Supplementary Information II — Structures and Computation Reliability

Layered $MoSi_2N_4$ as electrode material of Zn-air battery

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1. Structure dataset

Supplementary III contains the CIF files of typical structures, including the structure of $MoSi_2N_4$ lattice, Zn-filled structures along the convex hull, O_2 adsorption configuration, and $MoSi_2N_4$–ZnO_2 structures. The list is in the following.

MoSi2N4-AA.cif	$MoSi_2N_4$ with AA stacking (the most stable)
MoSi2N4-AB.cif	$MoSi_2N_4$ with AB stacking
MoSi2N4-AC.cif	$MoSi_2N_4$ with AC stacking
convex-hull-6.25%-state-I.cif	$MoSi_2N_4$ with 6.25% Zn in the convex hull (state I)
convex-hull-12.5%-state-I.cif	$MoSi_2N_4$ with 12.5% Zn in the convex hull (state I)
convex-hull-18.75%-state-I.cif	$MoSi_2N_4$ with 18.75% Zn in the convex hull (state I)
convex-hull-25%-state-I.cif	$MoSi_2N_4$ with 25% Zn in the convex hull (state I)
convex-hull-31.25%-state-I.cif	$MoSi_2N_4$ with 31.25% Zn in the convex hull (state I)
convex-hull-43.75%-state-I.cif	$MoSi_2N_4$ with 43.75% Zn in the convex hull (state I)
convex-hull-50%-state-I.cif	$MoSi_2N_4$ with 50% Zn in the convex hull (state I)
convex-hull-87.5%-state-III.cif	$MoSi_2N_4$ with 87.5% Zn in the convex hull (state III)
convex-hull-100%-state-III.cif	$MoSi_2N_4$ with 100% Zn in the convex hull (state III)
metastable-16.67%-state-I.cif	a configuration of $MoSi_2N_4$ with 16.67% Zn above the convex hull (state I)
MoSi2N4-4O2.cif	$\sqrt{7}\times\sqrt{7}$ $MoSi_2N_4$ surface with 4 O_2 molecules (100% O_2 coverage)
MoSi2N4-ZnO2-1ML.cif	$\sqrt{7}\times\sqrt{7}$ $MoSi_2N_4$ surface with 1ML ZnO_2
MoSi2N4-ZnO2-2ML.cif	$\sqrt{7}\times\sqrt{7}$ $MoSi_2N_4$ surface with 2ML ZnO_2
MoSi2N4-ZnO2-3ML.cif	$\sqrt{7}\times\sqrt{7}$ $MoSi_2N_4$ surface with 3ML ZnO_2
Zn-migration-state-I-gs.cif	The ground state in the Zn migration path **Figure 3(c)**

Zn-migration-state-I-ts.cif	The transition state in the Zn migration path **Figure 3(c)**
Zn-migration-state-III-gs.cif	The ground state in the Zn migration path **Figure 3(d)**
Zn-migration-state-III-ts.cif	The transition state in the Zn migration path **Figure 3(d)**
Zn-migration-state-III-ms.cif	The metastable state in the middle of Zn migration path **Figure 3(d)**

2. DFT kinetic energy cutoff

In order to determine an appropriate kinetic energy cutoff (ENCUT in VASP), tests are performed for two structures with ENCUT = 400 ~ 600 eV. The first structure is in the convex hull with 43.75% Zn (state I, **Figure S5(a)**, **convex-hull-43.75%-state-I.cif** in Supplementary III). The second is a metastable structure with 16.67% Zn (state I, **Figure S5(b)**, **metastable-16.67%-state-I.cif** in Supplementary III). The DFT energies of $MoSi_2N_4$ (in the most stable AA stacking) and Zn bulk (hexagonal lattice, two Zn atoms in one cell) are calculated. Then the Zn adsorption energy E_{ad}(Zn) is calculated by Eq. (1). The results are listed in **Table S1**. We can see that the resulted E_{ad}(Zn) changes little with ENCUT. To two decimal places, E_{ad}(Zn) keeps unchanged. In our calculations, ENCUT = 400 eV is then adopted to save computation time.

Table S1 Calculated DFT energy and Zn adsorption energy E_{ad}(Zn) under different kinetic energy cutoff ENCUT. The unit is in eV.

ENCUT		400	450	500	550	600
AA-$MoSi_2N_4$	DFT energy	-63.581	-63.590	-63.584	-63.584	-63.589
Zn bulk	DFT energy	-3.038	-3.038	-3.039	-3.038	-3.038
convex hull 43.75%	DFT energy	-1022.005	-1022.133	-1022.057	-1022.055	-1022.127
$Mo_{16}Si_{32}N_{64}Zn_7$	E_{ad}(Zn)	0.847	0.848	0.846	0.847	0.846
metastable 16.67%	DFT energy	-1143.322	-1143.469	-1143.375	-1143.373	-1143.453
$Mo_{18}Si_{36}N_{72}Zn_3$	E_{ad}(Zn)	1.900	1.901	1.899	1.901	1.899

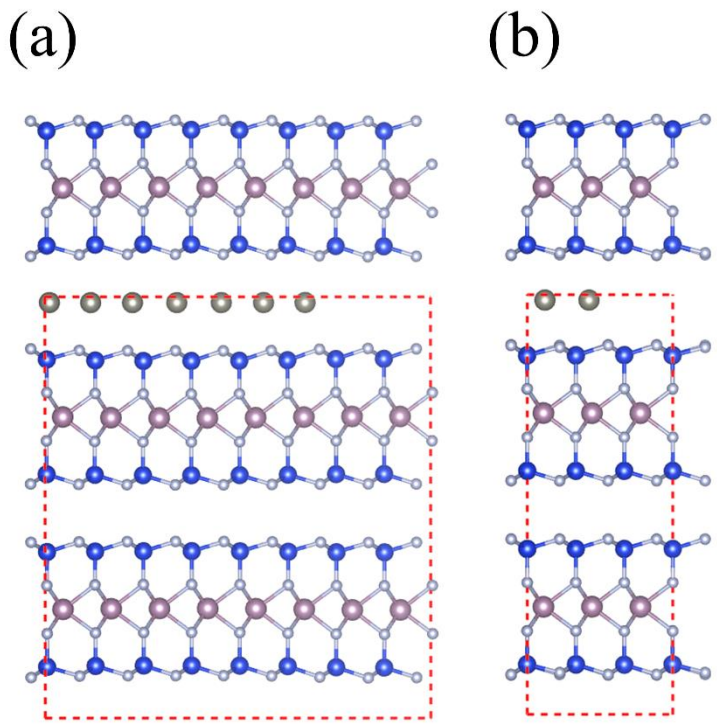


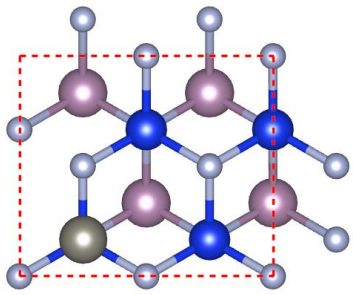
Figure S5 Structure of **(a)** the one in the convex hull with 43.75% Zn (corresponding to **convex-hull-43.75%-state-I.cif** in Supplementary III) and **(b)** metastable structure with 16.67% Zn (corresponding to **metastable-16.67%-state-I.cif** in Supplementary III). The violet, blue, white and gray balls denote Mo, Si, N and Zn atoms, respectively.

3. Zn migration barrier and transition state

In **Figure 3(c)** and **(d)**, we consider Zn atom migration in dilute (state I, an isolate Zn atom) and dense (state III, nearly full Zn filling) Zn concentration, respectively. For **Figure 3(c)**, the structure of ground state corresponds to **Zn-migration-state-I-gs.cif** in Supplementary III, and the structure of transition state corresponds to **Zn-migration-state-I-ts.cif**. For **Figure 3(d)**, the migration starts from a ground state, climbs over a barrier and reaches a metastable state, which are **Zn-migration-state-III-gs.cif**, **Zn-migration-state-III-ts.cif** and **Zn-migration-state-III-ms.cif** in Supplementary III, respectively. To verify the calculation of migration paths, frequency calculations are performed to identify the ground and transition states. For the transition states, one imaginary frequencies are found corresponding to the saddle point. See the data listed below.

dilute Zn concentration

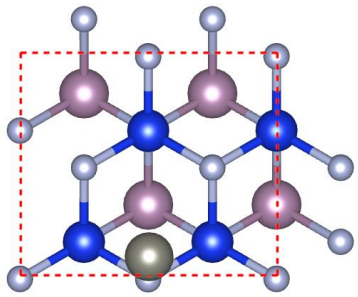
ground state



Zn-migration-state-I-gs.cif

vibration frequencies $h\gamma_i$ (meV)					
131.84	131.63	130.89	126.67	117.46	117.35
117.29	117.24	116.86	116.78	115.28	115.17
114.57	114.54	113.32	113.31	113.14	113.12
112.37	112.11	111.16	110.87	110.34	110.18
110.16	110.14	109.90	109.86	106.77	106.73
106.69	106.36	106.28	106.23	106.22	106.19
106.10	106.03	105.99	105.97	105.95	105.91
105.46	105.35	105.33	105.28	105.18	104.94
94.34	92.99	92.70	92.50	88.10	86.14
85.86	84.47	84.47	83.62	83.59	83.58
83.45	83.43	83.17	80.35	80.31	79.48
79.45	79.44	79.21	78.88	78.77	78.58
78.23	78.20	78.12	77.98	77.97	77.86
77.27	76.94	75.38	75.29	75.07	74.31
74.31	73.19	73.15	73.13	73.00	72.55
72.21	72.14	69.12	69.06	69.01	68.94
57.41	56.83	56.72	56.56	56.47	56.18
55.68	55.62	55.44	55.27	54.95	54.58
54.18	54.13	53.67	52.97	52.49	52.48
52.19	52.00	51.16	50.07	48.99	48.45
48.35	48.05	47.19	46.99	46.83	45.66
43.35	43.21	42.99	42.31	42.04	41.93
41.80	41.58	41.49	41.26	40.79	40.06
37.88	37.67	36.90	35.65	33.38	33.16
32.85	32.61	32.55	32.41	31.54	31.38
30.68	25.13	25.04	21.04	20.93	16.65
16.55	16.19	16.00	15.47	14.76	14.40
12.32	4.82	4.26	3.16	2.16	1.55

transition state

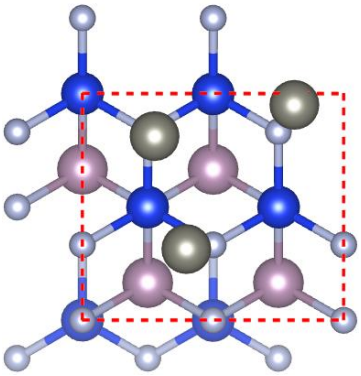


Zn-migration-state-I-ts.cif

vibration frequencies $h\gamma_i$ (meV)					
131.92	131.75	131.07	126.87	117.68	117.63
117.42	117.31	117.22	116.78	115.37	115.24
114.66	114.52	113.43	113.43	113.22	113.22
112.47	112.18	111.19	110.89	110.39	110.36
110.32	110.18	110.10	110.00	106.82	106.64
106.47	106.41	106.36	106.25	106.24	106.18
106.12	106.09	106.06	106.06	106.05	106.00
105.79	105.47	105.38	105.33	105.22	105.03
94.50	93.07	92.72	92.37	88.13	86.13
85.90	84.46	84.46	83.78	83.70	83.64
83.52	83.37	83.27	80.39	80.34	79.60
79.53	79.48	79.24	78.89	78.80	78.59
78.31	78.25	78.19	77.99	77.97	77.92
77.31	77.01	75.42	75.31	75.11	74.42
74.34	73.23	73.19	73.13	73.01	72.57
72.23	72.23	69.10	69.09	69.06	69.05
57.52	56.91	56.79	56.67	56.46	56.29
55.77	55.69	55.49	55.32	55.07	54.53
54.24	54.22	53.91	52.96	52.56	52.49
52.19	52.09	51.25	50.13	49.21	48.54
48.41	48.14	47.39	47.09	46.75	45.72
43.41	43.12	43.01	42.40	42.10	42.05
41.87	41.74	41.52	41.31	40.86	40.26
37.90	37.67	37.08	35.77	33.41	33.31
32.84	32.75	32.60	32.39	31.68	31.37
30.87	25.14	25.02	21.23	21.01	16.75
16.73	16.27	16.02	15.62	14.76	14.53
12.66	4.66	2.88	2.52	1.96	-0.52

dense Zn concentration

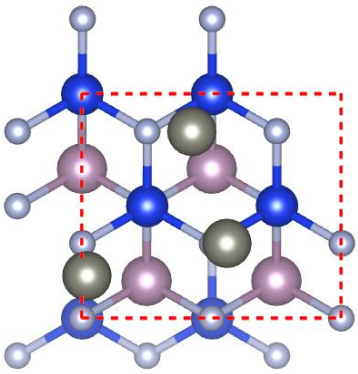
ground state



Zn-migration-state-III-gs.cif

vibration frequencies $h\gamma_i$ (meV)					
131.01	127.08	118.88	118.06	117.67	114.49
114.25	113.37	113.28	112.86	111.47	111.37
110.74	110.37	106.45	106.42	106.39	106.34
106.13	106.08	105.75	105.61	105.00	104.95
92.00	91.34	83.18	83.03	82.94	82.29
80.39	79.76	79.61	79.58	78.96	78.25
78.10	77.91	77.38	76.79	75.15	74.51
73.33	73.30	72.73	72.58	69.52	69.33
56.33	55.55	55.22	55.16	54.53	54.12
53.83	52.40	51.85	51.44	49.80	47.89
46.74	46.36	45.19	42.45	41.76	41.57
40.95	39.80	37.23	36.86	36.66	31.73
31.40	30.48	24.63	24.35	23.88	16.79
16.06	15.93	14.61	14.33	13.34	12.94
12.38	9.97	5.97	4.94	3.79	2.98

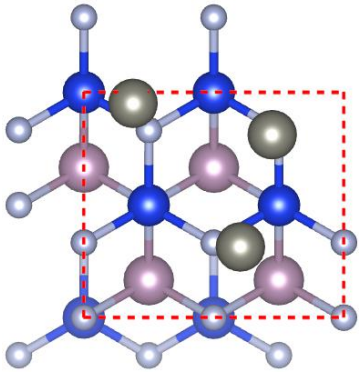
transition state



Zn-migration-state-III-ts.cif

vibration frequencies $h\gamma_i$ (meV)					
131.11	127.00	118.89	118.43	117.74	114.69
114.16	113.50	113.30	113.01	111.68	111.26
110.80	110.47	106.66	106.64	106.31	106.30
106.11	106.07	105.62	105.59	105.11	104.86
91.51	90.98	83.38	83.26	82.67	81.95
80.45	79.70	79.48	79.41	78.94	78.25
78.11	77.82	77.33	76.83	75.15	74.55
73.26	73.24	72.68	72.47	69.51	69.28
56.21	55.34	54.81	54.72	54.43	54.19
53.66	52.60	51.72	51.60	49.59	47.99
46.75	46.65	45.01	42.81	41.61	41.51
40.87	40.19	37.04	36.96	36.67	32.03
31.46	30.46	24.76	24.36	22.29	16.91
15.97	15.79	14.54	14.27	13.05	12.52
10.70	10.27	5.68	3.87	3.40	-3.82

metastable state



Zn-migration-state-III-ms.cif

vibration frequencies $h\gamma_i$ (meV)					
131.14	127.57	119.53	118.84	118.44	114.98
114.81	113.72	113.62	113.42	111.95	111.86
111.25	110.84	106.62	106.52	106.50	106.42
106.19	106.15	105.93	105.79	105.17	105.11
92.26	91.61	83.62	83.52	83.40	82.80
80.66	80.06	79.85	79.78	79.23	78.58
78.49	78.14	77.59	77.01	75.46	74.87
73.65	73.61	73.03	72.92	69.86	69.63
56.41	55.33	55.00	54.95	54.35	54.09
53.66	52.28	51.79	51.35	49.36	48.08
47.14	46.37	45.24	42.41	41.39	41.33
40.67	40.33	36.99	36.84	36.65	31.87
31.56	30.91	24.72	24.46	23.83	16.75
15.29	14.69	14.29	14.04	13.51	13.29
12.80	10.32	6.77	5.32	4.80	4.39