

## Stabilization of graphene / Silicon electrodes for Li-ion battery applications

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The energy density and performance of Li-ion batteries are highly dependent on physical and chemical properties of the electrode materials. The negative electrode materials still offer a wide area to explore in order to improve both their capacity and reversibility for lithium storage. In this context, the development of negative electrodes based on silicon led to many researches (1). Despite a high specific capacity of  $3850 \text{ mAh.g}^{-1}$ , the use of silicon has major drawbacks (volume expansion, formation of irreversible  $\text{Li}_x\text{Si}_x$  alloys...) which cause early deterioration of the electrodes. Various synthesis techniques of silicon/carbon composite materials have been used to overcome this phenomenon, including physisorption (2, 3, 4). Another original approach is to bridge the two components by chemical (covalent) bond. This link is obtained by chemical reduction of a diazonium salt (para-phenylenediamine) and allows the junction of the carbon surface with silicon nanoparticles through a phenyl bridge (Figure 1).

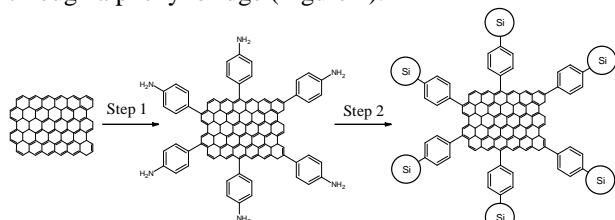


Figure 1: Step 1: functionalization of graphene carbon; Step 2: construction of a molecular bridge between graphene and silicon

This technique was previously used to bond silicon nanoparticles to carbon nanotubes (5), the molecular bridge helped to improve the stability of the electrodes during galvanostatic cycling. The work presented here focuses on a coupling between silicon nanoparticles and graphene sheets. Graphene is potentially interesting for Li-ion applications, it has a good electronic conductivity and its layered structure could promote an increased mechanical strength of the electrodes. The sheets could act as a "buffer" while the silicon particles expand thus helping to maintain the electrode cohesion upon galvanostatic cycling.

The synthesis of these graphene/silicon nanocomposites consists in two different steps. First, the functionalization of graphene sheets is performed in an aqueous or organic medium by aminophenyl groups (Figure 2). Then, the above grafted aminophenyl groups are diazotized, thus offering the possibility to link the silicon nanoparticles to graphene.

The obtained electrode materials are characterized by different physical and electrochemical techniques (TGA-MS, BET, SEM, IR / Raman spectroscopy, electrochemical experiments...) at different stages of the synthesis in order to confirm the presence of the grafted

molecules onto the graphene layers and to determine their influence on the cycling performance in lithium-ion cells.

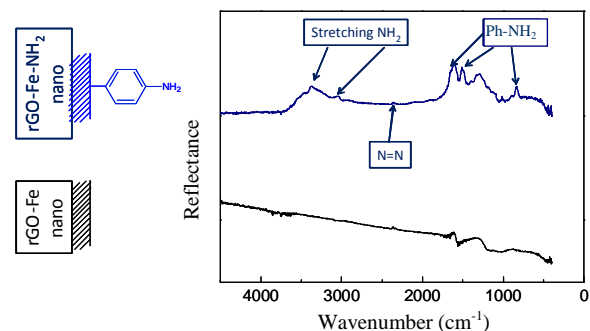


Figure 2: IR spectrum of (bottom) unmodified graphene samples (top) modified graphene samples.

Different graphene/silicon ratios were prepared and the composite materials were used as negative electrodes of lithium-ion batteries, their performance were evaluated by galvanostatic cycling at different cycling rates. The presence of molecular bridges clearly improves the specific capacity compared to a simple mixture of graphene and silicon (Figure 3), confirming the interest of such a technique for lithium-ion battery materials.

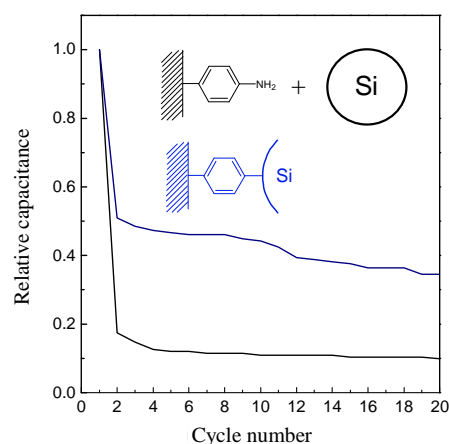


Figure 3: relative losses of capacitance toward first intercalation of (black curve) unbridged graphene/silicon and (blue curve) bridged graphene/silicon composite electrode

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