Polyoxometalate enabled Zn-air battery at near-neutral pH

Riccardo Argurio[1], Andrea Inclan[1], Rosa Maria-Gonzalez-Gil[1], Adrian Crespo-Villanueva[2], Leandro Bengoa Abraham[1], Nieves Casañ Pastor[2], Pedro Gomez-Romero[1]

[1]Institut Català De Nanociència I Nanotecnologia (ICN2), UAB Campus, Barcelona, Spain
[2]Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), UAB Campus, Barcelona, Spain

*riccardo.argurio@icn2.cat

Designing advanced electrocatalysts for catalyzing the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is of great importance for practical applications in metal-air batteries [1][2]. With the rising cost of benchmark catalysts that consist of noble metals (Pt, Ru, Ir) both for ORR (Pt/C) and OER (RuO_2, IrO_2, PdO), the research has shifted to low-cost transition metal alternatives, such as polyoxometalates (POMs) and their hybrids with carbon-based materials and doped carbon materials (N, P, S). POMs are an incredible variety of novel materials that can be used as electrocatalysts for Zn-air batteries to enhance the OER-charge and ORR-discharge – two main reactions at the O_2 cathode of a metal-air battery.

In this work, a Keggin-type ($Co^{3+}Co^{2+}W_{11}$) polyoxometalate (POM) has been anchored to reduced graphene oxide (rGO-POM) and activated carbon (YP80F-POM) via a hydrothermal reaction method. The synthesis approach consisted first of making graphene oxide (GO_x) by modified Hummer's method. The polyoxometalates were prepared in three batches consisting first of: $Co^{2+}Co^{2+}W_{11}$ POM, $Co^{2+}W_{12}$ POM, and intermediaries POM which were P_2W_{18}, P_2W_{12}, and P_8W_{48}. The physical characterization has been done using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Fourier-transfer infrared spectroscopy. The electrochemical characterization of the hybrids and POMs on their own was done using a rotating disk electrode (RDE) with a glassy carbon tip (GCE). The parameters studied include onset potential, overpotential, limiting current density, electron transfer number. A novel two Co-complex POM with two Co^{2+} and Co^{3+} oxidation state allows for enhanced ZAB performance with high open circuit potential (OCV) of 1.66 V in a near-neutral/acidic electrolyte.

The hybrid rGO-POM and YP80F-POM exhibit enhanced electrochemical activity at pH 4-7 range electrolyte solution, showing promising performance in Zn-air -near-neutral devices.

References

[1] Y. Li, J. Lu, ACS Energy Lett., 2, 6, (2017), 1370–1377.

[2] F. Cheng, J. Chen, Chem. Soc. Rev, 41, (2012), 2172-2192.

[3] S. P. Nandan, N. I. Gumerova, et al. ACS Materials Au, 2 (4), (2022), 505-515.

Figures

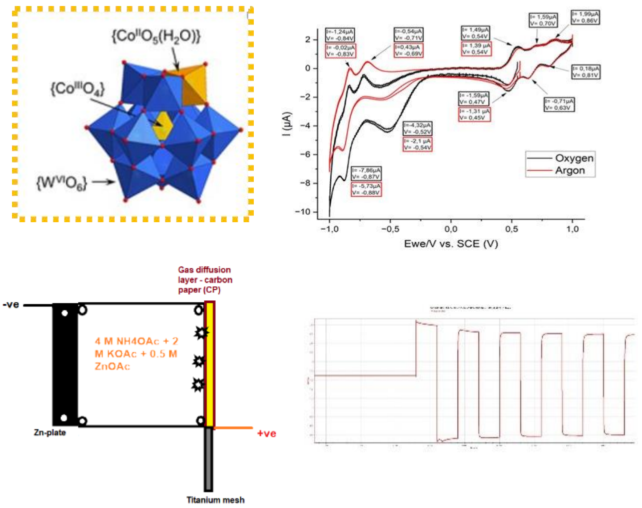

Figure 1. (a) $Co^{3+}Co^{2+}$W11 POM structure [3], (b) cyclic voltammetry (CV) of $Co^{3+}Co^{2+}$-POM in solution of 1.6 M NH_4OAc_2 + 0.5 M $ZnOAc_2$, (c)Zinc-air battery configuration, (d) ZAB charge-discharge performance.

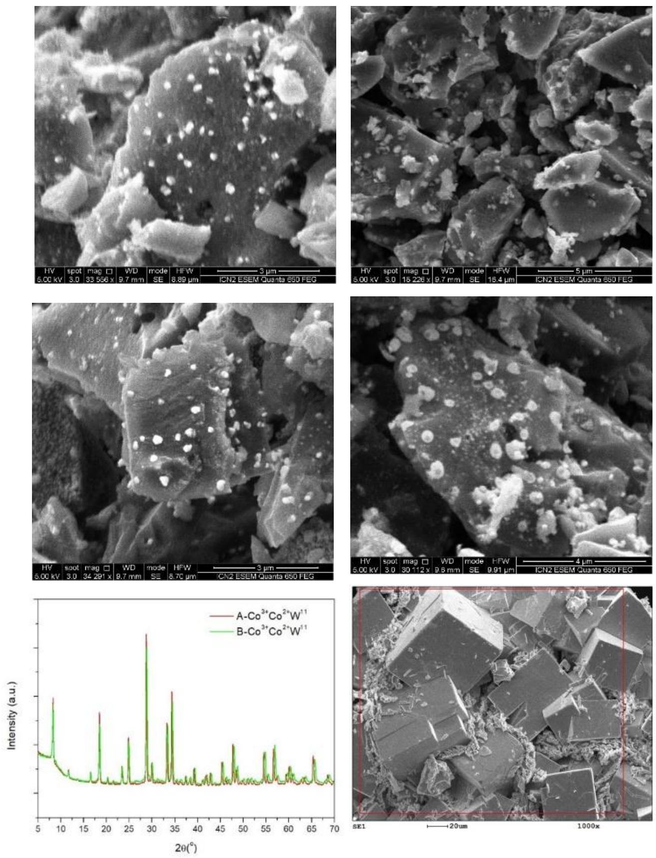

Figure 2. SEM of rGO-POM and YP80F-POM hybrids at high and low resolutions (a-d), XRD and SEM of $Co^{3+}Co^{2+}W_{11}$ (e-f)

Acknowledgments

The authors would like to acknowledge the financial support provided by Ministerio de Ciencia y Innovacion (MCIIN), the Agencia Estatal de Investigacion (AEI) and NextGenerationEU/PRTR (TED2021-130205B-C2) for this research activity. L.N. Bengoa wants to thank the European Union for providing a Marie Curie Postdoctoral Fellowship (Grant 101062498-POMZAB) to join ICN2. The ICN2 is funded by the CERCA programme/Generalitat de Catalunya and supported by the Severo Ochoa Centres of Excellence programme, Grant CEX2021-001214-S, funded by MCIN/AEI/10.13039.501100011033.