
In Situ NMR Studies of Hydrogen Storage Systems

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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

(b) *In Situ* NMR Studies

Background: The new classes of hydrogen-storing solids, such as sodium alanate, lithium borohydride, and the imides and amides, represent fundamental departures from the interstitial metallic hydrides that were formerly the focus of hydrogen storage interest. As light interstitials, the H atoms in metals typically display high diffusivity¹. In the new materials, the H diffusivity is quite low, at least in the pure, unreacted materials. Furthermore, recharging of the spent material (e.g., by addition of H₂ gas to the Al and NaH from dehydriding of NaAlH₄) must involve mobility of the metallic species (Na, Al) as well. Despite intensive study, the mechanistic details of the dehydriding and rehydriding reactions are not known. For NaAlH₄, the role of catalyst species is not understood.

Our project addresses these open questions by NMR studies at the conditions of the reactions, as distinct from NMR at ambient conditions on materials recovered from reaction in a separate vessel. *In situ* measurements will identify the mobile species present, which clearly have an important role in the chemistry, as well as reactive chemical intermediates. These *in situ* measurements involve temperatures to 300 C and pressures to 100 atm, depending on the system under study.

Results: The overall design approach of such an NMR apparatus has been reported² and a version for pressures to 55 atm constructed and tested. While it seems unlikely that anyone would want to construct an exact copy of the device, the ideas and strategies should be relevant to other *in situ* NMR and neutron scattering efforts. Thus, we present here the basic components of our design. The complete design appears as Figure 1.

The powdered NMR sample is held in a ceramic (or glass) tube, with an rf coil on its outside. The ceramic tube is 30 cm long with a closed bottom; it is heated near its bottom 8 cm by a resistive, non-inductive heater assembly. Thus, the top (open) end of the ceramic sample tube remains cold, so that an O-ring fitting can connect it to external gas plumbing. This plumbing allows H₂ gas to be removed or added during the NMR measurements, yielding true *in situ* capability.

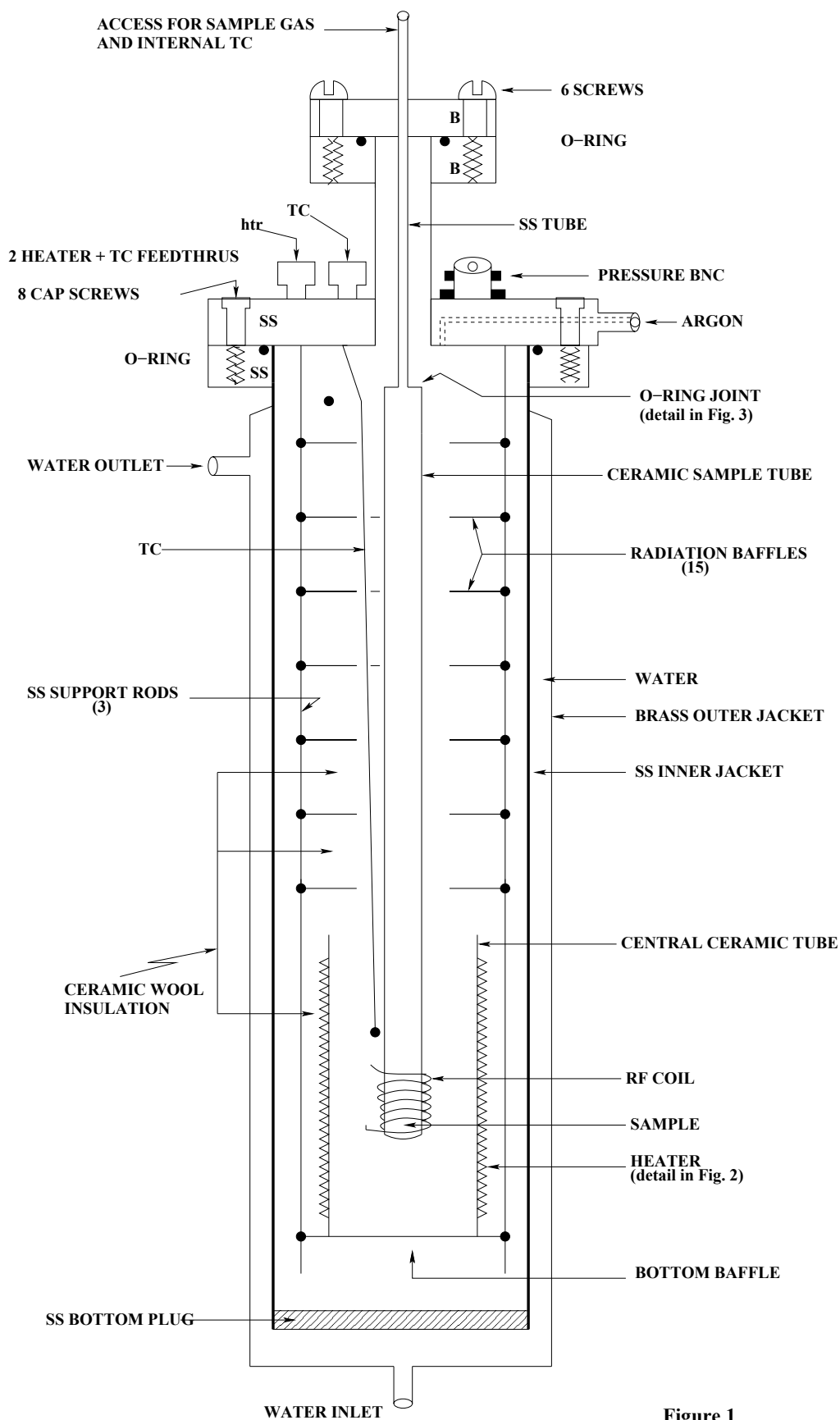


Figure 1

The ceramic tube has no particular strength and would rupture at the high pressures. Thus, argon gas surrounding the sample vessel is always maintained at a higher pressure than that inside the vessel, making use of the tube's strength under compressive forces.

The inner wall of the water cooling jacket is stainless steel and holds the argon gas pressure. The larger diameter of this tube and the larger volume of compressed gas (compared to pressurizing only the sample vessel) make this tube a crucial element of the design in terms of safety against rupture. Since this tube remains cold, its strength does not decrease as the sample temperature is increased.

The rf coil is tuned and coupled to appear as 50 ohms resistive with tuning capacitors in a shielded box on top of the apparatus. The design has been used at 21 and 53 MHz in a Varian iron-core electromagnet. Modifications for use in a superconducting solenoid have been thoroughly discussed.²

To eliminate the effects of the residual magnetic field from the nominally non-inductive heater winding, the current to the heater is disabled by a relay during NMR data acquisition. The effect upon temperature regulation (Omega temperature controller with thermocouple input and on-off output) is negligible.

Future Plans

The first system to be studied will be NaAlH_4 , because of its central role in the development of non-metallic hydrides. We will look for mobile H species; their signals should stand-out from the signals of NaAlH_4 , Na_3AlH_6 , and NaH because the mobile species will have long T_2 (and thus be the only signal remaining at long times). A sample of Sc-catalyzed NaAlH_4 will be studied by MAS-NMR to identify the chemical species of Sc present (e.g., Sc metal, Sc-Al alloy or compound, or ionic Sc as in ScCl_3). While catalysis by Sc is relatively new, the properties of its nucleus are much more favorable for NMR than is Ti (e.g., ^{45}Sc is 100% abundant while ^{47}Ti and ^{49}Ti have 8 and 5% abundances each, very large electric quadrupole moments, and small magnetogyric ratios).

In parallel with the hydrogen studies in the existing high-T, high-P apparatus, a student will build a second version for the high-field magnet (8.4 T). This device will be useful for examining metal nuclear spins, such as ^{29}Al , ^{23}Na , and ^7Li . Its first use will be to detect and identify mobile Al and Na species in the recharging of NaAlH_4 from the fully or partially dehydrided state.

References

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