

Probing Oxygen Reduction Mechanism of Copper/triazoles Complexes Based Electrochemicals by EPR Spectroscopy

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Developing active, inexpensive non platinum (Pt) based oxygen reduction reaction (ORR) electrocatalysts materials to replace expensive Pt-based catalysts is a necessary and essential endeavor for decreased dependence on combustion engines and commercialization of PEMFC to serve our daily need for automotive propulsion. Extensive research has been conducted on pyrolyzed Fe or Co-based electrocatalysts. Good activity and stability have been achieved for these sort of non precious metal catalysts. Questions about the fundamental understanding of ORR by these catalysts arise upon the achievement of these competitive alternatives. In our previous work, we have synthesized a series of copper/triazoles complexes based electrocatalysts and characterize their ORR activity substantially by electrochemical techniques.¹

To gain deeper understanding of the ORR mechanism, we took advantage of the paramagnetic property of copper (II), and its resultant EPR activity, and characterized the complexes prepared from different substituted triazoles extensively. In Figure 1, we show the EPR spectrum of different substituted copper(II) complexes obtained at the X band. The spectrum indicates that triplet states are significantly populated in our complexes, indicating a multinuclear feature of our complexes.^{2,3} The relative intensity of half field and full field transitions have been correlated to different exchange interactions between copper(II) centers qualitatively.⁴ An in-situ electrochemical flow cell was designed for the cavity of our EPR spectrometer to investigate both the evolution of the oxygen reduction reaction and copper EPR signal simultaneously. Hydrodynamic and electrochemical properties of the flow cell will be explored to enable a quantitative correlation between the EPR signal and current/potential response. In addition, possible intermediates and kinetic parameters of the oxygen reduction reaction will be reported in the presentation.

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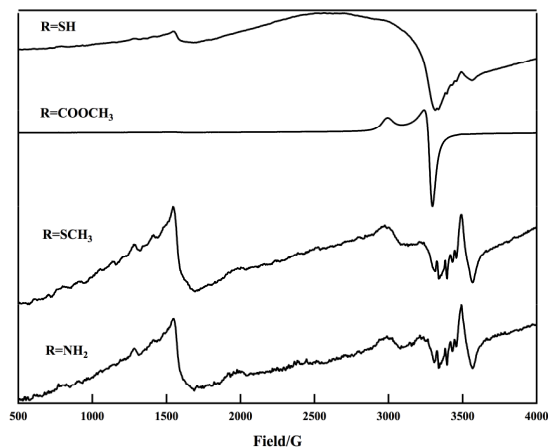


Fig. 1 EPR spectra of copper(II)/3-amino, 5-substituted-1,2,4-triazole complexes obtained at the X-band