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

**Aurora Gómez-Martín[1], Mirco Rutter[2], Tobias Placke[2], Julián Martínez-Fernández[1], Joaquín Ramírez-Rico[1].**

[1] *Dpto. Física de la Materia Condensada and Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla - CSIC, Sevilla, Spain*

[2] *MEET Battery Research Center, Institute of Physical Chemistry, University of Münster, Münster, Germany*

## 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 2400ºC[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 ºC and 2000 ºC 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 2800ºC.

## Materials and Methods

MDF wood pieces were first impregnated with 1.0 M $FeCl_3$ solution and then submitted to a pyrolysis process up to peak temperatures ranging between 850 °C and 2000 ºC (Fe content ≈11.6 wt. %). The remaining Fe catalyst was removed by ultrasonic stirring in concentrated $HNO_3$. 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. % graphitized carbons, 5 wt. % Na-CMC as binder and 5 wt. % Super C65 as conductive agent. Galvanostatic and cyclic voltammetry experiments were carried out in a potential range between 0.02 and 1.5 V vs. $Li/Li^+$.

## Results and Discussion

The graphitization process starts at ≈700 ºC when Fe is used as a catalyst, showing a microstructure characteristic of catalyst particle cores surrounded by several curved and ordered graphitic shells[2]. After acid etching, Fe particles are almost completely removed from the material (content 0.4 wt. %), leaving hollow ordered carbon nanostructures. Raman measurements (*Figure 1.a*) of catalyzed samples reflects a progressive improvement in the degree of structural order and crystalline orientation with increasing treatment temperature, observable by an enhancement of the G peak intensity with respect to the intensity of the $D_1$ 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 ($\alpha = I_G/I_G+I_{D1}$) was estimated and compared in *Figure 1.b* as a function of temperature with non-catalyzed carbons and a reference soft carbon (petroleum coke[1]). Non-catalyzed MDF samples do not reflect any abrupt development in the crystalline structure even when heat-treated up to 2800 ºC (α≈0.4), while when using Fe as catalyst, values close to 0.7 are reached at 2000 ºC, achieving comparable but slightly lower values than petroleum coke samples (α≈ 0.8 at 2000ºC).

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 2800ºC[1].

Without the effect of any catalyst, the trend is clear: a decrease up to ≈2000 ºC due to the release of remaining surface functional groups, followed by a slight increase up to 2800ºC due to the improved structural order (maximum reversible capacity of ≈160 $mAh \cdot g^{-1}$ and ≈310 $mAh \cdot g^{-1}$ for hard and soft carbons, respectively). However, by using Fe, the capacity increases directly from 1000ºC as the graphitization has already begun at this temperature. Fe-catalyzed sample at 2000 ºC delivered a remarkable specific capacity of 307 $mAh \cdot g^{-1}$, 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 ºC).

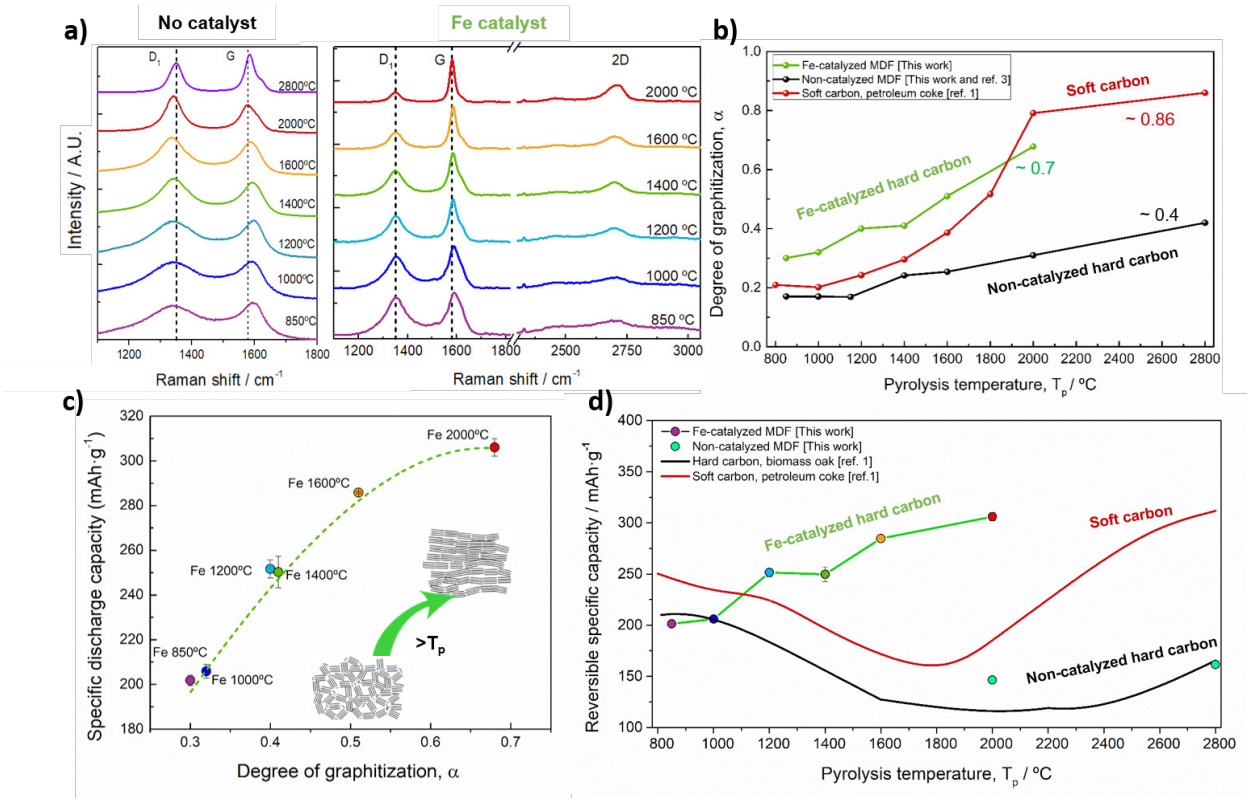


**Figure 1.** a) Raman spectra of Fe- catalyzed and non-catalyzed MDF carbons; b) Degree of graphitization vs. pyrolysis temperature [2]; c) Reversible capacity of Fe-graphitized MDF-derived carbon as a function of degree of graphitization from Raman fitting and d) Reversible specific capacity vs. pyrolysis 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

[1] O. Fromm, A. Heckmann, U.C. Rodehorst, J. Frerichs, D. Becker, M. Winter, et al., Carbons from biomass precursors as anode materials for lithium ion batteries: New insights into carbonization and graphitization behavior and into their correlation to electrochemical performance, Carbon 128 (2018) 147-163.

[2] A. Gomez-Martin, J. Martinez-Fernandez, M. Ruttert, A. Heckmann, M. Winter, T. Placke, et al., Iron-Catalyzed Graphitic Carbon Materials from Biomass Resources as Anodes for Lithium-Ion Batteries, ChemSusChem 0(0).

[3] A. Gutiérrez-Pardo, J. Ramírez-Rico, A.R. de Arellano-López, J. Martínez-Fernández, Characterization of porous graphitic monoliths from pyrolyzed wood, Journal of Materials Science 49(22) (2014) 7688-7696.