

# Spark Plasma Sintering: an efficient route to design energy storage devices

Fabien Lalère<sup>1,2</sup>, Rakesh Elango<sup>1,2</sup>, Matthieu Morcrette<sup>1,2</sup>, Christian Masquelier<sup>1,2</sup> and Vincent Seznec<sup>1,2</sup>

1. *Laboratoire de Réactivité et de Chimie des Solides (CNRS UMR 7314), Université de Picardie Jules Verne, 33 rue Saint Leu, 80039 Amiens Cedex, France.*
2. *Réseau de Stockage Electrochimique de l'Energie (CNRS FR3459), 33 rue Saint Leu, 80039 Amiens Cedex, France.*

Spark Plasma Sintering is a well-known sintering method involving the use of an electrical current added to the application of pressure. This technique presents some advantages over conventional methods such as pressureless sintering or hot pressing for example. These advantages include lower sintering temperature, shorter holding time (which may limit unexpected reactions) and marked improvements in the properties of materials consolidated by this method. For these reasons, we decided to use this technique to design devices for energy storage such as all solid state batteries or thick electrodes.

In a first part, an all-solid state symmetric monolithic sodium ion battery made by SPS and operating at 200 °C will be described, using NASICON-type electrodes and electrolyte.  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is used at both electrodes as the active material while  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  plays the role of the  $\text{Na}^+$  solid electrolyte. Both compositions present order-disorder phase transitions and present decent ionic conductivity properties,  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  and  $1.9 \times 10^{-4} \text{ S cm}^{-1}$  at 200 °C for  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , respectively. The full battery (560  $\mu\text{m}$  in thickness) was assembled in a 10' single step by spark plasma sintering at 900 °C. The electrochemical characteristics at high temperature (200 °C) were evaluated thanks to a new experimental set-up. The battery operates at 1.8 V with 85% of the theoretical capacity attained at C/10 with satisfactory capacity retention, for an overall energy density of  $1.87 \times 10^{-3} \text{ W h cm}^{-2}$  and a capacity of  $1.04 \text{ mA h cm}^{-2}$ .

In the second part of the talk, some results concerning the preparation of thick porous sintered electrodes thanks to SPS will be presented. Indeed, SPS is a technique of choice which limits unwanted side chemical reactions thanks to the rapidity of the process. Our preliminary works carried out at LRCS have already shown the feasibility to manufacture thick porous composites electrodes by SPS. By incorporating a salt (NaCl) in the electrodes, it is possible to dissolve it after sintering and therefore to generate porosity within the electrode. The porosity (pore size and volume) can be easily controlled by its percentage in volume and the particle size of NaCl.