

### Tuning the Cu(II)/(I) formal potential of Copper Phenanthrolines adsorbed on graphite electrodes for ORR maximum activity.

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In previous works it has been reported that the activity of MN4 macrocyclic transition metal complexes is related with the formal potential of catalyst and the reversible potential of the reaction in study [1-3]. The formal potential of the catalyst can be "shifted" by placing electro-withdrawing or electro-donor substituents on the ligand [4].

Based on these findings, the present work is focused on the study of the oxygen reduction reaction (ORR) catalyzed by copper bis-phenanthrolines with different substituents. Although the activity of copper 1,10-phenanthrolines for the oxygen reduction reaction is known [5], there are no systematic studies to understand the effect of the chelates on the catalyst activity. Figure 1 shows the effect of different substituents on the phenanthroline ligand, and they can tune the Cu(II)/(I) formal potential in a range of 200mV from the unsubstituted ligand. It is noteworthy that the position of the substituent brings significant changes in the formal potential (see differences between 5-Cl-phen and 2-Cl-phen). Complexes with more positive formal potential exhibit higher activity, but all the complexes present similar Tafel slopes between 120mV/dec and 200mV/dec in pH 5.8. Tafel slopes decrease to 60mV/dec in pH 13 solutions.

In this work we have found a first approximate correlation between the formal potential of different substituted copper phenanthrolines and the reversible potential of the ORR reaction. Hypothetically the highest catalytic activity can be reached by chemically shifting the formal potential of the catalyst to approach the reversible potential of the ORR.

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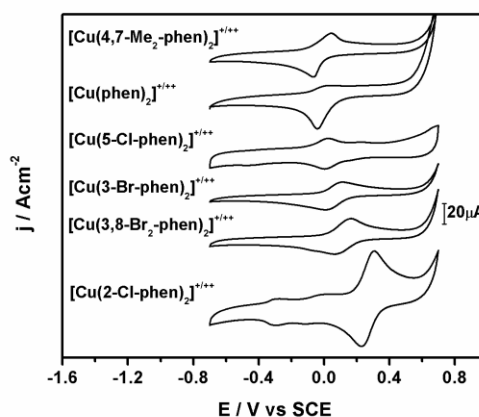


Fig. 1. Cyclic voltammograms of the EPG modified with  $\text{Cu}(\text{phen})_2$  with different substituents on phen ligands, recorded in  $\text{N}_2$  saturated 0.1M  $\text{NaClO}_4$  buffered solution, pH 5.2.