

Synthesis and characterization of hybrid materials based on Keggin Polyoxometalate fixed on carbon as oxygen reduction reaction electrocatalysts in near neutral aqueous media

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The development of high-performance energy storage devices has been increasing in demand to enable the widespread use of renewable energy sources.

The pursuit of efficient and sustainable energy storage technologies has induced the exploration of devices such as Zn-air batteries and fuel cells, whose performance largely relies on the efficacy of electrocatalysts for oxygen reduction reactions (ORR) at the cathode.^[1] These are the most suitable candidates to meet the energy storage demand.

Despite considerable efforts, the development of cost-effective electrocatalysts that exhibit exceptional activity for ORR remains a substantial challenge as it faces obstacles due to its dependence on expensive and limited metal catalysts, such as platinum.^[2] On top of this, most work in the ORR field is conducted in highly acidic or alkaline media.

These electrolytes might work for both technologies in principle, but the need for mild near-neutral electrolytes for Zn-based devices has become obvious ^[3] in order to extend battery life. However, even though these electrolytes avoid unwanted reactions at the Zn anode, it is necessary to develop catalysts optimized for these pH values instead of those traditionally used.

Hence, this study investigates the methodologies and catalytic performance of hybrid materials composed of polyoxometalates (POMs) and carbon as ORR electrocatalysts for near neutral electrolytes with potential application in Zn-air batteries. The hybrid materials exhibit promising ORR catalytic activity, facilitating efficient electron transfer among

clusters attributed to carbon while offering high surface area, global conductivity and substantial stability.

In this work, we present the synthesis and characterization (SEM, XPS, XRD, FTIR and CV) of hybrids materials Co-containing $K_5H[Co^{+2}W_{12}O_{40}]$ – Keggin-type POM in two different carbon materials, Ketjenblack EC600 JD (Carbon black) and YP-80F Active carbon, tested in different near neutral electrolytes (pH=5 - 7), as well as their clear role as ORR electrocatalysts.

References

- [1] Bruce PG. et al. *Nat Mater.* Li-O₂ and Li – S batteries with high energy storage. **2012**, *11*, 19 -30.
- [2] F. Dawood, M. et al., *Int. J. Hydrogen Energy.* **2020**, *45*, 3847–3869.
- [3] Aroa R. Mainar. et al. *Journal of energy storage.* An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc. **2018**, *15*, 304 – 328.

Figures

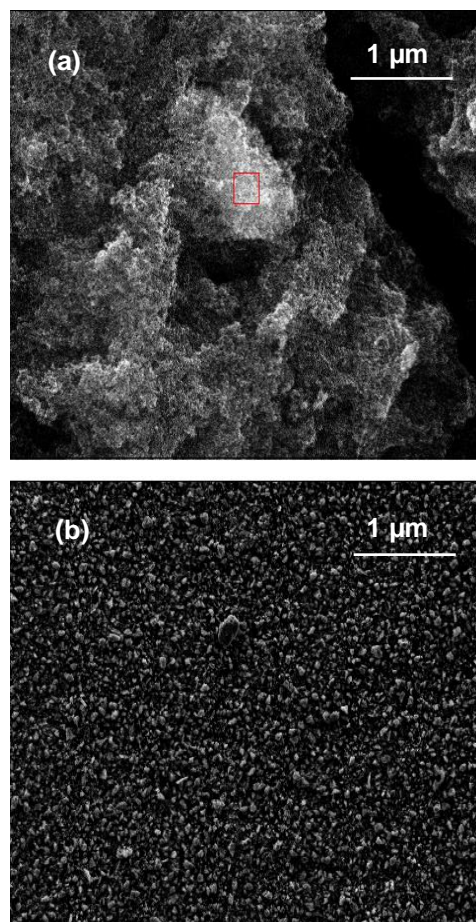


Figure 1. SEM images of (a) $Co^{+2}W_{12}@KB$ and (b) $Co^{+2}W_{12}@YP-80F$, at 20000 x magnification.

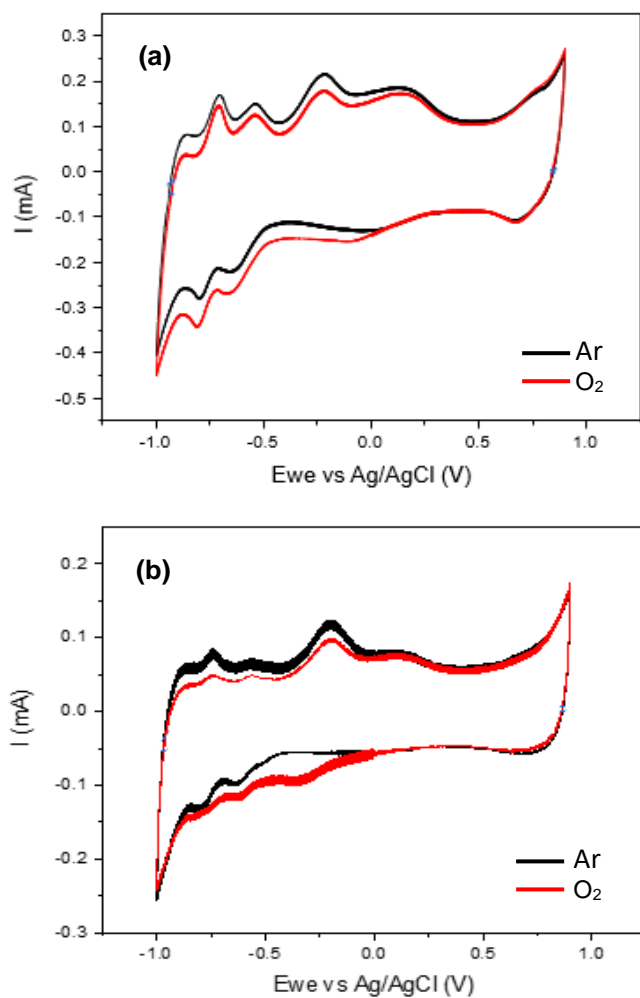


Figure 2. CV of (a) Co²⁺W₁₂@YP-80F (b) Co²⁺W₁₂@KB in Ar-saturated (black line) and O₂-saturated (red line) 0.5 M Zn (OAc)₂, pH=5 solution.