Supporting Information for:

Theoretical Insights into Nitrogen Fixation on Ti_2C and Ti_2CO_2 in a Lithium-Nitrogen Battery

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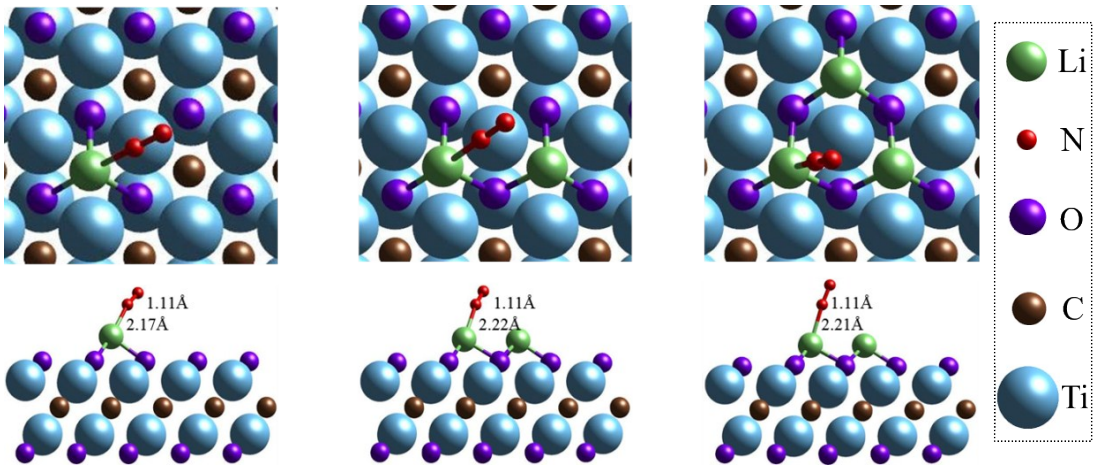

Figure S1 Schematic top- and side-view of optimized configurations of xLi+N_2 adsorption on Ti_2CO_2, and x=1-3. N_2 molecule is adsorbed with end-on model and unable to interact with each Li atoms simultaneously. Besides, the closest distance between Li and N atoms is ~2.2 Å and N≡N is constantly 1.11 Å equal to N_2 in gas, indicating the weak interaction.

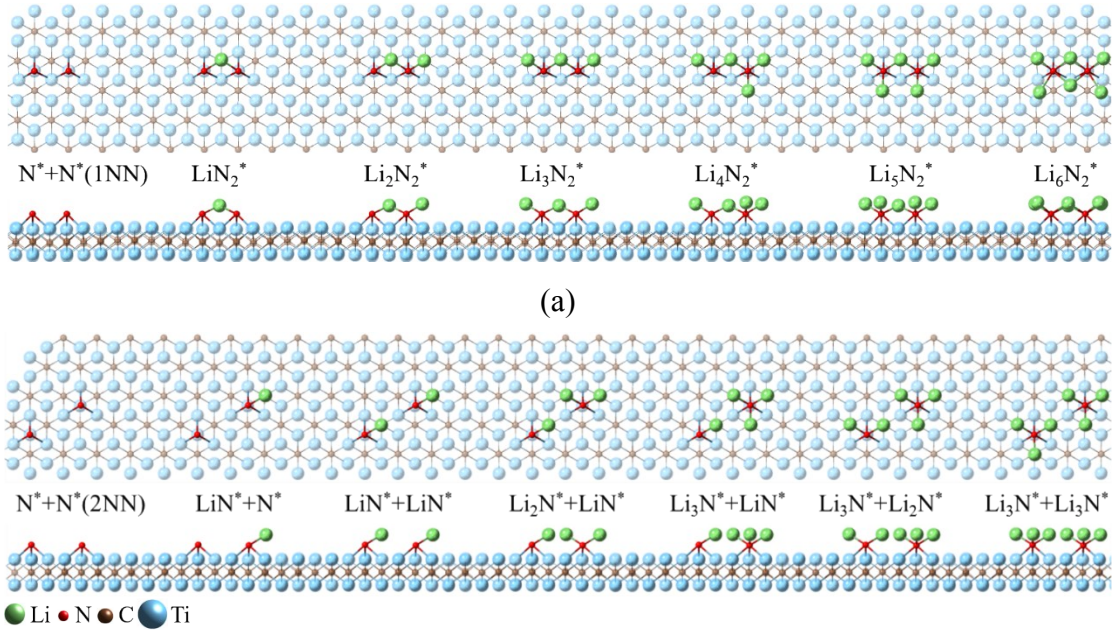

Figure S2 Schematic diagrams for two pathways of N_2 reduction reaction on Ti_2C, which start with N atoms located (a) at 1NN sites and (b) at 2NN sites. The red sphere represents N and green sphere represents Li.

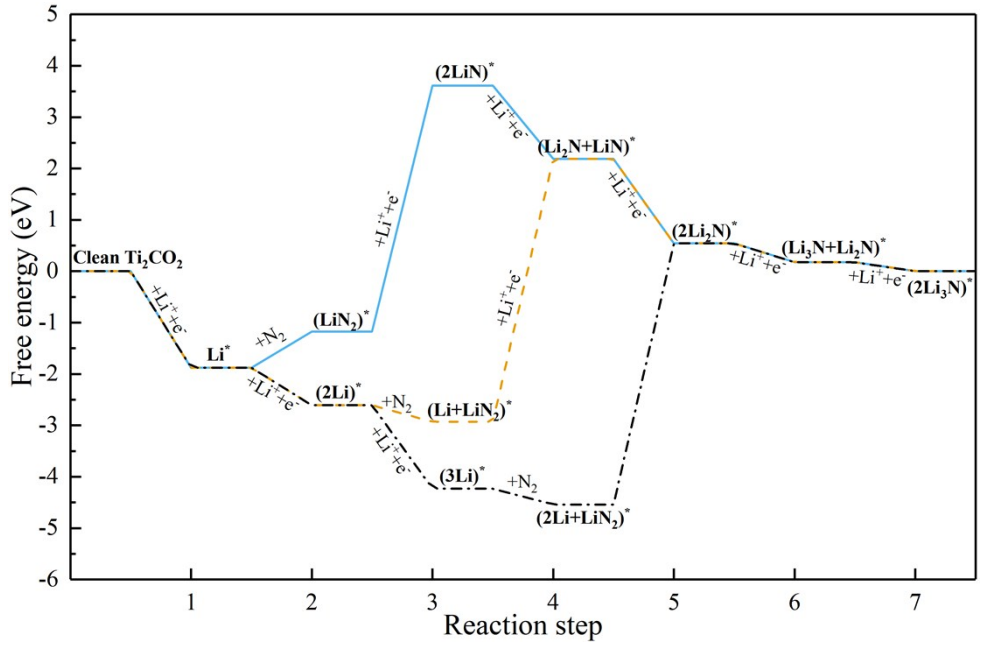

Figure S3 Calculated energy profiles for the formation of $(2Li_3N)^*$ on Ti_2CO_2 under the equilibrium potentials. There are three pathways in consideration that one, two or three Li atoms are pre-adsorbed before N_2 adsorbed on Ti_2CO_2. The equilibrium potential is 0.21 V, and the corresponding calculated discharge overpotentials are tabulated in Table S4.

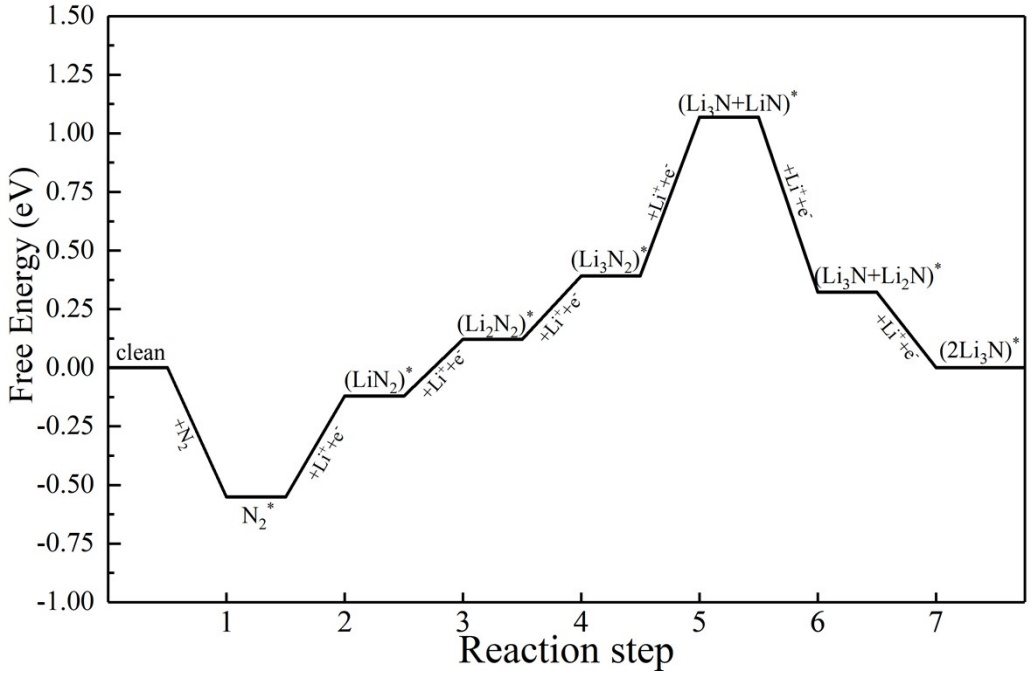

Figure S4 Calculated energy profiles for the formation of $(2Li_3N)^*$ on $Ti_2CO_2Li_2$ (already lithiated Ti_2CO_2) under the equilibrium potential. The equilibrium potential is 0.31 V. The step 5 and step 6 are controlling steps for discharge and charge respectively, and discharge and charge overpotentials are 0.68 V and 0.75 V.

Table S1 Adsorption energy (in eV) of N_2 molecule, N atom and Li atom adsorbed on the Ti_2C monolayer.

On Ti_2C	N_2		N	Li
	end-on	side-on		
fcc	-1.09	-3.52	-2.63	-0.91
hcp	-0.88	-3.52	-2.44	-0.90
atop	-0.85	-3.52	+0.52	-0.88

Table S2 Adsorption energy (in eV) of N_2 molecule, N atom and Li atom adsorbed on the Ti_2CO_2 monolayer.

On Ti_2CO_2	N_2		N	Li
	end-on	side-on		
On Ti	-0.12	-0.14	+6.22(+1.02)	-1.99
On C	-0.12	-0.15	+7.69(+2.49)	-2.17
On O	-0.09	-0.13	+4.72(-0.48)	-1.63

Table S3 Equilibrium potential (U_e), controlling steps for discharge (Step D), overpotentials for Li-pre-adsorption discharge ($\eta_{discharge}$) on Ti_2CO_2 substrate.[a]

Pathway	One Li Pre-adsorption	Two Li Pre-adsorption	Three Li Pre-adsorption
U_e(V)		0.21	
Step D	3rd	4th	5th
$\eta_{discharge}$ (V)	4.79	5.12	5.08

[a] as shown in Fig. S3, the controlling steps represent the dissociation of N_2 and N atom adsorption on Ti_2CO_2 substrate, however, the dissociation energy is high and the adsorption is unfavorable on Ti_2CO_2 which result in ultrahigh overpotentials.

Table S4 Adsorption energy (in eV) of N_2 molecule and Li atom adsorbed on the $Ti_2CO_2Li_2$ (already lithiated Ti_2CO_2) monolayer.

On $Ti_2CO_2Li_2$	N_2		N	Li
	end-on	side-on		
On Li	-0.51	-0.53	+2.20	+0.27
On O	-0.37	-0.50	+2.20	+0.27
On Ti	-0.47	-0.55	+2.30	+0.27