Development of electrocatalysts based on colloidal graphene by electrochemical methods and other carbon materials for energy generation

Desarrollo de electrocatalizadores basados en grafeno coloidal por métodos electroquímicos y otros materiales carbonosos para la generación de energía

Cristian Daniel Jaimes-Paez

Presented in May 2024, Group of Electrocatalysis & Polymer Electrochemistry (GEPE), Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante, 03080 Alicante, Spain

Supervisors: Emilia Morallón and Diego Cazorla-Amorós (Universidad de Alicante, Spain)

cristian.jaimes11@ua.es

Objectives and novelty

This Doctoral Thesis focuses on the development of carbon-based electrocatalysts to enhance efficiency and sustainability in energy production and storage, a field of global importance. The work involves the synthesis of electrocatalysts based on graphene, carbon fibers, activated carbons, and carbon black, using innovative techniques like electrochemical exfoliation, electrospinning, and microwave-assisted synthesis. The developed electrocatalysts are applied in key energy conversion reactions, such as the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER), with the aim of improving their performance.

The novelty of this work lies in the combination and optimization of advanced techniques to produce high-quality carbon-based materials, exploring the incorporation of metallic nanoparticles and modifying their structure with functional groups to enhance electrocatalytic activity. Additionally, the thesis develops bifunctional electrocatalysts, metal doped carbon fibers, and Pt-based materials with optimized characteristics, offering more efficient and sustainable alternatives for energy applications, such as in zinc-air batteries. The study includes a comprehensive characterization of the synthesized materials and a comparative analysis of their performance against commercial materials, significantly contributing to the advancement of electrocatalyst design for energy applications.

Results

This thesis achieved significant results in the development of carbon-based electrocatalysts. The synthesis of graphene materials through electrochemical exfoliation enabled the optimal incorporation of Pt nanoparticles, achieving excellent distribution and reduced particle size. This catalyst demonstrated superior performance in ORR and HER, with high stability and energy efficiency, outperforming the commercial Pt/C electrocatalyst while using less platinum (Figure 1).

Graphene-based materials enriched with nitrogen groups were also developed by integrating polyaniline and subsequent carbonization, which significantly enhanced their electrocatalytic properties towards ORR. Despite being metal-free, this material exhibited exceptional performance, opening the possibility of using metal-free catalysts for future applications. Additionally, a trifunctional composite material was created by combining poly(ionic liquids), graphene, and metal nanoparticles, achieving notable activity in ORR, HER, and oxygen evolution reaction (OER) with reduced platinum use.

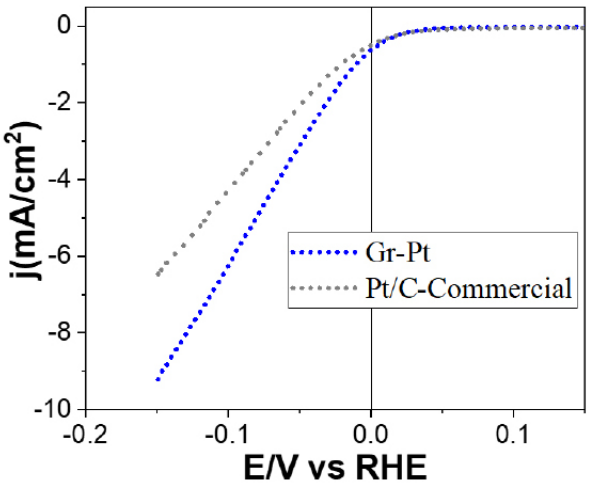

Figure 1. Linear sweep voltammograms for Gr-Pt and Pt/C-Commercial for HER, in 0.1M KOH saturated with N_2. Scan rate of 2 mV s^{-1} from 0.2 V to -0.15 v (vs RHE).

Furthermore, graphene-doped carbon fibers with metal nanoparticles were synthesized through electrospinning. These fibers demonstrated outstanding performance as electrodes in zinc-air batteries, showing improvements in charge-discharge voltage, durability, and stability, surpassing the commercial Pt/C material. Synergistic effects were observed between the carbon fibers and metal nanoparticles, particularly with palladium, resulting in high electrocatalytic activity with a lower metal loading.

Finally, Pt-based electrocatalysts on carbon supports were synthesized using a microwave-assisted method, achieving Pt nanoparticles smaller than one nanometer with high dispersion. These electrocatalysts showed high activity and selectivity for ORR and HER, as well as excellent stability and

resistance to CO poisoning, demonstrating superior performance compared to the commercial catalyst with lower platinum loading, highlighting their improved energy efficiency (Figure 2).

Conclusions

This PhD thesis has successfully developed and evaluated a variety of carbon-based electrocatalysts, demonstrating their significant potential in energy conversion and storage applications. Through innovative synthesis techniques, such as electrochemical exfoliation and electrospinning, graphene materials and carbon fibers were created with enhanced properties, including optimal distribution of metal nanoparticles and improved electrochemical performance. These materials exhibited superior activity in key reactions like ORR and HER, often outperforming commercial catalysts while using less metal content. The results also highlighted the successful development of metal-free graphene composites and multifunctional materials that demonstrated outstanding catalytic behavior across various conditions.

The work also emphasized the importance of material composition and synthesis methods in achieving high-performance electrocatalysts. For instance, nitrogen-doped graphene materials, polymer-ionic liquid composites, and fibers doped with palladium or platinum showcased excellent stability, durability, and activity. These findings underscore the potential of carbon-based materials, not only for their intrinsic properties but also for their ability to serve as effective supports for metal nanoparticles, leading to efficient, cost-effective, and sustainable alternatives in electrochemical applications, such as in zinc-air batteries and other energy storage devices.

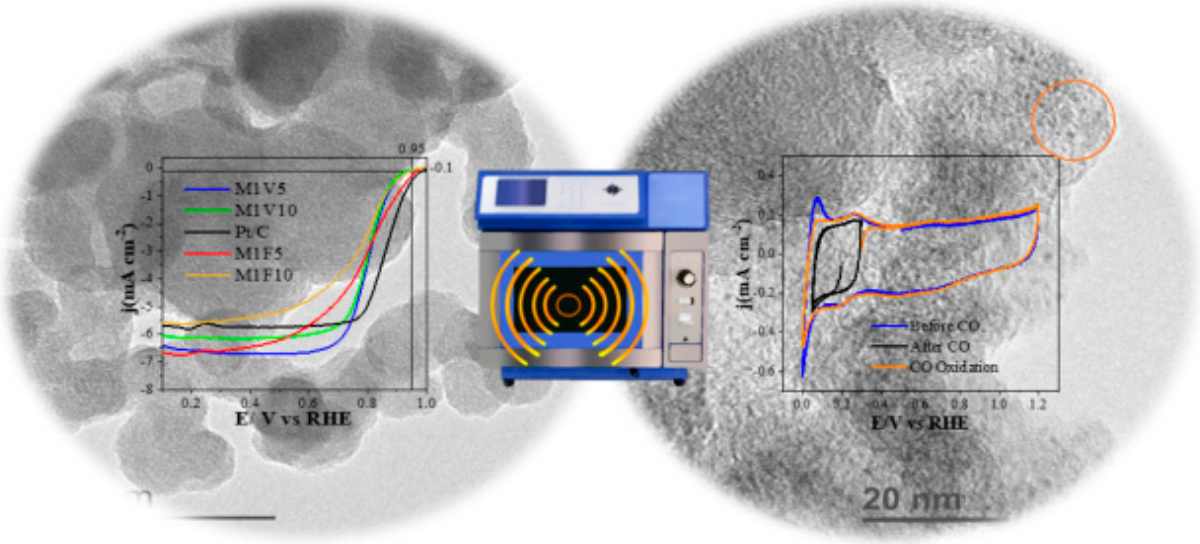

Figure 2. Linear sweep voltammograms for the electrocatalysts synthesized via microwave-assisted method, along with the evaluation of the CO poisoning resistance.

Acknowledgments

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Related publications

[1] C.D. Jaimes-Paez, E. Morallón, D. Cazorla-Amorós, Few layers graphene-based electrocatalysts for ORR synthesized by electrochemical exfoliation methods, Energy, Volume 278, Part A, (2023), 127888.

[2] C.D. Jaimes-Paez, E Vences-Alvarez, D. Salinas-Torres, E. Morallón, J.R Rangel-Mendez, D. Cazorla-Amorós. Microwave-assisted synthesis of carbon-supported Pt nanoparticles for their use as electrocatalysts in the oxygen reduction reaction and hydrogen evolution reaction, Electrochimica Acta, volume 464, (2023), 142871.

[3] C.D. Jaimes-Paez, F.J García-Mateos, R. Ruiz-Rosas, J. Rodríguez-Mirasol, T. Cordero, E. Morallón, D. Cazorla-Amorós, Sustainable synthesis of metal doped lignin-derived electrospun carbon nanofibers for the development of ORR electrocatalysts, Nanomaterials, 13 (22), 2921 (2023).

[4] C.D. Jaimes-Paez, M. García-Rollán, F.J García-Mateos, R. Ruiz-Rosas, J. M. Rosas-Martínez, J. Rodríguez-Mirasol, T. Cordero, E. Morallón, D. Cazorla-Amorós, Self-standing carbon fiber electrodes doped with Pd nanoparticles as electrocatalysts in Zinc-air battery, submitted for publication (2024).

Full Thesis can be downloaded from:
ttp://hdl.handle.net/10045/153375