High-performance and environmentally friendly electrocatalysts: perovskite, metal hexacyanoferrate, and carbon composites for Zn-batteries and beyond

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Objectives and novelty

The doctoral thesis investigates sustainable, low-cost, and safe alternatives for energy storage systems by developing advanced cathode materials for zinc-based batteries such as Zn-air (ZAB) and Zn-ion (ZIB) batteries, and electrocatalysts for the electrochemical reduction of nitrates (NO_3RR) to ammonia. The study focuses on synthesizing electrocatalysts based on perovskite-type metal oxides-carbon composites and metal hexacyanoferrates, optimizing green synthesis methodologies (including mechanochemical, hydrothermal, and sol-gel processes) to enhance electrochemical performance through improved particle size control, intimate phase interactions, and scalable, eco-friendly production routes.

A significant contribution of this work is its detailed examination of the role of the carbon material, which is pivotal in enhancing the electrocatalytic activity across all studied reactions yet often remain underemphasized in the literature, defined just as an "additive". By incorporating carbon materials, the results demonstrate improved electron transfer, increased exposure of active sites, and enhanced interfacial interactions with perovskite-type metal oxides, thereby enhancing the electrochemical performance in oxygen reduction (ORR) and oxygen evolution reactions (OER) for ZABs as well as the capacity in ZIBs. This comprehensive approach not only advances our understanding of electrocatalyst behavior but also paves the way for the development of more efficient and robust energy conversion systems based on materials mixed with carbon materials.

Results

The most significant outcomes of this doctoral work encompass the development and optimization of novel electrocatalysts that show enhanced performance in zinc-based energy storage systems and green ammonia synthesis. A major achievement is the successful synthesis of perovskite-type metal oxides-carbon composites and metal hexacyanoferrate-carbon materials-based electrocatalysts, which have been tailored for use as cathodes in ZABs and ZIBs, respectively. Through systematic studies using various synthesis methods, including mechanochemical processes (via a planetary ball mill), as well as hydrothermal and sol-gel treatments, this research demonstrated that optimizing key parameters in the mechanochemical approach (such as low rotation speeds, controlled atmospheres, and short milling times) produces electrocatalysts with smaller nanoparticles, more homogeneous phases, and stronger interactions between active metal oxides and the carbon material. These improvements directly translate into superior bifunctional for ORR and OER, key processes for the effective operation of these batteries.

Another remarkable result is the comprehensive investigation into the role of carbon materials in these electrocatalytic systems. The incorporation of carbon not only improves electrical conductivity but also enhances the dispersion of active sites, facilitates electron transfer, and increases the overall electrocatalytic efficiency. This synergistic effect was observed across multiple studies, including the *in-situ* synthesis of N-doped carbon encapsulated metal oxide nanostructures, followed by a CO_2 activation process, where the formation of porous carbon frameworks and active and well-distributed Co–N_x–C sites (Fig. 1A) significantly boosted electrocatalytic performance and ZAB durability. Additionally, by exploring the effect of Sr substitution in La-based perovskites, the work identified that lower levels of Sr doping (20 % molar ratio with respect La) preserve the perovskite structure while optimizing the oxidation states of Mn and Co, further enhancing the bifunctional electrocatalytic activity for ORR/OER in ZABs. Advanced characterization techniques, such as temperature-programmed desorption/reduction (TPD/TPR), X-ray photoelectron spectroscopy (XPS), and Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM) tomography, provided deep insights into the structural and interfacial properties of the electrocatalysts. Specifically, the interaction between perovskite-type metal oxides and the carbon material was measured using the TPD technique, serving as a descriptor of the bifunctional electrocatalytic activity toward ORR/OER (Fig. 1B).

Additionally, the distribution of elements in the GDL was analyzed before and after a stability experiment in the ZAB to understand degradation processes, even though the sample was stable up to 120 h of charge-discharge ZAB cycling (Fig. 2). A different distribution of La within the carbon matrix of the GDL was observed, moving away from the region near the electrolyte, while the electroactive elements remained unchanged. Moreover, the study introduced a green mechanochemical synthesis approach that not only reduced the environmental impact of

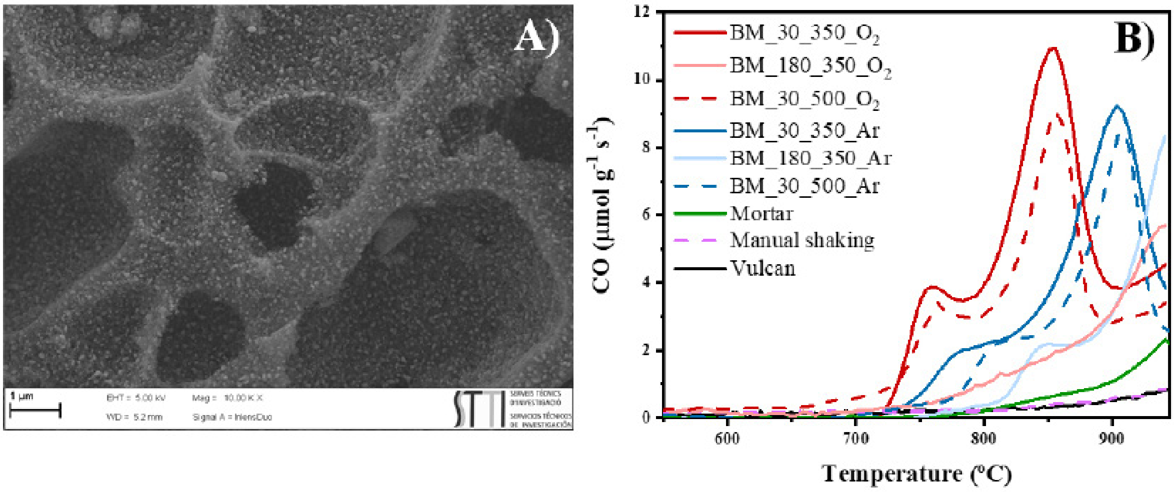

Figure 1. A) SEM image of the in-situ developed electrocatalyst. B) TPD technique results for the perovskite-type metal oxide-carbon composites.

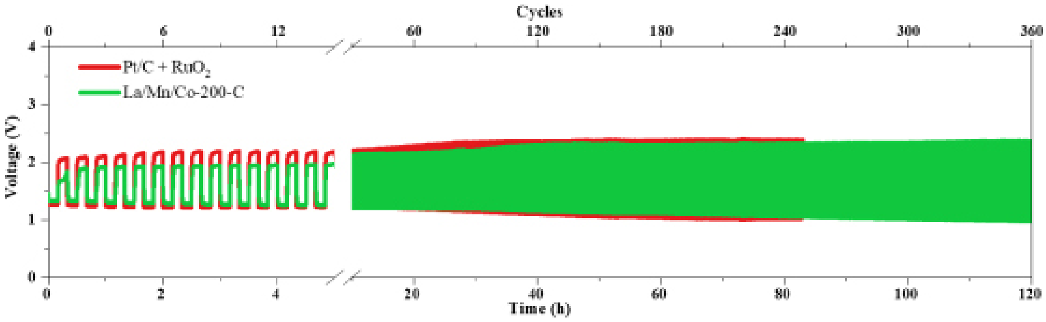

Figure 2. Long-term charge-discharge ZAB stability test. The La/Mn/Co-200-C sample is composed of a mixture of lanthanum, cobalt, and manganese (hydro-)oxides mixed with carbon black material (Vulcan XC72-R).

electrocatalyst production, measured by the E-factor, but also resulted in materials with outstanding electrochemical performance, thereby emphasizing the potential for scalable, eco-friendly manufacturing. Finally, the exploration of ZIBs cathodes through the structural modification of zinc hexacyanoferrate-carbon composites underscored the importance of phase transitions and $[Fe(CN)_6]$ vacancy formation in enhancing electroactivity, enhancing the capacity values.

Conclusions

The conclusions of this doctoral research underscore the potential of innovative cathode materials based on metal oxide perovskite-carbon composites and metal hexacyanoferrates for advanced zinc-based batteries and green ammonia synthesis. The work demonstrates that optimized green synthesis strategies, such as mechanochemical, hydrothermal and sol-gel processes, can significantly enhance the electrocatalytic performance.

Advanced characterization techniques such as XPS, TPD/TPR, and FIB-SEM have provided valuable insights into the interfacial interactions between electrocatalyst components and the gas diffusion layer, revealing differentiated behavior of Mn, Co, and La during operation. The study also introduces innovative synthesis strategies, including a CO_2 activation process for in-situ formation of metal nanoparticles encapsulated in nitrogen-doped carbon and a solid-state synthesis method with a low environmental impact. In Zn-ion batteries, the ball-milling of zinc hexacyanoferrate in the presence of carbon materials has been shown to preserve structural integrity and enhance performance through the creation of $[Fe(CN)_6]$ vacancies. Collectively, these findings not only advance the development of high-performance, sustainable energy conversion and storage systems but also underscore the crucial role of carbon materials in catalysis, a factor often underemphasized in the existing literature.

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Related publications

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