



INDIVIDUAL FELLOWSHIPS



**Project n°:** 253863

**Project Acronym:** MATERHY

**Project Full Name:** Development and characterisation of novel materials for hydrogen storage

## Marie Curie Actions

# IEF-IOF-IIF-IFFR Final Report

**Period covered:** from Aug/2010 to Aug/2012

**Period number:** 1

**Start date of project:** 03/Aug/2010

**Project beneficiary name:** IFE

**Project beneficiary organisation name:** INSTITUTT FOR ENERGITEKNIKK

**Date of preparation:** 01/Oct/2012

**Date of submission (SESAM):** 01/Oct/2012

**Duration:** 24 months

**Version:** 1

## 1. Final publishable summary report

Hydrogen storage is considered to be the key challenge in achieving hydrogen based energy economy. The long-term solution especially for mobile applications is hydrogen storage in solid materials. Light-weight complex hydrides are considered as the most promising materials. The project addresses synthesis of novel anion-substituted borohydrides by ball milling and characterisation with respect to thermodynamics, kinetics and structure. Partial substitution of an element, i.e. hydrogen, with a more electronegative element changes the bond strength of the remaining elements, and it may facilitate release of hydrogen.  $\text{Mg}(\text{BH}_4)_2$  undergoes a polymorphic phase transition around 190 °C and desorbs hydrogen around 300 °C. In order to reduce the temperature for hydrogen release, partial substitution of  $(\text{BH}_4)^-$  by halide anion has been achieved to form mixed phase  $\text{Mg}(\text{BH}_4)_{2-x}\text{X}_x$  and the effects on the thermodynamics and kinetics of hydrogen sorption has been investigated.

Mixtures of  $\text{Mg}(\text{BH}_4)_2 + \text{MgX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) were prepared by ball-milling using different milling times/speeds (Table 1).  $\text{Mg}(\text{BH}_4)_2$  was synthesized at Århus University by wet chemistry methods and the halides  $\text{MgX}_2$  were commercially available ( $\text{MgCl}_2$ : 98%, MERCK,  $\text{MgBr}_2$  and  $\text{MgI}_2$ : 98%, Aldrich). The samples were prepared in 1:1 molar ratio, 0.5 g in total with 1:30 sample to ball mass ratio. Ball milling was performed under 1 bar Ar atmosphere for 1 h and followed by 30 min pause, and repeated until reaching the total milling time listed in Table 1.

**Table 1** Samples prepared by ball milling (BM). The molar ratio is 1:1, the milling time and milling speed are listed in the table.

$\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$		$\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$		$\text{Mg}(\text{BH}_4)_2 + \text{MgI}_2$	
BM time	BM speed	BM time	BM speed	BM time	BM speed
2 h	280 rpm	2 h	280 rpm	10 min	by hand
12 h	280 rpm	12 h	280 rpm	30 min	280 rpm
12 h	360 rpm	12 h	360 rpm	1 h	280 rpm
12 h	505 rpm	12 h	505 rpm	2 h	280 rpm
				4 h	505 rpm
				12 h	280 rpm
				12 h	505 rpm

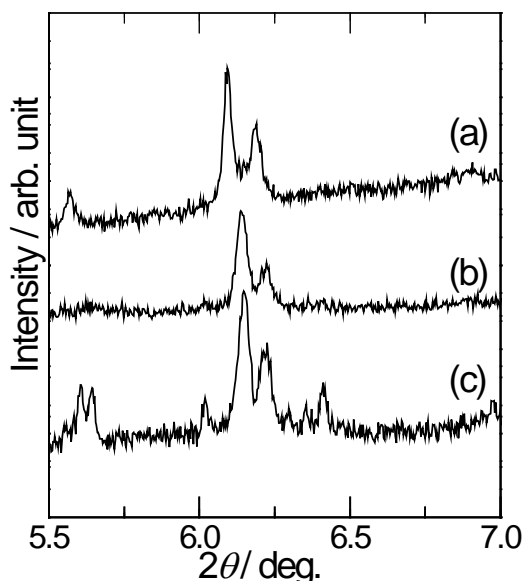
The samples were routinely investigated by laboratory powder X-ray diffraction (PXD) after milling. The diffraction data revealed mechanical mixtures of  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$  and the halide with no sign of chemical reaction. In-situ synchrotron radiation (SR) PXD measurements of selected samples were performed at Swiss-Norwegian beam line (SNBL) in European Synchrotron Radiation Facility (ESRF), France. In-situ SR-PXD patterns of  $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$  milled for 12 h with milling speed of 505 rpm shows that  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$  transformed to  $\varepsilon$ - $\text{Mg}(\text{BH}_4)_2$  at 123 °C, and then to  $\beta$ - $\text{Mg}(\text{BH}_4)_2$  at 162 °C. The  $\beta$  phase decomposed at 274 °C. The  $\varepsilon$  polymorph usually forms from  $\gamma$  phase and has not previously been observed to form from  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$ . Therefore it appears that substitution or ball-milling could alter the relative stability of the different  $\text{Mg}(\text{BH}_4)_2$  polymorphs.

The milled samples with  $\text{X} = \text{Cl}$  and  $\text{Br}$  were then annealed around the  $\alpha \rightarrow \beta$  transition temperature (200 °C) for 12 hours under 10 bar  $\text{H}_2$  back-pressure. Subsequent PXD

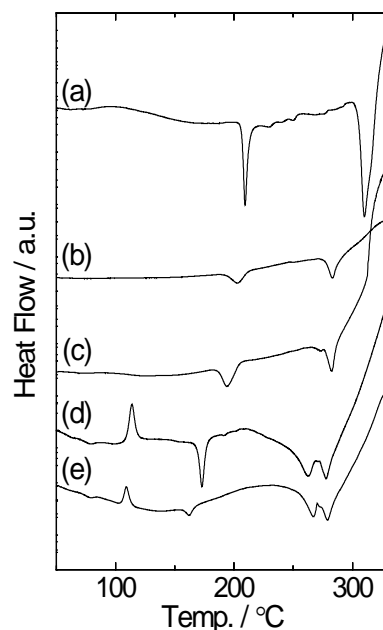
measurements (lab and/or synchrotron) always showed a complete conversion to  $\beta$ - $\text{Mg}(\text{BH}_4)_2$  which did not reverse  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$  on cooling to room temperature. There were clear shifts in the positions of Bragg peaks belonging to  $\beta$ - $\text{Mg}(\text{BH}_4)_2$  in both the Cl and Br containing samples after annealing, as compared to pure  $\beta$ - $\text{Mg}(\text{BH}_4)_2$ , as shown in Figure 1. Since  $\alpha$ - $\text{Mg}(\text{BH}_4)_2$  (without halide) milled and annealed under the same conditions does not show a similar peak shift, it is clear that the shifts are due to substitution of  $\text{BH}_4^-$  (ionic radius  $r = 2.05 \text{ \AA}$ ) by  $\text{Cl}^-$  ( $r = 1.81 \text{ \AA}$ ) or  $\text{Br}^-$  ( $r = 1.96 \text{ \AA}$ ). Structure refinement revealed that unit cell parameters decreased by about 0.1-0.2  $\text{\AA}$  for  $\beta$ - $\text{Mg}(\text{BH}_4)_2$  in the mixtures, which corresponds to a volume contraction of the unit cell of about 2%. This is estimated to correspond to approximately 10% substitution of  $\text{BH}_4^-$  by halides.

Figure 2 shows differential scanning calorimetry (DSC) profiles of as-received  $\text{Mg}(\text{BH}_4)_2$  and the mixtures of  $\text{Mg}(\text{BH}_4)_2 - \text{MgX}_2$  measured under 10 bar hydrogen back pressure. The as-received  $\text{Mg}(\text{BH}_4)_2$  transformed from  $\alpha$  phase to  $\beta$  phase at around 210  $^\circ\text{C}$  and desorbed hydrogen at around 310  $^\circ\text{C}$ . The temperature of  $\text{H}_2$  desorption for the mixtures are decreased by 30  $^\circ\text{C}$  compared to as-received  $\text{Mg}(\text{BH}_4)_2$ . Reversibility of the mixtures were investigated with Sieverts type apparatus, however, substitution does not have a beneficial influence on the reversibility under tested conditions.

In summary, substitution of  $\text{BH}_4^-$  ion by halide ion  $\text{Cl}^- / \text{Br}^-$  in  $\text{Mg}(\text{BH}_4)_2$  is observed for the first time. The substitution occurs in  $\beta$ - $\text{Mg}(\text{BH}_4)_2$  after annealing milled mixtures of  $\alpha$ - $\text{Mg}(\text{BH}_4)_2 + \text{MgX}_2$  ( $X = \text{Cl}, \text{Br}$ ). The substitution is evident from the shift of Bragg peaks to higher angles. A slight reduction in temperature of hydrogen desorption due to the halide substitution is observed. These efforts are expected to contribute to a scientific breakthrough in the search for more efficient hydrogen storage materials.



**Figure 1** SR-PXD ( $\lambda = 0.50123 \text{ \AA}$ ) profile for (a)  $\text{Mg}(\text{BH}_4)_2$  heated up to 300  $^\circ\text{C}$ , (b)  $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$  and (c)  $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$  milled for 12h at 280 rpm and annealed for 10h at 200  $^\circ\text{C}$ .



**Figure 2** DSC profiles (under 10 bar  $\text{H}_2$ ) for (a) as-received  $\text{Mg}(\text{BH}_4)_2$ , (b)  $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$  and (c)  $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$  milled for 12 h with 280 rpm, (d)  $\text{Mg}(\text{BH}_4)_2 + \text{MgCl}_2$  and (e)  $\text{Mg}(\text{BH}_4)_2 + \text{MgBr}_2$  milled for 12 h with 505 rpm. Heating rate is 2  $^\circ\text{C}/\text{min}$ .