Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

First-principles view of the interaction between Li and $Bi_4Ge_3O_{12}$ anode

HongXian Liu[1], Jassiel R. Rodriguez[2], Vilas G. Pol[2], Yanning Zhang[1*]

[1]Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, Sichuan, China.
[2]Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA.

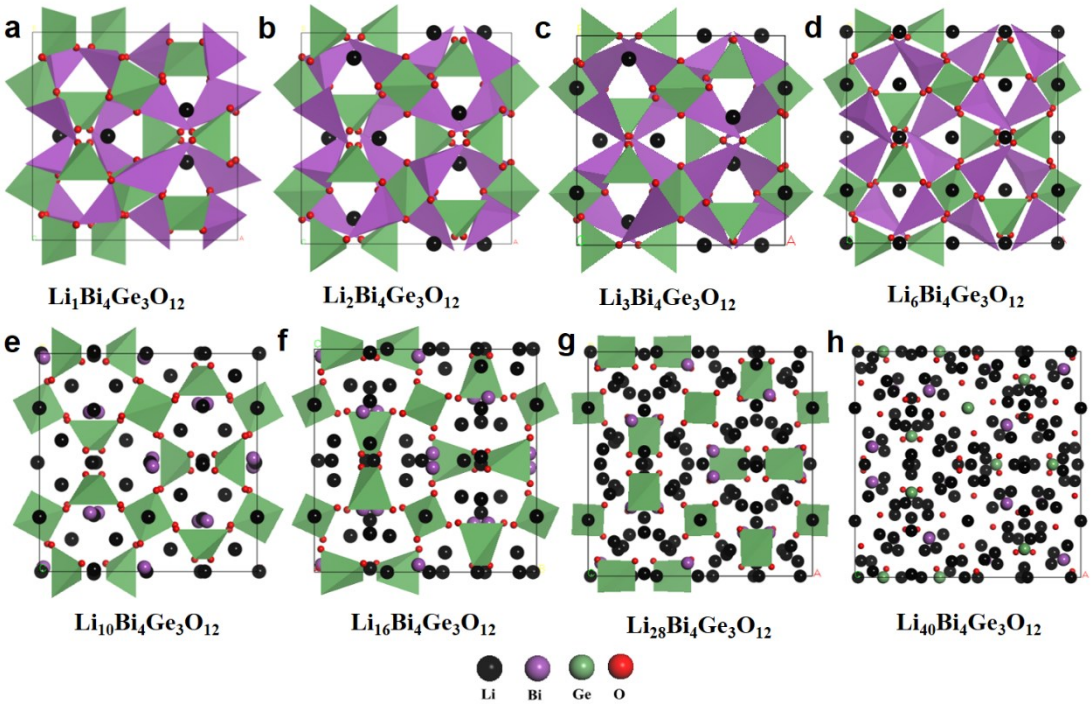

Figure S1. The optimized structures of (a)$Li_1Bi_4Ge_3O_{12}$, (b)$Li_2Bi_4Ge_3O_{12}$, (c)$Li_3Bi_4Ge_3O_{12}$, (d)$Li_6Bi_4Ge_3O_{12}$, (e)$Li_{10}Bi_{16}Ge_3O_{12}$, (f)$Li_{16}Bi_4Ge_3O_{12}$, (g)$Li_{28}Bi_4Ge_3O_{12}$, (h)$Li_{40}Bi_4Ge_3O_{12}$. The purple, green, red and black balls are for Bi, Ge, O and Li atoms，respectively.

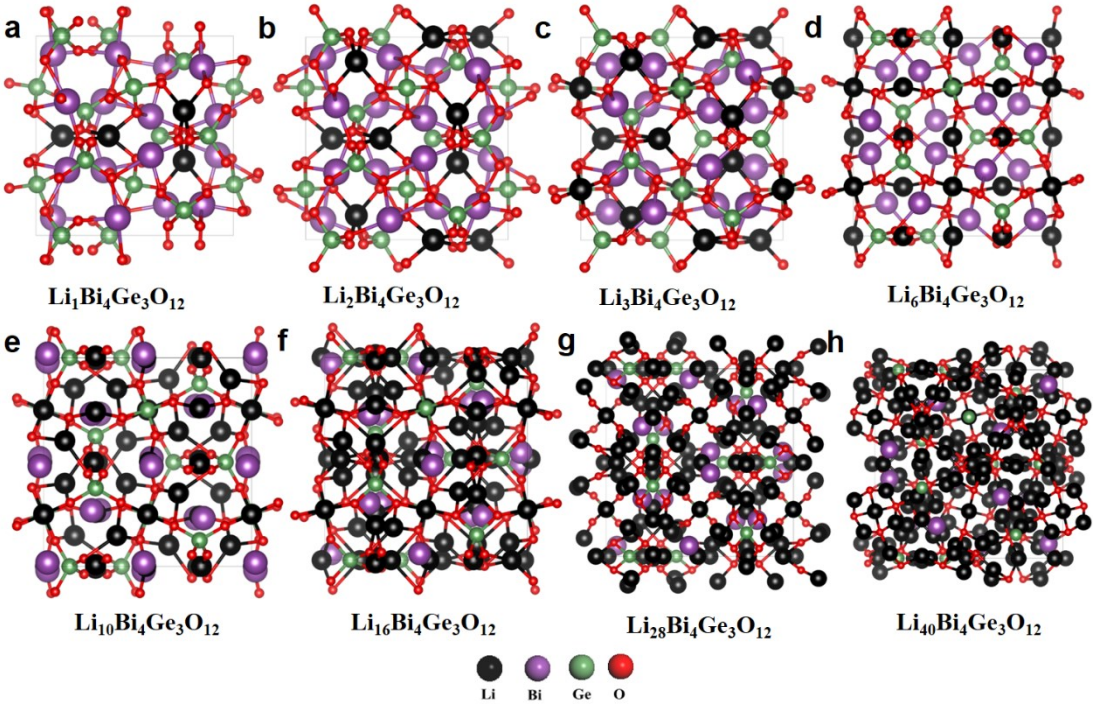

Figure S2. The optimized $Li_nBi_4Ge_3O_{12}$ configurations with the coordinates of atoms (a)$Li_1Bi_4Ge_3O_{12}$, (b)$Li_2Bi_4Ge_3O_{12}$, (c)$Li_3Bi_4Ge_3O_{12}$, (d)$Li_6Bi_4Ge_3O_{12}$, (e)$Li_{10}Bi_{16}Ge_3O_{12}$, (f)$Li_{16}Bi_4Ge_3O_{12}$, (g)$Li_{28}Bi_4Ge_3O_{12}$, (h)$Li_{40}Bi_4Ge_3O_{12}$. The purple, green, red and black balls are for Bi, Ge, O and Li atoms，respectively.

Table S1. The lattice parameters and volume of optimized $Li_nBi_4Ge_3O_{12}$.

$Li_nBi_4Ge_3O_{12}$	**Lattice** (Å)	**Vol** ($Å^3$)
bulk	10.68	1218.66
$Li_{0.25}$	10.76/10.72/10.72	1235.26
$Li_{0.5}$	10.79/10.79/10.74	1250.28
$Li_{0.75}$	10.83/10.83/10.72	1257.96
Li_1	10.80/10.92/10.74	1267.57
Li_2	11.02/11.02/10.78	1310.33
Li_3	11.06/11.09/11.09	1360.29
Li_6	12.44	1922.67
Li_{10}	12.35	1882.29
Li_{16}	12.62	2007.74
Li_{28}	13.87	2668.94
Li_{40}	14.73	3195.07

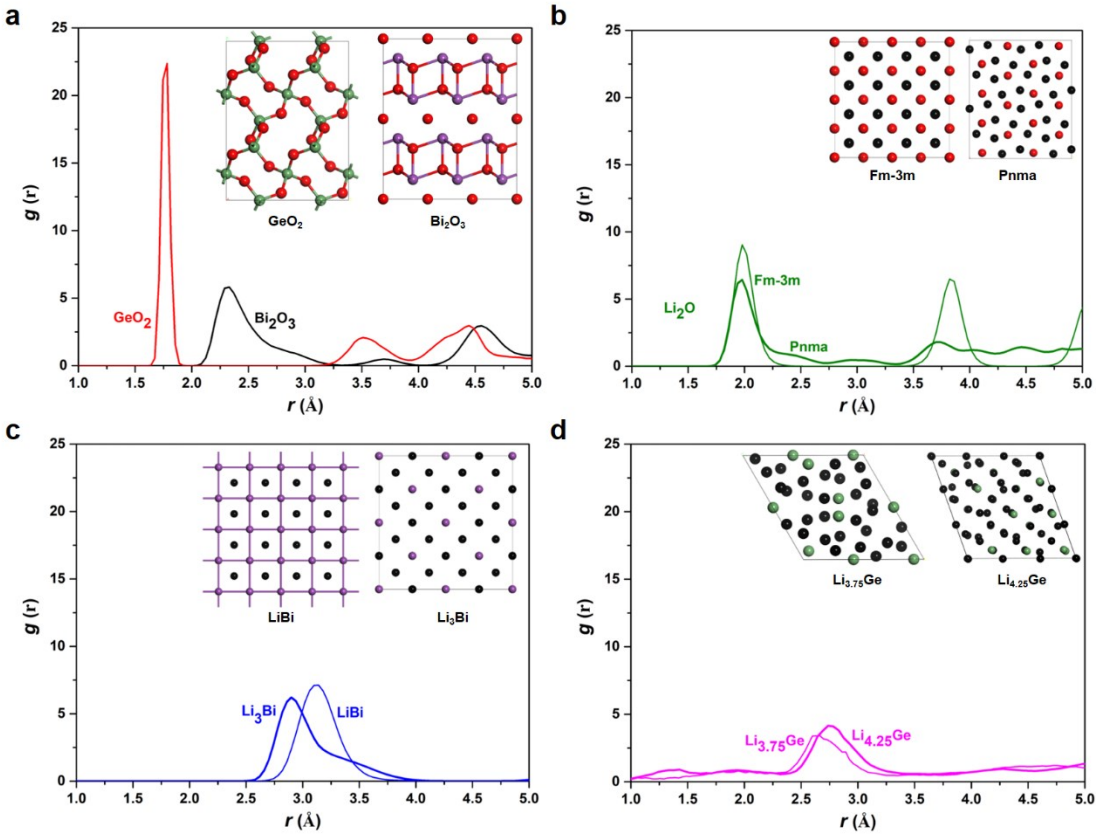

Figure S3. The calculated g(*r*) curves of (a)GeO_2 and Bi_2O_3, (b)Li_2O, (c)LiBi and Li_3Bi (d)$Li_{3.75}Ge$ and $Li_{4.25}Ge$. The zoom-in diagrams are the crystal structures of lithiation products adopted in MD simulations.

Table S2. The detailed information of lithiation products.[1, 2]

Compounds	Crystal	Formula	Energy (eV)
Li_2O	Fm-3m	Li_2O	-14.348
	Pnma	Li_8O_4	-56.356
LiBi	P4/mmm	LiBi	-6.592
Li_3Bi	Fm-3m	Li_3Bi	-11.796
$Li_{15}Ge_4$	I-43d	$Li_{30}Ge_8$	-106.044
$Li_{4.25}Ge$	F-43M	$Li_{85}Ge_{20}$	-285.060
Bi_2O_3	P-3m1	Bi_2O_3	-28.348
	Pn-3m	Bi_4O_6	-53.754
Li	Im-3m	Li_2	-3.815
	$P4_132$	Li_4	-6.546
Bi	Im-3m	Bi_1	-3.768
	Pmma	Bi_2	-8.031
Ge	Im-3m	Ge_1	-4.177
GeO_2	$P3_121$	Ge_3O_6	-57.724

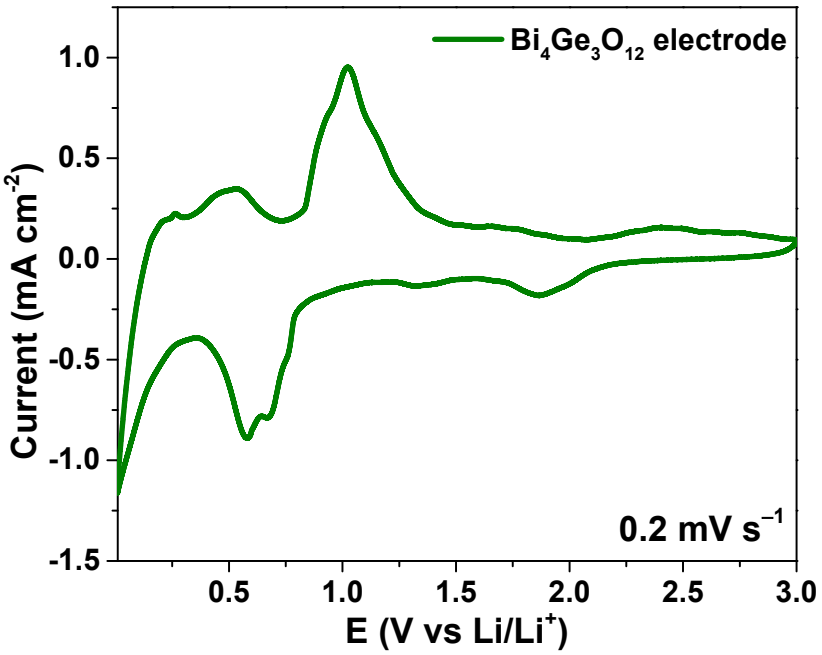

Figure S4. Cyclic voltammogram curve of the $Bi_4Ge_3O_{12}$-base electrode with 1 M $LiPF_6$ in EC:DEC.

References

1. M. de Jong, W. Chen, T. Angsten, A. Jain, R. Notestine, A. Gamst, M. Sluiter, C. Krishna Ande, S. van der Zwaag, J. J. Plata, C. Toher, S. Curtarolo, G. Ceder, K. A. Persson and M. Asta, *Scientific Data*, 2015, **2**, 150009.
2. A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Materials*, 2013, **1**, 011002.