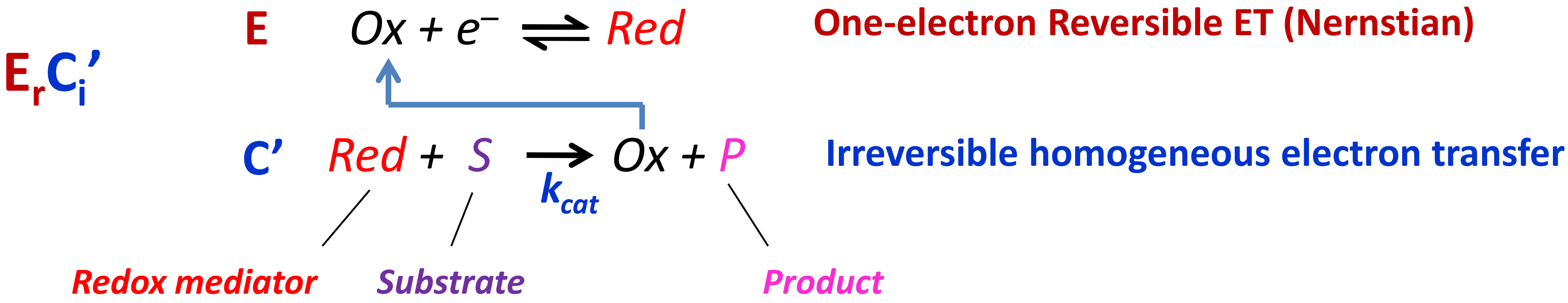
The homogeneous catalytic reaction mechanism (E_rC_i')



E_rC_i'

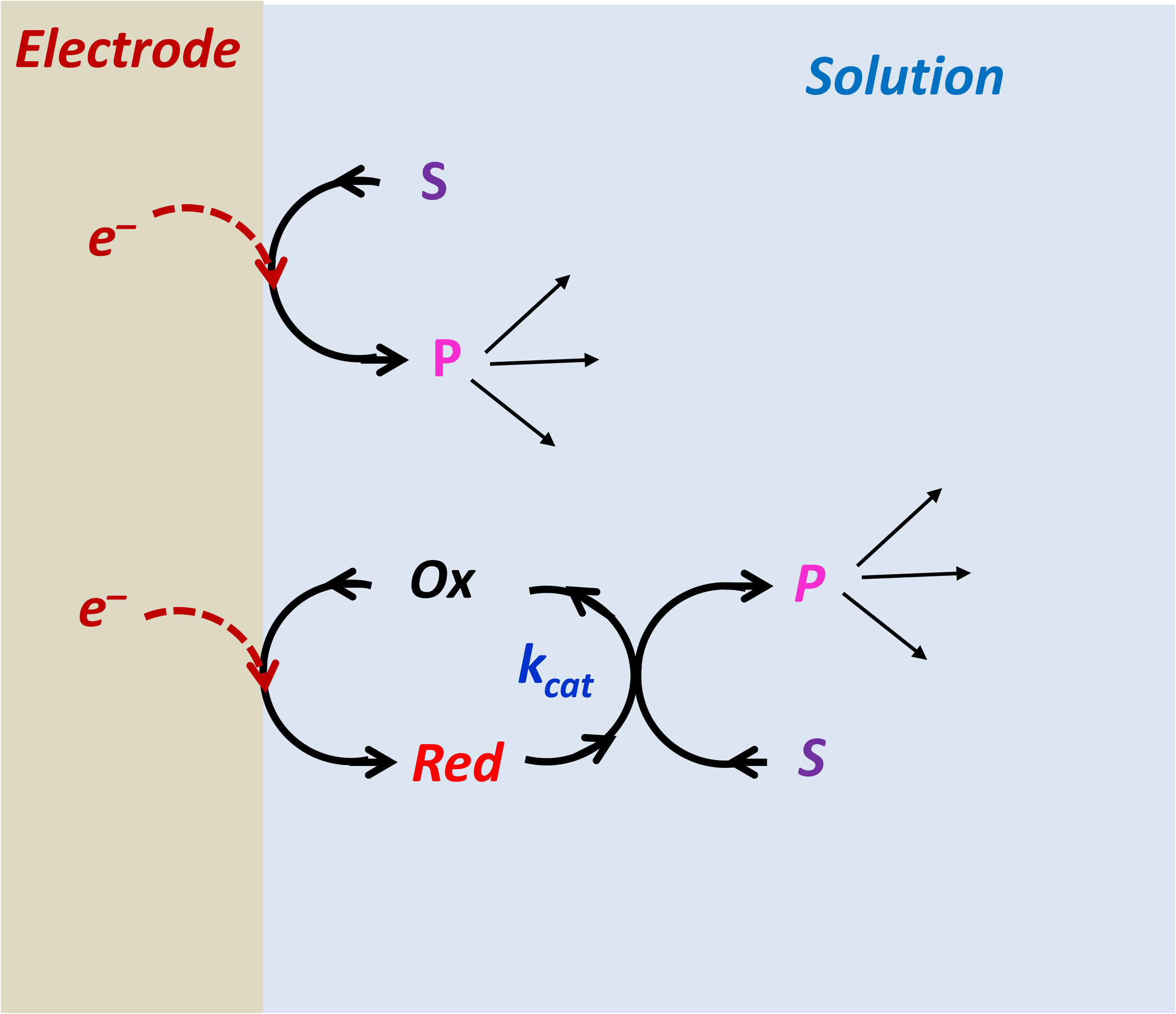
E $Ox + e^- \rightleftharpoons Red$ **One-electron Reversible ET (Nernstian)**

C' $Red + S \xrightarrow[k_{cat}]{} Ox + P$ **Irreversible homogeneous electron transfer**

Redox mediator ***Substrate*** ***Product***

- Ox/Red redox couple acts as a catalyst for the conversion (here reduction) of a substrate S into a product P
- The electrogenerated **Red** is the **active form of the catalyst** (here reduced) and acts as a **mediator** for the S conversion into P
- Unlike E_rC_i mechanism, the E_rC_i‘ scheme involves a **catalytic regeneration of the initial form of the catalyst** (Ox)
- Homogeneous ET (chemical step) is assumed to be **irreversible** and **rate-limiting**
- The substrate **S** is assumed to be **NOT electroactive** in the potential window of interest

The homogeneous catalytic reaction mechanism (E_rC_i')

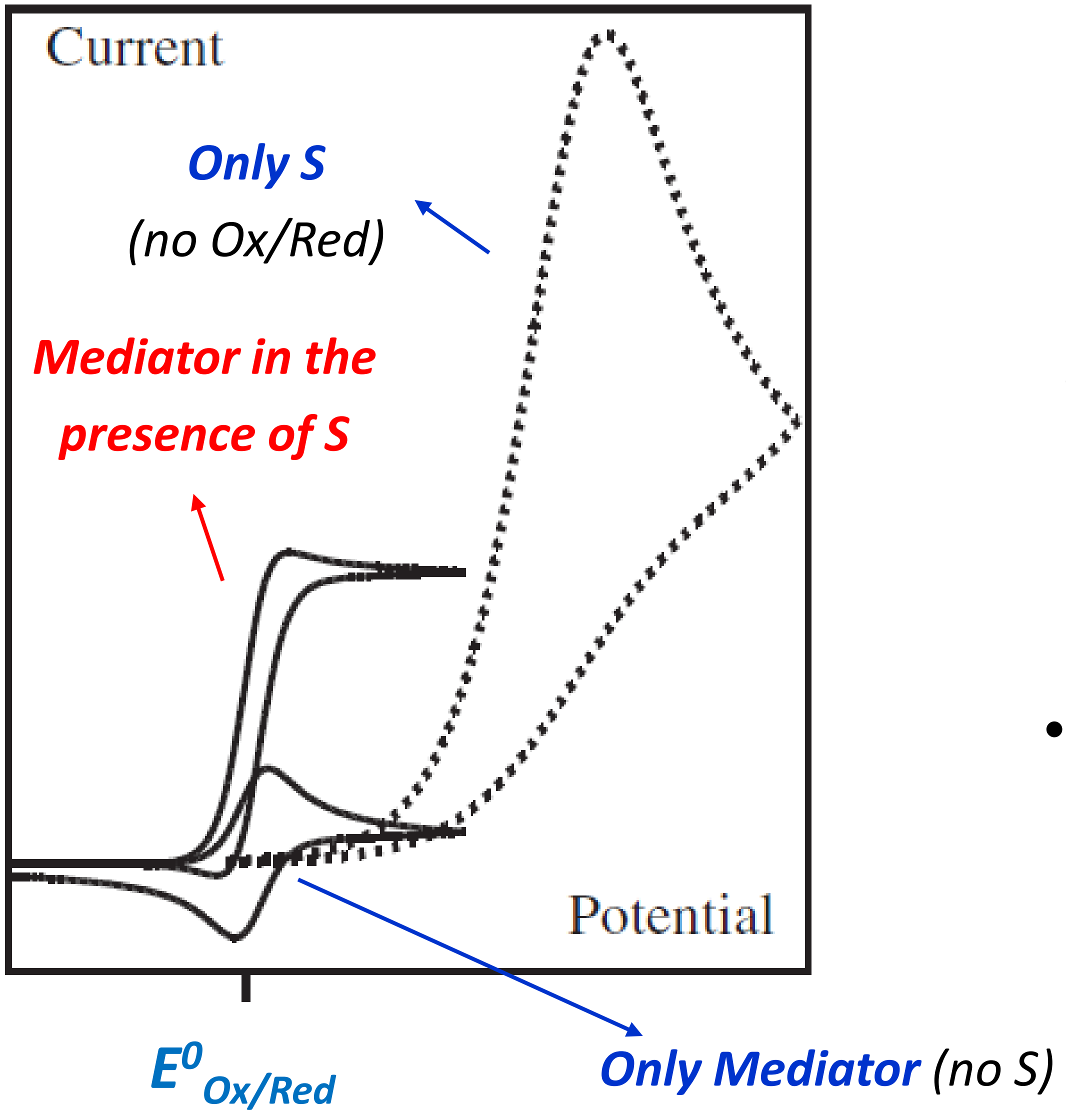


Direct electrochemical S reduction to P

Redox-mediated catalytic S reduction to P (Red = redox mediator)

The homogeneous catalytic reaction mechanism (E_rC_i')

Savéant, Elements of Molecular and Biomolecular Electrochemistry, 1st Ed., 2006



Only S (no Ox/Red)

Mediator in the presence of S

Only Mediator (no S)

$E^0_{Ox/Red}$

- ET to S is mediated by the reduced form of the catalyst (Red) rather than occurring directly at the electrode surface
- The reduction of S into P takes place at the mediator (Ox/Red) redox wave, i.e. at a **potential less negative** than the potential required for direct reduction of S
- Regeneration of the initial form of the catalyst (Ox) induces a **current enhancement** (catalytic current) and a **loss of reversibility** of the Ox/Red redox wave

Homogeneous molecular catalysis: voltammetric response

The voltammetric response may be dependent on multiple variables. For an E_rC_i' scheme, the CV responses is a function of **two dimensionless parameters**:

Rate constant of homogeneous ET from Red to S

$$\lambda = \frac{RT}{F}\frac{k_{cat}C_{Ox}^{*}}{v}$$

Kinetic parameter

Scan rate

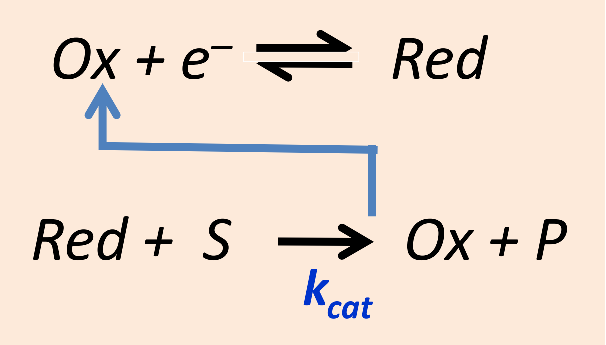
Bulk concentration of catalyst (Ox)

$$\gamma = \frac{C_S^{*}}{C_{Ox}^{*}}$$

Excess factor

Bulk concentration of the substrate

E_rC_i'

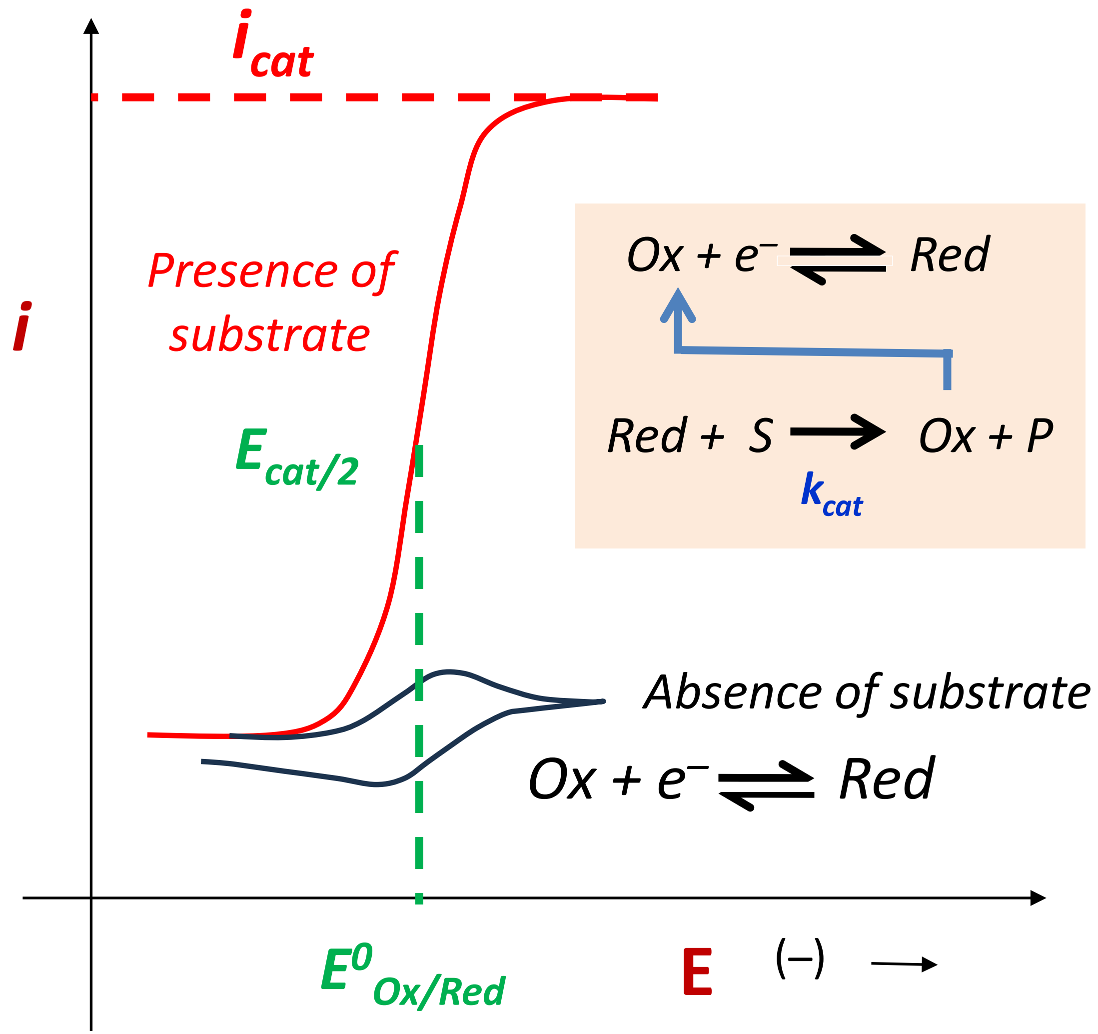


$$Ox + e^- \rightleftharpoons Red$$

$$Red + S \xrightarrow[k_{cat}]{} Ox + P$$

Rate-limiting homogeneous electron transfer

Canonical S-shape response: pure kinetic conditions



Pure kinetic conditions

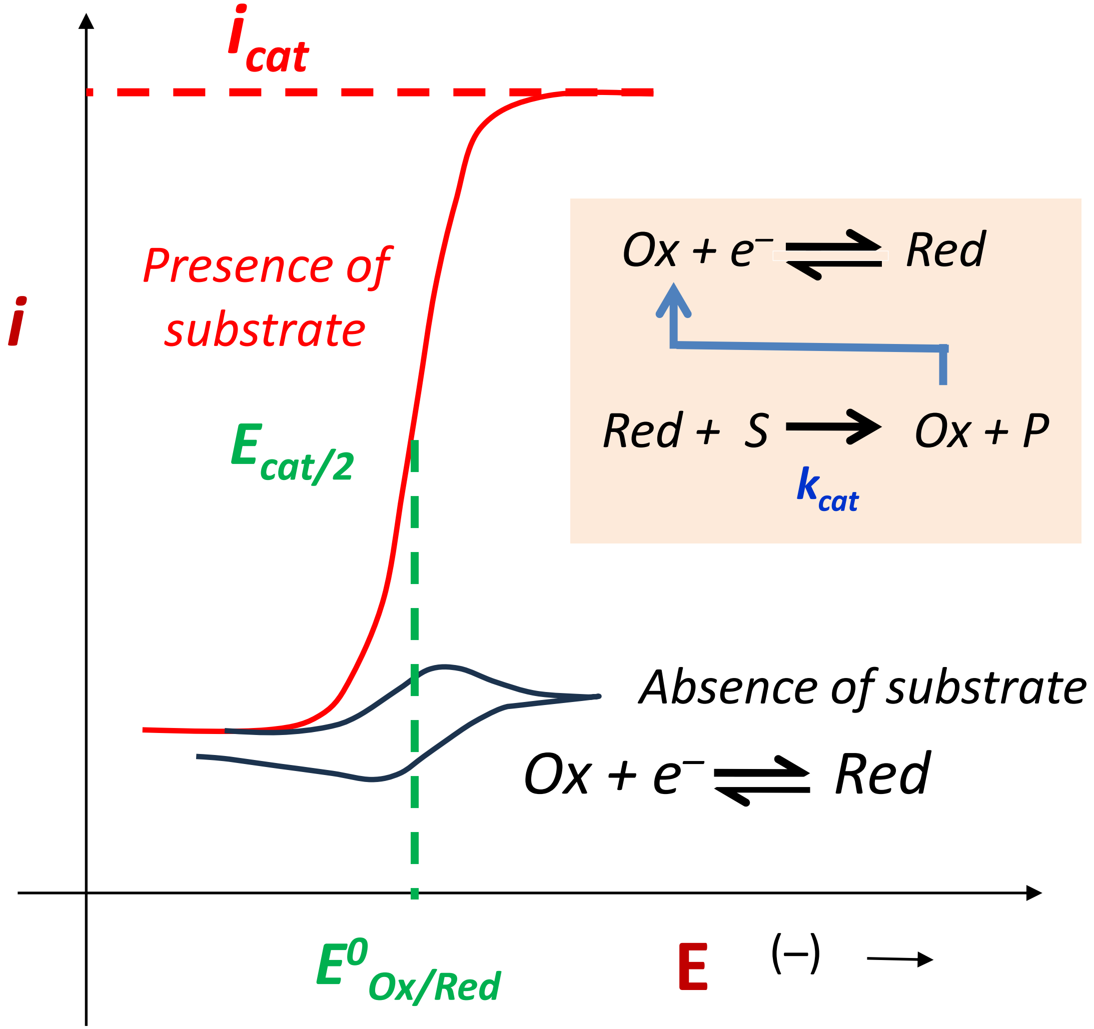
⇕

Canonical S-shaped CV response

(limiting current, i_{cat})

- **Large enough λ** (large k_{cat} and/or small v)
- **Large γ**: **excess of substrate** or **negligible substrate consumption** ($C_S^* >> C_{Ox}^*$)
- $E^0_{Ox/Red} = E_{cat/2}$ (half-wave potential)

Canonical S-shape response: pure kinetic conditions



$$i = \frac{FAC^*_{Ox}\sqrt{D_{Ox}}\sqrt{k_{cat}C^*_S}}{1+\exp\left[\frac{F}{RT}\left(E-E^0_{Ox/Red}\right)\right]}$$

for $E \ll E^0_{Ox/Red}$

$$i_{cat} = FAC^*_{Ox}\sqrt{D_{Ox}}\sqrt{k_{cat}C^*_S}$$

- **i_{cat} is independent on the scan rate (v)**
- rate constant is commonly extracted from i_{cat} normalized by i_p:

$$\frac{i_{cat}}{i_p} = \frac{1}{0.4463}\sqrt{\left(\frac{RT}{Fv}\right)k_{cat}C^*_S} \qquad (n = 1)$$

Non-catalytic peak current of the Ox/Red reversible wave
(absence of S), given by the Randles-Sevcik equation

Multistep multielectron mechanisms

- Several catalytic reactions of interest, including energy-conversion processes based on the activation of small molecules (e.g. O_2 reduction, water splitting, CO_2 reduction, etc.), are typically characterized by more complex mechanisms based on ***multiple ET and chemical steps***

- Large variety of possible scenarios, depending on the reaction conditions and the type of catalyst

- Moreover, catalytic processes often involve other species in addition to catalyst and substrate, such as **co-catalysts** (or co-substrates, e.g. acid for reductions, base for oxidations)

- ***Two-electron, two-steps reaction schemes*** are quite common in homogeneous molecular catalysis

Competitive side-phenomena: non-idealized CV responses

- Rigorous determination of rate constants and kinetic analysis of a catalytic reaction using previously derived equations strictly requires the achievement of classical S-shaped voltammograms (pure kinetic conditions), but often this is not the case

- In real systems, several **side-phenomena** may interfere with the catalytic reaction, preventing the observation of sigmoidal CVs (**peak-shaped catalytic CVs**)

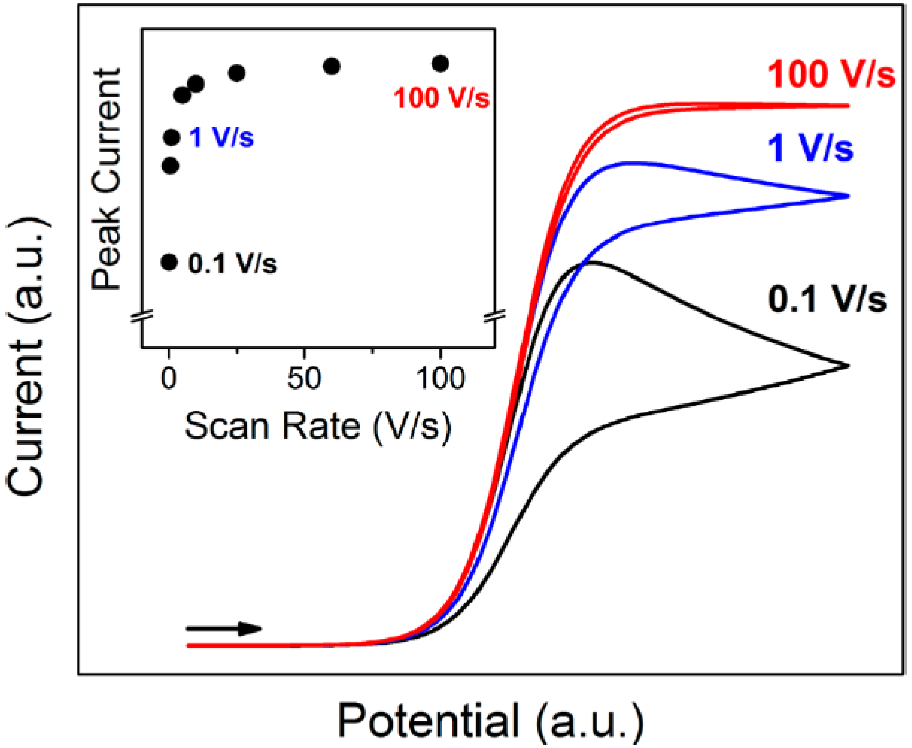
- These secondary phenomena may be related to **substrate consumption** (“total catalysis”), **catalyst deactivation**, **inhibition by products**, etc.

Non-idealized CV responses: increase of the scan rate

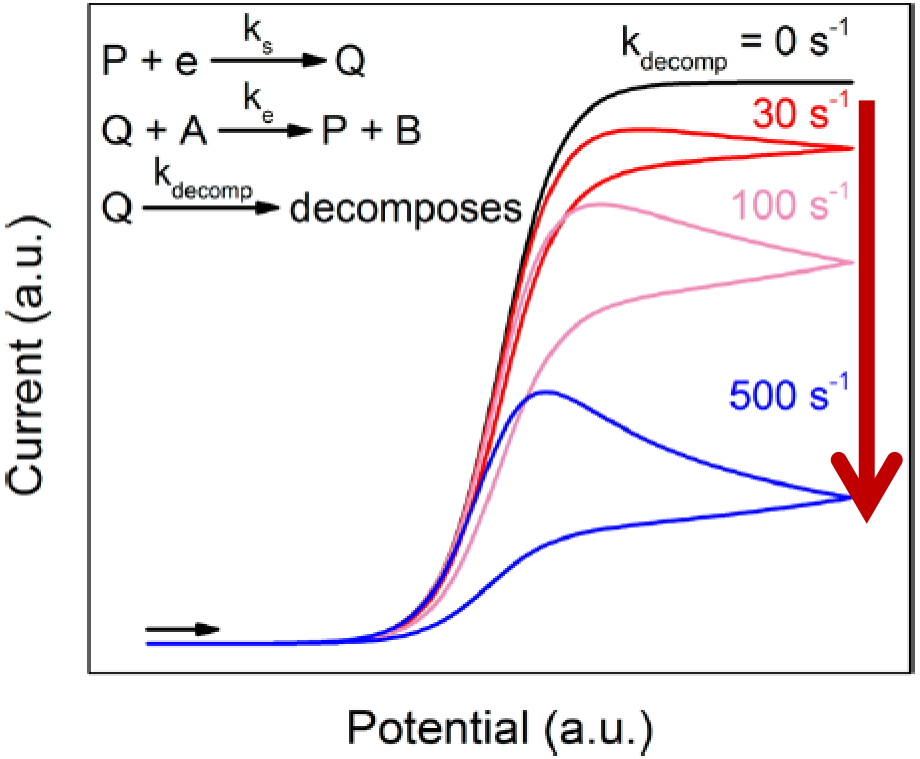
E_rC_i' mechanism (simulated CVs)

Low scan rate region:
scan rate-dependent peak current (peak-shaped CV)

High scan rate region:
scan rate-independent plateau (S-shaped CV)



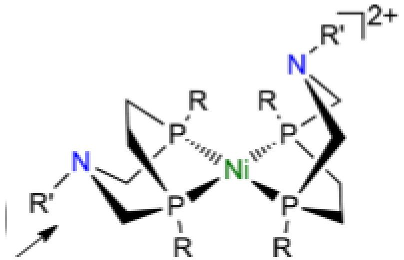
Catalyst deactivation (decomposition)



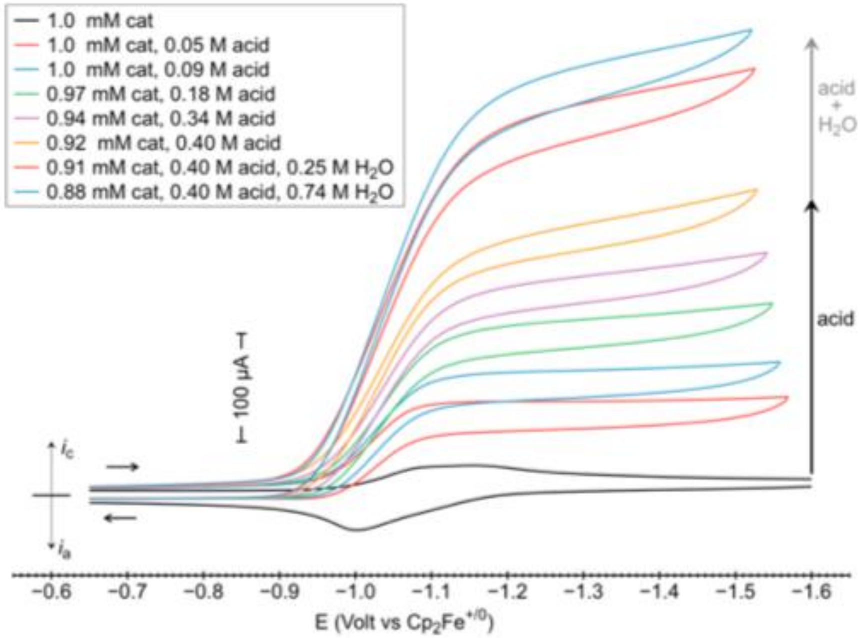
Faster decomposition

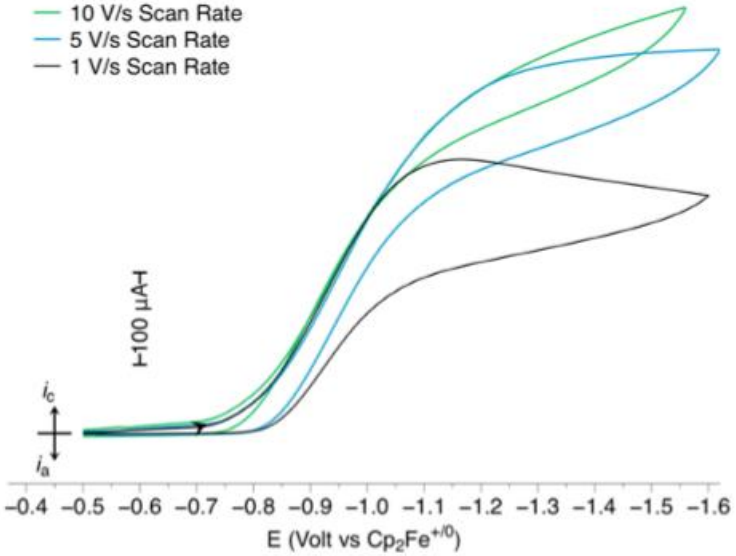
E. Rountree, B. McCarthy, T. Eisenhart, J. Dempsey, *Inorg. Chem.* **2014**, *53*, 9983–10002

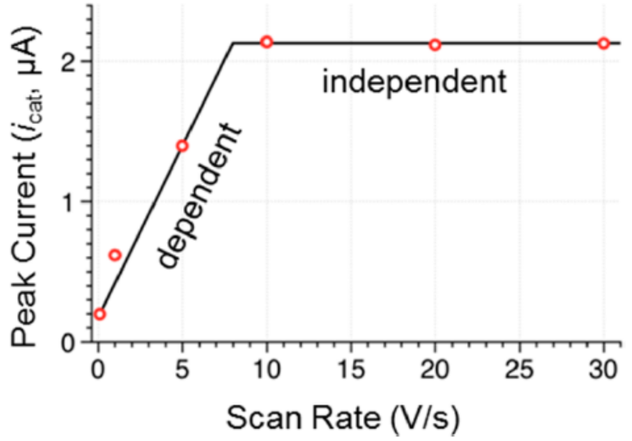
Non-idealized CV responses: examples



$$2H^+ + 2e^- \rightarrow H_2$$







E. Rountree, B. McCarthy, T. Eisenhart, J. Dempsey, *Inorg. Chem.* **2014**, *53*, 9983−10002

M. Stewart, M. Ho, S. Wiese, M. Lindstrom, C. Thogerson, S. Raugei, R. Bullock, M. Helm, *JACS* **2013**, 135, 6033−6046