Unraveling the elusive Oxygen Reduction Reaction electrokinetics and energetics in PEM Fuel Cells

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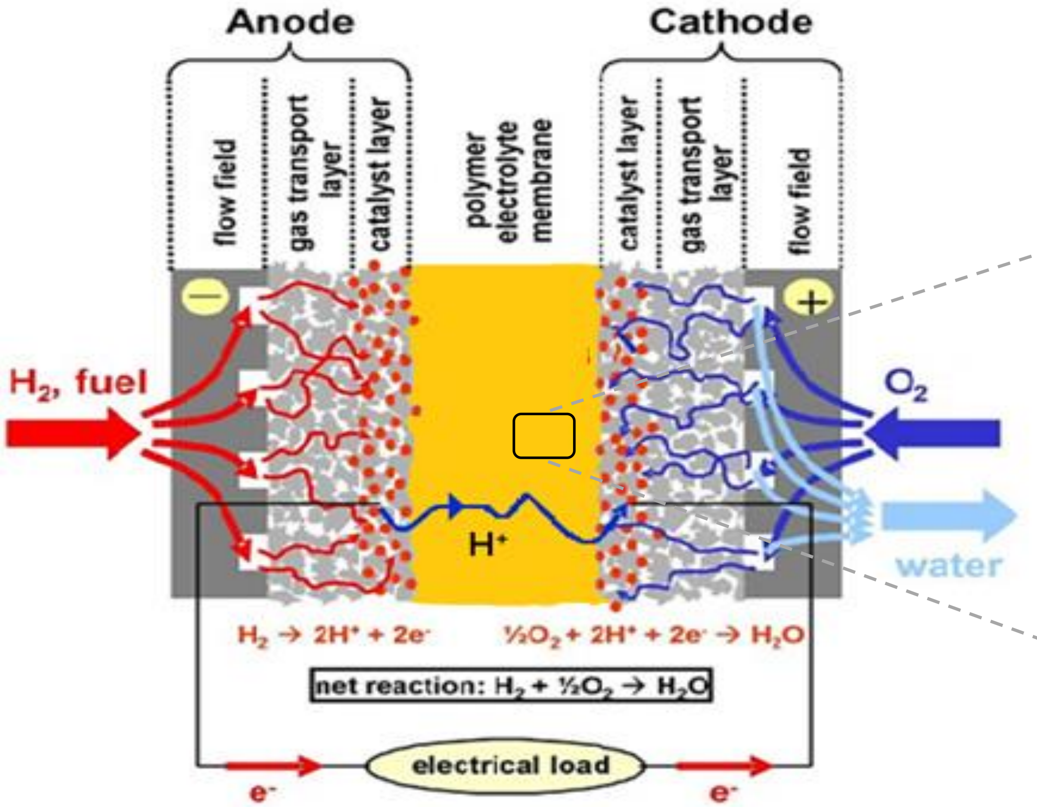
Outline

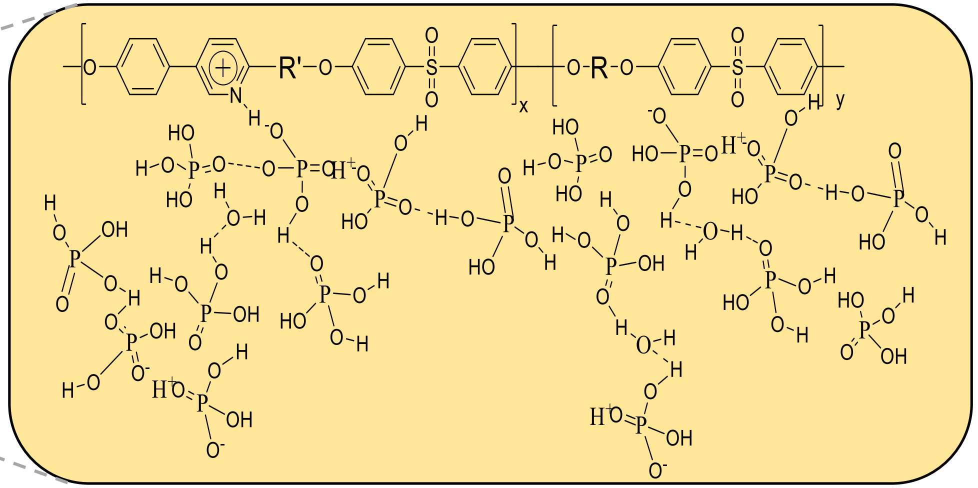
- High Temperature PEM Fuel Cells
- EIS as an experimental tool for Electrochemical Interfaces
- Physical Model for EIS simulation
- Fitting results of the EIS
- ORR Kinetic Constants and reaction energetics

High Temperature PEM Fuel Cells



Polymer Membrane : TPS & H3PO4 (PA)

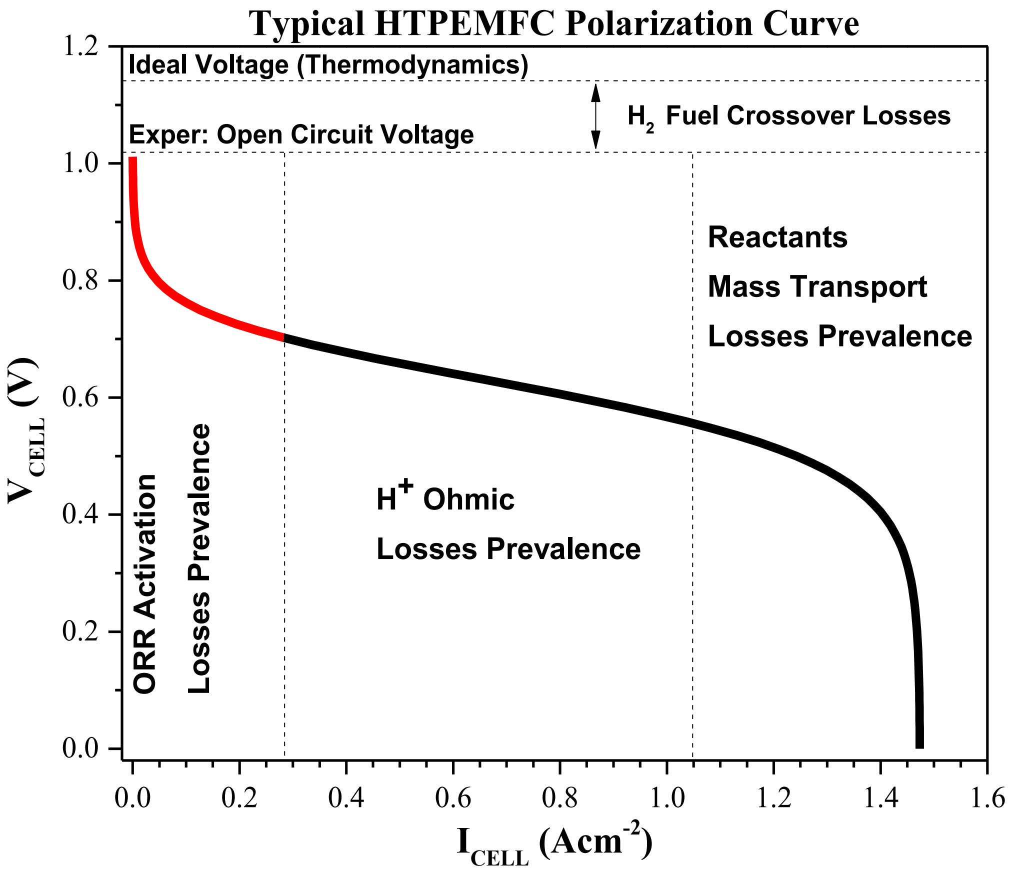
T_{cell} = 140 – 200°C

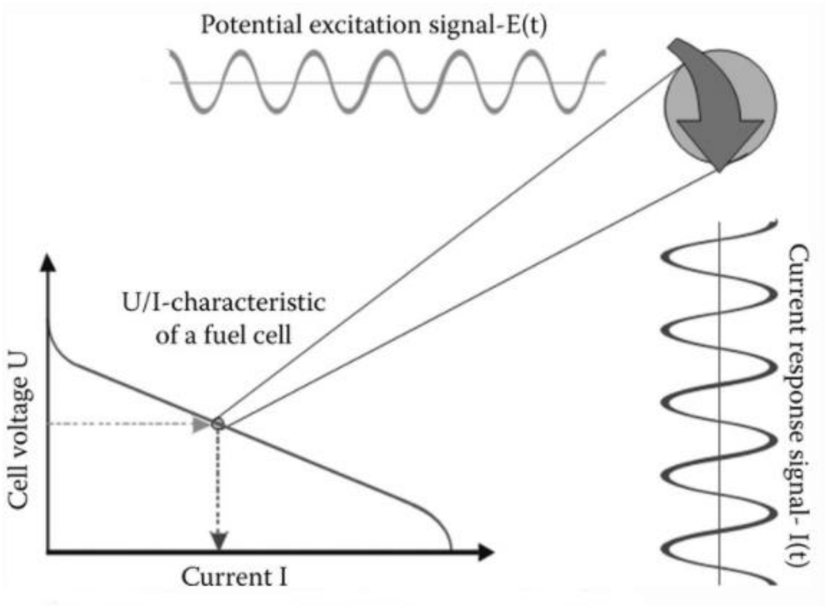


- ❑ Increased Kinetics
- ❑ Increased CO tolerance
- ❑ Simplified water and heat management

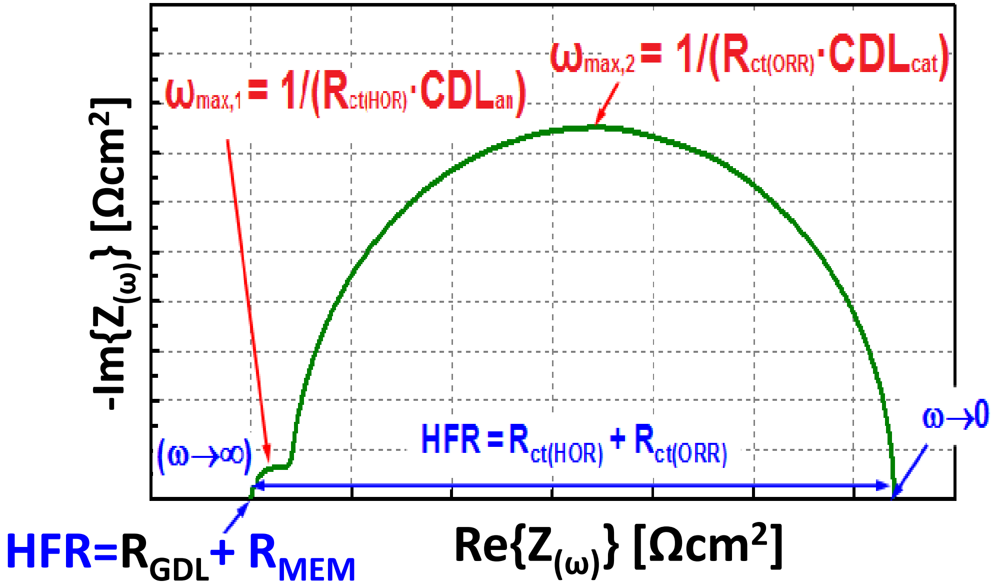
- ❑ H_3PO_4 network provides H^+ pathways
  - Membrane
  - CLs
- ❑ Dry reactants, self humidified

Why Electrochemical Impedance Spectroscopy?



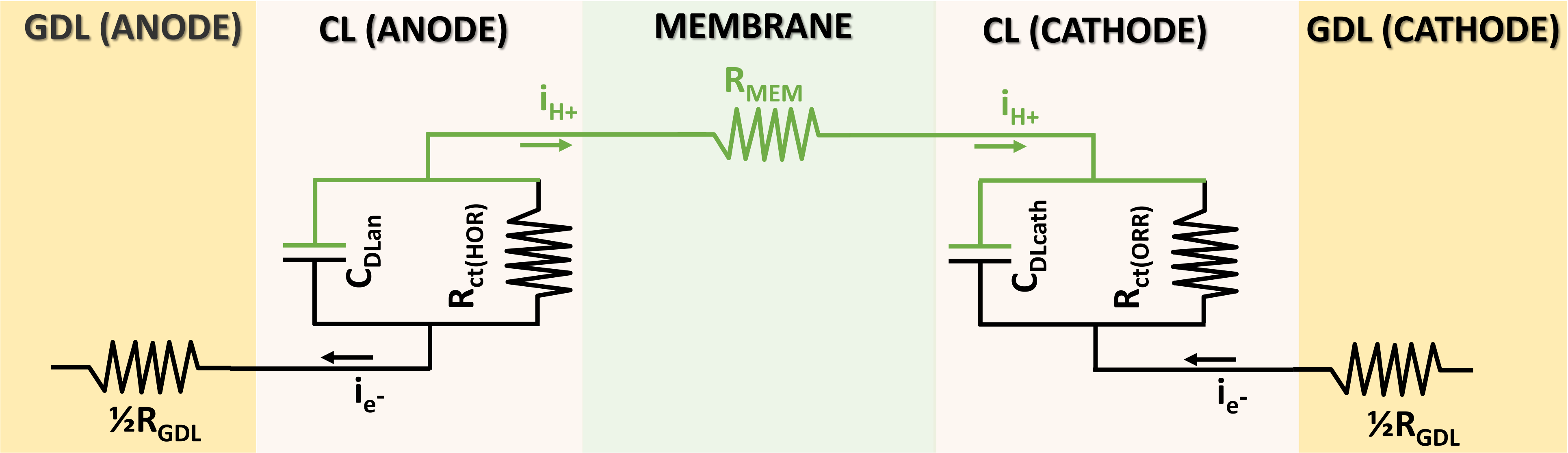


$$Z(\omega) = \frac{F[\Delta E(t)]}{F[\Delta I_{ORR}(t)]}$$



- ❑ Holistic approach
- ❑ Very difficult to deconvolute individual potential contributions

EQC Analysis of Electrochemical Impedance Spectra



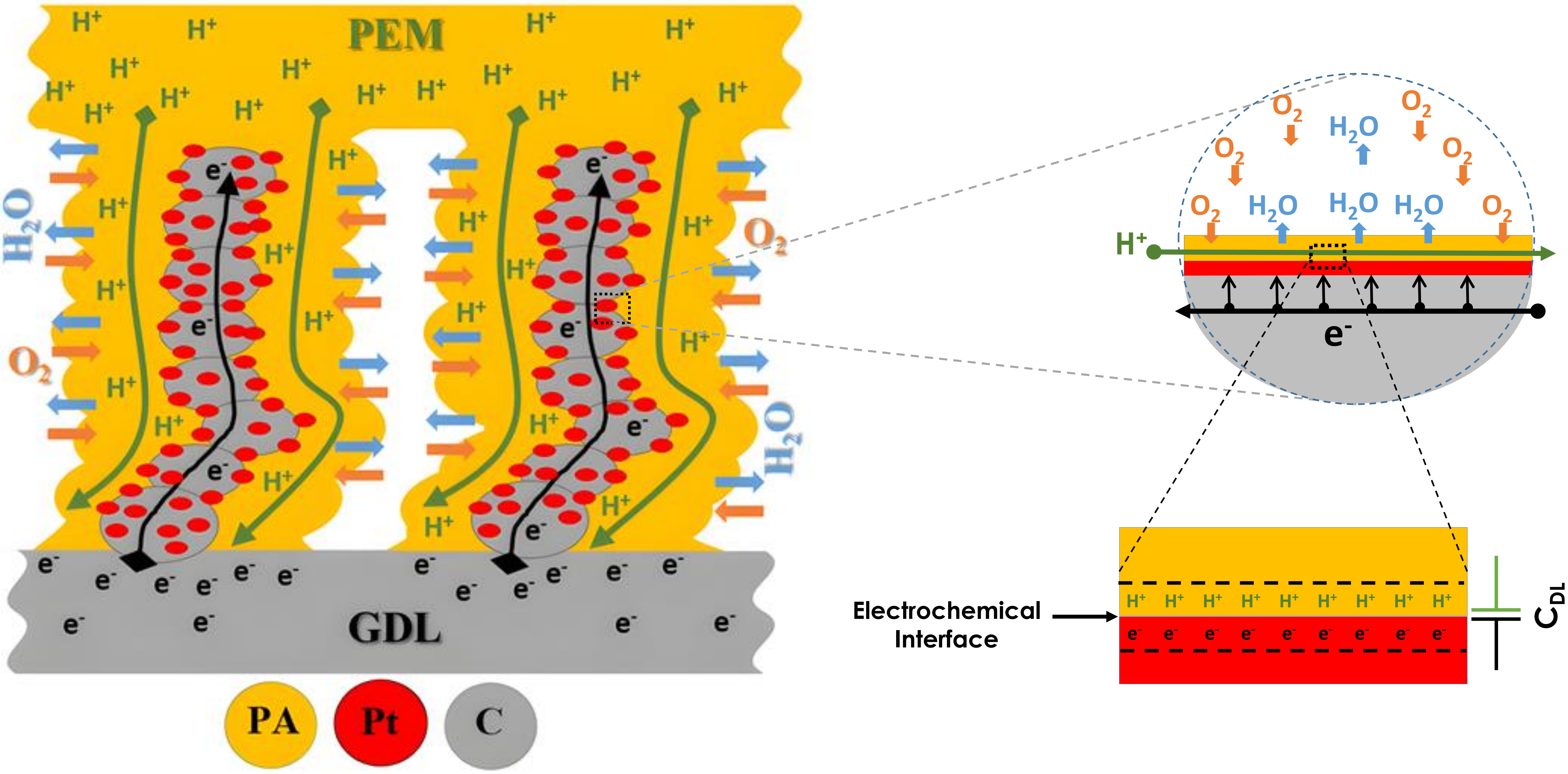
X **Main Draw Back :**

Equivalent Electrical Circuits (EQC) Representation:

1. **Not Unique!**
2. **Limited physicochemical insights**

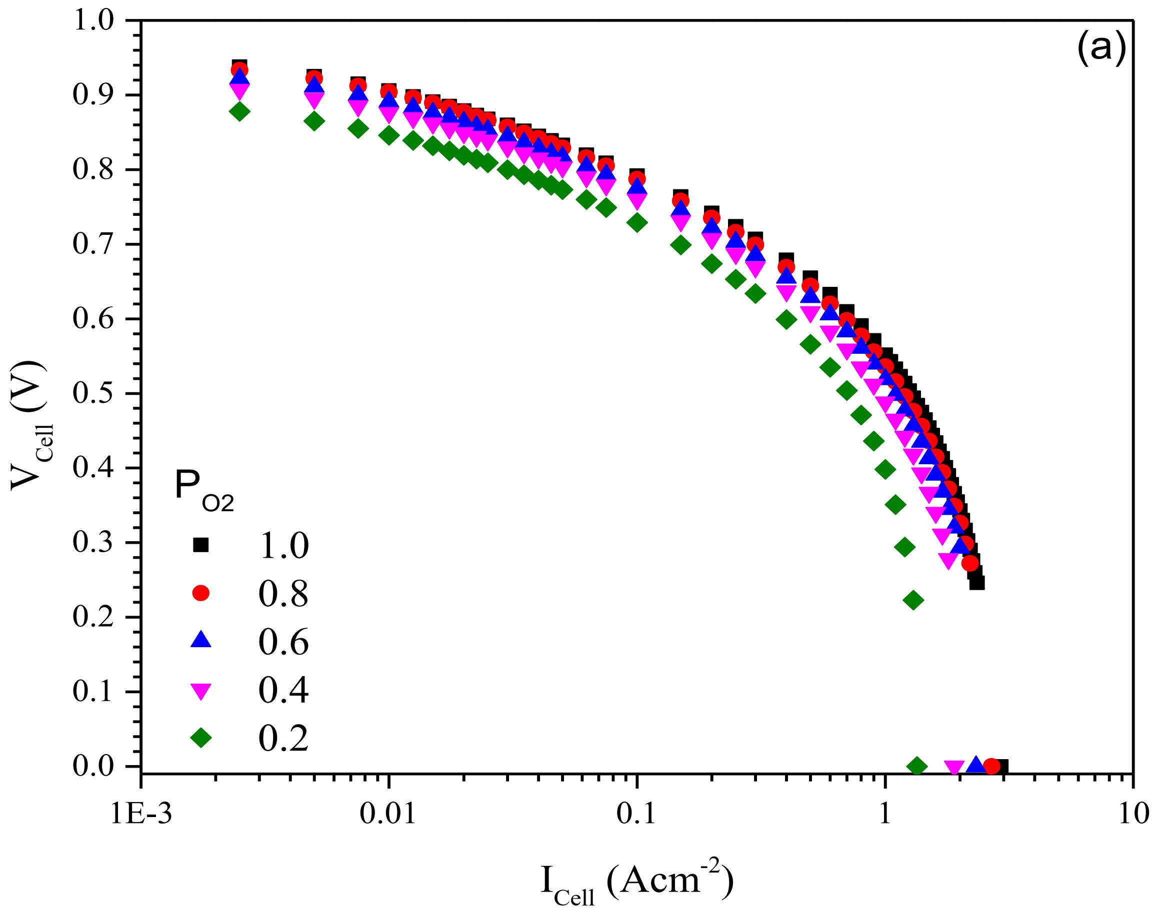
☑ **We developed a physical model to simulate EIS and study ORR kinetics**

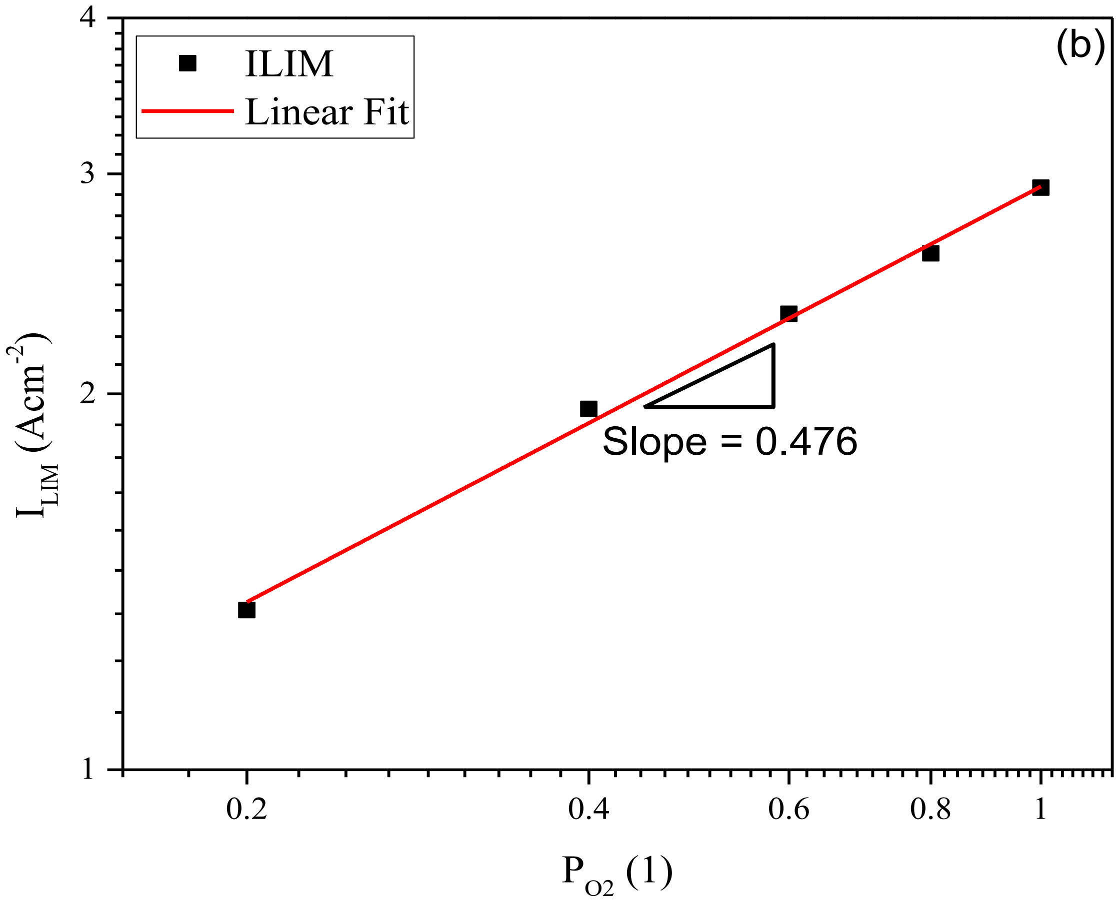
Cathode CL & CDL



Experimental Tafel & Limiting Current Plots

(Differential conditions- single 4cm² HTPEMFC)





- The $\mathbf{I_{LIM}}$ depends on $P_{O_2}^{0.5}$ indicating kinetic limitation due to O_2 dissociative adsorption

HT-ORR Mechanism & Physical macrokinetic Model

$$\frac{1}{2}O_{2(g)} + (Pt) \underset{k_{des}}{\overset{k_{ads}}{\rightleftarrows}} (O)_{ads}$$

$$(O)_{ads} + H^{+}/e^{-} \underset{k_{2b}}{\overset{k_{2f}}{\rightleftarrows}} (OH)_{ads}$$

$$(OH)_{ads} + H^{+}/e^{-} \underset{k_{3b}}{\overset{k_{3f}}{\rightleftarrows}} H_2O_{(g)} + (Pt)$$

$$r_1 = k_{ads} P_{O_2}^{1/2} \theta_{Pt} - k_{des}\theta_O$$

$$r_2 = k_{2f}\theta_O \exp\left(-\frac{E}{b}\right) - k_{2b}\theta_{OH}\exp\left(\frac{E}{b}\right)$$

$$r_3 = k_{3f}\theta_{OH} \exp\left(-\frac{E}{b}\right) - k_{3b}P_{H_2O}\theta_{Pt}\exp\left(\frac{E}{b}\right)$$

$$\Gamma_s \frac{d\theta_O}{dt} = r_1 - r_2$$

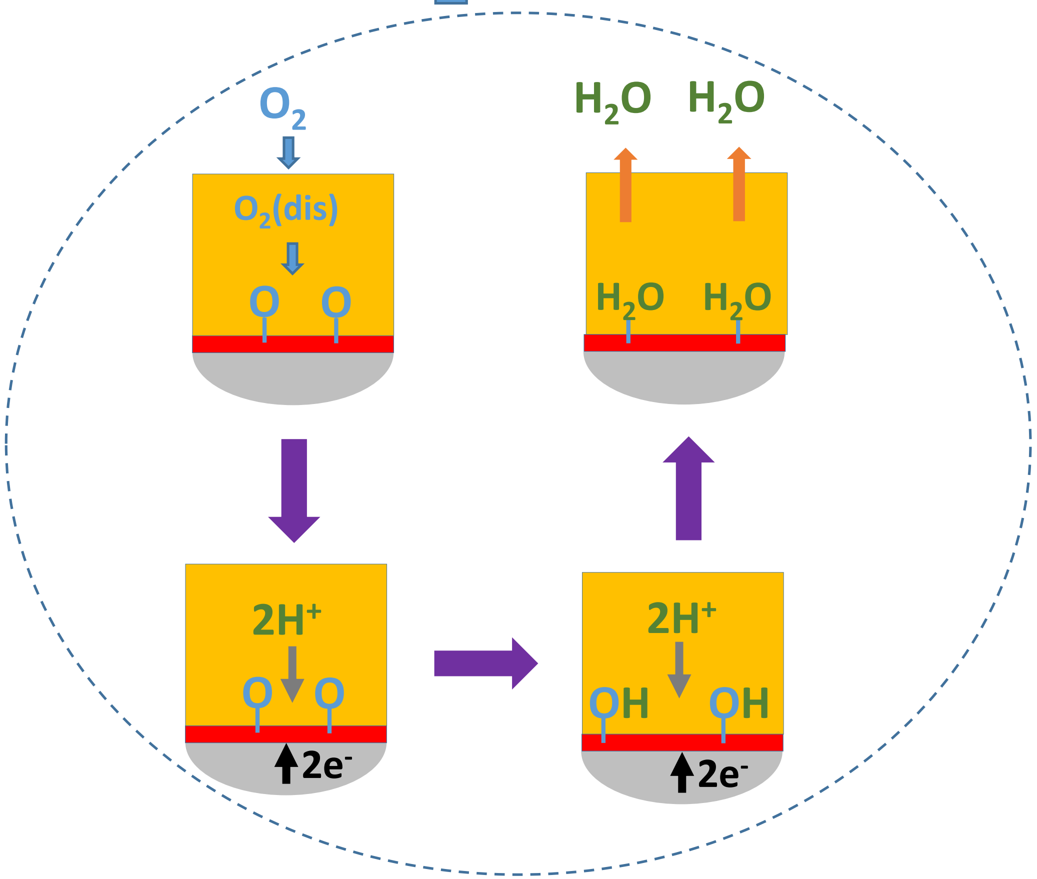
$$\Gamma_s \frac{d\theta_{OH}}{dt} = r_2 - r_3$$

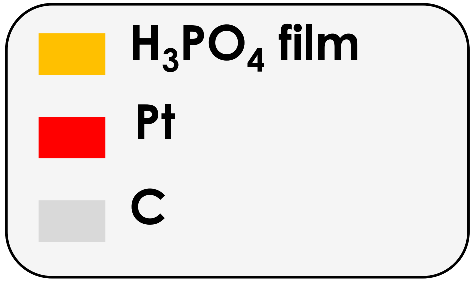
$$\theta_O + \theta_{OH} + \theta_{Pt} = 1$$

$$i_{Tot} = i_{ORR} + i_{CDL}$$

$$i_{ORR} = F(r2 + r3)$$

$$i_{CDL} = \left(\frac{\partial \phi_{ele}}{\partial t} - \frac{\partial \phi_{pro}}{\partial t}\right) \cdot C_{DL}$$





Regression Algorithm

✓ For the determination of the kinetic parameters:
13 experimental EIS and **13 I-V** points were fitted simultaneously (2309pts in total)

1. Choose with equal probability the parameter vector $\vec{P}\{k, C_{dl}, \sigma_p, \Delta_{Vi}\} = 45$ parameters

2. Minimize: $f\left(\vec{P}\right) = \sum_{i=1}^{13}\left(\mathrm{norm}_2\left(Z_{RE_i} - z_{re_i}\right) + \mathrm{norm}_2\left(Z_{IM_i} - z_{im_i}\right) + \mathrm{norm}_2\left(I_{CELL_i^{ss}} - i_{cell_i^{ss}}\right)\right)$

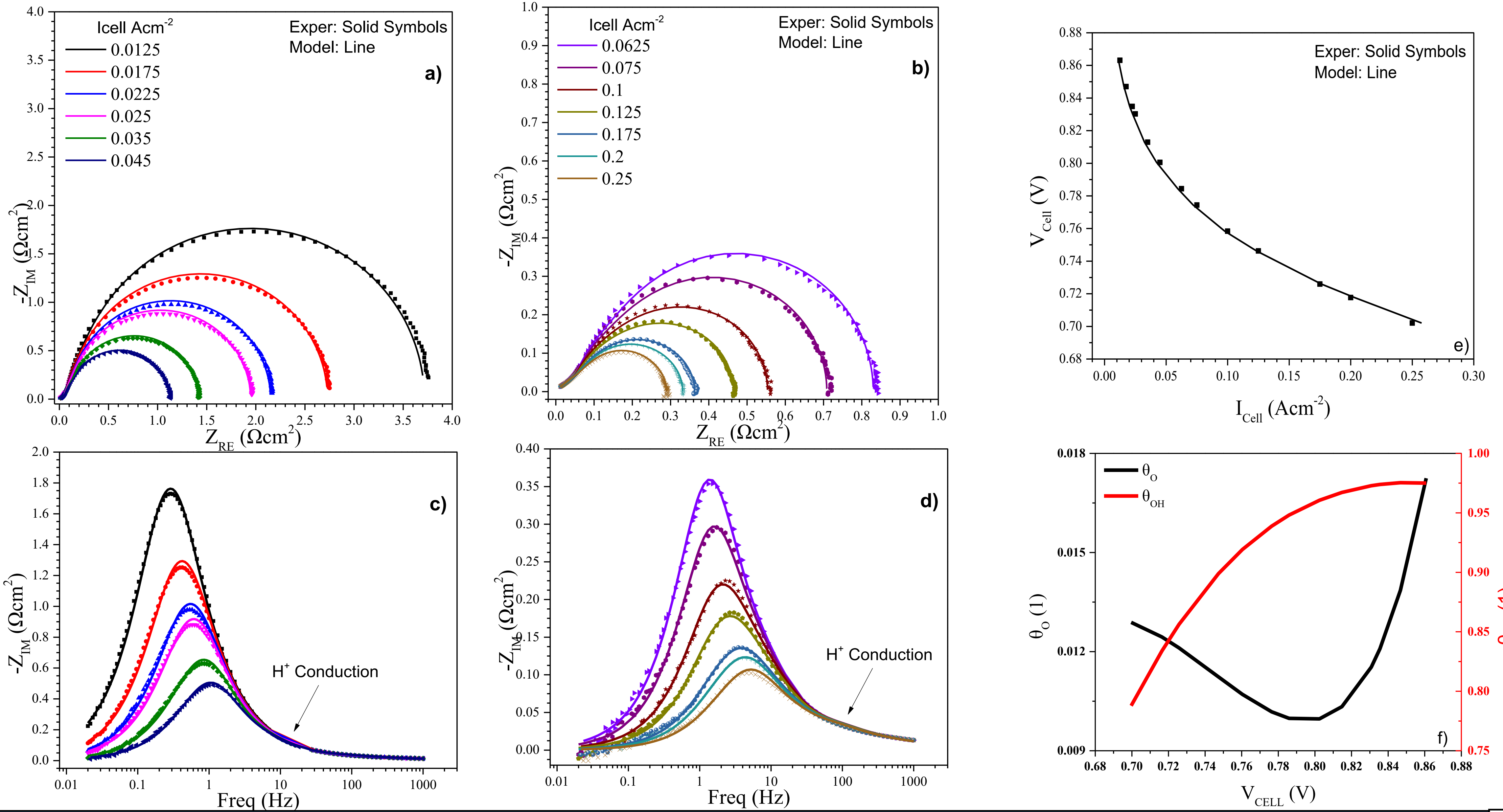
$$\text{w.r.t} : \vec{P} = \{k_{ads}, k_{2f}, k_{2b}, k_{3f}, k_{3b}\} \cup \{C_{dl1}, ..., C_{dl13}\} \cup \{\sigma_{p1}, ..., \sigma_{p13}\} \cup \{\Delta_{V1}, ..., \Delta_{V13}\}$$

3. Store $\vec{P}_{min}$ vector and $f\left(\vec{P}_{min}\right)$

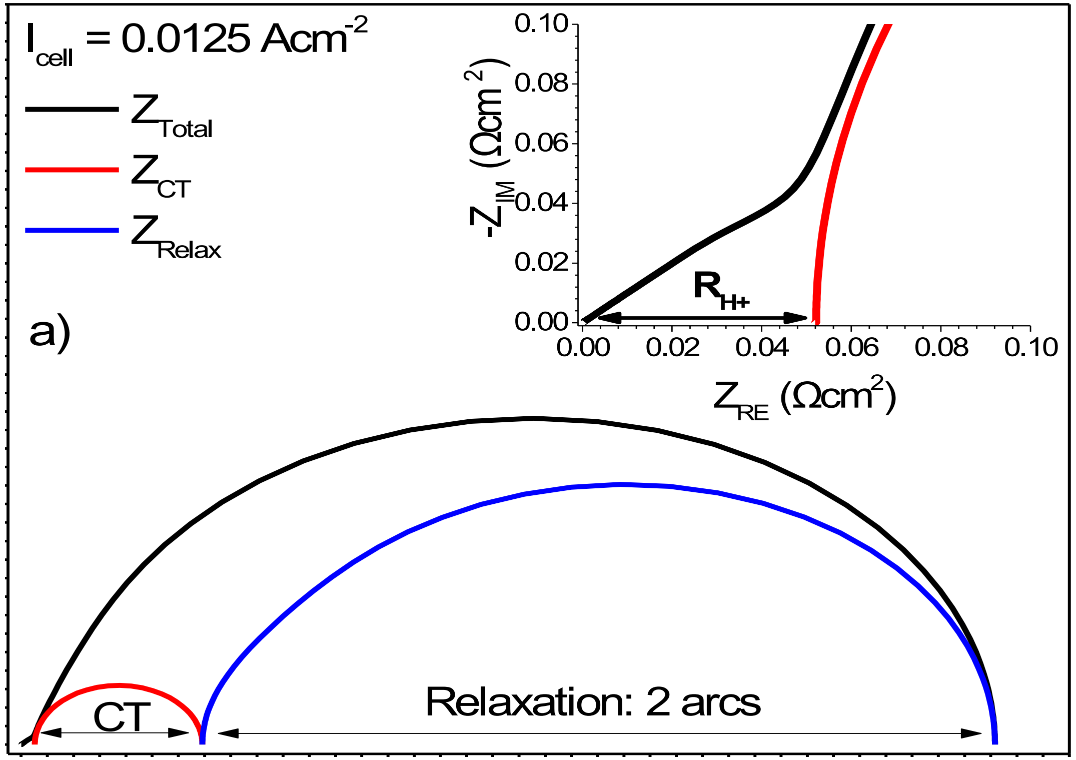
4. Repeat steps $(1\text{-}3)$ 10^5 times

5. Find the global minimum $\vec{P}_{min}$ vector among the converged local minima

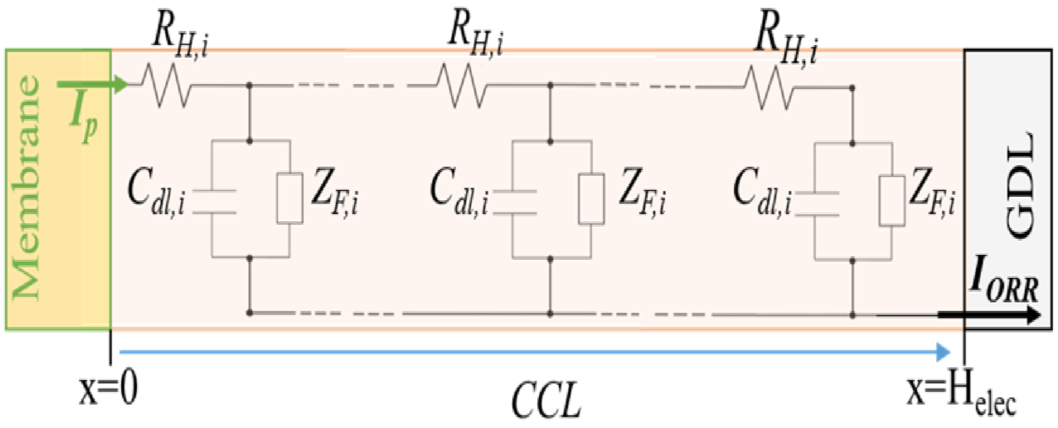
Experimental-Modeled Fitting Results (IV-EIS-Coverages)



Contributing components of the EIS



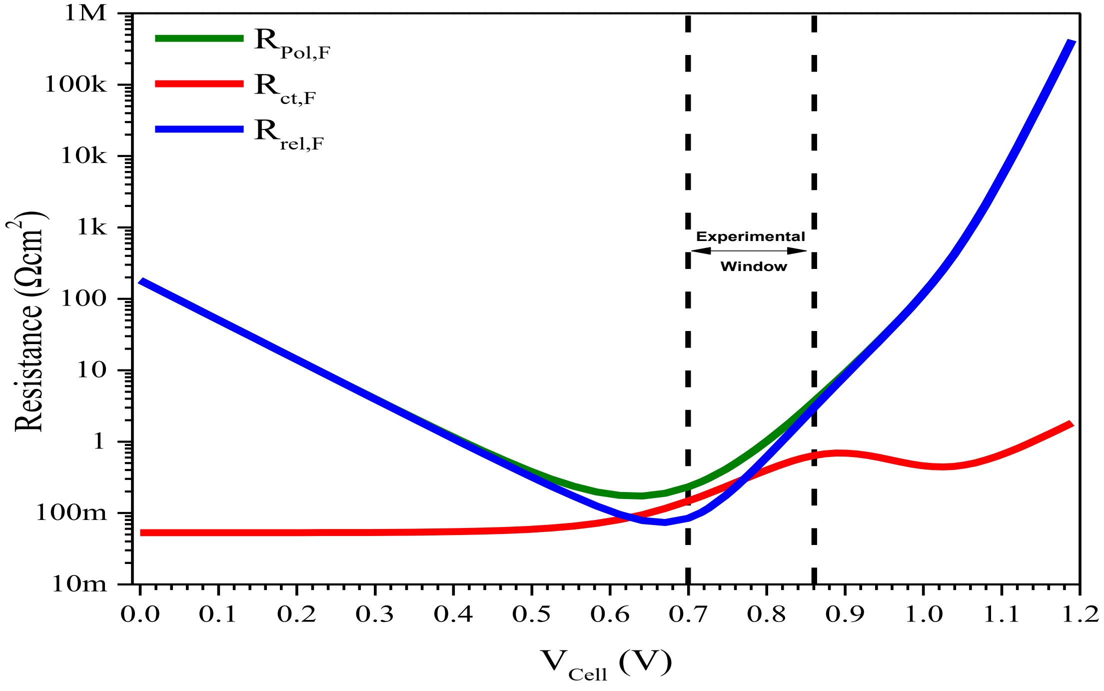
Transmission Line Model (TLM)



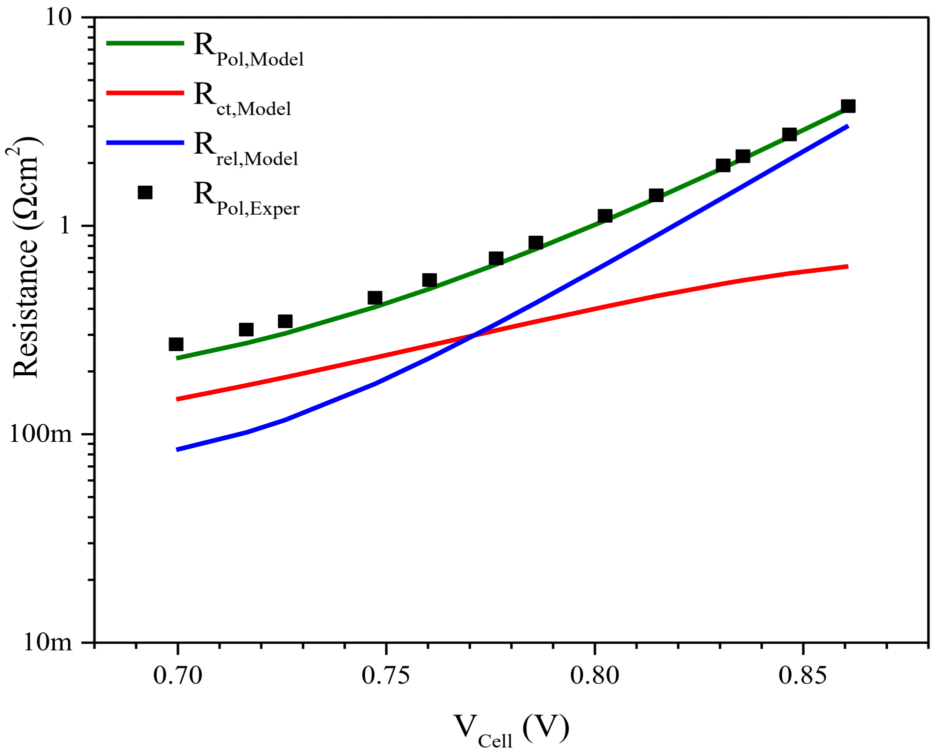
The EIS are composed of three types of contributions:

1. The effective proton resistance (**R_{H+}**) within the catalytic layer modeled by the use of **TLM**
2. The Charge transfer resistance (**R_{CT}**) representing the electrochemical reactions across the interface
3. The relaxation arc (**R_{Relax}**) related to hysteresis of the coverages on the catalytic surface –"**Intrinsic Kinetic Inertia**"

R_{Pol} Deconvolution : R_{CT} - R_{Relax}



Experimental Window

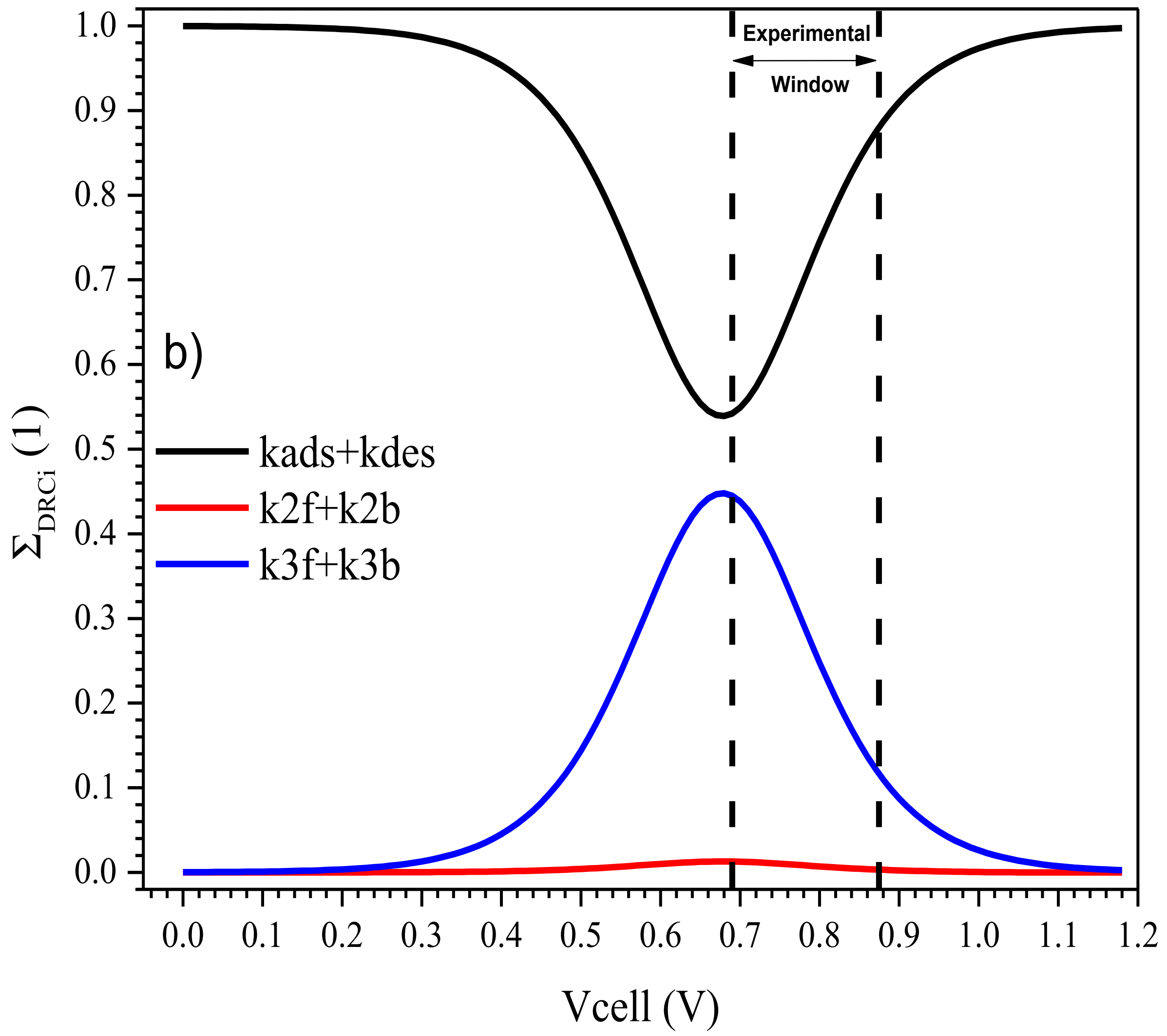


Determined Kinetics & Degree of Rate Control

Table I Model Fitted Parameters

Parameter	Value [Units]	Description
MSE (#pts)	1.95×10^{-4} (2309pts)	Regression Mean Squared Error
k_{ads}	2.965×10^{-4} $[mol\,m_{Pt}^{-2} s^{-1} atm^{-1/2}]$	Step 1: Forward chemical kinetic constant
k_{des}	4.251×10^{-12} $[mol\,m_{Pt}^{-2} s^{-1}]$	Step 1: Backward chemical kinetic constant
k_{2f}	1.614×10^{1} $[mol\,m_{Pt}^{-2} s^{-1}]$	Step 2: Forward chemical kinetic constant
k_{2b}	5.909×10^{-11} $[mol\,m_{Pt}^{-2} s^{-1}]$	Step 2: Backward chemical kinetic constant
k_{3f}	4.680×10^{-1} $[mol\,m_{Pt}^{-2} s^{-1}]$	Step 3: Forward chemical kinetic constant
k_{3b}	2.720×10^{-7} $[mol\,m_{Pt}^{-2} s^{-1} atm^{-1}]$	Step 3: Backward chemical kinetic constant

$$DRC_i = \frac{k_i}{r}\left(\frac{\partial r}{\partial k_i}\right)_{k_j \neq k_i, K_i} = \left(\frac{\partial \ln r}{\partial \ln k_i}\right)_{k_j \neq k_i, K_i}$$



List of the determined energetics

Table II Calculated reaction free energies

Free Energy (kJ/mol)	U = 0 [V] η=-1.147 [V]	U = 0.561 [V] η=-0.586 [V]	U = 0.795 [V] η=-0.352 [V]	U = 1.147 [V] η = 0 [V]
ΔG_{1f}	102.724	102.724	102.724	102.724
ΔG_{1b}	170.770	170.770	170.770	170.770
$\Delta G_1 = \Delta G_{1f} - \Delta G_{1b}$	-68.046	-68.046	-68.046	-68.046
ΔG_{2f}	61.638	88.702	99.991	116.976
ΔG_{2b}	160.854	133.790	122.501	105.510
$\Delta G_2 = \Delta G_{2f} - \Delta G_{2b}$	-99.216	-45.088	-22.510	11.466
ΔG_{3f}	74.978	102.040	113.331	130.317
ΔG_{3b}	129.076	102.010	90.723	73.737
$\Delta G_3 = \Delta G_{3f} - \Delta G_{3b}$	-54.098	0.030	22.608	56.580
$\Delta G_{ORR} = \Delta G_1 + \Delta G_2 + \Delta G_3$	-221.360	-113.104	-67.948	0.000

Calculated at Unit Activities and T=180°C

Kinetic constants according to Transition State Theory (TST)

$$k_{ads} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{1\rightarrow}}{RT}\right) \Gamma_s$$

$$k_{des} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{1\leftarrow}}{RT}\right) \Gamma_s$$

$$k_{2f} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{2\rightarrow}}{RT}\right) a_{H^+} \Gamma_s$$

$$k_{2b} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{2\leftarrow}}{RT}\right) \Gamma_s$$

$$k_{3f} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{3\rightarrow}}{RT}\right) a_{H^+} \Gamma_s$$

$$k_{3b} = \frac{\kappa k_B T}{h} \exp\left(-\frac{\Delta G^{0\neq}_{3\leftarrow}}{RT}\right) \Gamma_s$$

$\kappa = 1$ (transmission coeff.)

$a_{H^+} = 1$ (H^+ activity)

$\Gamma_s = 2.2 x 10^{-5} [mol/m^2_{Pt}]$ (Monolayer)

Gibbs Free Energies (energy states) and activation energies of ORR intermediate species

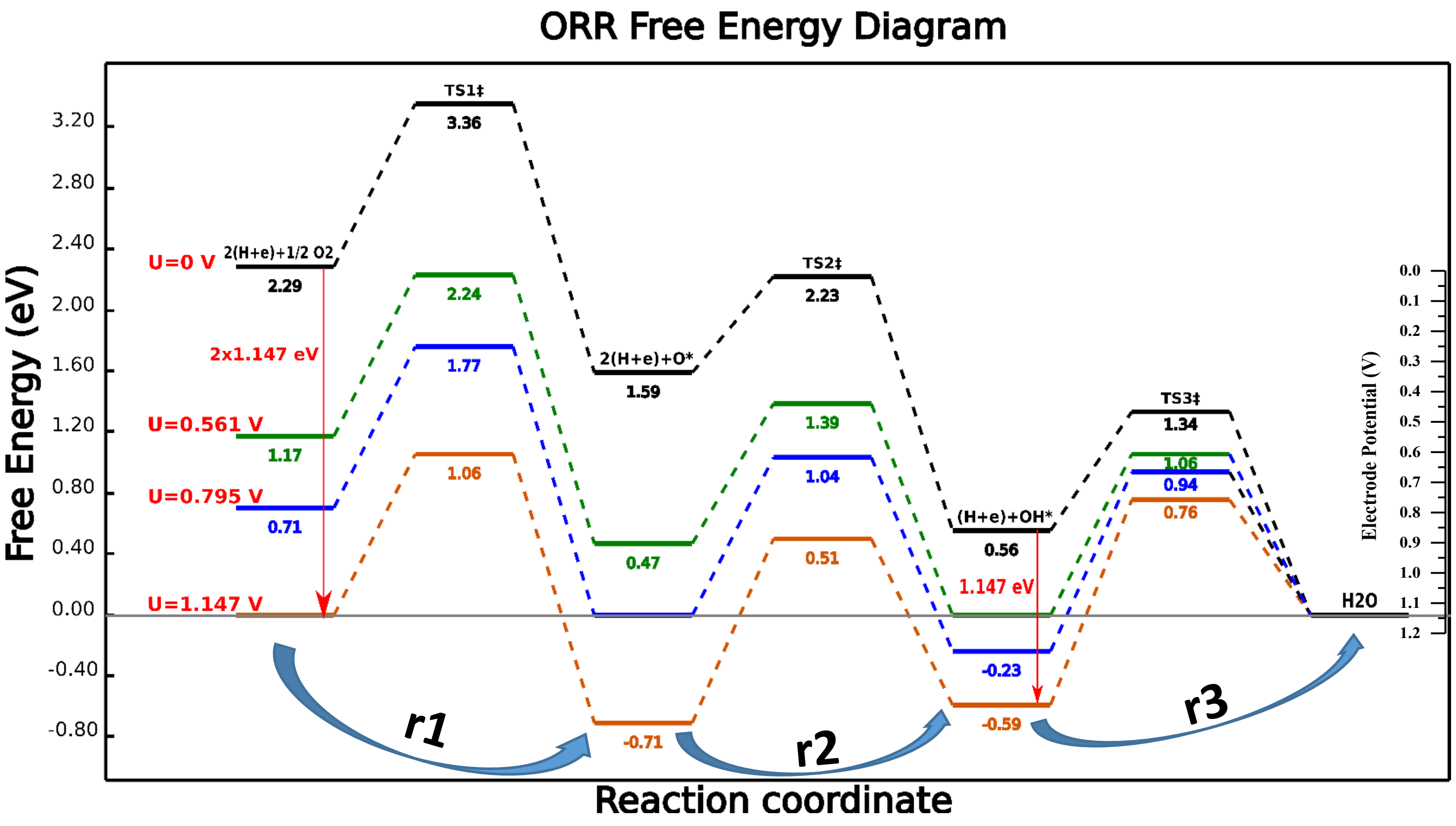
$$\Delta G_1 = \Delta G^{0\neq}_{ads\rightarrow} - \Delta G^{0\neq}_{des\leftarrow}$$

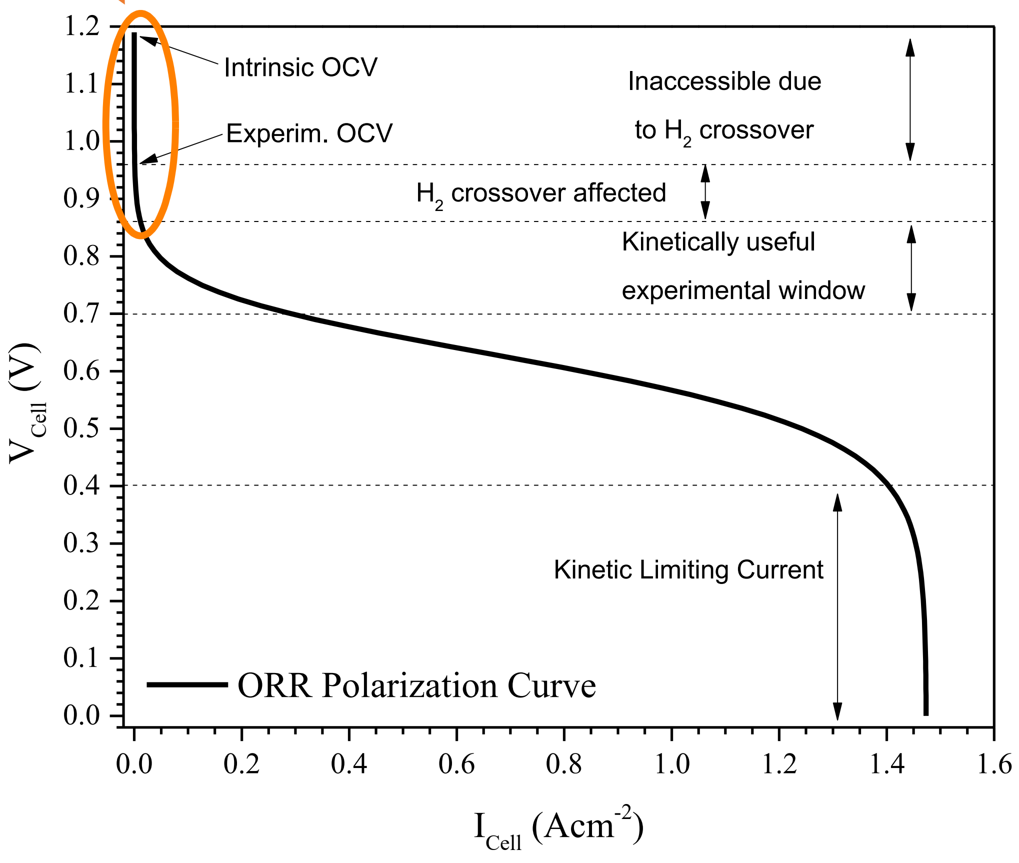
$$\Delta G_2 = \Delta G^{0\neq}_{2f\rightarrow} - \Delta G^{0\neq}_{2b\leftarrow}$$

$$\Delta G_3 = \Delta G^{0\neq}_{3f\rightarrow} - \Delta G^{0\neq}_{3b\leftarrow}$$

ORR Energetics @ Unit Activities and T=180°C

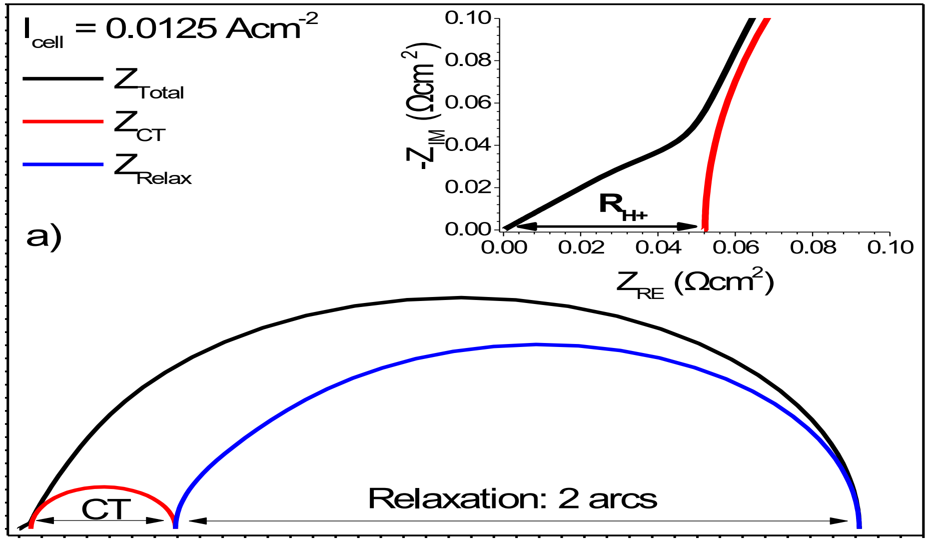
@ U=1.147V (Open Circuit) the activation overpotential is mainly related to the electrochemical energy spent to overcome the positive free energy change (uphill) of the two electrochemical reaction steps (2 and 3)





Conclusions I

➢ <u>*The ORR Spectrum In the activation region & under Differential Conditions consists of:*</u>



☑ **A small high frequency linear contribution due to H^+ ionic resistance of the catalytic layer**

☑ **A high frequency arc due to Charge Transfer Resistance of <u>both</u> electrochemical steps**

☑ **A large low frequency arc due to the intrinsic KINETIC INERTIA - RELAXATION of the accumulated adsorbed species (Oads, OHads) on catalyst surface, caused by the hysteresis between the competing ORR reaction steps**

Conclusions II

➢ *Regarding the Kinetics & Energetics of ORR:*

☑ **The limiting step of the whole process is the dissociative adsorption of O_2 (DRC)**

☑ **The energetics of the reaction steps can be estimated according to the Transition State Theory**

☑ **The activation overpotential is the electrochemical energy spent to overcome:**

i) the positive free energy change of the two electrochemical steps (thermodynamics)

ii) the high activation energy of the O2 adsorption step (kinetics)

Acknowledgements

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ΙΣΝ SNF ΙΔΡΥΜΑ ΣΤΑΥΡΟΣ ΝΙΑΡΧΟΣ
STAVROS NIARCHOS FOUNDATION

Regression Results

Name	Value	Units	Description
MSE	**1.950 x10^{-4}**	-	**Regression Mean Squared Error for 2309pts**
$\mathbf{k_{ads}}$	2.965x10^{-4}	$mol\ m_{Pt}^{-2}\ s^{-1}\ atm^{-1/2}$	Step 1: Forward chemical kinetic constant
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$\mathbf{k_{3b}}$	2.720 x10^{-7}	$mol\ m_{Pt}^{-2}\ s^{-1}\ atm^{-1}$	Step 3: Backward chemical kinetic constant
$\mathbf{CDL_{Pt}}$	1.107 x10^{-5}	$F\ cm_{Pt}^{-2}$	Avg. Pt Double Layer Capacitance, (min, max)= (10.5,12.3) $\mu F\ cm_{Pt}^{-2}$
$\boldsymbol{\sigma_{CL}}$	5.541	$S\ m^{-1}$	Avg. effective CL ionic conductivity, (min, max)= (5.1,5.9) $S\ m^{-1}$
$\boldsymbol{\Delta V_i}$	1.374 x10^{-3}	V	Avg. potential deviation, (min, max)= (0.14, 2.48) mV
E_{OCV}^{Nerst}	1.1899	V	Calculated OCV Potential for P_{H2}=1 atm, P_{O2}=0.2 atm, P_{H2O}=0.05 atm
E_{OCV}^{exp}	0.960	V	Experimentally measured OCV Potential due to H_2 crossover
E_{calc}^{0}	1.1471	V	Standard thermodynamic potential at 180°C and unit activities for reactants and products
J_0^{ORR}	2.135 x10^{-2}	$A\ cm_{CCL}^{-2}$	ORR Exchange Current Density per CCL area
$J_{0,Pt}^{ORR}$	3.558 x10^{-5}	$A\ cm_{Pt}^{-2}$	ORR Exchange Current Density per electrocatalyst active area
$J_{xover}^{H_2,model}$	1.124x10^{-3}	$A\ cm_{CCL}^{-2}$	$H_{2(g)}$ Crossover Current Density per CCL area

ORR Polarization Curve – Tafel Slope – Intermediates' Coverages