Performance of C/*c*Si Hybrids and Composites as Anode Material in Li-ion Batteries

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INTRODUCTION

In the development of advanced devices to improve energy utilization, lithium-ion batteries play an important role as power source due to their remarkable characteristics as low weight, compact size, high energy density, longevity and versatility. However, their optimization based on a higher energy density and better rate performance is still necessary. In this scenario, studies have been carried out on different materials capable of acting as an anode due to their ion intercalation or alloying capacity, being the most successful those involving ordered nanostructures based on carbon and silicon compounds (Shi et al., 2021). The structure of the based-carbon materials has a great influence on the reversibility of the lithium intercalation and electronic conductivity, while the crystalline silicon (*c*Si) has an electrochemically active structure that enhances the specific capacity. However, using C/Si materials in lithium-ion batteries, the aim is to combine the properties of both species (Pedrayes, 2016). While the contribution of carbon seeks to provide a stable structure that allows the transport of lithium without collapse, the *c*Si species provides a high capacity, enhancing the general performance (Zhang et al., 2016). In this work, C/*c*Si materials obtained by two different approaches (i.e. hybrid and composites), were characterized and evaluated as potential anode materials for lithium-ion batteries. The main differences conferred during the synthesis process of the materials revealed an important role in their electrochemical performance.

EXPERIMENTAL

In both, hybrid and composites materials, the carbon contribution comes from pyrolysis of resorcinol-formaldehyde (RF) species, while silicon comes from tetraethylorthosilicate (TEOS). Using these reactants as precursors, RF, Si and hybrid gels were synthesized via microwave heating, through a one-pot, quick and efficient process. Synthesis variables such as molar ratio of reagents, volume of catalyst and dilution ratio were employed to design their properties. In the case of hybrid materials, AEAPTMES as catalyst and molar ratios R/F=0.5, D=5.6 y EtOH/TEOS=4.7 were employed, whilst R/TEOS was adjusted in 0.1 or 0.5 to modify the Si content. For comparison with hybrids, Si gel was synthesized following a similar procedure (i.e. molar ratios and basic conditions), whilst RF gels were designed based on a comparable pore size. Hybrid and RF gels were carbonized under N_2 atmosphere at 1000ºC for 2h.

To obtain the C/*c*Si materials, C/SiO_2 hybrid gel or a physical mixture of carbon and silica gels (i.e. composite with the same C:SiO_2 proportion than hybrids) were powdered and homogeneously mixed with Mg to carry out a magnesiothermic reduction. This reduction was performed at 750ºC

under Ar atmosphere for 12h. The heating ramp and Si:Mg ratio were optimized with hybrid samples. Samples were washed with HCl 1M to eliminate sub-products.

The reduced materials were evaluated with adsorption-desorption N_2 isotherms to determine S_{BET}, and pore volumes. X-ray diffraction was employed to analyze the crystalline compounds formed, whilst XPS and SEM/EDX were employed to determine their chemical composition.

Finally, the C/cSi were studied as anodes in Li-ion batteries. For the electrochemical experiments, two-electrode (working, WE, and counter, CE) Swagelok-type cells were used. The WE composition was 70% wt. of active material, 20% wt. of NaCMC and 10% wt. of carbon black. A metallic lithium disc was the CE. WE and CE were separated by two microfiber glass discs soaked with 150 µl of electrolyte $LiPF_6$. Galvanostatic cycling tests of the cells were carried out in a BioLogic Potenciostat, in the 0.003-2.1 V and 0.01-0.9 V voltage ranges, at 500 mA g^{-1} during 200 charge-discharge cycles. As a reference, electrodes composed of the same carbon and a commercial cSi (nanocrystalline silicon 97%, Strem Chemicals) were also tested.

RESULTS AND DISCUSSION

From the results obtained with the magnesiothermic reduction of hybrid materials, it was concluded that the most effective via to obtain the cSi specie is the use of materials with higher Si content, slow heating ramp and a Mg:Si ratio slightly above the stoichiometric one. After these treatments, around 10% wt. of cSi was developed on these samples and, in most cases, the crystalline specie SiC was formed. Due to the macroporous character of the hybrid precursors (c.a. 4 µm), materials with Si crystalline structures well distributed on an accessible matrix were obtained. However, the magnesiothermic treatment of composites produced different results. Unlike hybrid materials, in the case of composites, the absence of Si-C bonds increases the formation of Si with high crystallinity (see Figure 1a). In this case, crystalline SiC is not formed when a macroporous gel of high pore size is employed (c.a. 4µm) due to the low interaction between carbon and silica components. However, when the pore size decreases to 100nm, similar XRD profile and percentage composition are obtained (see Figure 1b). In terms of porous properties, small differences were observed between hybrid and composite reduced samples.
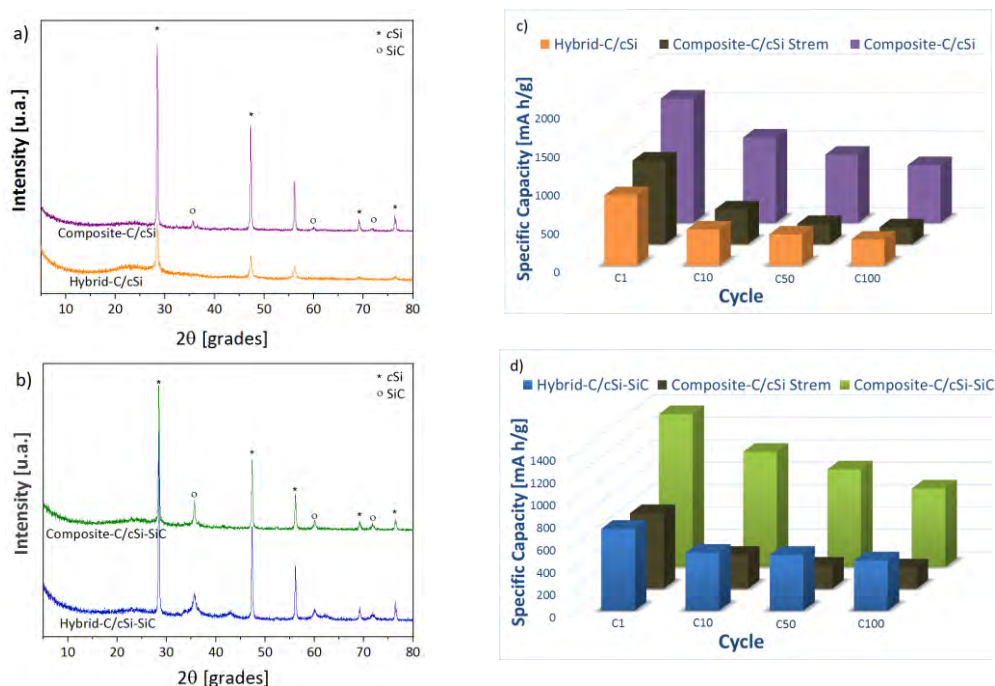

FIGURE 1: a,b) XRD patterns of hybrid and composite materials after reduction treatments. c,d) Specific capacity from cycles 1th, 10th, 50th and 100th of the materials.

The electrochemical performance of reduced materials was defined mainly by its constituent crystalline species. The presence of SiC should provide higher capacity retention, however, this benefit is better appreciated in the case of the hybrid-*C/c*Si-SiC material. On the other hand, *c*Si was determinant to increase the capacity of the material, especially for composites. In comparison with hybrids, the presence of individual species in composites precursors leads to high crystalline structures with better distribution, which impacts positively on their electrochemical performance (see Figures 1c and d). However, competitive performances can be achieved with both types of materials, as their capabilities are superior to those of commercial C/*c*Si Strem composite.

CONCLUSIONS

The use of hybrid materials as the precursor of C/cSi materials with electrochemical purposes has some advantages in terms of processing time and cost. However, the arrangement of the different chemical bonds presents in this hybrid structure limits its availability during the reduction processes. On the other hand, when similar quantities of the same components are used in a composite, the efficiency of this process increases, favoring not only the crystalline properties of the final material but also their electrochemical performance. Therefore, composites are a more promising option in the development of anode materials for lithium-ion batteries.

References

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