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

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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:

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- [2] Zhang et al., *Energy Storage Mater.* **20**, 118-38 (2019)
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Figure 1: Evolution of the phase concentrations at the In and Sb *K*-edges along the first magnesiation of a InSb/Mg cell.

