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Unraveling Ethanol Electro-Oxidation Mechanisms and Interfacial pH Changes via Rotating Ring-Disk Electrode Analysis

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The rotating ring-disk electrode (RRDE) system, introduced by Albery and Calvo [1], is a robust technique for analyzing mass transport by convection, mathematically based on the Koutecký-Levich equation. Its unique configuration, which spatially separates the working electrodes (disk and ring), enables real-time monitoring of reactive products generated at the disk [2]. This feature is particularly valuable for understanding the ethanol electro-oxidation mechanism, which is the focus of this study. In this work, an electrochemical cell equipped with a disk-ring electrode—comprising a platinum (Pt) disk and a platinum (Pt) ring - was used. coupled to a bipotentiostat and operated under an argon atmosphere. Measurements were conducted at rotation rates of 0, 400, and 1600 rpm to evaluate and compare mass transport effects, as well as at scan rates of 30 and 50 mV·s⁻¹. Initially, the system was conditioned in a 0.1 mol·L⁻¹ NaOH solution (pH 13) to ensure a high concentration of hydroxyl ions. The primary objective in this initial step was to measure the hydrogen evolution reaction (HER) region in the RRDE under varying rotation and scan rates. Subsequently, ethanol (1 mol·L⁻¹) was added to the electrolyte to investigate its electro-oxidation, and the HER region was measured again under the same conditions. The ring was polarized at 0 V vs. RHE, while cyclic voltammetry was applied to the disk to monitor the deprotonation of ethanol at the disk. The interfacial pH variation (ΔpH) was estimated using the method proposed by Figueiredo et al. [3]. The results indicated progressive acidification of the electrode/solution interface, with ΔpH values ranging from -0.829 to -1.116 units for scan rates of 30 and 50 mV·s⁻¹. Additionally, the ring current response was monitored during oscillatory dynamics techniques applied to the disk to examine alcohol dehydrogenation. This approach revealed the potential for detecting ethanol intermediates through controlled mass transport dynamics, offering new insights into the reaction mechanism and advancing ongoing research in this field.

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References:

[1] W. J. Albery, E. J. Calvo, J. Chem. Soc., <u>Faraday Trans</u>. 1 1983, **79**, 2583–2596.

(Ring-disc electrodes. Part 21. - pH measurement with the ring.)

[2] S. Hessami, C. W. Tobias, <u>AIChE Journal</u>. 1993, **39**, 149–162.

(In-situ measurement of interfacial pH using a rotating ring-disk electrode.)

[3] M. C. Figueiredo, R. M. Arán-Ais, V. Climent, T. Kallio, J. M.

Feliu, ChemElectroChem 2015, 2, 1254-1258.

(Evidence of local pH changes during ethanol oxidation at Pt electrodes in alkaline media.