green solid line) and with 1.2 wt.% SLMP (red dashed line) at C/3 rate. The cell with SLMP was rested under open circuit for four days before cycling and the cell without SLMP was cycled at C/3 after assembling. (b) The cycle performance and Coulombic efficiency for graphite half cells with (diamonds) and without SLMP (circles and squares) at C/3 rate. Solid symbols are for capacity (left *y*-axis) and open symbols are for Coulombic efficiency (right *y*-axis). The cell without SLMP with formation (circles) was cycled at C/25 for two cycles, followed by C/10 for five cycles, then cycled at C/3 rate. The cell without SLMP without formation (squares) was cycled at C/3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
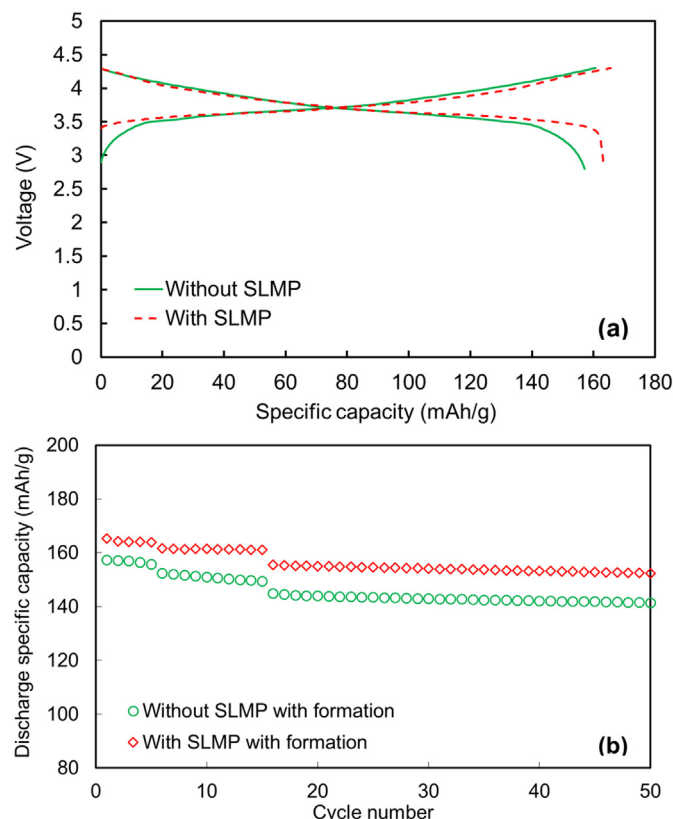
full cells. Several full cells with graphite (with or without SLMP) anode and NMC cathode have been constructed. Since lithium source is limited in full cells, impact of SLMP on the cell performance is expected to be seen on cell capacity (cycleable lithium amount) as well. For this purpose, two full cells, one with SLMP prelithiated graphite anode and one with regular graphite anode, were assembled. The SLMP-contained cell was allowed to rest for one day before cycling. Both cells were put in a formation process consisting five C/20 cycles and ten C/10 cycles prior to C/3 cycling test. The first cycle voltage profiles at C/20 rate of both cells are shown in Fig. 3(a). With SLMP in the anode, the open circuit voltage before cycling (at the end of resting) is about 2.2 V, significantly higher than that of the regular full cell at around 0.16 V, and this is consistent with what is observed in SLMP-contained graphite half cells described above, e.g., ∼0.2−0.4 V OCV after resting. Compared with the regular cell without SLMP, the voltage profile at both ends (start of charge and end of discharge) are distinctly different, indicating different lithiation and delithiation of graphite during these two regions. During formation and following C/3 cycling, the cell with SLMP constantly shows a larger capacity (∼10% higher) than the regular cell, and the C/3 cycle stability of the cells with and without SLMP are comparable. However, it was not clear at this point how SLMP affect the SEI formation, and whether SEI was developed during rest or formation cycles. To identify this, another test was conducted on a group of three full cells.

Fig. 3. (a) The first cycle voltage profile for graphite/NMC full cells without SLMP (green solid line) and with SLMP (red dashed line) at C/20 rate. The cell with SLMP was rested at open circuit for one day before cycling. (b) The cycle performance for graphite/NMC full cells without SLMP (circles) and with SLMP (diamonds). Both cells were cycled at C/25 for five cycles, followed by C/10 for ten cycles, then cycled at C/3 rate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

In addition to the regular full cell tested above (without SLMP cell), two more graphite/NMC full cells were assembled, one with SLMP and one without. The cell with SLMP was allowed to rest at open circuit for four days before cycled at C/3 rate, and the cell without SLMP was cycled at C/3 rate right after assembling. No small external current driven formation process was applied for
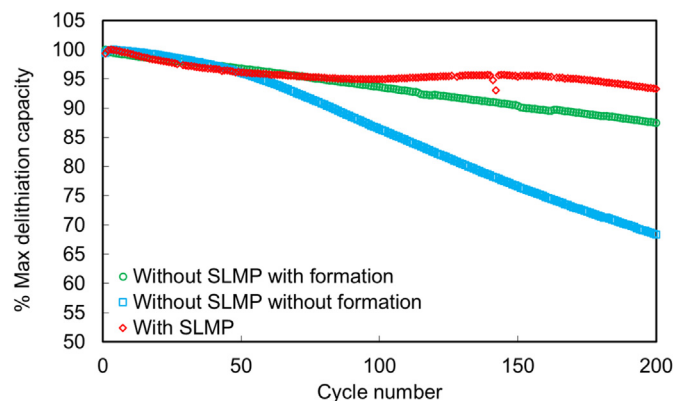

Fig. 4. Cycle performance for graphite/NMC full cells without SLMP (squares and circles) and with SLMP (diamonds) at C/3 rate. The cell with SLMP was rested at open circuit for four days before cycling. The cell without SLMP with formation (circles) was cycled at C/25 for five cycles, followed by C/10 for ten cycles, then cycled at C/3 rate. The cell without SLMP without formation (squares) was cycled at C/3 after assembling.

these two cells. Cycle performance for the first 200 cycles of these two cells, as well as the above discussed regular cell after formation process, are shown in Fig. 4. As expected, the cell without SLMP and without formation decays the fastest, most likely due to the poor quality of formed SEI. After 200 cycles, the capacity decays to only 68.2% of its initial value. Meanwhile, capacity retention of the cell with SLMP and the one without SLMP but with formation was 93.2% and 87.3%, respectively. Among these three cells, SLMP-contained cell displays the highest capacity retention upon cycling, regardless no low current formation process involved. These results indicate that SEI formation in the SLMP prelithiated cell occurred during its resting time and the quality of the developed SEI is the same effective or even better than that developed in the regular cell upon low current formation.

This study, therefore, has provided direct evidence that SLMP can effectively help SEI formation. Particularly, after the cell with SLMP prelithiated anode is assembled, it could be rested at open circuit and the SEI formation occurred spontenously. It is possible to skip the external current driven formation process to reduce lithium battery manufacturing cost by applying this strategy.

4. Conclusions

SLMP has been successfully applied into graphite anode. With SLMP prelithiation, after resting at open circuit for a few days, both graphite half cells and graphite/NMC full cells showed higher first cycle capacity and Coulombic efficiency than their corresponding regular cells without SLMP. Cycle performance of SLMP-contained cells are better than that without SLMP, even some of them are subject to low external current driven formation processes. Cells with SLMP have developed full functional SEI on graphite during the resting time. Development of such SEI (using SLMP method) is equivalent to or even better than the slow formation protocols used in regular lithium ion cells. This implies that the manufacturing cost for cell formation can be significantly reduced with additional of SLMP and elimination of regular cell formation process. This new prelithiation method also implies that the promising future of application of SLMP in other higher energy density anodes such as Si and Sn, which are currently unlikely used in commercial lithium-ion batteries because of the large first cycle irreversible capacity loss.

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