

# Insights on the Electrochemical Magnesiumation of InSb from Combined Operando X-ray Diffraction and X-ray Absorption Spectroscopy

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## ABSTRACT

The continued acceleration of the lithium demand combined with its relatively low abundance and uneven concentration on the Earth's crust might dramatically increase its price in a near future. Mg-batteries are promising candidates to replace Li-ion batteries thanks to Mg abundance, theoretical capacity (2.2Ah/g - 3.8Ah/cm<sup>3</sup>), low cost and safety. However, metallic Mg reacts with standard electrolytes to form a blocking layer on its surface, preventing cation exchange, and thus dramatically limiting reversible stripping/deposition. An interesting alternative is to substitute Mg metal with another negative electrode made of *p*-block elements as they electrochemically alloy with Mg and possess adequate stability in standard electrolytes [1].

In a recent work, we investigated the InSb alloy as a negative electrode [2] in order to fundamentally understand the electrochemical reactions occurring in alloys in Mg batteries. A strong synergy between In and Sb has been evidenced with the promotion of the electrochemical activity of Sb towards magnesiumation along few cycles, in contrast to what was already reported in other studies.

Using complementary information from *operando* X-Ray diffraction (XRD) and X-Ray Absorption Spectroscopy (XAS), we further characterized in-depth the peculiar electrochemical behavior of InSb. *Operando* XRD measurements demonstrate the formation of the Mg<sub>3</sub>Sb<sub>2</sub> phase almost all along the first magnesiumation, accompanied by the extrusion of In metal. While crystalline MgIn has always been detected in the case of pure In or InBi electrodes [3], 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 Mg<sub>3</sub>Sb<sub>2</sub> and In crystalline phases but also the formation of MgIn. It gives us further insights on the atomic environment of In and Sb during the first magnesiumation. 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 InSb has been followed. These results are of paramount importance to shed light on synergetic effects between *p*-block elements and to study the relation between *in situ* amorphization and electrochemical behavior.

## REFERENCES

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[2] Blondeau et al., *Phys. Chem. C* 123, 1120–1126 (2019)  
[3] Murgia et al., *Electrochem. Acta.* 209, 730-736 (2016)