

Derivation of generalized kinetic equation for RR'CHOH oxidation:

Start with the equation for film surface coverage where Γ is surface coverage (mol area⁻²), $N_{\text{Ru}^{\text{II}}}$ is moles of Ru^{II} , A is film surface area, d is film thickness, n is number of electrons transferred per reaction, F is the Faraday constant, and Q_{cat} is charge passed during the catalysis,

$$\Gamma = \frac{N_{\text{Ru}^{\text{II}}}}{A} = [\text{Ru}_{\text{red}}]d = \frac{Q_{\text{cat}}}{nFA} \quad (1s)$$

rearrange (1s) to get

$$Q_{\text{cat}} = nFAd[\text{Ru}_{\text{red}}] \quad (2s)$$

Differentiation with respect to time gives i_{cat} , the catalytic current,

$$\frac{dQ_{\text{cat}}}{dt} = i_{\text{cat}} = nFAd \frac{d[\text{Ru}_{\text{red}}]}{dt} \quad (3s)$$

Convert to current density, j_{cat} , by the relation

$$j_{\text{cat}} = \frac{i_{\text{cat}}}{A} \quad (4s)$$

This gives catalytic current density as a function of $[\text{Ru}_{\text{red}}]$

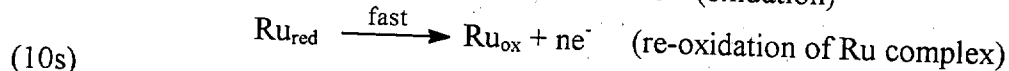
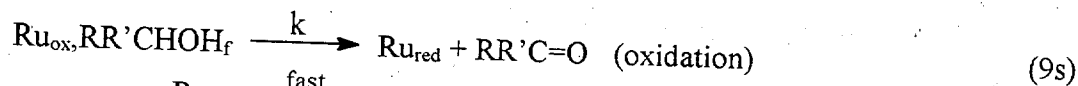
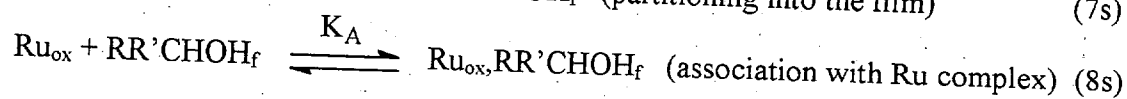
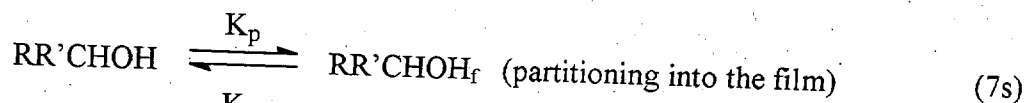
$$j_{\text{cat}} = nFd \frac{d[\text{Ru}_{\text{red}}]}{dt} \quad (5s)$$

Correct for the fact that not all Ru sites are catalytically active by multiplying by a factor f , the fraction of sites which are catalytically active,

$$j_{\text{cat}} = nFdf \frac{d[\text{Ru}_{\text{red}}]}{dt} \quad (6s)$$

This is the catalytic current density due to catalytically active Ru sites.

Assume the following kinetic scheme:



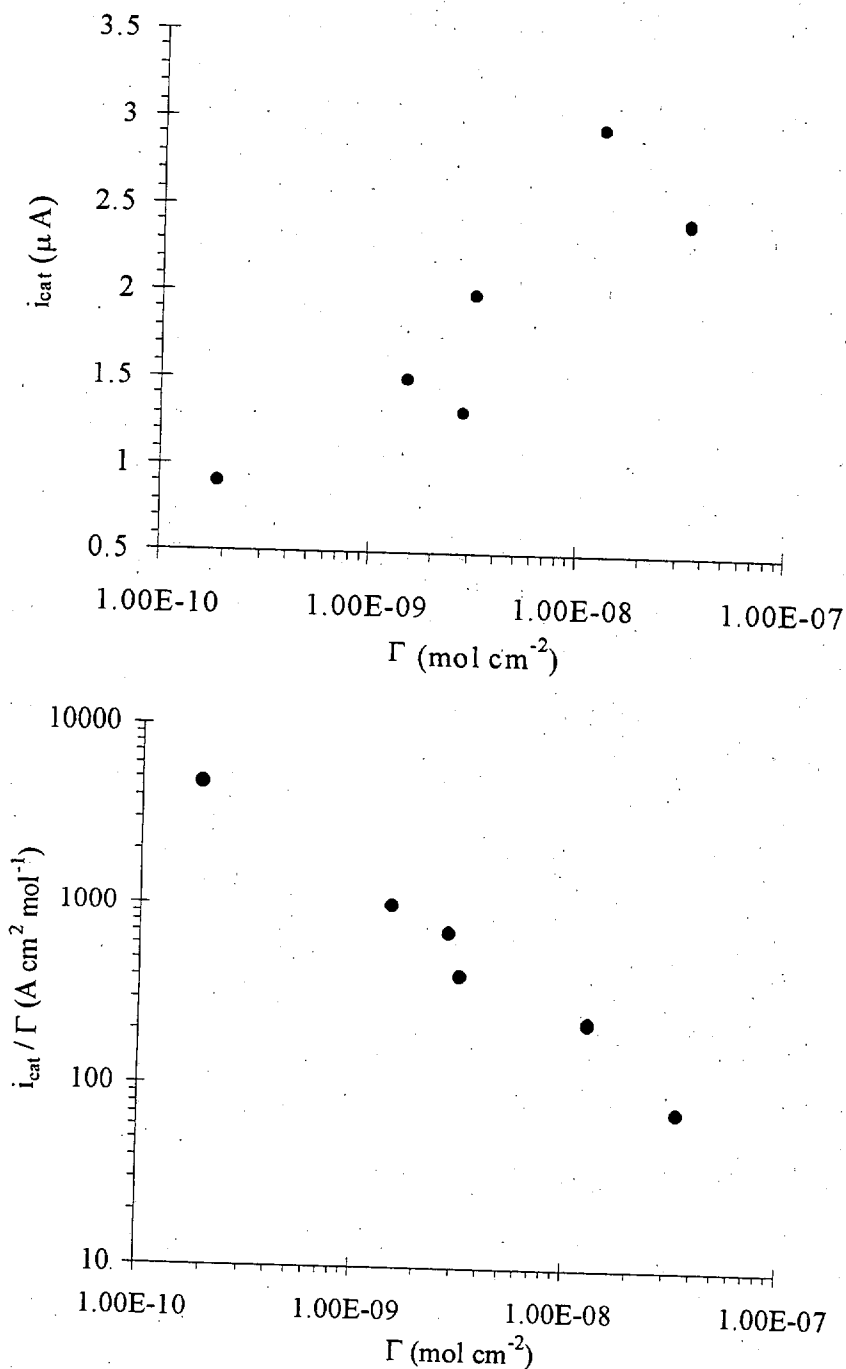


Figure S1. Catalytic current (a) and normalized catalytic current (i_{cat} / Γ) (b) versus surface coverage, Γ , for oxidation of 2-propanol (0.1 M) by poly-*cis*- $[\text{Ru}(\text{vbpy})_2(\text{OH}_2)_2](\text{ClO}_4)_2$ on a 3 mm glassy carbon electrode. The electrode was held at 1.25 V in a stirred 0.1 M HClO_4 solution and a 77 μL aliquot of 2-propanol was injected after the film oxidation current dropped to a steady baseline. The catalytic current was measured in the limiting current region, 550 s after addition of the 2-propanol.