Supplementary Information

Ab initio molecular dynamics study on disordered Li-Ga-Sn system

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Calculation methods for some properties:

I). Mixing enthalpy, thermal expansion coefficient and open cell voltage

The mixing enthalpy ΔH_{mix} can be calculated by:

$$\Delta H_{mix}\left(A_x B_y\right) = E\left(A_x B_y\right) - xE(A) - yE(B), \qquad (1)$$

where $E(A_x B_y)$, $E(A)$ and $E(B)$ are the free energies of $A_x B_y$, A and B, and x and y are the molar fractions of A and B, respectively. In our AIMD simulation, the free energy is the time-averaged DFT energy.

The thermal expansion coefficient at constant pressure α_v can be calculated by [1, 2]

$$\alpha_v = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad (2)$$

where V is the volume and T is the absolute temperature. For a specific component and volume at different temperatures, the thermal expansion coefficient can be obtained by calculating the slope of the volume vs. temperature plot.

For an anode material, the open cell voltage is directly related to the difference in the Gibbs free energy between its charged state (lithiated phase) and discharged state (delithiated phase), taking into account the reference state of lithium on the cathode. Due to the small Gibbs free energy difference contributed from entropy and volume, we approximate the voltage using the time-averaged DFT energy differences computed from AIMD; thus, the open cell voltage V is calculated by:

$$V = -\frac{E\left(Li_x - GaSn\right) - E\left(Li_y - GaSn\right) - (x - y)E(Li)}{x - y}, \qquad (3)$$

where x and y are the number of Li atoms before and after delithiation, $E(Li_x\text{-}GaSn)$ and $E(Li_y\text{-}GaSn)$ are the free energies of Li_x-GaSn and Li_y-GaSn, respectively, and $E(Li)$ is the energy of pure Li per atom, namely, the chemical potential, in liquid Li.

II). Radial distribution function, structure factor and angular distribution function

As one of the main functions describing the disordered structure, the radial distribution function (RDF) $g(r)$ represents the probability of finding a particle in a shell dr at the distance r from a reference particle, which can be calculated as follows:

$$g(r) = \frac{dN(r)}{4\pi r^2 \rho_0 dr}, \qquad (4)$$

where ρ_0 is the atomic number density of the system and $dN(r)$ is the number of atoms at a distance between r and $r + dr$.

Similarly, for a multivariate system, the partial radial distribution function $g_{\alpha\beta}$, also known as the pair correlation function, describes the probability of finding β atoms at the distance of r from an α atom:

$$g_{\alpha\beta}(r) = \frac{dN_{\alpha\beta}(r)}{4\pi r^2 \rho_\beta d(r)}, \qquad (5)$$

where ρ_β is the density of species β and $dN_{\alpha\beta}(r)$ is the number of β atoms in the range of r-$r+dr$ from α species.

It is possible to estimate the coordination numbers from the partial pair correlation functions:

$$N_{\alpha\beta} = 4\pi\rho_\beta \int_0^{r_{min}} g_{\alpha\beta}(r)r^2 dr, \qquad (6)$$

r_{min} is the position of the first peak valley of the RDF. The coordination number $N_{\alpha\beta}$ means the number of β-type atoms lying in a sphere of radius r_{min} centered on an α-type atom.

Although RDF is an important structural characteristic to describe structural information, it cannot be obtained directly from experimental measurements, and thus, it is difficult to compare the simulated results with experiments. In contrast, structure factors $S(k)$ are obtained directly in experiments. $S(k)$ is obtained by the Fourier

transformation from the RDF and is more useful when theoretical predictions are compared with experimental measurements.

To further describe the local structure of the disordered system, we also calculate the angle θ_{ijk} among three atoms i, j, k, where j is the center atom to obtain the angular distribution function (ADF), which can reflect the bond orientation. The definition of θ_{ijk} is as follows:

$$\theta_{ijk} = \left\langle \cos^{-1} \frac{r_{ji}^2 + r_{jk}^2 - r_{ik}^2}{2r_{ji}r_{jk}} \right\rangle. \qquad (7)$$

r represents the distance between two atoms within the selected cut-off radius r_{min}, and angular brackets denote the average value. Once θ_{ijk} is known, we can obtain the ADF $g(\theta_{ijk})$, which represents the probability of finding a specific angle θ_{ijk} from a cut off radius.

III). Diffusion coefficient and viscosity

The kinetic properties of molten and liquid metals have played an important role in the mass transport, nucleation and growth of crystals. Combined with MSD, the time-averaged diffusion coefficient for species α and D_α can be estimated through the Einstein expression:

$$D_\alpha = \lim_{t \to \infty} \frac{(MSD)_\alpha}{6t} \qquad (8)$$

The final atomic diffusion coefficient of the system is extracted from the slope of the *MSD* at long times. Moreover, to minimize the statistical error as much as possible, the *MSD* here takes all the time nodes after the system reaches equilibrium as the time origin. The *MSD* for species α is calculated by the following equation:

$$(MSD)_\alpha = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} |\vec{r}_{\alpha i}(t + t_0) - \vec{r}_{\alpha i}(t_0)|^2 \right\rangle, \qquad (9)$$

where N_α is the number of α atoms, $\vec{r}_{\alpha i}$ is the position vector of the α atom after time interval t, and the angular brackets denote the average over various time origins t_0.

After obtaining the diffusion coefficient D, the Arrhenius equation can be used to linearly fit the relationship between $1/T$ and $\ln D$ to obtain the diffusion activation energy and the diffusion pre-exponential factor:

$$D = D_0 \exp\left(\frac{-E_a}{k_B T}\right), \qquad (10)$$

where k_B is the Boltzmann constant, E_a is the activation energy and D_0 is a pre-exponential factor.

Since the viscosity and diffusion coefficient conform to the Stocks-Einstain relationship, it is calculated by the following formula[3]:

$$\mu = \frac{k_B T}{C R_{S-E} D}, \qquad (11)$$

where C is a numerical constant with a value of 6π, and R_{S-E} is the effective particle diffusion radius; here, we take the radius of an atomic sphere.
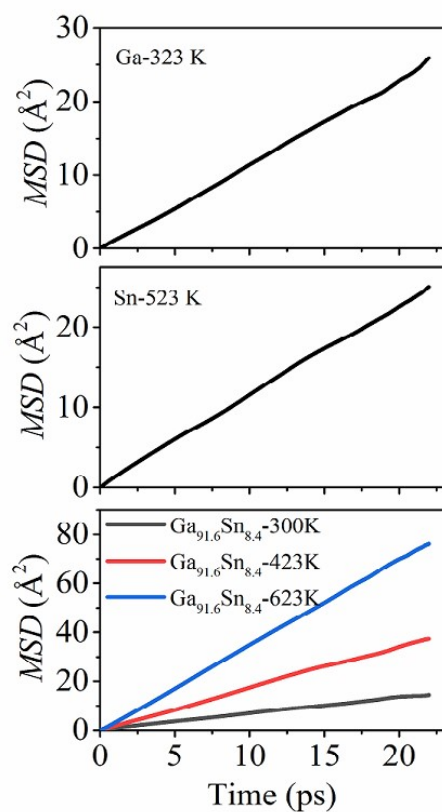
Fig. S1. *MSD* of liquid Ga, Sn and Ga$_{91.6}$Sn$_{8.4}$ at different temperatures.

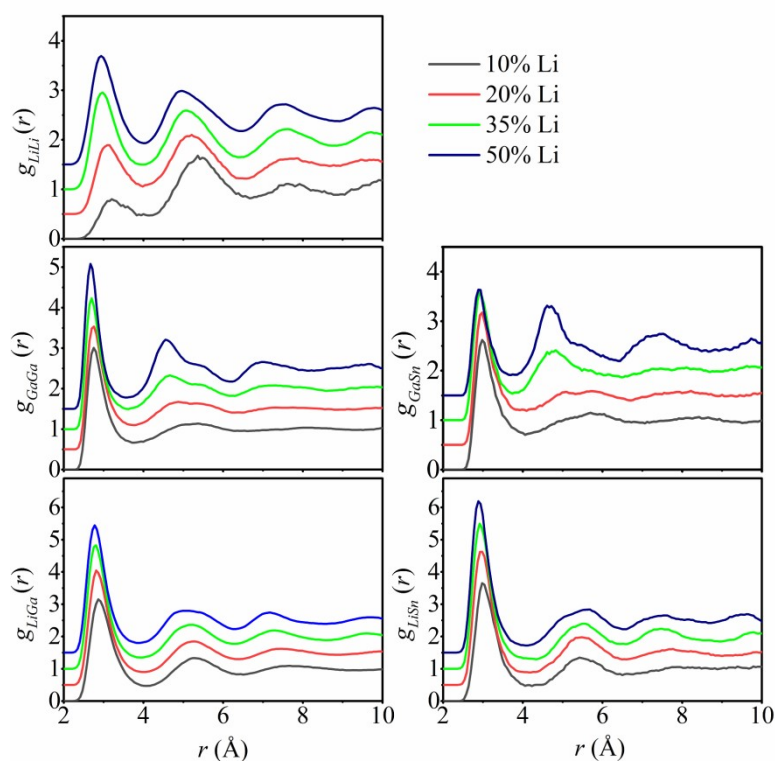Fig. S2. Partial radial distribution functions of the Li-Ga-Sn system at 423 K. The curves for Li$_{20}$-GaSn, Li$_{35}$-GaSn, and Li$_{50}$-GaSn are shifted upwards by 0.5, 1, and 1.5,
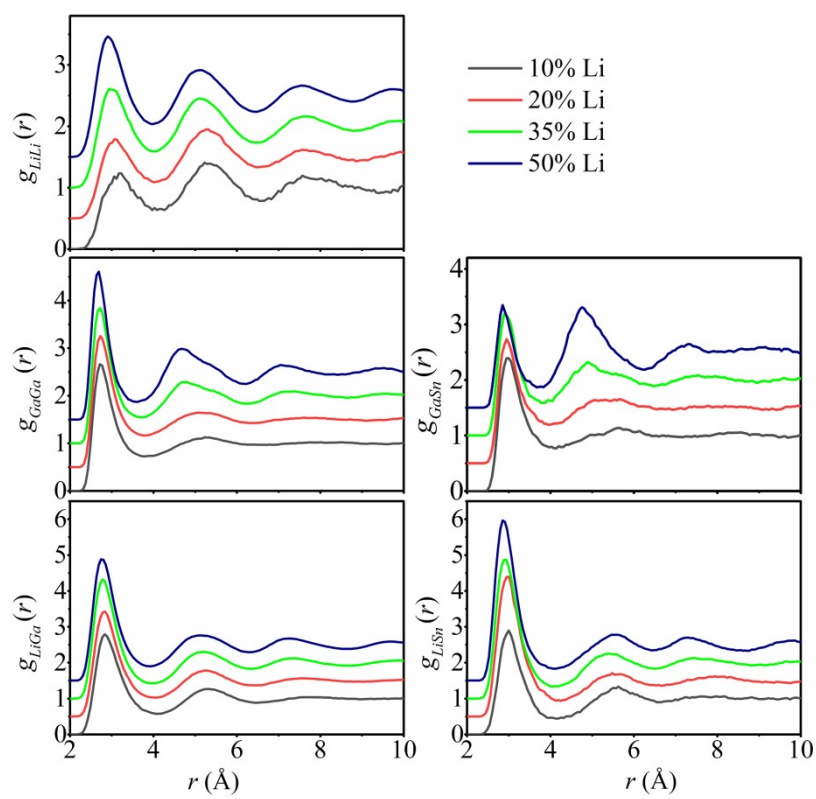
respectively.

Fig. S3. Partial radial distribution functions of the Li-Ga-Sn system at 623 K. The curves for Li_{20}-GaSn, Li_{35}-GaSn, and Li_{50}-GaSn are shifted upwards by 0.5, 1, and 1.5, respectively.
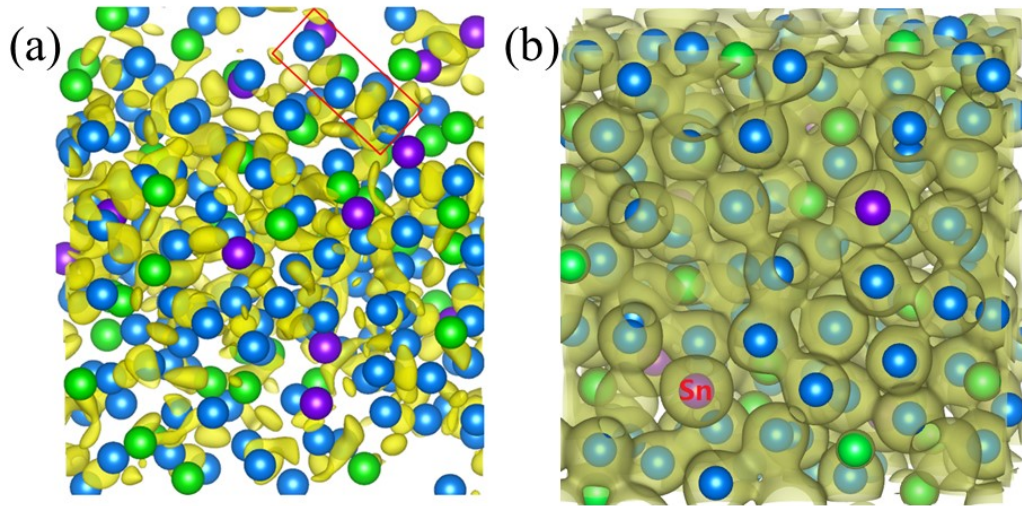
Fig. S4. (a) The charge density difference plot for Li_{20}-GaSn at 300 K with isosurface level of $0.04e/Bohr^3$. The yellow color means positive change of charge density, which represents gain electron. (b) Charge distribution of Li_{20}-GaSn at 300 K with isosurface level of $0.03e/Bohr^3$. The green, blue and pink balls represent Li, Ga and Sn atoms, respectively.
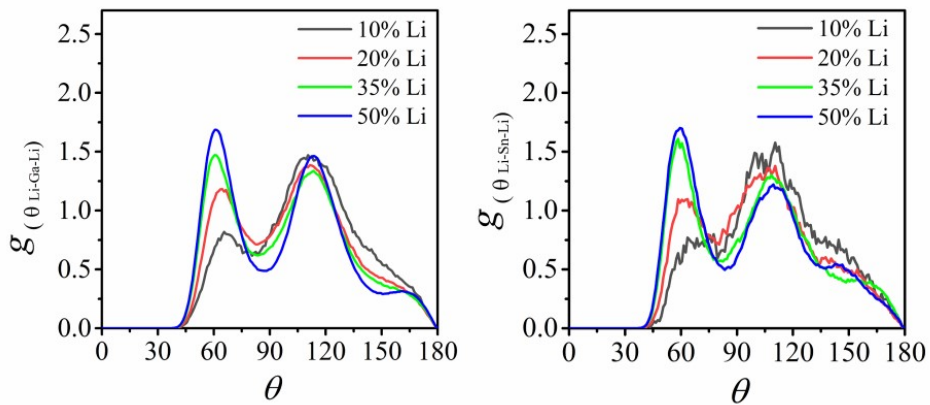

Fig. S5. Calculated angle distribution functions for Li-Ga-Li and Li-Sn-Li in the Li-Ga-Sn system at 423 K.
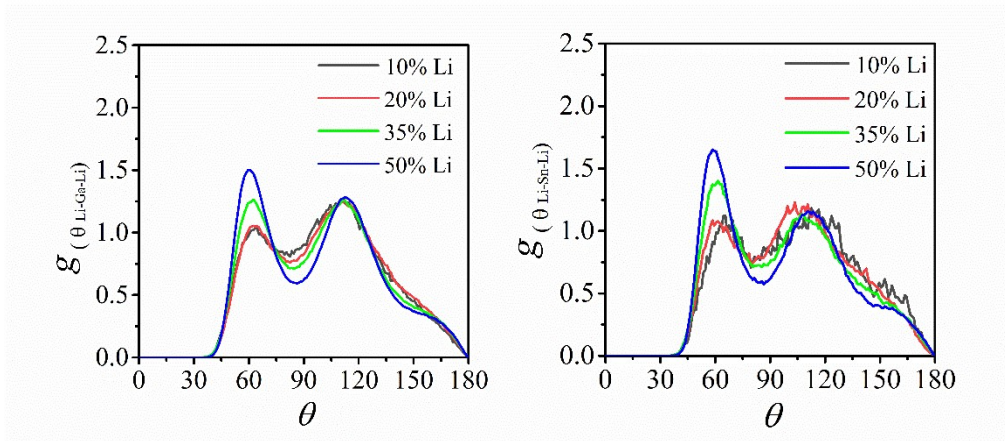
Fig. S6. Calculated angle distribution functions for Li-Ga-Li and Li-Sn-Li in the Li-Ga-Sn system at 623 K.

Table S1. The number of atom used in the simulation of the disordered Li-Ga-Sn system.

Composition	$N_{\text{Li}} : N_{\text{Ga}} : N_{\text{Sn}}$
$\text{Ga}_{91.6}\text{Sn}_{8.4}$	$0 : 183 : 17$
$\text{Li}_{10}\text{-GaSn}$	$20 : 165 : 15$
$\text{Li}_{20}\text{-GaSn}$	$40 : 147 : 13$
$\text{Li}_{35}\text{-GaSn}$	$70 : 119 : 11$
$\text{Li}_{50}\text{-GaSn}$	$100 : 92 : 8$

Table S2. Diffusion activation energy E_a and pre-exponential D_0 of the Li-Ga-Sn system at various temperatures.

Composition	E_a (kJ/mol)			D_0 (10^{-5} cm^2/s)		
	Li	Ga	Sn	Li	Ga	Sn
Li$_{10}$-GaSn	11.79	10.98	11.21	22.60	33.04	24.23
Li$_{20}$-GaSn	12.4	10.91	9.61	19.85	22.21	13.09
Li$_{35}$-GaSn	13.15	12.74	7.02	11.23	11.65	0.96
Li$_{50}$-GaSn	17.52	16.16	15.46	23.71	10.97	6.00

References

1.   A. Bengtson, H. O. Nam, S. Saha, R. Sakidja and D. Morgan, First-principles molecular dynamics modeling of the LiCl–KCl molten salt system, *Comput. Mater. Sci.*, 2014, **83**, 362-370.
2.   C. Woodward, M. Asta, D. R. Trinkle and J. Lill, Ab initio simulations of molten Ni alloys, *J. Appl. Phys.*, 2010, **107**(11), 1861-1888.
3.   Frenkel and I. Ia., *Kinetic theory of liquids*, Dover Publications, 1955.