Description of complicated reaction systems with optimal mathematical complexity

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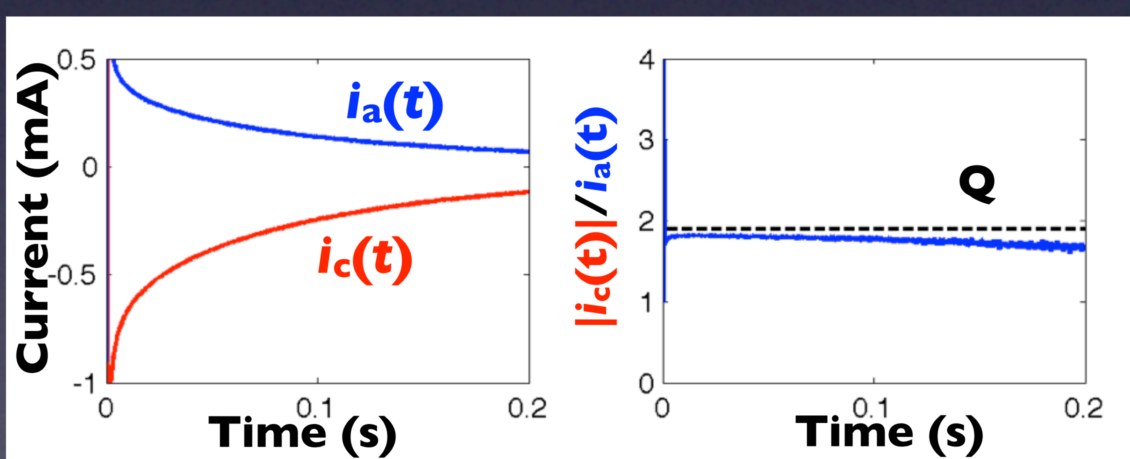
- Electrochemical systems have complicated underlying mathematical description because of interplay of chemical and various physical (e.g., diffusion) processes
- Simplified kinetic techniques are applied to describe dynamic features

Thermodynamic reciprocal trajectories

- From certain initial conditions the ratio cathodic [$i_c(t)$] and anodic [$i_a(t)$] relaxation current = reaction quotient (Q)
- Experimental confirmation in reaction system

$$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$$



Thermodynamics governs far-from-equilibrium behavior!

Dynamics of cathode-anode interactions

- Effect of cathode size on Faradayic resistance and dynamical features in anode-cathode (A-C)cells
- At intermediate electrode sizes strongly enlarged Faradaic resistance causes instabilities (oscillations) in Ni dissolution (anode)-hydrogen reduction (Ni cathode) cells

Small cathode (Area=0.05 cm^2) | Medium cathode (Area=1.00 cm^2) | Large cathode (Area=6.00 cm^2)