UNDERSTANDING THE MECHANISMS LIMITING THE CONVERSION REACTION OF IRON OXIDE NANOSTRUCTURES IN LI- AND NA-ION BATTERIES

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Na-ion batteries have attracted renewed interest during the last decades due their attractive features, which could establish this technology as a potential alternative to Li-ion cells for large-scale stationary storage of electrical energy. However, the route towards the development of effective Na-ion batteries runs into bigger challenges than those faced for Li-ions. Indeed, the noticeable differences in both mass and size between Li\textsuperscript{+} and Na\textsuperscript{+} ions severely influence the resulting electrochemical reactions. This fact limits the choice of suitable materials for Na-ion batteries, especially for negative electrodes, since graphite cannot be employed as reliable insertion host [1]. However, Na\textsuperscript{+} incorporation via solvent co-intercalation phenomena [2] in graphite has been proposed as well. So far, the most promising materials for negative electrodes in Na-ion batteries are hard carbons [3], since they offer the best trade-off in terms of capacities, performances and cycle life. However, these aspects could be further improved and more abundant and cheaper materials, which can be easily fabricated at lower temperatures, have been proposed as well. Among these, iron oxide is certainly one of the most attractive and some preliminary studies in Na-half cells have been carried out [4-5]. The reaction pathway of iron oxide upon sodiation at first glance resembles that occurring upon lithiation. However, important differences do exist in the respective electrochemical processes, being the conversion reaction [6] of iron oxide into Fe and Na\textsubscript{2}O clearly hindered compared to its analogue in presence of Li\textsuperscript{+} ions [4, 7].

A careful comparative analysis via cyclic voltammetry on various types of iron oxide nanostructures (e.g. nanopowders, nanowires and thin-films) cycled in parallel in Li- and Na-half cells with analogous electrolytes will be presented, in order to clarify the different behaviours observed for these two electrochemical systems. The roles played by the characteristic structures, textures and their electrical wiring through the related electrode architectures will be highlighted. The limiting factors arising from the conversion of iron oxide upon lithiation and sodiation will be discussed and the related issues addressed.

References