

CORE SHELL AMORPHOUS SILICON-CARBON NANOPARTICLES SYNTHESIS BY DOUBLE STAGE LASER PYROLYSIS, APPLICATION TO ANODE MATERIAL

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Li-ion battery is reaching a limit in its energy density. In particular the capacity of graphite is too low (372 mAh.g⁻¹) to meet the increasing energy demand. Silicon (Si) anode appears as a possible solution as carbon replacement in LIB thanks to its high theoretical specific capacity (3579 mAh.g⁻¹). However, rapid pulverization of the particles and SEI instability cause capacity fading in few cycles. Silicon nanostructuration together with association of carbon to Si greatly enhance the performances in terms of both cyclability and capacity. Using a-Si as core material, instead of c-Si, is a less considered option but appears promising to enhance cyclability. Indeed, a-Si is not subject to the drastic crystalline state alteration upon its first lithiation. In order to cumulate all the benefits cited above, active material should be a composite of an a-Si core covered with a carbon shell. A major drawback of such structures is related to their synthesis processes not meeting the quantity requirement for industrial development. Having this point in mind, the Laser Pyrolysis (LP) process was adapted for the one step synthesis of C-coated nanoparticles. This versatile process was used with success to synthesize many types of nanoparticles. Interestingly, the amount of final product is directly correlated to the flow of gas precursor, thus leading to easily scalable process. However the synthesis of a complex material such as nanoparticles composed of a-Si core covered with a carbon shell implies the development of specific reactor. We demonstrate here the successful use of a two stage reactor. This reactor, composed of two reaction zones, allow the synthesis of Si@C nanoparticle in a one-step process, without manipulation of nanopowders. We develop the synthesis of a-Si and a-Si@C core shell nanoparticles, with the exact same silicon core, and we bring in evidence the protective effect of the carbon shell. The two active materials were characterized and studied as anode materials versus metallic lithium in cyclic voltammetry and galvanostatic experiment. We highlighted the beneficial effects related to the use of a-Si over c-Si and the beneficial of a carbon covered active material over a bare one. Results show that a-Si without any carbon coverage presents very poor cycling capacity, due to the presence of a thick and electronically insulant silicon oxide shell. At the opposite, a-Si protected with a carbon shell presents outstanding electrochemical properties: In coin cell configuration, it can be cycled for more than 500 cycles, with a specific capacity superior to 1000 mAh.g⁻¹ and with an exceptional coulombic efficiency of 99,91% at the end of the 500th cycle. This very high stability can be explained by the low oxidation of silicon through the carbon shell that act as an efficient barrier to oxygen diffusion. In good agreement with the stability of the device, post mortem SEM analysis shows an important residual porosity in the electrode.