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

A facile surface alloy-engineering route to enable robust lithium metal anode

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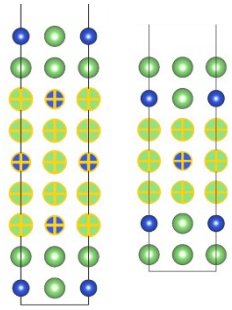

Figure S1. The two types of exposed Li_3Cu (001) surfaces. The atomic layers in bulk were constrained and only the atoms at top two layers were free to relax. The green atoms are Li, and the blue atoms are Cu.

Table S1. The calculated data of the surface energy of Li_3Cu.

	Bulk		Surface area Å^2	E_{unrel}	E_{rel}	½ △E	σ	Esurface(μLi) J/m^2
Li_3Cu	-18.91	001	16.17	-41.56	-41.86	-0.15	24.44	24.22
				-41.56	-41.86	-0.15	24.44	24.22
				-40.41	-40.57	-0.08	19.43	19.24
		100	30.13	-82.43	-82.83	-0.20	43.67	23.22
				-82.43	-82.83	-0.20	43.67	23.22
		110	22.12	-41.02	-41.26	-0.12	24.74	17.92
				-41.02	-41.26	-0.12	24.74	17.92
				-40.13	-40.19	-0.03	19.62	14.21
		111	48.36	-76.38	-76.92	-0.27	44.73	14.82
				-75.38	-75.69	-0.15	39.68	13.15

Table S2. The calculated data of the surface energy of Li_3Ga.

	Bulk		Surface area Å^2	E_{unrel}	E_{rel}	½ △E	σ	Esurface(μLi) J/m^2
Li_3Ga	-38.01	001	40.21	-82.03	-82.33	-0.15	145.10	57.81
				-82.03	-82.33	-0.15	145.10	57.81
				-81.32	-81.46	-0.07	115.11	45.86
		110	28.44	-82.80	-83.03	-0.11	129.54	72.98
				-82.80	-83.03	-0.11	129.54	72.98
		111	80.43	-98.82	-99.31	-0.25	174.63	34.78
				-116.01	-116.25	-0.12	234.60	46.73

Table S3. The calculated data of the surface energy of Li_3Mg.

	Bulk		Surface area Å^2	E_{unrel}	E_{rel}	½ △E	σ	Esurface(μLi) J/m^2
Li_3Mg	-14.68	001	37.06	-63.77	-63.79	-0.01	34.18	14.77
		100	30.48	-41.45	-41.68	-0.12	23.21	12.20
				-47.99	-48.07	-0.04	30.91	16.25
				-56.42	-56.44	-0.02	30.50	16.03
		110	52.79	-61.24	-61.41	-0.08	38.92	11.81
				-62.80	-62.95	-0.08	31.05	9.42
		111	62.12	-61.31	-61.40	-0.04	35.38	9.12

Table S4. The calculated data of the surface energy of Li_3Zn.

	Bulk		Surface area Å^2	E_{unrel}	E_{rel}	½ △E	σ	Esurface(μLi) J/m^2
Li_3Zn	-14.47	001	32.94	-62.76	-62.81	-0.02	33.70	16.39
		100	26.85	-46.95	-47.17	-0.11	30.49	18.20
				-54.91	-55.60	-0.70	29.72	17.73
		110	46.50	-59.87	-60.14	-0.13	38.48	13.25
				-62.30	-62.66	-0.18	30.33	10.45
		111	54.82	-60.33	-60.76	-0.22	34.72	10.15

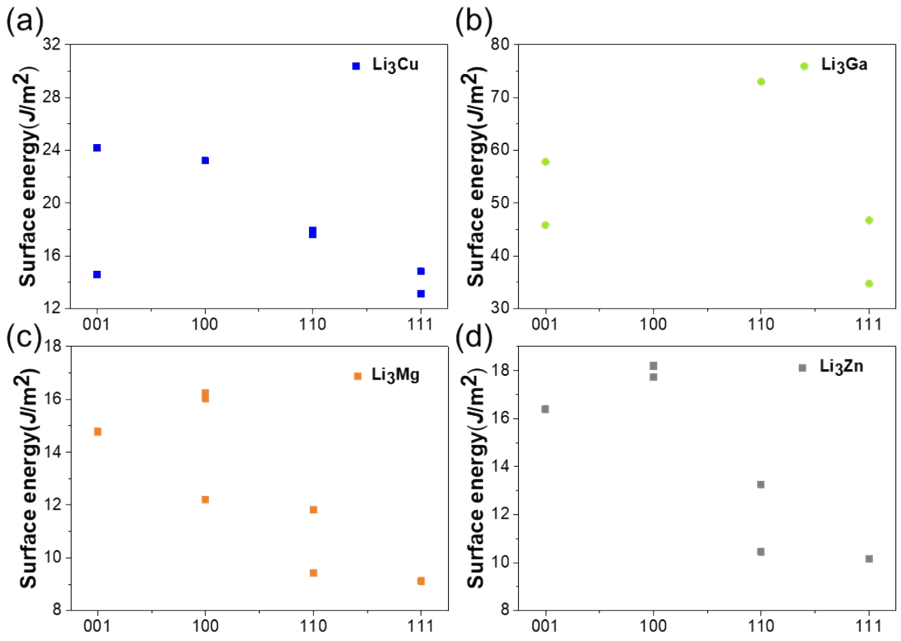

Figure S2. The graph results of the surface energies of Li_3Cu, Li_3Ga, Li_3Mg and Li_3Zn.

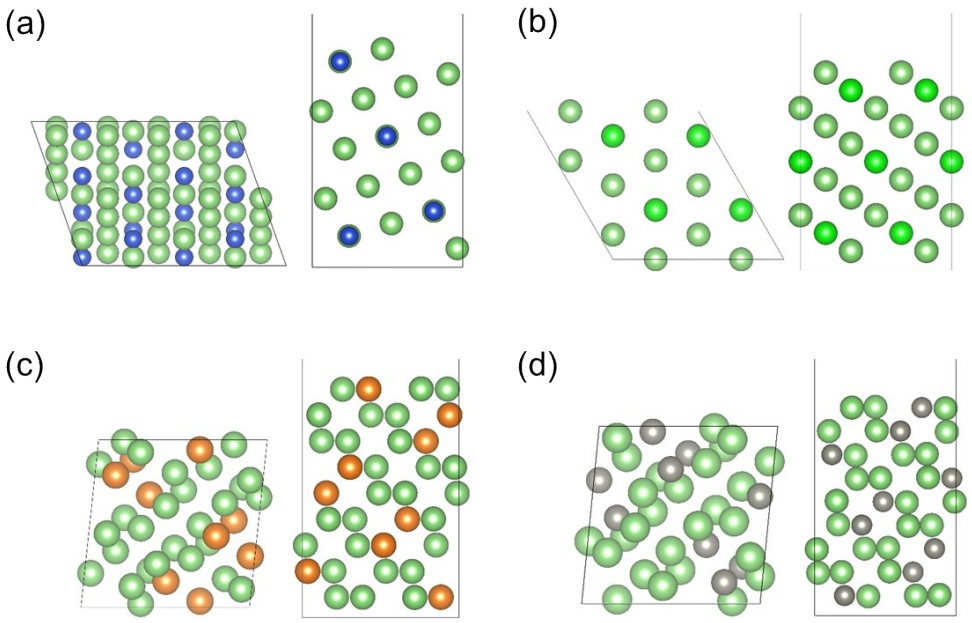

Figure S3. The optimized Li_3Cu (111) (a), Li_3Ga (111) (b), Li_3Mg (111) (c) and Li_3Zn (111) surface (d). The green atoms are Li, blue atoms are Cu, cyan atoms are Ga, brown atoms are Mg and grey atoms are Zn.

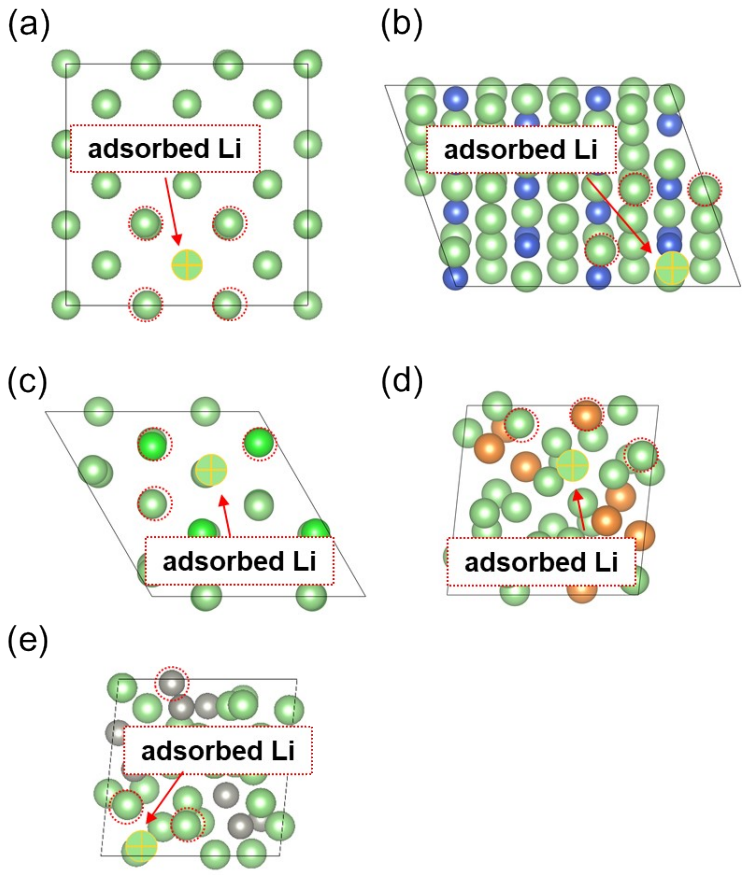

Figure S4. Li atom adsorbed on the pure Li (001) (a), Li_3Cu (111) (b), Li_3Ga (111) (c), Li_3Mg (111) (d) and Li_3Zn (111) surfaces (e). The green atoms are Li, blue atoms are Cu, cyan atoms are Ga, brown atoms are Mg and grey atoms are Zn.

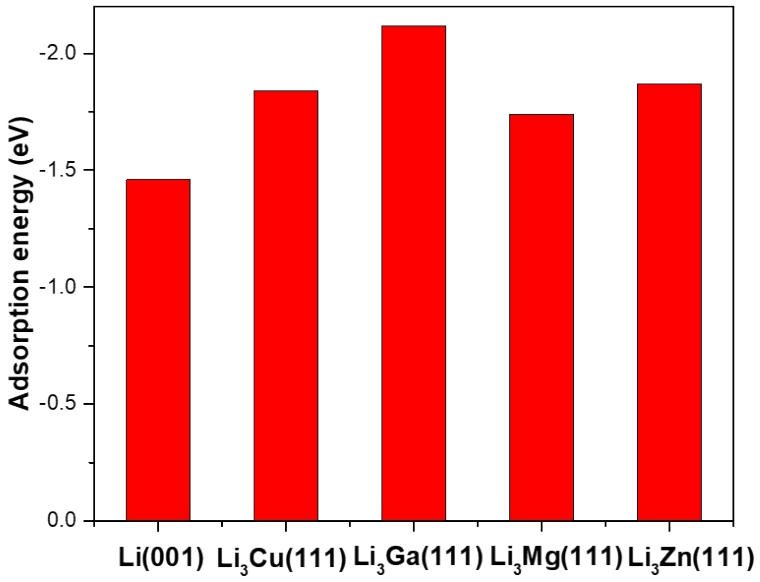

Figure S5. The highest adsorption energy for the Li atom adsorbed at the pure Li meal and Li alloy surfaces.

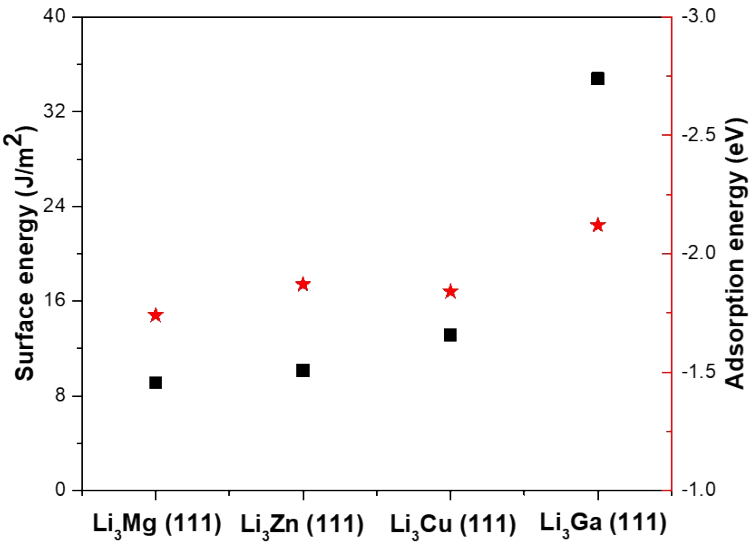

Figure S6. The scatter plot of the surface energy *vs.* adsorption energy at different alloy surfaces.

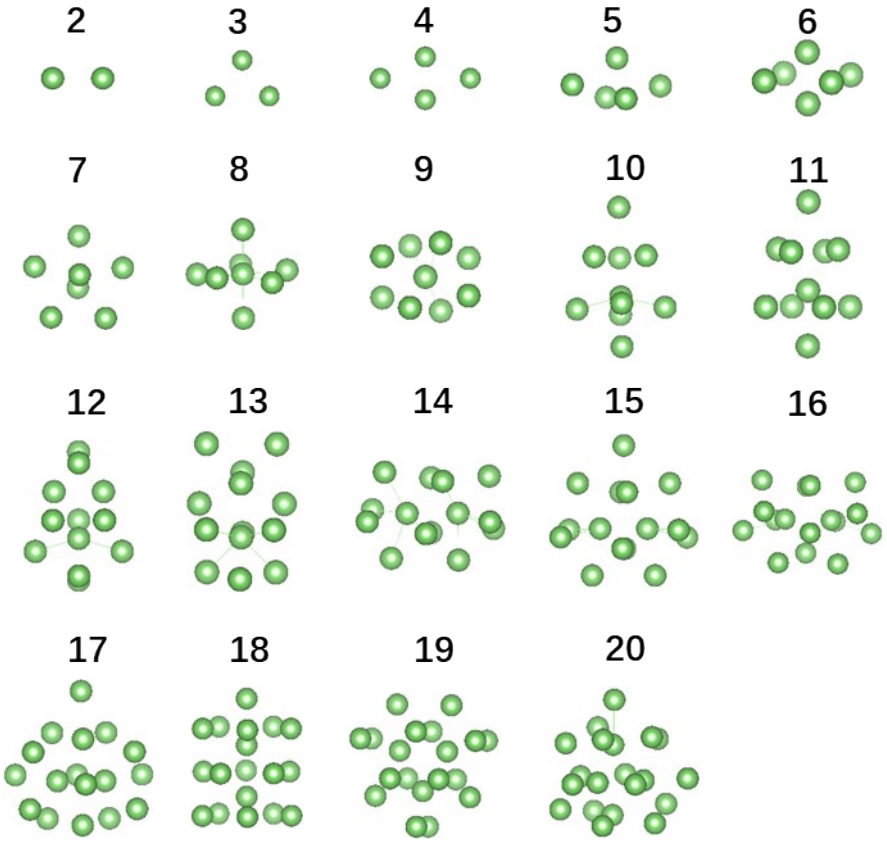

Figure S7. The structures of the optimized Li_n (n = 2 - 20) clusters.

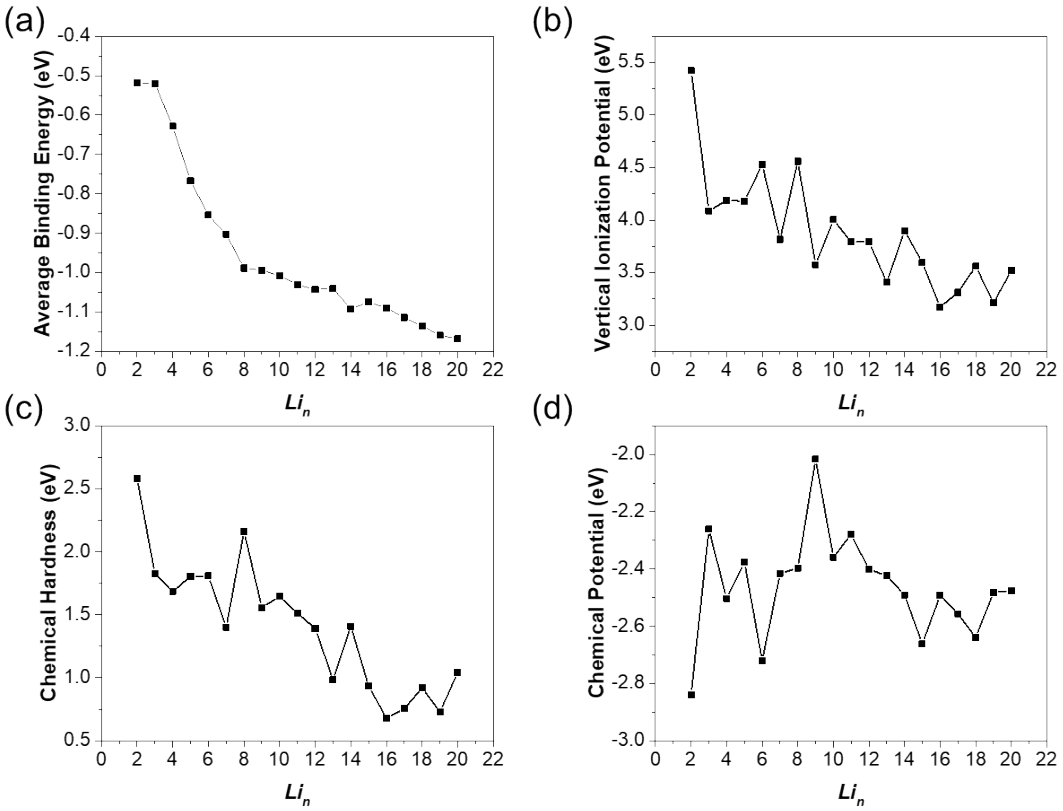

Figure S8. The average binding energy (a), vertical ionization potential (b), chemical hardness (c), and the chemical potential of the Li clusters (d).

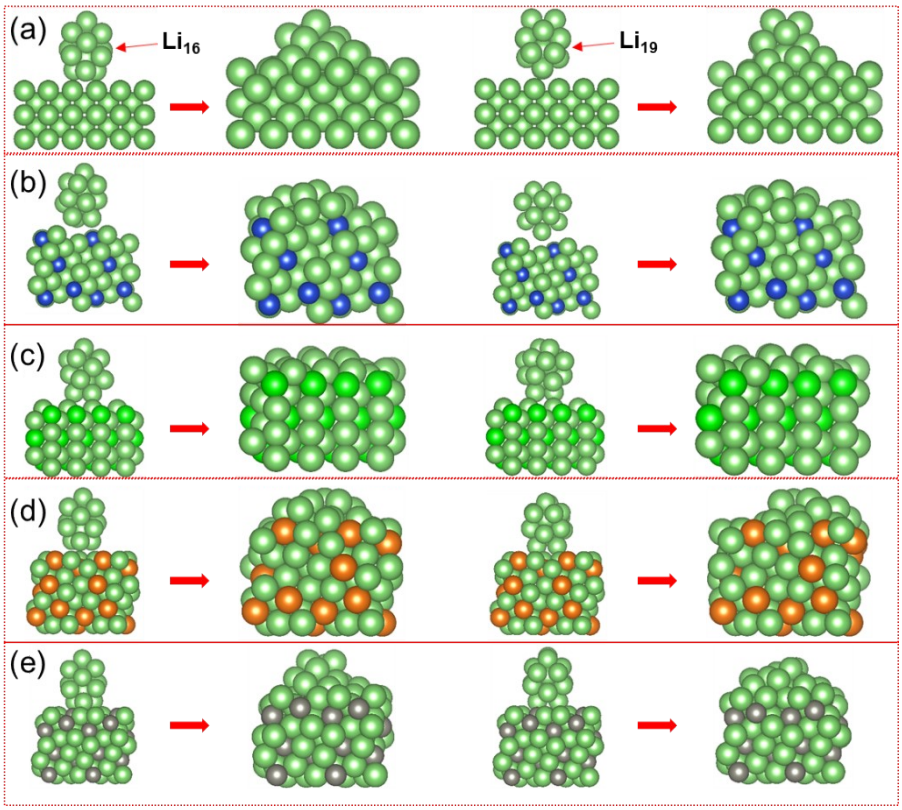

Figure S9. The Li_{16} and Li_{19} clusters adsorbed at pure Li (001) (a), Li_3Cu (111) (b),

Li_3Ga (111) (c), Li_3Mg (111) (d) and Li_3Zn (111) surfaces (e). The green atoms are Li, blue atoms are Cu, cyan atoms are Ga, brown atoms are Mg and grey atoms are Zn.

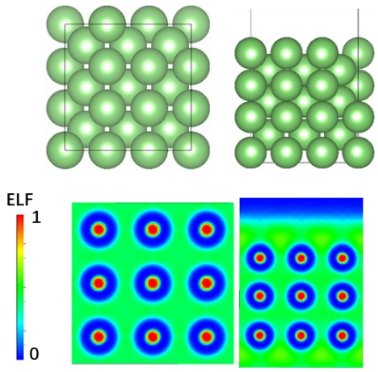

Figure S10. The configuration and electron localization functional of the pure Li (001) surface.

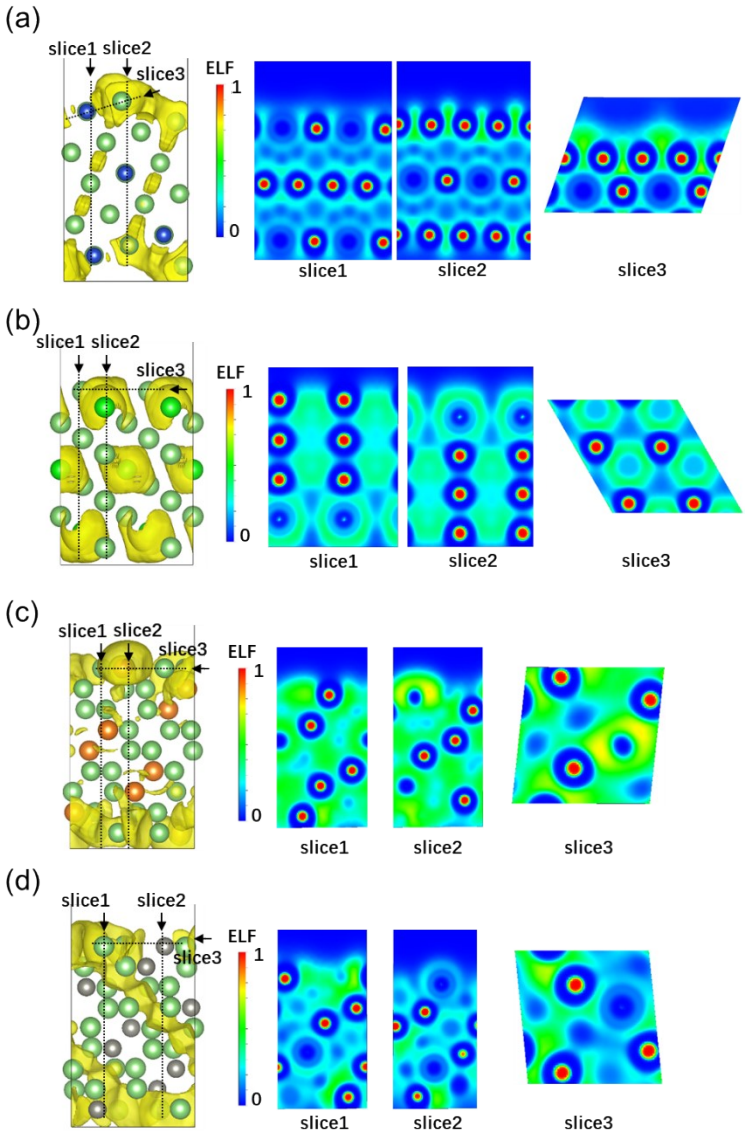

Figure S11. The ELF and corresponding sliced 2D displayed ELF of the Li_3Cu (111)

(a), Li_3Ga (111) (b), Li_3Mg (111) (c) and Li_3Zn (111) surfaces (d). The green atoms are Li, blue atoms are Cu, cyan atoms are Ga, brown atoms are Mg and grey atoms are Zn.

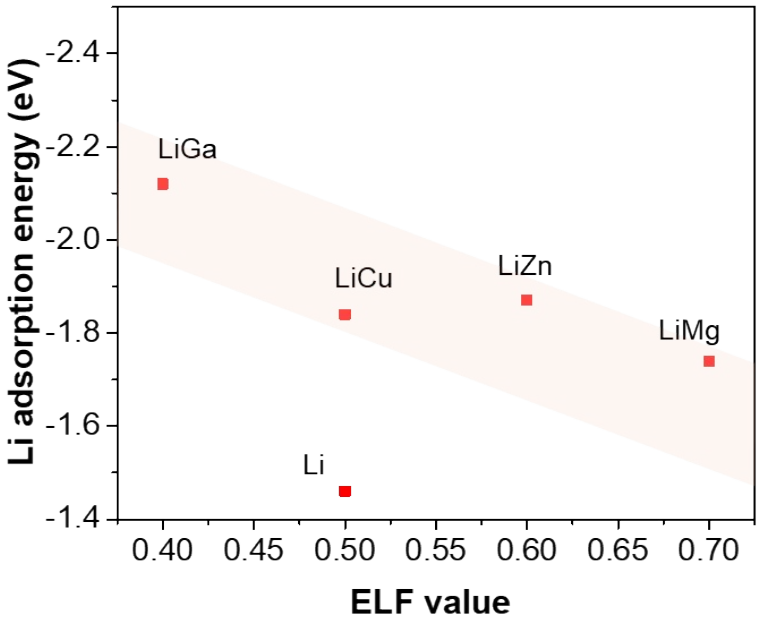

Figure 12. The relationship of highest Li adsorption energy and ELF value.

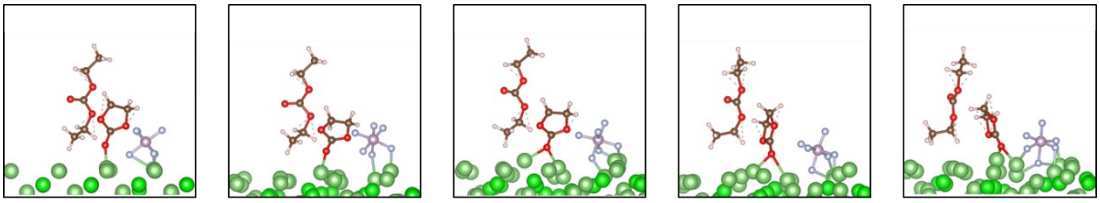

Figure S13. The molecular dynamics at 360 K for simulating the interaction between electrolyte molecules and LiGa alloy surface.

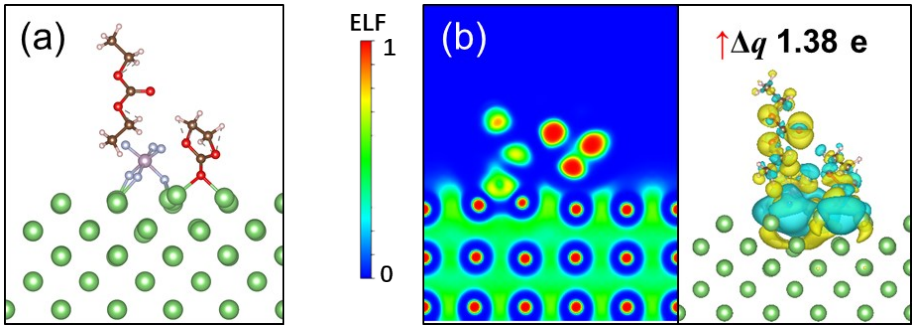

Figure S14. The optimized structure of Li (001) with adsorbed electrolyte molecules (a). The corresponding 2D displayed ELF and charge density difference (b). The green atoms are Li, pink atoms are H, the saddle-brown atoms are C, red atoms are O, silver atoms are F and plum atoms are P.

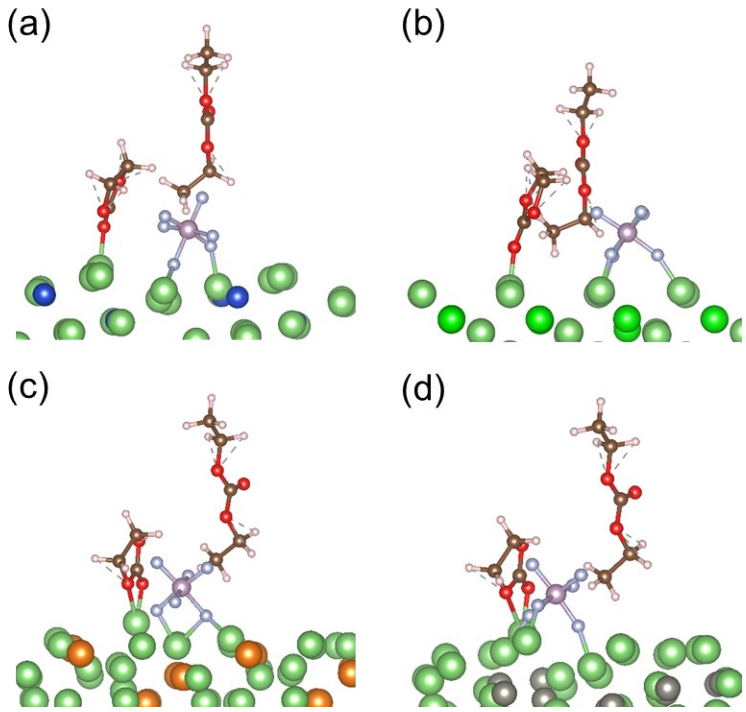

Figure S15. The optimized structure of alloy surfaces with adsorbed electrolyte molecules: Li_3Cu (111) (a), Li_3Ga (111) (b), Li_3Mg (111) (c) and Li_3Zn (111) (d). The green atoms are Li, blue atoms are Cu, cyan atoms are Ga, brown atoms are Mg and grey atoms are Zn, pink atoms are H, the saddle-brown atoms are C, red atoms are O, silver atoms are F and plum atoms are P.

Table S5. The transferred charge on the oxygen atoms in EC within the alloy systems.

	O_t	O_{b1}	O_{b2}
Li_3Cu	1.22	1.01	1.04
Li_3Ga	1.24	1.02	1.01
Li_3Mg	1.21	1.01	1.07
Li_3Zn	1.21	1.02	1.07

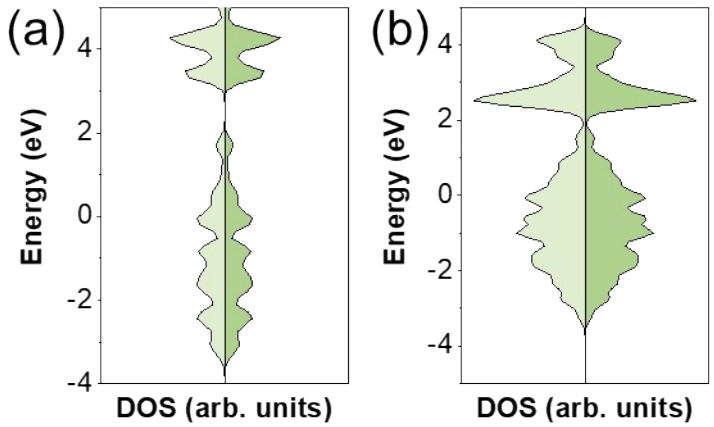

Figure S16. The density of states of the Li *s* orbital in bulk (a) and Li (001) surface (b).

Table S6. The Bader charge of EC and DEC molecules on Li (001) surface.

EC	Charge	DEC	Charge
H	0.920388	H	0.960047
H	0.888458	H	0.939755
H	0.819047	H	0.9427
H	0.904753	H	0.947391
C	1.882382	H	0.978973
C	3.680304	H	0.946888
C	3.669961	H	0.95815
O	7.327072	H	0.95098
O	7.039065	H	0.957928
O	7.044682	H	0.963881
		C	3.594062
		C	1.932769
		C	3.599117
		C	4.084666
		C	4.054022
		O	7.051271
		O	7.121027
		O	7.056847

Table S7. The Bader charge of EC and DEC molecules on Li_3Cu surface.

EC	Charge	DEC	Charge
H	0.914277	H	0.9437
H	0.921732	H	0.944107
H	0.845939	H	0.894089
H	0.879369	H	0.942829
C	1.894836	H	0.976009
C	3.672024	H	0.949917
C	3.645194	H	0.971908
O	7.226394	H	0.940665
O	7.012683	H	0.954936
O	7.045591	H	0.963356
		C	3.581941
		C	1.901887
		C	3.655754
		C	4.046629
		C	4.07545
		O	7.054233
		O	7.157097
		O	7.061957

Table S8. The Bader charge of EC and DEC molecules on Li_3Ga surface.

EC	Charge	DEC	Charge
H	0.943568	H	0.927329
H	0.93731	H	0.911539
H	0.882854	H	0.924173
H	0.884647	H	0.940091
C	1.862994	H	0.943957
C	3.607073	H	0.941405
C	3.623878	H	0.958097
O	7.245723	H	0.954654
O	7.020908	H	0.960661
O	7.016524	H	0.996574
		C	3.636828
		C	1.902125
		C	3.615695
		C	4.100996
		C	4.098425
		O	7.053707
		O	7.15198
		O	7.052654

Table S9. The Bader charge of EC and DEC molecules on Li_3Mg surface.

EC	Charge	DEC	Charge
H	0.894442	H	0.929691
H	0.946112	H	0.904868
H	0.877274	H	0.897708
H	0.876744	H	0.937379
C	1.885191	H	0.964254
C	3.662103	H	0.952992
C	3.615346	H	0.937276
O	7.211725	H	0.939578
O	7.014666	H	0.967875
O	7.069138	H	0.970575
		C	3.648618
		C	1.888337
		C	3.632496
		C	4.08014
		C	4.095203
		O	7.054267
		O	7.167811
		O	7.056317

Table S10. The Bader charge of EC and DEC molecules on Li_3Zn surface.

EC	Charge	DEC	Charge
H	0.901867	H	0.930487
H	0.903834	H	0.910724
H	0.883049	H	0.890931
H	0.87283	H	0.948792
C	1.879269	H	0.959497
C	3.655194	H	0.952499
C	3.669604	H	0.975432
O	7.208084	H	0.940626
O	7.020287	H	0.955036
O	7.072674	H	0.986589
		C	3.674296
		C	1.889685
		C	3.634682
		C	4.02537
		C	4.1209
		O	7.039799
		O	7.162742
		O	7.068001