Electrooxidation of Ethanol: From Electrochemical Oscillations to Molecular Mechanisms

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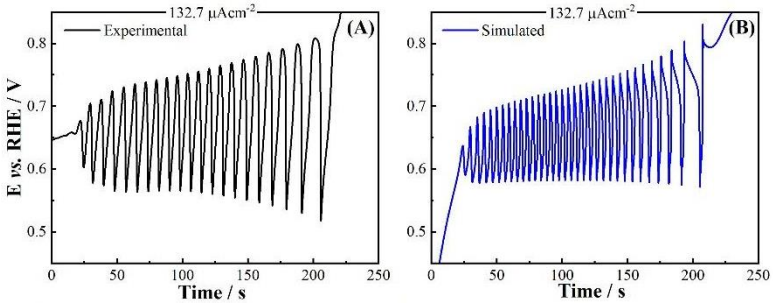
This study presents an innovative microkinetic model that elucidates both the complex electrochemical oscillations during galvanostatic ethanol electrooxidation reaction (EEOR) and the long-standing mechanistic uncertainties. [1-2] By integrating experimental data with theoretical simulations, our model deconstructs the EEOR mechanism into 16 elementary steps. The model accurately reproduces experimental oscillations at 132.7 μAcm^{-2} (Figure 1 A-B), revealing the competitive dynamics between OH_{ad} and CO_{ad} intermediates. Surface analysis shows CH_x accumulation reaching 60% coverage, driving progressive potential increase during oscillations. Partial oxidation products dominate through pathways avoiding C-C bond cleavage, with CO_{ad} oxidation ($k = 1.31 \times 10^{-6}\ s^{-1}$) identified as the rate-determining step. These mechanistic insights provide crucial guidance for rational catalyst design, representing a significant advancement toward more efficient ethanol fuel cell technology.

Figure 1: (A) Experimental and (B) simulated potential profiles at j_{app}= 132.7 µA cm^{-2}. Electrolyte: aqueous solution containing 0.5 mol L^{-1} H_2SO_4 + 0.05 mol L^{-1} CH_3CH_2OH.



References:

[1] Rizo, R.; Ferre-Vilaplana, A., Herrero, E.; Feliu, J. M. Acs Sustain Chem Eng, 11, 4960–4968, (2023).

[2] Calderón-Cárdenas, A.; Paredes-Salazar, E. A.; Varela, H. New J. Chem., 46, 6837-6846, (2022).