Comment

What is old is new again

Drew A. Sheppard*, **Terry D. Humphries,**
Craig E. Buckley
Fuels & Energy Technology Institute |Hydrogen Storage Research Group| Department of Imaging & Applied Physics, Curtin University, Australia
d.sheppard@curtin.edu.au

Fluorine stabilized metal hydrides for high-temperature thermal storage

The most efficient way to use sunlight for base-load power generation is via concentrating solar power (CSP) [1]. Advanced CSP plants can supply base-load power generation by storing solar energy as heat that can be used to generate electricity during the night-time. However, as with many clean energy technologies, economic constraints influence how well energy storage can spread through the emerging market for commercial-scale solar power. Molten nitrate salts are the first generation of heat storage materials but they have a number of drawbacks: low heat storage capacity, large volumes, high costs and an operating temperature that is limited to 565°C [2]. Metal hydrides are a class of thermochemical heat storage materials that are 5–30 times more energy dense than molten salts and have the potential to reduce the heat storage costs of next generation CSP [1,3].

The term ''metal hydrides'' incorporates thousands of metals, alloys and complex compounds that can reversibly react with gaseous hydrogen [4]. They absorb heat to release hydrogen (endothermic) and release heat (exothermic) when they absorb hydrogen gas. This property can be exploited to release and store heat on-demand. Since the early 1990s, the development of low-cost magnesium hydride (MgH_2) [5–7] and Mg-based hydrides (such Mg_2FeH_6) [8–13] with rapid hydrogen absorption/desorption kinetics has led to interest in combining CSP with high-temperature metal hydrides for storing solar energy as heat but are limited to operating temperatures below ~500°C due to the high hydrogen pressures they generate. However, the US Department of Energy Sunshot program [14] has set targets for the next generation of CSP to operate at temperatures of between 600 and 800°C and there are relatively few low-cost metal hydrides that can operate in this temperature range (TiH_x is one high-cost example).

Research at Curtin University is addressing this ''gap'' by applying an ''old idea'' to increase the operating temperature and stability of metal hydrides for thermal storage in next-generation CSP: fluorine for hydrogen substitution. The comparable ionic size of the hydride and fluoride ions and the structural similarity of their compounds were recognized before the 1960s [15]. Maeland and Lahar [16] used this analogy to synthesise new ternary metal hydrides based on known fluoride structures and, in the process, illustrated evidence for solid solution behaviour in the ternary hydride – fluoride systems. In the context of heat storage in metal hydrides, this partial substitution of hydrogen for fluorine has a number of economic advantages: (1) Metal fluorides are more stable than their hydride equivalents, a property that can be exploited to increase the thermal stability, operating temperature and efficiency of electricity generated from metal hydrides partially substituted for fluorine [15]; (2) the increased thermal stability of the fluorine substituted hydride means less H_2 is needed to generate the same amount of heat. With less H_2 in the system, the cost to store this H_2 (until it is needed to generate heat) is reduced; and (3) the raw material cost of the high temperature metal hydride is reduced[17] as metal fluorides are cheaper than the metal hydrides they partially replace.

Curtin University has recently applied this approach to compare the properties of $NaMgH_2F$ and its pure hydride equivalent, $NaMgH_3$ [17,18]. For example, $NaMgH_2F$ requires 545°C to release hydrogen at a pressure of 10 bar compared to a temperature of 493°C required by $NaMgH_3$. Though $NaMgH_2F$ has a lower heat storage capacity compared to other Mg-based hydrides, its higher operating temperature and thermal stability results in a lower system installed cost [17,19]. Even without optimisation of the engineering design, initial techno-economic assessments of $NaMgH_2F$ for thermal storage estimate an installed system cost of US$30–US$60/kWh_{th}: comparable with the estimates of molten salt technology (US$30–US$80/KWh_{th}) [20,21].

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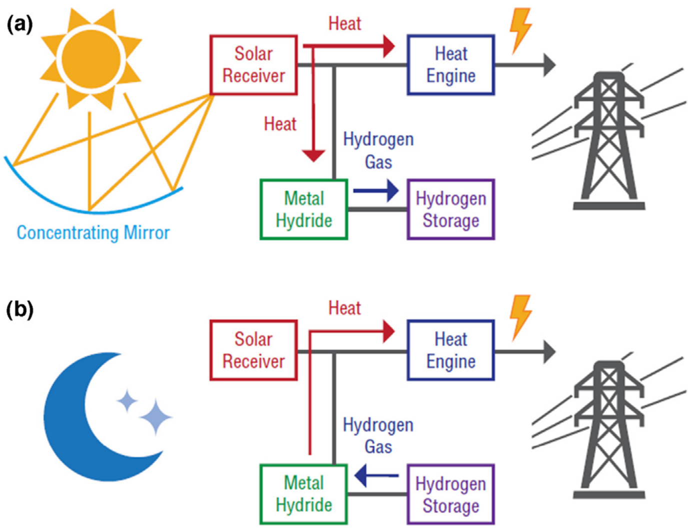

A schematic of the concentrating solar thermal system coupled with metal hydrides as a thermal storage medium during (a) daytime and (b) nighttime operations.

With several hundred known ternary and quaternary fluorides containing low-cost alkali or alkaline earth metals there are numerous synthesis targets for low-cost mixed hydride-fluorides compounds with the potential to operate at temperatures of 600°C and above. The mutual solubility between hydride and fluoride analogues means that properties, such as operating temperature and thermal stability, can be tuned by the choice of hydrogen to fluorine ratio.

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