Phase transformation and amorphization upon alloys magnesium: combining operando X-Ray diffraction and X-Ray Absorption Spectroscopy

Lucie Blondeau, Eddy Foy, Stéphanie Belin, Suzy Surblé, Fabienne Testard,
Hicham Khodja, Magali Gauthier

► To cite this version:

Lucie Blondeau, Eddy Foy, Stéphanie Belin, Suzy Surblé, Fabienne Testard, et al.. Phase transformation and amorphization upon alloys magnesium: combining operando X-Ray diffraction and X-Ray Absorption Spectroscopy. 237th ECS Meeting, May 2020, Montréal, Canada. cea-02491929

HAL Id: cea-02491929

<https://hal-cea.archives-ouvertes.fr/cea-02491929>

Submitted on 26 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Phase transformation and amorphization upon alloys magnesianation: combining *operando* X-Ray diffraction and X-Ray Absorption Spectroscopy

Lucie Blondeau¹, Eddy Foy², Stéphanie Belin³, Suzy Surblé¹, Fabienne Testard⁴, Hicham Khodja¹, Magali Gauthier¹

¹ LEEL, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette France

²LAPA-IRAMAT, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif sur Yvette Cedex, France

³Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin 91192 Gif-sur-Yvette, France

⁴LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette France

e-mail: magali.gauthier@cea.fr

Magnesium appears as a great alternative to lithium due to its high capacity, low cost, abundance and largely smaller reactivity compared to lithium [1]. Magnesium metal has however a tendency to react with conventional electrolytes to form a barrier on its surface [1], impeding cations exchange, and thus dramatically limiting reversible stripping/deposition of Mg. An interesting alternative is to replace Mg metal with negative electrode materials based on *p*-block elements (In, Sn, Sb, Bi...) as they electrochemically alloy with Mg and possess adequate stability in standard electrolytes [2]. These substitute electrodes can thus prove a promising solution to overcome the problem of compatibility with electrolytes, even if the reaction mechanisms behind their operation in conventional electrolytes remain partly unsolved.

In a recent work, we investigated the electrochemical reactivity and performance of the InSb alloy as a negative electrode for Mg-ion batteries [3]. A strong synergy between In and Sb has been evidenced with the promotion of the electrochemical activity of Sb towards magnesianation/demagnesianation, in contrast to what was already reported for pure Sb electrodes where Mg²⁺ ions cannot be pulled out of the Mg₃Sb₂ phase after the first magnesianation [4].

Using complementary information from *operando* X-Ray diffraction (XRD) and X-Ray Absorption Spectroscopy (XAS), we further characterized in-depth the electrochemical behavior of InSb to understand its peculiar performance. *Operando* XRD measurements demonstrate the formation of the Mg₃Sb₂ phase almost all along the first magnesianation, accompanied by the extrusion of In metal. While crystalline MgIn has always been detected in the case of pure In or InBi electrodes [5], we observed a kinetically dependent electrochemically-driven amorphization of MgIn. This behavior suggests a possible competition between crystallization and amorphization in the material. EXAFS data, obtained at the In and Sb *K*-edges at the ROCK beamline of synchrotron Soleil, corroborate the formation of Mg₃Sb₂ and In crystalline phases and the formation of MgIn, and give further insights on the atomic environment of In and Sb during the first magnesianation. Thanks to the evolution of EXAFS spectra as well as the changes in scattering paths, the phase proportions evolution as function of the number of Mg inserted into the alloy is followed (Figure 1).

These results shed light on synergetic effects between *p*-block elements for Mg-ion batteries and more generally raise questions on the relation between *in situ* amorphization and electrochemical behavior.

References:

[1] Yoo *et al.*, *Energy Environ. Sci.* **6**, 2265–2279 (2013)

- [2] Zhang et al., *Energy Storage Mater.* **20**, 118-38 (2019)
- [3] Murgia et al., *Electrochim. Acta*, **259**, 276 – 283 (2018)
- [4] Blondeau et al., *Phys. Chem. C* **123**, 1120–1126 (2019)
- [5] Murgia et al., *Electrochim. Acta*. **209**, 730-736 (2016)

Figure 1: Evolution of the phase concentrations at the In and Sb *K*-edges along the first magnesiation of a InSb/Mg cell.