

## Hydride Chemistry in Nanoporous Scaffolds

John J. Vajo<sup>a</sup>, Adam F. Gross<sup>a</sup>, Robert D. Stephens<sup>b</sup>,  
Tina T. Salguero<sup>a</sup>, Sky. L. Van Atta<sup>a</sup>, Ping Liu<sup>a</sup>

<sup>a</sup>*HRL Laboratories, LLC, Malibu, California, USA*

<sup>b</sup>*General Motors Research and Development Center, Warren, Michigan, USA*

Light element and complex anion hydrides (such as LiH, MgH<sub>2</sub>, NaAlH<sub>4</sub>, and LiBH<sub>4</sub>) are attractive for fuel cell-based transportation applications because they have high gravimetric and volumetric capacities. However, the thermodynamic properties of these materials, which determine the operating temperatures, are often not compatible with proton exchange membrane (PEM) fuel cells. In many cases, the thermodynamic stability and, consequently, the temperatures for hydrogen delivery are too high. We have addressed this problem by combining stable hydrides with additional elements or compounds to form destabilized chemical systems that have much lower operating temperatures; examples include LiH/Si and LiBH<sub>4</sub>/MgH<sub>2</sub>. The additives are chosen such that new compounds or alloys are formed during dehydrogenation. The stability of these new phases lowers the enthalpy for dehydrogenation, thereby lowering the operating temperature. In this talk we will briefly describe our efforts using this approach.

In addition to issues associated with thermodynamic properties, the *rates* at which hydrogen absorbs into and desorbs from light metal and complex hydrides are typically much too slow at PEM fuel cell temperatures. The slow rates originate, at least in part, from the high activation energies for hydrogen diffusion associated with the ionic and covalent bonds found in these hydrides. Small quantities of catalytic additives have been shown to greatly improve the rates of hydrogen exchange in MgH<sub>2</sub> and NaAlH<sub>4</sub>. We have explored another approach in which hydride materials are incorporated into nanoporous scaffolds. The pores of the scaffold limit the crystallite sizes of the hydride and thus the diffusion lengths to nanoscale dimensions. The limitation of diffusion lengths reduces overall diffusion times and increases overall rates of hydrogen exchange. The limited crystallite sizes also increase the interfacial area between reacting phases, which improves hydrogen capacity retention during cycling. This talk will focus on the hydrogenation and dehydrogenation chemistry of hydrides such as LiBH<sub>4</sub>, MgH<sub>2</sub> and NaAlH<sub>4</sub> incorporated into nanoporous carbon aerogels.