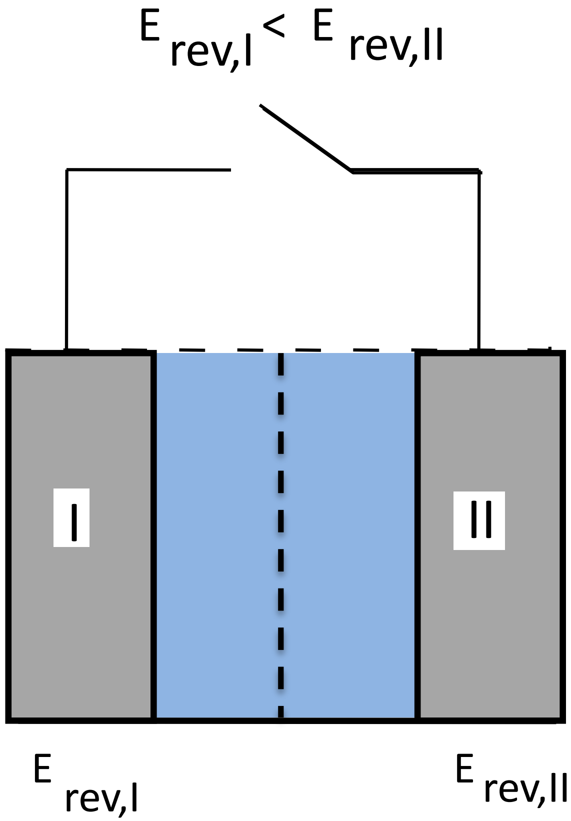
Electrochemistry for materials technology

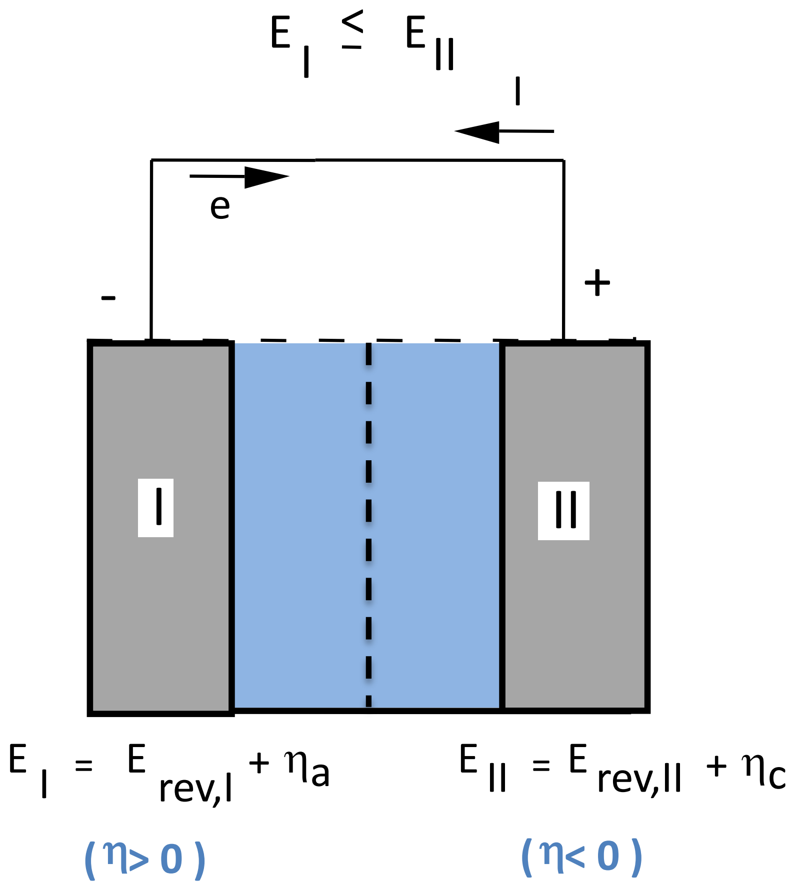
Chapter 6

Electrochemical cells and mixed electrodes

Electrochemical cell: block diagram

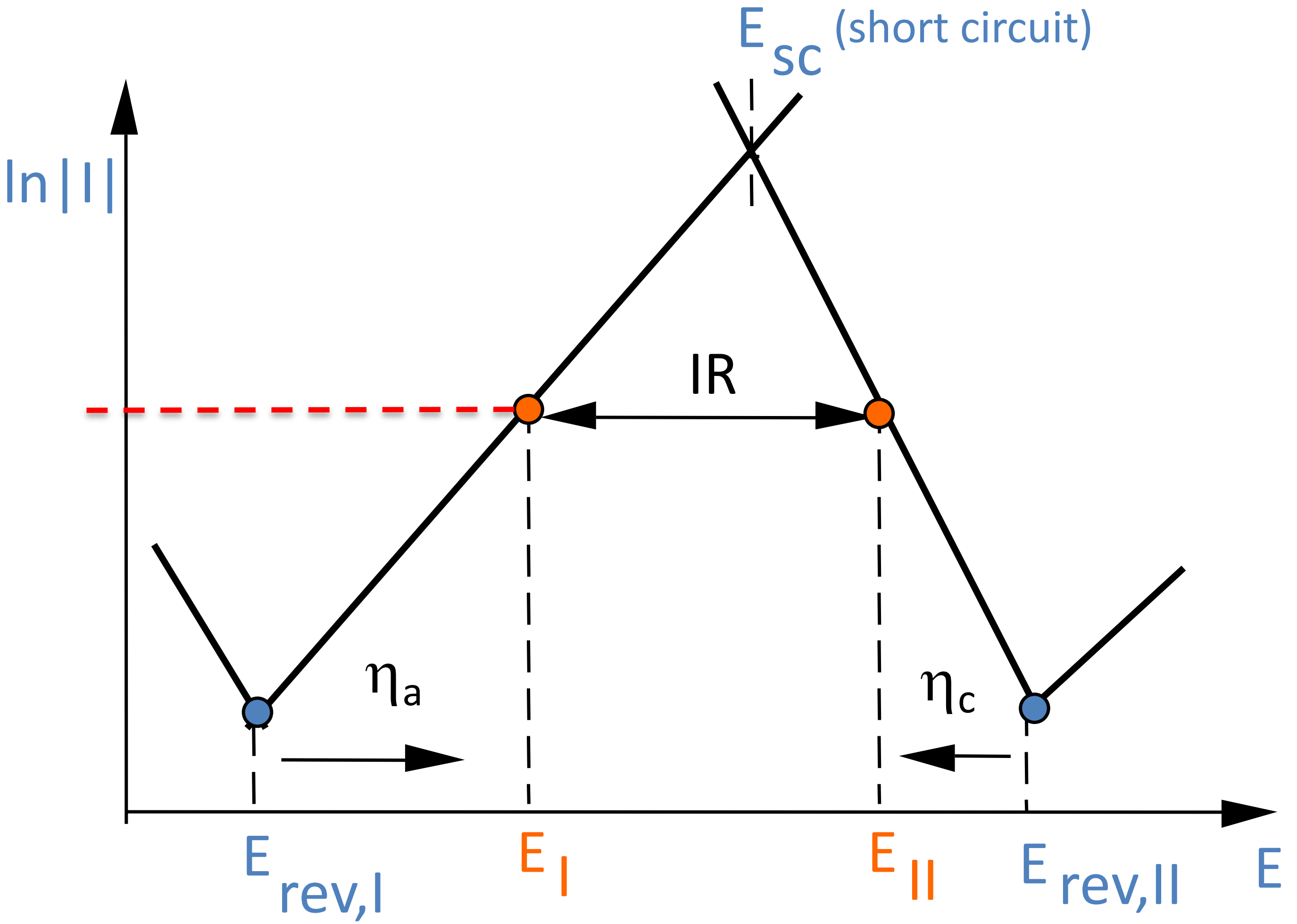


open circuit

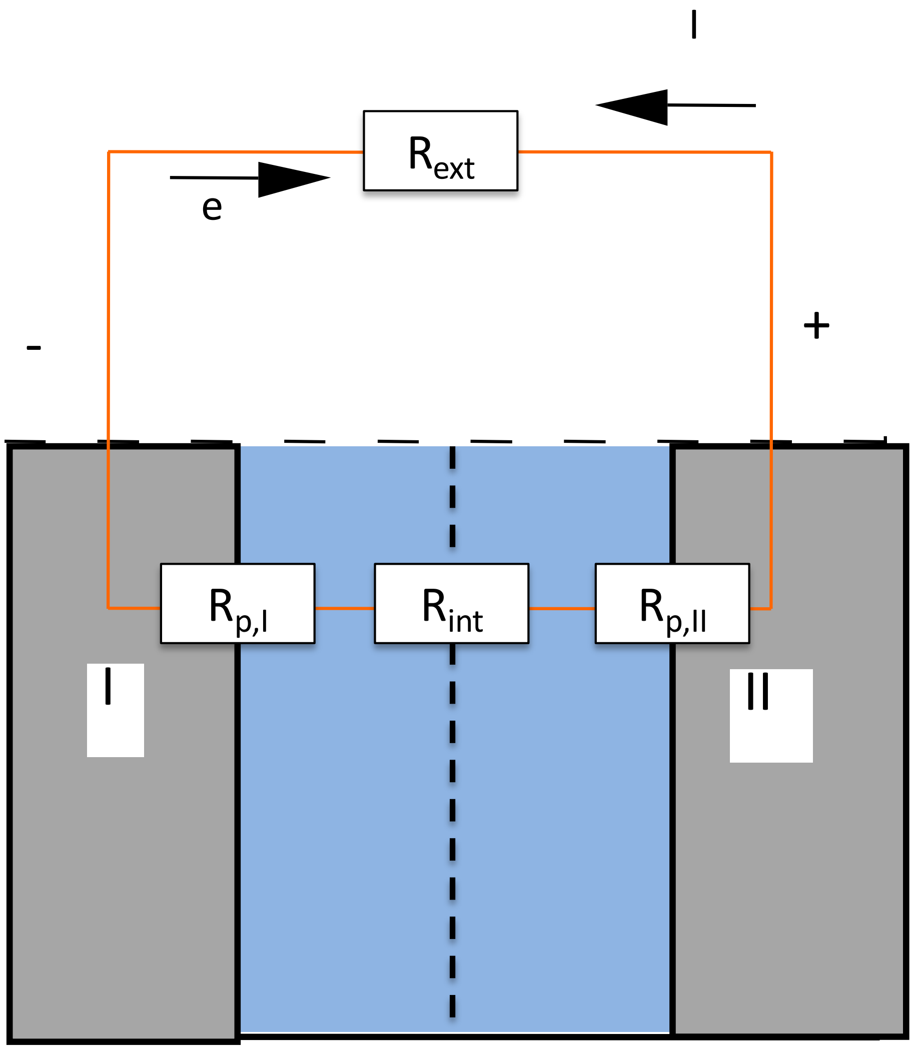


closed circuit

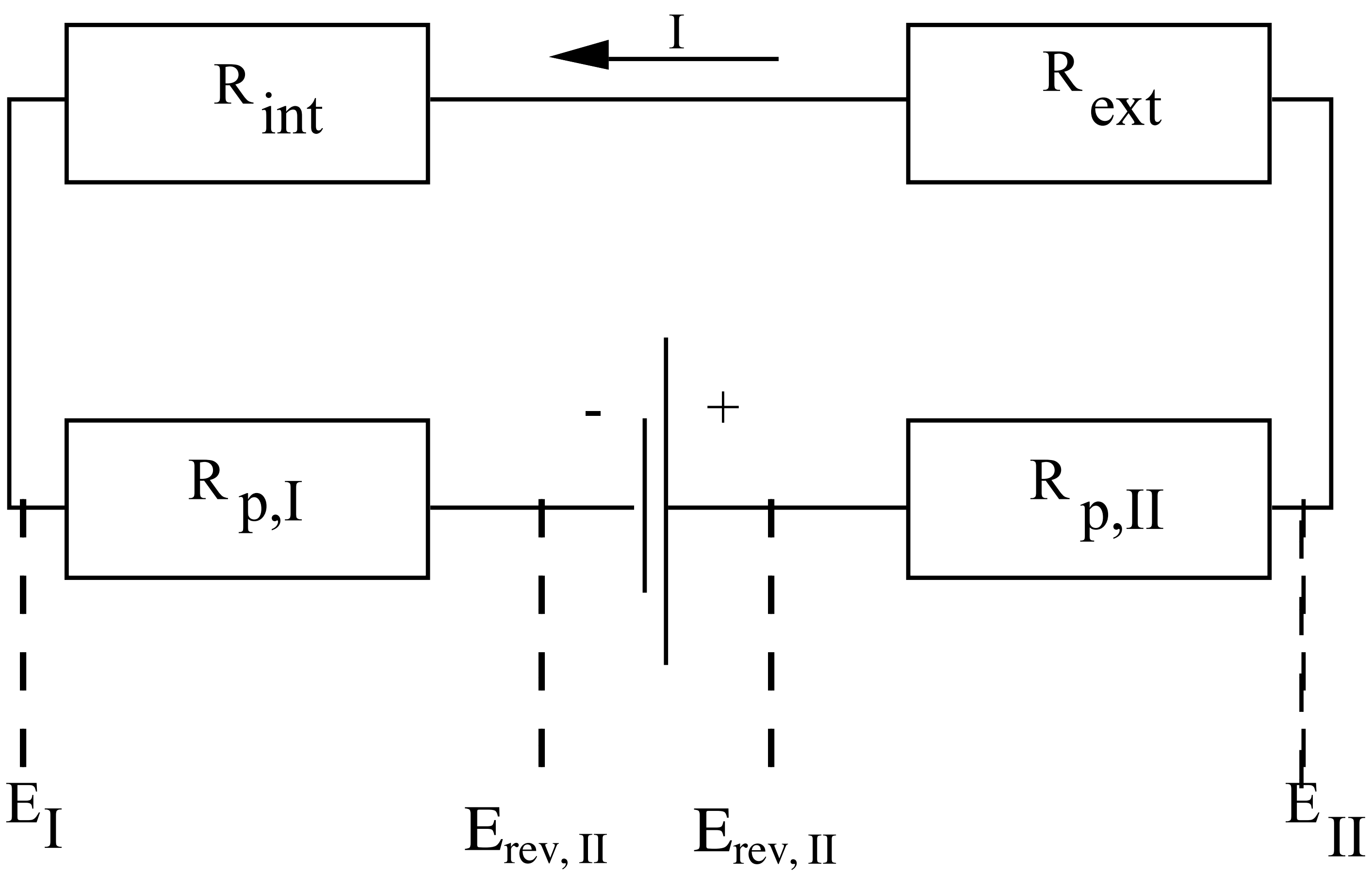
Evans diagram of an electrochemical cell



Resistances in electrochemical cells



Electrical equivalent circuit



$$I = \frac{E_{rev,\,II} - E_{rev,\,I}}{R_{int} + R_{ext} + R_{p,I} + R_{p,II}}$$ (dc conditions)

Effect of electrode surface area

In electrochemical cells, a constant current "I" [A] flows through cathode and anode.
As a consequence the current density "i" [A/m^2] and the overvoltage η of each electrode depend on the electrode surfaces areas "A".

$I_I = - I_{II} = i_a A_I = -i_c A_{II}$

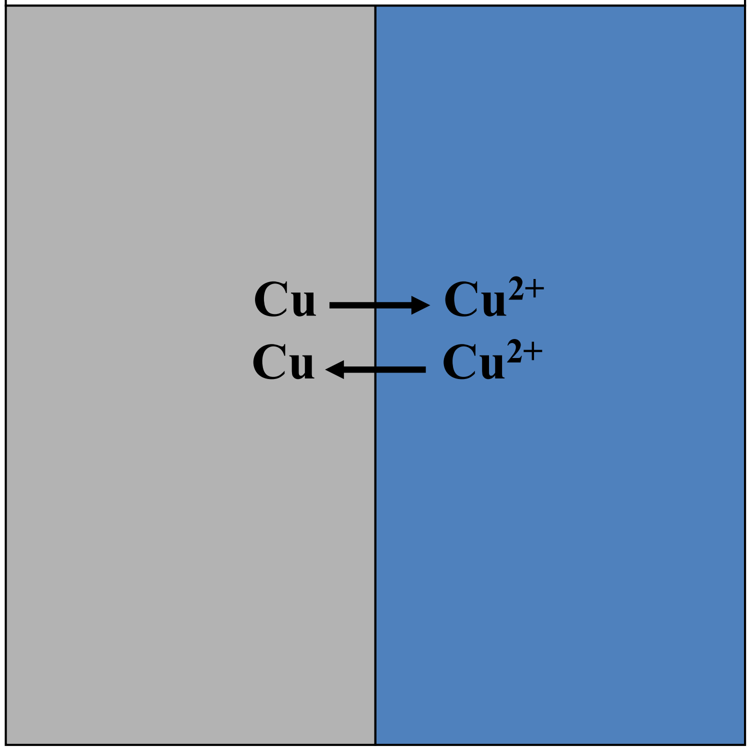
$i_I = -i_{II} (A_{II}/A_I)$

$i = i_0 \exp(\eta / \beta)$ (Butler-Volmer equation)

(NB: sometimes small area WE (working electrode) and large area CE (counter electrode) are used to limit the CE overvoltage) to concentrate the study on the WE overvoltage)

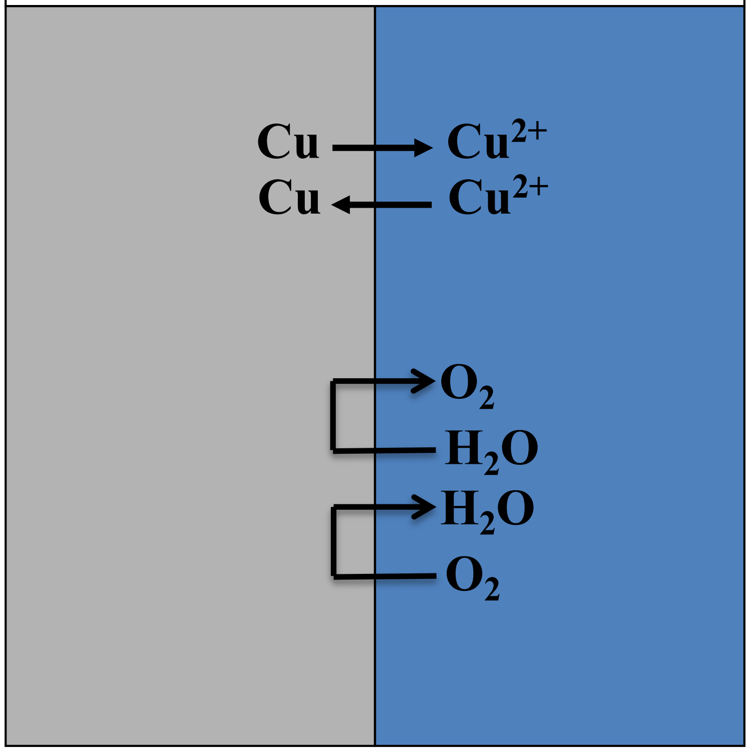
Mixed electrodes (='corrosion')

Simple electrode:
1 half cell reaction occurs on the electrode



$Cu^{2+} + 2\ e = Cu$

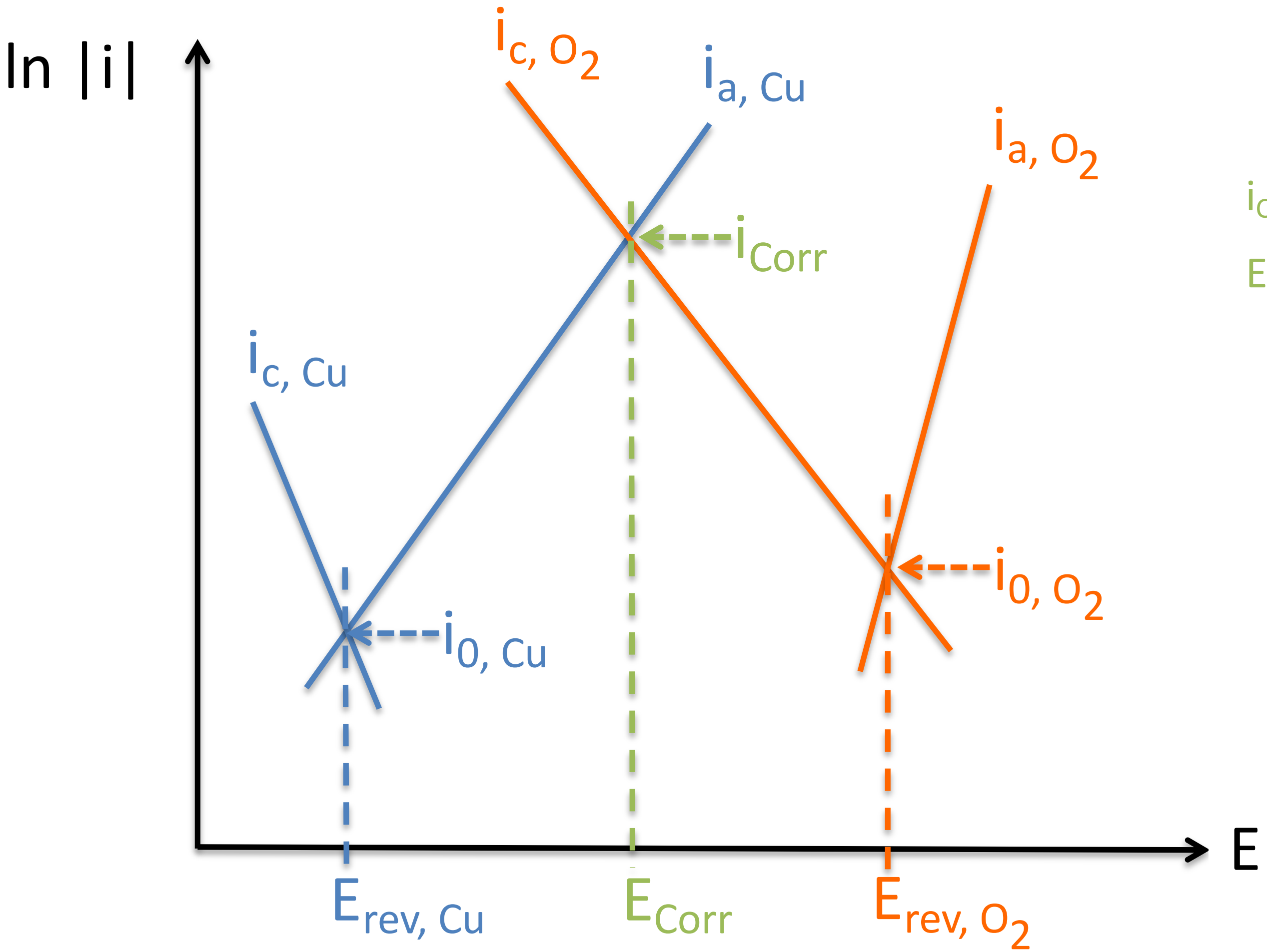
Mixed electrode:
2 or more half cell reactions occur on the electrode



$Cu^{2+} + 2\ e = Cu$

$O_2 + 4\ H^+ + 4\ e = 2H_2O$

Evans diagram of mixed electrodes



i_{Corr}: corrosion current density

E_{corr}: corrosion potential

Corrosion current =
the anodic branch of one reaction overlaps with the cathodic branch of another, different reaction

Total and partial currents in mixed electrodes

$i = i_{a,Cu} + i_{c,Cu} + i_{a,O2} + i_{c,O2}$

At E_{corr} $\quad i \approx i_{a,Cu} + i_{c,O2} = 0$ (if $i_{c,Cu}$ and $i_{a,O2} \approx 0$)

$i_{corr} = i_{a,Cu} = - i_{c,O2}$

$i_{corr} = i_{a,Cu} = i_{0,Cu} \exp ((E_{corr}-E_{rev,Cu})/\beta_{a,Cu})$

$i_{corr} = - i_{c,O2} = -i_{0,O2} \exp ((E_{corr}-E_{rev,O2})/\beta_{c,O2})$

Butler-Volmer equation for a mixed electrode

$i_a = i_{corr} \exp(\xi / \beta_a)$ anodic current density

$i_c = - i_{corr} \exp(- \xi / \beta_c)$ cathodic current density

$i = i_a + i_c = i_{corr} \exp(\xi / \beta_a) - i_{corr} \exp(- \xi / \beta_c)$

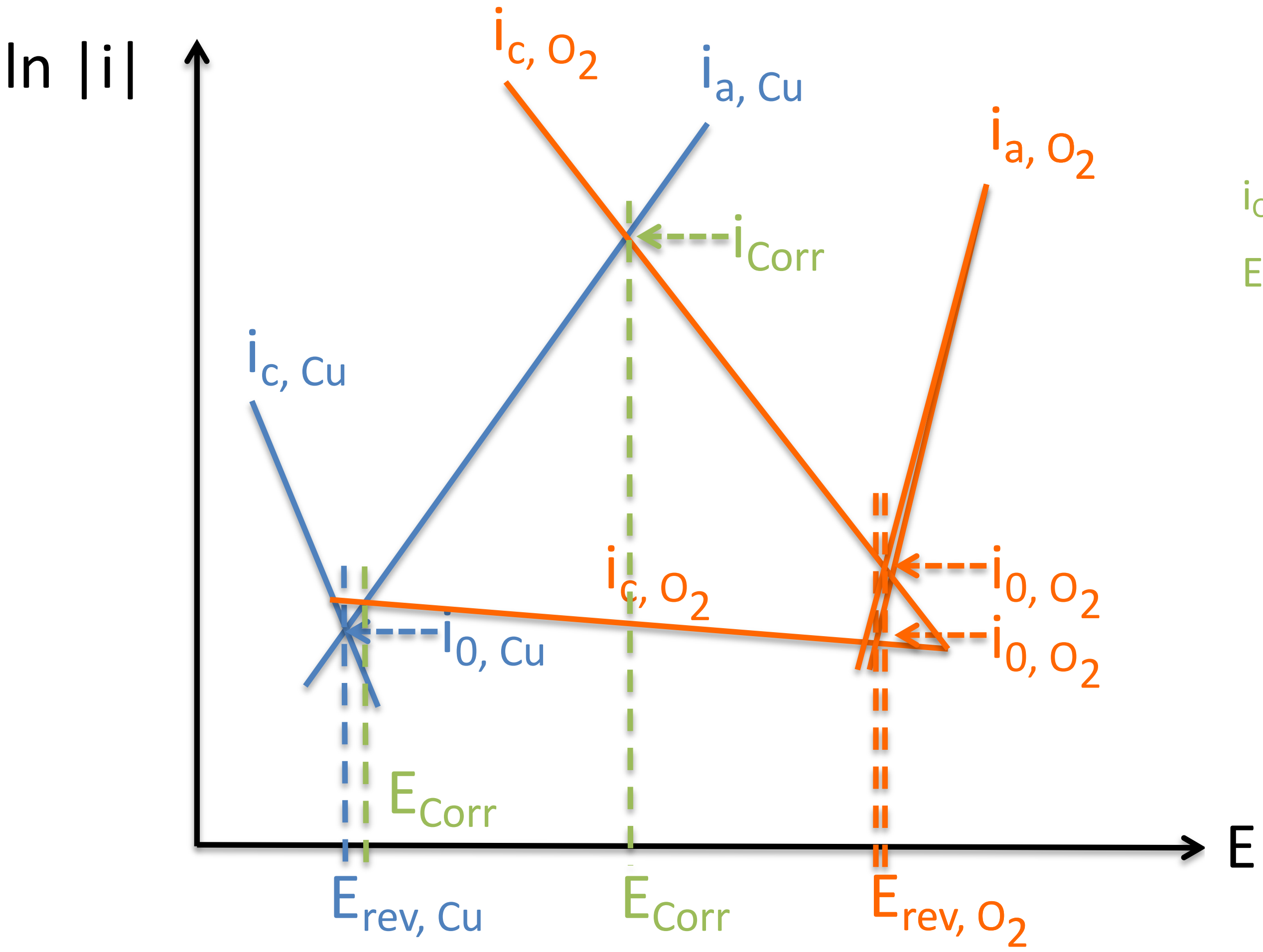
ξ : *polarisation* $= E - E_{corr}$

$\beta_a = RT / \alpha n F$

$\beta_c = RT / (1-\alpha') n F$

i_{corr} : *corrosion current density*

E_{corr} and i_{corr} depend on kinetics



i_{Corr}: corrosion current density

E_{corr}: corrosion potential