

ORNL Manufacturing Demonstration Facility
Technical Collaboration **Final Report**

Demonstration of Deposition and Integration of Stabilized Lithium Metal Powder (SLMP) into Electrode Surfaces and Packaging in Battery Pouch Cell¹

FMC Lithium

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Summary

This Oak Ridge National Laboratory (ORNL) research objective was to demonstrate dry application of FMC's proprietary Stabilized Lithium Metal Powder (SLMP[®]) material through roll compaction onto the electrode substrate. This would allow for the minimal change to current electrode processing practices and is expected to be on a fast track for industry adoption.

The work entailed relocating existing equipment into ORNL's dry room, tooling that equipment to accommodate the SLMP material, and performing roll compaction of SLMP materials onto electrode substrates to demonstrate semi-continuous processing. Three coating trials with various loads of SLMP were conducted, pouch cell built, and electrochemical testing was performed.

This study demonstrated the dry application of SLMP by roll compaction onto an electrode in a roll to roll manufacturing environment. Electrochemical testing of pouch cells manufactured with roll compacted SLMP improved electrochemical performance, reduced first cycle efficiency and improved capacity retention compared to baseline materials without SLMP to some extent.

Background

SLMP Technology was developed by FMC Lithium and provides an independent source of lithium for increasing the energy density of lithium ion batteries along with enhancement of calendar life performance. Normal lithium metal powder is pyrophoric and can only be handled under heavy organic oils or in an inert atmosphere. SLMP has a continuous stabilizing coating layer which renders the powder non-pyrophoric and

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safe to handle under controlled environmental conditions such as in a dry room of -30°C dew point or better. SLMP contains about 98% metallic lithium and can be shipped by air or sea.

SLMP breaks the current limitation that all lithium in a battery must be supplied by the cathode. This opens up the choice of cathode materials to non-lithium containing compounds that are more charge tolerant and potentially have higher capacity than the current state of the art lithium providing cathode materials. SLMP can be used with current battery chemistries to compensate for anode first cycle inefficiencies resulting in improvements in energy density of up to 30%. SLMP is an enabling material and allows for the adoption of high capacity materials which have high irreversible capacity such as silicon and tin based materials. After electrolyte addition, lithium diffuses into the active anode matrix and there is no metallic lithium left in the cell.

The benefits of SLMP technology have been validated by the majority of battery manufacturers worldwide. However, adoption of the technology on the commercial scale has been hindered due to the difficulties associated with technology integration. FMC is pursuing the development of a tool that could be retrofitted into the existing battery manufacturing processes, or conceptually new designs that specifically target large format battery production to enable use of SLMP. This will bridge the gap between laboratory validation of SLMP technology and the ability to use this revolutionary technology for large format high energy density Li-ion batteries.

Technical Results

Pouch cell assembly and test

The anode used in this work is graphite A12 anode (ConocoPhillips) with A12/Super P Li/Kureha 9300 PVDF in 92/2/6 wt while the cathode is LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (Toda America, NMC532) with NMC532/Denka carbon black/Solvay 5130 PVDF in 90/5/5 wt. The anode and cathode areas are 50.1 and 47.3 cm², respectively. The solid loadings are 6.93 and 12.92 mg/cm² for anodes and cathodes, respectively. The electrode balance (anode capacity/cathode capacity) is 1.1. 3 ml of electrolyte (1.2 M LiPF₆ in EC/DMC (3/7 wt)) was loaded into each pouch cell.

Three single layer pouch cells were cycled at 0.1C/-0.1C between 2.5 and 4.2V. One cell is without SLMP; another cell is with excess amounts of SLMP (21.9 mg); the 3rd cell is with adequate SLMP.

Procedure to add SLMP to the graphite anodes

A rolling trial with SLMP screened onto the current collector of graphite / copper anode using a single 64 mm diameter Ø stainless steel roll against a granite surface plate was performed. A single cell lithium ion battery pouch was produced from the SLMP imbedded anode. A baseline cell without SLMP was produced from the same lot of graphite / Cu anode material. Cathode material was also from the same lot for both cells.

A sandwich method was used to retain the SLMP material on the graphite current collector prior to rolling. The SLMP was applied by hand vibration screening through a

325 mesh screen to create an approximate monolayer on the current collector. The copper anode and current collector are depicted schematically in figure 1.

The bare copper measured 12 μm in thickness; Copper plus coated graphite measured 96 to 98 μm . The estimated rolling load was between 50 and 70 pounds. Figure 2 shows the equipment used to perform the rolling, and a plan view of the graphitic anode showing that SLMP distribution to be heterogeneous.

It was observed that the SLMP did appear as a monolayer under stereoscopic examination. The apparent high concentration areas shown in figure 2 are lateral connectivity of SLMP powder, not stacked connectivity as shown in the stereographic images of figure 3a, 3b and 3c. The morphology of the spherical SLMP has changed to a flattened shape with evidence of good adherence and mechanical embedment. The electrode surface indicates some SLMP patches which in turn indicates a need for future optimization in dispersion of particles on the surface and an optimization in pressure applied to fully activate all particles.

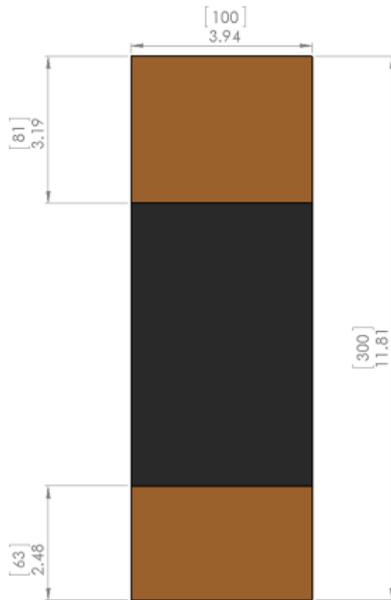


Figure 1: Schematic of the copper (brown)/ graphite (black) anode raw material used to imbed SLMP® onto the anode via sandwich rolling with a top copper foil (brown).

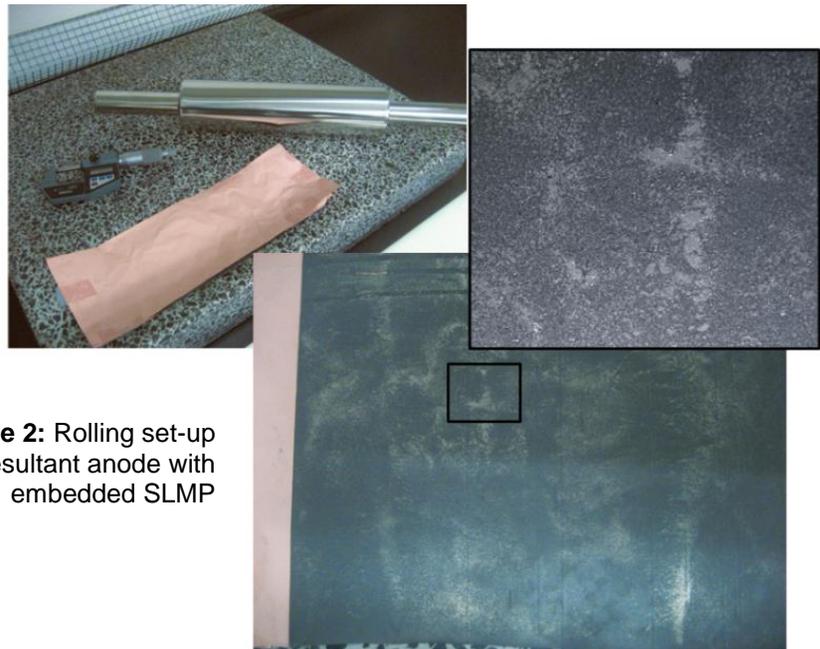


Figure 2: Rolling set-up and resultant anode with embedded SLMP

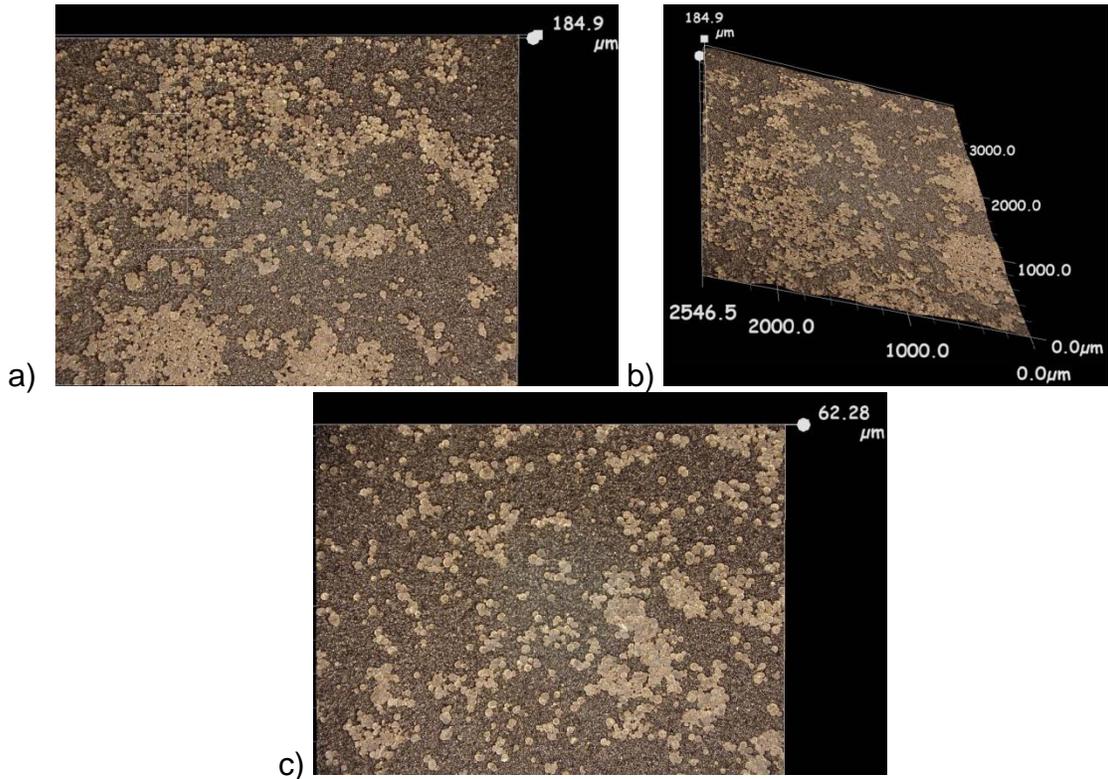


Figure 3: Rolled SLMP into graphitic / Cu anode a) Overview; b) Tilted; c) Close up

Electrochemical performance

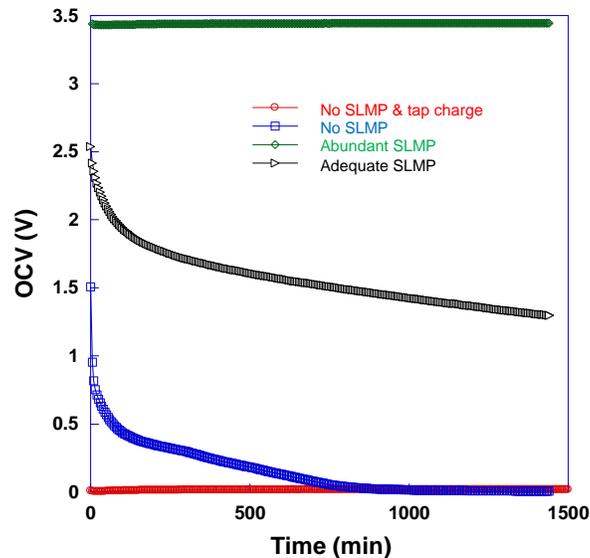


Figure 4: Open circuit voltage of the pouch cells during 24 hours test.

The pouch cell shows an open circuit voltage (OCV) of ~0 V without SLMP. The OCV increases to 1.8 V and 0.7 V with abundant SLMP and adequate SLMP, respectively. The drop in voltage over time is as expected and indicates the diffusion of lithium into the graphite structure. However, after 24hrs we have observed that SLMP diffusion should be complete for carbon anode and the voltage should start out higher. This may indicate future need in optimizing rolling pressure. The pouch cells were tap charged at

C/20 for 10 min after they were assembled to avoid corrosion on Cu current collector. The OCV increases during the 10 min tap charge to 1.5V, 3.5V and 2.5 V for the cases without SLMP, with abundant SLMP and with adequate SLMP, respectively. The OCV was recorded during the subsequent 24 h test as shown in figure 4. The OCV degrades to 0 V after 15 h for the cell without SLMP and to 1.4 V after 24 h for the one with adequate SLMP, respectively. In contrast, the OCV remains constant at 3.5 V during the 24 h test for the cell with abundant SLMP. 3.5 V is the potential between Li/Li⁺ and NMC532 thus indicating there is abundant SLMP on the graphite anode even after part of the SLMP diffuses from the rolled surface into the active graphite anode material.

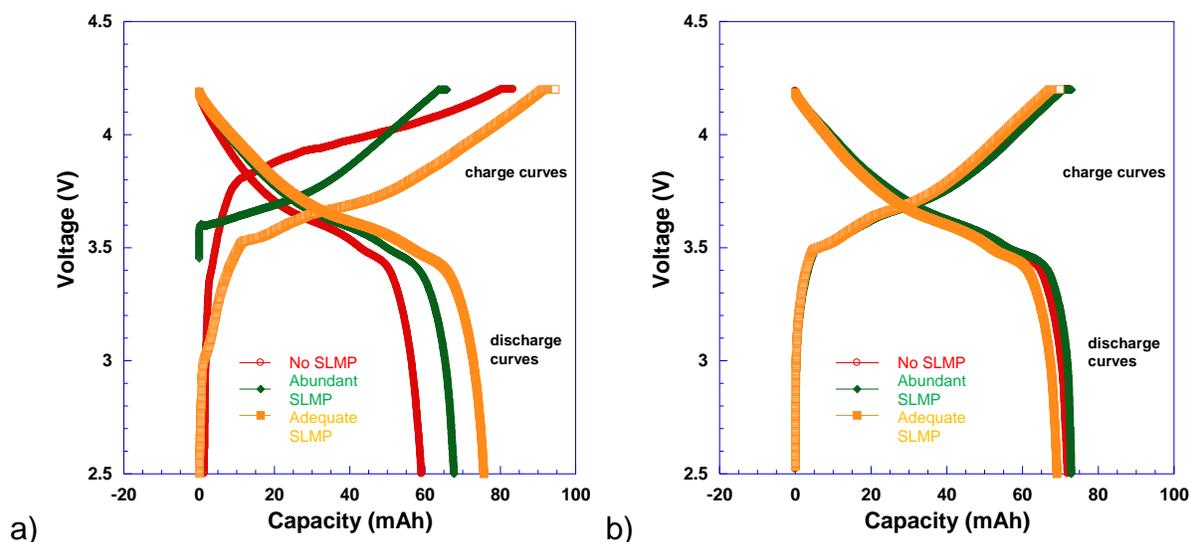


Figure 5: Voltage profiles a) 1st cycle and b) 10th cycle.

Figure 5 shows the voltage profiles during the 1st cycle and 10th cycle. The addition of SLMP reduces the over potential (polarization) in the 1st cycle. Without SLMP, the voltage plateau is between 3.8 and 4.0 V and it decreases to 3.6-3.8 and 3.5-3.7 V for the cells with abundant SLMP and adequate SLMP, respectively. In addition, the voltage plateaus in discharge step increases with the addition of SLMP and follows: No SLMP < with abundant SLMP < with adequate SLMP. This leads to over potentials in those cells: No SLMP > with abundant SLMP > with adequate SLMP. Consequently, the capacity follows the opposition order. In contrast, the effect of SLMP on voltage plateau reduces and eventually disappears when the cells go through more cycles. This is verified by the voltage profiles at the 10th cycle shown in figure 5 b). The voltage profiles are almost identical.

Figure 6 shows the capacity of the pouch cells. Due to non-optimized pressure and amounts of SLMP, it is difficult to develop a full understanding of the trend. However, differences are measurable and future works will need to optimize amounts and parameters for the integration of SLMP in full cells.

The cell without SLMP exhibits substantial irreversible capacity loss (ICL) in the 1st cycle (figure 7). The ICL reduces with adequate SLMP and goes to slightly negative with abundant SLMP. The ICL also reduces in the subsequent cycles and are almost identical after 10 cycles which can be seen from the excellent Coulomb efficiency (figure 8). The Coulomb efficiency is above 99.5% after 10 cycles. The cell without SLMP

shows substantial capacity fade and only remains 85% capacity after 50 cycles (figure 9). In contrast, the addition of abundant SLMP significantly improves the capacity retention, maintaining 95%+ after 50 cycles.

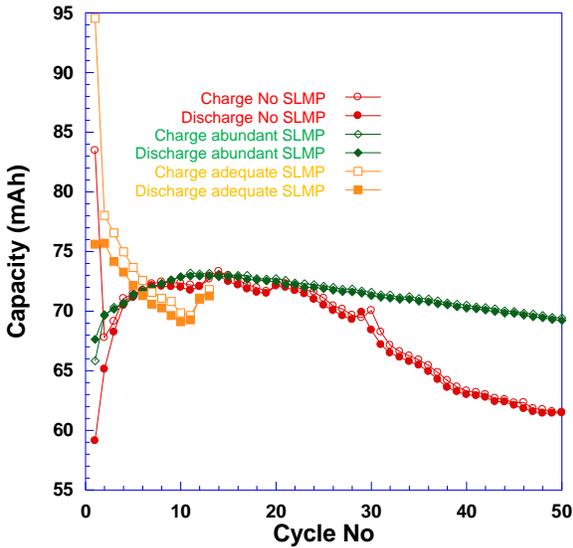


Figure 6. Discharge capacity vs. cycle No.

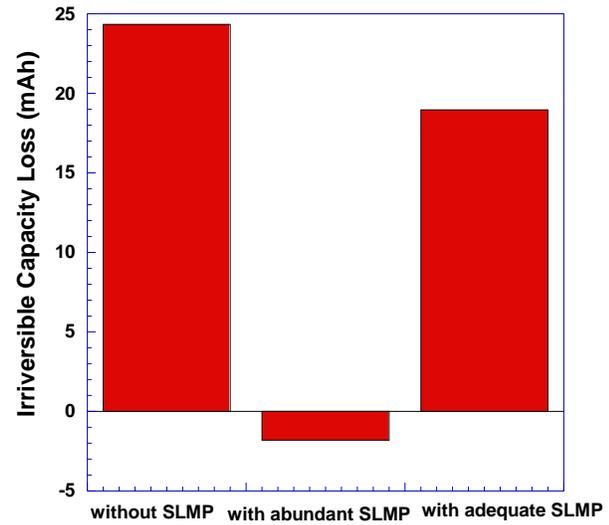


Figure 7. Irreversible capacity loss at the 1st cycle.

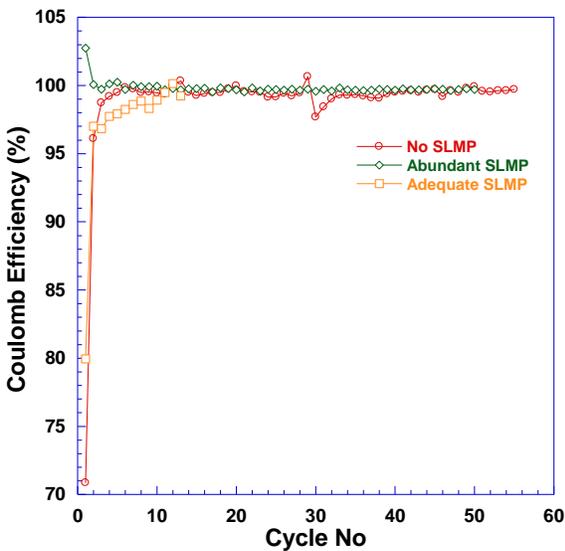


Figure 8. Coulomb efficiency vs. cycle No.

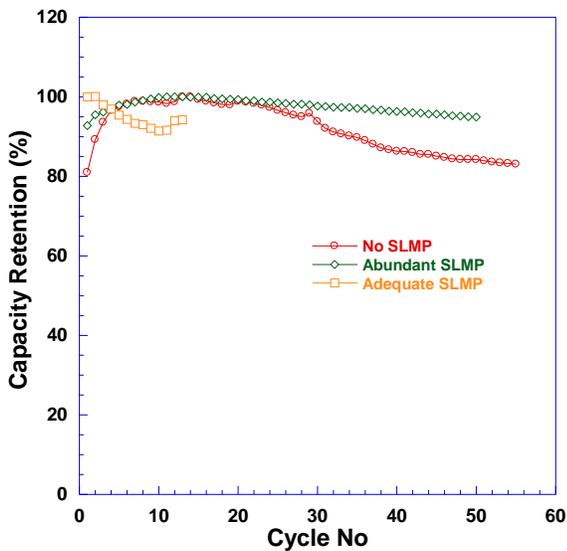


Figure 9. Capacity retention vs. cycle No.

Impacts

A roll to roll integration of SLMP into electrode surfaces would enable a mass manufacturing process to include SLMP in battery manufacturing and allow for a reduction in first cycle efficiency loss and better performing batteries for a variety of applications. The process would be able to allow for a shorter formation cycle and lower cost production of lithium ion batteries.

Conclusions

This study demonstrated the dry application of SLMP by roll compaction onto an electrode in a roll to roll manufacturing environment. Electrochemical testing of pouch cells manufactured with roll compacted SLMP improved electrochemical performance, reduced first cycle efficiency and improved capacity retention compared to baseline materials without SLMP to some extent.

This technology assessment demonstrated the general feasibility but also allowed for the observation of some major challenges for this technology. The biggest challenge is the homogeneous distribution and application of very small amounts of SLMP on an electrode surface in an industrial manufacturing environment. Industry will need to continue working on an adequate dispensing system and optimize compression.

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