

## Characterization of Complex Metal Hydrides by High-Resolution Solid State NMR

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Insights on the compositions, chemical bonding, and structures of complex metal hydrides (i.e., alanates, borohydrides, and amides/imides) are being obtained via multinuclear nuclear magnetic resonance (NMR) studies. By implementing advanced solid-state NMR techniques such as Magic Angle Spinning (MAS), cross-polarization (CP) MAS, and multi-quantum (MQ) MAS; these NMR measurements can provide very detailed information on the complicated relationships amongst various processes accompanying the formation of hydride phases and their transformations, including reaction kinetics, reversibility, and the roles of catalysts. Because short range interactions dominate NMR parameters, highly disordered as well as amorphous materials can be more thoroughly evaluated via solid state NMR than is typically possible with x-ray or neutron diffraction studies since the latter usually require good crystallinity as well as sufficiently large domain sizes. Several examples are taken from our recent investigations on high-capacity hydrogen storage candidates to illustrate how these high-resolution NMR techniques can address and often resolve diverse issues on phase formation and decomposition processes. First, the behavior of Sc-doping on the phase compositions and reactivity of the sodium tetra- and hexa-alanates has been assessed from the <sup>45</sup>Sc, <sup>27</sup>Al, and <sup>23</sup>Na spectra following mechanical milling and hydrogen absorption/desorption treatments. Second, the formation and subsequent hydrogen desorption from several borohydride phases based upon Li, Mg, and Sc was investigated using <sup>11</sup>B MAS and CPMAS spectra that included clear evidence for the formation of highly stable intermediate “B<sub>n</sub>H<sub>m</sub>” species in their x-ray amorphous decomposition products that severely impact their ability to reform the initial borohydride phases. Finally, NMR was used to assess the reversibility of several combinations in the Li-Mg-Al-N-H system that independently validated proposed reactions that could not be confirmed by x-ray diffraction or other methods.