NMR studies of metal-hydrides: MgScHx

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Program Scope

Our research program focuses on in situ NMR studies of solid-state hydrogen storage systems. In particular, NMR measurements at the high temperatures and/or high pressures of the dehydriding and rehydriding reactions offer the best opportunity of detecting and identifying the mobile species that must be present, as well as the chemical intermediate species that are crucial to the reactions. For example, we expect to identify mobile H atoms in partially dehydrided NaAlH4. From high-field measurements on the nuclear spins of catalytically active species like Ti and Sc, we will determine the local environment of the catalyst atoms in terms of the neighboring nuclear spins, using spin-echo double resonance.

Recent Progress

(a) Kinetics of hydrogen atom hopping in Mg-Sc alloy hydride.

(Paper presentation by Mark Conradi)

Background: The research group of Notten at Philips has recently shown Mg-Sc metastable alloys to be effective systems for hydrogen storage and metal-hydride battery electrodes1-3. The motivation behind this alloy system is to capture desirable features of both end-members. At one end, MgH2 has a high hydrogen storage capacity of 8 wt%. However, the binding is of ionic character and this is believed to result in the very slow diffusion kinetics of H in MgH2. The equilibrium H2 pressure is on the low side at 1 atm at T = 278 C, but this is not a severe disability for electrochemical applications. At the other end is ScH2 with approximately 4 wt% storage but the superior diffusion kinetics typical of interstitial metallic hydrides. The H2 equilibrium pressure of the two-phase plateau region is very low at 1 Torr at 740 C.

The Mg-Sc alloy hydrides take on the fluorite structure3, as does ScH2, for Mg fractions ≤ 80%. At higher Mg fractions the structure is rutile-like as for MgH2 and it appears the charging kinetics suffer markedly as a result. The alloys show high storage capacity of 6.7 wt%, in approximate agreement with the simplistic (local) view that each Mg supports 2H and each Sc supports 3H; here the expanded lattice is believed to allow the additional H on Sc beyond the usual ScH2. Mg-Ti alloys have similar behavior to Mg-Sc, but should be much less costly4. However, even in thin films for electrochemical applications, the charge/discharge kinetics of MgScHx are slower than one would like. The kinetic bottleneck may be slow diffusion of H through the alloy or slow kinetics at the electrode surface (despite use of a Pd overlayer).

While gearing-up for in situ studies of complex hydrides, we have measured and report here the temperature dependence of the H hopping rate \( \omega_H \) in MgScHx as determined by NMR relaxation times.

Methods: Bulk Mg65Sc35Pd2.4 was synthesized by WPK at TUE and loaded with H2 to \( x = [H]/[M] = 2.2 \) from the gas phase. Samples were loaded into glass NMR tubes under 0.9 atm of N2 and sealed at a neck with a flame. RF field penetration into the powdered metallic sample was
judged to be good from measurements of rf pulse lengths for $\pi/2$ and $\pi$ nutations, compared to a water reference sample.

Relaxation times were measured with a homebuilt pulsed, superheterodyne NMR spectrometer with 4 transmitter phases and quadrature-detected receiver. The transmitter power to the probe was about 80 W. Pulse sequences were generated with a combination of TTL hardware and a Pulse Blaster card. The NMR acquisition and analysis software was written locally. $T_1$ was determined with inversion-recovery and repeated-saturation-recovery schemes. $T_2$ was measured from the decays of free-induction signals ($T_2^*$), two-pulse (Hahn) echoes, and CPMG echo trains. Continuous (not chopped) spin-locking with $\gamma B_1/2\pi = 50$ kHz was used to measure $T_{1\rho}$. The relaxation of the dipolar-ordered state ($T_{1D}$, essentially $T_{1\rho}$ in zero amplitude field) was measured using a phase-alternated version of the Jeener-Broekaert three-pulse method.

**Results:** The relaxation times for Mg$_{65}$Sc$_{35}$Pd$_{2.4}$H$_{220}$ are presented as a function of reciprocal temperature in the figure below. The data can be understood by realizing that $T_2$ begins to increase (motional averaging) when the H atomic hopping rate $\omega_H$ is about $10^5$ s$^{-1}$. The $T_{1\rho}$ minimum corresponds to $\omega_H = 5 \times 10^5$ s$^{-1}$, and a $T_1$ minimum at 21 MHz would reflect $\omega_H = 2 \times 10^8$ s$^{-1}$, but evidently the available temperature range is too low to reach such a fast rate of H motion. One sample was heated to 300 C for about one hour and suffered irreversible changes (e.g., $T_1$ was different upon returning to 25 C). The time $T_{1D}$ is, to within a factor of two, equal to the mean hopping time, $1/\omega_H$, a strong-collision result.
For comparison, similar data for LaNi$_5$H$_{6.8}$ are presented in the above figure. This material was synthesized at JPL and hydrided at WU by MPM. Comparing the figures, it is obvious that specific features such as the $T_{1p}$ minimum occur at much higher temperatures in MgScH$_x$ than in LaNi$_5$H$_{6.8}$. Thus, at a given temperature the H motion in MgScH$_x$ is much slower (by factor of ~3000) than in LaNi$_5$H$_{6.8}$. This demonstrates that slow internal kinetics are a substantial reason for the slow kinetics of MgSc film electrodes.

The relaxation map of the lower figure shows the log of $\omega_H$ as a function of reciprocal temperature for both materials. The data points are from a $T_1$ minimum, $T_{1p}$ minima, and the onset of line narrowing (lengthening of $T_2$). In each case, the attempt frequency $\omega_a$ is approximated as $10^{13}$ s$^{-1}$, corresponding to $1/T=0$, providing an additional point on each line. The straight line fits correspond to $\omega_H = \omega_a \exp{(-\Delta E/kT)}$; the activation energies $\Delta E/k$ are 6000 K and 3500 K for MgScH$_x$ and LaNi$_5$H$_{6.8}$, respectively. This approach is more reliable than obtaining activation energies from the temperature dependence of one relaxation time (e.g., $T_1$ or $T_{1p}$) in cases with broad distributions of hopping rates at a fixed temperature (particularly true of LaNi$_5$H$_{6.8}$).
Future Plans

The study of new interstitial metallic alloys will be extended to Mg-Ti, because Ti is so much less costly than Sc. Only a small quantity of Mg-Ti is expected to be available, requiring measurement in a microcoil at high field strength. The H kinetics in Mg-Sc hydride will also be studied as a function of the Mg:Sc ratio, to test the view that the rutile-fluorite structural transition controls the H hopping rate. When MgScDx is available, deuterium magic-angle spinning NMR will be used to try to resolve distinct resonance lines for distinct hydrogenic sites.

References


Publications