On the Role of Carbonate and Bicarbonate Electrolytes in the Electrochemical Oxidation of Water to Hydrogen Peroxide

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Electrochemical two-electron water oxidation (2e-WOR) is currently being explored as an alternative and more sustainable method for the production of hydrogen peroxide (H2O2), which is currently produced industrially using the highly energy-intensive anthraquinone process. [1] Metal oxide-based catalysts such as CaSnO3, BiVO4 and ZnO have been shown to be highly active catalysts for WOR. Additionally, boron-doped diamond (BDD) electrodes have been suggested as active and stable electrodes (2,3).

Despite the growing interest in electrochemical oxidative peroxide formation, little knowledge so far exists about the reaction mechanism, the contribution of the electrolyte, and concerns remain regarding the actual product distribution and the concentration of free hydrogen peroxide.

The objective of this study is to provide mechanistic insights and to elucidate the impact of electrolyte composition on 2e-WOR. Rotating ring disc experiments (RRDE) with a BDD disk electrode were employed to achieve rotation-rate dependent in-situ detection of hydrogen peroxide. Our analysis indicates a strong dependency of electrolyte composition and concentration, rotation rate and applied potential on the sensitivity for hydrogen peroxide detection. The role of chemical equilibria is discussed, and evidence is provided for an electrolyte-dependent indirect oxidation and hydrolysis reaction mechanism.

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