Reaction Pathways in the Reactive Composite Mg(NH\(_2\))\(_2\) + LiH

DENIZ CAKIR, University of Twente, GILLES A. DE WIJS, Radboud University Nijmegen, GEERT BROCKS — Chen et al [1] reported reversible hydrogen storage in a mixture of LiH + LiNH\(_2\) with a storage capacity of 6.5 wt %. However, this system requires an operating temperature in excess of 250 °C to achieve a hydrogen pressure of 1 bar. Several efforts including cation substitution have been considered in order to improve the operating conditions, which is necessary for onboard applications. For instance, replacing LiH with MgH\(_2\) markedly reduces the operating temperature through the reaction MgH\(_2\) + 2LiNH\(_2\) → Li\(_2\)Mg(NH)\(_2\)+ 2H\(_2\) ↔ Mg(NH\(_2\))\(_2\) + 2LiH. Recent experimental results however indicate that the latter is not a simple one-step reaction and full hydrogenation of Li\(_2\)Mg(NH)\(_2\) occurs in a two-step sequence via an intermediate Li\(_2\)Mg(NH)\(_2\)\(_3\) [2]. In this work we examine the stability and structure of possible intermediates compounds, namely Li\(_{2-2x}\)Mg\(_x\)NH, Li\(_{1-2x}\)Mg\(_x\)NH\(_2\), and Li\(_{2-x}\)Mg(NH)\(_2-x\)(NH\(_2\))\(_x\), by means of first-principles DFT calculations. All intermediate compounds are thermodynamically stable with respect to the elements. The hydrogenation reaction of Li\(_2\)Mg(NH)\(_2\) via the intermediate imides Li\(_{2-2x}\)Mg\(_x\)NH is energetically favorable compared to other intermediates.