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Voltammetry at a single nano-electrode by varying electrode diameters: Review

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Abstract

Steady-state voltammetric responses at a single nanometer-sized electrode are reviewed, in the light of 1) the basic properties of Saito's (diffusion-controlled) equation, 2) the heterogeneous charge transfer reaction kinetics, 3) reactions of non-charged redox species without supporting electrolyte, and 4) a limitation of diffusion equations. These data are supported by more than 100 fabricated electrodes, of which diameters range from 1 nm to 10 μm. Inlaid disk-electrodes are fabricated by polishing a glass-coated platinum wire with a help of the time-variation of ac-current. The four subjects are specified as follows. 1) Small sizing yields the high current density, which is related with scan rates of cyclic voltammetry and the ac-frequency. Effects of deformed disks on the current are discussed. 2) Heterogeneous rate constants for six redox species are attempted to be determined from the variations of their potential shift with a decrease in the diameters. No potential shift is found although fast scan voltammetry exhibits potential shift. The disagreement is discussed from the view of the double layer capacitance. 3) Sigmoidal voltammograms for non-charged redox species is obtained without adding salt in acetonitrile solution when electrode diameters are less than 400 nm. Di-anion of the redox species is not generated without salt. 4) Electrodes of which diameters are less than 4 μm exhibit the steady-state diffusion-controlled currents less than those calculated from Saito's equation. Simple diffusion is not valid at nano-meter electrodes.

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