

# Correction to Turnover Numbers, Turnover Frequencies, and Overpotential in Molecular Catalysis of Electrochemical Reactions. Cyclic Voltammetry and Preparative-Scale Electrolysis

Cyrille Costentin, Samuel Drouet, Marc Robert, and Jean-Michel Savéant\*

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Page 11236. A stoichiometric factor of 2, corresponding to the requirement that two molecules of catalyst are involved in the production of one molecule of product, was omitted in the original paper. Correction of this omission leads to the following changes in Scheme 1, several equations, and Figures 1, 2, and 6.

Scheme 1

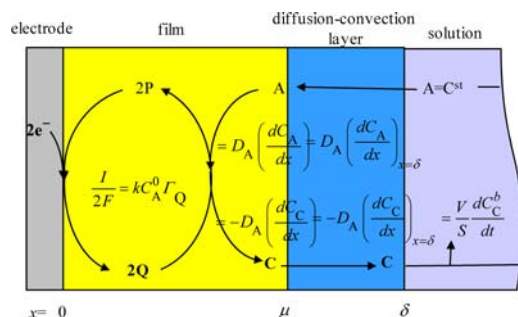
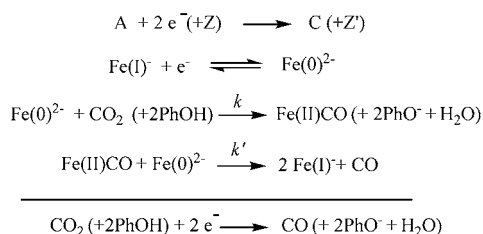
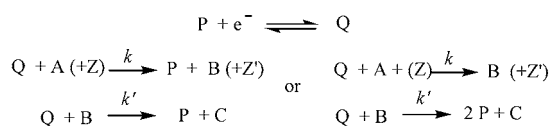


Figure 1. Catalysis and diffusion for a heterogeneous catalytic reaction under preparative scale steady-state conditions.

Page 11237. The latter concentration is thus obtained, from the combination of the various equations in Figure 1, as

$$\frac{dC_C^b}{dt} = -\frac{SD_A}{V} \left( \frac{dC_C}{dx} \right)_{x=\delta} = \frac{IS}{2FV}$$

Since,

$$\frac{I}{F} = \frac{2kC_A^0 \Gamma_P^0}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]}$$

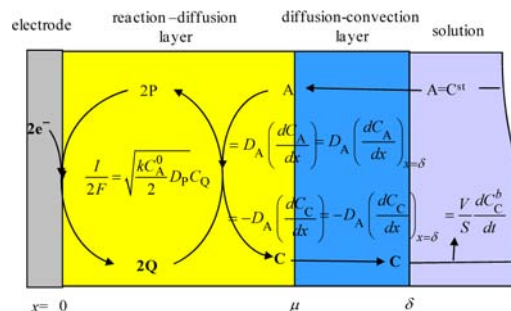


Figure 2. Catalysis and diffusion for a homogeneous catalytic reaction under preparative scale steady-state conditions.

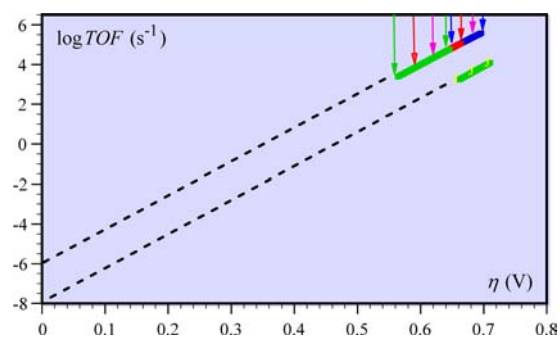


Figure 6. TOF<sup>(2)</sup> vs overpotential Tafel lines for, from bottom to top, 0.1, 0.75, 3 M PhOH. The green segments are derived from 0.1 V/s experiments. The red, magenta, and blue segments shown for [PhOH] = 3M, were obtained at 1, 10, 50 V/s, respectively. The colored arrows indicate the length of the overpotential interval browsed at each scan rate. The yellow dots represent the electrolyses at −1.335, −1.36, and −1.385 V vs SHE (see text and Figure 7 in original paper).

then:

$$C_C^b = \frac{kC_A^0 \Gamma_P^0}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]} \frac{S}{V} \times t$$

The turnover number is defined as the number of moles of substrate transformed by one mole of both forms of the catalyst present on the surface:

$$\text{TON} = \frac{\text{molC}}{\text{mol}(P + Q)} = \frac{C_C^b \times V}{\Gamma_P^0 \times S} = \frac{kC_A^0 \times t}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]}$$

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and the turnover frequency ( $s^{-1}$ ):

$$\text{TOF} = \frac{kC_A^0}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]}$$

$$\text{TON}^{(2)} = \frac{k \times t}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]} \quad (1)$$

$$\text{TOF}^{(2)} = \frac{k}{1 + \exp\left[\frac{F}{RT}(E - E_{PQ}^0)\right]} \quad (2)$$

$$\text{TOF}^{(2)} = \frac{k}{1 + \exp\left[\frac{F}{RT}(E_{AC}^0 - E_{PQ}^0 - \eta)\right]} \quad (4)$$

$$\log \text{TOF}^{(2)} = \log k - \frac{F}{RT \ln 10}(E_{AC}^0 - E_{PQ}^0) + \frac{F\eta}{RT \ln 10} \quad (5)$$

The corresponding intrinsic turnover frequencies ensue as measures of the intrinsic properties of the catalyst + phenol system:  $\text{TOF}^{(2)} = 3.1 \times 10^{-8}$ ,  $2.45 \times 10^{-9}$ , and  $1.75 \times 10^{-7}$  for  $[\text{PhOH}] = 0.1, 0.75$ , and  $3 \text{ M}$ , respectively.

Page 11241. The values of the rate constant,  $2k = 1.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  and  $\text{TOF}^{(2)} = 0.8 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ , are in good agreement with the values derived from the foot-of-the-wave analysis in CV ( $2k = 1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $\text{TOF}^{(2)} = 0.75 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ) for the same concentration of PhOH.

#### ■ ACKNOWLEDGMENTS

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