Electrochemical Electron Paramagnetic Resonance (EPR): Instrumentation and Application

M. A. Tamski [(1)], E. Braxton,[(2)] B. G. Breeze[(1)] and M. E. Newton[(1*)]

[1]Department of Physics, University of Warwick, Coventry, UK; [2]Department of Chemistry, University of Warwick, Coventry, UK

Resumo: Due to its high sensitivity towards paramagnetic species, Electron Paramagnetic Resonance (EPR) can provide key information about radical species generated or consumed during electrode reactions. EPR thus complements electrochemical data by directly identifying radical species, confirming reaction mechanisms, and revealing subtle interactions, for example, between the radical and its environment. As such, EPR has not only provided a wealth of information to electrochemists, but EPR spectroscopists have also found electrochemical generation to be a feasible option to standard chemical and optical generation of radical species. Two aspects are focused on in this talk.

(1) In electrochemistry, micro-electrodes are extremely advantageous due to properties such as e.g. diminished ohmic drop, shorter cell time constants and enhanced mass transport, etc. It is thus of considerable interest to deploy microelectrodes with EPR, however no commercial in-situ electrochemical EPR systems coupled to microelectrodes currently exist. We thus describe the development of integrated in-situ EPR cells for combined microelectrode-EPR measurements, showcasing experimental design and results with finite element modelling, the latter used to optimise the hydrodynamic properties of the EPR cell and predict the electrochemical performance.[1,2] (2) In the second application we focus on a specific electrochemical problem, identifying hydroxyl radical generation on boron doped diamond (BDD) electrodes using combined electrochemical-EPR methodologies. Hydroxyl radicals are incredibly important in the oxidative breakdown of organic pollutants and BDD, due to its low electrocatalytic activity can produce hydroxyl radicals via an alternative water oxidation route. Here was show how using EPR it is possible to determine switch on potential for hydroxyl radical generation and track quantitatively radical numbers as a function of applied potential.

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Referências:
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* **e-mail do autor principal:** m.e.newton@warwick.ac.uk