

ABSTRACT

The effects of different redox mediators on the oxygen reduction reaction (ORR) catalyzed by an iron porphyrin complex, iron(III) *meso*-tetra(*N*-methyl-4-pyridyl)porphine chloride [Fe^{III}TMPyP], in 0.1 M triflic acid were investigated by cyclic voltammetry (CV) and spectroelectrochemistry in conjunction with density functional theory (DFT) calculations. The formal potentials of the Fe^{III}TMPyP catalyst and the redox mediators, as well as the half-wave potentials for the ORR, were determined by CV in the absence and presence of oxygen in acidic solutions. UV/Vis spectroscopic and spectroelectrochemical studies confirmed that only the 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)diammonium salt (C₁₈H₂₄N₆O₆S₄) showed effective interactions with Fe^{III}TMPyP during the ORR. DFT calculations suggested strong interaction between Fe^{III}TMPyP and the C₁₈H₂₄N₆O₆S₄ redox mediator. The redox mediator caused lengthening of the dioxygen iron bond, which thus suggested easier dioxygen reduction. Consistent results were observed in electrochemical impedance spectroscopic measurements for which the electron-transfer kinetics were also evaluated.