

Supporting Information:

Anomalous H₂ Desorption Rate of NaAlH₄ Confined in Nitrogen-Doped Nanoporous Carbon Frameworks

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Experimental Procedures:

Chemicals: Phenol, Formalin, tetraethyl orthosilicate (TEOS), Pluronic F-127 tri-block copolymer, dicyandiamide, carbon tetrachloride (CTC) and ethylenediamine (EDA) were purchased from Sigma-Aldrich. SBA-15 silicate hard template was purchased from ACS Materials. Deionized water was used in all experiments.

NPC produced using inorganic/organic self-assembly method:¹

Resol precursors: In a typical process, 6.1 g of phenol was melted in a Schlenk flask at 40 °C and added to 1.3 g of 20 wt.% NaOH solution under stirring. At the end of 10 minutes, 10.5 g of formalin was added at a temperature below 50 °C dropwise. The resulting mixture was placed in

a water bath at 70 °C under stirring for 80 minutes and then allowed to cool to room temperature (RT). Using 1 N HCl the pH of the solution was adjusted to ~7.0. Water was removed from the solution under vacuum at 45 °C, producing a gel-like product. Ethanol was added to dissolve the product, producing a 20 wt.% resol-ethanol solution after mixing. The solution was allowed to settle and then poured off into a separate flask, leaving behind the salt from the acid-base neutralization.

NPC synthesis: In a typical process to produce 2D hexagonal carbon, 16 g F-127 tri-block copolymer was added to a solution consisting of 80 g ethanol and 10 g 0.2 M HCl. After stirring for 1 hour at 40 °C, 20.8 g TEOS and 50 g of 20 wt.% resol-ethanol solution were added sequentially, followed by stirring for 2 hours at 40 °C. The solution was poured into a glass pan and allowed to evaporate overnight at RT, producing a transparent film. In order to thermopolymerize the sample, heat treatment at 100 °C was carried out in an oven for 24 hours. The sample was scraped from the pan, ground into a fine powder, and placed into a tube furnace under flowing nitrogen for calcination at 350 °C for 3 hours, followed by carbonization at 900 °C for 2 hours. During the heat treatment the ramp rate was 1 °C/min below 600 °C and 5 °C/min after. To remove the silicate, the sample was etched in 5 wt.% HF solution overnight twice under stirring, followed by washing with ethanol and deionized water. Finally, the carbon sample was dried for 24 hours at 100 °C and additionally overnight at 300 °C under dynamic vacuum. The final sample was transported without air exposure to an argon-filled glovebox for storage.

NNPC produced using inorganic/organic self-assembly method:²

In a typical process, 8 g of F-127 tri-block co-polymer and 7.5 g dicyandiamide are added to a solution consisting of 100 g ethanol, 50 g H₂O, and 10 g 0.2 M HCl. After stirring for 1 hour at 40 °C, 10.4 g TEOS and 25 g of 20 wt.% resol-ethanol solution were added sequentially, followed by stirring for an additional 2 hours at 40 °C. In order to evaporate the solvent, the mixture was poured into pans and placed in an oven at 45 °C for 8 hours resulting in the formation of uniform films. In order to thermopolymerize the sample, heat treatment at 100 °C was carried out in an oven for 24 hours. The sample was scraped from the pan, ground into a fine powder, and placed into a tube furnace under flowing nitrogen for calcination at 250 °C for 2 hours, followed by carbonization at 700 °C for 3 hours. During the heat treatment the ramp rate was 1 °C/min. To remove the silicate, the sample was etched in 5 wt.% HF solution overnight twice under stirring, followed by washing with ethanol and deionized water. Finally, the carbon sample was dried for 24 hours at 100 °C and additionally overnight at 300 °C under dynamic vacuum. The final sample was transported without air exposure to an argon-filled glovebox for storage.

CMK-3 produced using the nanocasting method:³

In a typical synthesis, 6.25 g sucrose was dissolved in a mixture consisting of 0.7 g H₂SO₄ and 25 g H₂O, followed by the addition of 5 g SBA-15 silicate hard template material. After 15 minutes of stirring, a uniform white slurry was obtained. Heat treatments of the sample at 100 °C for 6 hours and 160 °C for 6 hours were performed sequentially. The resulting black/brown powder sample was added to a solution consisting of 4 g sucrose dissolved in 0.45 g H₂SO₄ and 25 g H₂O. After 25 minutes of stirring the previous heat treatments were repeated, followed by carbonization of the sample in a tube furnace at 900 °C under flowing argon for 3 hours. During

the heat treatment the ramp rate was 1 °C/min below 600 °C and 5 °C/min after. To remove the hard silicate template, the sample was etched in 5 wt.% HF solution overnight twice under stirring, followed by washing with ethanol and deionized water. Finally, the carbon sample was dried for 24 hours at 100 °C and additionally overnight at 300 °C under dynamic vacuum. The final sample was transported without air exposure to an argon-filled glovebox for storage.

NCMK-3 produced using the nanocasting method:⁴

In a typical process using Schlenk line techniques, 6.75 g EDA and 15 g CTC were added to a jacketed flask under stirring at RT. Next, 2.5 g SBA-15 silicate template was added to the mixture of EDA and CTC under stirring slowly. The resultant mixture was allowed to stir for 1 hour until a uniform white slurry was obtained. Under continuous stirring, the temperature was increased to 90 °C, at which the mixture was refluxed and stirred for 6 hours. The obtained brown colored solid mixture was placed in a drying oven at 100 °C for 12 hours, and subsequently ground into a fine powder. Sample calcination was carried out in a tubular furnace under flowing nitrogen at 600 °C for 5 hours. A ramp rate of 3 °C/min was used to bring the sample up to 600 °C. After calcination, the composite carbon/silica powder was immersed in 5 wt.% HF acid solution under stirring to dissolve the silica template. Carbon powder was recovered following filtration and several washings with ethanol and deionized water. Finally, the carbon sample was dried for 24 hours at 100 °C and additionally overnight at 300 °C under dynamic vacuum. The final sample was transported without air exposure to an argon-filled glovebox for storage.

Nitrogen Sorption Supporting Information:

Scans were recorded on a Coulter SA3100 at 77 K.

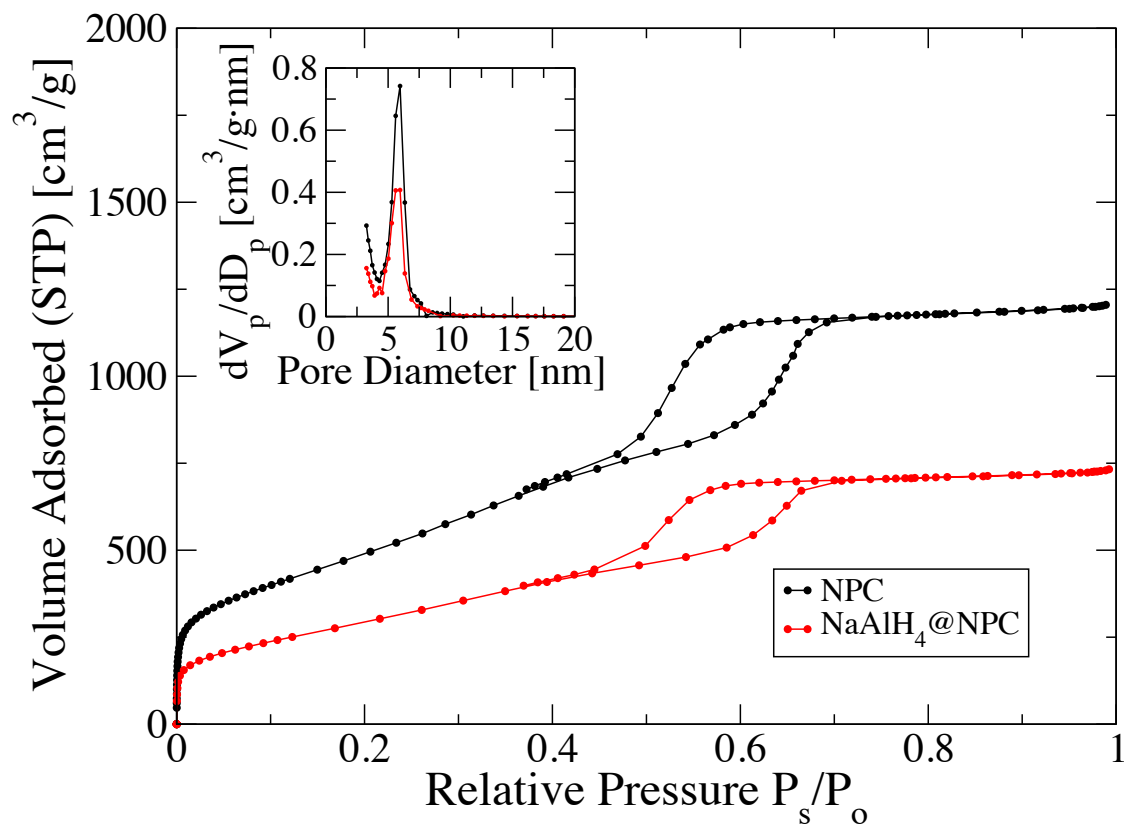


Figure S1. Nitrogen sorption isotherms and pore volume distributions (inset) for the NPC carbon substrate before and after infiltration with NaAlH_4 . The decreased volume adsorbed over the whole of the isotherm indicates some portion of the available surface area is now inaccessible to the adsorbate, as a result of the filling or blocking of the substrate pores.

PXRD Supporting Information:

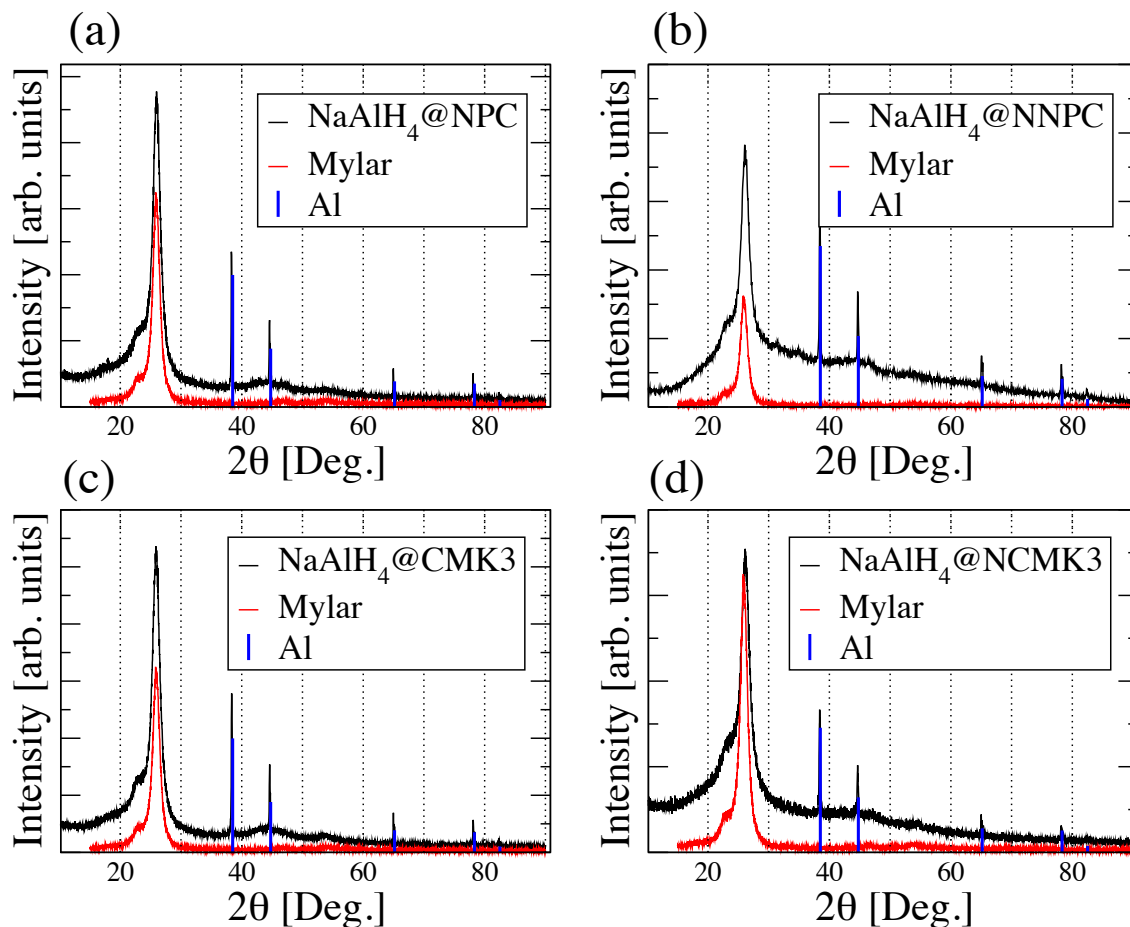


Figure S2. PXRD scans of infiltrated carbons: (a) NPC, (b) NNPC, (c) CMK-3, and (d) NCMK-3. Mylar film was used to cover the sample to avoid air exposure. No peaks from crystalline NaAlH_4 were detected, indicating the presence of little or no NaAlH_4 outside the pores, and indicating NaAlH_4 contained inside the pores is amorphous.

Table S1. NaAlH_4 and Al Metal Content of Infiltrated Carbon Scaffolds

Sample	NaAlH_4	Al metal	Al_2O_3
NaAlH_4 @CMK-3	26.5%	73.5%	0%
NaAlH_4 @NCMK-3	68.0%	32.0%	0%
NaAlH_4 @NPC	89.2%	10.8%	0%
NaAlH_4 @NNPC	20.1%	22.3%	26.9%

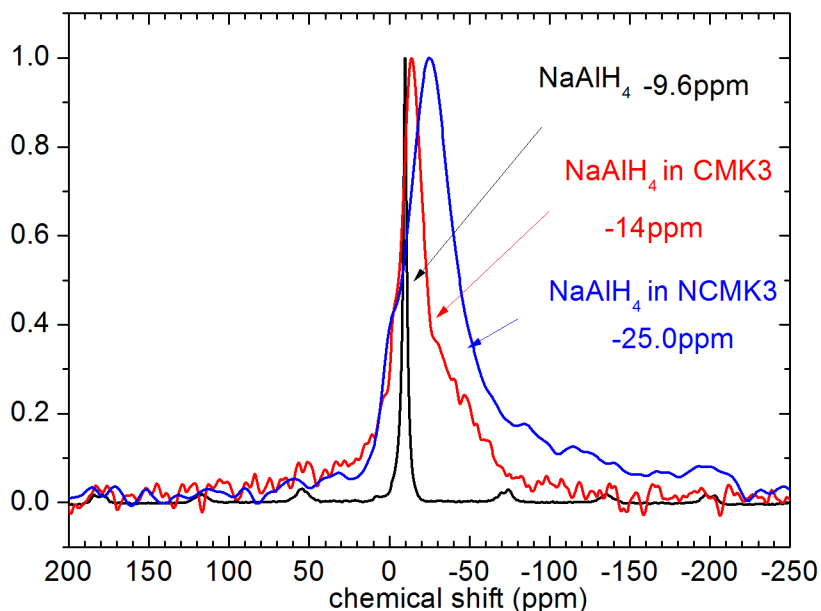


Figure S3. ^{23}Na 5 kHz MAS NMR spectra referenced to a 6 M NaCl solution showing measured chemical shifts for bulk NaAlH_4 , NaAlH_4 @CMK-3, and NaAlH_4 @NCMK-3 indicating NaAlH_4 remains intact after confinement in the carbon scaffolds. The position of the observed NaAlH_4 line is consistent with previous studies of the bulk hydride.⁵

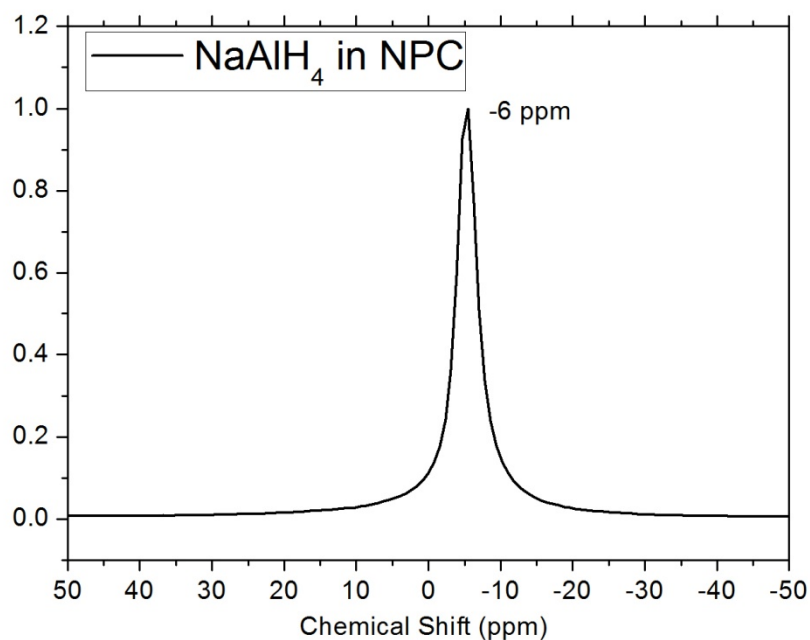


Figure S4. ^{23}Na 25 kHz MAS NMR spectra referenced to a 6 M NaCl solution at 156.022 MHz for NaAlH_4 @NPC. The observed NaAlH_4 line position is consistent with previous studies of bulk NaAlH_4 .⁵

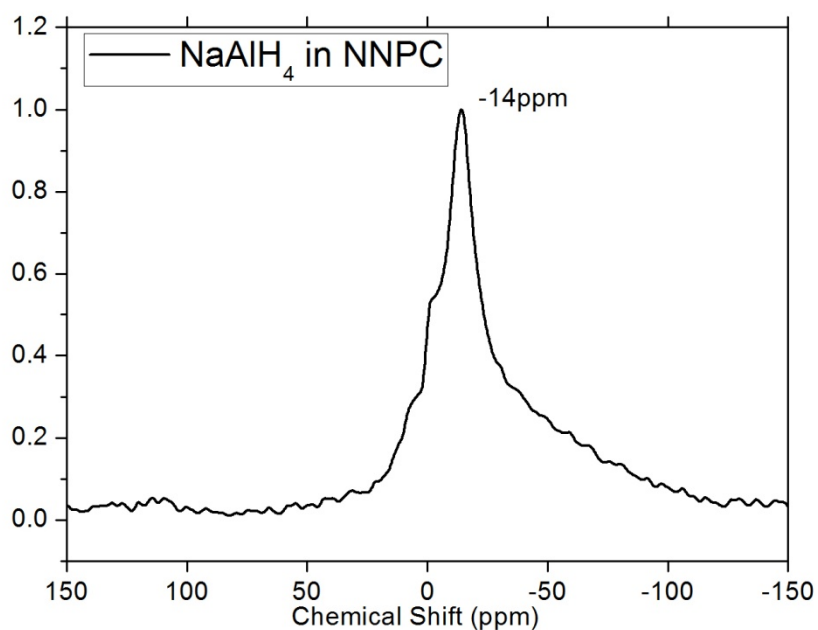


Figure S5. ^{23}Na 9 kHz MAS NMR spectra referenced to a 6 M NaCl solution at 79.27 MHz for NaAlH_4 in NNPC. The observed NaAlH_4 line position is consistent with previous studies of bulk NaAlH_4 .⁵

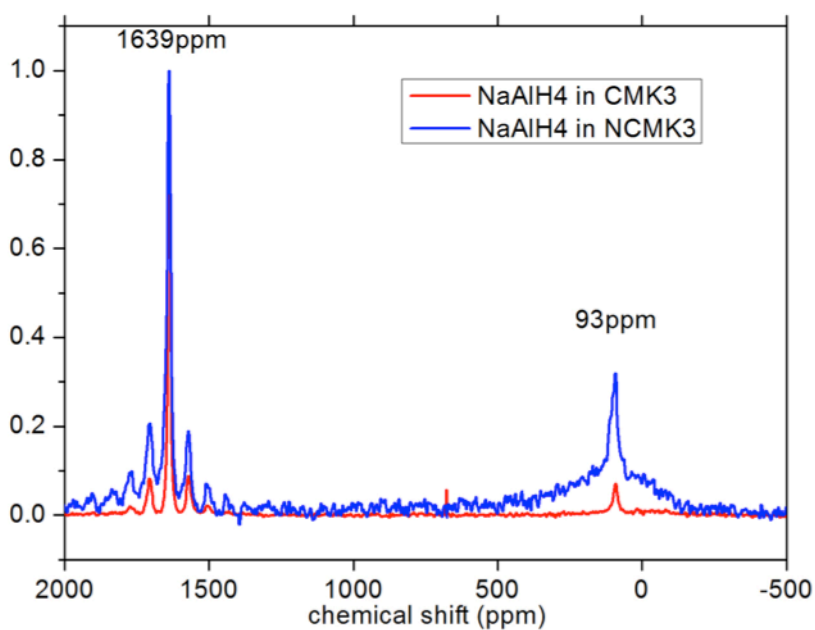


Figure S6. ^{27}Al 5 kHz MAS NMR referenced to 1 M $\text{Al}(\text{NO}_3)_3$ solution. NaAlH_4 -infiltrated carbon samples have one Al metal peak at 1639 ppm and a NaAlH_4 peak at 93 ppm.⁵

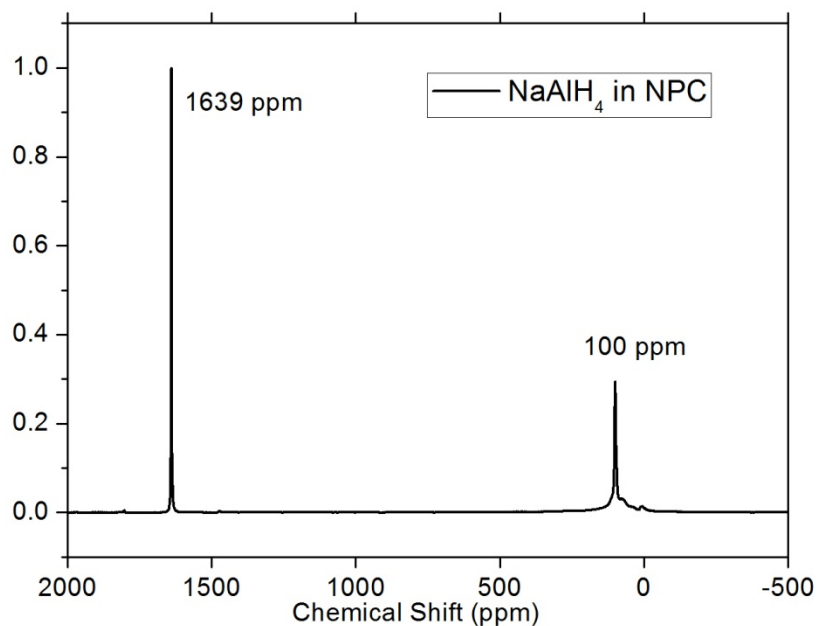


Figure S7. ^{27}Al 25 kHz MAS NMR referenced to 1 M $\text{Al}(\text{NO}_3)_3$ solution at 153.69 MHz for NaAlH_4 @NPC. There is one Al metal peak at 1639 ppm and one NaAlH_4 peak at 100 ppm.⁵

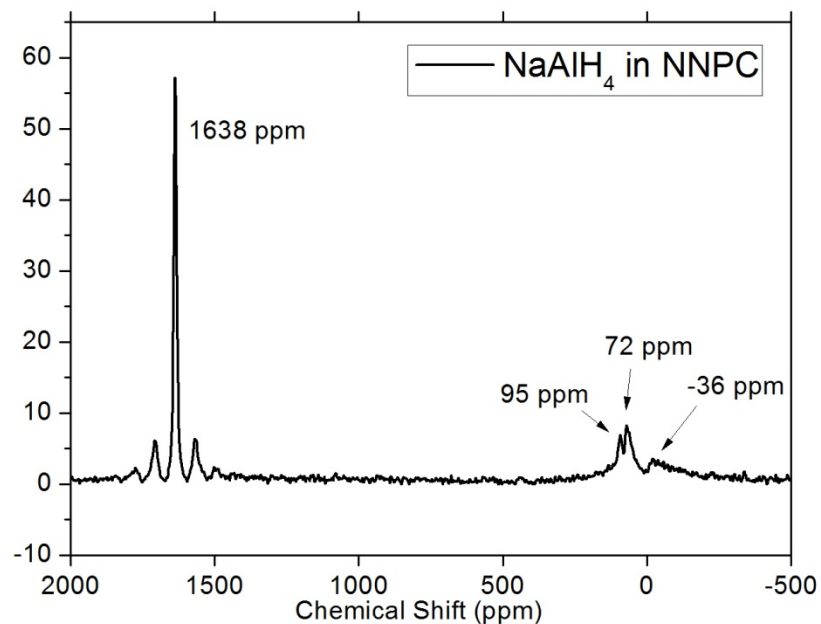


Figure S8. ^{27}Al 5 kHz MAS NMR referenced to 1 M $\text{Al}(\text{NO}_3)_3$ solution at 78.085 MHz. Although the samples are sealed in separate containers, some oxygen contamination is unavoidable given the surface areas and reactivity of the nanoparticle Al-containing phases. For this reason, peaks corresponding to Al_2O_3 are evident in the ^{27}Al spectra. There is still one Al metal peak at 1639 ppm and a NaAlH_4 peak at 95 ppm.⁵

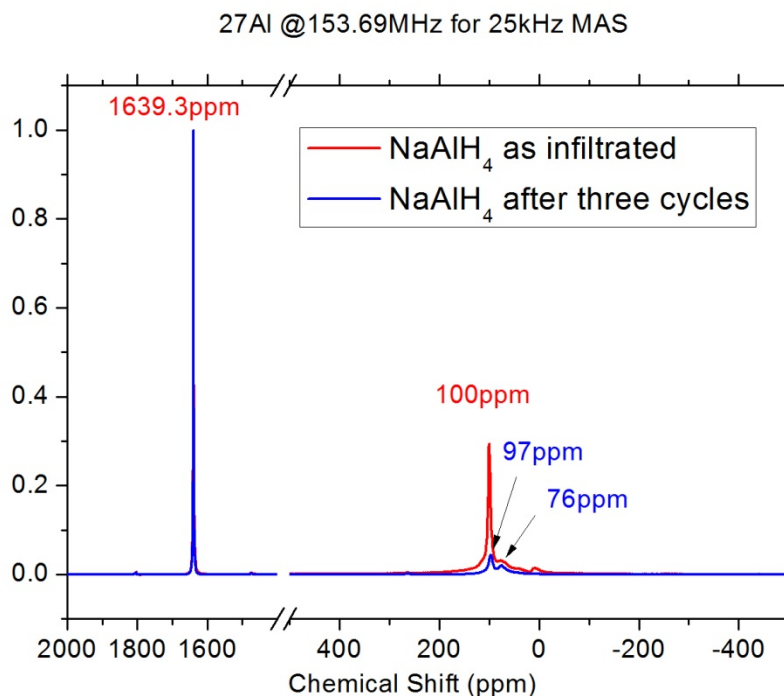


Figure S9. NaAlH_4 @NPC as infiltrated and after three cycles ^{27}Al 25 kHz MAS NMR. Reference 1M $\text{Al}(\text{NO}_3)_3$ solution at 153.69 MHz. There is one Al metal peak at 1639 ppm and a NaAlH_4 peak at 97 ppm after 3 cycles.⁵ Although the samples are sealed in separate containers, some oxygen contamination is unavoidable given the surface areas and reactivity of the nanoparticle Al-containing phases. For this reason, peaks corresponding to Al_2O_3 are evident in the ^{27}Al spectra.

References:

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