Building an Interfacial Framework: Li/Garnet Interface Stabilization Through a Cu₆Sn₅ Layer

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EXPERIMENTAL

1. Preparation of LLCZNO Garnet Electrolyte

LLCZNO pellet was synthesized by sol-gel method. Stoichiometric amounts of starting materials: LiNO₃ (99.99%, Sigma-Aldrich, 10% excess), Ca(NO₃)₂ (99.99%, Sigma-Aldrich), La(NO₃)₃.6H₂O (99%, Macklin), ZrO(NO₃)₂.xH₂O (99.99%, Sigma-Aldrich), NbCl₅ (99.99%, Alfa Aesar), citric acid and ethylene glycol were dissolved in de-ionized water. The mole ratio of citric acid and ethylene glycol was 1:1. The precursors were dried at 90 °C for 12 h to evaporate the water and then sintered at 400 °C and 800 °C. The Garnet powder was uniaxially pressed into pellets under the pressure of 400 MPa and sintered at 1100 °C for 10 h to acquire stable cubic phase with the coverage of LLCZNO mother powder. The as prepared pellet was polished and stored in glovebox.

2. Preparation of Cu₆Sn₅ modification layer

Cu and Sn were deposited on garnet substrate simultaneously by magnetron sputtering. The ratio of deposition rate of Cu and Sn is crucial to form Cu_6Sn_5 thin film as pure as possible and the final alloy production. The power of radio frequency generators for Cu target and Sn target were adjusted to 45W and 100W, respectively. With 8 cm target-substrate distance and 60 min deposition, the amount of Cu and Sn were measured to be 0.392 mg/cm² and 0.625 mg/cm². During Cu-Sn co-sputtering, the substrate was heated to 250 °C to facilitate the alloying of Sn and Cu to form Cu_6Sn_5 , then cooled slowly to room temperature in the cooling rate of 2 °C /min. 60 min deposition time is applied for XRD analysis. When it came to symmetric cell or full cell assembly, the

deposition time is 90 s for Sn and o 60 s for Cu_6Sn_5 interlayers. The thickness of both Sn and Cu_6Sn_5 were about 50 nm.

3. Assembly of Li/Garnet/Li Symmetric Cells and Li/Garnet/LiCoO₂ Hybrid Solid State Full Cells

Garnet pellets with and without Cu_6Sn_5 modification were attached with Li foils on both sides. Two stainless steels current collectors were attached outside the Li foils under the pressure of about 4000 Pa. The symmetric cells were heated in 200 °C for 10 minutes to ensure intimate contact with both garnet pellets and stainless steels current collectors. With respect to the full cell, LiTFSI (99%, Aldrich) was dissolved in PY14TFSI (Moni Chem. Eng. Sci. & Tech. Co., Ltd.) with a concentration of 0.3 M. LiCoO₂ and Super-P with a mass ratio of 3:1 were then composited and remained toothpaste like.¹ The percentage of the active material was 40 wt%, the solid content of the composited cathode was about 60 % and the loading was about 2 mg. A stainless steel was attached on the top side as current collector. The full cells were assembled and tested in swagelok cells.

4. Characterization

A layer of Au (~ 300 nm) was deposited on both sides of the garnet pellet acting as a blocking electrode to measure the ionic conductivity of the garnet electrolyte. The electrochemical impedance spectroscopy (EIS) was performed in a frequency range from 7 MHz to 0.1 Hz with 50 mV perturbation amplitude. The morphology, elemental line scanning and mapping of Li/garnet interfaces were characterized by scanning electron microscopy (SEM) (Phenom Prox). X-ray absorption (XRD) data was characterized by Bruker D8 advance diffractometer by Cu K α radiation. Sn and Cu₆Sn₅

deposition were operated by magnetron sputtering (Xinruibo nanotech. co., ltd.). Galvanostatic stripping and plating of the symmetric cell and cyclic properties of the full cells were operated on LAND CT2001A Battery Cycler (Wuhan, China).

Table S1. Space group and volume of the crystal lattice of the reactants and products at anode side.

	Li	Sn	Cu ₆ Sn ₅	Li _{4.4} Sn	Li ₂ CuSn	Cu
Space Group	Im3m	I41/amd	C2/c	F23	Fm-3m	Fm-3m
Volume	43.2	108.2	781.7	1547.8	245.3	47.2

The expansion rate of Sn interlayer: $\eta_{Sn} = [V_{Li4.4Sn} / (V_{Sn} + 4.4 V_{Li})] \times 100 \%$

The expansion rate of Cu₆Sn₅ interlayer:

 $\eta_{Cu6Sn5} = \left[\left(3.75 \ V_{Li2CuSn} + 2.25 \ V_{Cu} + 1.25 \ V_{Li4.4Sn} \right) / \left(V_{Cu6Sn5} + 13 \ V_{Li} \right) \right] \times 100 \ \%$

Table S2. Comparison of the state-of-the-art Li/Garnet modifications and corresponding electrochemical performance of the hybrid solid state full cells.

Li/Garnet modification	ASR without modification ($\Omega \text{ cm}^2$)	ASR with modification ($\Omega \text{ cm}^2$)	Cathode, Cathode/Garnet modification	Cycles / Rate	Ref.
Sn	758	46.6	LiFePO4, liquid electrolyte	100 / 0.1 C	2
Al	950	20	LiFePO4, liquid electrolyte	100 / 0.1 mA.cm ⁻²	3
Al ₂ O ₃	1710	1	Li ₂ FeMn ₃ O ₈ , liquid electrolyte	50 / 0.1 C	4
Gel Electrolyte	> 1400	214	LiFePO4, gel electrolyte	70 / 170 mA.g ⁻¹	5
Graphite	1350	25	LiNi0.5C00.2Mn0.3O2, ionic liquid	500 / 0.5 C (80 °C)	6
In situ thermal reaction	1210	28	LiFePO4, liquid electrolyte	50 / 0.1 mA.cm ⁻² (65 °C)	7
Li _x Al bulk anode	unknown	< 1	LiFePO4, liquid electrolyte	100 / 0.5 C	8
$\mathrm{Li}_{\mathrm{x}}\mathrm{C}$ bulk anode	381	11	LiFePO4, liquid electrolyte	100 / 0.5 C	9

Note that liquid electrolyte has been applied in most of the hybrid solid state full cell researches, but the amount of liquid electrolyte is unclear, which could probably lead to the diverse of battery performance.



Figure S1. (a) Nyquist plot of LLCZNO electrolyte, (b) XRD pattern of LLCZNO electrolyte.



Figure S2. Schematic diagram of co-deposition of Cu and Sn on Garnet pellet.



Figure S3. XRD pattern of the Cu_6Sn_5 thin film.



Figure S4. XRD pattern of the alloyed Li-Sn interlayer during thermal reaction and DCP test.

Figure S4 demonstrates the XRD pattern of the alloyed Li-Sn interlayer during thermal reaction and subsequently DCP test. Bulk Li was scraped from the pellet to facilitated XRD characterize. Li and Sn interlayer were originally reacted in 200 °C for 10 minutes to ensure intimate contact with both garnet pellets and stainless steels current collectors. Low alloy state of Li₁₃Sn₅ and Li₇Sn₂ were indexed, indicating the alloying process is incomplete. After 3 h DCP test, the Li plated side was characterized and the highest alloy state of Li_{4.4}Sn was indexed, indicating the alloy reaction is one step forward. After 5 h DCP test, all of the low alloy state, such as Li₁₃Sn and Li₇Sn₂ had disappeared, and there only remained Li_{4.4}Sn, which manifests that the Li-Sn interlayer is fully alloyed.



Figure S5. (a) XRD pattern of the Li/Sn-Garnet interface after Li plating and after Li striping. (b) XRD pattern of the Li/Cu₆Sn₅-Garnet interface after Li plating and after Li striping.

In order to diminish the disturb peaks from the cubic garnet, both of the Sn and Cu₆Sn₅ interlayers were deposited 60 times thicker. Regardless of the significantly increased Sn or Cu₆Sn₅ thickness, it has little effect on their mass ratio with bulk Li. The amount of Li plating and striping was also 60 - fold increased (= 0.5 mAh/cm^2). Li₂₂Sn₅ can be clearly indexed in Figure S5a after Li plating while other Li-Sn phases cannot be found, indicating the Sn interlayer was fully alloyed with Li. Lower alloying state phases such as Li₇Sn₂ and Li₁₃Sn₅ were indexed after Li striping, indicating there exited the shrinkage of the interlayer. As shown in Figure S5b, both Li₂₂Sn₅ and Li₂CuSn peaks were indexed after Li striping also confirm the volume shrinkage of Cu₆Sn₅ interlayer. The Li₂CuSn peaks stayed still after Li striping while Cu₆Sn₅ peak cannot be indexed. The volume shrinkage rate of both interlayers is definitely smaller than the expansion rate because the interlayers cannot be fully dealloyed.



Figure S6. (a) Cross sectional SEM images of Li/Sn-Garnet interface, (b) EDS and (c) Mapping of Sn element at Li/Sn-Garnet interface. (d) Cross sectional SEM images of Li/Cu₆Sn₅-Garnet interface, (e) EDS and (f) Mapping of Sn element at Li/ Cu₆Sn₅-Garnet interface.



Figure S7. Initial charge/discharge curves and coulombic efficiency of the hybrid solid state full cells at 0.1 C.

The initial capacity of cell with Pristine Garnet is 7.8 mAh/g and 6.7 mAh/g smaller than that with Sn and Cu_6Sn_5 modification, respectively.



Figure S8. Cycling of the Li/Garnet/LiCoO₂ hybrid solid state full cells at 0.25 C

As shown in Figure S8, the initial discharge capacity of Li/Pristine-Garnet/LiCoO₂ was 19.1 mAh/g and 18.4 mAh/g smaller than that with Sn and Cu₆Sn₅ modification, and the capacity retention decreased to 51 % after only 50 cycles. Comparatively, batteries with Sn and Cu₆Sn₅ modification layers displayed a much higher initial discharge capacities of 108.6 mAh/g and 107.9 mAh/g, and capacity retentions of 73.6 % and 85.8 %, respectively. Moreover, the watershed appeared earlier at about 18th cycle, indicating the advantage of the more stable Li/Cu₆Sn₅-Garnet interface came into sight at a higher cycling rate.

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