Electrochimica Acta 230 (2017) 132–140

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Anodic Materials for Lithium-ion Batteries: TiO_2-rGO Composites for High Power Applications

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ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form 27 January 2017
Accepted 29 January 2017
Available online 31 January 2017

Keywords:
Li-ion Batteries
Anode material
High Power
TiO_2
Reduced Graphene Oxide

ABSTRACT

Titanium dioxide/reduced graphene oxide (TiO_2-rGO) composites were synthesized at different loadings of carbonaceous phase, characterized and used as anode materials in Lithium-ion cells, focusing not only on the high rate capability but also on the simplicity and low cost of the electrode production. It was therefore chosen to use commercial TiO_2, GO was synthesized from graphite, adsorbed onto TiO_2 and reduced to rGO following a chemical, a photocatalytic and an in situ photocatalytic procedure. The synthesized materials were in-depth characterized with a multi-technique approach and the electrochemical performances were correlated *i*) to an effective reduction of the GO oxidized moieties and *ii*) to the maintenance of the 2D geometry of the final graphenic structure observed. TiO_2-rGO obtained with the first two procedures showed good cycle stability, high capacity and impressive rate capability particularly at 10% GO loading. The photocatalytic reduction applied in situ on preassembled electrodes showed similarly good results reaching the goal of a further simplification of the anode production.

1. Introduction

The Li-ion batteries world has undergone marked changes during the last years, and it is continuously evolving. Limited initially by the high price, as Asian manufactures started to compete in this field after the year 2000, the cells price has drastically lowered [1] as a consequence of the increased commercial diffusion (from 2 GWh in 2000 to 34 GWh in 2012). Moreover, in the last few years the application field of the Li-ion systems has been extended from electronics and portable devices to the transportation field. This kind of cell is actually replacing the NiMH technology especially in hybrid and micro-Hybrid Electric Vehicles (micro-HEVs) [2–4]. Hybrid vehicles are today the 3% of all cars, but the most recent studies predict that their number will quickly increase in the next few years [2].

As for HEV mobility, the main requirement of the accumulator is the high power density, while energy density is secondary [3]. In this context safety comes out to be of paramount importance [1].

To optimize the Li-ion system with respect to the recalled requirements, new electrode materials have to be considered, in particular regarding the anode aiming at substituting graphite, the currently most employed anode material, which cannot sustain the high currents needed to reach high power and is limited from the safety viewpoint [5]. Recently, the attention of researchers has focused on titanium oxide, in particular its crystallographic form anatase [3,4,6–10,13], due to its high chemical stability, low cost, environmental sustainability, combined to interesting electrochemical performances, including a higher charging potential that prevents lithium dendrite formation. In fact, TiO_2 is intrinsically safer than graphite (showing a reversible intercalation of Li-ions at about 1.5 V vs. Li^+/Li) while delivering comparable theoretical capacity (around 335 $mAh\,g^{-1}$). Moreover, it reveals enhanced stability and long cycle life thanks to the negligible lattice changes during reactions [11].

A major drawback of TiO_2 is its poor conductivity. Some authors proposed different methods to overcome the poor TiO_2 anode conductivity, as embedding noble metal nano-particles on TiO_2 fibers [12] or nanostructuring TiO_2 and adding a C layer [13,14]. However, all these synthesis approaches are not suitable for an

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http://dx.doi.org/10.1016/j.electacta.2017.01.190
0013-4686/