ES01

Differential Pulse Voltammetry for a First-Order EC Process: A Ratio of Half-Peak-Widths as a New Diagnostic Parameter

펄스차이 전압전류법의 반봉우리 나비의 비를 이용한 E_rC_i 메카니즘 진단

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Theoretical expressions for the differential pulse voltammetry (DPV) for a reversible electron transfer coupled with an irreversible follow-up first order chemical reaction (E_rC_i) is derived. The peaks as given by the current expressions are analyzed in terms lf several parameters such as a ratio of anodic-to-cathodic peak currents (i_p^a/i_p^c) a separation of peak- potentials ($E_p^c-E_p^a$), and a ratio of anodic-to-cathodic half-peak-widths ($W_{½}^a/W_{½}^c$) in order to characterize the E_rC_i process and distinguish it from other types of electrode processes. The anodic peak is found to be more sensitive to the post kinetics than the cathodic peak. The new parameter of $W_{½}^a/W_{½}^c$ ratio is much more sensitive to the post kinetics than the peak separation ($E_p^c-E_p^a$). The peak current ratio (i_p^a/i_p^c) and the peak width ratio ($W_{½}^a/W_{½}^c$) have comparable sensitivities to the kinetics. Hence, peak width ratio is better diagnostic criteria than peak separation which has a poor sensitivity. This is different from cyclic voltammetry(CV) in which peak separation is as sensitive as current ratio. The new criteria for EC with DPV is tested and successfully applied to several Co(Ⅲ) complex systems, including coenzyme B_{12}. The homogeneous rate constant for the follow-up step is estimated from the measurements of the experimental values of the parameters.