Effect of transition metals on the electrocatalytic activity of N-doped carbon composites derived from polydopamine for oxygen evolution and oxygen reduction reactions

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In recent years, renewable energies have played an essential role in the technological development to meet energy demand and replace fossil fuels. At the same time, new challenges have arisen in order to implement clean energy production. The problem to store renewable energy that is obtained intermittently in the long term has led the development of fuel cells, electrolyzers and unitized regenerative fuel cells (URFC) to use hydrogen as an energy vector. URFCs can be used for both electric power production and hydrogen generation by adapting to the energy needs of the power grid. The most recent studies using an anion exchange membrane as electrolyte have opened up a range of possibilities for synthesizing new catalysts by replacing noble metals such as Pt, Ir or Ru with cheaper transition metals in combination with N-doped carbon structures [1]

This work focuses on the development of noble metal-free bifunctional electrocatalysts for the oxygen electrode of unitized regenerative alkaline fuel cell (UR-AFC), where oxygen evolution (OER) and reduction (ORR) reactions take place [2]. Composites based on non-precious metals such as Ti, Mn, Fe, Co, Ni or Zn, and nitrogen-doped carbonaceous nanostructures obtained from polydopamine have been prepared.

For the physiochemical characterization, transmission electron microscopy (TEM) to determine the morphology of the carbonaceous materials and metallic particles, X-ray photoelectron spectroscopy (XPS) to determine the surface composition and chemical state, X-ray diffraction (XRD) to determine the crystalline phases, and chemical analysis (ICP-MS) and elemental analysis to determine the bulk composition have been used. For the electrochemical characterization, ORR and OER electrocatalysis performance have been carried out in a three-electrode electrochemical cell in 0.1 M NaOH, using a rotating disk electrode as working electrode.
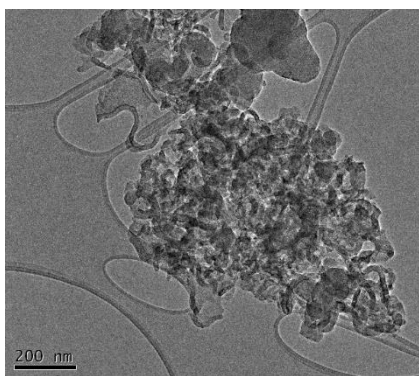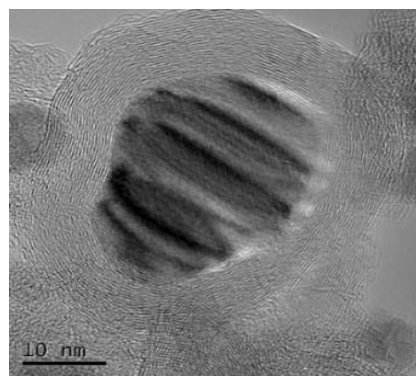

Figure 1. Carbon structure of Zn-NC.

Figure 2. Co nanoparticle encapsulated in N-doped carbon layer in Co-NC catalyst.

The synthesis of the catalysts is based on the coordination of the different transition metals with the dopamine monomers forming coordination compounds in solution. The ligands are then polymerized to generate a polymer that traps the metals inside [3]. This "encapsulation" of the metal protects it during electrochemical reactions and keeps it more stable. The carbonization process is performed in two steps. First of all, the materials are subjected to hydrothermal carbonization and then, pyrolysis is carried out at high temperature to form active and stable composites in the ORR and OER. Figure 1 shows the carbon structure of Zn-NC, where zinc was evaporated during pyrolysis. Figure 2 shows Co nanoparticle encapsulated in N-doped carbon layer in Co-NC catalyst.

The electrochemical measurements show an important effect of the transition metal on the ORR and OER in alkaline environment. The addition of metal to the polymer modifies carbon structure and the electrocatalytic properties of the carbonaceous materials. For ORR, the catalysts with Fe, Mn and Co prove to be the most promising with the onset potential around 0.87 V vs RHE, as well as the limiting current obtained is above 3.6 mA/cm². In the case of OER, some of the composites are not active and others suffer degradation from the high potentials applied during the measurement. The Co-NC is the closest to the Iridium oxide standard with an overpotential of 0.4 V at 10 mA/cm² without hard

degradation of the carbon. Comparing the activity of all composites prepared in the two reactions, Co-NC shows the best activity and properties to for performing both reactions in the oxygen electrode of UR-AFC. Besides, bifunctional grade of Co-NC, measured as the overpotencial in both reactions, is better than commercial catalyst such as PtC 20% or IrO_2.**Acknowledgments**
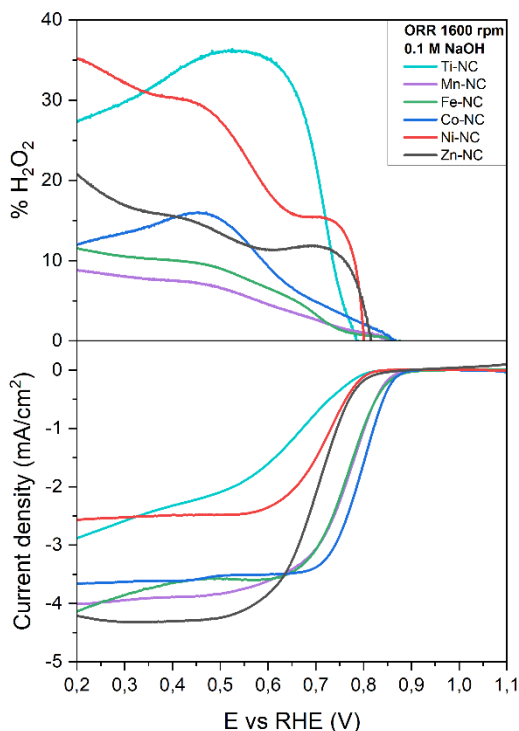

Figure 3. ORR electrochemical characterization with RRDE at 1600 rpm in O_2-saturated 0.1 M NaOH. ORR current density at the disk and %H_2O_2 measured during ORR at the ring.
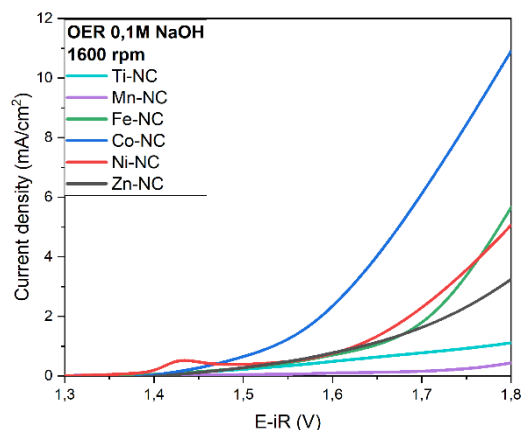
Figure 4. OER electrochemical characterization with RRDE at 1600 rpm in Ar-saturated 0.1 M NaOH.

Acknowledgments

References

[1] J.M. Luque-Centeno et al., Electrochim. Acta **331** (2020) 135396
[2] I. Katsounaros et al., Angew. Chem. Int. Ed. Engl. **53(1)** (2014) 102-21.
[3] Y. Liu, K. Ai, L. Lu, Chem. Rev. **114** (2014) 5057-5115