

†Electronic Supplementary Information (ESI) for

## New insights into Li diffusion in Li-Si alloy for Si anode materials: role of Si microstructure

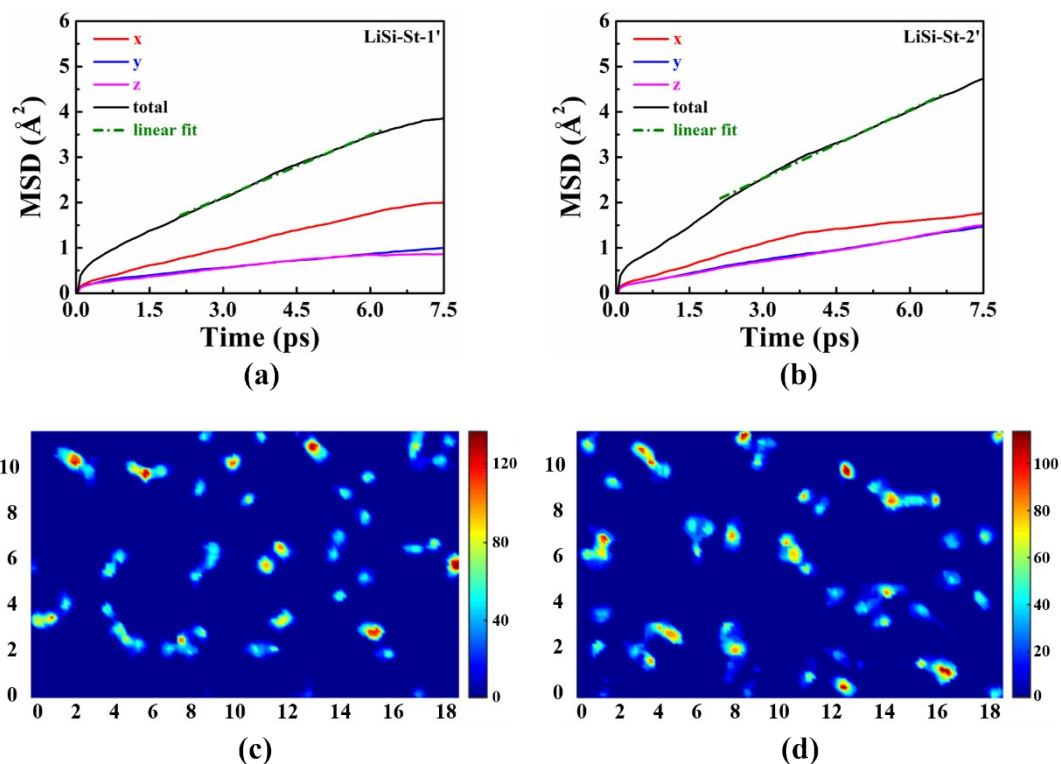
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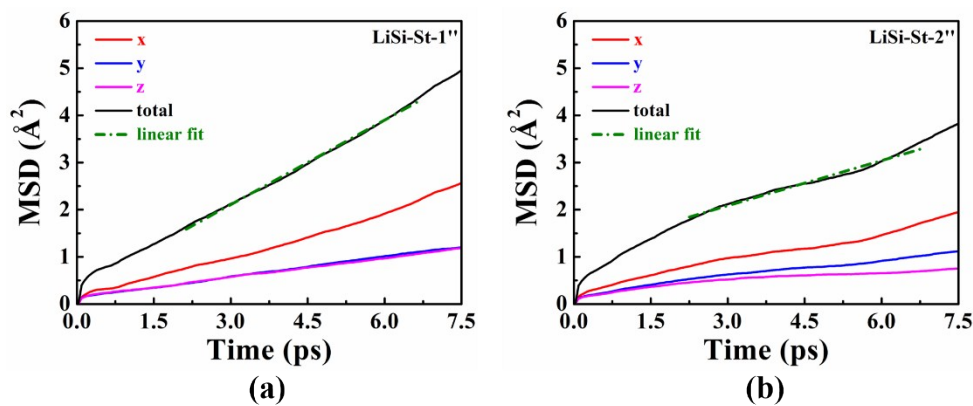
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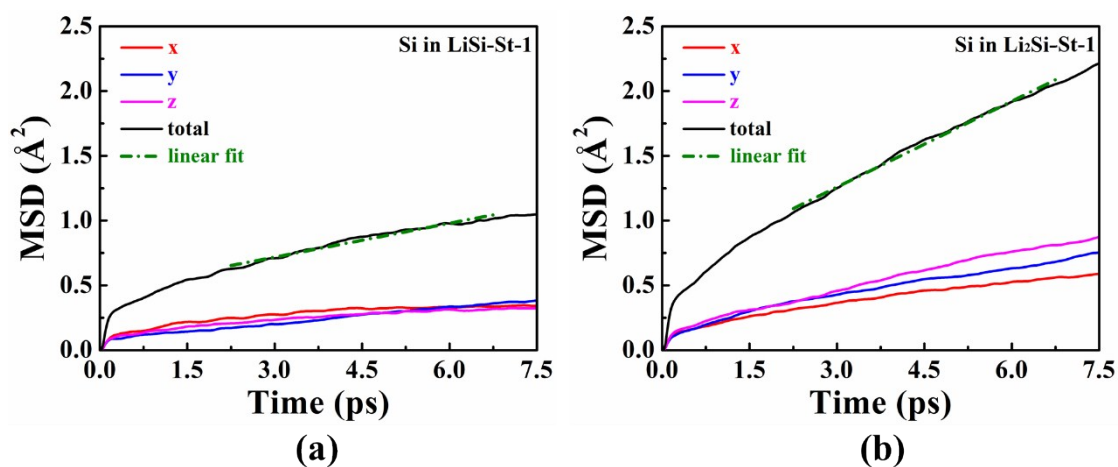
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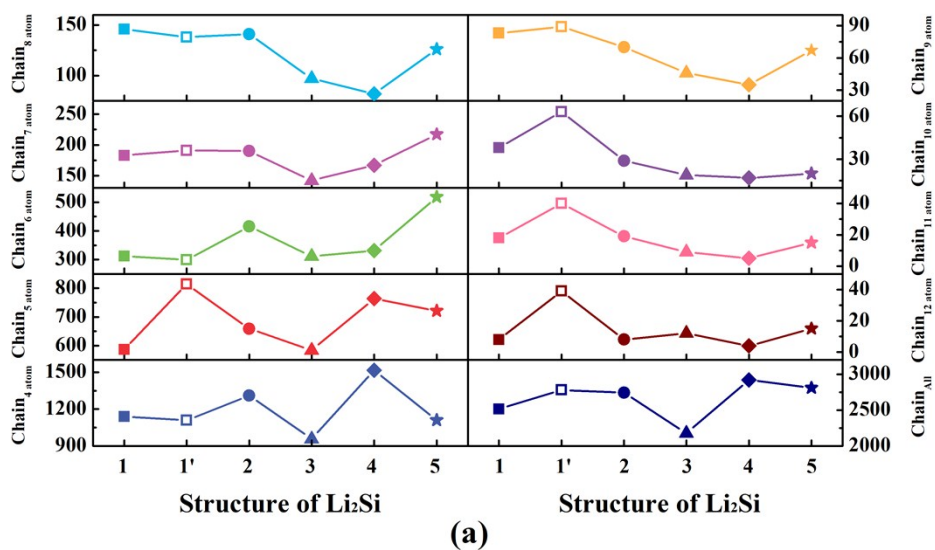
**Fig. S1** Total and projected MSD profiles along x, y and z directions for all Li ions in (a) LiSi-St-1' and (b) LiSi-St-2' at 800 K. The density map of the projected plane of the Si atoms along x direction in (c) LiSi-St-1' and (d) LiSi-St-2', the brighter the region is, the denser the distribution of Si atoms is.

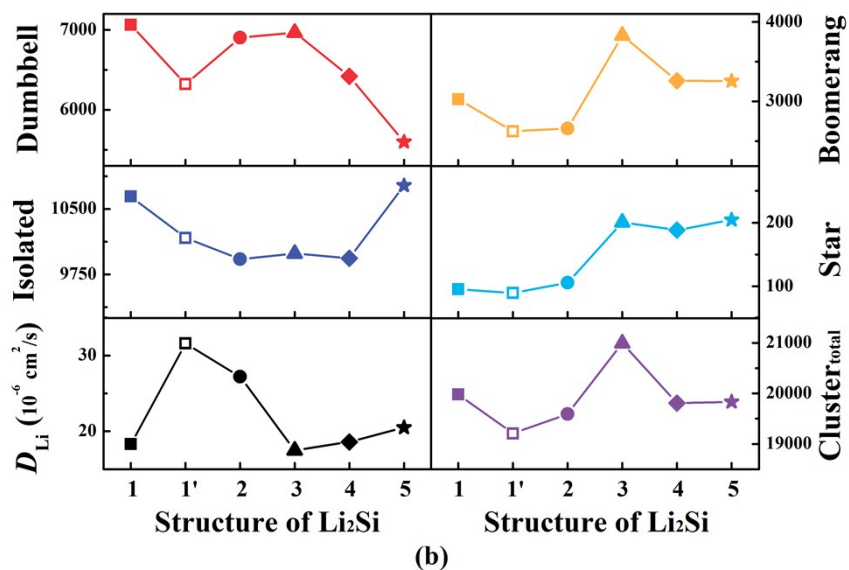


**Fig. S2** Total and projected MSD profiles along x, y and z directions for all Li ions in (a) LiSi-St-1'' and (b) LiSi-St-2'' at 800 K.



**Fig. S3** Total and projected MSD profiles along x, y and z directions for all Si atoms in (a) LiSi-St-1 and (b) Li<sub>2</sub>Si-St-1 at 800 K.





**Fig. S4** (a) Number of chains with different Si atomic number for various  $\text{Li}_2\text{Si}$  structures. (b) Number of small clusters with different Si atomic number, total number of clusters and diffusion coefficients for various  $\text{Li}_2\text{Si}$  structures.

Table S1 Diffusion coefficient ( $D_{\text{Li}}$ ) of Li ions (unit:  $10^{-6} \text{ cm}^2/\text{s}$ ) and channel area ratio for Li diffusion for various  $\text{LiSi}$  structures

	St-1	St-1'	St-1''	St-2	St-2'	St-2''	St-3	St-4	St-5
$D_{\text{Li}}$	5.0	7.5	9.8	11.3	8.4	5.3	6.7	10.3	10.8
$S_x$ (%)	67.2	71.1	70.2	73.4	69.9	67.6	68.1	71.4	73.3

Table S2 Number of rings with different Si atomic number for various  $\text{LiSi}$  structures

	rings3	rings4	rings5	rings6	rings7	rings8	r-total
St-1	373	624	450	268	162	344	2221
St-1'	162	197	524	629	82	100	1694
St-1''	322	218	636	383	171	132	1862
St-2	265	212	691	323	111	144	1746
St-2'	226	181	772	617	93	81	1970
St-2''	381	285	683	513	176	93	2131
St-3	404	336	564	364	147	51	1866
St-4	183	452	431	276	80	38	1460
St-5	282	374	237	486	85	93	1557

Table S3 Diffusion coefficient ( $D_{Li}$ ) of Li ions (unit:  $10^{-6}$  cm<sup>2</sup>/s) and number of small clusters for various Li<sub>2</sub>Si structures

	$D_{Li}$	Isolated	Dumbbell	Boomerang	Star	total
St-1	18.3	10642	7064	3025	97	19978
St-1'	31.6	10169	6323	2624	91	19207
St-2	27.2	9926	6903	2657	108	19594
St-3	17.5	9990	6968	3830	207	20995
St-4	18.6	9934	6421	3259	194	19808
St-5	20.5	10769	5598	3255	211	19833

Table S4 Number of chains with different Si atom number for various Li<sub>2</sub>Si structures

	ch-4	ch-5	ch-6	ch-7	ch-8	ch-9	ch-10	ch-11	ch-12	total
St-1	1140	587	312	183	146	83	38	18	8	2527
St-1'	1108	814	299	191	138	89	63	40	39	2781
St-2	1310	659	416	190	141	70	29	19	8	2842
St-3	956	584	311	142	97	46	19	9	12	2176
St-4	1516	764	331	167	82	35	17	5	4	2921
St-5	1109	721	518	217	126	67	20	15	15	2808