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Effect of the central metal in Schiff bases for the electroreduction and evolution of oxygen for energy storage systems.

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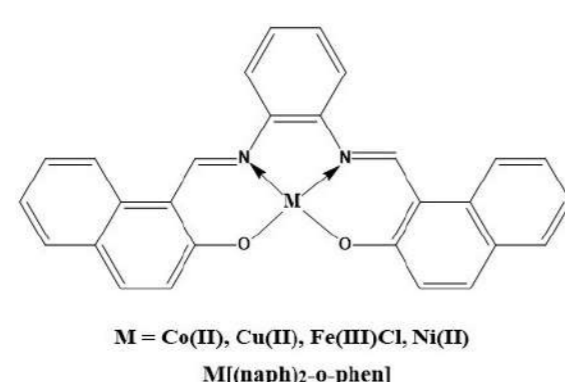
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1. Introduction

The oxygen reduction reaction (ORR) and evolution reaction (OER) are widely used in systems such as fuel cells and metal-air batteries. The search for stable, low-cost bifunctional electrocatalysts, that is, not based on precious metals, and environmentally friendly that present high activity toward these reactions is very important for progress in the development of new technologies associated with the storage of energy. Schiff base complexes have received a great deal of attention due to their potentially diverse applications in many fields, such as catalysts for ORR and OER, among others. These complexes can form adducts with oxygen, presenting catalytic activity toward ORR through charge transfer under specific conditions. On the other hand, the performance of these complexes is related to the structure of the ligands, the central metal as well as the interactions between the ligand and the metal. This study compares the catalytic effect of the central metal of a Schiff base ($M[(naph)(o-phen)]$) with different central metals ($M = Fe, Co, Ni$ and Cu) toward RRO and EOR.

2. Experimental

Two equivalents of 2-hydroxybenzaldehyde were mixed with one equivalent of 2,3-diaminonaphthalen in ethanol which resulted in a dark yellowish orange precipitate of $(naph)_2-o-phen$. This was complexed with one equivalent of the corresponding metal salt to give the product $M[(naph)_2-o-phen]$, which was then filtered, washed with cold water, and air dried.



Electrochemical measurements were carried out using a bipotentiostat (CHI900B) in a three compartment electrochemical cell. A rotating ring disk electrode (RRDE) with a disk of glassy carbon, and a ring of Pt were used as working electrodes. A Pt wire was the counter electrode and Ag/AgCl (KCl sat.) was the reference electrode.



The ink was prepared with active material, 833 μ L of deionized water, 167 μ L isopropanol and 20 μ L of 5% Nafion solution.

3. Results

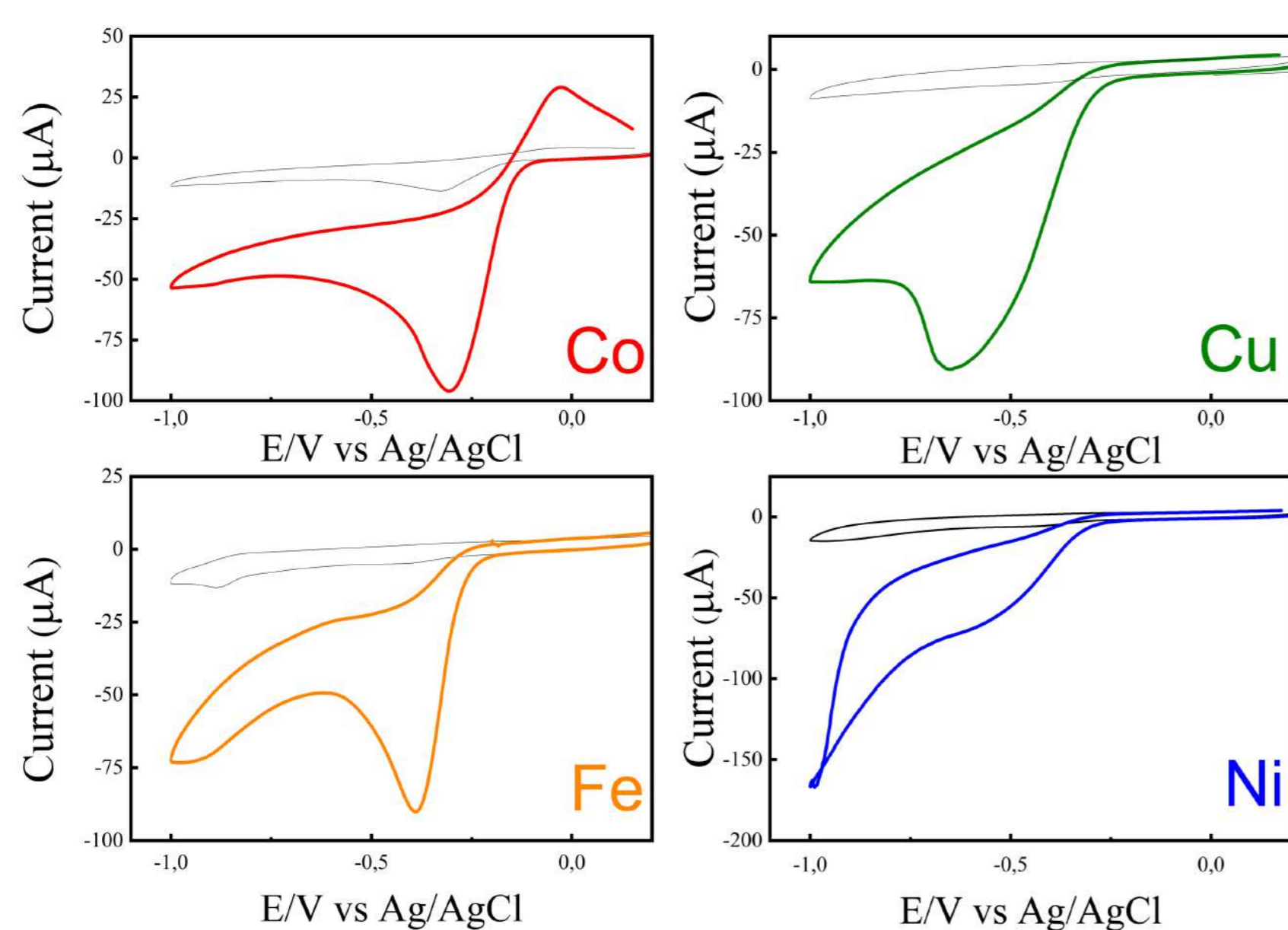


Fig. 1. Cyclic voltammograms of $M[(naph)(o-phen)]$ catalysts in 0.1 M KOH solution in O_2 saturated (color line) and N_2 saturated (grey line) at a scan rate of 10 mV s^{-1}

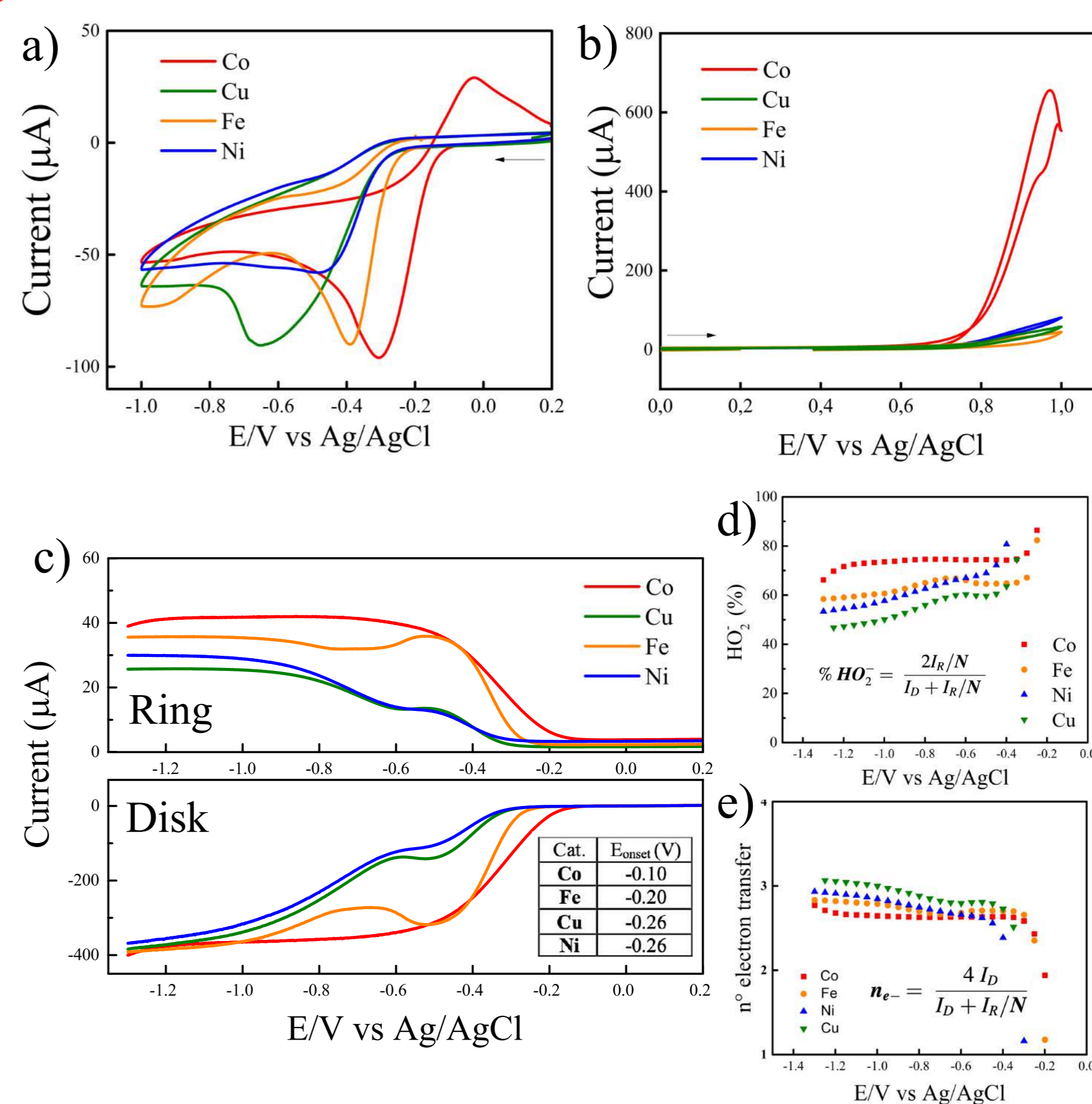


Fig.2. Cyclic voltammograms of $M[(naph)(o-phen)]$ for ORR(a) and OER(b). LSV profiles for ORR using RRDE, with disk modified with different catalysts at 1600 rpm at a scan rate of 10 mV s^{-1} , at a fixed potential of 0.47 V on the ring electrode (c) percentage of peroxide (d) and number of transferred electrons (e).

4. Conclusions

The preliminary results suggest that for the ORR reaction, the Cu complex is the one that presented the best response in terms of lower peroxide formed and high number of transferred electrons, (values close to 4 electrons). Co, instead generates a large amount of peroxide. In the case of OER, to avoid the use of Co, Ni can be used which shows reasonable catalysis toward this reaction, followed by Fe. Preliminary results indicate that a combination of Cu, Ni and Fe complexes in bifunctional oxygen catalysis would be a viable alternative to the use of Co.

5. References

[1] J. Amici et al. *Journal of Power Sources* 546 (2022) 231942

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