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Supporting Information

Ammine Bimetallic (Na, Zn) Borohydride for Advanced Chemical Hydrogen Storage

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Table S1. Experimental structural parameters of the as-prepared $NaZn(BH_4)_3 \cdot 2NH_3$.

Atom	Site	x/a	y/b	z/c
Zn1	4a	0.69084(43)	0.24742(24)	0.41352(13)
Na1	4a	0.77549(77)	0.04133(50)	0.84756(32)
B1	4a	0.17713	0.65232	0.89356
H1a	4a	0.21145	0.74453	0.93845
H1b	4a	0.23517	0.56537	0.93713
H1c	4a	0.02312	0.64791	0.88505
H1d	4a	0.24181	0.65716	0.81450
B2	4a	0.22393	0.30326	0.07086
H2a	4a	0.22247	0.34961	0.15007
H2b	4a	0.27619	0.37956	0.01460
H2c	4a	0.31367	0.21262	0.07474
H2d	4a	0.08033	0.27309	0.04832
B3	4a	0.44443	0.70997	0.17091
H3a	4a	0.53779	0.62110	0.17035
H3b	4a	0.40833	0.73384	0.08828
H3c	4a	0.32071	0.68461	0.21941
H3d	4a	0.51782	0.79684	0.20654
N5	4a	0.21841	0.05904	0.89697
H5a	4a	0.10116	0.02214	0.92232
H5b	4a	0.24492	0.02341	0.82749
H5c	4a	0.31846	0.03431	0.94476
N6	4a	0.92192	0.17945	0.36130
H6a	4a	1.00606	0.19851	0.41929
H6b	4a	0.91471	0.08298	0.35053
H6c	4a	0.96845	0.22215	0.29786

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Table S2. Interatomic bond distances (Å) in the crystal structure of $NaZn(BH_4)_3 \cdot 2NH_3$.

Atoms		Bond distances (Å)	Atoms		Bond distances (Å)
Zn1	H3a	1.8113	B1	H1c	1.2095
	H2d	1.8566		H1b	1.2225
	H3d	2.0876		H1a	1.2475
	H2b	2.1572		H1d	1.2671
	H6b	2.4006	B2	H2b	1.2061
	H5b	2.4031		H2a	1.2199
	H2c	2.4254		H2c	1.2388
	H6a	2.5378		H2d	1.2561
	H5c	2.5584	B3	H3d	1.2125
	B2	2.1185		H3c	1.2199
	B3	2.1392		H3a	1.2332
	N6	1.9435		H3b	1.2335
	N5	1.9853	N5	H5c	1.0338
				H5a	1.0404
				H5b	1.0487
			N6	H6c	1.0339
				H6b	1.0428
				H6a	1.0430

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Table S3. Interatomic distances (Å) and Angles (°) for apparent dihydrogen bonds in the $NaZn(BH_4)_3 \cdot 2NH_3$.

Distance		Angle		Angle	
H1b···H6a	1.987	B1-H1b···H6a	113.14	H1b···H6a-N6	160.16
H1d···H6b	2.053	B1-H1d···H6b	119.01	H1d···H6b-N6	172.82
H1a···H5a	2.132	B1-H1a···H5a	165.91	H1a···H5a-N5	128.25
H1d···H5b	2.147	B1-H1d···H5b	116.29	H1d···H5b-N5	158.58
H3d···H5b	2.201	B3-H3d···H5b	137.81	H3d···H5b-N5	95.19
H3b···H6a	2.352	B3-H3b···H6a	129.41	H3b···H6a-N6	122.28

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Table S4. Summarization of dehydrogenation peak temperature (D_p), Pauling electronegativity (χ_p), and selected atomic distances from $NaZn(BH_4)_3{\cdot}2NH_3$, $NaZn(BH_4)_3$, and several borohydride ammonites. All units are measured in Å.

Samples	$NaZn(BH_4)_3(NH_3)_2$	$NaZn(BH_4)_3$ [S1]	$Li(BH_4)(NH_3)$ [S2]	$Mg(BH_4)_2(NH_3)_2$ [S3]	$Ca(BH_4)_2(NH_3)_2$ [S4]	$Li_2Al(BH_4)_5(NH_3)_6$ [S5]
χ_p	Zn: 1.65 Na: 0.93	Zn: 1.65 Na: 0.93	Li: 1.0	Mg: 1.31	Ca: 1.0	Al: 1.61 Li: 1.0
D_p (ºC)	130	140	~280	~200	~280	138
Metal-H	Zn-H 1.81-2.56 Na-H 2.11-2.84	Zn-H 1.59-2.86 Na-H 2.26-2.85	1.96-2.73	2.02-2.66	2.41-2.98	Al-H 2.57-2.73 Li-H 2.06-2.94
Metal-B	Zn-B 2.11-2.14	Zn-B 2.44-2.86	2.52-2.56	2.26-2.39	2.77-2.96	Al-B 4.56-6.3
Metal-N	Zn-N 1.94-1.99	---	2.01	2.14	2.52	Al-N 2.05
H···H	1.99-2.35	---	1.91-2.55	2.08-2.23	2.03-2.44	2.06-2.26

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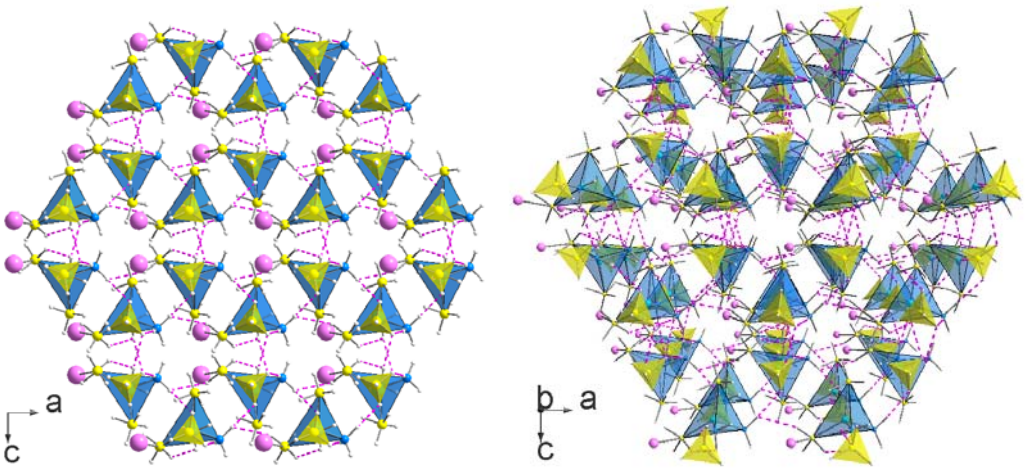

(a) (b)

Figure S1. The packed architecture viewing of $NaZn(BH_4)_3 \cdot 2NH_3$ from *b* direction.

The dash lines represent the dihydrogen bindings between NH_3 and BH_4 units.

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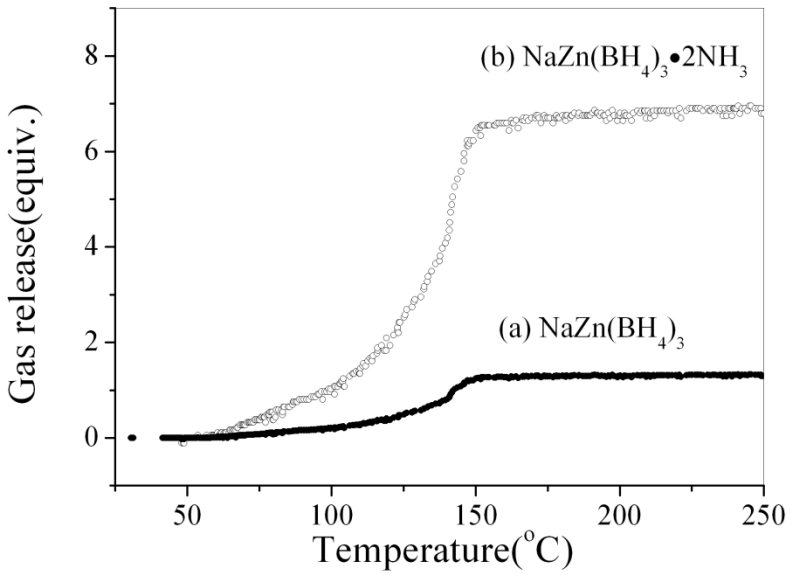

Figure S2. The gas release curves as a function of temperature for the synthesized $NaZn(BH_4)_3$ and $NaZn(BH_4)_3{\cdot}2NH_3$ in 1 atm Ar atmosphere. The heating ramp is 10 ^{o}C/min.

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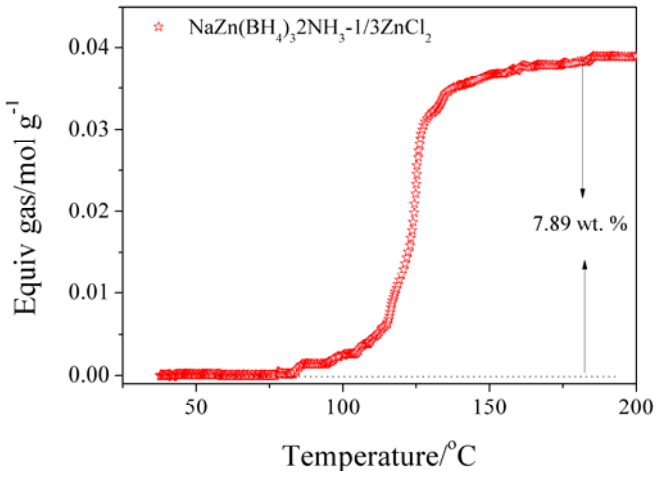

Figure S3. Volumetric gas release measurement for the as-prepared $NaZn(BH_4)_3{\cdot}2NH_3$-$1/3ZnCl_2$. The heating rate is 10 ^{o}C/min in argon.

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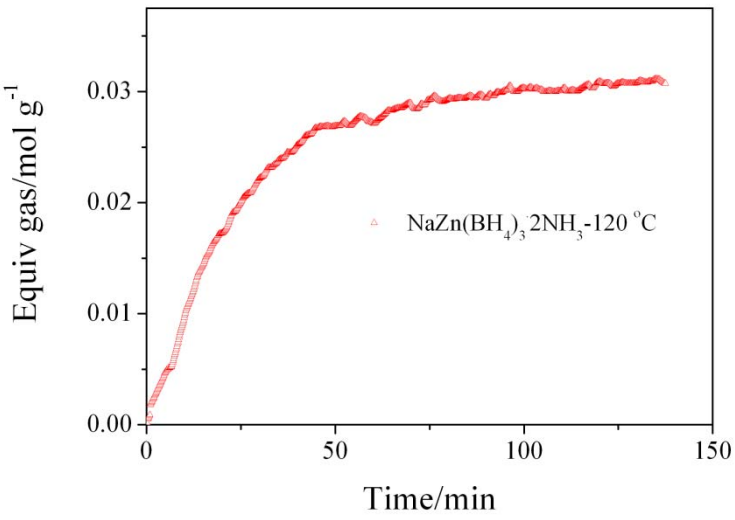

Figure S4. Isothermal TPD curve for the decomposition of $NaZn(BH_4)_3 \cdot 2NH_3$ at 120 ^oC.

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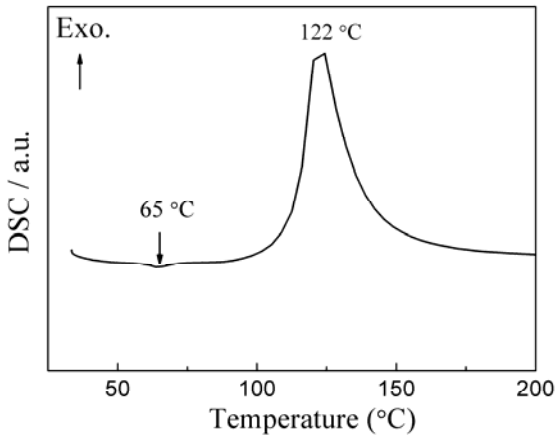

Figure S5. DSC curve for the as-prepared $NaZn(BH_4)_3 \cdot 2NH_3$-1/3$ZnCl_2$ composite. The heating rate is 10 ^oC min^{-1}.

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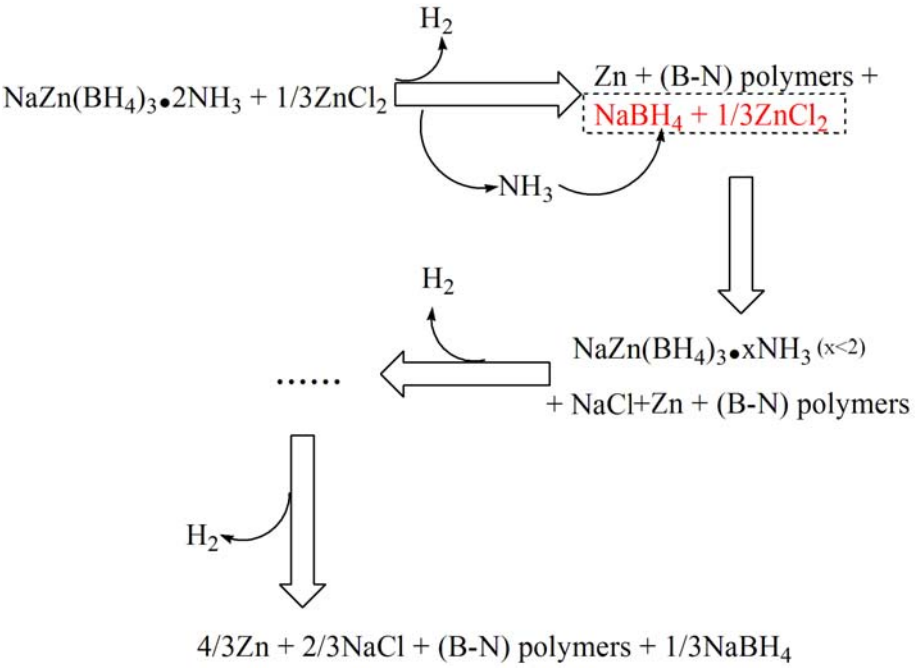

Scheme S1. Proposed mechanism for the dehydrogenation of the as-prepared $NaZn(BH_4)_3{\cdot}2NH_3$-$1/3ZnCl_2$ sample. Note: $NaZn(BH_4)_3{\cdot}xNH_3$ was designated as ammoniates of $NaZn(BH_4)_3$ with coordination number $x < 2$.