

Hydrogen storage: The major technological barrier to the development of hydrogen fuel cell cars

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Abstract

In this paper, we review the current technology for the storage of hydrogen on board a fuel cell-propelled vehicle. Having outlined the technical specifications necessary to match the performance of hydrocarbon fuel, we first outline the inherent difficulties with gas pressure and liquid hydrogen storage. We then outline the history of transition metal hydride storage, leading to the development of metal hydride batteries. A viable system, however, must involve lighter elements and be vacuum-tight. The first new system to get serious consideration is titanium-activated sodium alanate, followed by the lithium amide and borohydride systems that potentially overcome several of the disadvantages of alanates. Borohydrides can alternatively produce hydrogen by reaction with water in the presence of a catalyst but the product would have to be recycled via a chemical plant. Finally various possible ways of making magnesium hydride decompose and reform more readily are discussed. The alternative to lighter hydrides is the development of physisorption of molecular hydrogen on high surface area materials such as carbons, metal oxide frameworks, zeolites. Here the problem is that the surface binding energy is too low to work at anything above liquid nitrogen temperature. Recent investigations of the interaction mechanism are discussed which show that systems with stronger interactions will inevitably require a surface interaction that increases the molecular hydrogen–hydrogen distance.

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1. Introduction

Both from the point of view of global warming and from that of the inevitable exhaustion of Earth's oil reserves, it has become highly desirable to develop an alternative energy source for automobiles. Since the development of the proton exchange membrane (PEM) fuel cell, which is fuelled by hydrogen and oxygen (air) and produces only water, hydrogen has generally been seen to be the most promising approach (see accompanying article in this issue). However, although the development of fuel cell technology appears to be progressing smoothly towards eventual commercial exploitation, a viable method for storing hydrogen on board a vehicle is still to be established. The US Department of Energy (DoE) has taken what is perhaps an extreme view of what the

technology needs to deliver. By rejecting taxation as a means of persuading the public to change their fuel, the DoE starts from the position that the hydrogen-fuelled vehicle must be able to match the performance of a hydrocarbon-fuelled car and must do so at a comparable cost (based on the costs of oil in the recent past). This has led them to establish a series of targets which, given the remarkable advantages of petrol and diesel for this purpose, will be very tough to meet [1]

- gravimetric energy density: 2 kWh/kg,
- volumetric energy density: 1.5 kWh/l,
- H₂ storage capacity (mass fraction) of 6 wt% (on a system basis),
- operating temperature: –30 to +50 °C,
- re-fuelling time < 5 min,
- re-fuelling rate: 1.5 kg H₂/min,
- recoverable amount of hydrogen: 90%,

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- cycle life: 500 times (requirements for the physical properties of storage material),
- cost target: US\$5/kWh (storage material only, without peripheral components).

From our present point of view, the most significant of these targets are that (1) the fuel tank system when charged should contain 6% gravimetric hydrogen density; and (2) the system should be capable of being recharged at the filling station in less than 5 min. In addition, (3), the hydrogen should be available at the inlet of the fuel cell at a pressure of a few bar without it being necessary to heat the store to a temperature of more than 50 °C. If (2) cannot be met, we could consider using replaceable fuel tanks that can be recharged off-line at the fuel station. If one goes this way, one could also consider the use of chemical hydrides that will liberate hydrogen on the addition of water [1,2] but here the product would have to be sent back to a factory to be recycled.

Four different methods of hydrogen storage are currently being considered, namely liquid hydrogen, high-pressure hydrogen, solid-state hydride storage (including chemical hydrides) and porous solid adsorption of molecular hydrogen. The first two methods have reached the engineering prototype stage while for the last two methods, there is still much to be done in selecting the optimum system for further development. This paper will concentrate on the present status of these last two approaches. Before doing that, however, we should discuss the disadvantages of the first two methods, given that they have actually been demonstrated to work.

2. Liquid and high-pressure hydrogen storage

Liquid hydrogen can be stored on board the vehicle, as has been demonstrated by BMW who have produced a limited series of cars fuelled in this way [3]. In this case, most of the hydrogen is supplied to a conventional internal combustion engine (ICE) with some going to a fuel cell which provides the electrical power for air conditioning etc. This approach yields a gravimetric storage density of 100% H₂. However, if you include the mass of the tank, this is reduced to about 10% gravimetric H₂. Moreover, it has two major disadvantages: (1) there is inevitably a boil-off rate which is currently ~1%/day; (2) there is an inevitable energy loss due to the refrigeration process which amounts to 30% of the energy available from burning the hydrogen, even in the largest plant size [4].

The second approach is to store the hydrogen at high pressures. A conventional steel hydrogen cylinder achieves about 1% gravimetric hydrogen. Recent developments of fibre-reinforced resin have reached pressures of 700 bar, corresponding to about half the density of liquid hydrogen. The CUTE hydrogen-fuelled buses [5], as have been operating recently in London, actually use conventional steel hydrogen cylinders (150 bars). However, while we are all happy to have buses driving round with high-pressure

hydrogen cylinders on board—after all, gas suppliers are doing this all the time using properly designed lorries—there are some anxieties about letting the general public loose with the really high-pressure cylinders that are now being developed.

3. Metal hydride stores

Turning to metal hydride stores, here the hydrogen splits into atoms at the surface of the metal and then enters the metallic lattice in the atomic form, diffuses through the metal, jumping between interstitial sites; and finally forms a hydride phase with a more or less ordered hydrogen sublattice. If the (inter) metallic lattice contains d or f electron states at the Fermi surface, the hydrogen s electron can be partly donated to the conduction band and the bare proton, screened electrostatically by electrons at the Fermi surface, can move relatively freely through the lattice. Most binary or intermetallic hydrides are either very stable or very unstable but a number do show an equilibrium hydrogen pressure at room temperature of about 1 bar. The prime example of such a system (apart from palladium, which is rather too expensive!) is lanthanum nickel hydride (LaNi₅H₆). This system was first investigated by Buschow and Miedema at Philips in Eindhoven [6] and subsequently, its use in rechargeable metal hydride batteries operated in KOH was demonstrated by Notten [7]. LaNi₅/H is not itself a practical system for a battery as the lattice tends to fragment after a few hydrogenation cycles but, in the following years, a series of AB₅ compounds based on this system were developed, mainly in Japan [8]. Batteries made from these compounds (called nickel—metal-hydride (NiMH) batteries) have largely replaced Ni—Cd rechargeable batteries. Indeed, in China, which has large deposits of rare earths, bicycles with electric motors powered by metal hydride batteries are in mass production [9]. However, batteries on their own have to be recharged by plugging into the mains electricity overnight (and AB₅ compounds can only provide about 1% hydrogen by mass) so, while they have a role for powering bicycles, they do not seem capable of providing a long-term substitute for petrol or diesel fuel.

The hunt is therefore on to find lighter metal lattices that will work as well as these AB₅ materials while satisfying the gravimetric storage requirement. However, there are a number of major problems that will have to be dealt with. First, the protonic transport system that works for the transition metal hydrides (where the metal atom effectively changes valency as the hydrogen is added) is not available where the bonding is either ionic (H⁻) or covalent; because here the chemical reaction involves the transfer of integral numbers of electrons. Hence the addition of hydrogen must involve the complete geometric rearrangement of the lattice. This inevitably results in much smaller diffusion coefficients for hydrogen in the solid phase and hence a practical system has to involve nanoscale materials with large surface areas. Secondly, most potential systems are

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