Student Prize: Fe-Catalyzed graphitic carbon materials from biomass resources as anodes for Lithium-ion batteries

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Introduction

The ongoing raising environmental and economic concerns have currently lead the research community to investigate the use of biomass-derived carbons as electrodes for lithium-ion batteries (LIBs) with the main aim of sustainability management. However, carbons from the pyrolysis of most biomass resources are considered hard or non-graphitizing since subsequent heat treatment does not lead to perfectly ordered graphitic domains even when heat treated at temperatures above 2400°C[1]. When tested as anode materials for LIBs, they deliver a limited capacity due to the cross-linked and disordered structure, suffer from a large irreversible capacity in the first charge/discharge cycles and a large voltage hysteresis on the potential profile.

An alternative pathway for developing synthetic graphitic materials from non-graphitizing carbons consists of the catalytic graphitization by the prior addition of a transition metal into the raw precursor[2,3]. The graphitization can be induced in situ during pyrolysis within a solid carbon template from temperatures below 1000 °C, with enhancements in crystallinity and electronic conductivities with increasing treatment temperature. In this work, a renewable biomass precursor, a medium density fibreboard (MDF) recycled-wood, was graphitized by means of an iron catalyst at temperatures between 850 °C and 2000 °C and systematically studied as anode materials for LIBs. The microstructural parameters are correlated with the anodic behaviour, compared with high-temperature soft and hard carbons without catalyst up to 2800°C.

Materials and Methods

MDF wood pieces were first impregnated with 1.0 M FeCl₃ solution and then submitted to a pyrolysis process up to peak temperatures ranging between 850 °C and 2000 °C (Fe content =11.6 wt. %). The remaining Fe catalyst was removed by ultrasonic stirring in concentrated HNO₃. The crystallinity and microstructural parameters were evaluated by SEM, TEM, Raman spectroscopy and Nitrogen adsorption/desorption measurements. Electrochemical investigations were carried out in a three-electrode set-up. Carbon electrodes consisted of 90 wt. % Fe-Catalyzed graphitic carbon materials from non-graphitizing carbons up to 2800 ºC. The crystallinity and electronic conductivities with increasing treatment temperature, observable by an enhancement of the G peak intensity with respect to the intensity of the D band, along with the narrowing of the full-width at half-maximum of the G peak. By fitting Raman spectra using pseudo-Voigt line shapes, the degree of graphitization (α= I_D/I_G) was estimated and compared in Figure 1.b as a function of temperature with non-catalyzed carbons and a reference soft carbon (petroleum coke[4]). Non-catalyzed MDF samples do not reflect any abrupt development in the crystalline structure even when heat-treated up to 2800 °C, while when using Fe as catalyst, values close to 0.7 are reached at 2000 °C, achieving comparable but slightly lower values than petroleum coke samples (α≈ 0.8 at 2000°C).

When used as anode for LIBs, an increasing structural order within the carbon structure goes along with an increase in specific capacity of more than 50% within the range of temperatures investigated herein (Figure 1.c). Figure 1.d shows the effect of the treatment temperature on specific reversible capacities of MDF when using Fe as catalyst[2], compared with the usual trend of soft and hard carbon up to 2800°C[1].

Without the effect of any catalyst, the trend is clear: a decrease up to ≈2000 °C due to the release of remaining surface functional groups, followed by a slight increase up to 2800°C due to the improved structural order (maximum reversible capacity of ≈160 mAh·g⁻¹ and ≈310 mAh·g⁻¹ for hard and soft carbons, respectively). However, by using Fe, the capacity increases directly from 1000°C as the graphitization has already begun at this temperature. Fe-catalyzed sample at 2000 °C delivered a remarkable specific capacity of 307 mAh·g⁻¹, a value up to twice as much as that of non-catalyzed MDF-derived carbons at the same temperature and comparable to synthetic graphite derived from petroleum coke precursor at higher temperatures (=2600-2800 °C).
Figure 1. a) Raman spectra of Fe-catalyzed and non-catalyzed MDF carbons; b) Degree of graphitization vs. pyrolysis temperature [2]; c) Reversible capacity of Fe-graphitized MDF-derived carbon as a function of degree of graphitization from Raman fitting and d) Reversible specific capacity vs. pyrolysis temperature compared with soft and hard carbons [1]. Electrolyte: 1.0 M LiPF_6 in 3:7 EC/EMC + 2 wt. % VC.

Conclusions
Graphitized carbon materials from biomass resources were successfully synthesized at moderate temperatures by means of an iron catalyst, and their electrochemical performance as anode materials for lithium-ion batteries (LIBs) was systematically investigated. An enhancement in the degree of graphitization was corroborated by Raman analysis with increasing treatment temperature. Fe-catalyzed MDF sample at 2000 ºC delivered a specific discharge capacity of 307 mAh·g\(^{-1}\) as anode for LIBs, a value comparable to synthetic graphite derived from soft carbons at higher temperatures (~2600-2800 ºC). The results reported here demonstrate that the catalytic graphitization of biomass resources, by a low cost and environmental friendly process using iron as a catalyst, is a promising synthesis route to develop synthetic graphitic anode materials for LIBs.

References