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Benchmark Density Functional Theory Approach for the Calculation of Potential Redox Applied in the Study of CO_2 Electroreduction Reactions

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Molecular electrocatalysis based on 3d transition metal compounds plays a crucial role in various applications, including CO_2 reduction, [1-3] water splitting, [4,5] oxygen reduction, [6] and hydrogen evolution reactions. [7] In this context, Quantum Chemistry (QC) approaches can be employed to study reaction mechanisms, optimize ligand structures, and enhance selectivity toward products of industrial interest.

The first step in these theoretical studies is to identify a reliable Quantum Chemistry (QC) method, such as density functional theory (DFT), to accurately describe key thermodynamic properties commonly used in this type of application. One such property is the redox potential. [8] For first-row (3d) transition metal electrocatalysts, it is particularly challenging to establish a well-defined protocol for calculating redox potentials, as these systems can be large and often exhibit complex electronic structures.

This work presents preliminary results from the investigation of two methods available in the literature for calculating the redox potential for a one-electron reduction in a copper-based porphyrin employed in CO_2 reduction reactions. [9-11] Furthermore, a brief benchmark study was conducted to determine the most suitable functional for calculating the redox potential of these species. The selected methodology will be used in subsequent studies on the CO_2 reduction reaction mechanism for this system as reported in the literature.

(a)

$$E^{\circ}_{O/R} = \frac{G^{\circ}(O,aq) + n_p G^{\circ}(H^{+},aq) + n_e G^{\circ}(e^{-},g) - G^{\circ}(R,aq)}{n_e \mathrm{F}} - E^{\circ}_{SHE}$$

(b)

$$E^{\circ}_{O/R} = \frac{G^{\circ}(O,aq) + G^{\circ}(FeCp^{0},aq) - G^{\circ}(\mathrm{R,aq}) - G^{\circ}(FeCp^{+},aq)}{n_e \mathrm{F}} + 0.64\mathrm{V}$$

(c)

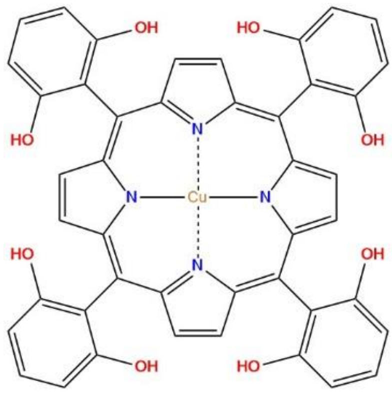

Figure 1. (a) Direct method to calculate redox potential in liquid-phase, (b) Isodesmic method to calculate redox potential in liquid-phase, here a theoretical redox coupe is employed. (c) Catalyst that was chosen to further studies in the mechanism of CO_2RR.

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