

# **Modifying specific Li-Sites of LiNH<sub>2</sub> by Na: Study of Multi-cation Hydride Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> in Electrochemical Applications**

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## Supporting information

### **S-I. Sample preparation**

As-milled powder of Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> was prepared by ball-milling 500 mg mixtures of LiNH<sub>2</sub> and NaNH<sub>2</sub> (both are purchased from Aldrich, Japan) in 3:1 molar ratio for 5 h (400 rpm; 20 stainless-steel balls; ball-to-powder mass ratio 60:1) under high purity Ar gas. The as-milled powder (typically 150 mg) was heat treated isothermally at temperatures 373 K for 12 h under the dynamical vacuum.

### **S-II: X-ray Diffraction**

The crystal structure of Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> was confirmed by the X-ray diffraction (XRD) in PANalytical X'PERT with Cu K $\alpha$  radiation to collect the XRD profiles at room temperature with transmission geometry. Samples for XRD measurement were prepared inside the glove box kept under constant circulation of high purity Ar gas. The water level inside the glove box was very low (dew point below -363 K).

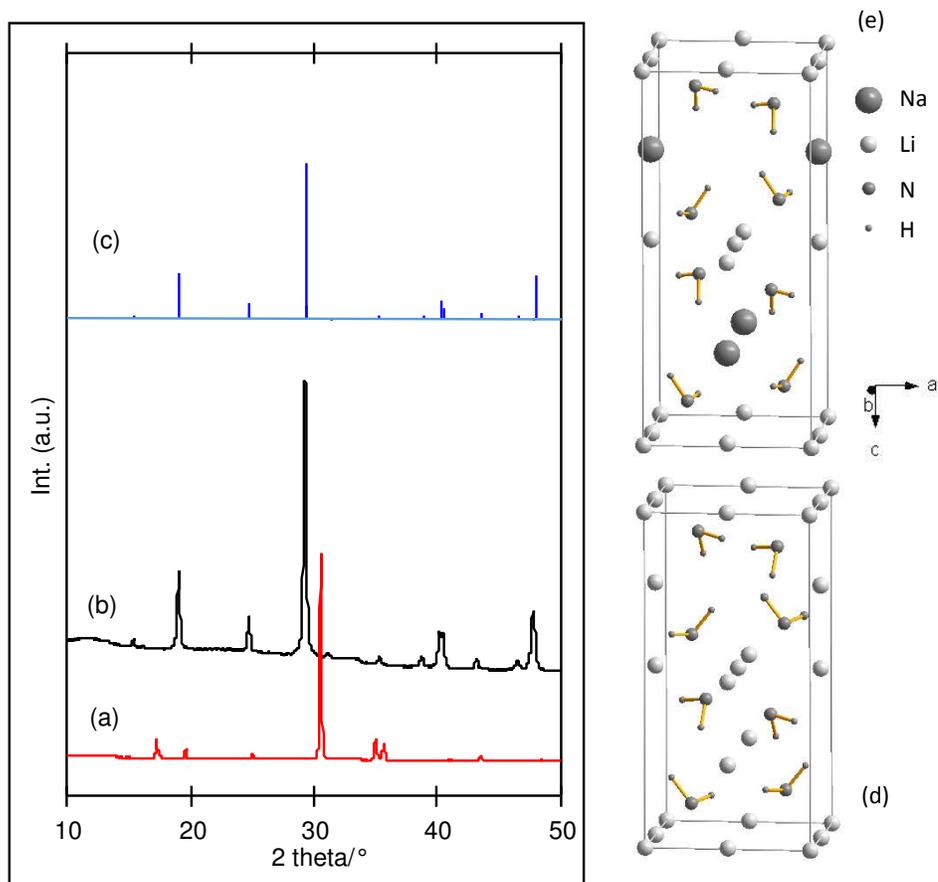


Fig. S1: XRD profiles of (a) as-purchased LiNH<sub>2</sub>, (b) as-synthesized Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> (c) ICDD# 98-016-0614 (Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>). Unit cell of LiNH<sub>2</sub> and Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> are shown in (d) and (e), respectively. Na<sup>+</sup> cations replace Li<sup>+</sup> cations from the 2c sites in Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>.

### S-III: Raman spectroscopy

Raman spectroscopy (Nicolet Almega-HD, Nd:YVO<sub>4</sub> laser with wavelength 532 nm) was employed to collect the vibration energies of the LiNH<sub>2</sub>-NaNH<sub>2</sub> compositions. The sample, taken in an Al pan, was loaded in a specially designed container in the glove box to prevent the samples from any exposure to the air/oxygen during the experiment.

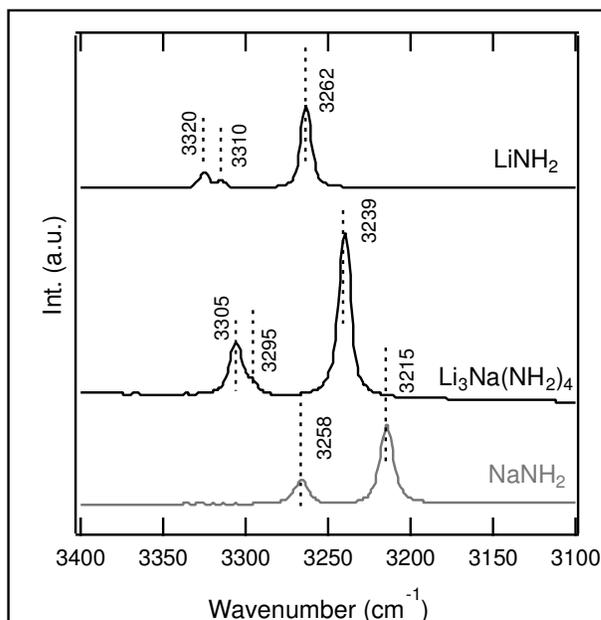


Fig. S2: Comparing the stretching vibrations of [NH]<sup>-</sup> anions in the Raman spectra of Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>, LiNH<sub>2</sub> and NaNH<sub>2</sub>.

### S-IV: Measurement of ac and dc conductivity

The ionic conductivity of Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub> was measured by both ac and dc impedance spectrometry. The ac impedance measurement was carried out using the impedance meter Hioki 3532-80 by sandwiching the pressed complex hydride pellet (diameter 8 mm, thickness typically 1 mm, density > 95% of the calculated value) between two lithium plates to collect the impedance of the pellet at ac frequencies ranging from 10-10<sup>6</sup> Hz at every 5-10 K temperature interval over a temperature window of 300-373 K. The Nyquist plot (semi-circle) observed in the symmetrical cell Li/[Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>]/Li was fitted into simple R-C circuit to

estimate the value of dc resistance  $R$  (in ohm), giving the ionic conductivity  $\sigma = t/(R \cdot A)$ ; where  $t$  and  $A$  are, respectively, the thickness (in cm) and flat-surface area (in  $\text{cm}^2$ ) of the pressed complex hydride pallet.

The dc impedance measurement was carried out by applying a suitable dc voltage at 343 K across a symmetrical impedance cell  $M/[\text{Li}_3\text{Na}(\text{NH}_2)_4]/M$  where  $M = \text{Li}$  (non-blocking electrode) and  $\text{Mo}$  (blocking electrode). The applied dc voltage for the  $\text{Li}/[\text{Li}_3\text{Na}(\text{NH}_2)_4]/\text{Li}$  cell was 0.1 V and that for the  $\text{Mo}/[\text{Li}_3\text{Na}(\text{NH}_2)_4]/\text{Mo}$  cell was 1.0 V. The current was measured at every 0.01 s for 1 h. The dc resistance was estimated from the voltage-current data at every data point. From the known thickness and the diameter of the  $\text{Li}_3\text{Na}(\text{NH}_2)_4$  pallet, we estimated the resistance and, hence, the conductivity using the equation  $\sigma = t/(R \cdot A)$  as a function of time.

#### **S-VI: Voltammogram**

The cyclic voltammogram (CV) of  $\text{Li}_3\text{Na}(\text{NH}_2)_4$  was obtained at various temperatures using the lithium plate (the reference electrode) and molybdenum plate (the working electrode) sandwiching the pressed powder. Range of the voltage used was (-) 2.0 V to (+) 5.0 V. Voltage scan rate was  $5 \text{ mV} \cdot \text{s}^{-1}$ . We obtained CV for up to 5 cycles. Figure 3 in the main text shows a representative voltammogram of  $\text{Li}_3\text{Na}(\text{NH}_2)_4$  obtained at 363 K.

### S-VII: Lattice vibrations in LiNH<sub>2</sub>, NaNH<sub>2</sub> and Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>

Table S1: Lattice vibrations in LiNH<sub>2</sub> and Li<sub>3</sub>Na(NH<sub>2</sub>)<sub>4</sub>.

LiNH <sub>2</sub> (calc.) <sup>1</sup>	Symmetry <sup>1</sup>	LiNH <sub>2</sub> (obs., at RT) <sup>1</sup>	LiNH <sub>2</sub> (at RT, this study)	Li <sub>3</sub> Na(NH <sub>2</sub> ) <sub>4</sub> (this study) <sup>2</sup>
109	E	132.7	137.1	103.3
184	B	177.6	179.5	166.0
195	E			
210	A			214.2
239	E	237.8	238.3	
257	B			
275	A	272.7	276.9	268.2
279	E	289.1	~ 294 <sup>§</sup>	
305	A			
312	B	322.3		
317	E	322.3	~ 327 <sup>§</sup>	328.0
338	B	322.3		
348	A	342.7	344.4	
385	E	372.9	376.2	360.8
404	A			
419	B	406.2	407.9	
457	B			
500	E			
515	A	513.3	513.1	518.0
569	E			
600	B	563.4	~ 570	
669	A	654.5	657.3	652.0
679	E			
719	B			

<sup>§</sup>These weak peaks are not labelled in Fig.3 of the main text for clarity in the figure.

Table S2: Comparing the observed NaNH<sub>2</sub> lattice vibrations in different studies.

Wood <i>et al.</i> <sup>3</sup> (Raman spect.)	Liu <i>et al.</i> <sup>4</sup> (Raman spect.)	Cunningham <i>et al.</i> <sup>5</sup> (Raman spect.)	Day <i>et al.</i> <sup>6</sup> (Neutron scattering)	This study (Raman spect.)
				63.8 <sup>†</sup>
110	115 <sup>a</sup>			110.1
177	177 <sup>a</sup>			177.6
				205.5
246	251 <sup>a</sup>			248.9
				277.0
		349		370.0
469	464 <sup>b</sup>		400 <sup>c</sup>	
		468		475.5
		522		
532	535 <sup>b</sup>			535.3
			550/560 <sup>d</sup>	

<sup>a</sup>Translational modes (tentatively assigned in ref 4).

<sup>b</sup>Librational modes (ref 4).

<sup>c</sup>Wagging of [NH<sub>2</sub>]<sup>-</sup> (ref 6).

<sup>d</sup>Torsion of [NH<sub>2</sub>]<sup>-</sup> (ref 6).

<sup>†</sup>This peak has not been reported in NaNH<sub>2</sub> by previous studies.

## Notes and references

- 1 Michigoe, A.; Hasegawa, T.; Ogita, N.; Ichikawa, T.; Kojima, Y.; Isobe, S.; Udagawa, M. Raman scattering study of hydrogen storage material LiNH<sub>2</sub>. *J. Phys. Soc. Jap.*, **2012**, *81*, 94603.

- 2 The tabulation/arrangement of the observed lattice vibrations of  $\text{Li}_3\text{Na}(\text{NH}_2)_4$  in Table S1, against specific modes of  $\text{LiNH}_2$ , is not intended to suggest any assignment for the Raman peaks of  $\text{Li}_3\text{Na}(\text{NH}_2)_4$ ; they are merely tabulated against the closest-matching vibrations reported for  $\text{LiNH}_2$ .
- 3 Wood, T.J.; Makepeace, J.W.; Hunter, H.M.A.; Jones M.O.; David, W.I.F. Isotopic studies of the ammonia decomposition reaction mediated by sodium amide. *Phys. Chem. Chem. Phys.*, **2015**, *17*, 22999-23006.
- 4 Liu, A.; Song, Y. In situ high-pressure study of sodium amide by Raman and infrared spectroscopies. *J. Phys. Chem. B*, **2011**, *115*, 7-13.
- 5 Cunningham, P.T.; Maroni, V.A. Laser Raman spectra of solid and molten  $\text{NaNH}_2$ : Evidence for hindered rotation of the  $\text{NH}_2^{-1}$  ion. *J. Chem. Phys.*, **1972**, *57*, 1415-1418.
- 6 Day, D.H; Sinclair, R.N. Studies of vibration spectra of bonded hydrogen atoms using a pulsed neutron source. *J. Chem. Phys.*, **1971**, *55*, 2807-2811.