Diseño de materiales carbonosos porosos de alta durabilidad y bajo coste para el almacenamiento y producción de energía

Design of porous carbon materials of high durability and low cost for the storage and production of energy

Jessica Alejandra Chaparro Garnica

Presented in 2021, Instituto de Materiales, Universidad de Alicante, 03690, Alicante, Spain

Supervisors: Diego Cazorla-Amorós (Universidad de Alicante, Spain) and David Salinas-Torres (Univ. de Alicante, Spain)

jessica.chaparro@ua.es

Objectives and Novelty

Currently, one of the main challenges for the scientific community is to mitigate environmental and energy problems, and that is why much of the research has focused on searching alternatives for green and efficient energy generation. In this context, the use of biomass residues as a precursor for various products with high added value, among which fuels and activated carbons stand out, is becoming increasingly important. Activated carbons obtained from biomass residues are widely used in many environmental and energy applications. Activated carbons with excellent properties such as high surface area, high pore volume, and high thermal and chemical stability, can be prepared by simple synthesis methodologies.

One of the most common synthesis method used to prepare activated carbons is the conventional chemical activation. However, the main disadvantages of this method is the use of activating agents in high concentrations together with the low yield. An attractive alternative to produce activated carbons is the combination of treatments that contribute to an effective concentration of organic matter. Therefore, in this Doctoral Thesis, an innovative methodology was implemented for the synthesis of activated carbons using biomass residues as precursors, which consists of combining a hydrothermal carbonization method assisted by H_3PO_4 with an activation treatment. Using this methodology, it is possible to reduce the concentration of the activating agent and increase the yield of activated carbon. Thus, the main objective of this Doctoral Thesis is to prepare activated carbon from lignocellulosic biomass residues with appropriate characteristics for their use in environmental and energy applications.

Results

Activated carbons were prepared from biomass residues (i.e. almond shell (AS) and hemp residue (HR)) using a H_3PO_4-assisted hydrothermal carbonization and a subsequent activation treatment. The activated carbons obtained were then modified by: (1) a thermal treatment, to improve its electrical conductivity and electrochemical stability; (2) incorporation of nitrogen functional groups, through an organic reaction under mild conditions to improve their electrochemical stability and their properties as catalyst support.

All the synthesized activated carbons, were used as electrodes for supercapacitors and their electrochemical behavior was assessed in both aqueous and organic electrolytes, evaluating the influence of the introduction of nitrogen functional groups and the effect of thermal treatment in the electrochemical behavior displayed by these activated carbons.

It was shown that both the thermal treatment and the introduction of nitrogen-containing functional groups improved the electrical conductivity and electrochemical stability of the activated carbons, obtaining materials with properties comparable to those of a commercial activated for their use as electrodes in supercapacitors (see Figure 1).

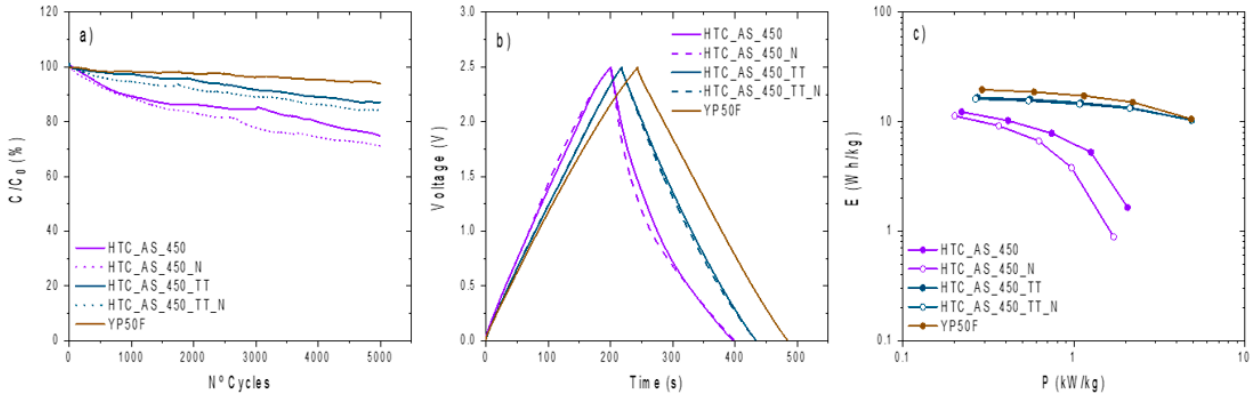

Figure 1. (a) Capacitance retention (C/C_0) a 2.5 V (j = 1 A g^{-1}); (b) galvanostatic charge-discharge cycles after durability test (j = 0.25 A g^{-1}); y (c) Ragone plot at 2.5 V after durability test (j = 0.25 A g^{-1}). Electrolyte: 1M TEMA-BF_4/PC.

To expand the promising scenario of the implementation of as-prepared activated carbons, both nitrogen-free and nitrogen-containing activated carbons were used as catalyst support of Pd-based catalysts, which were evaluated towards the production of hydrogen from formic acid decomposition reaction. The preparation of the catalysts was carried out through a conventional impregnation method and subsequent reduction with sodium borohydride (Pd/HTC_HR and Pd/N-HTC_HR, for the nitrogen-free and nitrogen-containing catalyst, respectively). The effect of the preparation of the catalysts was also checked by preparing an additional sample in which the reduction with sodium borohydride was skipped (Pd/HTC_HR (n.r.)). The resulting catalysts displayed a very promising catalytic activity and excellent stability under reaction conditions, which is a highly desirable yet challenging aspect of the catalysts studied for this reaction. Figure 2 shows the gas evolution profiles attained in the first reaction cycle (Figure 2 a)) and those registered during the stability tests for the three studied catalysts (only the results of the 1st, the 3rd and the 6th cycles are plotted for the sake of clarity). Among the catalysts studied, Pd/HTC_HR (n.r.) showed the most promising results, displaying an excellent stability even after 12 consecutive reaction cycles (results not shown here).

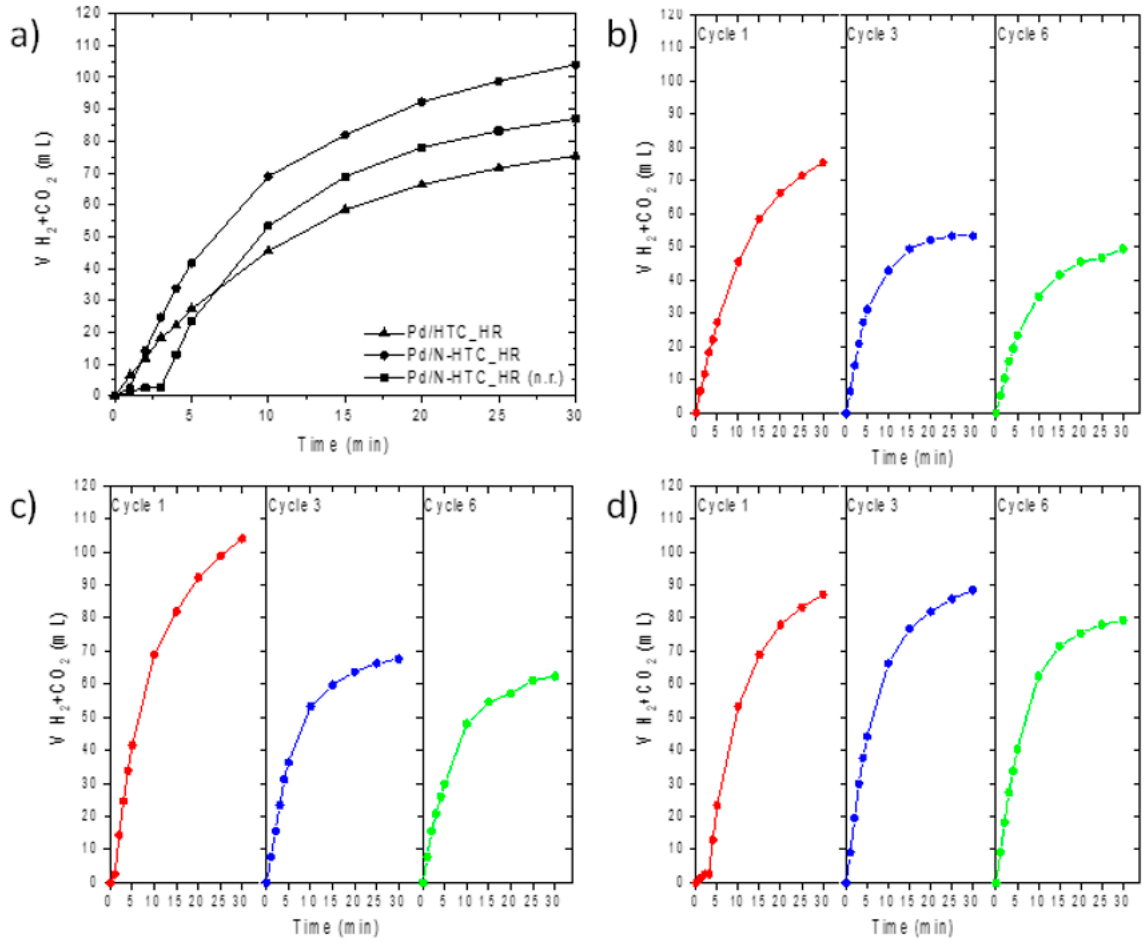

Figure 2. (a) Gas evolution profiles achieved in the 1st reaction cycle for Pd/HTC_HR, Pd/N-HTC_HR, and Pd/N-HTC_HR (n.r.); (b) Gas evolution profiles of Pd/HTC_HR in the 1st, 3rd and 6th cycle; (c) Gas evolution profiles of Pd/N-HTC_HR in the 1st, 3rd and 6th cycle; and (d) Gas evolution profiles of Pd/N-HTC_HR (n.r.) in the 1st, 3rd and 6th cycle.

Finally, to determine if the methodology of H_3PO_4-assisted hydrothermal carbonization and subsequent activation treatment implemented in this Doctoral Thesis, can be considered as a sustainable alternative to obtain products with high added value, the use not only of the solid phase but also of the liquid phase resulting from the hydrothermal treatment has been proposed, obtaining as products of the process: activated carbon and levulinic acid. The environmental impacts that are generated during this process were analyzed. In this sense. the Life Cycle Assessment (LCA) methodology is a useful tool to assess the environmental impacts and the resources employed in the life cycle of a product. This analysis methodology was used to determine the environmental impacts generated in each stage of the H_3PO_4-assisted hydrothermal carbonization followed by activation treatment and subsequent functionalization. From LCA, it was demonstrated the importance of considering environmental criteria to support the development of new processes that allow the conversion of biomass residues into high value-added products, including alternatives to reduce the resources used in each stage of the process.

Conclusions

This Doctoral Thesis has demonstrated the opportunities offered using biomass residues

for the preparation of activated carbons by H_3PO_4-assisted hydrothermal carbonization and subsequent activation treatment. This methodology allows the preparation of activated carbons using lower concentrations of H_3PO_4 compared to the conventional methodology, obtaining higher yields and greater porosity development. This is not only relevant from an economic point of view, but it is also an effective way to approach a more environmentally friendly protocol. Therefore, a notable contribution was made towards the implementation of new methodologies for the use of biomass residues. Therefore, this Doctoral Thesis presents a promising outlook towards a new world of possibilities to obtain high-performance activated carbons for energy storage and production applications, which could be competitive in the market.

Related Publications

[1] Chaparro-Garnica, J.; Mostazo-López, M. J.; Salinas-Torres, D.; Morallón, E.; Cazorla-Amorós, D. Residuos de biomasa como plataforma para obtener materiales carbonosos porosos mediante carbonización hidrotermal en presencia de H_3PO_4. Boletín del Grupo Español del Carbón. 2020, 55:22-27.

[2] Chaparro-Garnica, J.; Navlani-García, M.; Salinas-Torres, D.; Morallón, E.; Cazorla-Amorós, D. Highly Stable N-Doped Carbon-Supported Pd-Based Catalysts Prepared from Biomass Waste for H_2 Production from Formic Acid. ACS Sustain. Chem. Eng. 2020, 8, 15030-15043.

[3] Chaparro-Garnica, J.; Salinas-Torres, D.; Mostazo-López, M. J.; Morallón, E.; Cazorla-Amorós, D. Biomass Waste Conversion into Low-Cost Carbon-Based Materials for Supercapacitors: A Sustainable Approach for the Energy Scenario. J. Electroanal. Chem. 2021, 880, 114899.

[4] Chaparro-Garnica, J.; Navlani-García, M.; Salinas-Torres, D.; Morallón, E.; Cazorla-Amorós, D. H_2 production from formic acid using highly stable carbon-supported Pd-based catalysts derived from soft-biomass residues. Effect of heat treatment and functionalization of the carbon support. Materials 2021, 14(21), 6506.

[5] Chaparro-Garnica, J.; Navlani-García, M.; Salinas-Torres, D.; Berenguer-Murcia, Á.; Morallón, E.; Cazorla-Amorós, D. Efficient production of hydrogen from a valuable CO_2-derived molecule: Formic acid dehydrogenation boosted by biomass waste-derived catalyst. Fuel 2022, 320, 123900.

[6] Chaparro-Garnica, J.; Guiton, M.; Salinas-Torres, D.; Morallón, E.; Benetto, E; Cazorla-Amorós, D. Life Cycle Assessment of biorefinery technology producing activated carbon and levulinic acid. Journal of Cleaner Production.

The full Thesis can be downloaded from **http://rua.ua.es/dspace/handle/10045/124810**