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Effects of point defects and impurities on kinetics in hydrogen storage materials[1]

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First-principles calculations are playing an important role in developing a fundamental understanding of the physics and chemistry of hydrogen storage materials. In order to accurately describe the mechanisms of hydrogen uptake and release that are at the core of the hydrogen storage process, it is necessary to consider the addition or removal of individual hydrogen atoms. We have performed supercell calculations to model addition or removal of hydrogen, corresponding to the formation of hydrogen interstitials or vacancies. While the concepts discussed here are general, they will be illustrated with detailed results for sodium alanate, a viable hydrogen storage material. The calculations are based on density functional theory in the generalized gradient approximation, using the projector-augmented-wave approach. We find that hydrogen-related point defects are the dominant defect species involved in (de)hydrogenation of sodium alanate. These defects are positively or negatively charged, and hence their formation energies are Fermi-level dependent - an important feature that has not been recognized in past studies. This dependence enables us to explain why small amounts of transition-metal additives drastically alter the kinetics of dehydrogenation. The rate-limiting step for hydrogen release is the creation of charged hydrogen-related defects, while transition-metal additives (such as Ti) act as electrically active impurities that lower the formation energy of these defects. Comparisons with experimental measurements that confirm the proposed mechanisms will be discussed. The ideas outlined here suggest improved preparation methods for complex hydrides through enhanced control of the addition of small concentrations of impurities.

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