Comparison of Solid State Lithium Batteries Assembled with $Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ (LAGP) and $Li_2Al_2SiP_2TiO_{13}$ (LICGC) Solid Electrolyte Sheets

This application note shows the assembling and testing operations of solid state lithium batteries with $Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ (LAGP) and $Li_2Al_2SiP_2TiO_{13}$ (Lithium Ion Conductive Glass Ceramic, LICGC) solid electrolyte sheets. The performance of LAGP and LICGC solid state lithium batteries are compared.

Experimental Materials and Equipments

Solid Electrolyte Sheets

LAGP

Li1.5Al0.5Ge1.5P3O12 Conductive Ceramic Separator Sheets with Optional Sizes for Li-Air & Solid Rechargeable Batteries - EQ-LAGP-LD

Sale Price: USD$249.00

LICGC

Li2Al2SiP2TiO13 Conductive Glass Ceramic Separator Sheets with Optional Sizes for Li-Air Batteries - EQ-CGCS-LD

Sale Price: USD$298.00

Cathode, Anode, Separator, and Liquid Electrolyte

Cathode

Li-Ion Battery Cathode - Aluminum Foil Single Side Coated by LiCoO2 (241 mm L x 200 mm W x 55 um Thickness) 5 sheets/bag - bc-af-241co-ss-55

Sale Price: USD$189.95

Anode

Lithium Chip 15.6 mm Dia x 0.25 mm thickness for Li-ion Battery R&D 100 g/bottle (4000 pcs) - EQ-Lib-LiC25

Sale Price: USD$459.00

Separator

Ceramic Coated Membrane (16 um thick x 60 mm W x 500 mL) as Separator of Li-ion Battery - EQ-bsf-0016-500A

Sale Price: USD$498.00

Liquid Electrolyte

Electrolyte LiPF6 for LiCoO2 Lithium-ion Battery R&D, 1 kg in Stainless Steel Container - EQ-LBC3051C

Sale Price: USD$549.00

Equipments

Split Cell

Pressure Controlled Split Coin Cell with Optional Size up to 20 MPa For SSB Research - EQ-PSC

Sale Price: USD$589.00

Pipette

Precision Electronic Single Channel Pipette: 20 – 200 uL with Battery & Charger - BD-200UL-LD

Sale Price: USD$495.00

Disc Cutter

Compact Precision Disc Cutter with 4 Sets of Cutting Die (15, 19, 20 & 24 mm) - MSK-T-07

Sale Price: USD$1,998.00

Glove Box

Glove Box with H2O & O2 Purification System and Openable Front Window - EQ-VGB-6OP-LD

Sale Price: RFQ

Press

1T Compact Pneumatic Compressing Jig - YLJ-01

Sale Price: USD$1,995.00

Load Cell

Pressure Calibration Kit: NIST certificated Load cell + Digital Meter - BS-070-LD

Sale Price: USD$1,469.00

Battery Analyzer

8 Channel Battery Analyzer (0.005 -1 mA, up to 5 V) w/ Adjustable Cell Holders Laptop & Software - BST8-WA

Sale Price: USD$3,698.00

Solid State Lithium Battery Assembly

Experimental Setup and Battery Assembly

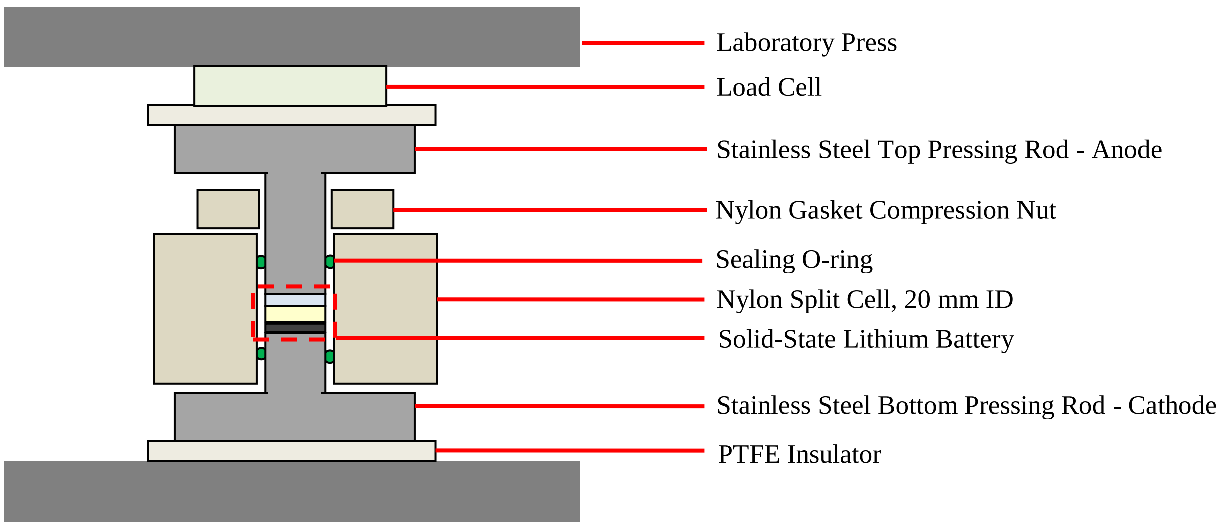


Fig. 1 Schematic of the split cell experimental setup.

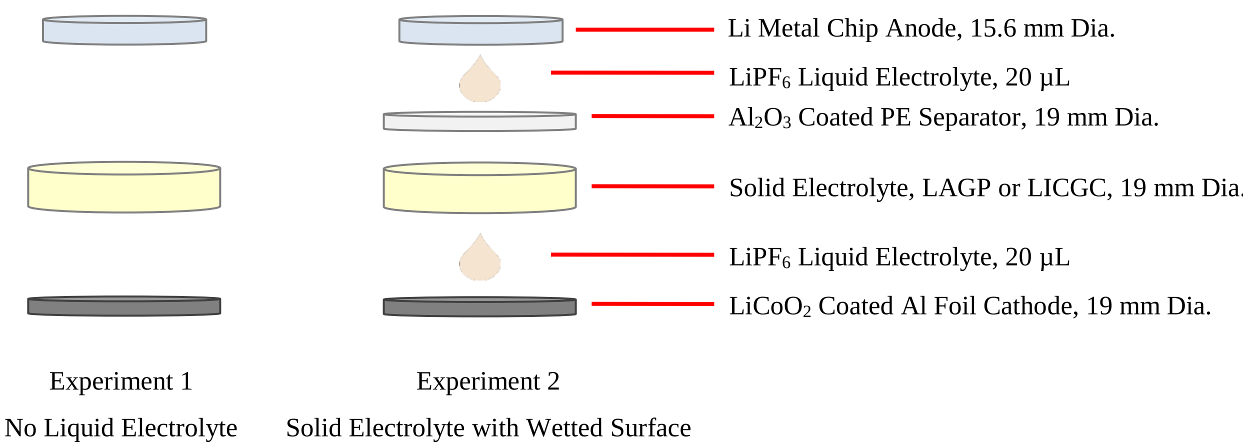


Fig. 2 Schematic of the solid state lithium battery assembled with solid state electrolyte.

Table 1 Specification of the assembled solid state lithium batteries.

Solid Electrolyte	LAGP or LICGC. 19 mm Dia. 0.3 mm or 0.15 mm Thickness 4×10^{-4} S/cm Ion Conductivity at 25 °C (See Table 2 for Details)
Cathode	$LiCoO_2$ Coated Al Foil, Single Sided Cut into 19 mm Dia. Chip by Disc Cutter. 0.055 mm Thickness
Anode	Li Metal Chip 15.6 mm Dia., 0.25 mm Thickness
Separator	Al_2O_3 Coated Polyethylene (PE) Membrane. Cut into 19 mm Dia. Chip by Disc Cutter. 0.016 mm Thickness
Liquid Electrolyte	1M $LiPF_6$ Liquid Electrolyte. 1×10^{-2} S/cm Ion Conductivity at 25 °C 20 µL on Each Side of Solid Electrolyte. 40 µL Total
Pressing Rods	Stainless Steel Rods. 20 mm Dia.
Assembled Size	19 mm Dia., 0.62 mm (LAGP) or 0.47 mm (LICGC) Thickness
Specific Capacity $LiCoO_2$	145 mAh/g (Reported)
$LiCoO_2$ Weight	3.6×10^{-2} g (Reported)
Expected Capacity	5.2 mAh
Temperature	25 °C
Gas Environment	Glove box filled with high purity Ar gas. H_2O and O_2 level < 1 ppm

Table 2 Comparison between LAGP and LICGC solid electrolyte sheets.

	LAGP	LICGC
Composition	$Li_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$	$Li_2Al_2SiP_2TiO_{13}$
Structure	NASICON (Na Super Ionic Conductor)	NASICON (Na Super Ionic Conductor)
Ion Conductivity at 25 °C	4×10^{-4} S/cm (Reported)	4×10^{-4} S/cm (Reported)
Average Grain Size	~25 µm (Reported)	1-10 µm (Reported)
Chemical Resistance	Water and Mild Acid Resistance	Water and Mild Acid Resistance
Stable in Air and Water	Yes	Yes
Stable with Li Metal	Yes	No (Separator Needed)
Size	19 mm Dia	19 mm Dia
Thickness	0.3 mm	0.15 mm
Part Number	**EQ-LAGP-LD**	**EQ-CGCS-LD**

Battery Assembling Procedures

1. Use the disc cutter to cut $LiCoO_2$ (LCO) coated Al foil and Al_2O_3 coated polyethylene (PE) membrane into 19 mm Dia. chips. Move the experimental materials and equipments into the glove box from the openable front window. Install the power, gas, and testing cable feedthroughs on the glove box. Seal the glove box, purge and cycle until both H_2O and O_2 levels drop < 1 ppm.

2. Open the Li metal chip container only after both H_2O and O_2 levels drop < 1 ppm. Prepare the work space in the glove box, and make sure the experimental materials and tools are ready for use.

3. Use tweezers to put LCO/Al cathode chip on top of the bottom pressing rod with LCO coated side facing up.

4. Use the digital pipette to draw 20 uL $LiPF_6$ liquid electrolyte, and spread the liquid electrolyte evenly on the cathode chip. Put the solid electrolyte sheet (LAGP or LICGC) right on top of the wetted cathode chip. For Experiment 1, no liquid electrolyte is used, and solid electrolyte sheet is directly put on top (See Fig. 2 for details).

5. Due to the instability of LICGC solid electrolyte when in contact with Li metal, a separator between Li metal anode and LICGC solid electrolyte sheet is needed for LICGC protection and dendrite growth prevention. Use tweezers to put the Al_2O_3 coated PE separator chip on top of the solid electrolyte as a protection interlayer. Use the digital pipette to draw 20 uL $LiPF_6$ liquid electrolyte, and spread the liquid electrolyte evenly on the separator chip. For Experiment 1, no liquid electrolyte is used. Also, no separator chip is used to ensure physical contact between LICGC and Li metal anode when pressed together.

6. Use tweezers to put the Li metal anode on top of the separator chip and solid electrolyte sheet. Make sure the anode chip is right at the center to avoid shorting between anode and cathode.
7. Put the top pressing rod through the compression nut, and press the rod through the top sealing O-ring. Carefully press down the top pressing rod until it is in contact with the Li metal anode. Rotate the gasket compression nut tight to seal the assembled battery inside the split cell.
8. Adjust the input gas pressure of the pneumatic press and set it to be the lowest pressure needed to raise the pressing stage. Insulate the top and bottom pressing rods of the split cell with the PTFE insulators. Position the split cell at the center of the pneumatic press. Raise the pressing stage to hold the split cell in place. Gradually adjust the input gas pressure and check the load cell force reading to reach the desired pressing force / pressure.
9. Connect the split cell to the battery analyzer outside of the glove box using the testing cable feedthrough. Connect the red clips to the bottom pressing rod (cathode); connect the black clips to the top pressing rod (anode). Start the battery testing.
10. Please refer to the instruction video for details.

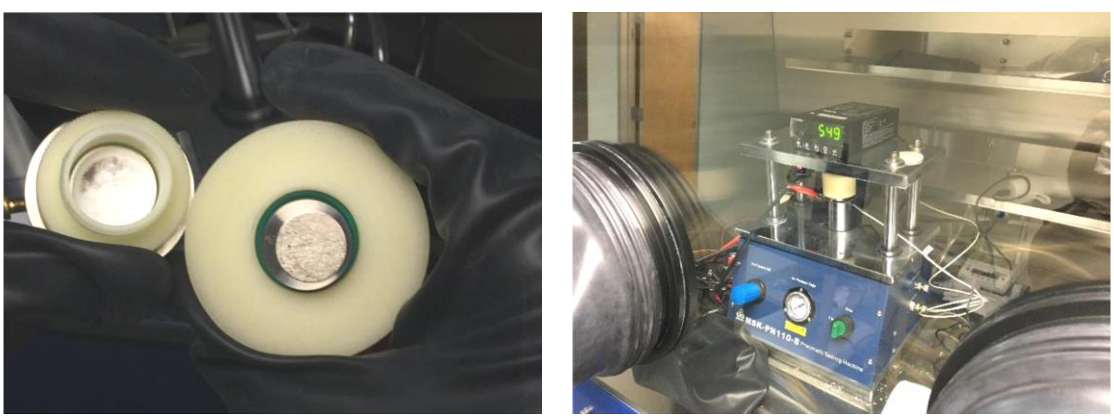


Fig. 3 Battery assembling procedures of solid state lithium battery.

Solid State Lithium Battery Testing

Experiment 1 - Solid Electrolyte with No Liquid Electrolyte

Table 3 Experiment 1 – battery testing parameters.

Solid Electrolyte	LAGP	LICGC
Pressing Force	50 – 5000 N	
Pressure	0.16 – 16 MPa	
Charge	Constant Current Discharge to 5.0 V. Current – 0.5 mA, 0.1 mA, 0.05 mA	
Discharge	Constant Current Discharge to 2.5 V. Current – 0.5 mA, 0.1 mA, 0.05 mA	
Current Density	0.25 mA/cm^2, 0.05 mA/cm^2, 0.025 mA/cm^2	

For solid state lithium batteries assembled with no liquid electrolyte, the assembled battery shows very large internal resistance.

A pressing force of 500 N (1.6 MPa pressure) is applied to the battery, and maintained during charge – discharge cycles. For LAGP solid state battery, it shows an open circuit voltage of ~2.4 V before charging; while for LICGC solid state battery, ~3.3 V before charging. When charged with a constant current as low as 0.05 mA, both batteries quickly raise to 5.0 V, indicating very large internal resistance. After charging, the open circuit voltage cannot be maintained, and will slowly drop to the initial voltage before charging (~2.4 V for LAGP, ~3.3 V for LICGC).

The cause of large internal resistance is attributed to the poor solid-solid interface contact between electrolyte sheet and electrode chips. The resulting large interface resistance dominates the battery internal resistance, and making it difficult to charge energy into the solid state batteries.

The pressing force is varied from 50 to 5000 N. No obvious change on the battery performance is observed. The solid-solid interface contact between electrolyte sheet and electrode chips cannot be improved by increasing the pressing force (up to 5000 N) alone.

Experiment 2 - Solid Electrolyte with Liquid Electrolyte Wetted Surfaces

Table 4 Experiment 2 – battery testing parameters.

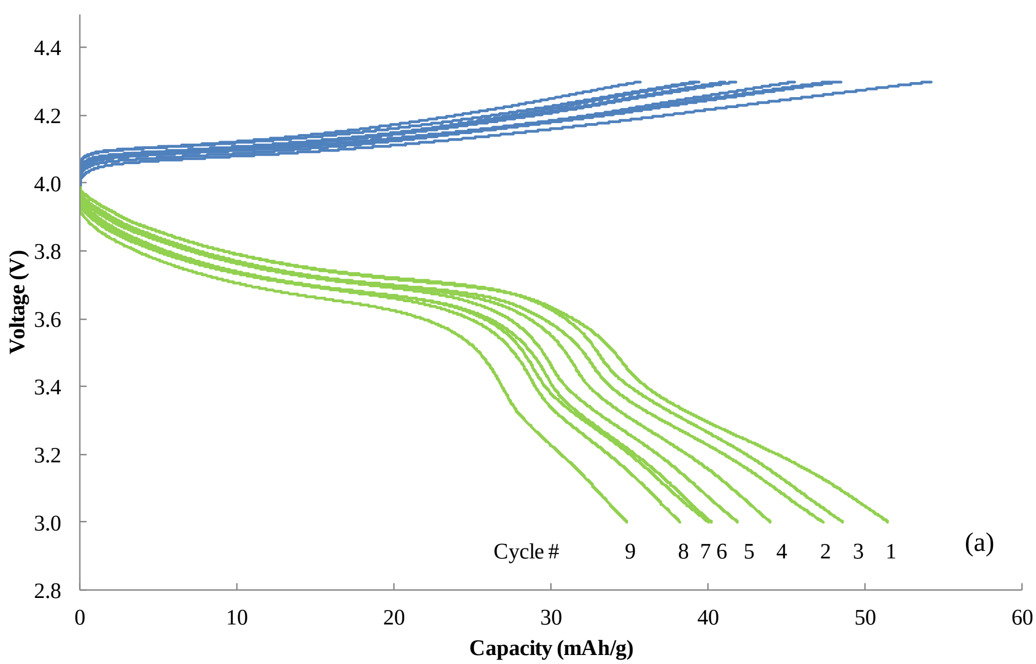
Solid Electrolyte	LAGP	LICGC
Pressing Force	500 N	500 N, 800 N
Pressure	1.6 MPa	1.6 MPa, 2.6 MPa
Charge	Constant Current Discharge to 4.3 V. Current – 0.5 mA	
Discharge	Constant Current Discharge to 3.0 V. Current – 0.5 mA	
Current Density	0.25 mA/cm^2	

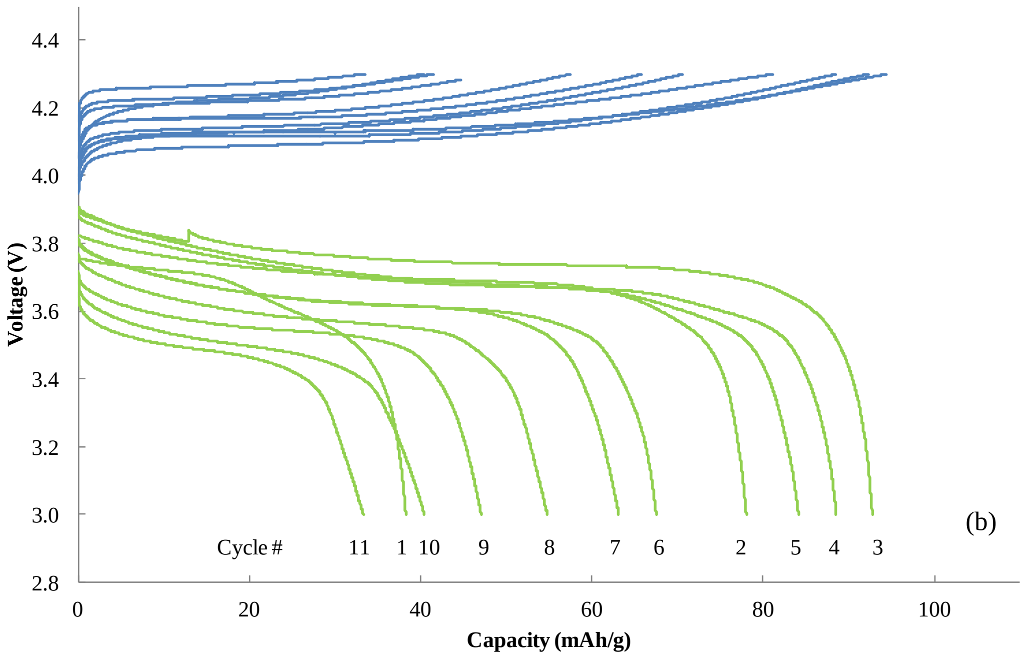
For solid state lithium batteries with $LiPF_6$ liquid electrolyte wetted solid electrolyte, the solid-solid interface contact are greatly improved by the small amount of liquid electrolyte sandwiched between solid electrolyte sheet and electrode chips. As a result, the battery performance is significantly improved compared to Experiment 1.

Figures of charge-discharge profile and cycle performance are shown in Fig. 4. A pressing force of 500 N (1.6 MPa pressure) is applied to the battery, and maintained during charge – discharge cycles. For both LAGP and LICGC solid state batteries, an open circuit voltage of ~3.1 V is observed before charging. Then, both batteries are tested with multiple charge – discharge cycles, and the battery performance is compared between LAGP and LICGC solid electrolytes. Moreover, the pressing force for the LICGC solid state battery is increased to 800 N (2.6 MPa pressure) after 9 cycles to study the mechanical pressure effect.

Under the 500 N pressing force, LAGP solid state battery shows an initial specific capacity of 52 mAh/g at cycle 1, and decreases linearly in the following cycles. At cycle 9, the specific capacity drops to 35 mAh/g. For LICGC solid state battery tested under the same conditions, the specific capacity starts with a low value of 38 mAh/g at cycle 1, and then increase rapidly to reach 93 mAh/g at cycle 3. After cycle 3, the specific capacity drops in a linear trend to 55 mAh/g at cycle 8. Both LAGP and LICGC solid state batteries give a high efficiency around 96% or higher throughout the multiple cycles. In terms of battery capacity, the LICGC solid state battery with $LiPF_6$ wetted solid electrolyte exhibits better battery performance than the LAGP solid state battery.

To study the effect of pressing force on solid state lithium batteries with $LiPF_6$ wetted solid electrolyte, the pressing force is increased from 500 N (1.6 MPa) to 800 N (2.6 MPa) before the start of cycle 9 of LICGC solid state battery (See Fig. 4c). No significant improvement on battery performance is observed thereafter, while the specific capacity keeps decreasing in the same linear trend over cycle / time. This result is expected, as the main improvement on the solid-solid interface is from the incorporation of $LiPF_6$ liquid electrolyte, which would not be affected much by a higher mechanical pressure.





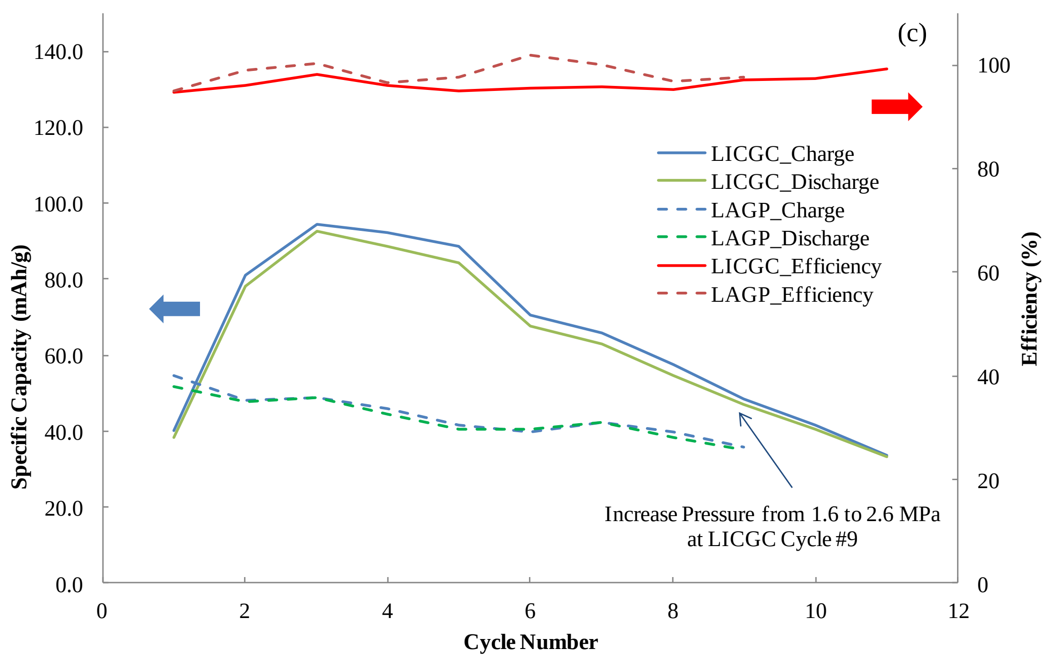


Fig. 4 (a) Charge-discharge profile of battery with $LiPF_6$ surface wetted LAGP. (b) Charge-discharge profile of battery with $LiPF_6$ surface wetted LICGC. (c) Comparison of cycle performance between LAGP and LICGC solid state batteries. The batteries are charged / discharged at a constant current of 0.5 mA from 3.0 – 4.2 V.

After the above experiment of solid state lithium battery with $LiPF_6$ surface wetted LAGP, the LAGP battery is dissembled and 20 µL of $LiPF_6$ liquid electrolyte is re-applied to each side of the LAGP solid electrolyte for re-wetting the surfaces. Keeping the same LCO/Al cathode and Li metal anode from the previous experiment, the LAGP solid state battery is re-assembled in the split cell with the re-wetted LAGP solid electrolyte. Then the battery is tested under the same conditions as the previous experiment (500 N pressing force, same charge-discharge parameters). The measured specific capacity goes back up and reaches the capacity of the original first cycle, which is ~52 mAh/g (See Fig. 5). This reveals that the degradation of battery performance is mainly from the consumption / evaporation of the small amount of the $LiPF_6$ liquid electrolyte sandwiched between LAGP and electrodes, which deteriorates the solid-

solid interface contact, increases the interface resistance, and lowers the capacity over cycle / time.

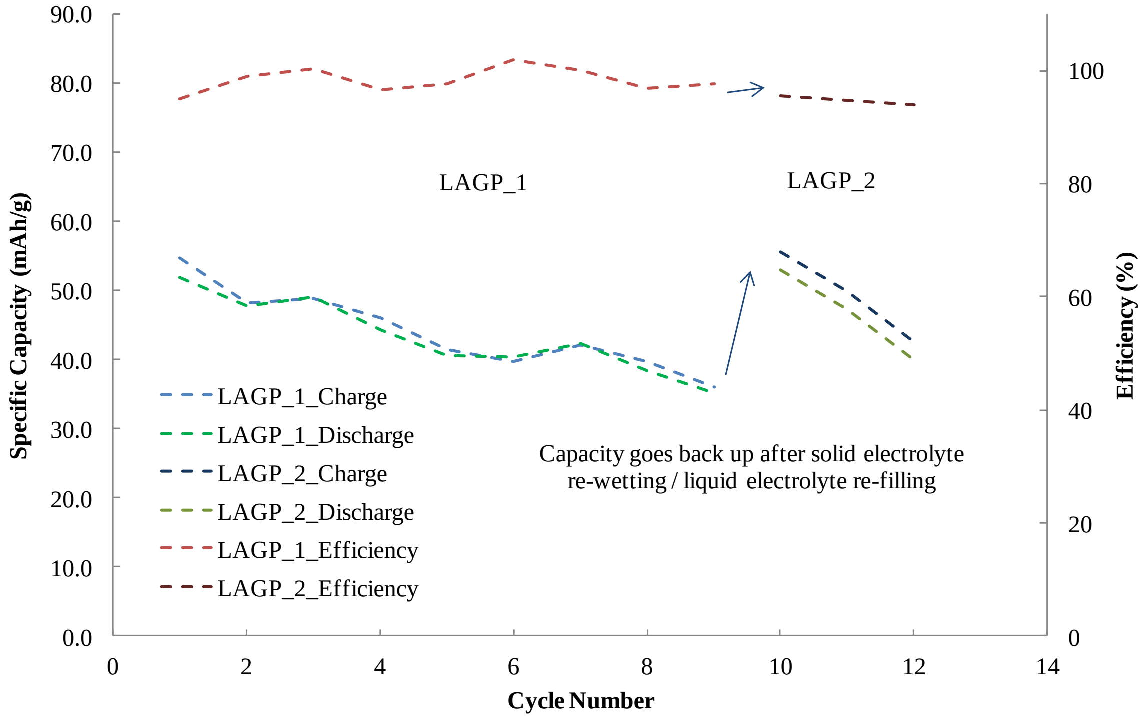


Fig. 5 Comparison of cycle performance between the original LAGP solid state battery (LAGP_1 in the figure) and the re-assembled the LAGP solid state battery with LAGP solid electrolyte re-wetted (LAGP_2 in the figure). The batteries are charged / discharged at a constant current of 0.5 mA from 3.0 – 4.2 V.

Conclusion

1. The interface resistance between electrolyte sheets and electrode chips is crucial for the battery performance of solid state lithium batteries. Wetting the surfaces of solid electrolyte with a small amount of liquid electrolyte can greatly reduce the interface resistance and improve the battery performance.

2. The battery performance of LAGP and LICGC solid electrolytes are compared under the same testing conditions and the LICGC battery exhibits higher battery capacity. The LICGC solid state battery with $LiPF_6$ wetted solid electrolyte achieves a specific capacity of 93 mAh/g at cycle 3, while the LAGP solid state battery with $LiPF_6$ wetted solid electrolyte gives the highest specific capacity at cycle 1, which is 52 mAh/g.

3. The pressing force has no obvious effect on the battery performance of solid state lithium battery assembled with surface wetted solid electrolyte.