

SYNTHESIS AND NANO-STRUCTURATION OF ENERGY STORAGE MATERIALS BY BALL-MILLING

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In the field of energy storage, ball-milling has emerged since the 1990's as a powerful technique for the nano-structuration of different phases allowing an enhancement of their performances and a convenient method for the synthesis of new phases.¹ This presentation will focus on two main applications: hydrogen storage materials and electrode materials for Li-ion batteries.

For hydrogen storage, ball-milling is a simple method for preparing nano-structured powders with enhanced hydrogen absorption/desorption kinetics. This has been largely applied, for instance, to magnesium, for which ball-milling leads to the formation of grains boundaries acting as hydrogen diffusion paths. The ball-milling of Mg with suitable catalysts has allowed the development of composite materials, which are very interesting for hydrogen storage applications.² The reactive ball-milling under different gases is also very interesting. Ball-milling under hydrogen appears as a very convenient synthesis method for metallic hydrides.³ Similarly, ball-milling under other gases can be conducted: for example, metal amides such as LiNH_2 or $\text{Mg}(\text{NH}_2)_2$ are easily prepared by ball-milling of the corresponding metals under ammonia.⁴ The preparation of various hydrogen storage materials by ball-milling will be discussed as well as their hydrogen storage performances.

For electrode materials, ball-milling is often used for the electrode preparation by mixing the electro-active material with carbon and other additives. Ball-milling allows at the same time a decrease of the particles size of the active material and an intimate mixture with the conductive carbon.⁵ Thus, the electrochemical performances are much better than the pristine material. More recently, the preparations of phases usually obtained under high pressure/high temperature conditions have been reported by ball-milling. We will especially discuss about the synthesis of superdense graphite intercalation compounds (LiC_3 with a Li content twice that of the classical LiC_6 phase),⁶ the single phase LiSi ,⁷ and a new family of electro-active phases: LiMSO_4OH with $\text{M} = \text{Fe}, \text{Co}, \text{Mn}$.⁸ Ball-milling in liquid media can be also useful for the preparation of electrode materials: the addition of a solvent in the milling jar can prevent the particles agglomeration or, in some cases, the solvent can be used as a reactant. The presentation will make a review of the important inputs brought by the ball-milling method in the field of energy storage materials in the last few years.

¹ Janot, R.; Guérard, D., *Progress Mat. Sci.* **2005**, 50, 1

² Janot, R.; Darok, X.; Rougier, A.; Nazri, G. A.; Tarascon, J.-M., *J. All. Comp.* **2005**, 404-406, 293

³ Elansari, L.; Antoine, L.; Janot, R.; Gachon, J. C.; Kuntz, J. J.; Guérard, D., *J. All. Comp.* **2001**, 329, L5

⁴ Janot, R.; Eymery, J.B.; Tarascon, J.M., *J. Phys. Chem. C* **2007**, 111, 2335

⁵ Tarascon, J.M.; Morcrette, M.; Saint, J.; Aymard, L.; Janot, R., *C.R. Chimie Acad. Sci.* **2005**, 8, 17

⁶ Guérard, D.; Janot, R., *J. Phys. Chem. Sol.* **2004**, 65, 147

⁷ Tang, W.S.; Chotard, J-N.; Janot, R., *J. Electrochem. Soc.* **2013**, 160, A1232

⁸ Subban, C.; Ati, M.; Rousse, G.; Abakumov, A.; Van Tendeloo, G.; Janot, R.; Tarascon, J.-M., *J. Am. Chem. Soc.* **2013**, 135, 3653