

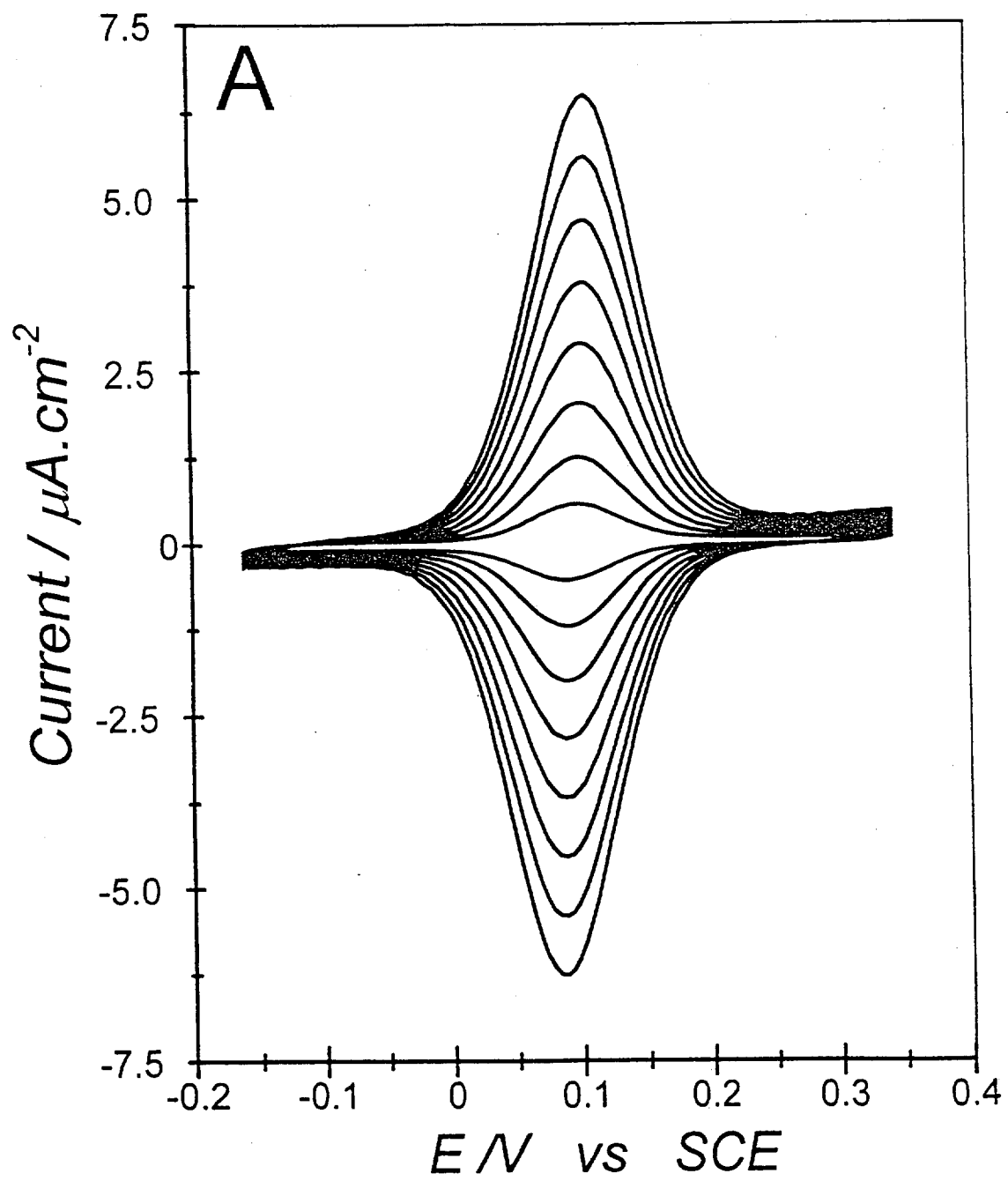
Legends for figures in the supporting information

Figure S1. (A) Cyclic voltammograms of Az-CH₃(CH₂)₁₁S-Au(111) in 20 mM NH₄Ac (pH = 4.6) with scan rates of 200, 300, 400, 500, 600, 700, 800 and 900 mV s⁻¹, and (B) the dependence of redox peak currents on scan rate.

Figure S2. (A) Cyclic voltammograms of Az-CH₃(CH₂)₁₁S-Au(111) in 20 mM NH₄Ac (pH = 4.6) with a scan rate of 500 mV s⁻¹. (B) Variation of the half-wave width with scan rates: (Δ) and (□) are experimental data for cathodic and anodic peaks, respectively; solid line indicates theoretical expectation for a single-electron Nernst surface reaction at 20 °C (i.e. 89.2 mV).

Figure S3. Variation of the peak-to-peak potential separation vs scan rates for Az-CH₃(CH₂)_nS-Au(111) (n = 4, 7, 9, 11, 13, 15, 17).

Figure S4. Electrochemical impedance spectra of Az-CH₃(CH₂)_nS-Au(111) in 20 mM NH₄Ac (pH = 4.6). n = 11 (A), 13 (B), 15 (C), 17 (D). Measurements were conducted at given surface formal potentials corresponding to n (see Table 2) with a frequency range of 0.05-2000 Hz. The inset in (A) is an equivalent circuit for simulation.



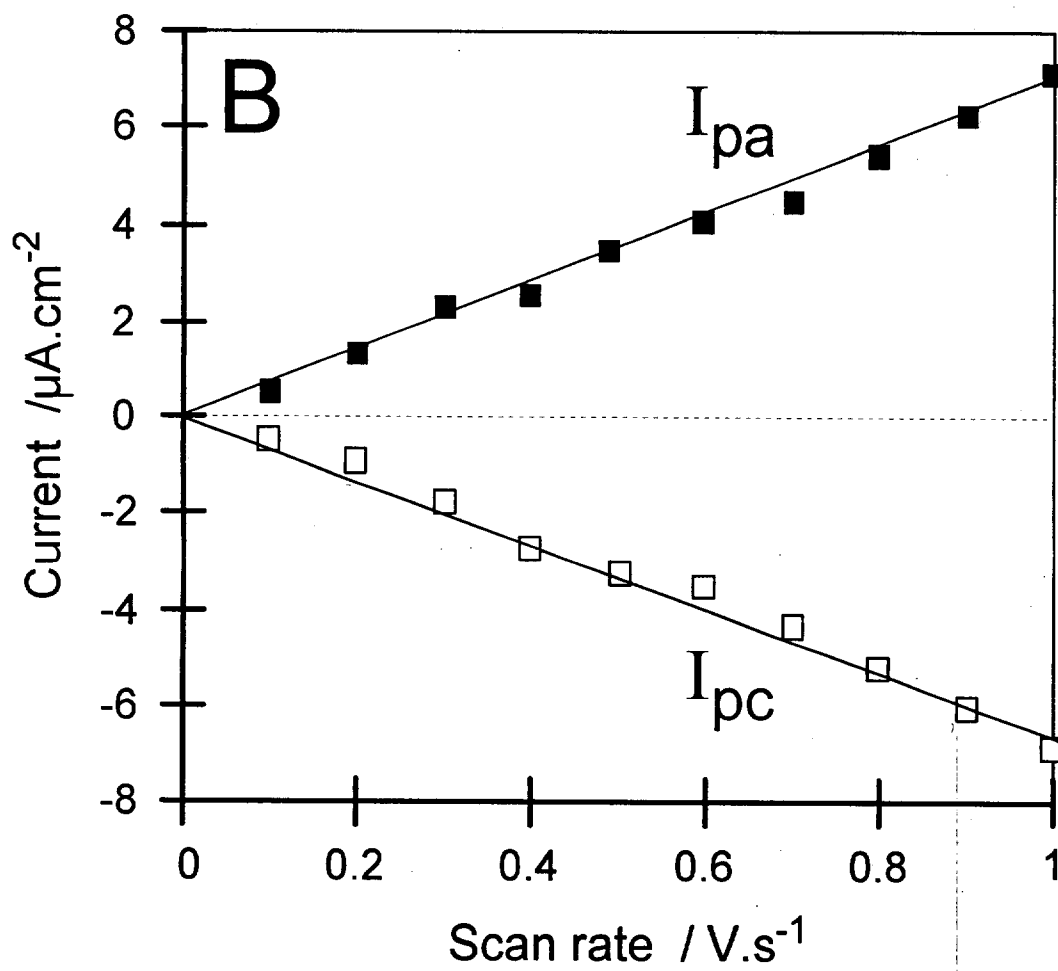
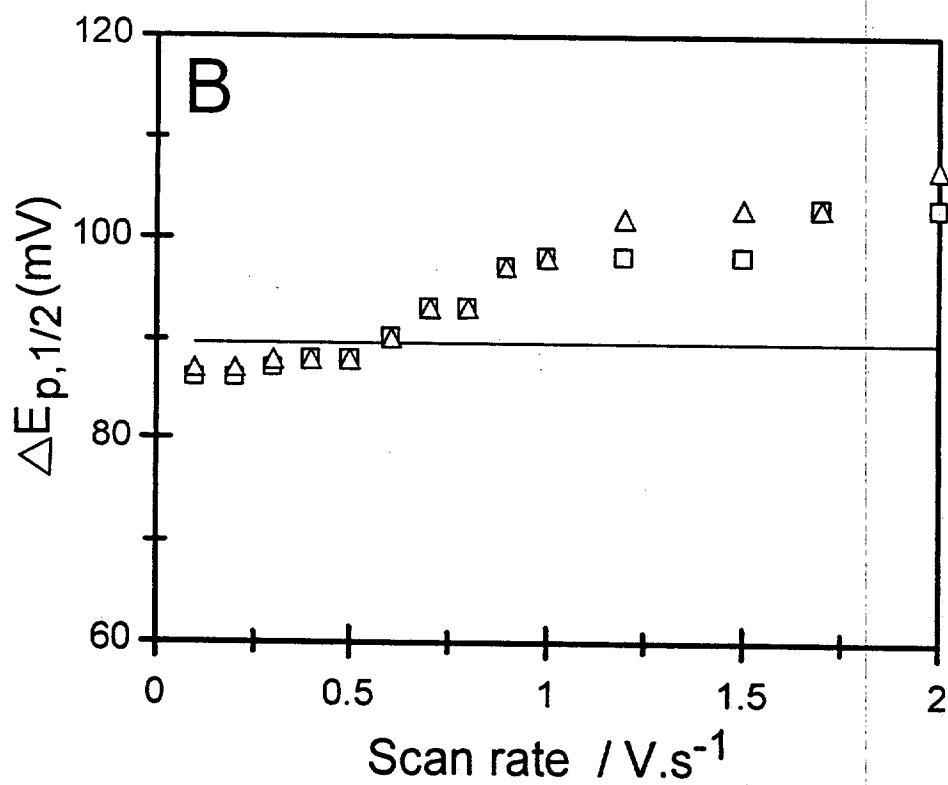
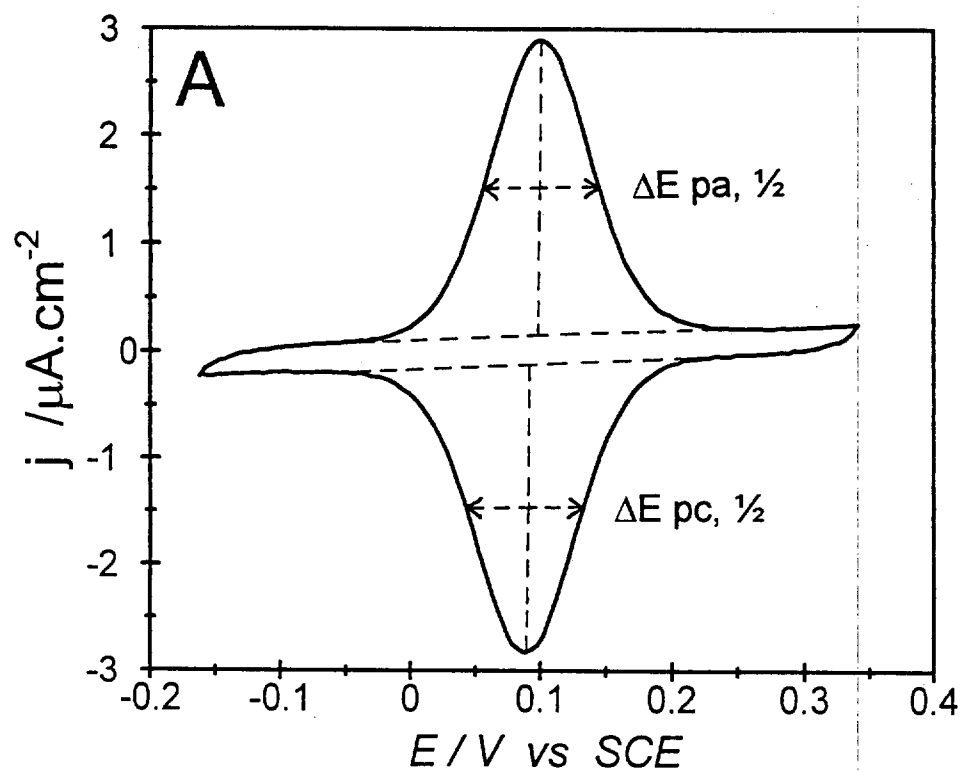


Figure S1B



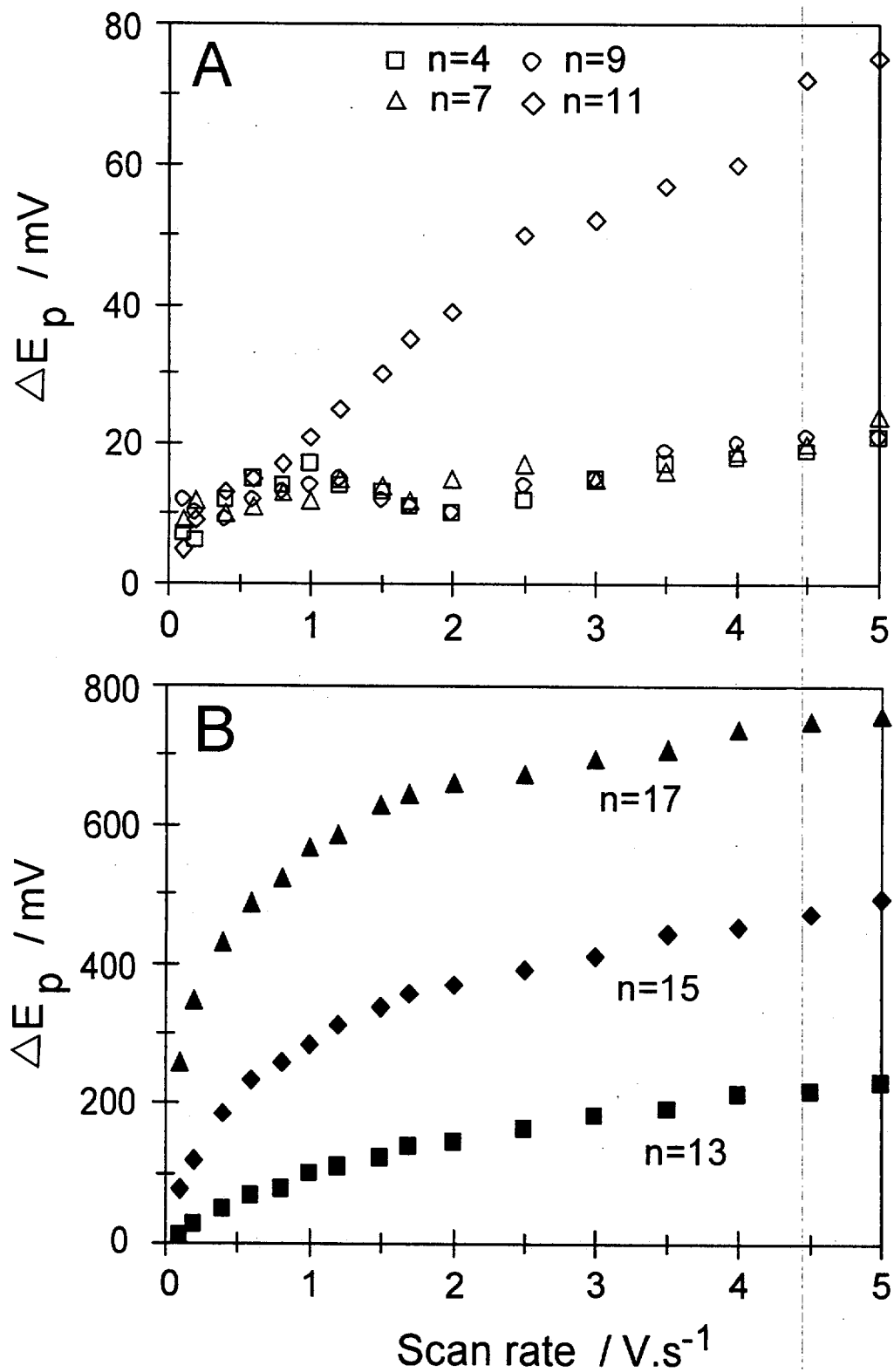


Figure S3

