Institute Interest Seminar Series, I2CNER
September 7, 2016

Advanced Amide/Hydride Composites for Hydrogen Storage

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Mission of the hydrogen storage division: Research and develop new carrier materials for mobile and stationary hydrogen storage as well as for hydrogen delivery.

The amide-based composite system is one of the most promising candidates for hydrogen storage because they include a stable FCC sub-lattice of N which is capable of retaining its structural symmetries upon hydrogen sorption/desorption. Moreover, hydrogen storage capacity is well above 5 wt%[1]. However, there are still some drawbacks to be solved: a) temperatures for dehydrogenation above 200^{o}C, b) emission of NH_3during dehydrogenation, c) sluggish hydrogen absorption/desorption kinetics. Recently, we focus on improving all of above mentioned hydrogen storage properties of amide-based composite using two strategies: forming three-component Li-Mg-N-H composites, and doping with Ce-based catalysts.

We previously reported a three-component $Mg(NH_2)_2$-$LiNH_2$-4LiH composite which reversibly stores hydrogen exceeding 5 wt% at temperature as low as 150^{o}C[2]. To further improve the hydrogen storage kinetics, thermodynamics and cycling properties, a number of additives such as CeF_4, CeO_2, $TiCl_3$, TiH_2, NaH, KBH_4 and KH are doped to the $Mg(NH_2)_2$-$LiNH_2$-4LiH composite by ball milling. Addition of 3wt% of KH reduces the dehydrogenation onset temperature of the $Mg(NH_2)_2$-$LiNH_2$-4LiH composite to below 90^{o}C without emission of NH_3 during the whole dehydrogenation process. Moreover, dehydrogenation kinetics and cycling ability are remarkably enhanced upon KH-addition. Reaction model is altered upon KH-addition with active molecule density improved by about 200 times. Last but not least, by optimization of the ratio of Mg^{2+} to Li^+ in the $Mg(NH_2)_2$-$LiNH_2$-LiH system, several novel composites with hydrogen storage capacity >6 wt% without emission of NH_3below 250 ^{o}C are developed[3].

Doping is an efficient strategy to improve hydrogen storage property of materials. We recently studied the effect of Ce-based additives, including Ce, CeO_2, CeF_3 and CeF_4, on hydrogen storage property of amide/hydride composites. Emission of NH_3 from the $LiNH_2$-LiH composite during hydrogen desorption is completely suppressed with addition of any of the Ce-based additives investigated. CeF_4 remarkably enhanced the dehydrogenation kinetics by ~3 times. More importantly, even after repeats of cycling at 150^{o}C, NH_3 emission from CeF_4-doped $LiNH_2$-LiH composite is completely suppressed. It is found that 1 wt% of CeF_4 is enough to efficiently suppress the emission of NH_3 from amide/hydride composites. XRD, Raman and XPS experiments indicate that the F-containing CeF_x species formed during reaction takes an important role in suppression of NH_3 formation and enhancement of kinetics.

References:

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