MS13-P5 **Mg/Zn Mixed-Metal Borohydride for hydrogen storage: ab-initio periodic computational study of the phase stability and decomposition.** Bartolomeo Civalleri,[a] Elisa Albanese,[a] Eugenio Pinatel,[a] Marcello Baricco[a]
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Metal borohydrides are considered promising materials for applications in efficient and reversible hydrogen storage. However, pure metal borohydrides are either too thermodynamically stable or kinetically too slow. Therefore, current research is seeking for mixed metal systems. Indeed, the manipulation of multi-cation combination may provide a general route for tuning the thermodynamic stability of borohydrides [1]. In this work, we investigate the Mg-Zn system by means of theoretical DFT calculations.

Calculations have been carried out at PBE-D* level of theory (PBE with Grimme's DFT-D2 dispersion correction [2], as modified for solids [3]) and performed with the periodic ab-initio CRYSTAL09 [4] program.

For both Mg and Zn pure compounds, the phase stability of four different structures has been calculated, as well as their decomposition enthalpy. Mg/Zn mixed metal borohydrides, $Mg_{(1-x)}Zn_x(BH_4)_2$, have then been studied by generating different solid solutions from the most stable structure of $Mg(BH_4)_2$ (á-phase, space group $P6_122$) with several Mg/Zn atomic ratios. The formation enthalpies of these compounds were calculated considering the following reaction paths:

$$(1-x)Mg(BH_4)_2 + xZn(BH_4)_2 \rightarrow Mg_{(1-x)}Zn_x(BH_4)_2$$

$$Mg(BH_4)_2 + xZnCl_2 \rightarrow Mg_{(1-x)}Zn_x(BH_4)_2 + xMgCl_2$$

Considering an ideal entropy of mixing, calculated free energies indicate that $Mg_{(1-x)}Zn_x(BH_4)_2$ compounds can be formed. The enthalpy of dehydrogenation has been estimated, considering MgH_2, Zn, B and H_2 as products and the value obtained for x=0.7 is ≈ 30 kJ/mol H_2, in the range of interest for practical applications. Therefore, Mg-Zn mixed metal borohydrides appears to be promising candidate for hydrogen storage and deserve to be also explored experimentally.

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Keywords: hydrogen storage; mixed borohydrides; ab-initio calculations

MS13-P6 **Structural and functional analysis of a GH12 from *Aspergillus terreus*.** Bruno Augusto Dias [ab], Fernando Segato [ac], Tatiana Souza [d], André Damásio [a], Rodrigo Almeida [ae], Ana Citadini [a], Dioni Oliveira [f], Mario Murakami [d], Eleni Gomes [b], Fábio Squina [a] *[a] CTBE - Laboratório Nacional de Ciencia e Tecnologia do Bioetanol - CNPEM, Brazil, [b]UNESP - Universidade Estadual Paulista, Brazil, [c] VTT Technical Research Centre, Brazil, [d] LNBIO - Laboratório Nacional de Biociências - CNPEM, Brazil, [e] UNIP - Universidade Paulista, Brazil, [f] UEM - Universidade Estadual de Maringá, Brazil.*
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The production of renewable fuels, especially bio-ethanol derived from lignocellulosic biomass, holds remarkable potential as environmentally friendly alternatives to petroleum-derived fuels. Advanced biofuels from non-food plant materials, such as dedicated crops or by-products of existing agricultural production, are of particular interest. Endoglucanases randomly cleaves cellulose chain internally and create relatively many chain-ends for exoglucanases and â-glucosidases actions. Those enzymes are useful in the process of second-generation ethanol production, particularly for biomass deconstruction. In this work, a GH12 endoglucanase from *Aspergillus terreus* was cloned and expressed in *A. nidulans* A773 for functional and structural characterization. The expression was confirmed by MS/MS and enzymatic characterization showed that the optimum pH and temperature for enzyme activity were 5.0 and 55 °C, respectively. Crystals were obtained in 2M Lithium sulfate 2M, 5 % 2-Propanol, 0.1M Magnesium sulfate and 0.1M Sodium acetate pH 4.5. Thestructural data show the GH12 is mainly comprised of β-sheets. SAXS experiments showed that GH12 ismonomeric in solution. These results allowed the understanding of the GH12 mode of action and useful generate information for the development of enzymatic cocktails to plant biomass degradation.

Keywords: bio-ethanol; biomass; hydrolysis; endoglucanase