

**Electronic Supporting Information**

For

**Recent Progress and Future Perspective on Atomic Layer Deposition to**

**Prepare/Modify Solid-State Electrolytes and Interface between Electrodes**

**for Next-Generation Lithium Batteries**

Table 1. Solid-state inorganic electrolytes formed by ALD.

Type of SSEs	Chemical formula	ALD temp. (°C)	ALD synthesis/operation/substrate	GPC (Å/cycle)	Ionic conductivity (S/cm)	Ref.
LiPON	$\text{Li}_{0.99}\text{PO}_{2.55}\text{N}_{0.30}$	250	<ul style="list-style-type: none"> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, <math>\text{H}_2\text{O}</math>, TMP</li> <li>● Plasma <math>\text{N}_2</math> (pN)</li> <li>● Pressure: 200 mTorr</li> </ul>	1.05	$3 \times 10^{-7}$ at room temperature	[20]
	$\text{Li}_{0.95}\text{PO}_{3.00}\text{N}_{0.60}$	270–310	<ul style="list-style-type: none"> <li>● Precursor: LiHMD, DEPA</li> <li>● Pressure: ~5 mbar</li> </ul>	0.7	$6.6 \times 10^{-7}$ at 25 °C	[21]
	LiPON	300	<ul style="list-style-type: none"> <li>● Precursor: LiHMD, DEPA</li> <li>● Pressure: ~5 mbar</li> </ul>	0.7	ND	[22]
	$\text{Li}_2\text{PO}_2\text{N}$	200 300	<ul style="list-style-type: none"> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, DEPA</li> <li>● Pressure: 200 mTorr</li> </ul>	0.15 0.9	$6.51 \pm 0.36 \times 10^{-7}$ at 35 °C	[24]
	$\text{Li}_2\text{PO}_2\text{N}$	250	<ul style="list-style-type: none"> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, DEPA</li> <li>● Pressure: 200 mTorr</li> </ul>	0.6	ND	[25]
	Al-doped	225	<ul style="list-style-type: none"> <li>● Precursor:</li> </ul>	ND	$7.8 \times 10^{-5}$ (200 °C)	[26]

Garnet	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$		<p>LiO<sup>t</sup>Bu, Tris(N,N'- diisopropylforma midinato)lanthan um (LaFAMD), Tetrakis(dimethyl amido)zirconium (DMAZ), trimethylaluminu m (TMA)</p> <ul style="list-style-type: none"> <li>● Pressure: ~7 mTorr</li> </ul>		$1.2 \times 10^{-6}$ (100 °C) $1 \times 10^{-8}$ (25 °C)	
Oxide	$\text{Li}_{5.1}\text{TaO}_z$	225	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, H<sub>2</sub>O, Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub></li> <li>● Subcycle: Li<sub>2</sub>O, Ta<sub>2</sub>O<sub>5</sub></li> <li>● Pressure: ND</li> </ul>	2.1	$2 \times 10^{-8}$ at 26 °C	[29]
	$\text{LiAlO}_x$	225	<ul style="list-style-type: none"> <li>● Precursor: TMA, LiO<sup>t</sup>Bu, H<sub>2</sub>O</li> <li>● Subcycle: Al<sub>2</sub>O<sub>3</sub>, LiOH</li> <li>● Pressure: ~1 Torr</li> </ul>	1.54	ND	[31]
	$\text{LiNbO}_x$	235	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, [Nb(OEt)<sub>5</sub>], H<sub>2</sub>O</li> <li>● Subcycle: Li, Nb</li> <li>● Pressure: ND</li> </ul>	ND	$6 \times 10^{-8}$ at 30 °C	[32]
	$\text{Li}_x\text{SiO}$	225–300	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, tetraethylorthosilane (TEOS), H<sub>2</sub>O</li> <li>● Compound: Li<sub>2</sub>O, SiO<sub>2</sub> (Subcycle: Li<sub>2</sub>O- SiO<sub>2</sub>)</li> <li>● Pressure: ND</li> </ul>	0.80–1.36	$1.45 \times 10^{-6}$ at 30 °C	[33]

	$\text{Li}_x\text{Al}_y\text{Si}_z\text{O}$	290	<ul style="list-style-type: none"> <li>● Compound: LiOH, <math>\text{Al}_2\text{O}_3</math>, <math>\text{SiO}_2</math> (Subcycle: LiOH-<math>\text{Al}_2\text{O}_3</math>-<math>\text{SiO}_2</math>)</li> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, TMA, TEOS, <math>\text{H}_2\text{O}</math></li> <li>● Pressure: 60 mTorr</li> </ul>	ND	$10^{-7}$ – $10^{-9}$ at room temperature	[34]
Pervoksite	$\text{Li}_{0.32}\text{La}_{0.30}\text{TiO}_z$	225	<ul style="list-style-type: none"> <li>● Precursor: La(thd)<math>_3</math>, <math>\text{TiCl}_4</math>, <math>\text{LiO}^t\text{Bu}</math>, <math>\text{H}_2\text{O}</math>, <math>\text{O}_3</math></li> <li>● Subcycle: <math>\text{TiO}_2</math>-<math>\text{La}_2\text{O}_3</math>-<math>\text{Li}_2\text{O}</math></li> <li>● Pressure: 3mbar</li> </ul>	0.48	ND	[36]
Sulphide	$\text{Li}_x\text{Al}_x\text{S}$	150	<ul style="list-style-type: none"> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, tris (dimethylamido) aluminum (III) (TMDA-Al), <math>\text{H}_2\text{S}</math></li> <li>● Subcycle: (<math>\text{LiO}^t\text{Bu}</math>)-<math>\text{H}_2\text{S}</math>, TMDA-Al-<math>\text{H}_2\text{S}</math></li> <li>● Pressure: 1.2 torr</li> </ul>	0.50	$2.5 \times 10^{-7}$	[40]
LBCO	$\text{Li}_3\text{BO}_3$ - $\text{Li}_2\text{CO}_3$	200, 260	<ul style="list-style-type: none"> <li>● Precursor: <math>\text{LiO}^t\text{Bu}</math>, TIB and <math>\text{O}_3</math></li> <li>● Subcycle: <math>\text{LiO}^t\text{Bu}</math>-<math>\text{O}_3</math> and TIB-<math>\text{O}_3</math></li> <li>● Pressure: ND</li> </ul>	0.65	$2.23 \times 10^{-6}$ at 25 °C	[48, 49]
NASICON	$\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$	250	<ul style="list-style-type: none"> <li>● Precursor: TMA, <math>\text{H}_2\text{O}</math></li> </ul>	ND	$1.5 \times 10^{-4}$ at 25 °C	[51]

Remark: ND: Non-detected

Table 2. Various SSEs on electrodes modified by ALD.

Electrode material	SSE	ALD temp. (°C)	ALD synthesis/ operation/substrate	GPC (Å/cycle)	LIB Performance (mAh/g)	Ref.
LITP anode	LiPON	300	<ul style="list-style-type: none"> <li>● Precursor: LiHMD, DEPA</li> <li>● Pressure: ~5 mbar</li> </ul>	0.7	350	[22]
MWCNT @RuO <sub>2</sub>	LiPON	225	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, DI H<sub>2</sub>O, TMP, N<sub>2</sub> gas</li> <li>● Pressure: 200 mTorr</li> </ul>	1.1	ND	[23]
NMC cathode	LiTaO <sub>3</sub>	225	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, tantalum ethoxide (Ta(OEt)<sub>5</sub>, H<sub>2</sub>O)</li> <li>● Subcycle: 1 Li<sub>2</sub>O- 6Ta<sub>2</sub>O<sub>5</sub></li> <li>● Pressure: ND</li> </ul>	ND	122-145	[30]
Li metal anode	Li <sub>x</sub> Al <sub>x</sub> S	150	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, tris (dimethylamido) aluminum (III) (TMDA-Al), H<sub>2</sub>S</li> <li>● Subcycle: Li<sub>2</sub>S-Al<sub>2</sub>S<sub>3</sub></li> <li>● Pressure: 1.2 torr</li> </ul>	0.50	ND	[40]

Remark: ND: Non-detected

Table 3. Modification of ALD layer at interface between SSEs and electrodes.

SSE/ electrode	ALD layer	ALD temp. (°C)	ALD synthesis/ operation/substrate	GPC (Å/cycle)	Interfacial impedance	Ref.
Garnet /Li-metal	Al <sub>2</sub> O <sub>3</sub>	250	<ul style="list-style-type: none"> <li>● Precursor: TMA, H<sub>2</sub>O</li> <li>● Pressure: ND</li> </ul>	0.7	34 Ω cm <sup>2</sup>	[27]
Garnet/ Li-metal	ZnO	150	<ul style="list-style-type: none"> <li>● Precursor: diethyl zinc, H<sub>2</sub>O</li> <li>● Pressure: ND</li> </ul>	ND	20 Ω cm <sup>2</sup>	[28]
Perovskite /anode	Li <sub>2</sub> O- Al <sub>2</sub> O <sub>3</sub>	225	<ul style="list-style-type: none"> <li>● Precursor: LiO<sup>t</sup>Bu, TMA, H<sub>2</sub>O</li> <li>● Pressure: 3mbar</li> </ul>	2.8	ND	[37]
Sulphide/ cathode	LiNbOx	235	<ul style="list-style-type: none"> <li>● Precursor: [LiO<sup>t</sup> Bu], [Nb(OEt)<sub>5</sub>]</li> <li>● Pressure: ND</li> </ul>	2	ND	[42]
LATP/Li metal anode	Al <sub>2</sub> O <sub>3</sub>	85	<ul style="list-style-type: none"> <li>● Precursor: TMA, Water</li> <li>● Pressure:ND</li> </ul>	ND	150 KΩ	[51]
LATP/ sulphur cathode	Al <sub>2</sub> O <sub>3</sub>	120	<ul style="list-style-type: none"> <li>● Precursor: TMA, Water</li> <li>● Pressure: ND</li> </ul>	1	ND	[52]

Remark: ND: Non-detected