Electrochemical Engineering
Lecture 03
Electrochemical Kinetics

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Electrochemical Kinetics

❑Definition

"…a field of electrochemistry studying the rate of electrochemical processes." (Wikipedia)

"The main goal of the electrochemical kinetics is to find **a relationship between the electrode overpotential and current density** …" (S. N. Lvov)

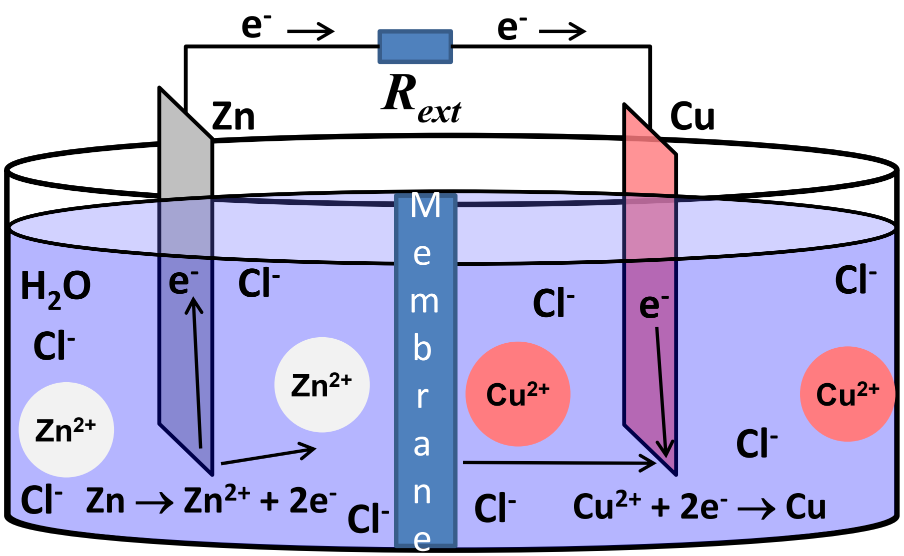
Rate - represented by **current (density)** for electrochemical reactions

❑Contents

- Cell potential, voltage loss, and overpotential (η)
- Charge transfer overpotential & **Butler-Volmer equation**
    - Tafel relationship
    - Linear approximation
- Mass transfer limitation

Cell Potential for Galvanic & Electrolytic Cells

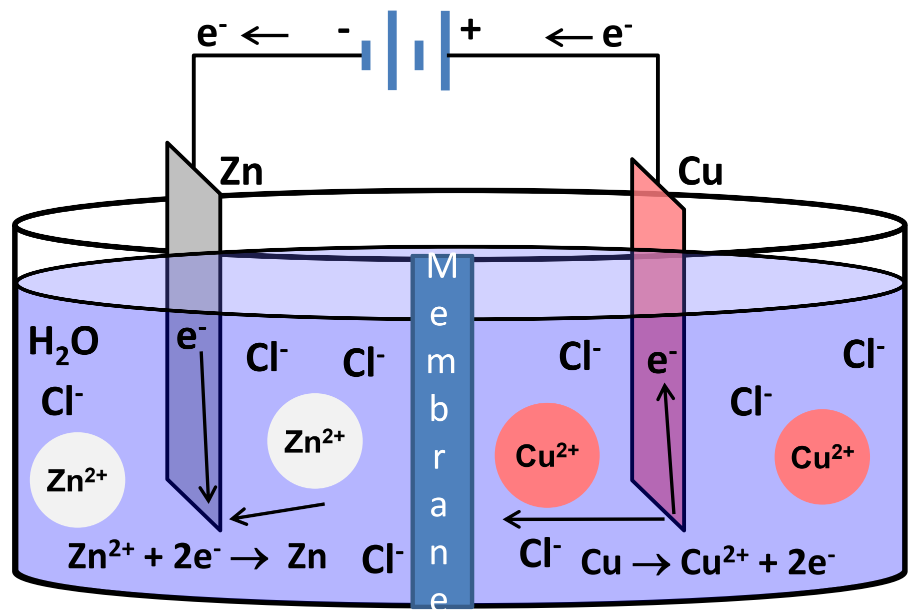
Galvanic cell (GC)



$$E_{eq} = I\,(R_{ext} + R_{int})$$

$$E_{cell} = IR_{ext} = E_{eq} - IR_{int}$$

Electrolytic cell (EC)



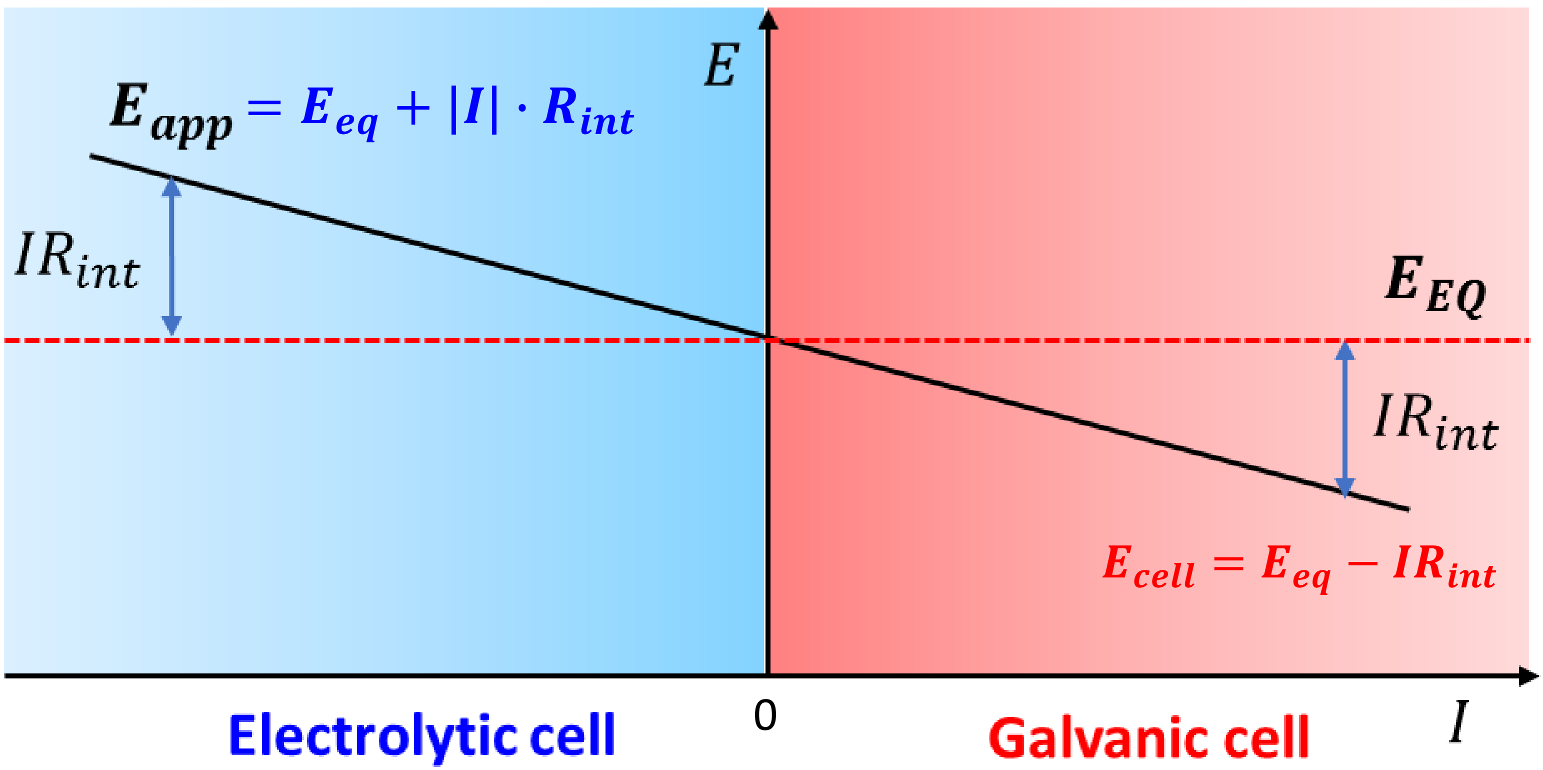
$$E_{cell} = E_{App} = E_{eq} + |I| \cdot R_{int}$$

Cell (External) Potential vs. Current Relationship

Actual cell (external) potential E_{cell} is related to equilibrium cell potential E_{eq} and the current passing through the cell

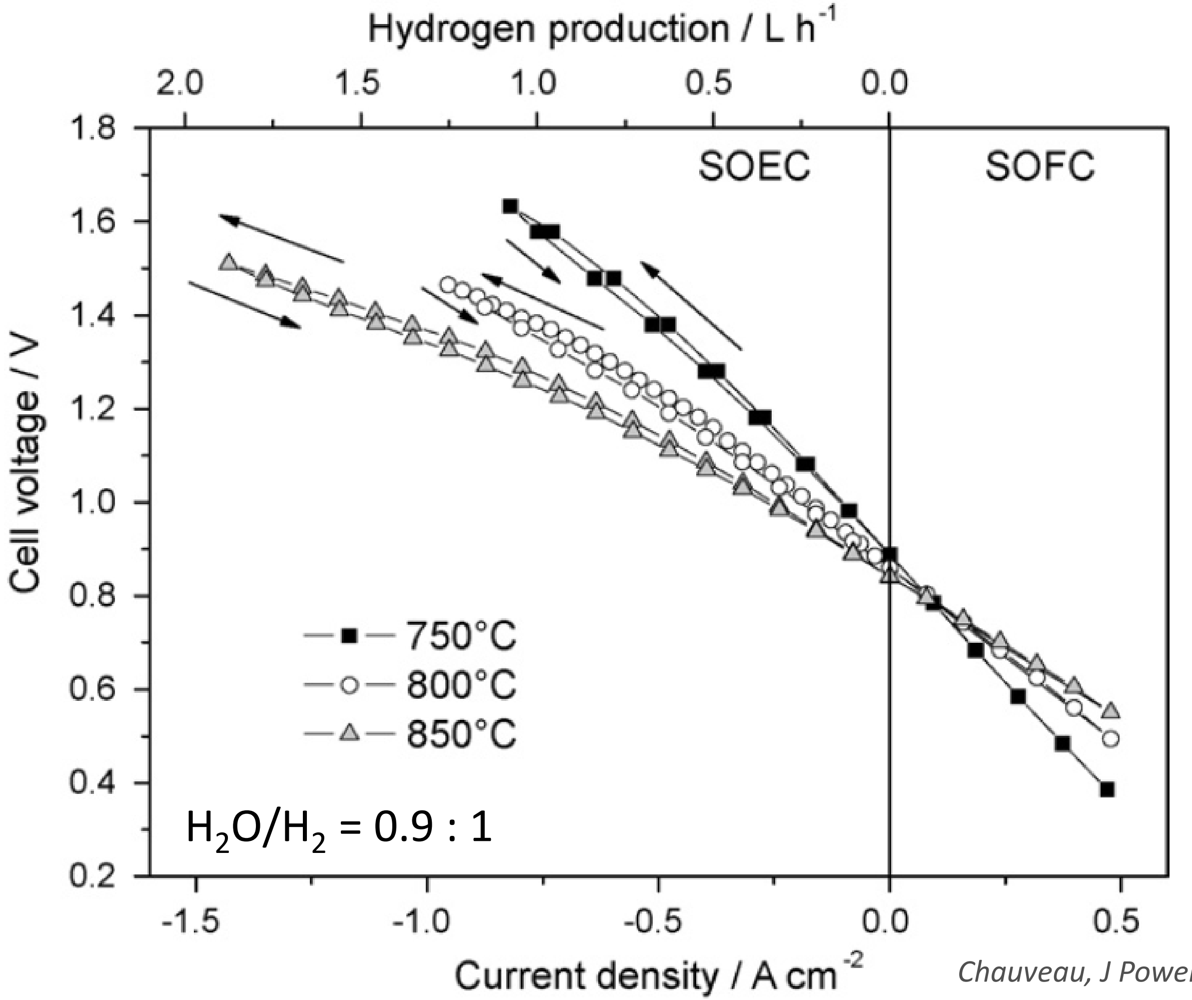
If cell internal resistance R_{int} a constant (an oversimplification) → **linear** relationship

Cell potential E vs. Current I



Cell (External) Potential - Current Example (1)

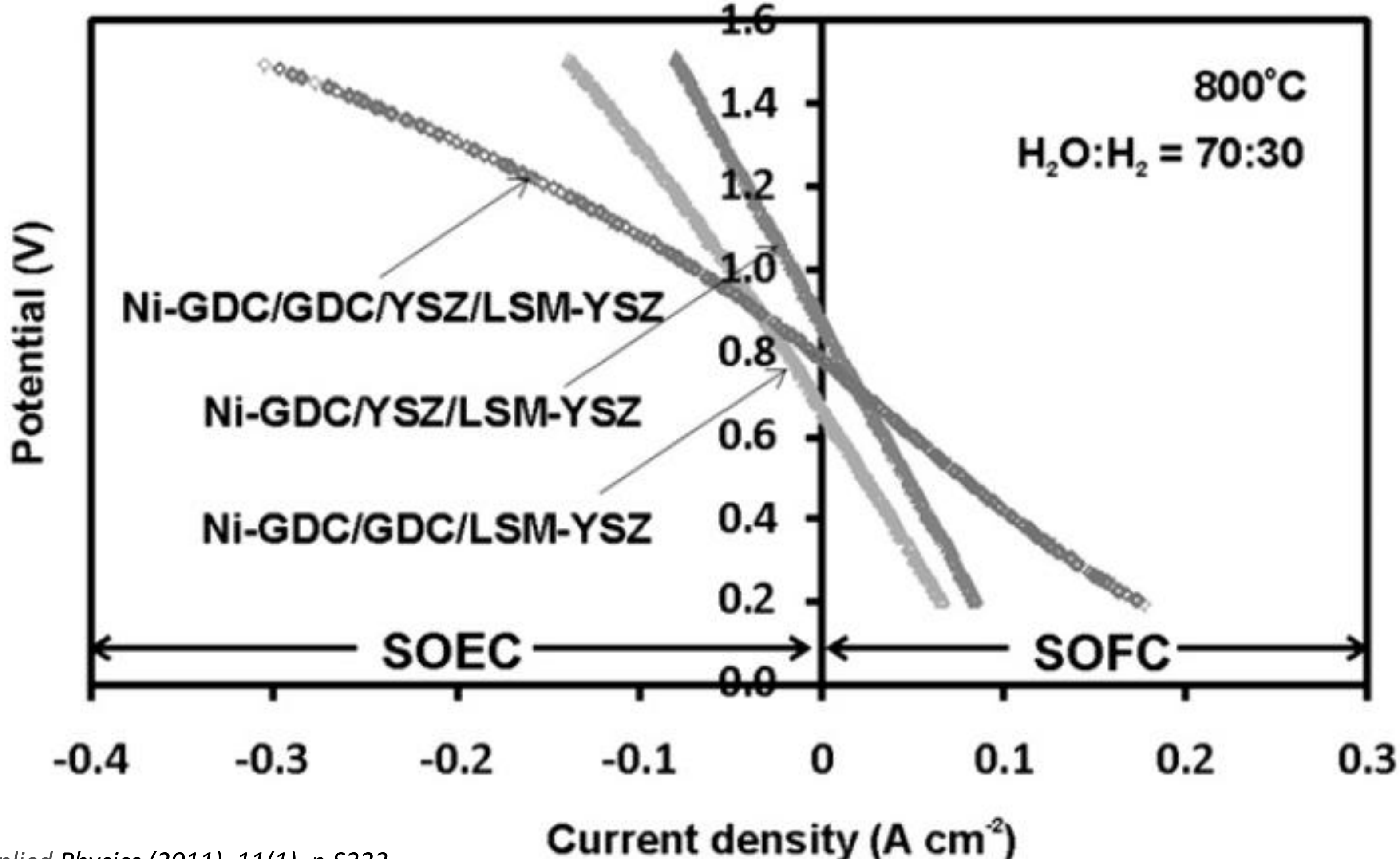
j-V for a reversible solid oxide fuel cell (SOFC, a galvanic cell, j > 0)/solid oxide electrolysis cell (SOEC, an electrolytic cell, j <0) in both modes



Chauveau, J Power Sourcesv195 (2010) p. 744

Cell (External) Potential - Current Example (2)

j-V for a reversible solid oxide fuel cell (SOFC, a galvanic cell, j > 0)/solid oxide electrolysis cell (SOEC, an electrolytic cell, j <0) in both modes



Current Applied Physics (2011), 11(1), p.S223

Voltage Loss from Equilibrium Cell Potential in an Electrochemical Cell

- **Difference between cell equilibrium potential E_{eq} and actual cell (external) potential E_{cell} is due to <u>cell internal resistance</u> R_{int}**

  If current takes <u>**absolute**</u> value:

  Galvanic cell (GC)

$$\Delta E_{GC} = E_{eq} - E_{cell} = IR_{int} = \eta_{electrodes} + IR_{\Omega}$$

  IR_{Ω} voltage loss due to ohmic resistance (mostly in electrolyte)

  $\eta_{electrodes}$ voltage loss or overpotential due to electrode processes

  $E_{cell} < E_{eq}$ → less energy is converted to outside electrical work (i.e., $E_{cell}Q$) than predicted under <u>equilibrium</u> condition, i.e., $E_{eq}Q$

  Electrolytic cell (EC)

$$\Delta E_{EC} = E_{App} - E_{eq} = IR_{int} = \eta_{electrodes} + IR_{\Omega}$$

  $E_{cell} > E_{eq}$ → electrical energy provided $E_{App}Q$ is higher than what is actually stored as chemical energy, $E_{eq}Q$

- $\eta_{electrodes}$ from both anode & cathode $\eta_{electrodes} = |\eta_{an}| + |\eta_{cat}|$
- R_{int} often **not** constant and $\eta_{electrodes}$ often non-linear with I
- Overpotential for an individual electrode (reaction) cannot be separated without using a third electrode or reference electrode

Overpotential η

❑ Definition

Difference between actual potential (e.g., measured) E and the equilibrium potential E_{eq} for an **electrode (or redox or half cell) reaction**:

$$\eta = E(Ox/Red) - E_{eq}(Ox/Red)$$

- For situation when i ≠ 0 or electrode (half cell) reaction is NOT at equilibrium
- Changes with current density & direction

❑ Significance

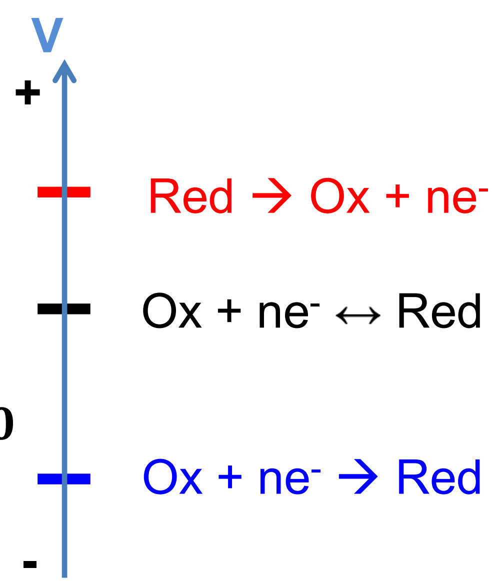
$E(Ox/Red) > E_{eq}(Ox/Red),\ \eta > 0$

Anodic polarization (or bias)

$E_{eq}(Ox/Red)$

$E(Ox/Red) < E_{eq}(Ox/Red),\ \eta < 0$

Cathodic polarization (or bias)

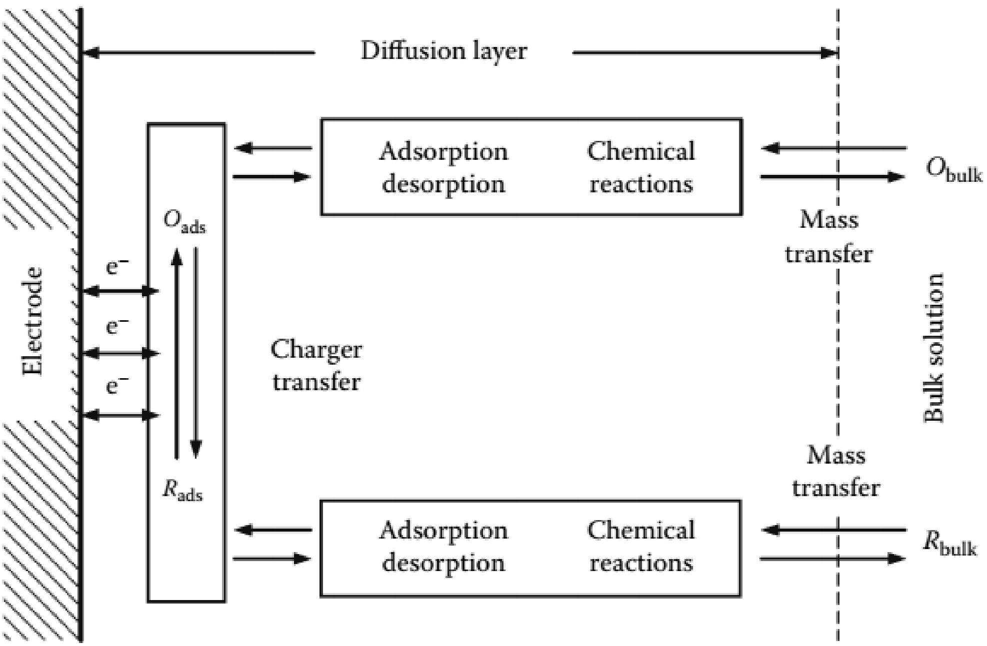


❑ Often takes **absolute value** with note about nature (anodic or cathodic)

Contributions to Overpotential for a Single Electrode (Reaction)

- **Charge transfer overpotential η_{ct}**
  Voltage loss associated with charge (or electron) transfer for an electrode (half-cell) reaction, usually across the electrode/electrolyte interface
- **Mass transfer overpotential η_{mt}**
  Voltage loss related to delivering of reactants to or removing of products from the electrode/electrolyte interface, significant at high current (density)
- **Others**
  - Adsorption/desorption
  - Chemical reactions (away from electrode interface)
- **Total overpotential for a <u>single electrode</u> (either anode or cathode) <u>reaction</u> is sum of contributions from charge transfer, mass transfer, and, maybe, other effects:**

$$\eta = \eta_{ct} + \eta_{mt} + \eta_{others}$$

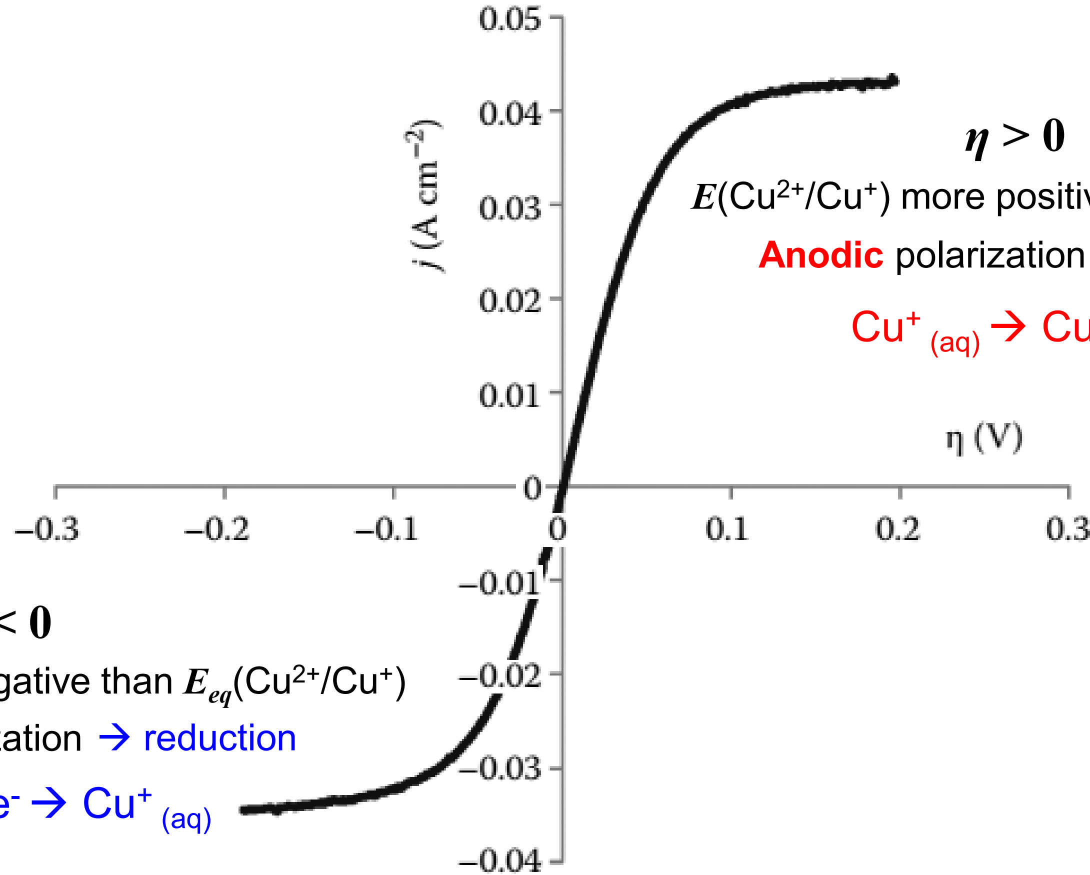


Possible processes in an electrochemical electrode (or half cell) reaction

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9

Polarization Curve for Electrode Reaction & an Example

- Plot of current density *j* vs electrode overpotential η is called **polarization curve**
- Often **<u>nonlinear</u>**



$\eta > 0$

$E(Cu^{2+}/Cu^{+})$ more positive than $E_{eq}(Cu^{2+}/Cu^{+})$

Anodic polarization → oxidation

$Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + e^{-}$

$\eta < 0$

$E(Cu^{2+}/Cu^{+})$ more negative than $E_{eq}(Cu^{2+}/Cu^{+})$

Cathodic polarization → reduction

$Cu^{2+}_{(aq)} + e^{-} \rightarrow Cu^{+}_{(aq)}$

Polarization curve of for Cu^{2+}(aq, 0.1 mol/kg) / Cu^{+}(aq, 0.1 mol/kg) electrode (redox or half cell) reaction at 25°C 1 atm with HCl (aq) supporting electrolyte of 8 mol/kg

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9

Butler-Volmer Equation <u>without</u> Mass Transport Limitation

For a one-step electrode (half cell) reaction **<u>without</u> mass transport limitation**

$$Ox + ne^- \leftrightarrow Red$$

Butler-Volmer equation describes net current density j as a function of total overpotential for that electrode (half cell) reaction $\eta = E(Ox/Red) - E_{eq}(Ox/Red)$

$$\boldsymbol{j = j_a + j_c = j_o\left\{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right)\right\}}$$

j_a	Anodic (oxidation) current density, in A/cm^2
j_c	Cathodic (reduction) current density, in A/cm^2
j_o	Exchange current density, in A/cm^2
β	Symmetry factor, unitless
R	Gas constant 8.314 J/(mol·K)
T	Absolute temperature, K

Notes:

- **Assuming <u>uniform concentration</u>** for all active species:
  - Extensively stirring and/or keep current relatively low
- **Sign convention**
  - For η & j: Anodic (oxidation) as positive (+); Cathodic (reduction) as negative (-)

Butler-Volmer Equation - Anodic Bias

For a one-step electrode (half cell) reaction:

$$Ox + ne^- \leftrightarrow Red$$

Butler-Volmer equation describes net current density j as a function of total overpotential for that electrode (half cell) reaction $\eta = E(Ox/Red) - E_{eq}(Ox/Red)$

$$j = j_a + j_c = j_o\left\{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right)\right\}$$

Anodic polarization or bias:

$$\eta = E(Ox/Red) - E_{eq}(Ox/Red) > 0$$

Ratio of anodic (oxidation) to cathodic (reduction) current absolute value:

$$\frac{j_a}{|j_c|} = \frac{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right]}{\exp\left(-\frac{\beta nF\eta}{RT}\right)} = \exp\left[\frac{(1-\beta)nF\eta}{RT} + \frac{\beta nF\eta}{RT}\right] = \exp\left(\frac{nF\eta}{RT}\right) > 1$$

Net current density $j > 0$

Electrode (half cell) reaction proceeds along anodic/oxidation direction

$$Red \rightarrow Ox + ne^-$$

Butler-Volmer Equation - Cathodic Bias

For a one-step electrode (half cell) reaction:

$$Ox + ne^- \leftrightarrow Red$$

Butler-Volmer equation describes net current density j as a function of total overpotential for that electrode (half cell) reaction $\eta = E(Ox/Red) - E_{eq}(Ox/Red)$

$$j = j_{\mathrm{a}} + j_{\mathrm{c}} = j_{\mathrm{o}} \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

Cathodic polarization or bias:

$$\eta = E(Ox/Red) - E_{eq}(Ox/Red) < 0$$

Ratio of anodic (oxidation) to cathodic (reduction) current absolute value:

$$\frac{j_{\mathrm{a}}}{|j_{\mathrm{c}}|} = \frac{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right]}{\exp\left(-\frac{\beta nF\eta}{RT}\right)} = \exp\left[\frac{(1-\beta)nF\eta}{RT} + \frac{\beta nF\eta}{RT}\right] = \exp\left(\frac{nF\eta}{RT}\right) < 1$$

Net current density $j < 0$

Electrode (half cell) reaction proceeds along cathodic/reduction direction

$$Ox + ne^- \rightarrow Red$$

Butler-Volmer Equation at Equilibrium

For a one-step electrode (half cell) reaction:

$$Ox + ne^- \leftrightarrow Red$$

Butler-Volmer equation describes change of net current density *j*, as a function of overpotential, $\eta = E(Ox/Red) - E_{eq}(Ox/Red)$

$$j = j_{\mathrm{a}} + j_{\mathrm{c}} = j_{\mathrm{o}} \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

At equilibrium,

$$\eta = E(Ox/Red) - E_{eq}(Ox/Red) = 0$$

Anodic (oxidation) current density $j_a = j_{\mathrm{o}} exp\left[\frac{(1-\beta)nF\eta}{RT}\right] = j_{\mathrm{o}} > 0$

Cathodic (reduction) current density $j_c = -j_{\mathrm{o}} exp\left(-\frac{\beta nF\eta}{RT}\right) = -j_{\mathrm{o}} < 0$

Net current density $j = j_{\mathrm{a}} + j_{\mathrm{c}} = 0$

→ No net reaction i.e., reaction at equilibrium

→ No change in (local) concentration of different (active) species

From Butler Volmer Equation to Polarization Curve

$$j = {\color{red}j_a} + {\color{blue}j_c} = j_o \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

- At equilibrium

  $\eta = 0, j = 0$

  $j_a = j_0$

  $j_c = -j_0$

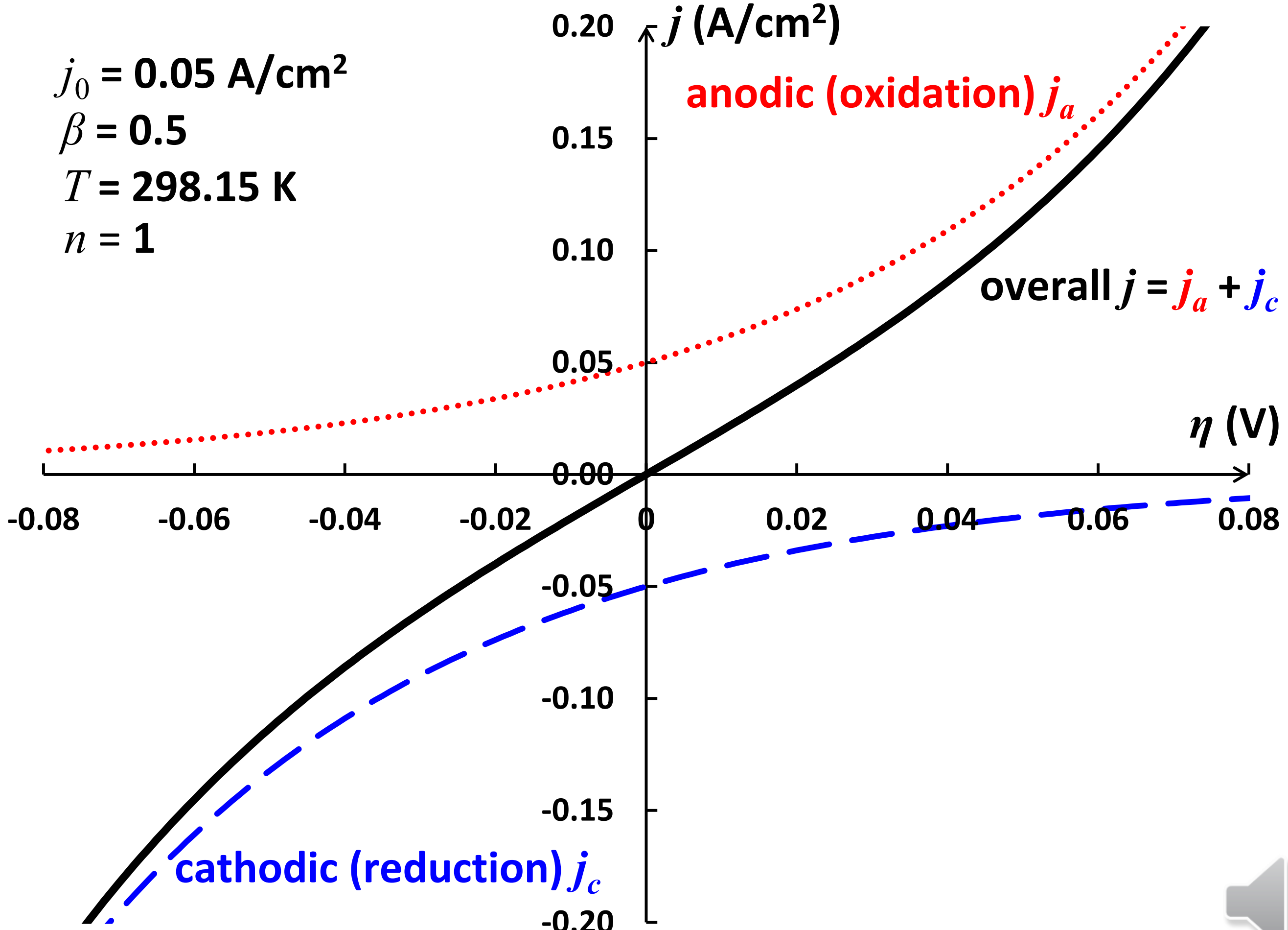
  $j = {\color{red}j_a} + {\color{blue}j_c} = 0$

- $\eta > 0, j > 0$

  Anodic/oxidation

- $\eta < 0, j < 0$

  Cathodic/reduction



Exchange Current Density j_0

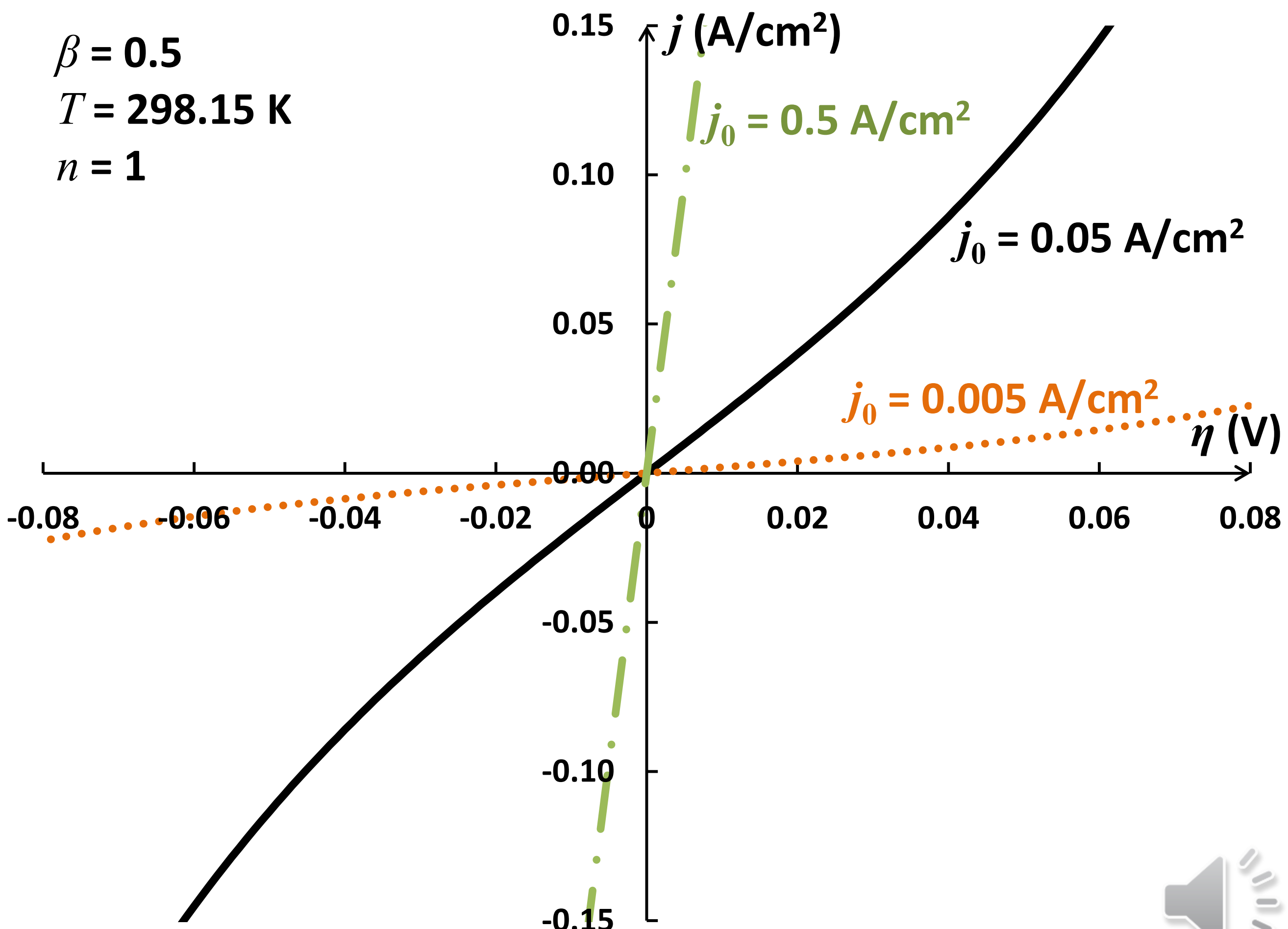
$$j = j_a + j_c = j_o\left\{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right)\right\}$$

Larger j_0 →

at the same η,

much higher j

→ intrinsically faster reaction (both ways)

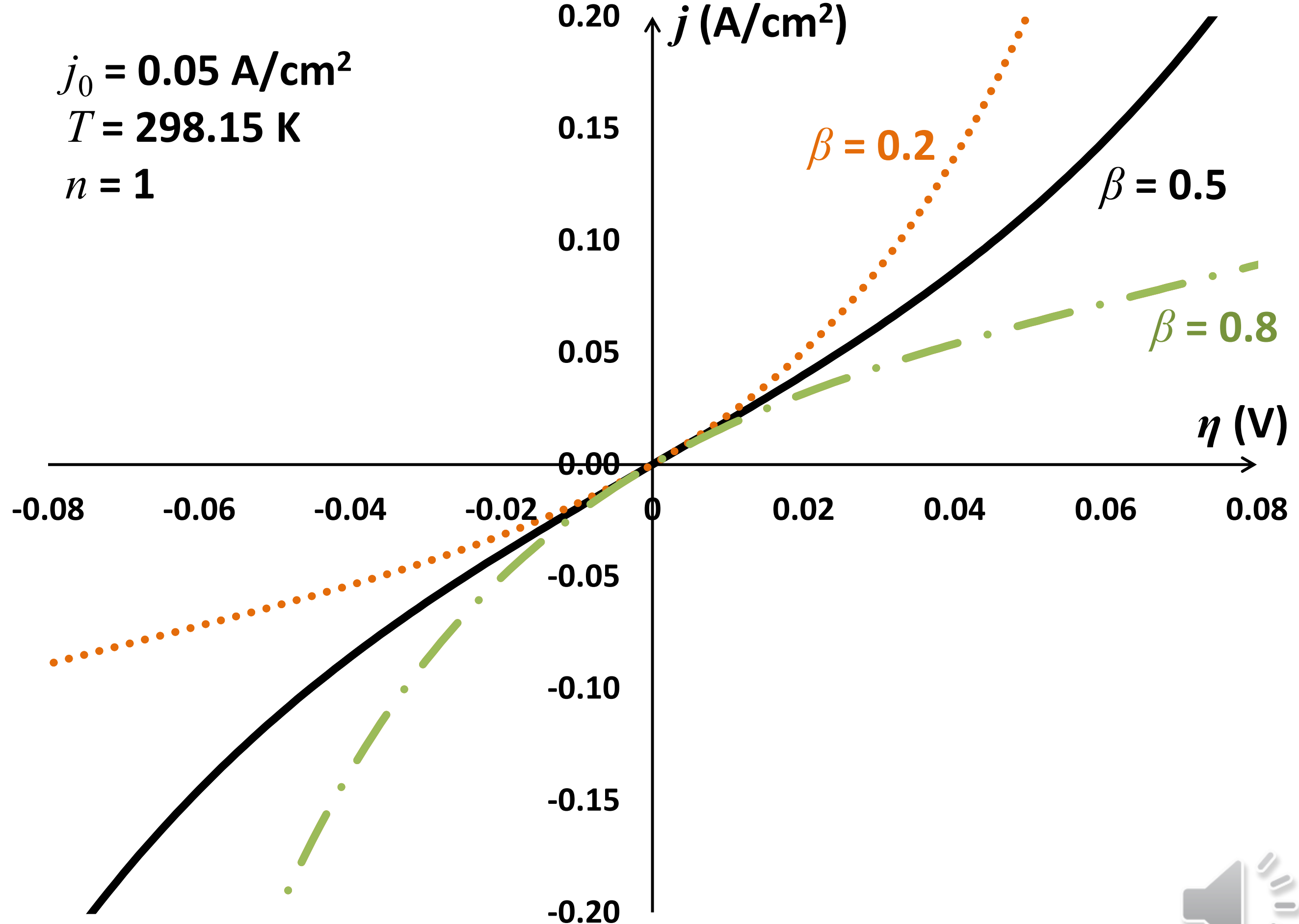


Symmetry Factor β

$$j = j_a + j_c = j_o \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

β is an indicator of symmetry of the polarization curve, ranges from 0 to 1

- β = 0.5
  Symmetrical
- β < 0.5
  anodic (oxidation) direction "easier"
- β > 0.5
  cathodic (reduction) direction "easier"



Experimental Data on β and j_o and Notes

- Exchange current density & symmetry factor data limited due to experimental difficulties & insufficient studies
- Different electrode/half cell reactions have different j_0
  - Fe^{3+}/Fe^{2+}
  - $K_3Fe(CN)_6/K_4Fe(CN)_6$
  - H^+, O_2/H_2O
- The same electrode/half cell reaction may have different j_0 values, depending on catalyst or (inert) electrode material
  - H^+/H_2 on **Hg**
  - H^+/H_2 on **Pt**

Experimental Values of Exchange Current Density, Standard Exchange Current Density and Symmetry Coefficient

S. Lvov, CRC Press (2015). ISBN: 978-1-4665-8285-9

Electrode and Concentration of Aqueous Species	Aqueous Electrolyte	t (°C)	Electrode	j_o (A cm^{-2})	j_o^o (A cm^{-2})	β
Fe^{3+}/Fe^{2+} (0.005 mol/L)	1 mol/L H_2SO_4	25	Pt	2×10^{-3}	4×10^{-1}	0.42
$K_3Fe(CN)_6/K_4Fe(CN)_6$ (0.02 mol/L)	0.5 mol/L K_2SO_4	25	Pt	5×10^{-3}	5	0.51
Ag^+/Ag (0.001 mol/L)	1 mol/L $HClO_4$	25	Ag	1.5×10^{-1}	13.4	0.35
Cd^{2+}/Cd (0.01 mol/L)	0.4 mol/L K_2SO_4	25	Cd	1.5×10^{-3}	1.9×10^{-2}	0.45
$Cd^{2+}/Cd(Hg)$ (0.0014 mol/L)	0.5 mol/L Na_2SO_4	25	Cd(Hg)	2.5×10^{-2}	4.8	0.2
$Zn^{2+}/Zn(Hg)$ (0.02 mol/L)	1 mol/L $HClO_4$	25	Zn(Hg)	5.5×10^{-3}	0.10	0.25
Ti^{4+}/Ti^{3+}(0.001 mol/L)	1 mol/L $C_2H_4O_2$	0	Pt	9×10^{-4}	0.9	0.45
H_2O/H_2, OH^-	1 mol/L KOH	25	Pt	10^{-3}	10^{-3}	0.5
H^+/H_2	1 mol/L H_2SO_4	25	Hg	10^{-12}	10^{-12}	0.5
H^+/H_2	1 mol/L H_2SO_4	25	Pt	10^{-3}	10^{-3}	0.5
H_2O/O_2, OH^-	1 mol/L KOH	25	Pt	10^{-6}	10^{-6}	0.7
H^+, O_2/H_2O	1 mol/L H_2SO_4	25	Pt	10^{-6}	10^{-6}	0.75

Butler-Volmer Equation Near Equilibrium

For B-V equation: $j = j_o\left\{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right)\right\}$

At very small overpotential ($|\eta| < 10\ \mathrm{mV}$), exponents in the B-V equation are small:

e.g., β = 0.5, n = 1, T = 298.15 K

$$\frac{(1-\beta)nF\eta}{RT} = \frac{\beta nF\eta}{RT} = \frac{0.5 \times 1 \times 96485C/mol \times 0.01V}{\frac{8.314J}{(mol \cdot K)} \cdot 298.15K} = 0.195$$

Consider $e^x \approx 1 + x$ when $x \to 0$ $\quad e^{0.195} = 1.215 \approx 1 + 0.195$

We have $j \approx j_o\left[1 + \frac{(1-\beta)nF\eta}{RT} - \left(1 - \frac{\beta nF\eta}{RT}\right)\right] = j_o\left[\frac{(1-\beta)nF\eta}{RT} + \frac{\beta nF\eta}{RT}\right] = j_o \cdot \frac{nF\eta}{RT}$

$$\boldsymbol{j = j_o \frac{nF}{RT} \cdot \eta}$$

Current density **linearly** proportional to overpotential under very small bias ($< 10\ \mathrm{mV}$)

Define charge transfer resistance $R_{ct} = \frac{\eta}{j} = \frac{RT}{nFj_o}$ a way of determining j_o - under very small bias

Tafel Equation (1)

For B-V equation: $j = j_o \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$

When $\eta \gg 0$, large anodic polarization (still no mass transport limitation):

$$j \approx j_o \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \Rightarrow \ln j = \ln j_o + \frac{(1-\beta)nF\eta}{RT} \Rightarrow \frac{(1-\beta)nF\eta}{RT} = -\ln j_o + \ln j$$

$$\eta = -\left[\frac{RT}{(1-\beta)nF}\right] \ln j_o + \left[\frac{RT}{(1-\beta)nF}\right] ln j$$

When $\eta \ll 0$, large cathodic polarization (still no mass transport limitation):

$$|j| \approx j_o \exp\left(-\frac{\beta nF\eta}{RT}\right) \Rightarrow \ln|j| = \ln j_o - \frac{\beta nF\eta}{RT} \Rightarrow -\frac{\beta nF\eta}{RT} = -\ln j_o + \ln|j|$$

$$-\eta = -\left(\frac{RT}{\beta nF}\right) \ln j_o + \left(\frac{RT}{\beta nF}\right) ln|j|$$

Tafel Equation (2)

B-V equation:

$$j = j_o \left\{ \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

$\eta \gg 0$

$$\eta = -\left[\frac{RT}{(1-\beta)nF}\right] \ln j_o + \left[\frac{RT}{(1-\beta)nF}\right] ln j$$

$\eta \ll 0$

$$-\eta = -\left(\frac{RT}{\beta nF}\right) \ln j_o + \left(\frac{RT}{\beta nF}\right) ln|j|$$

Tafel equation – general form

$$\boldsymbol{|\eta| = a + b \cdot \ln|j| = a + b' \cdot \log_{10}|j|}$$

Anodic overpotential (bias)

$$a = -\left[\frac{RT}{(1-\beta)nF}\right] \ln j_o \quad b = \left[\frac{RT}{(1-\beta)nF}\right]$$

Cathodic overpotential (bias)

$$a = -\left(\frac{RT}{\beta nF}\right) \ln j_o \qquad b = \left(\frac{RT}{\beta nF}\right)$$

- Fitting of experimental η - j data yields Tafel intercept a and slope b (or $b' = 2.303b$), which allows estimation of j_o and β
- Applicable when η > ~100 mV
- NOT applicable near equilibrium or $|j| \rightarrow 0$

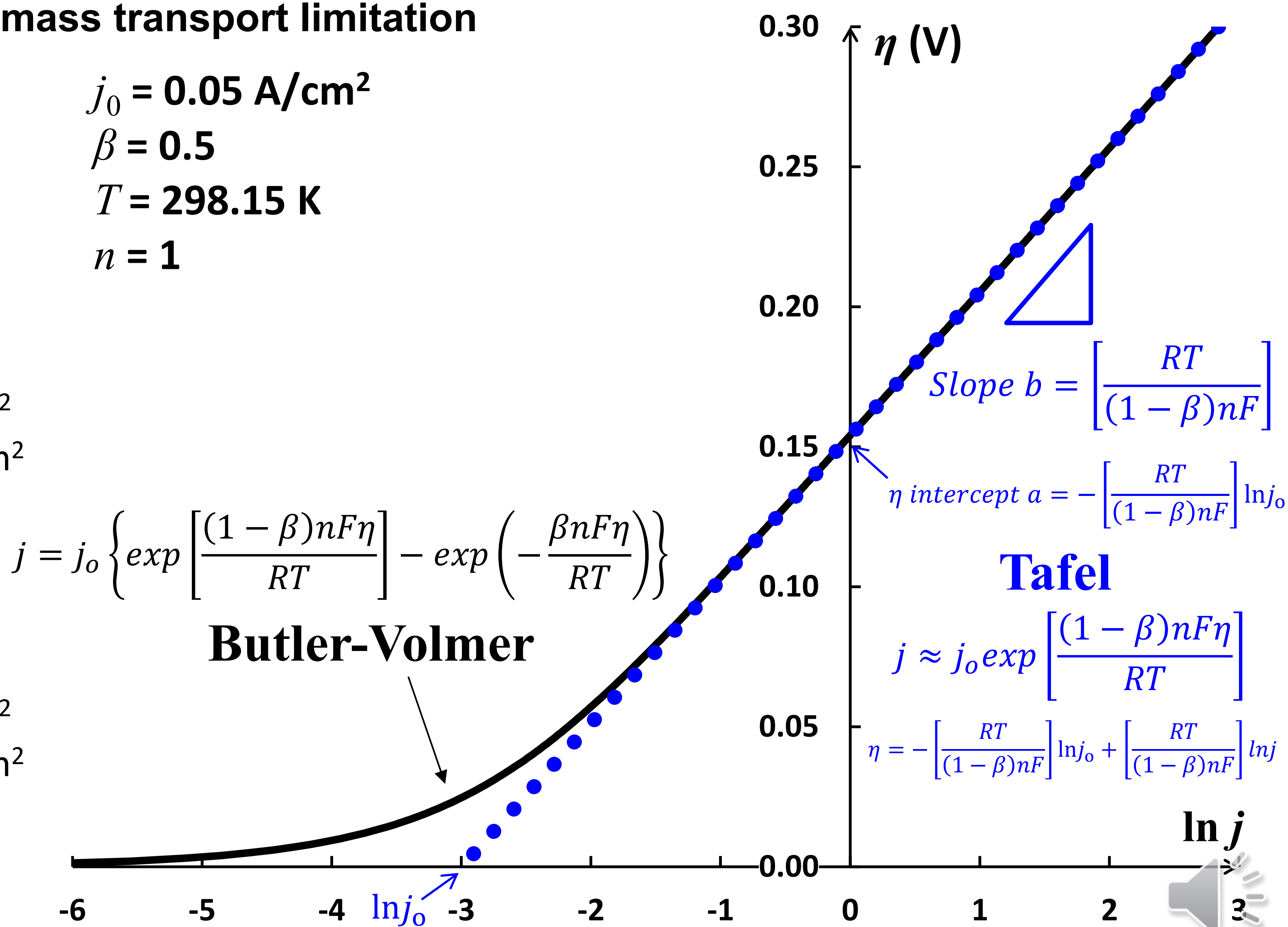
Deviation of Tafel from Butler-Volmer

Assuming NO mass transport limitation

j_0 = **0.05 A/cm^2**
β = **0.5**
T = **298.15 K**
n = **1**

η = 100 mV,
$j_{B\text{-}V}$ = 0.343 A/cm^2
j_{Tafel} = 0.350 A/cm^2
~2% error

η = 60 mV,
$j_{B\text{-}V}$ = 0.145 A/cm^2
j_{Tafel} = 0.161 A/cm^2
~11% error



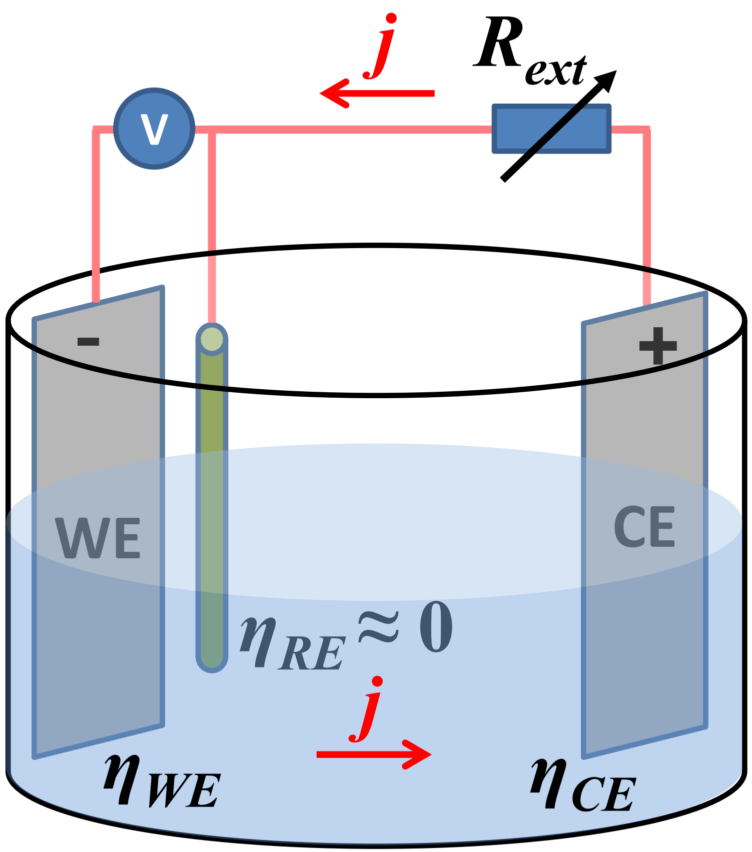
Measurement of Overpotential for an Electrode (half cell) Reaction

- Overpotential for an electrode (reaction) of interest that is passing a current (**working electrode, WE**) *cannot* be measured with respect to the other current-carrying electrode reaction (**counter electrode, CE**) in an electrochemical cell.
  →A third electrode (reaction) must be introduced as the **reference electrode (RE)**
- Measure potential difference for WE vs. RE under equilibrium (j = 0) and with different current density j,
  then the "overpotential" for WE

  $$\eta_{WE} = [E\,(\text{WE}) - E\,(\text{RE})] - [E_{eq}\,(\text{WE}) - E_{eq}(\text{RE})]$$

  $$\eta_{WE} \approx E\,(\text{WE}) - E_{eq}\,(\text{WE})$$

  could be obtained as a function of j
- To avoid overpotential contribution from RE, no significant current must pass through RE, which is achieved with **a high impedance voltmeter**

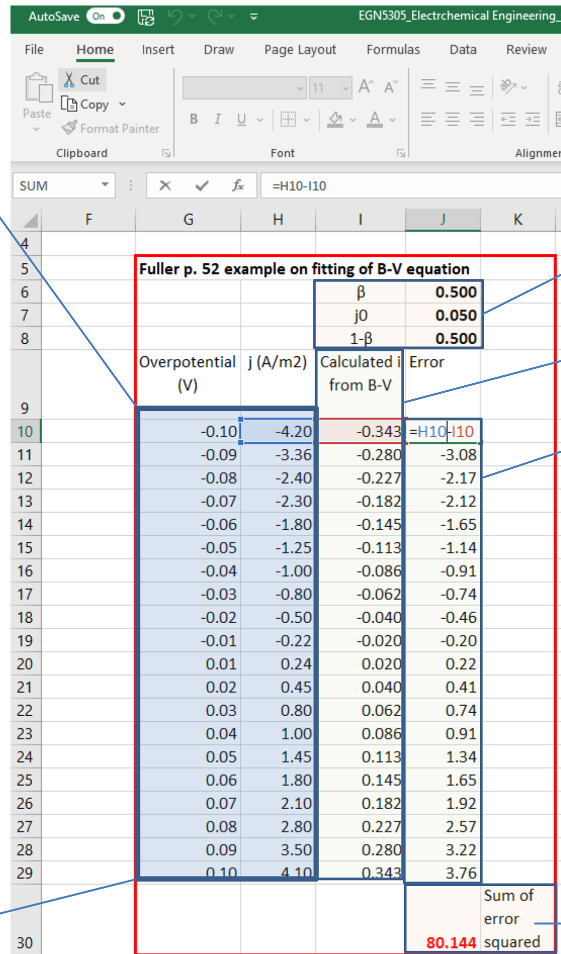


Example of Data Fitting to B-V Equation (1)

Data below were taken for a NiOOH electrode reaction involving a single electron. Fit the data to obtain kinetic parameters in the Butler-Volmer equation.

Overpotential (V)	j (A/m^2)
-0.10	-4.20
-0.09	-3.36
-0.08	-2.40
-0.07	-2.30
-0.06	-1.80
-0.05	-1.25
-0.04	-1.00
-0.03	-0.80
-0.02	-0.50
-0.01	-0.22
0.01	0.24
0.02	0.45
0.03	0.80
0.04	1.00
0.05	1.45
0.06	1.80
0.07	2.10
0.08	2.80
0.09	3.50
0.10	4.10

Enter the data into MS Excel



Fuller p. 52 example on fitting of B-V equation

β	0.500
j0	0.050
1-β	0.500

Overpotential (V)	j (A/m2)	Calculated i from B-V	Error
-0.10	-4.20	-0.343	=H10-I10
-0.09	-3.36	-0.280	-3.08
-0.08	-2.40	-0.227	-2.17
-0.07	-2.30	-0.182	-2.12
-0.06	-1.80	-0.145	-1.65
-0.05	-1.25	-0.113	-1.14
-0.04	-1.00	-0.086	-0.91
-0.03	-0.80	-0.062	-0.74
-0.02	-0.50	-0.040	-0.46
-0.01	-0.22	-0.020	-0.20
0.01	0.24	0.020	0.22
0.02	0.45	0.040	0.41
0.03	0.80	0.062	0.74
0.04	1.00	0.086	0.91
0.05	1.45	0.113	1.34
0.06	1.80	0.145	1.65
0.07	2.10	0.182	1.92
0.08	2.80	0.227	2.57
0.09	3.50	0.280	3.22
0.10	4.10	0.343	3.76
		80.144	Sum of error squared

Initial guessed values for j_0 and β

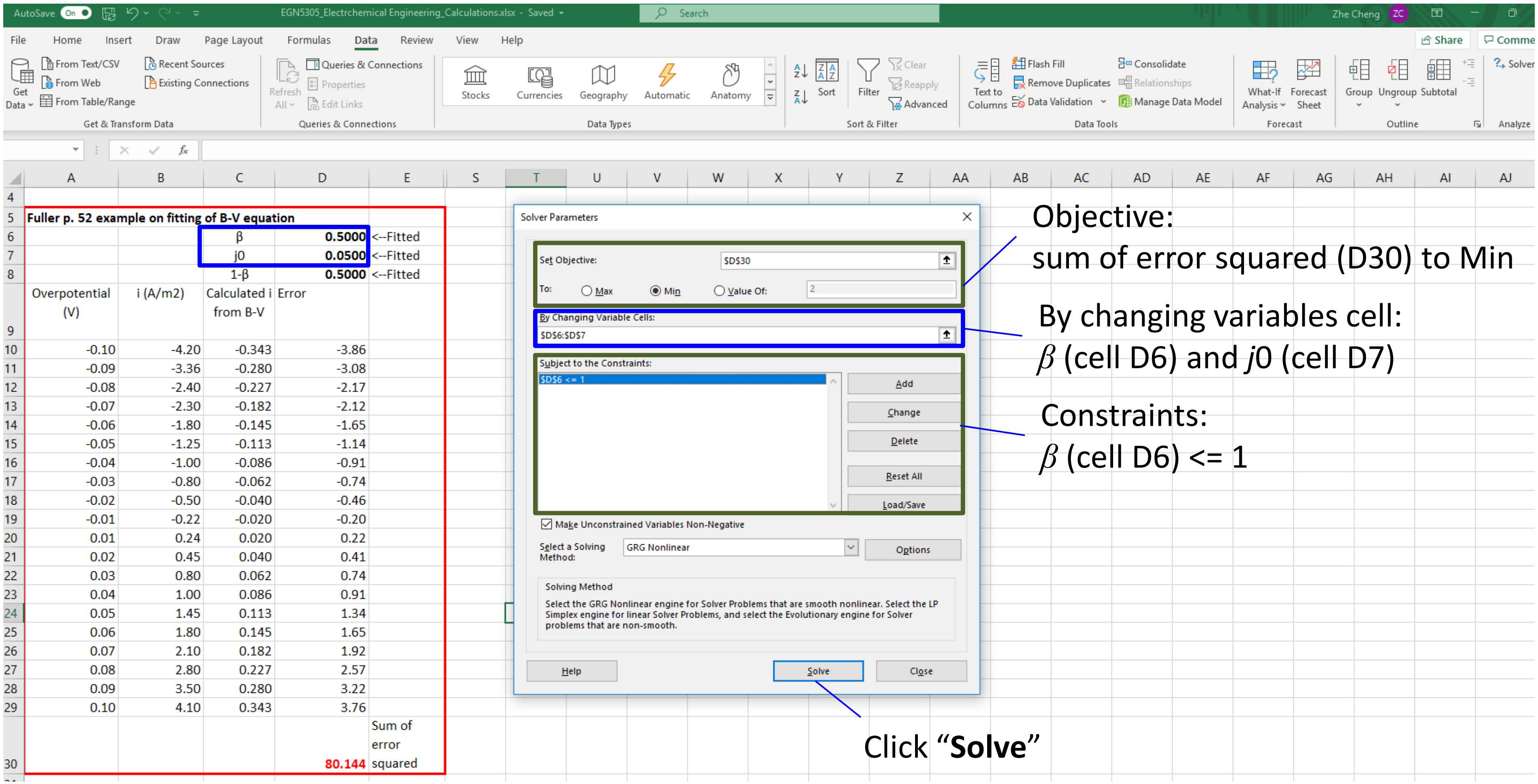
Calculated from B-V equation

Error = j – Calculated from B-V

= SUMSQ(J10:J29)

Example of Data Fitting to B-V Equation (2)

Use Excel **Solver** to fit for j_0 and β values



Fuller p. 52 example on fitting of B-V equation

		β	0.5000	<--Fitted
		j0	0.0500	<--Fitted
		1-β	0.5000	<--Fitted
Overpotential (V)	i (A/m2)	Calculated i from B-V	Error	
-0.10	-4.20	-0.343	-3.86	
-0.09	-3.36	-0.280	-3.08	
-0.08	-2.40	-0.227	-2.17	
-0.07	-2.30	-0.182	-2.12	
-0.06	-1.80	-0.145	-1.65	
-0.05	-1.25	-0.113	-1.14	
-0.04	-1.00	-0.086	-0.91	
-0.03	-0.80	-0.062	-0.74	
-0.02	-0.50	-0.040	-0.46	
-0.01	-0.22	-0.020	-0.20	
0.01	0.24	0.020	0.22	
0.02	0.45	0.040	0.41	
0.03	0.80	0.062	0.74	
0.04	1.00	0.086	0.91	
0.05	1.45	0.113	1.34	
0.06	1.80	0.145	1.65	
0.07	2.10	0.182	1.92	
0.08	2.80	0.227	2.57	
0.09	3.50	0.280	3.22	
0.10	4.10	0.343	3.76	
			80.144	Sum of error squared

Objective:
sum of error squared (D30) to Min

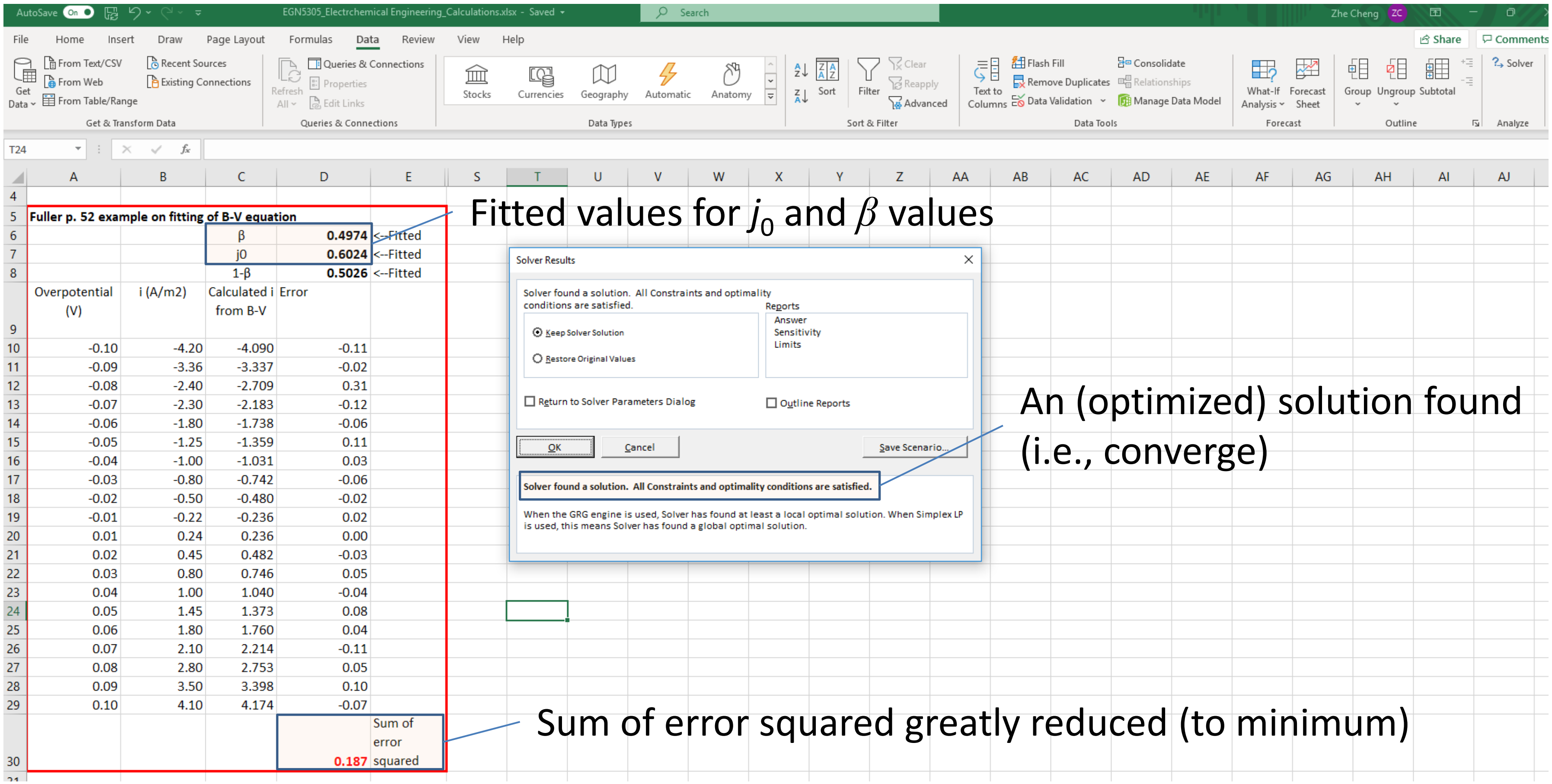
By changing variables cell:
β (cell D6) and $j0$ (cell D7)

Constraints:
β (cell D6) <= 1

Click "**Solve**"

Example of Data Fitting to B-V Equation (3)

Excel **Solver** provides fitted j_0 and β that minimize sum of error squared (cell D30)



Fuller p. 52 example on fitting of B-V equation

	β	0.4974	<--Fitted
	j0	0.6024	<--Fitted
	1-β	0.5026	<--Fitted

Overpotential (V)	i (A/m2)	Calculated i from B-V	Error
-0.10	-4.20	-4.090	-0.11
-0.09	-3.36	-3.337	-0.02
-0.08	-2.40	-2.709	0.31
-0.07	-2.30	-2.183	-0.12
-0.06	-1.80	-1.738	-0.06
-0.05	-1.25	-1.359	0.11
-0.04	-1.00	-1.031	0.03
-0.03	-0.80	-0.742	-0.06
-0.02	-0.50	-0.480	-0.02
-0.01	-0.22	-0.236	0.02
0.01	0.24	0.236	0.00
0.02	0.45	0.482	-0.03
0.03	0.80	0.746	0.05
0.04	1.00	1.040	-0.04
0.05	1.45	1.373	0.08
0.06	1.80	1.760	0.04
0.07	2.10	2.214	-0.11
0.08	2.80	2.753	0.05
0.09	3.50	3.398	0.10
0.10	4.10	4.174	-0.07
			0.187 Sum of error squared

Fitted values for j_0 and β values

An (optimized) solution found (i.e., converge)

Sum of error squared greatly reduced (to minimum)

Fitting to Tafel & Comparison w/ BV (1)

Anode polarization data on for chlorine gas production from 5 M NaCl solution at 20°C is provided (Kunh and Mortimer, *J Electrochem Soc* v120, 231 (1973)).
By fitting data to Tafel equation, determine exchange current density j_0 and symmetry factor β for the anode reaction.

$2Cl^- \rightarrow Cl_2 + 2e^-$

$n = 2$

j (A/m2)	Overpotential (V)	lnj
60300	0.20910	11.01
41300	0.19940	10.63
22300	0.17030	10.01
12400	0.15150	9.43
8080	0.13590	9.00
6180	0.12080	8.73
4110	0.10360	8.32
2070	0.07934	7.64
1230	0.05512	7.11
817	0.04727	6.71
621	0.04047	6.43
427	0.03433	6.06
240	0.02547	5.48
173	0.02204	5.15
116	0.01658	4.75
58	0.01175	4.07
30	0.00489	3.40

Fitted slope b	0.0398
Fitted intercept a	-0.2258
r^2	0.9978
1-β	0.317
j_0 (A/m2)	291

#1 Calculate ln$j$

#2 Linear fit for Overpotential (as y) vs. lnj (as x) for η >50 mV

#3 Calculate (1-β) and j_0 from fitted slope b and η axis intercept a :

$$Slope\ b = \left[\frac{RT}{(1-\beta)nF}\right]$$

$$\eta\ intercept\ a = -\left[\frac{RT}{(1-\beta)nF}\right]\ln j_0 = -b\ln j_0$$

Fuller textbook: $\alpha_a = (1-\beta)n = 0.635$

Fitting to Tafel & Comparison w/ BV (2)

j (A/m2)	Overpotential (V)	lnj	j from B-V	error
60300	0.20910	11.01	3935.5	56365
41300	0.19940	10.63	2680.6	38619
22300	0.17030	10.01	847.1	21453
12400	0.15150	9.43	402.4	11998
8080	0.13590	9.00	217.0	7863
6180	0.12080	8.73	119.4	6061
4110	0.10360	8.32	60.4	4050
2070	0.07934	7.64	23.1	2047
1230	0.05512	7.11	8.8	1221
817	0.04727	6.71	6.3	811
621	0.04047	6.43	4.8	616
427	0.03433	6.06	3.6	423
240	0.02547	5.48	2.4	238
173	0.02204	5.15	2.0	171
116	0.01658	4.75	1.4	115
58	0.01175	4.07	1.0	57
30	0.00489	3.40	0.4	30
	Fitted slope b	0.0398		
	Fitted intercept a	-0.2258		
	r^2	0.9978		
	1-β	0.317	0.500 <-- initial gu	
	j_0 (A/m2)	291	1 <-- initial gu	
			Sum of error squared	5.395E+09

Calculated from B-V equation based on initial guessed values for (1-β) and j_0 (e.g., 0.5 and 1, respectively)

Error between experimental j and calculated j from B-V equation, i.e., $j - j$ from B-V

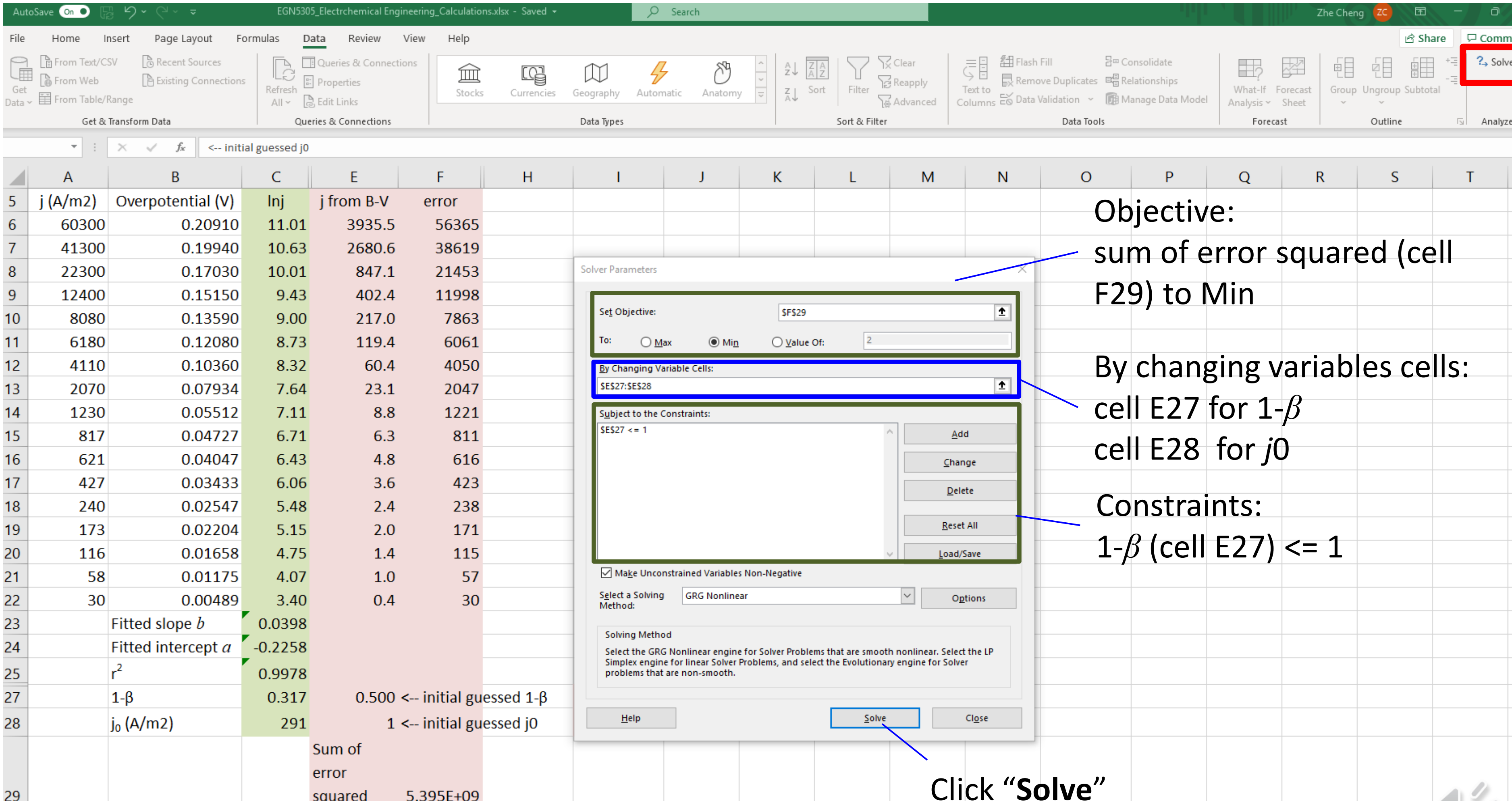
Anode polarization data on for chlorine gas production from 5 M NaCl solution at 20°C. (Kunh and Mortimer, J Electrochem Soc v120, 231 (1973)).

Fitting all polarization data to B-V equation

= SUMSQ(J10:J29)

Fitting to Tafel & Comparison w/ BV (3)

Excel <u>Solver</u> provide fitted 1–β (E27) and j_0 (E28) values, minimizing sum of error squared (F29)



	A	B	C	E	F
5	j (A/m2)	Overpotential (V)	lnj	j from B-V	error
6	60300	0.20910	11.01	3935.5	56365
7	41300	0.19940	10.63	2680.6	38619
8	22300	0.17030	10.01	847.1	21453
9	12400	0.15150	9.43	402.4	11998
10	8080	0.13590	9.00	217.0	7863
11	6180	0.12080	8.73	119.4	6061
12	4110	0.10360	8.32	60.4	4050
13	2070	0.07934	7.64	23.1	2047
14	1230	0.05512	7.11	8.8	1221
15	817	0.04727	6.71	6.3	811
16	621	0.04047	6.43	4.8	616
17	427	0.03433	6.06	3.6	423
18	240	0.02547	5.48	2.4	238
19	173	0.02204	5.15	2.0	171
20	116	0.01658	4.75	1.4	115
21	58	0.01175	4.07	1.0	57
22	30	0.00489	3.40	0.4	30
23		Fitted slope b	0.0398		
24		Fitted intercept a	-0.2258		
25		r^2	0.9978		
27		1-β	0.317	0.500 <-- initial guessed 1-β	
28		j_0 (A/m2)	291	1 <-- initial guessed j0	
29				Sum of error squared	5.395E+09

Objective:
sum of error squared (cell F29) to Min

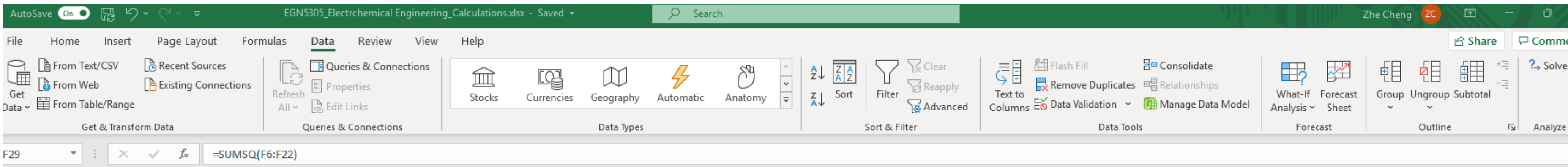
By changing variables cells:
cell E27 for 1-β
cell E28 for $j0$

Constraints:
1-β (cell E27) <= 1

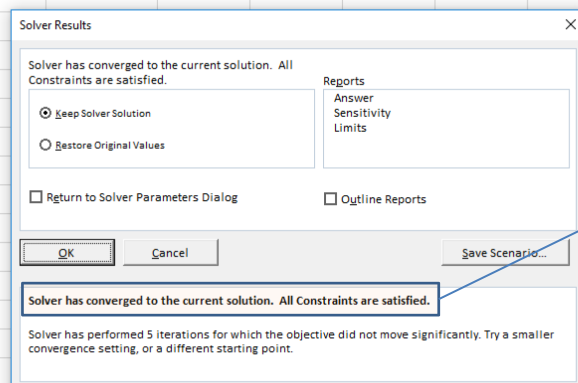
Click "**Solve**"

Fitting to Tafel & Comparison w/ BV (4)

Excel <u>Solver</u> provides fitted $1\!-\!\beta$ and j_0 values that minimizes sum of error squared (cell F29)



	A	B	C	E	F
5	j (A/m2)	Overpotential (V)	lnj	j from B-V	error
6	60300	0.20910	11.01	58105.0	2195
7	41300	0.19940	10.63	44905.8	-3606
8	22300	0.17030	10.01	20728.5	1572
9	12400	0.15150	9.43	12579.5	-180
10	8080	0.13590	9.00	8311.5	-231
11	6180	0.12080	8.73	5564.7	615
12	4110	0.10360	8.32	3523.0	587
13	2070	0.07934	7.64	1846.4	224
14	1230	0.05512	7.11	959.7	270
15	817	0.04727	6.71	770.4	47
16	621	0.04047	6.43	632.0	-11
17	427	0.03433	6.06	522.6	-96
18	240	0.02547	5.48	383.3	-143
19	173	0.02204	5.15	333.2	-160
20	116	0.01658	4.75	255.2	-139
21	58	0.01175	4.07	186.0	-128
22	30	0.00489	3.40	82.2	-52
23		Fitted slope b	0.0398		
24		Fitted intercept a	-0.2258		
25		r^2	0.9978		
27		1-β	0.317	0.336 <-- fitted 1-β	
28		j_0 (A/m2)	291	225 <-- fitted j0	
29				Sum of error squared	2.132E+07



An (optimized) solution found (i.e., converge)

Fitted values for $(1\!-\!\beta)$ (cell E27) and j_0 (cell E28) values

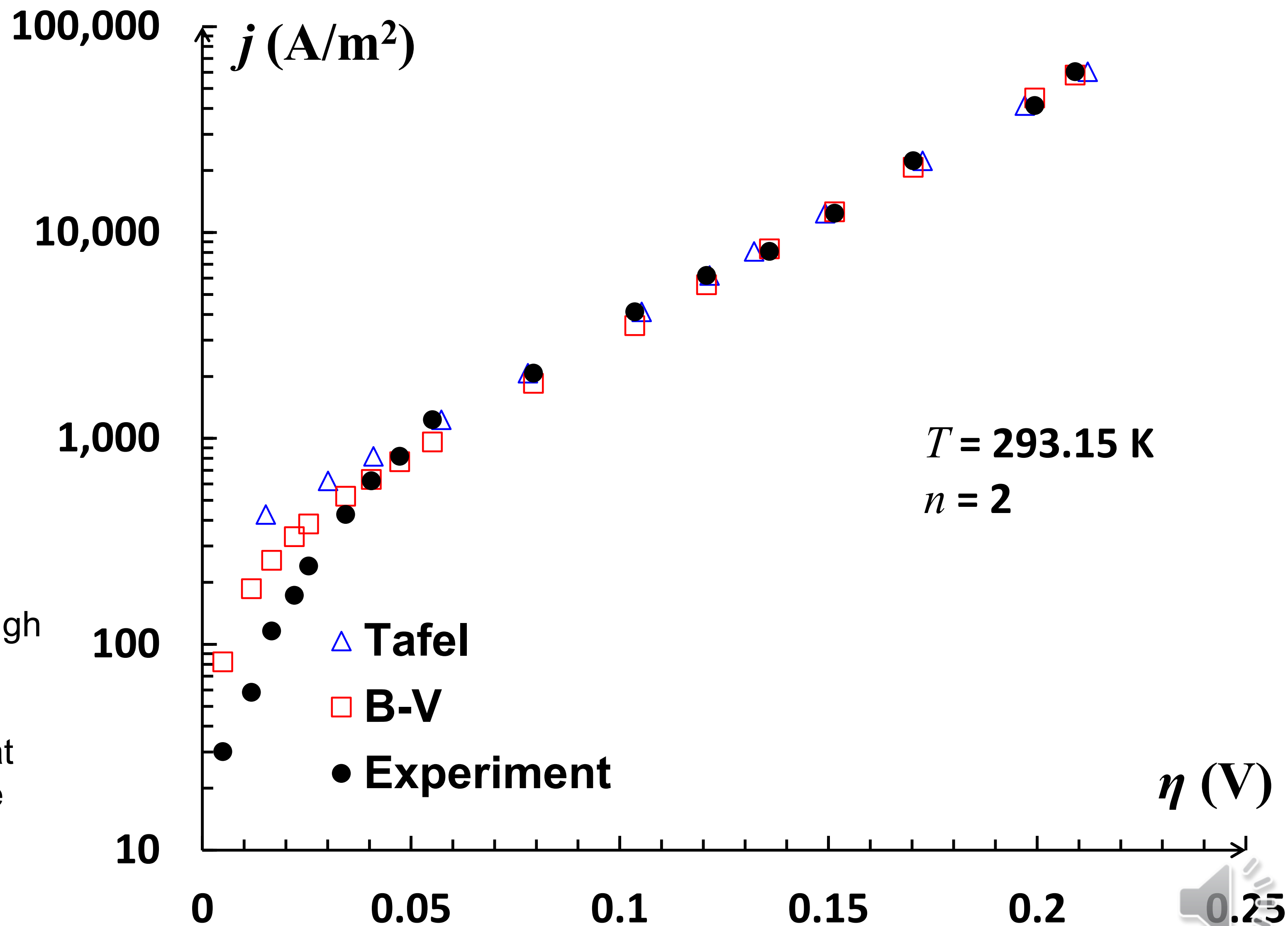
Sum of error squared (cell 29) greatly reduced (to minimum)

Fitted values by Tafel (0.317, 291 A/m^2) different from B-V (0.336, 225 A/m^2), but <u>close</u> – on same order!

Fitting to Tafel & Comparison w/ BV (5)

Anode polarization data for Cl_2 production from NaCl solution at 20°C (Kuhn and Mortimer, *J Electrochem Soc* v120, 231 (1973))

Good fitting at high overpotential (> ~0.05 V), but overestimation at <u>lower bias</u>, more obvious for Tafel than B-V



Voltage Loss in Electrochemical Cell

For an actual electrochemical cell, voltage loss from cell equilibrium potential E_{eq} is coming from several contributions

Galvanic cell (GC)

$$\Delta E_{GC} = E_{eq} - E_{cell} = |I|R_{int} = \eta_{electrodes} + |I|R_{\Omega} = |\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega}$$

$$E_{cell\,GC} = E_{eq} - |I|R_{int} = E_{eq} - (|\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega})$$

Electrolytic cell (EC)

$$\Delta E_{EC} = E_{App} - E_{eq} = |I|R_{int} = \eta_{electrodes} + |I|R_{\Omega} = |\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega}$$

$$E_{cell\,EC} = E_{App} = E_{eq} + |I|R_{int} = E_{eq} + |\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega}$$

Voltage Loss in Electrochemical Cell Example (1)

Consider a system with an Zn anode and a NiOOH cathode in an alkaline solution.

Electrode reactions are:

Anodic (oxidation) half cell

$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

Cathodic (reduction) half cell

$NiOOH + H_2O + e^- \rightarrow$

$Ni(OH)_2 + OH^-$

kinetic parameters are given

a) Determine cell potential at galvanic current density of 1000 A/m^2

b) Determine discharge current density that corresponds to total cell voltage of 1.3 V

$\alpha_a = (1-\beta)n$

$\alpha_c = \beta n$

Symbol	Value (unit)	Meaning
$R_{a,\,Ni}$	100	Surface roughness factor for Ni electrode
$R_{a,\,Zn}$	2	Surface roughness factor for Zn electrode
$j_{0,\,Ni}$	0.61 A/m^2	Exchange current density for Ni electrode
$j_{0,\,Zn}$	60 A/m^2	Exchange current density for Zn electrode
E_{eq}	1.74 V	Equilibrium cell potential for $NiOOH/Ni(OH)_2$ relative to $Zn(OH)_2/Zn$
$\alpha_{a,\,Ni}$	0.5	Anodic transfer coefficient for Ni electrode
$\alpha_{c,\,Ni}$	0.5	Cathodic transfer coefficient for Ni electrode
$\alpha_{a,\,Zn}$	1.5	Anodic transfer coefficient for Zn electrode
$\alpha_{c,\,Zn}$	0.5	Cathodic transfer coefficient for Zn electrode
κ	60 S/m	Electrolyte conductivity
L	2 mm	Electrolyte thickness

Voltage Loss in Electrochemical Cell Example (2)

Part a) Want $E_{cell\,GC} = E_{eq} - (|\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega})$

	Zn surface roughness factor	2	Ni surface roughness factor	100
	i0 (Zn) A/m2	60	i0 (Ni) A/m2	0.61
	alfa-a Zn	1.5	alfa-a Ni	0.5
	alfa-c Zn	0.5	alfa-c Ni	0.5
Overpotential (V)		j Zn by BV (A/m2)		j Ni by BV (A/m2)
-0.300		-41194.4		-20940.3
-0.299		-40400.5		-20536.7
-0.298		-39621.8		-20140.9
-0.297		-38858.1		-19752.7
-0.296		-38109.2		-19372.0
-0.295		-37374.7		-18998.6
-0.294		-36654.3		-18632.4
0.036		922.2		92.6
0.037		982.4		95.6
0.038		1046.1		98.7
0.039		1113.6		101.8
-0.145		-2017.2		-1021.8
-0.144		-1978.3		-1001.9
-0.143		-1940.2		-982.5

Knowing net j → back calculate η (for both Zn anode and Ni cathode) based on B-V equation

Zn electrode anodic (oxidation) current corresponding to positive overpotential

Interpolation for Zn anodic +1000 A/m^2

$$\eta_{a,Zn} = 0.037 + \frac{0.038 - 0.037}{1046.1 - 982.4} \times (1000 - 982.4)$$

$$\eta_{a,Zn} = 0.0373V$$

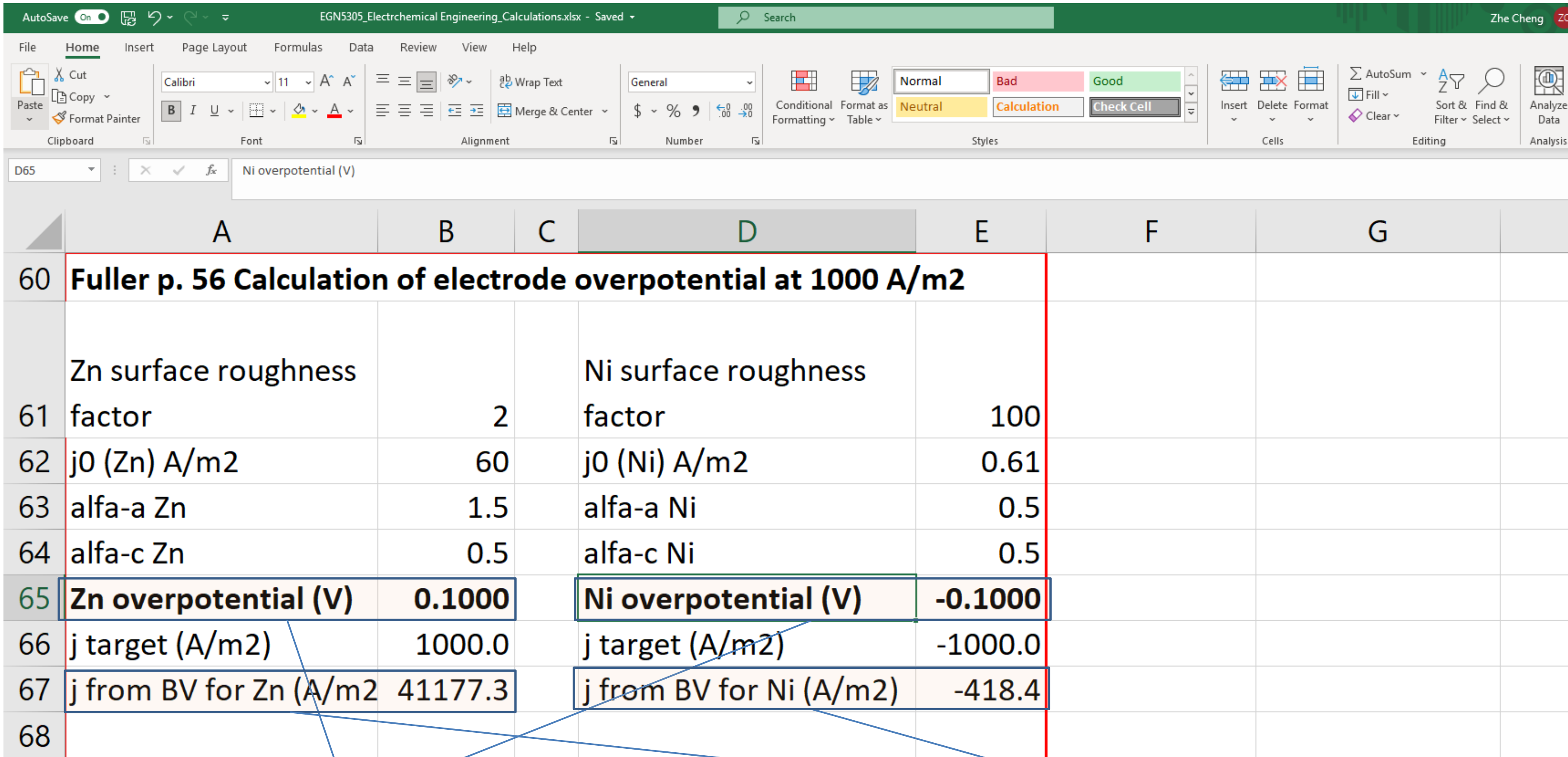
Ni electrode cathodic (reduction) current corresponding to negative overpotential

Interpolation for Ni cathodic -1000 A/m^2

$$\eta_{c,Ni} = -0.1439V$$

Voltage Loss in Electrochemical Cell Example (2: Alternative-1)

Set up problem in Excel: calculate current density (B67,E67) using overpotential (B65,E65) values



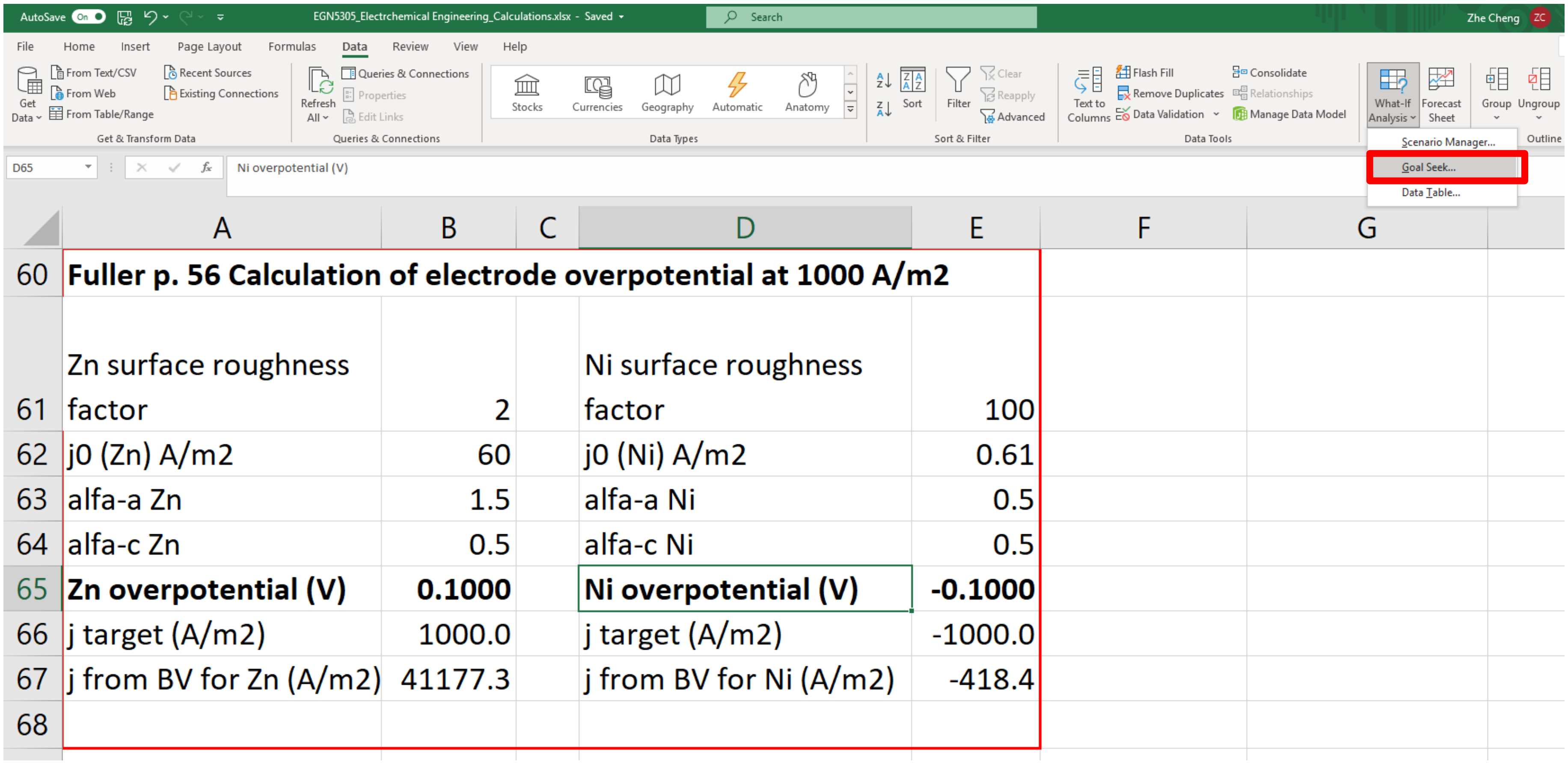
	A	B	C	D	E
60	**Fuller p. 56 Calculation of electrode overpotential at 1000 A/m2**				
61	Zn surface roughness factor	2		Ni surface roughness factor	100
62	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.61
63	alfa-a Zn	1.5		alfa-a Ni	0.5
64	alfa-c Zn	0.5		alfa-c Ni	0.5
65	**Zn overpotential (V)**	**0.1000**		**Ni overpotential (V)**	**-0.1000**
66	j target (A/m2)	1000.0		j target (A/m2)	-1000.0
67	j from BV for Zn (A/m2	41177.3		j from BV for Ni (A/m2)	-418.4
68					

Initial guessed values for overpotential for both Zn and Ni electrodes

Calculated j values from B-V equation using the overpotential values

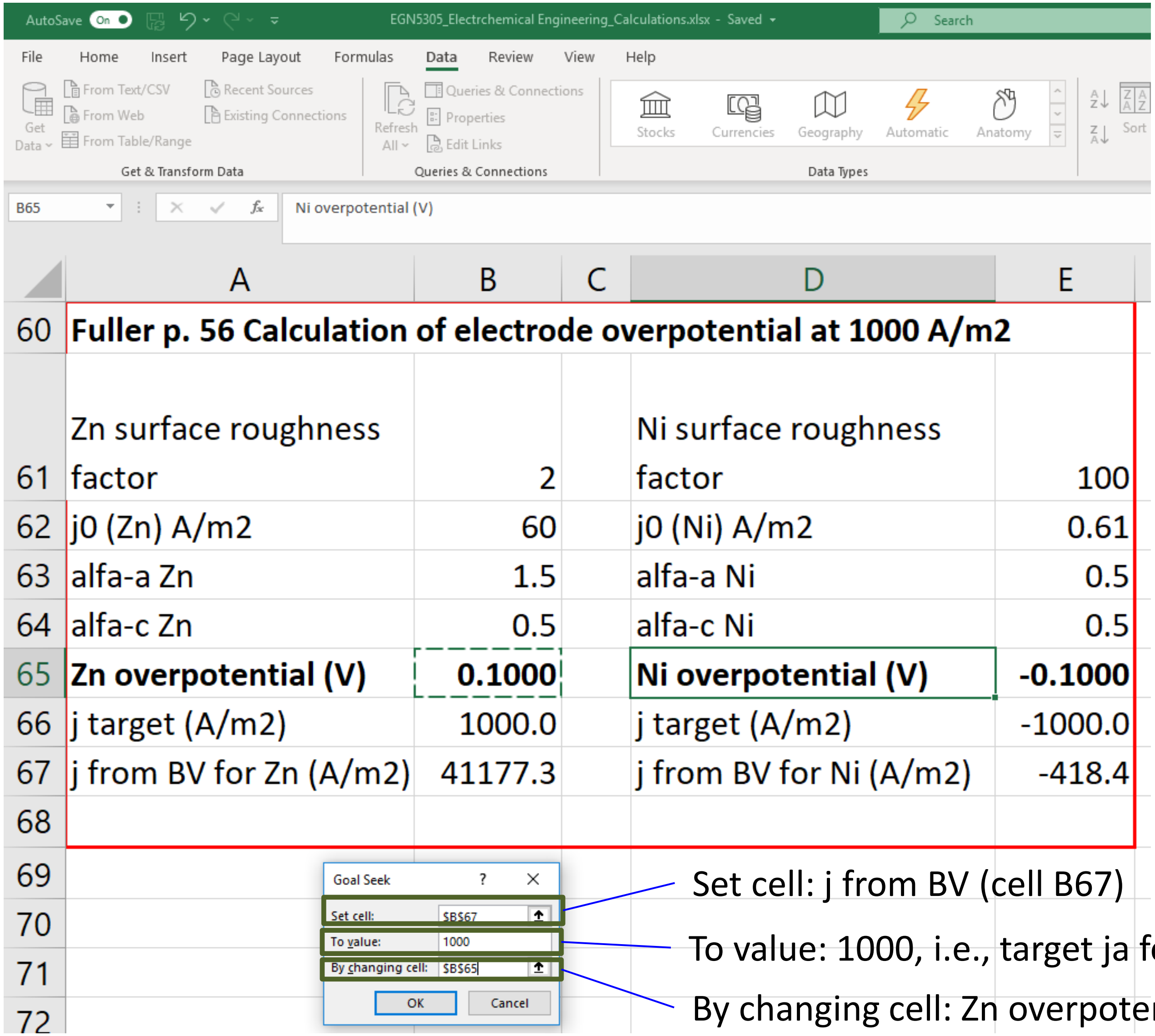
Voltage Loss in Electrochemical Cell Example (2: Alternative-2)

Excel <u>Goal Seek</u> to provide fitted overpotential (B65, E65) for target current density (B67, E67)



	A	B	C	D	E
60	**Fuller p. 56 Calculation of electrode overpotential at 1000 A/m2**				
61	Zn surface roughness factor	2		Ni surface roughness factor	100
62	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.61
63	alfa-a Zn	1.5		alfa-a Ni	0.5
64	alfa-c Zn	0.5		alfa-c Ni	0.5
65	**Zn overpotential (V)**	**0.1000**		**Ni overpotential (V)**	**-0.1000**
66	j target (A/m2)	1000.0		j target (A/m2)	-1000.0
67	j from BV for Zn (A/m2)	41177.3		j from BV for Ni (A/m2)	-418.4
68					

Voltage Loss in Electrochemical Cell Example (2: Alternative-3)



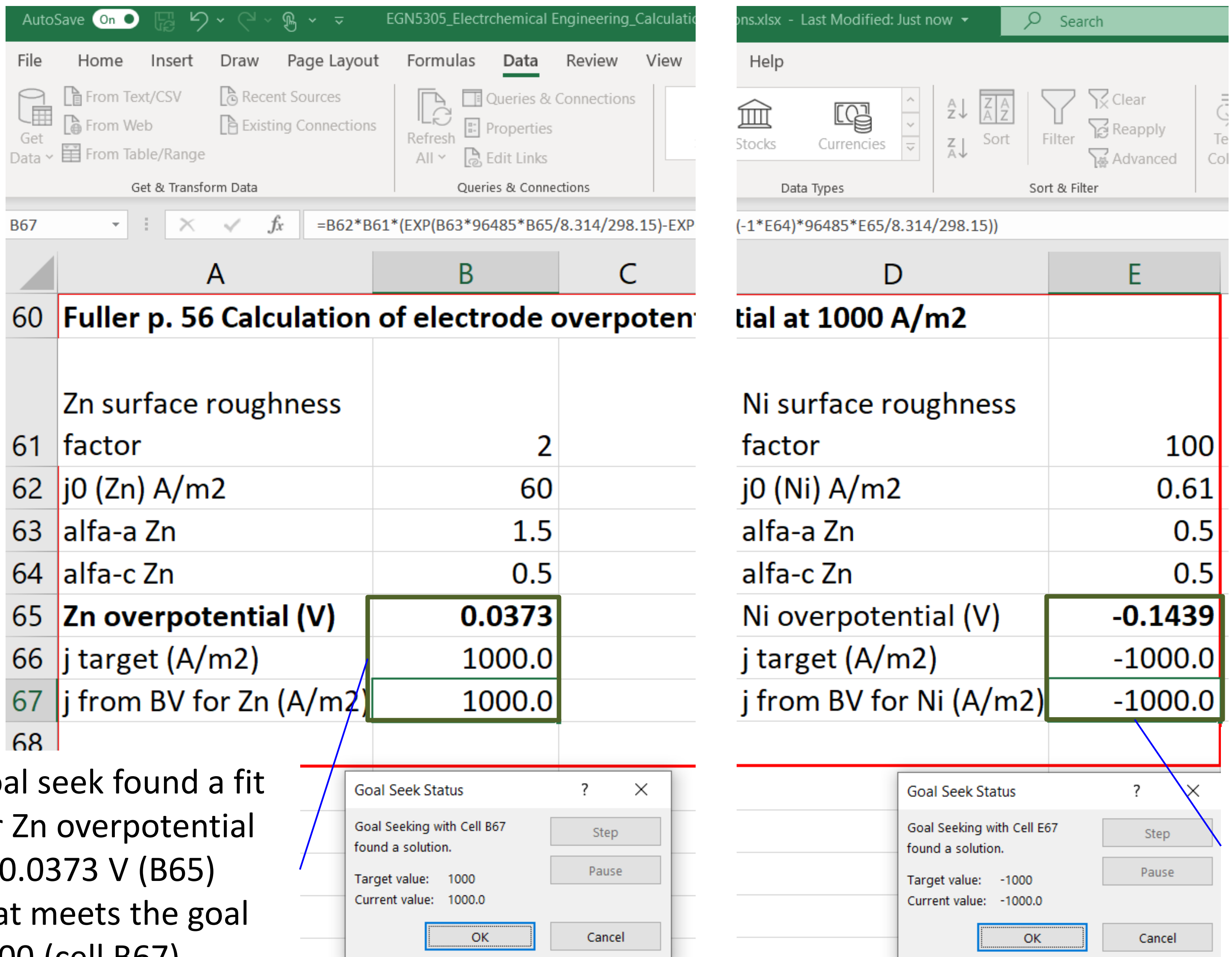
Excel Goal Seek provide fitted overpotential (e.g., B65) value for target current density (e.g., B67)

Set cell: j from BV (cell B67)

To value: 1000, i.e., target ja for Zn

By changing cell: Zn overpotential (B65)

Voltage Loss in Electrochemical Cell Example (2: Alternative-4)



	A	B	C	D	E
60	**Fuller p. 56 Calculation of electrode overpotential at 1000 A/m2**				
61	Zn surface roughness factor	2		Ni surface roughness factor	100
62	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.61
63	alfa-a Zn	1.5		alfa-a Zn	0.5
64	alfa-c Zn	0.5		alfa-c Zn	0.5
65	**Zn overpotential (V)**	**0.0373**		Ni overpotential (V)	**-0.1439**
66	j target (A/m2)	1000.0		j target (A/m2)	-1000.0
67	j from BV for Zn (A/m2)	1000.0		j from BV for Ni (A/m2)	-1000.0
68					

Goal seek found a fit for Zn overpotential at 0.0373 V (B65) that meets the goal 1000 (cell B67)

Goal seek found a fit for Ni overpotential at -0.1439 V (E65) that meets the goal -1000 (cell E67)

Voltage Loss in Electrochemical Cell Example (3)

Total cell voltage:

$$\boldsymbol{E_{cell\,GC} = E_{eq} - (|\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega})}$$

$$|I|R_{\Omega} = |j \cdot A| \cdot \rho \cdot \frac{L}{A} = |j \cdot A| \cdot \frac{1}{\kappa} \cdot \frac{L}{A} = |j| \cdot \frac{L}{\kappa}$$

$$= 1000\frac{A}{m^2} \times \frac{0.002m}{60S/m}$$

$$= 0.0333\frac{A}{S}$$

$$= 0.0333\frac{A}{1/\Omega}$$

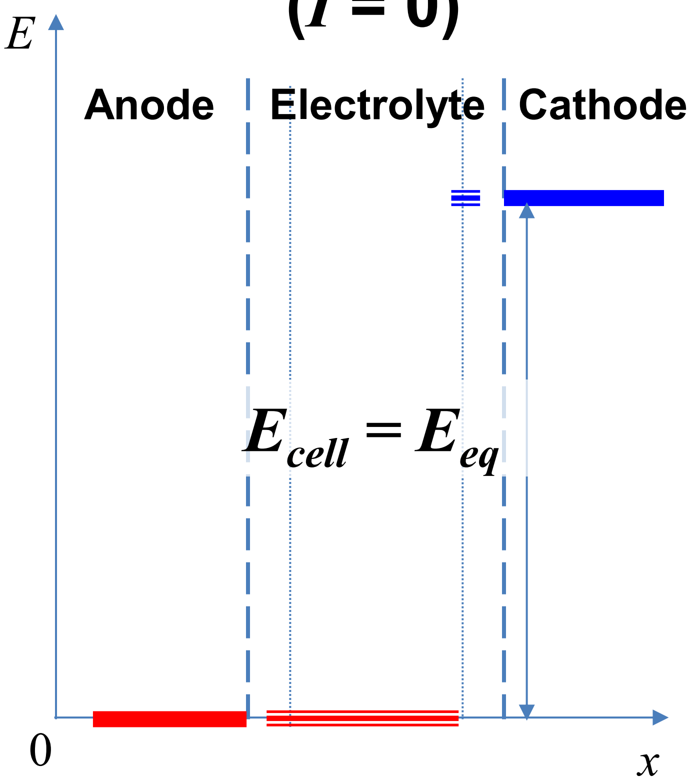
$$= 0.0333V$$

$$E_{cell\,GC} = 1.74V - (|0.0373V| + |-0.1439V| + 0.0333V) = 1.526V$$

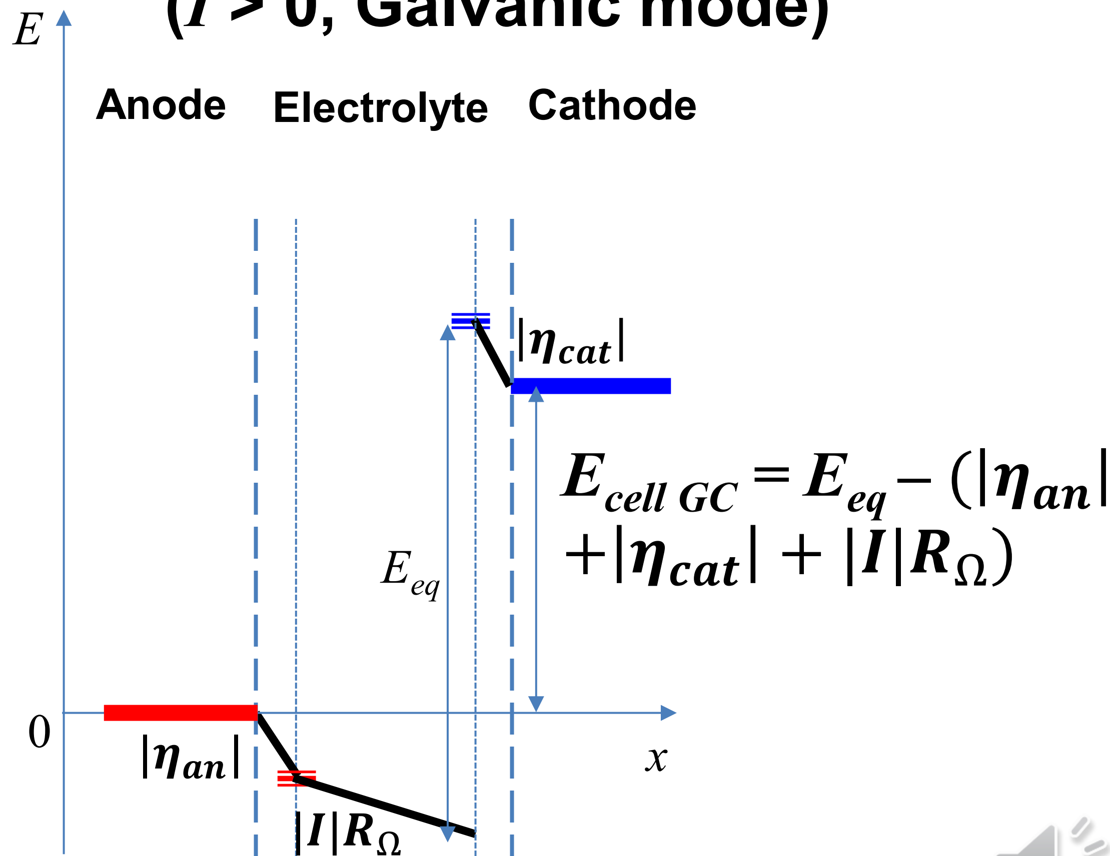
Voltage Loss in Electrochemical Cell Example (4)

Total cell voltage: $E_{cell\,GC} = E_{eq} - (|\eta_{an}| + |\eta_{cat}| + |I|R_{\Omega})$

Open Circuit ($I = 0$)



Closed Circuit ($I > 0$, Galvanic mode)



Voltage Loss in Electrochemical Cell Example (5)

Part b) Want j so that $E_{cell\ GC} = E_{eq} - (|\eta_{an}| + |\eta_{cat}| + |I|R_\Omega) = 1.30V$

Or $|\eta_{an}| + |\eta_{cat}| + |I|R_\Omega = E_{eq} - E_{cell\ GC} = 1.74V - 1.30V = 0.34\ V$

	A	B	C	D	E	F	G	H
75	**Fuller p. 56 Estimation of cell current for a given cell voltage of 1.3V**							
76	Zn surface roughness factor	2		Ni surface roughness factor	100		Electrolyte conductivity κ (S/m)	60
77	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.6		Electrolyte thickness L (m)	0.002
78	alfa-a Zn	1.5		alfa-a Ni	0.5			
79	alfa-c Zn	0.5		alfa-c Ni	0.5			
80	**ηa(Zn)(V)**			**ηc(Ni) (V)**				$\|I\|R$ = |j|avg*L/κ (V)
81	**0.0000**			**0.0000**				0.0000
82	ja(Zn) by BV (A/m2)			jc(Ni) by BV (A/m2)		|ja+jc| (A/m2)	|j|avg (A/m2)	
83	0.00			0.00		0.0	0.0	<--abs(ja-jc)/2
84	**Cell voltage E_{GC} (V)**	**1.740**	<-- = Eeq - |ηa(Zn)|-|ηc(Ni)|-|I|R					
85	Initial Eta-a(Zn) = 0, Eta-c(Ni) = 0; Solver with i sum<=2, Eta-a(Zn) in range (0, 2); Eta-c(Ni) in range (-2, 0)							

Initial guessed overpotential for Zn anode (cell A81) and Ni cathode (cell D81)

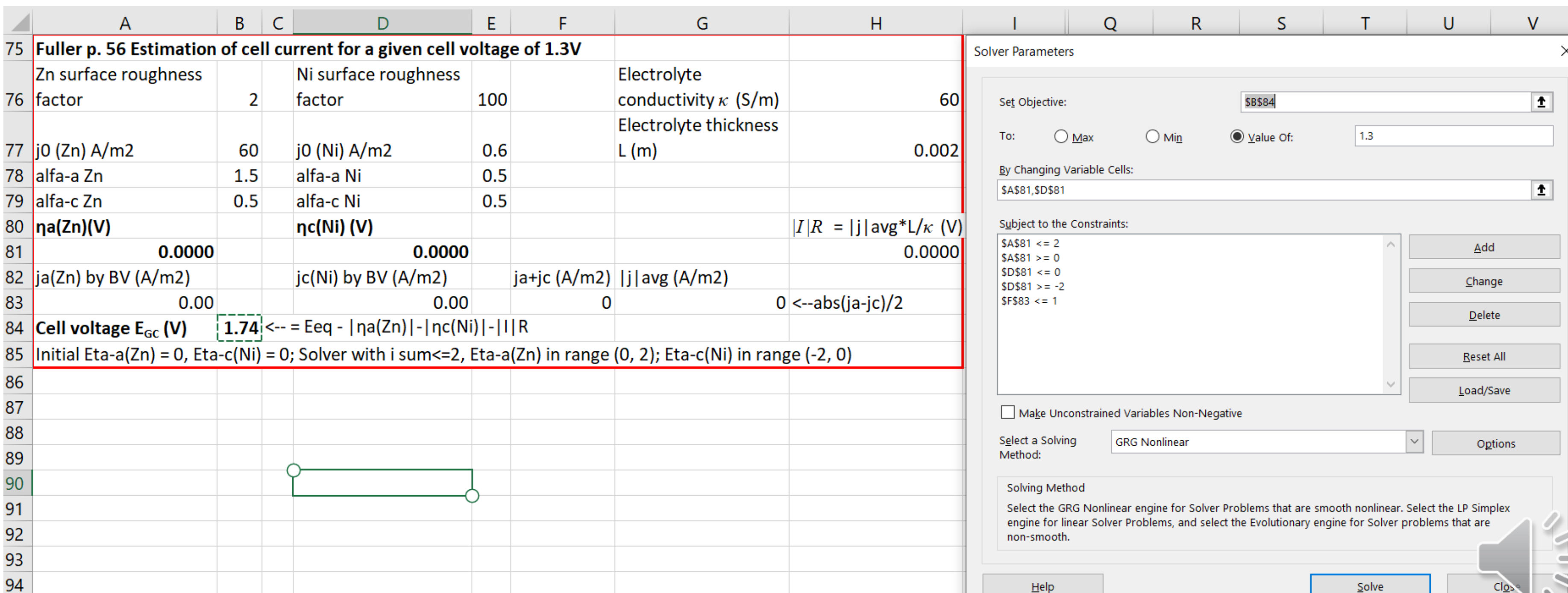
Difference in absolute values between anodic/positive (on Zn) and cathodic/positive current (on Ni); should be small (< 1 A/m2)

Average absolute current for |ja| and |jc|, to calculate |I|R

Voltage Loss in Electrochemical Cell Example (6)

Excel <u>Solver</u> to provide fitted ηa(Zn) (cell A81) and ηc(Ni) (cell D81) values

- Objective E_{GC} (cell B84) of 1.3 V
- By changing ηa(Zn) (cell A81) and ηc(Ni) (cell D81)
- Subject to the constraints:
  - ηa(Zn) (cell A81) in range of 0 to 2
  - ηc(Ni) (cell D81) in range of -2 to 0
  - ja+jc (cell F83) <=1, meaning ja and jc close in absolute value, but with opposite sign



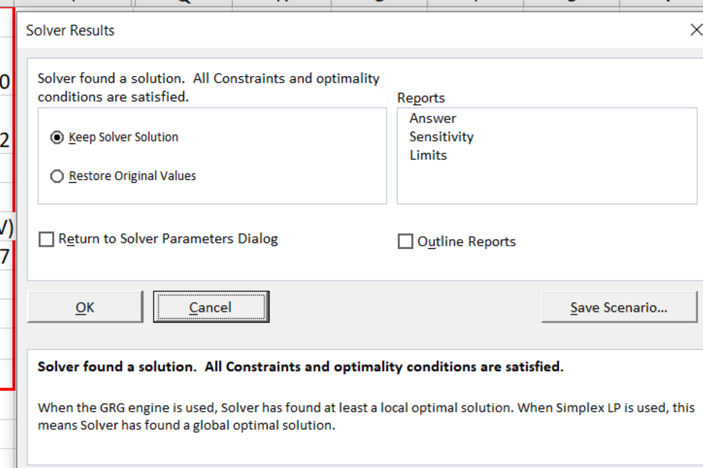
	A	B	C	D	E	F	G	H
75	**Fuller p. 56 Estimation of cell current for a given cell voltage of 1.3V**							
76	Zn surface roughness factor	2		Ni surface roughness factor	100		Electrolyte conductivity κ (S/m)	60
77	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.6		Electrolyte thickness L (m)	0.002
78	alfa-a Zn	1.5		alfa-a Ni	0.5			
79	alfa-c Zn	0.5		alfa-c Ni	0.5			
80	**ηa(Zn)(V)**			**ηc(Ni) (V)**				|I|R = |j|avg*L/κ (V)
81	**0.0000**			**0.0000**				0.0000
82	ja(Zn) by BV (A/m2)			jc(Ni) by BV (A/m2)		ja+jc (A/m2)	|j|avg (A/m2)	
83	0.00			0.00		0	0	<--abs(ja-jc)/2
84	**Cell voltage E_{GC} (V)**	1.74	<-- = Eeq - |ηa(Zn)|-|ηc(Ni)|-|I|R					
85	Initial Eta-a(Zn) = 0, Eta-c(Ni) = 0; Solver with i sum<=2, Eta-a(Zn) in range (0, 2); Eta-c(Ni) in range (-2, 0)							

Voltage Loss in Electrochemical Cell Example (7)

Excel <u>Solver</u> found a solution:

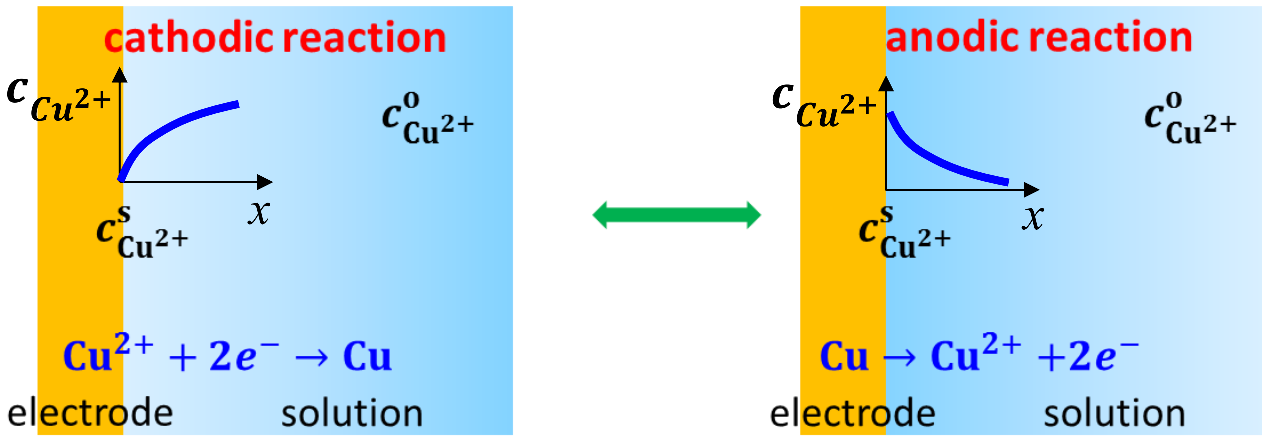
- Objective E_{GC} (cell B84) became 1.300 V
- ηa(Zn) (cell A81) = 0.0627 V (anodic overpotential)
- ηc(Ni) (cell D81) = -0.2226 V (cathodic overpotential)
- ja (Zn) = +4641.1 A/m2, jc(Ni) = -4640.1 A/m2, ja+jc (cell F83) = 1.0 A

	A	B	C	D	E	F	G	H
75	**Fuller p. 56 Estimation of cell current for a given cell voltage of 1.3V**							
76	Zn surface roughness factor	2		Ni surface roughness factor	100		Electrolyte conductivity κ (S/m)	60
77	j0 (Zn) A/m2	60		j0 (Ni) A/m2	0.6		Electrolyte thickness L (m)	0.002
78	alfa-a Zn	1.5		alfa-a Ni	0.5			
79	alfa-c Zn	0.5		alfa-c Ni	0.5			
80	**ηa(Zn)(V)**			**ηc(Ni) (V)**				$\|I\|R$ = |j|avg*L/κ (V)
81	**0.0627**			**-0.2226**				0.1547
82	ja(Zn) by BV (A/m2)			jc(Ni) by BV (A/m2)		ja+jc (A/m2)	|j|avg (A/m2)	
83	4641.11			-4640.11		1.0	4640.6	<--abs(ja-jc)/2
84	**Cell voltage E_{GC} (V)**	1.300	<-- = Eq - |ηa(Zn)|-|ηc(Ni)|-|I|R					
85	Initial Eta-a(Zn) = 0, Eta-c(Ni) = 0; Solver with i sum<=2, Eta-a(Zn) in range (0, 2); Eta-c(Ni) in range (-2, 0)							



Concentration Overpotential

Once electrochemical reaction starts, active species concentration often **NOT uniform**



Nernst equation roughly **estimates <u>overpotential</u>** due to **concentration gradient** of electrochemically active species between electrode/electrolyte interface and the bulk:

If concentration of **<u>an</u>** active species (e.g., Ox) in $Ox + ne^{-} \rightarrow Red$ at the surface is c^{s}_{active} and in bulk is c^{o}_{active},

Electrode **concentration** overpotential $\eta = \frac{RT}{nF} \ln \frac{c^{s}_{active}}{c^{o}_{active}}$

- η can be positive ($c^{s}_{active} > c^{o}_{active}$) or negative ($c^{s}_{active} < c^{o}_{active}$)
- c^{s}_{active} often unknown

Mass Transfer Overpential (1)

When a reaction is limited by mass transfer, e.g., bringing of an active species from the bulk to the electrolyte/electrode interface, current density often satisfy:

$$\boldsymbol{j \approx nFk(c^{o}_{active} - c^{s}_{active})}$$

When $\boldsymbol{c^{s}_{active} = 0}$, current density reaches the max or limiting value, $\boldsymbol{j_{\lim}}$:

$$\boldsymbol{j_{lim} \approx nFkc^{o}_{active}}$$

The ratio

$$\frac{j}{j_{\lim}} \approx 1 - \frac{c^{s}_{active}}{c^{o}_{active}}$$

Therefore,

$$\frac{c^{s}_{active}}{c^{o}_{active}} \approx 1 - \frac{j}{j_{\lim}}$$

- $j = 0$, $c^{s}_{active} = c^{o}_{active}$, uniform concentration
- $j = j_{\lim}$, $c^{s}_{active} = 0$, largest concentration gradient
- Applicable when **migration** is negligible ⇨ mass transport is dominated by diffusion and NOT electromigration

Mass Transfer Overpential (2)

From previous

$$\frac{c^{s}_{active}}{c^{o}_{active}} \approx 1 - \frac{j}{j_{\lim}}$$

In this case, concentration overpotential due to mass transfer (e.g., diffusion) can be approximated by:

$$\boldsymbol{\eta = \frac{RT}{nF} \ln \frac{c^{s}_{active}}{c^{o}_{active}}}$$

$$\boldsymbol{\eta = \frac{RT}{nF} \ln \left(1 - \frac{j}{j_{lim}}\right)}$$

- Also called **mass transfer** (diffusion in this case) **overpotential**
- Can be estimated if j and j_{lim} are measured

Generalized Butler-Volmer Equation (1)

For a general one-step electrode (half cell) reaction:

$$Ox + ne^- \leftrightarrow Red$$

<u>Generalized</u> Butler-Volmer equation for net current density j as a function of overpotential for that electrode or half cell reaction $\eta = E(Ox/Red) - E_{eq}(Ox/Red)$

$$\boldsymbol{j = j_a + j_c = j_o \left\{ \frac{c_{Red}^{s}}{c_{Red}^{o}} \cdot \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \frac{c_{Ox}^{s}}{c_{Ox}^{o}} \cdot \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}}$$

j_a	Anodic current density, often in A/cm^2
j_c	Cathodic current density, often in A/cm^2
j_o	Exchange current density, often in A/cm^2
β	Symmetry factor, unitless
c_{Red}^{s}	Electrode surface concentration for reduced species Red
c_{Red}^{o}	Bulk concentration for reduced species Red
c_{Ox}^{s}	Electrode surface concentration for oxidized species Ox
c_{Ox}^{o}	Bulk concentration for oxidized species Ox
R	Gas constant 8.314 J/(mol·K)
T	Absolute temperature, K

Generalized Butler-Volmer Equation (2)

If mass transfer limited by diffusion only, for the generalized Butler-Volmer equation

$$j = j_o \left\{ \frac{c_{Red}^{s}}{c_{Red}^{o}} \cdot \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \frac{c_{Ox}^{s}}{c_{Ox}^{o}} \cdot \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

$(c_{Red}^{s}/c_{Red}^{o})$ and (c_{Ox}^{s}/c_{Ox}^{o}) are for the anodic and the cathodic processes of the same electrode (half cell) reaction.

$$\frac{c_{Red}^{s}}{c_{Red}^{o}} \approx 1 - \frac{j}{j_{\lim,a}} \qquad \frac{c_{Ox}^{s}}{c_{Ox}^{o}} \approx 1 + \frac{j}{j_{\lim,c}}$$

j positive if anodic,
j negative if cathodic

Therefore,

$$j = j_o \left\{ \left(1 - \frac{j}{j_{\lim,a}}\right) \cdot \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \left(1 + \frac{j}{j_{\lim,c}}\right) \cdot \exp\left(-\frac{\beta nF\eta}{RT}\right) \right\}$$

Expand, we have

$$j = \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] j_o - \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \frac{j_0}{j_{\lim,a}} j - \exp\left(-\frac{\beta nF\eta}{RT}\right) j_o - \exp\left(-\frac{\beta nF\eta}{RT}\right) \frac{j_0}{j_{\lim,c}} j$$

Generalized Butler-Volmer Equation (3)

From previous

$$j = \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] j_o - \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \frac{j_0}{j_{\text{lim},a}} j - \exp\left(-\frac{\beta nF\eta}{RT}\right) j_o - \exp\left(-\frac{\beta nF\eta}{RT}\right) \frac{j_0}{j_{\text{lim,c}}} j$$

$$j + \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \frac{j_0}{j_{\text{lim},a}} j + \exp\left(-\frac{\beta nF\eta}{RT}\right) \frac{j_0}{j_{\text{lim,c}}} j = \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] j_o - \exp\left(-\frac{\beta nF\eta}{RT}\right) j_o$$

Therefore,

$$j = \frac{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] j_o - \exp\left(-\frac{\beta nF\eta}{RT}\right) j_o}{1 + \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] \frac{j_0}{j_{\text{lim,a}}} + \exp\left(-\frac{\beta nF\eta}{RT}\right) \frac{j_0}{j_{\text{lim,c}}}}$$

or

$$j = \frac{\exp\left[\frac{(1-\beta)nF\eta}{RT}\right] - \exp\left(-\frac{\beta nF\eta}{RT}\right)}{\frac{1}{j_o} + \left(\frac{1}{j_{\text{lim,a}}}\right) \exp\left[\frac{(1-\beta)nF\eta}{RT}\right] + \left(\frac{1}{j_{\text{lim},c}}\right) \exp\left(-\frac{\beta nF\eta}{RT}\right)}$$

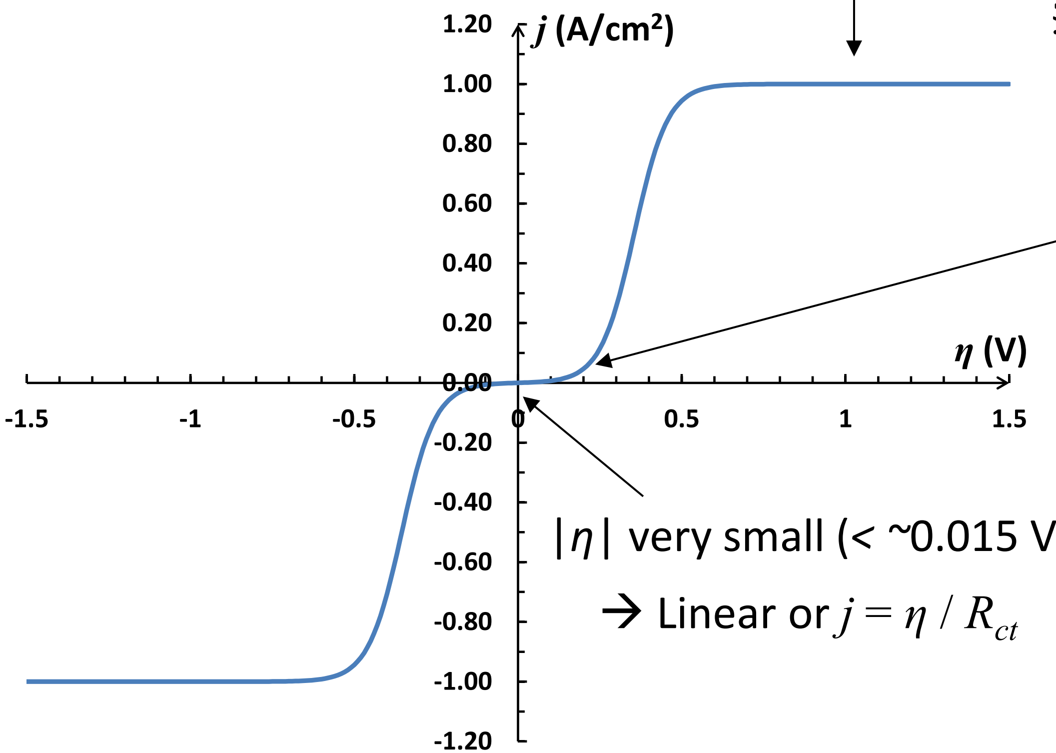
j vs. *η* Plots for Generalized B-V Equation

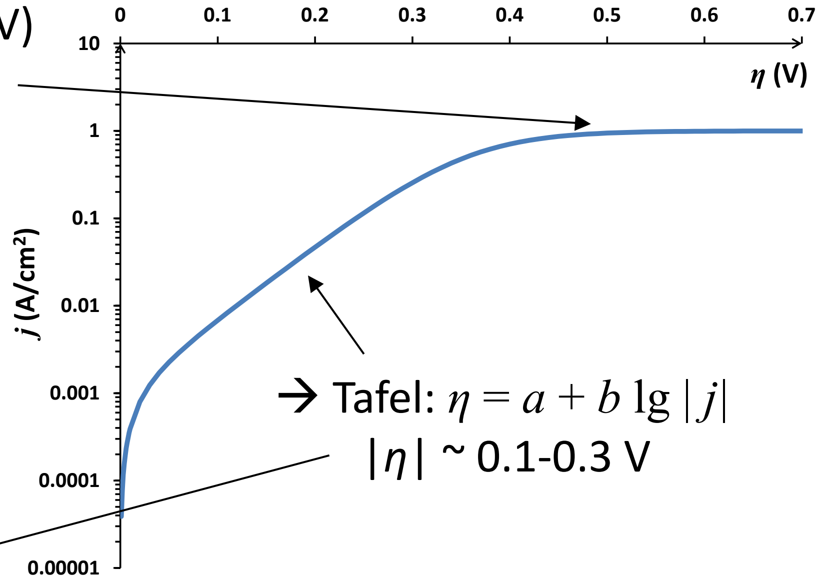
n = 1, β = 0.5,
T = 298.15 K,
j_o = 0.001 A/cm^2,
$j_{lim,a}$ = $j_{lim,c}$ = 1 A/cm^2

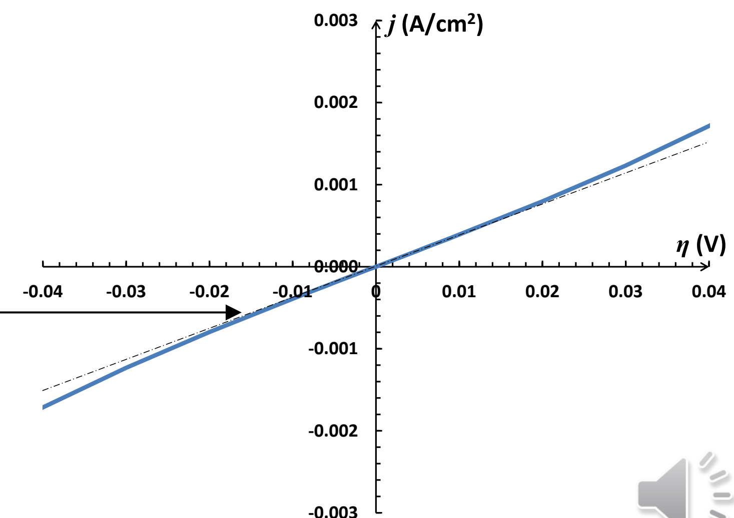
|*η*| very large (> ~0.5 V)
j → limiting values

→ Tafel: $\eta = a + b \lg |j|$
|*η*| ~ 0.1-0.3 V

|*η*| very small (< ~0.015 V)
→ Linear or $j = \eta / R_{ct}$







Homework

- **Read textbook chapter 3 and give an honor statement confirm reading**

- **Raise THREE (3) question that you don't understand for lecture videos**

  In case you have understood everything and don't have that many questions, please give corresponding number of multiple-choice problem (together with your answer) that you feel can be used to check a student's understanding.

  An example multiple-choice problem could be:
  Which of the units below can be the unit for current density j?
  a) *A*
  b) *A/cm^2 (Answer)*
  c) *V*
  d) *C*

- **Problems**
  - **Textbook** 3.3, 3.4, 3.8, 3.9, 3.10, 3.13

Exchange Current Density j_0 (Fuller Eq. 3.19)

From (3.11), anodic & cathodic reaction rate are the same at equilibrium:

$$\frac{j_0}{F} \equiv r_a = k_a c_{Red} \exp\left[\frac{(1-\beta)nFU}{RT}\right] = k_c c_{Ox} \exp\left(-\frac{\beta nFU}{RT}\right) = r_c$$

Therefore,

$$\exp\left(\frac{nFU}{RT}\right) = \frac{k_c c_{Ox}}{k_a c_{Red}}$$

$$\frac{nFU}{RT} = \ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)$$

$$U = \frac{RT}{nF}\ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)$$

which is (3.19)

Exchange Current Density j_0 (Fuller Eq. 3.20a)

From (3.11), when anodic & cathodic reaction rate are the same at equilibrium:

$$\frac{j_0}{F} \equiv r_a = k_a c_{Red} \exp\left[\frac{(1-\beta)nFU}{RT}\right] = k_c c_{Ox} \exp\left(-\frac{\beta nFU}{RT}\right) = r_c$$

From (3.19),

$$U = \frac{RT}{nF} \ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)$$

or

$$\frac{nFU}{RT} = \ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)$$

Therefore,

$$\frac{j_0}{F} \equiv r_a = k_a c_{Red} \exp\left[(1-\beta) \cdot \frac{nFU}{RT}\right] = k_a c_{Red} \exp\left[(1-\beta) \cdot \ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)\right]$$

$$\frac{j_0}{F} = k_a c_{Red} \exp\left[\ln\left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)^{1-\beta}\right] = k_a c_{Red} \cdot \left(\frac{k_c c_{Ox}}{k_a c_{Red}}\right)^{1-\beta}$$

$$\frac{j_0}{F} = (k_a c_{Red}) \cdot (k_c c_{Ox})^{1-\beta} \cdot (k_a c_{Red})^{\beta-1}$$

$$\frac{j_0}{F} = (k_c c_{Ox})^{1-\beta} \cdot (k_a c_{Red})^{\beta}$$

which is essentially (3.20a)

Mass Transfer on Reaction Rate (Fuller Eq 3.33-1)

Mass transfer rate from bulk to surface:

$$N_R = k_m\left(c_{R,b} - c_{R,s}\right)$$

At steady state, mass transfer and electrochemical reaction (charge transfer) match at the electrode/electrode interface, where Tafel equation is assumed

$$j = nFk_m\left(c_{R,b} - c_{R,s}\right) = j_{0,ref} \cdot \left(\frac{c_{R,s}}{c_{R,ref}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)$$

Assuming bulk concentration equals reference/standard concentration

$$c_{R,ref} = c_{R,b}$$

To solve for $c_{R,s}$

$$nFk_m c_{R,b} - nFk_m c_{R,s} = j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right) c_{R,s}$$

$$nFk_m c_{R,b} = nFk_m c_{R,s} + j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right) c_{R,s}$$

Mass Transfer on Reaction Rate (Fuller Eq 3.33-2)

From previous:

$$nFk_m c_{R,b} = \left[nFk_m + j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)\right] c_{R,s}$$

Therefore,

$$c_{R,s} = \frac{nFk_m c_{R,b}}{nFk_m + j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)}$$

Recall

$$j = j_{0,\,b} \cdot \left(\frac{c_{R,s}}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)$$

We have

$$j = j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right) \cdot \frac{nFk_m c_{R,b}}{nFk_m + j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)}$$

$$j = j_{0,\,b} \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right) \cdot \frac{nFk_m}{nFk_m + j_{0,\,b} \cdot \left(\frac{1}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)}$$

Mass Transfer on Reaction Rate (Fuller Eq 3.33-3)

From previous,

$$j = j_{0,\,b} \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right) \cdot \frac{1}{1 + j_{0,\,b} \cdot \left(\frac{1}{nFk_m c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)}$$

$$j = \frac{1}{\frac{1}{j_{0,b} \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)} + \frac{1}{nFk_m c_{R,b}}}$$

which is (3.33)

Note when $c_{R,s} = 0$, electrode anodic/oxidative current as limited by mass transfer

$$j = nFk_m\left(c_{R,b} - c_{R,s}\right)$$

,
reaches max or limiting value:

$$j_{lim} = nFk_m c_{R,b}$$

Mass Transfer on Reaction Rate (Fuller Eq 3.33-4)

On the other hand, if $c_{R,ref} = c_{R,b}$, for current density from Tafel relationship

$$j = j_{0,b} \cdot \left(\frac{c_{R,s}}{c_{R,b}}\right) \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)$$

We have

$$\frac{1}{j_{0,b} \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)} = \frac{c_{R,s}}{c_{R,b}} \cdot \frac{1}{j}$$

Therefore,

$$j = \frac{1}{\frac{1}{j_{0,b} \cdot exp\left(\frac{\alpha_a F}{RT}\eta_s\right)} + \frac{1}{nFk_m c_{R,b}}} = \frac{1}{\frac{c_{R,s}}{c_{R,b}} \cdot \frac{1}{j} + \frac{1}{j_{lim}}}$$

$$\frac{c_{R,s}}{c_{R,b}} + \frac{j}{j_{lim}} = 1$$

$$\frac{c_{R,s}}{c_{R,b}} = 1 - \frac{j}{j_{lim}}$$