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Oxidation State and Local Structure of Ti-Based Additives in the Reactive Hydride Composite 2LiBH₄ + MgH₂

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Nowadays, the technological utilization of reactive hydride composites (RHC) as hydrogen storage materials is limited by their reaction kinetics. However, addition of transition-metal-based additives, for instance titanium isopropoxide (Ti-iso), to the 2LiBH₄+MgH₂ system, results in a significant improvement of sorption kinetics. In this work, the evolution of chemical state and local structure of the Ti-based additive has been investigated by means of X-ray absorption (XAS) and photoemission (XPS) spectroscopy. X-ray absorption near-edge structure (XANES) as well as extended X-ray absorption fine structure (EXAFS) analysis have been undertaken at the Ti K-edge. The measurements reveal the formation of a highly dispersed and disordered TiO₂-like phase during ball milling. During first desorption reduced titanium oxide and titanium boride are formed and remain stable upon cycling. The surface analysis performed by XPS shows that the reduction processes of the Ti-based additive during first desorption is coupled to the migration of the Ti species from the surface to the bulk of the material. Several factors, related to favoring heterogeneous nucleation of MgB₂ and the increase of interfacial area through grain refinement are proposed as potential driving force, among other effects, for the observed kinetic improvement.

A comparative study of the role of additive in the MgH₂ vs. the LiBH₄–MgH₂ hydrogen storage system

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ABSTRACT

The objective of the present work is the comparative study of the behaviour of the Nb- and Ti-based additives in the MgH₂ single hydride and the MgH₂ + 2LiBH₄ reactive hydride composite. The selected additives have been previously demonstrated to significantly improve the sorption reaction kinetics in the corresponding materials. X-Ray Diffraction (XRD), X-Ray Absorption Spectroscopy (XAS), X-Ray Photoelectron Spectroscopy (XPS) and Electron Microscopy (TEM) analysis were carried out for the milled and cycled samples in absence or presence of the additives. It has been shown that although the evolution of the oxidation state for both Nb- and Ti-species are similar in both systems, the Nb additive is performing its activity at the surface while the Ti active species migrate to the bulk. The Nb-based additive is forming pathways that facilitate the diffusion of hydrogen through the diffusion barriers both in desorption and absorption. For the Ti-based additive in the reactive hydride composite, the active species are working in the bulk, enhancing the heterogeneous nucleation of MgB₂ phases during desorption and producing a distinct grain refinement that favours both sorption kinetics. The results are discussed in regards to possible kinetic models for both systems.

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1. Introduction

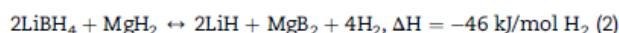
Light metal hydrides are the favoured materials for solid hydrogen storage applications. In particular magnesium hydride is a good candidate with a theoretical gravimetric storage capacity of 7.6%. Its limitation for practical application lies mainly in the slow hydrogen sorption kinetics and in the high thermodynamic stability of its hydride [1]. The reversible reaction for hydrogen storage occurs according to following reaction:



Major progress toward technical application has been achieved by using magnesium hydride in nanocrystalline form obtained by mechanical milling [2] and by using

transition-metal oxides during the milling process as additives [3–6]. This has led to big improvements in the hydrogen sorption kinetics. In particular, Nb₂O₅ has been shown to behave as one of the best additives [5–8] at the present time.

More recently, Vajo et al. [9,10] and Barkhordarian et al. [11,12] introduced the concept of reactive hydride composite (RHC) combining MgH₂ and borohydrides. As a representative example the reversible system with LiBH₄ operates according to the following reaction:



In this system the chemical reaction between the two hydrides lowers the overall reaction enthalpy while the gravimetric hydrogen storage capacity remains high (10.5 wt%).

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