

Structural Changes on Silicon-Graphite Anodes for Lithium-Ion Batteries by In-Situ Synchrotron X-ray Diffraction

Eng Weicheng Hua¹, Msc Pedro A Sanchez², Dr Javier Campo Ruiz³, Dr Federico H Cova⁴, Dr Maria V Blanco²

¹Norwegian University of Science and Technology, ²University of Zaragoza, ³CSIC, Zaragoza, ⁴ALBA Synchrotron, Barcelona, weicheng.hua@ntnu.no

Due to their potential to contribute to zero-emission mobility and storage of renewable energy, Lithium-ion batteries are a technological pathway to climate-change mitigation and energy sustainability. To achieve this, design of battery components with high energy density and high specific capacity is a must. A primary component of LIBs is the negative electrode, which is commonly made of graphite. Graphite anodes exhibit high stability and long durability, but with very limited storage capacity (372 mAhg^{-1}). Alternatively, Silicon (Si) has emerged as an excellent anode candidate, displaying a theoretical storage capacity 10 times higher than graphite (3579 mAhg^{-1}). However, one of the major drawbacks hindering the commercialization of Si anodes is the large volume changes that Si undergoes upon electrochemical cycling, which causes great structural and mechanical instabilities and dramatically shortens the cycle life of the anode. Due to its low-cost, high mechanical flexibility and excellent electrical conductivity, graphite has been highlighted as a desirable matrix for Si-based anodes. In Si/graphite composite electrodes (SiG), graphite compensates for the low electrical conductivity of Si and mitigates the severe electrode swelling with its low volume change. However, even though the introduction of graphite in Si electrodes reduces swelling, the practical application of SiG anodes is still challenging due to the problem of Si swelling in SiG composites. Studies on SiG composite electrodes have confirmed that the cracking of silicon particles occurs not just on a local level but also over the entire electrode volume. However, so far, no study has evaluated the effect of Si/graphite ratio on the structural evolution of both silicon and graphite upon electrochemical cycling, specially at high currents. The analysis of the effect of Si volume variation on the structure of graphite is key to develop durable SiG composite anodes that can outperform current state-of-the-art negative electrodes. In addition to this, recent results obtained at our laboratory suggest the formation of a less reversible phase at low working potentials when the cut-off voltage is close to 50 mV, leading to a progressive decrease on the achievable storage capacity of the electrode. The understanding of this phenomena is essential to set the operating conditions of SiG anodes. In this work, we analyze: the formation of the less reversible Si-based crystalline phase that so far has not been experimentally evidenced upon the electrochemical cycling of SiG anodes as well as the effect of Si/graphite ratio on the structural evolution of both graphite and Si. For this, we present time-resolved in situ synchrotron X-ray diffraction studies on SiG anodes for Li-ion Batteries. Experiments were performed at the BM01 of the European Synchrotron Radiation Facility on pure graphite and silicon-graphite anodes in half-cell configuration. The structural changes of the SiG anodes were quantified from the time-dependent alteration in a and c lattice constants on the graphite structure. The results clearly confirm that Li⁺ ions are inserted in the Si domain prior to graphite during the charge, and the delithiation takes place later in Si during the discharge consistently.