Control of High Efficiency PEM Fuel Cells for Long Life, Low Power Applications

Part 2

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Outline

- Review
- PEM Fuel Cell Degradation
- Catalyst Dissolution Chemistry
- Reaction Kinetics
- Physical Implications
- Effect on Fuel Cell Life
- Effective Control to Mitigate Degradation

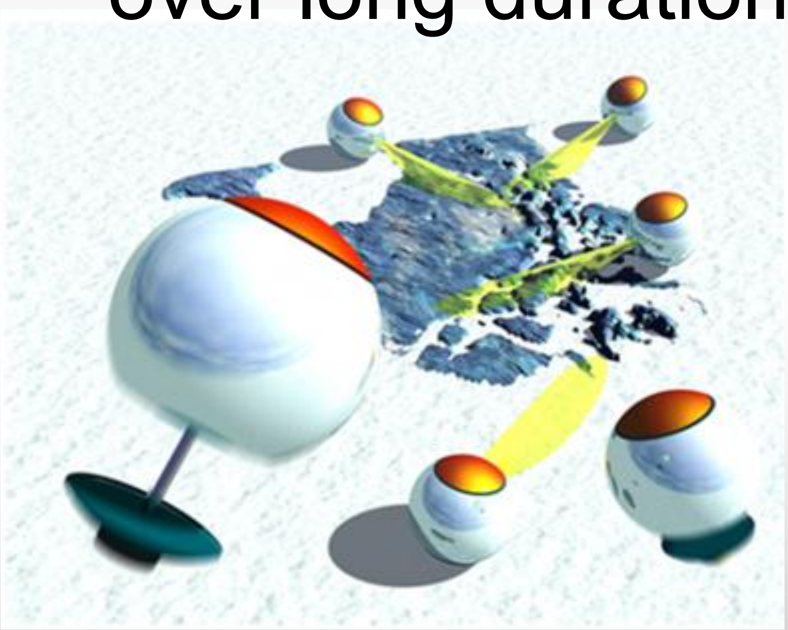
Review

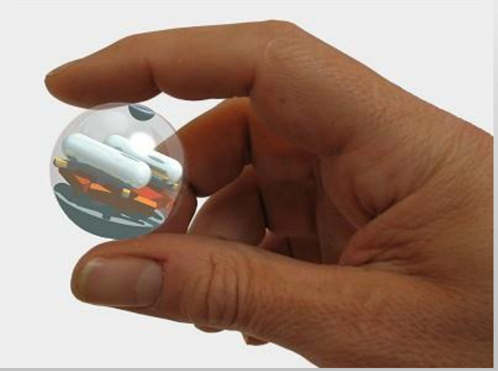
Motivation: Present

- Mobile electronic devices are energy hungry, battery have limited energy density could benefit from backup or alternative power sources.

Motivation: Future

- Mobile sensor networks can be an important tools to monitor the environment over long durations…



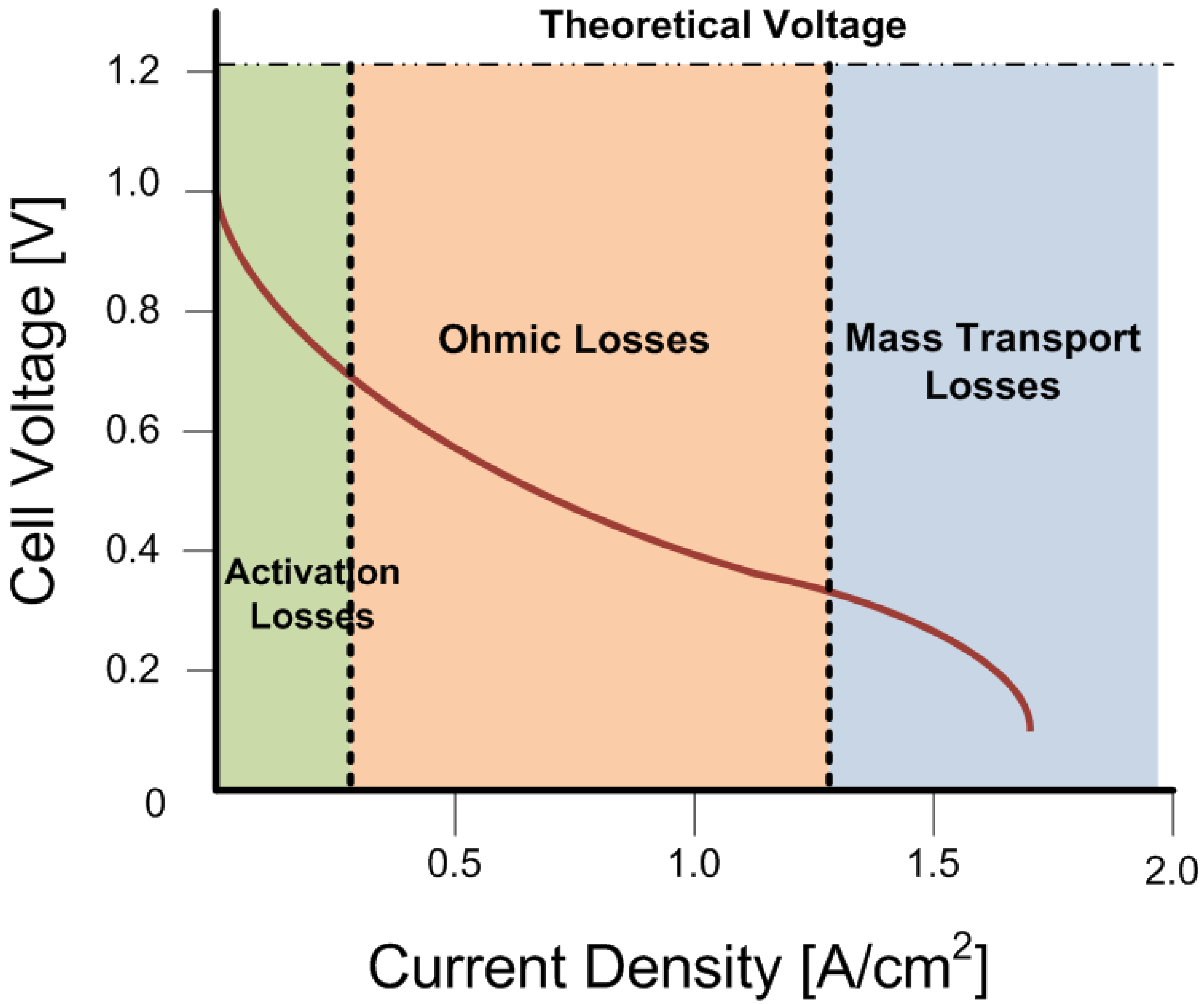


Fuel Cells

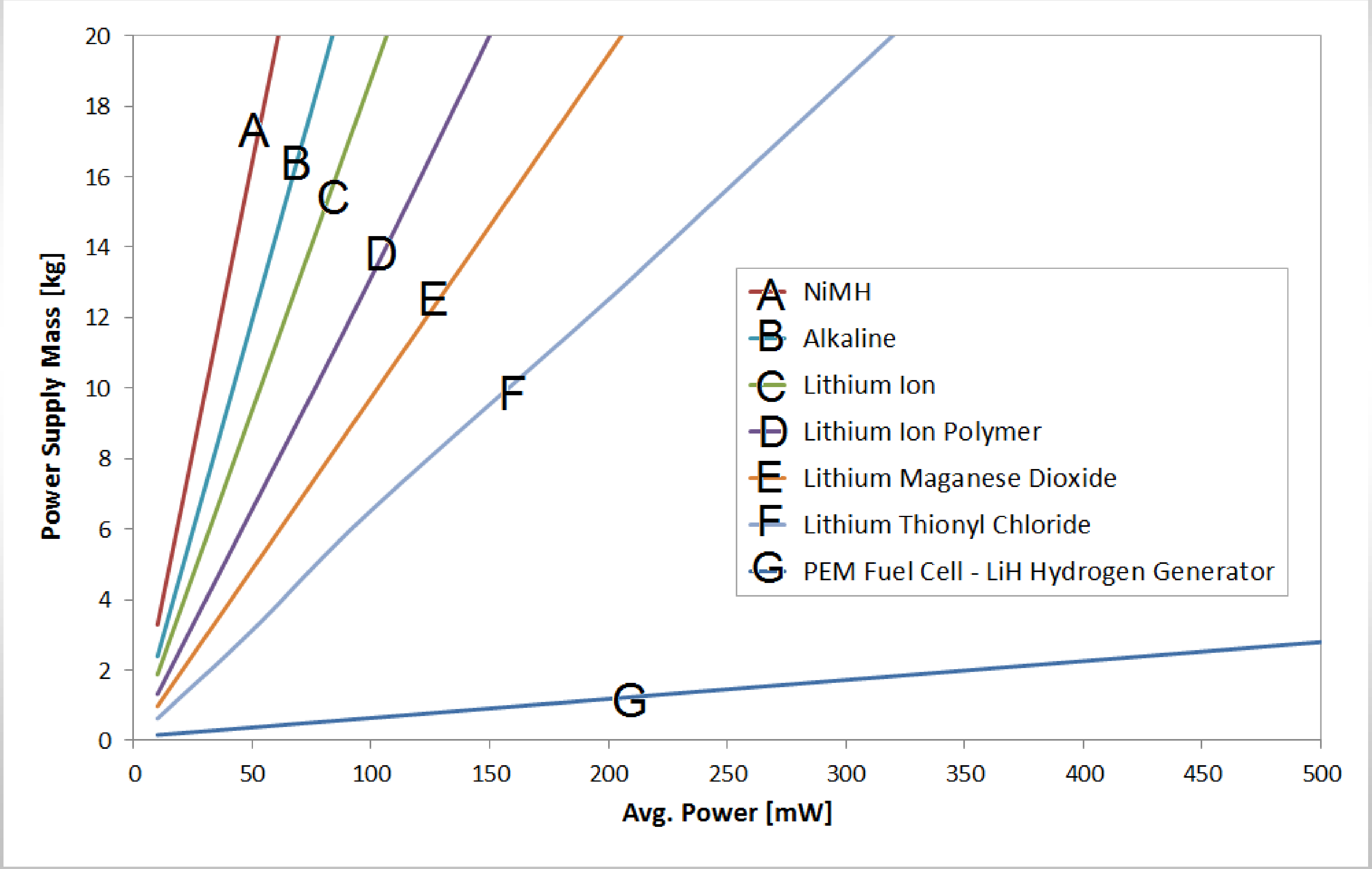
Fuel Cell	Electrolyte	Fuel & Oxidizer	Efficiency	Operating Temp
Alkaline	Potassium Hydroxide	H_2 and O_2 (pure)	40 - 60 %	90 – 100 °C
PEM	Polymer Membranes (typically Nafion®)	H_2 and O_2	40 - 70 %	5 – 100 °C
Direct Methanol	Polymer Membranes	CH_3OH and O_2	20 - 40 %	15 – 100 °C
Phosphoric Acid	Phosphoric Acid	H_2 and O_2	40 %	150 - 200 °C
Solid Oxide*	Oxide ion conducting ceramic	F: Methane, Propane, Butane, H_2 O_2	40 - 70 %	700 – 1000 °C

* No need for catalyst.

Fuel Cell Polarization Curve



Power Supply Mass for 3 Years



Challenges

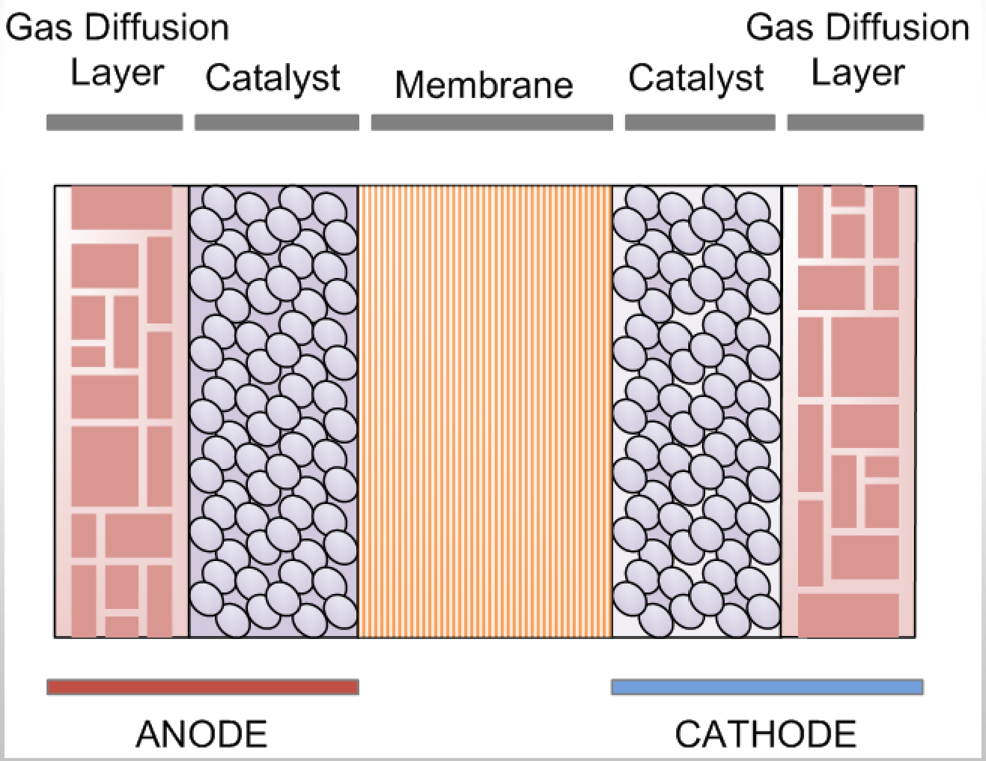
- PEM Fuel cells face 4 major problems:
  - Unreliable – due to degradation [Shao-Horn et al., 2007], [Rubio et al., 2004], [Wu et al., 2008], [Borup et al., 2009], [Madden et al., 2010]
  - Inefficient fuel storage [Schlapbach & Zuettel, 2001]
  - Low power density [Barbir, 2005], [O'Hayre et al., 2005]
  - High cost [Barbir, 2005]

- Significant progress being made in all these areas.

Fuel Cell Degradation

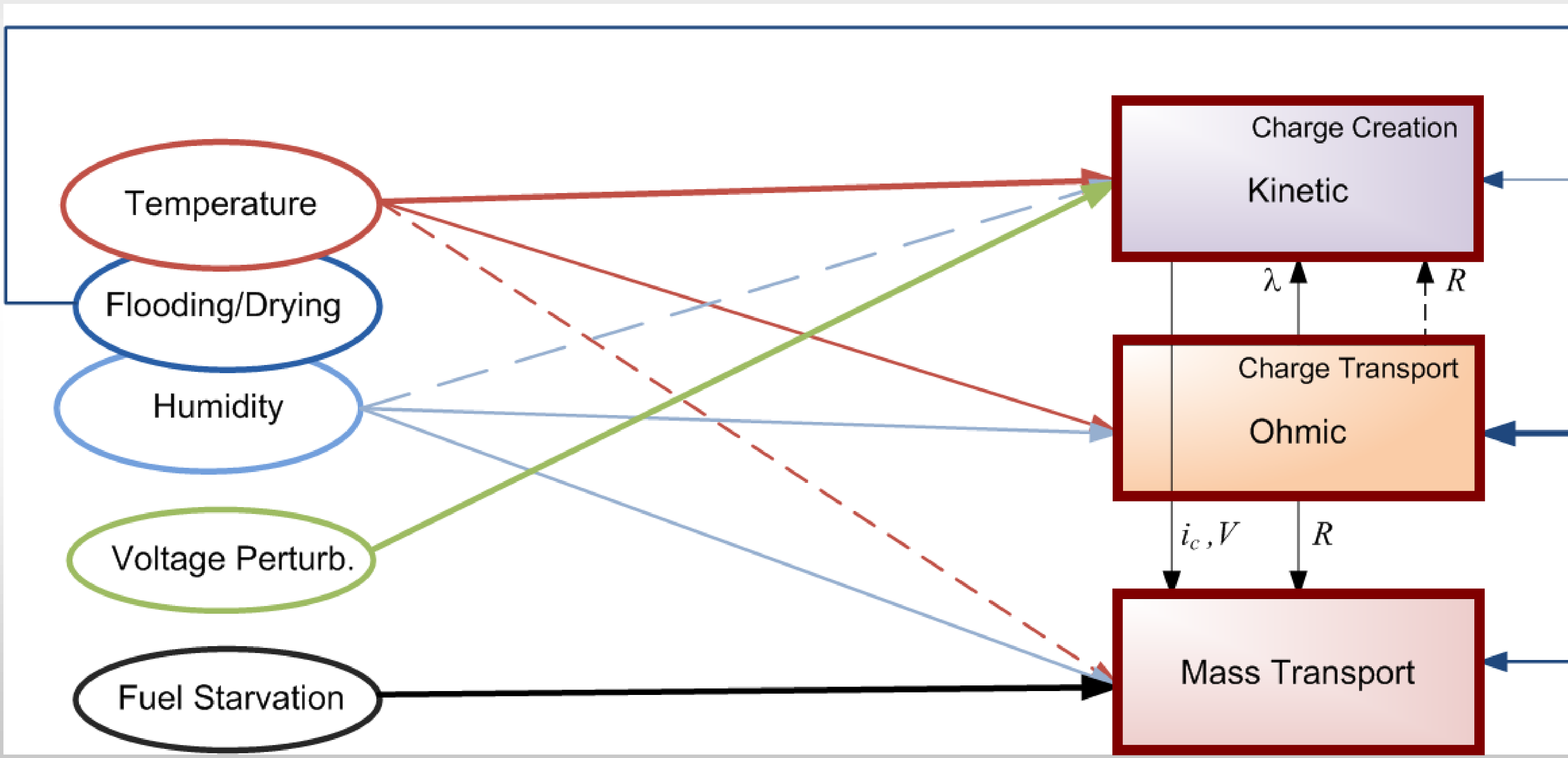
Key components that can degrade

- Catalyst Layer
- Membrane
- Gas Diffusion Layer



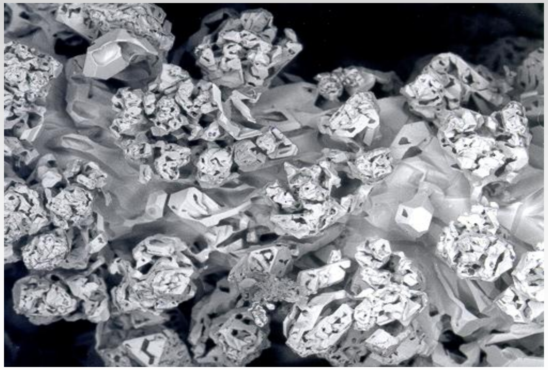
Fuel Cell Degradation Model

Fuel Cell Component: Gas Diffusion Layer
Membrane
Catalyst



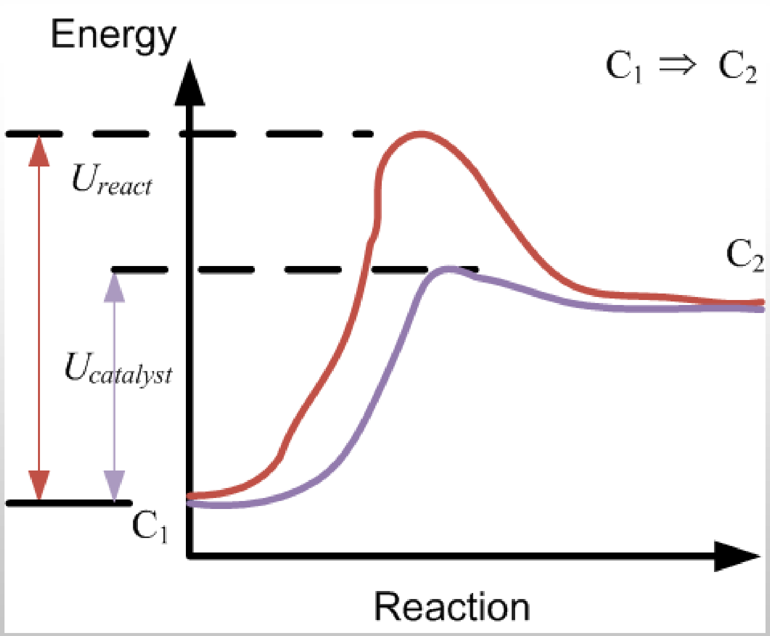
Role of Platinum Catalyst

- Speeds up and lower energy required for reactions
- Site for ionizing protons
- Site for assembly of water in the cathode



- Key metric – platinum surface area

$$S = \sum_{x} \sum_{i=S,L} N_{x,i} 4\pi R_{x,i}^2$$



Platinum Loss

- Loss of platinum is irreversible
- Starts as slow-steady degradation of FC power performance
- Accelerates membrane structure degradation leading to catastrophic loss [Wu et al., 2008]

Platinum Oxidation & Dissolution

Platinum Dissolution:

$$Pt = Pt^{2+} + 2e^{-} \qquad [1.188\ V]$$

Precipitation:

$$Pt^{2+} + H_2 = Pt + 2H^{+}$$

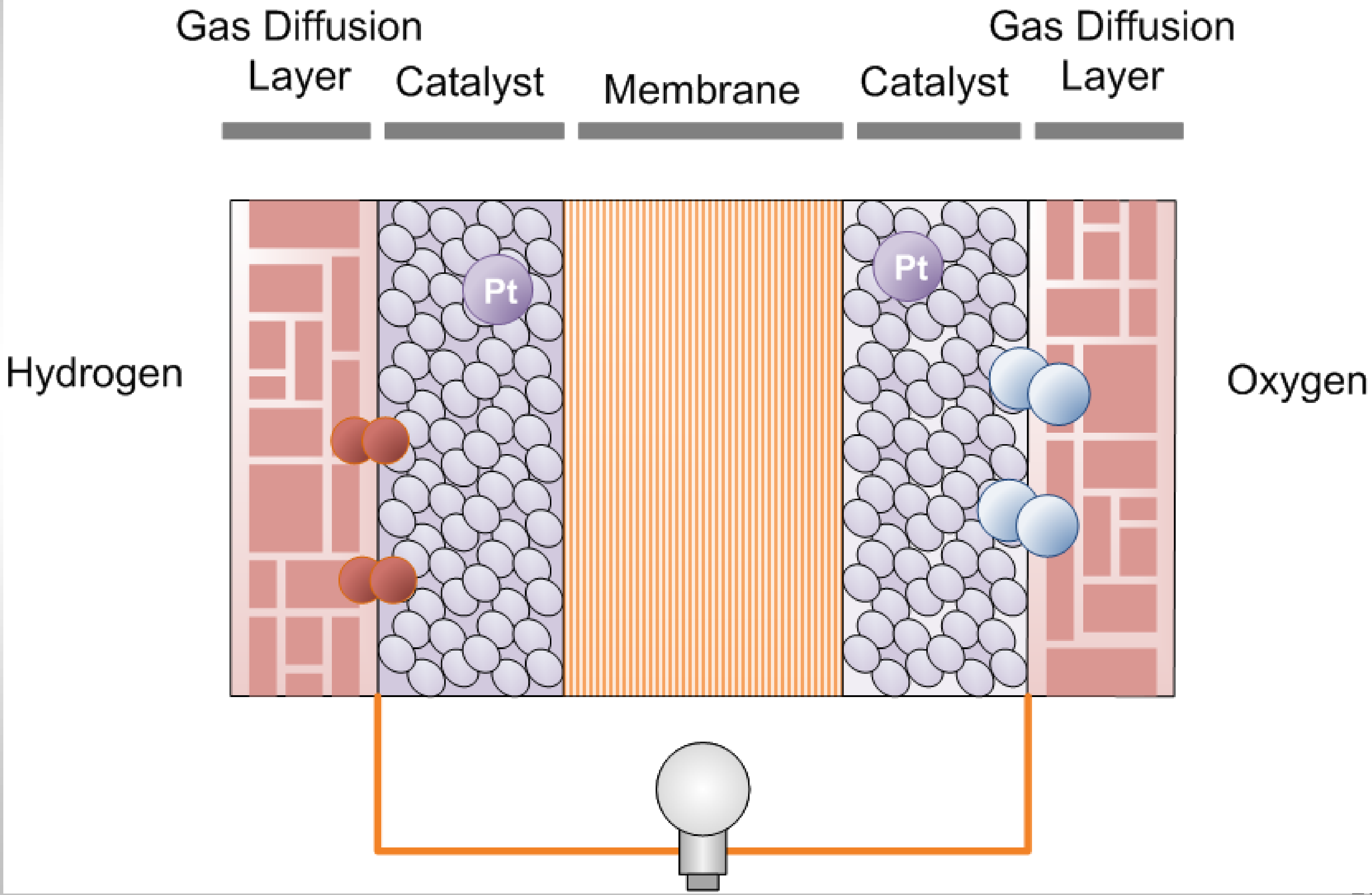
Platinum Oxidation:

$$Pt + H_2O = PtO + 2H^{+} + 2e^{-} \qquad [0.98\ V]$$

$$PtO + 2H^{+} = Pt^{2+} + H_2O$$

Ignored

Platinum Dissolution - Anode



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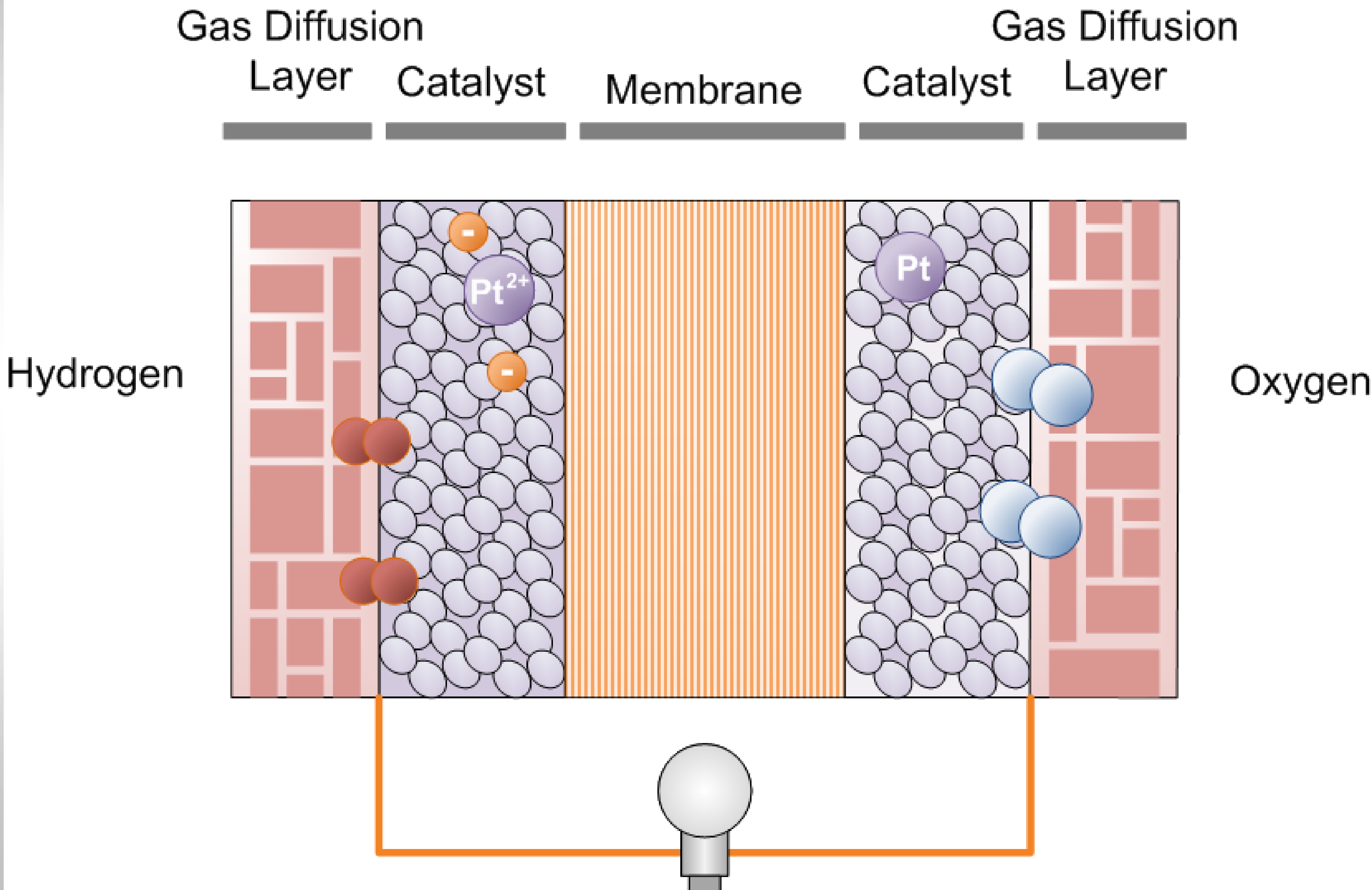

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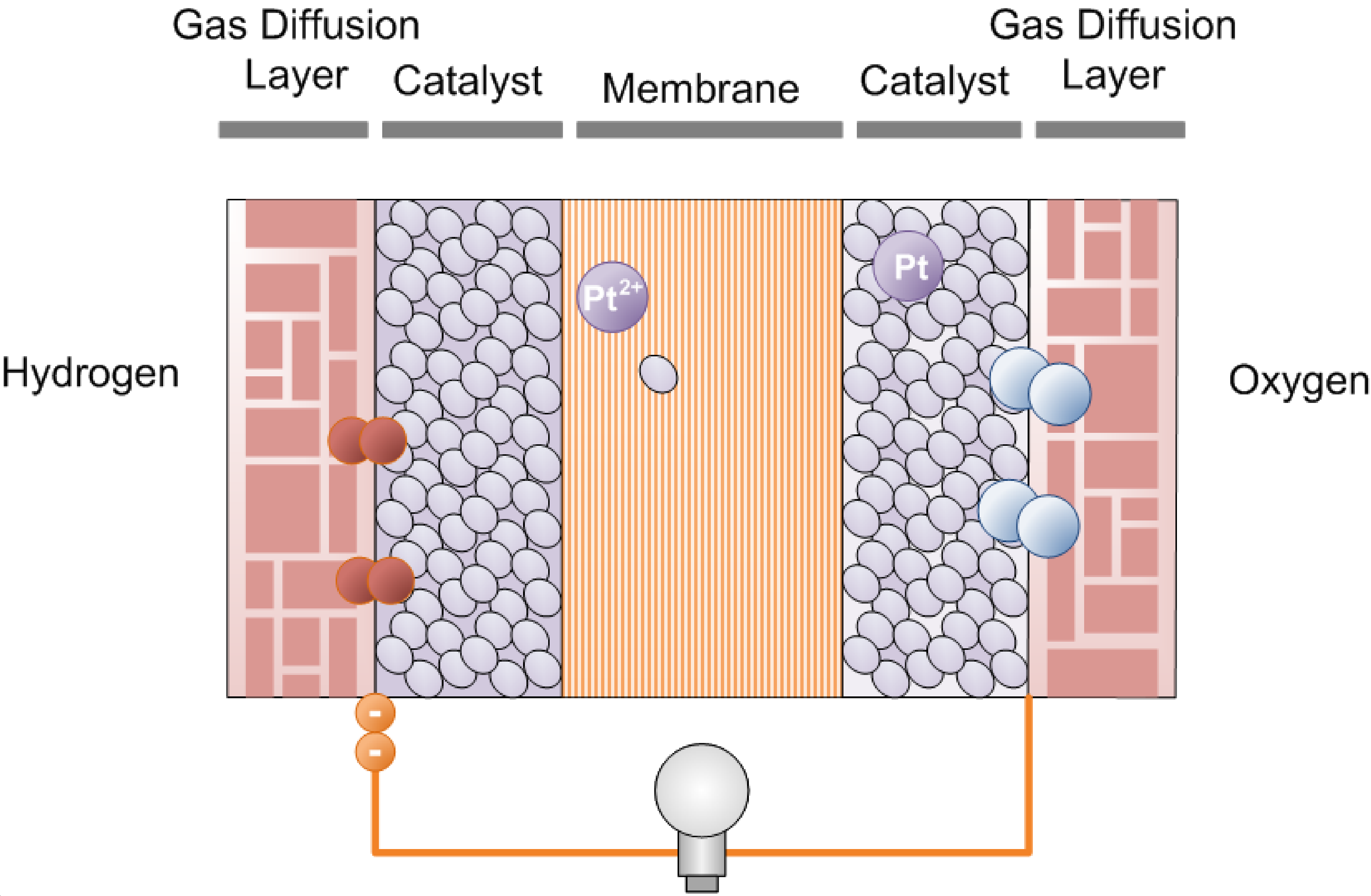

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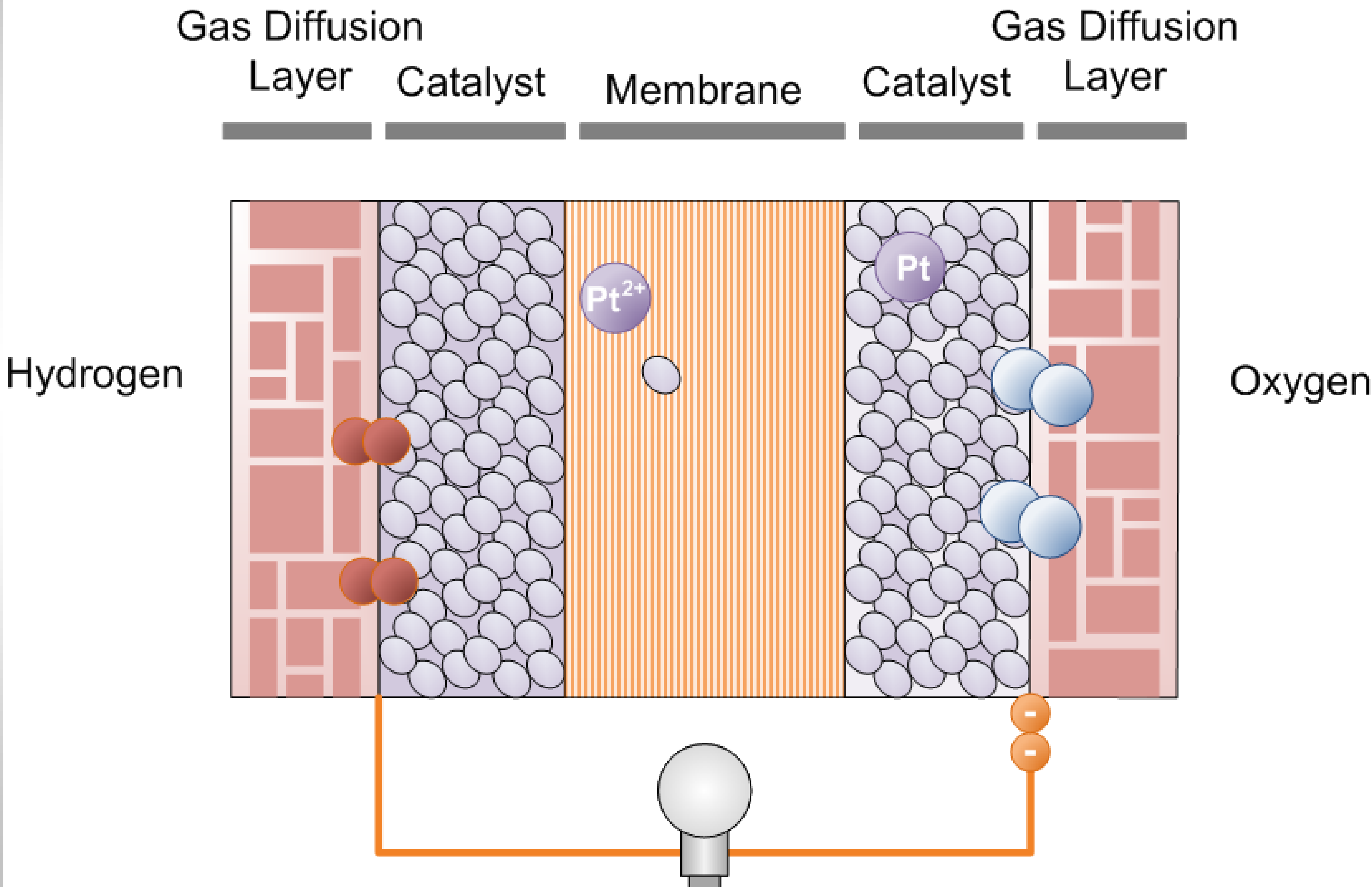

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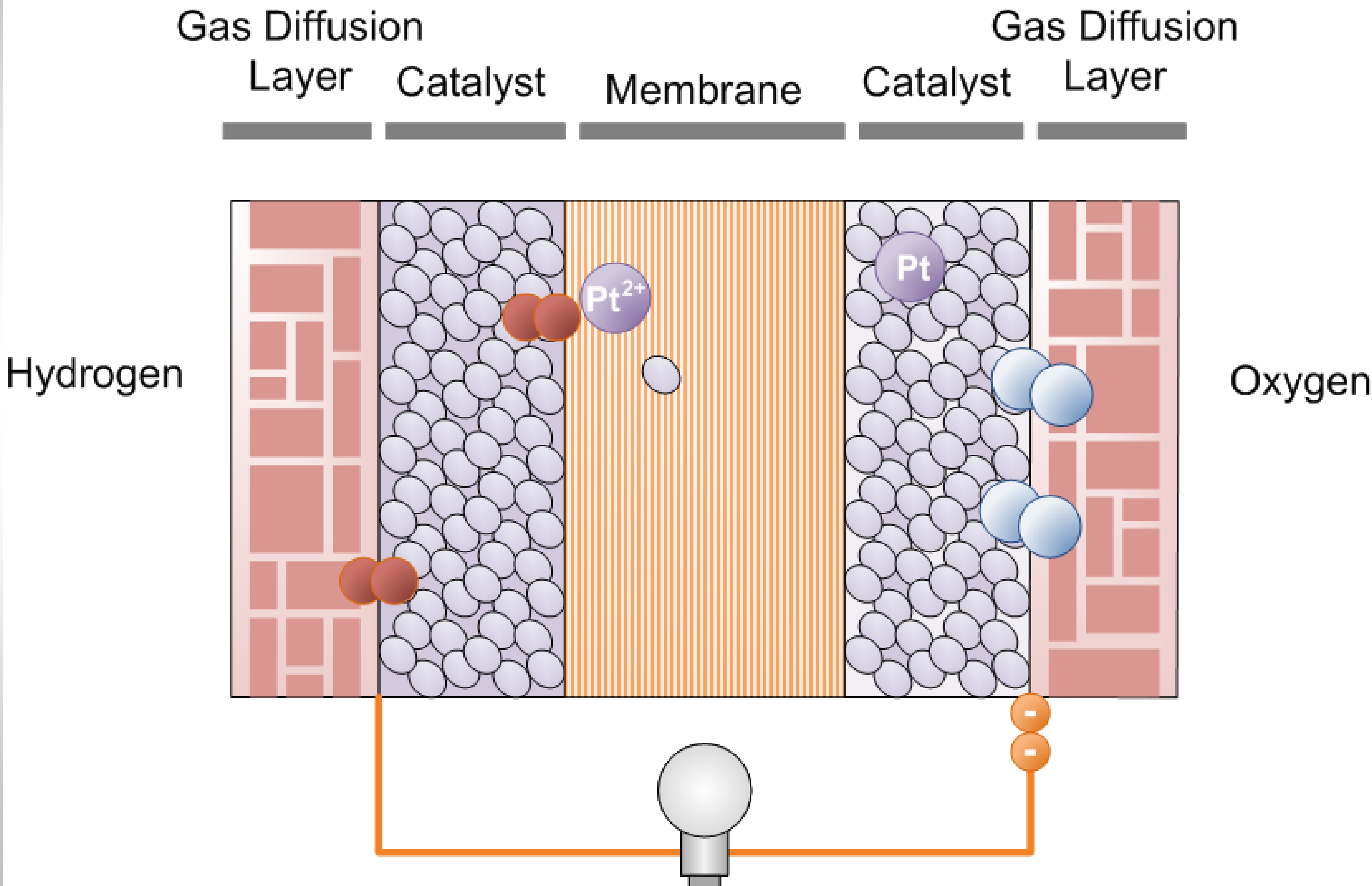

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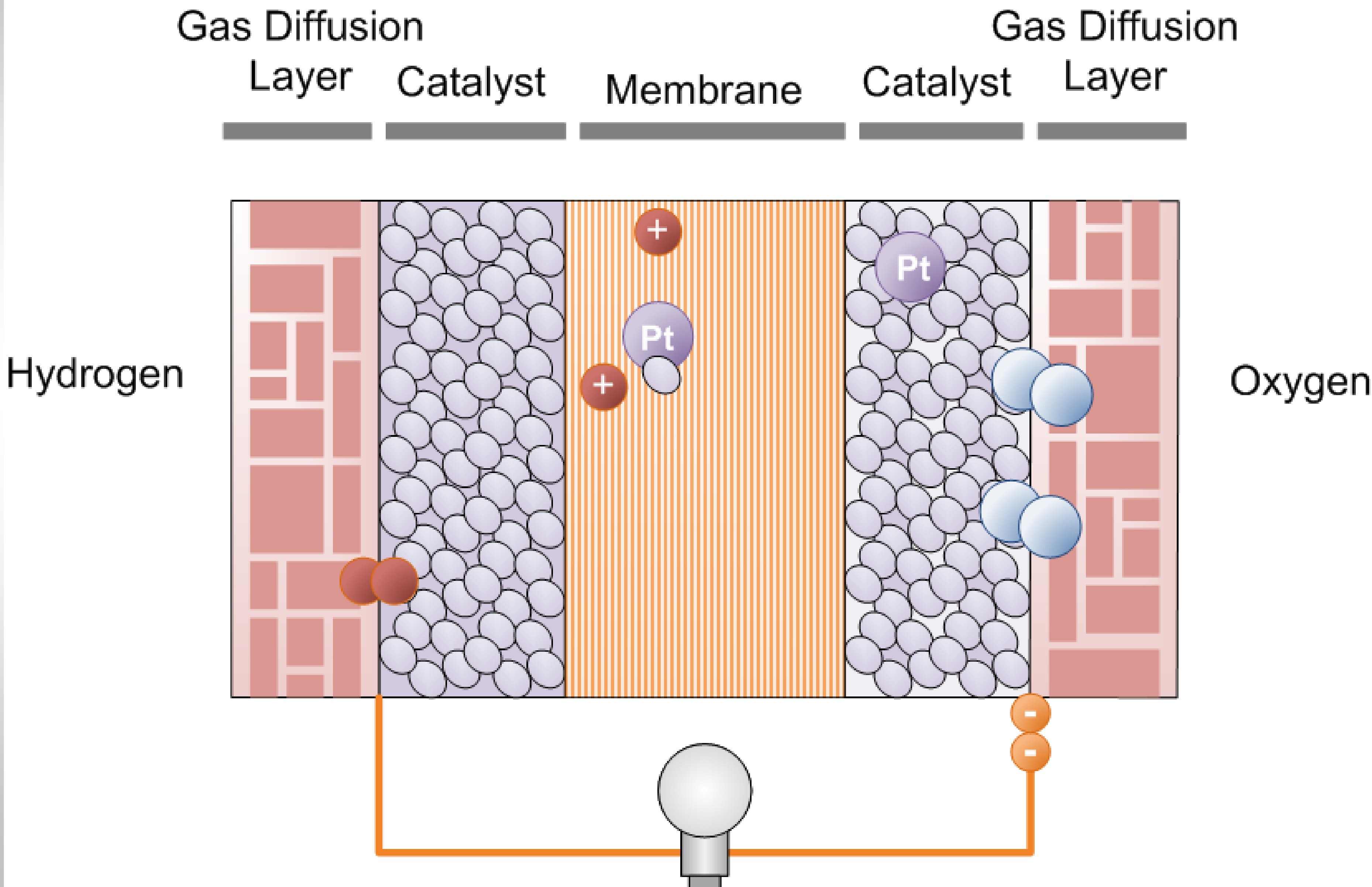

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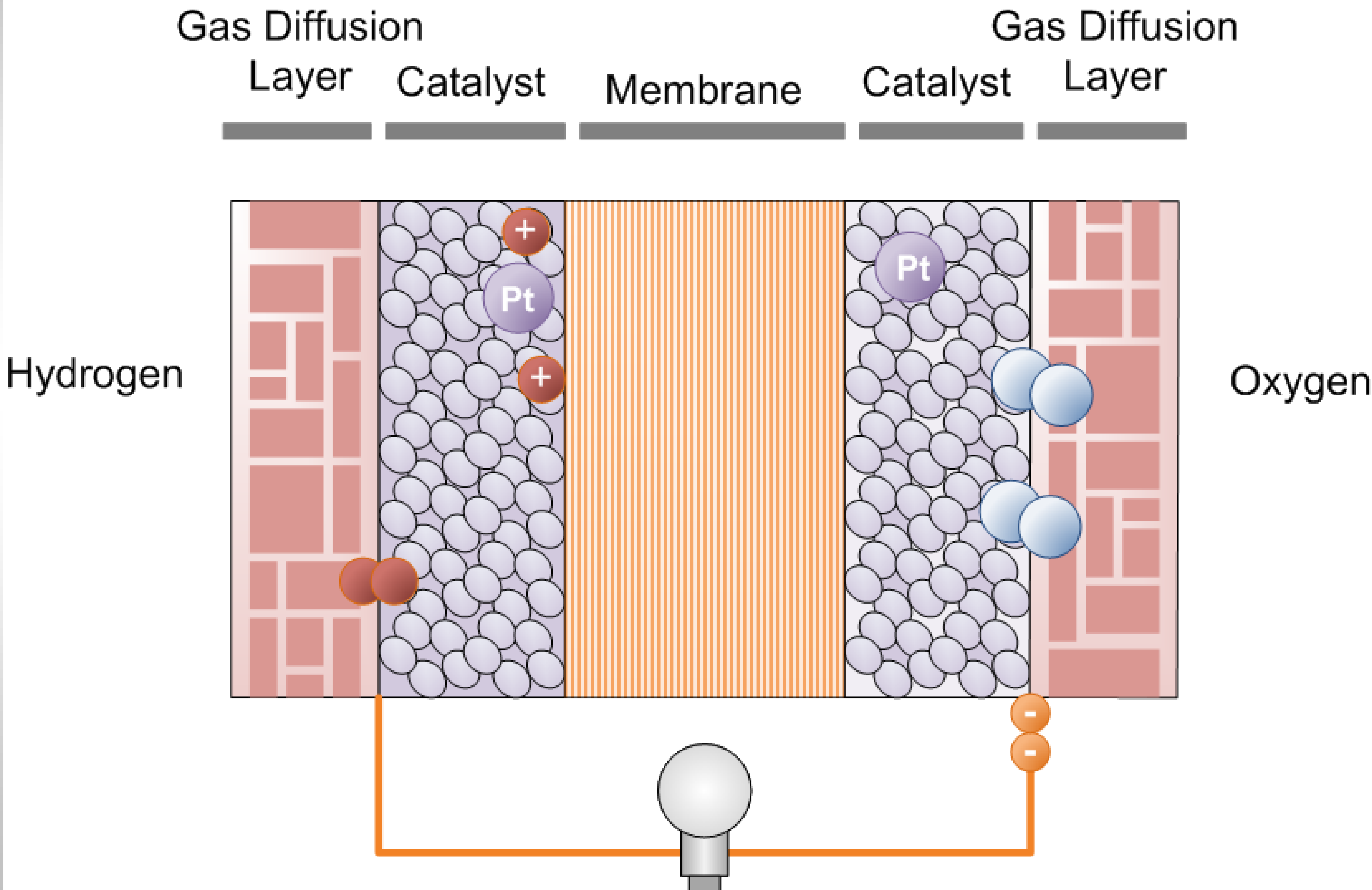

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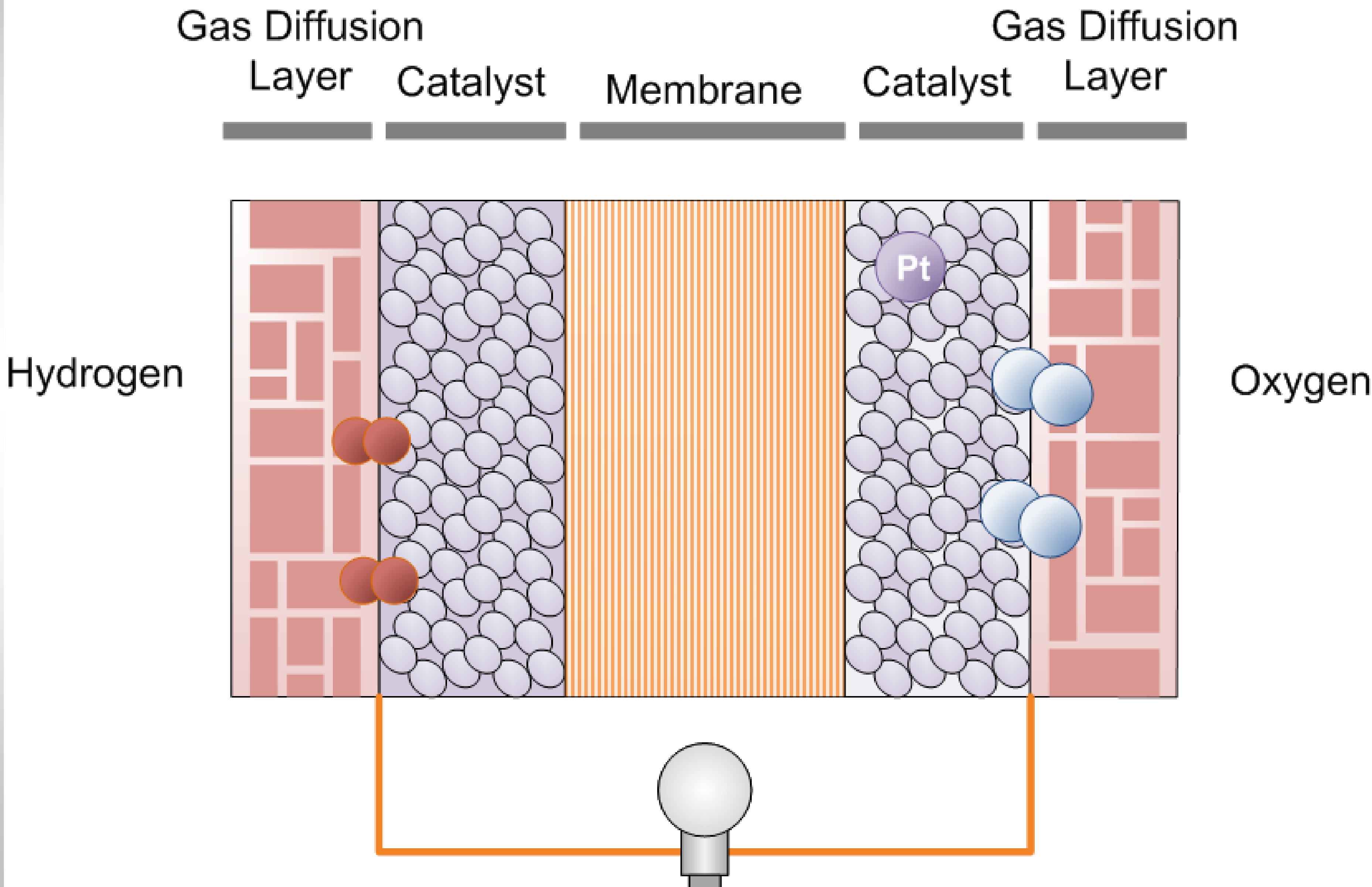
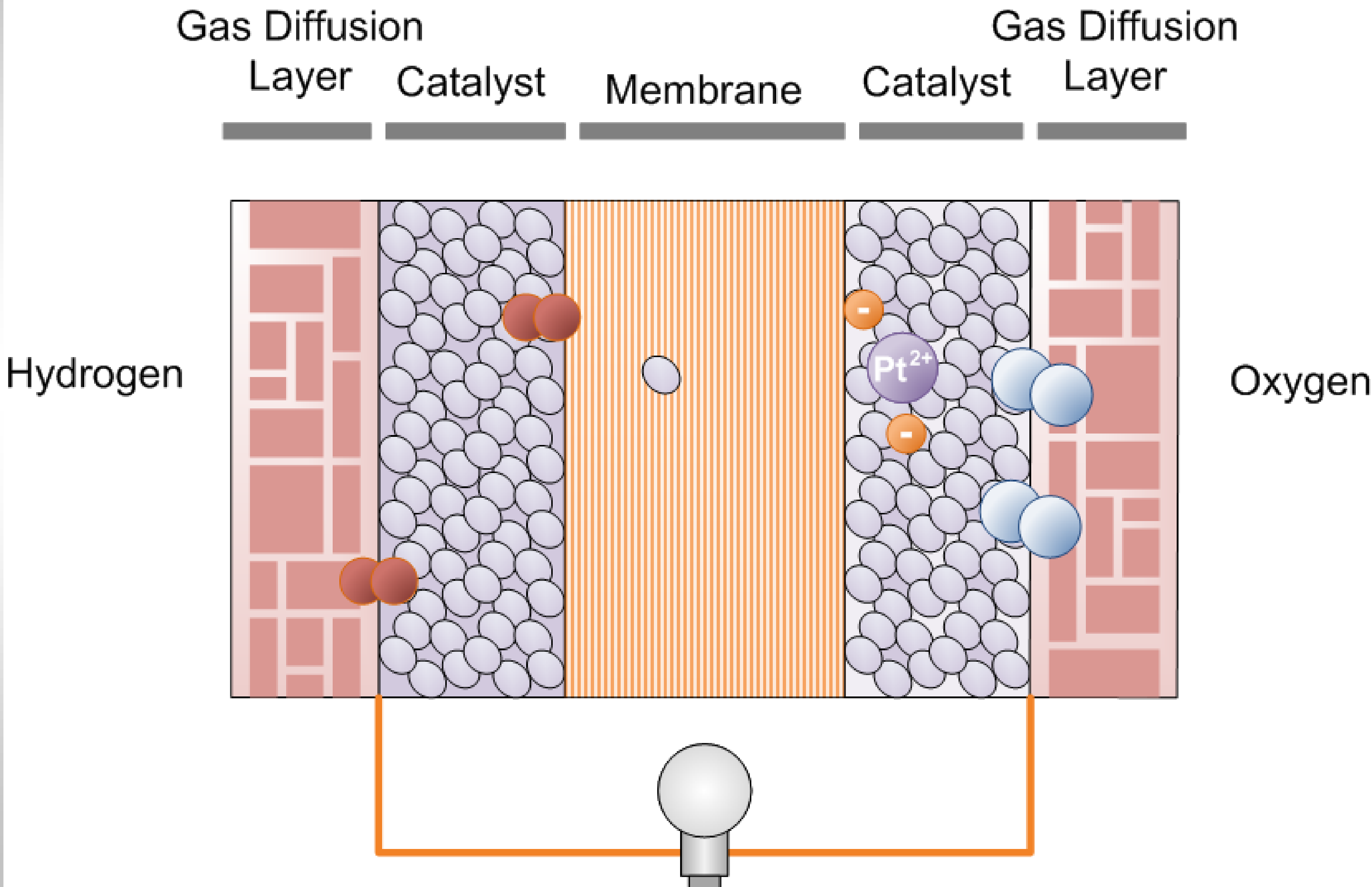


Platinum Dissolution – Cathode



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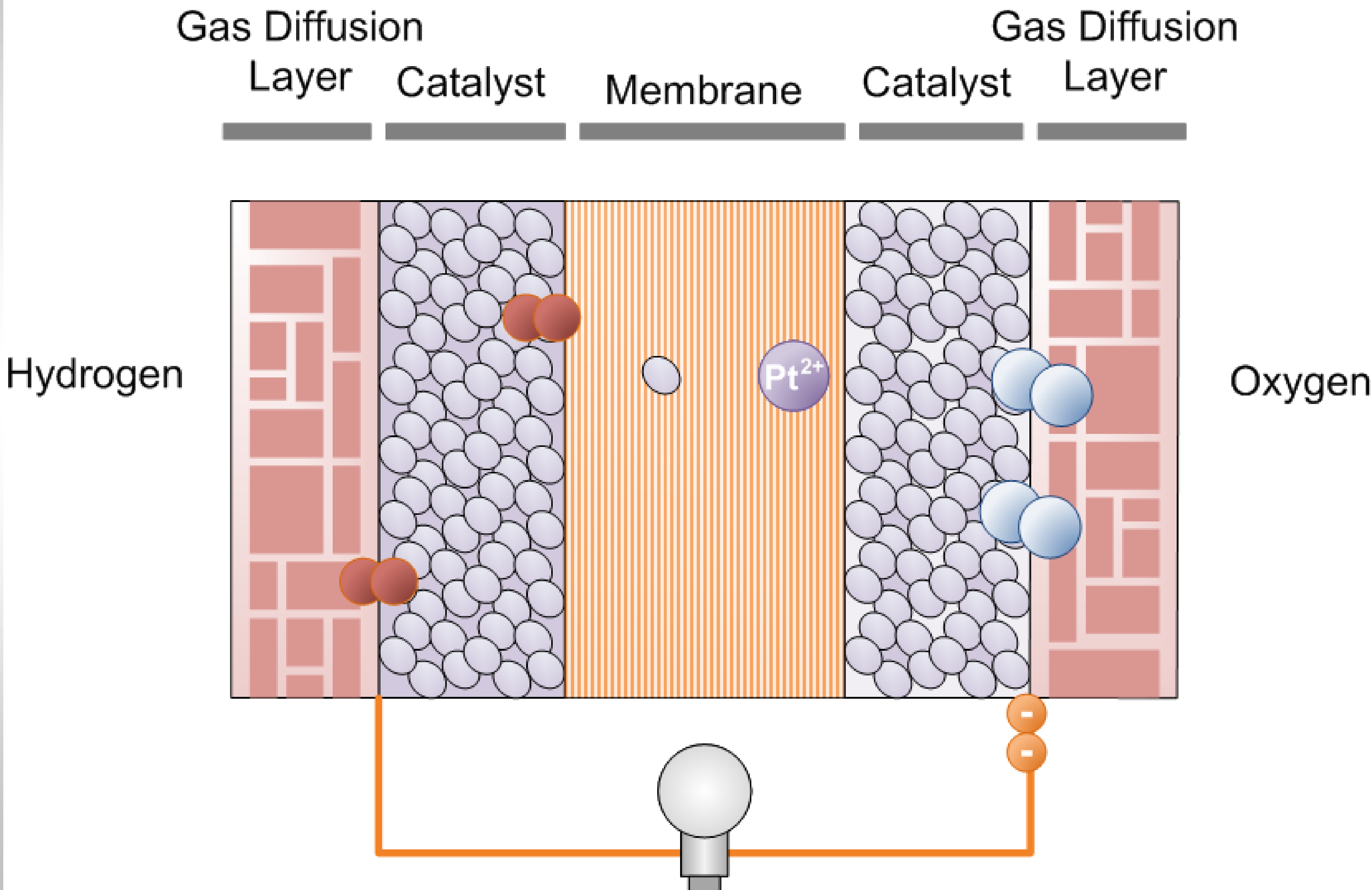

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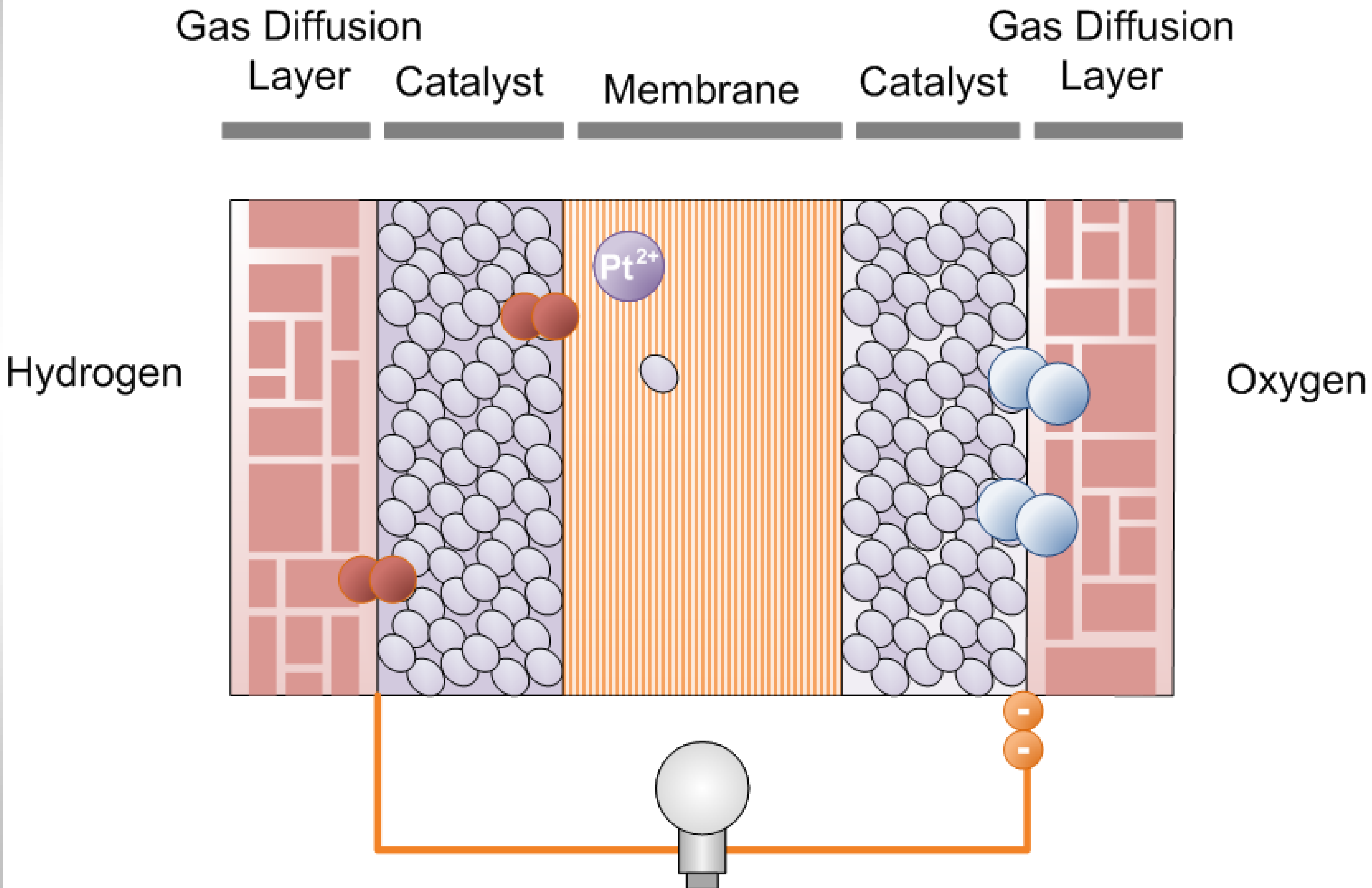

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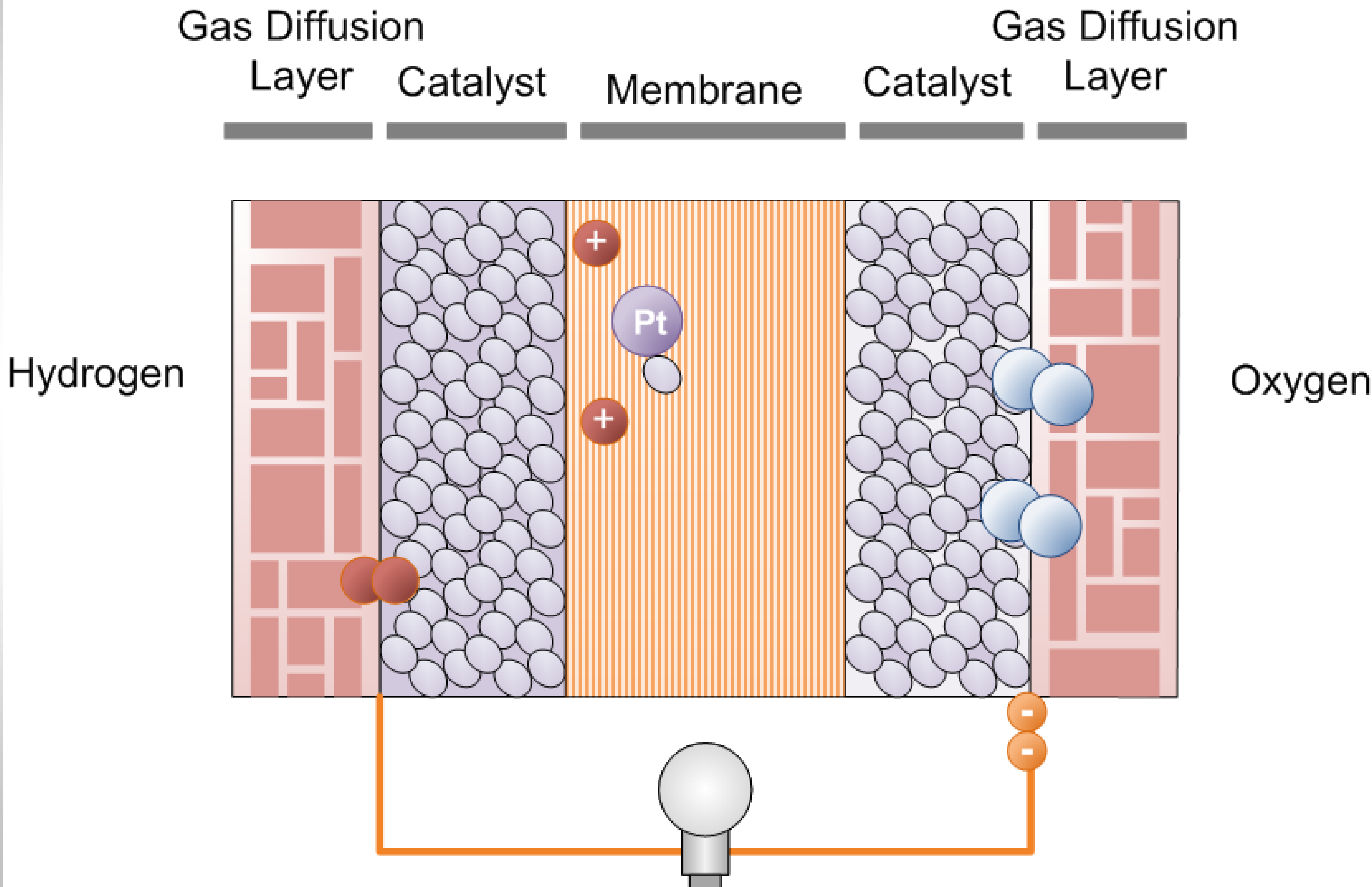


Kinetics of Catalyst Degradation

- Rate of Platinum dissolution using Butler-Volmer equations [Darling & Meyers, 2003], [Bi & Fuller, 2008]:

$$r_{\mathrm{Pt}^{2+}i} = k_{1a} RH_c \theta_{iV} \left[\exp\left\{ \frac{\alpha_{1a} n_1 F (V - U_{1i})}{RT} \right\} - \frac{c_{\mathrm{Pt}^{2+}}}{c_{\mathrm{Pt}^{2+}\ ref}} \exp\left\{ \frac{-\alpha_{1c} n_1 F (V - U_{1i})}{RT} \right\} \right]$$

- Rate of Platinum Oxidation [Darling & Meyers, 2003], [Bi & Fuller, 2008]:

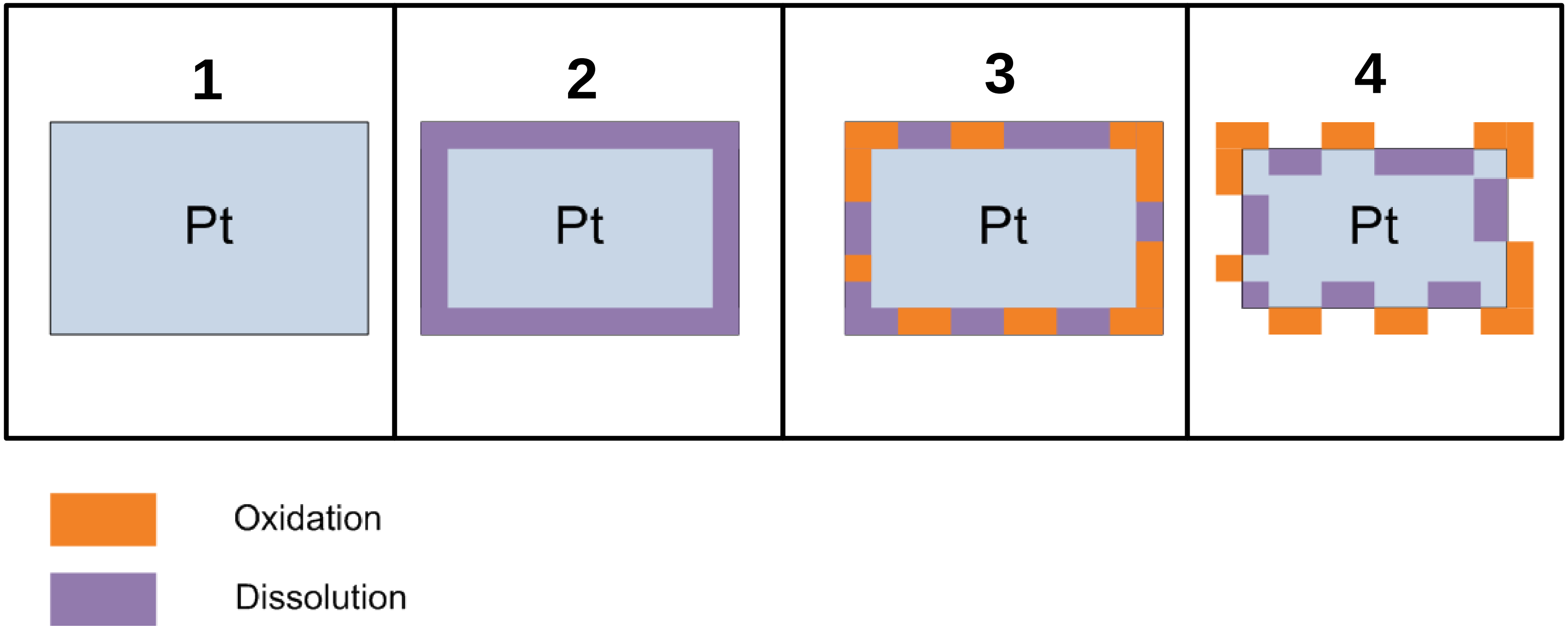
$$r_{\mathrm{PtO}i} = k_{2C} RH_c \theta_i \exp\left\{ \frac{\alpha_{2a} n_2 F (V - U_{2i})}{RT} \right\} - k_{2C} c_{\mathrm{H}+}^2 \theta_i \exp\left\{ \frac{-\alpha_{2c} n_2 F (V - U_{2i})}{RT} \right\}$$

Kinetics of Catalyst Degradation

i is the index of small and large categories of platinum particles.
k_{1a} is the platinum ion (Pt^{2+}) dissolution constant.
RH_a is the relative humidity of the anode.
RH_c is the relative humidity of the cathode.
θ is the oxide coverage of the catalyst surface.
θ_V is the vacant catalyst surface (i.e. not covered by oxide).
α_{1a} is the anodic transfer coefficient.
α_{1c} is the cathodic transfer coefficient.
n_1 is the equivalent number of electrons transferred per mole of Pt^{2+}.
n_2 is the equivalent number of electrons transferred per mole PtO.
F is Faraday's constant.
R is the universal gas constant.
V is the fuel cell operating voltage.
U_{1i} is the adjusted dissolution potential of Pt^{2+} [Darling & Meyer, 2003]
U_{2i} is the adjusted dissolution potential of PtO [Darling & Meyer, 2003]
T is the temperature.
c_{H+} is the relative proton activity.
c_{Pt2+} is the concentration of Pt^{2+}.
$c_{Pt2+\,ref}$ is the reference concentration of Pt^{2+}.

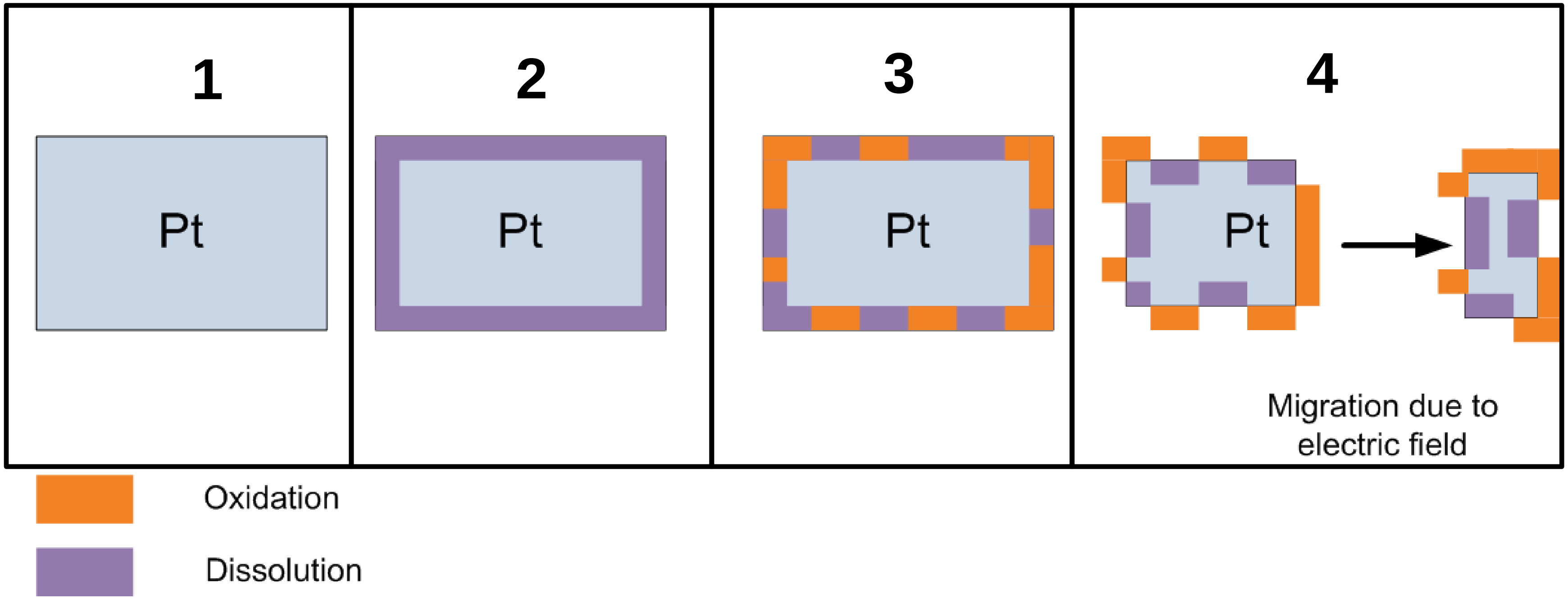
Catalyst Degradation: Current Model

[Bi & Fuller, 2008]

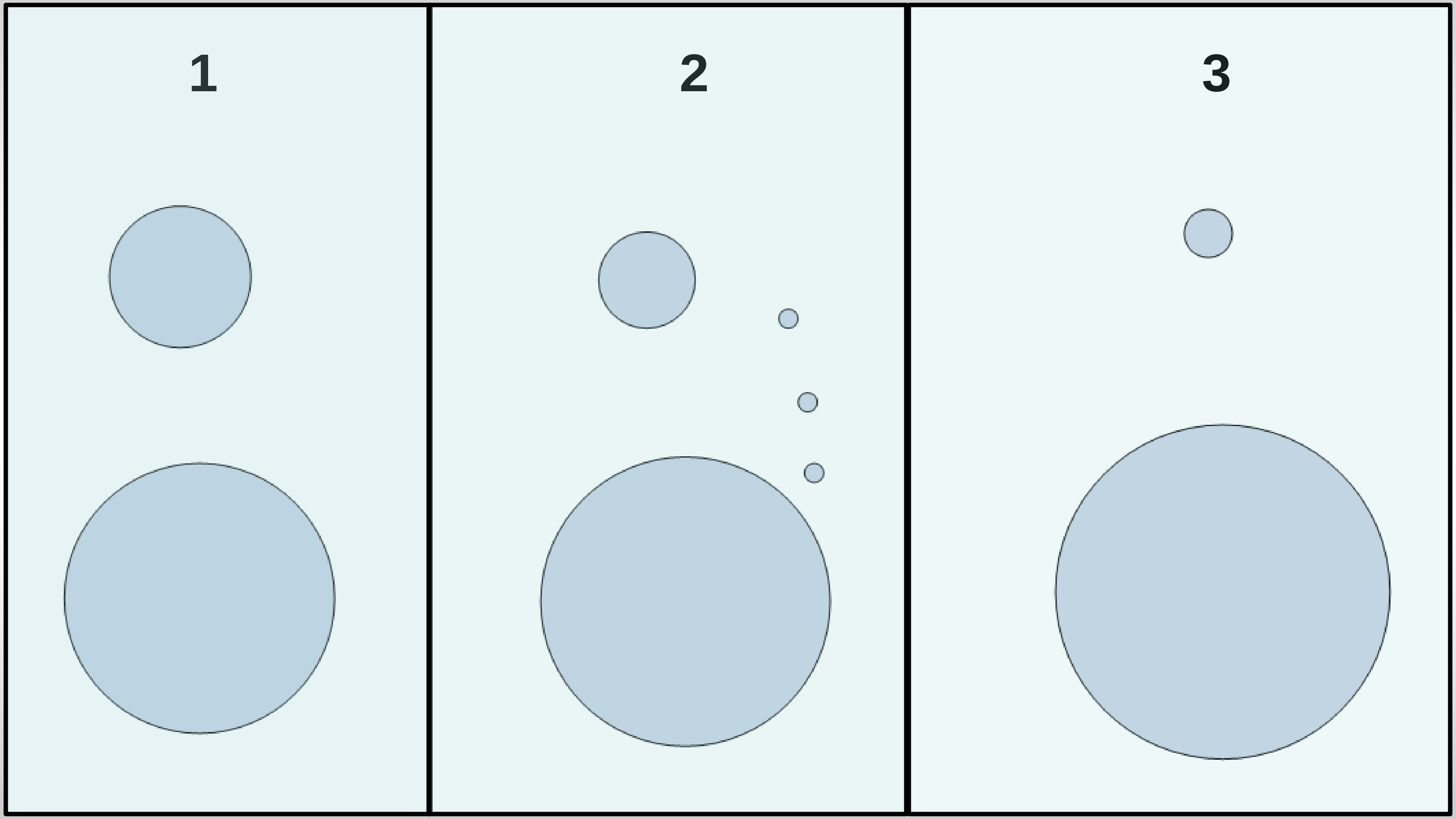


Catalyst Degradation: Current Model

[Thangavelautham & Dubowsky, 2012]



Ostwald Ripening



Effect of Humidity

- Effects of humidity to the kinetic model
- Relates humidity with proton activity:

$$c_{H+} = \frac{1}{\dfrac{EW}{\rho_{Nafion}} + \lambda \dfrac{M_{\mathrm{H_2O}}}{\rho_{\mathrm{H_2O}}}}$$

- Accounts for water content λ [Springer et al., 2008]:

$$\lambda = C_0 + C_1 RH + C_2 RH^2 + C_3 RH^3$$

- Change in Nafion® density with λ [Sethuraman, 2008]:

$$\rho_{Nafion} = \frac{C_4 + C_5 \lambda}{1 + C_6 \lambda}$$

Kinetics of Catalyst Degradation

- Two competing reactions occurring, dissolution and oxidation.
- Dissolution results in breakup of platinum into ions that mix into the water
- Oxidation results in film of platinum oxide forming over the platinum.
- Both reduce electrochemically active surface area.
- Platinum has an affinity to both the oxygen molecules and protons
- However oxidation in fact also reduces the effect of dissolution

Kinetics of Catalyst Degradation

- The reactions are dependent on:
- Operating Voltage
- Temperature
- Humidity

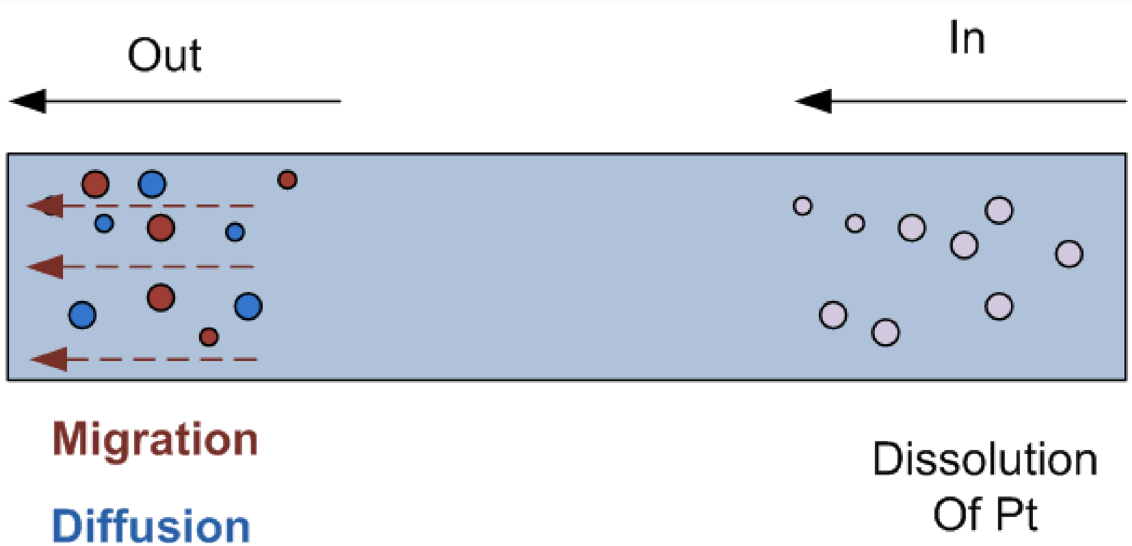
Mass Balance Equation

$$\varepsilon_j \frac{\partial c}{\partial t} = (1 + kd) \cdot D \varepsilon_j^{1.5} \frac{\partial^2 c}{\partial x^2} + \sum_{i=S,L} A_i r_{Pti}$$

Change in Platinum Ion Concentration

Diffusion and Migration Losses

Dissolution of Platinum Ions



Net Mass of Platinum Left

$$M(t) = M(t=0) + A(1+kd)\int_0^t \varepsilon_M D \left.\frac{\partial c}{\partial x}\right|_{x=L} dt$$

Diffusion and Migration Losses

- Total mass of platinum at time *t* is the initial mass minus the mass that diffuses and migrates away.

Migration vs. Dissolution

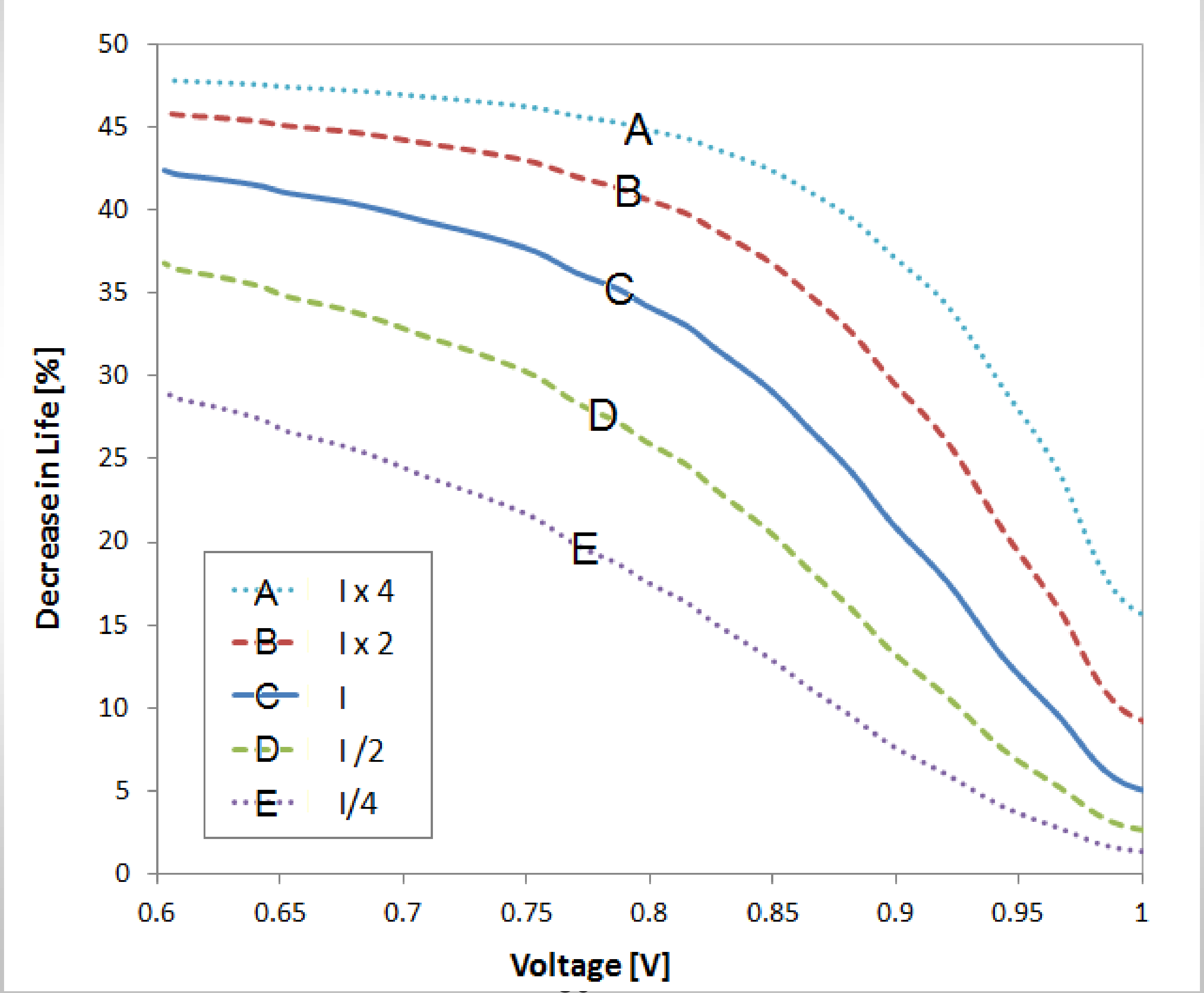
- Migration – movement of particles due to external electric field.
- Importance of migration dependent on primarily on current and but also temperature.

$$k = \frac{N_{migr}}{N_{diff}} \approx \frac{2FiR_{FC}}{RT}$$

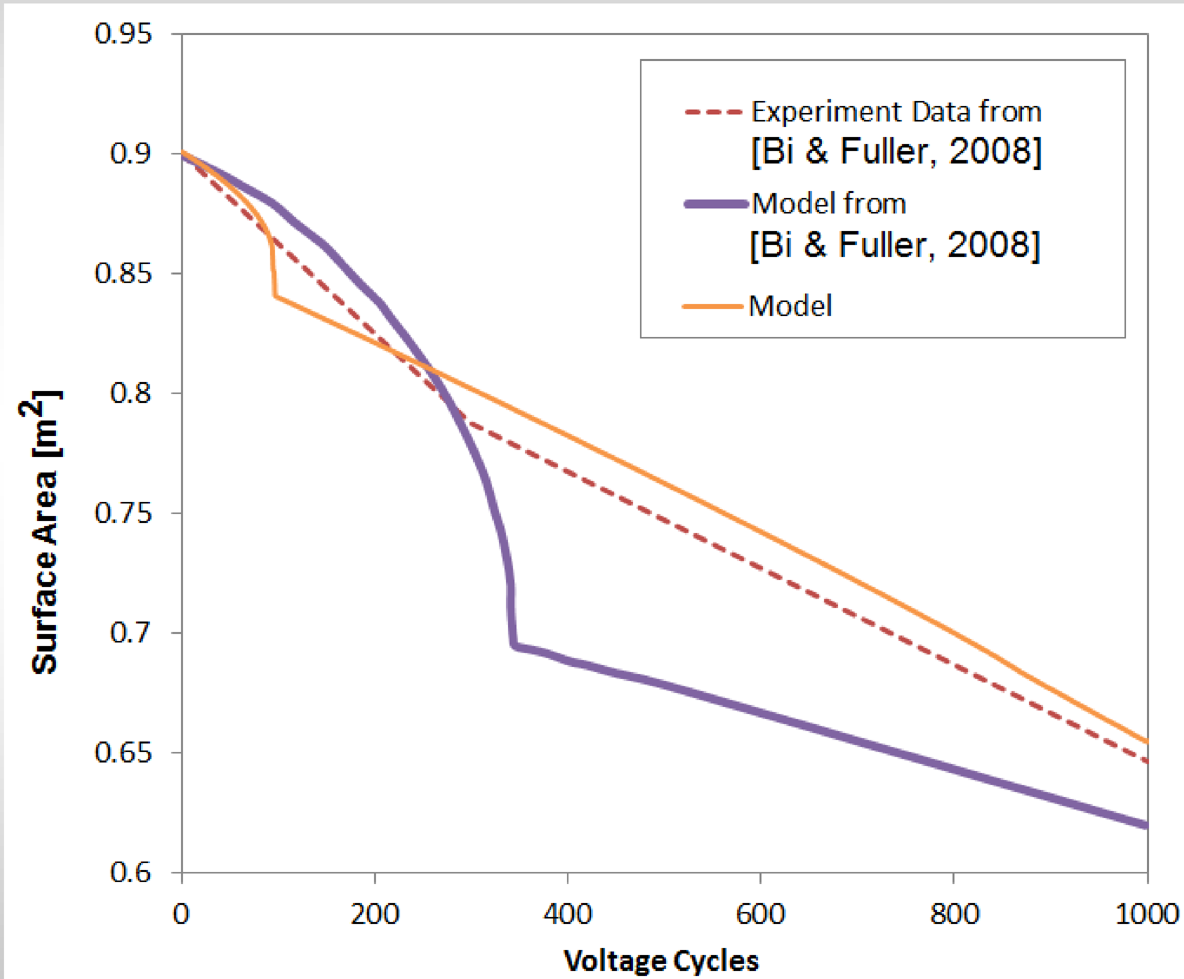
End of Life

- End of life is taken as when the platinum surface area decreases by 25 % of original.
- Rate of area decrease is expected to be linear followed by a non-linear “crash”

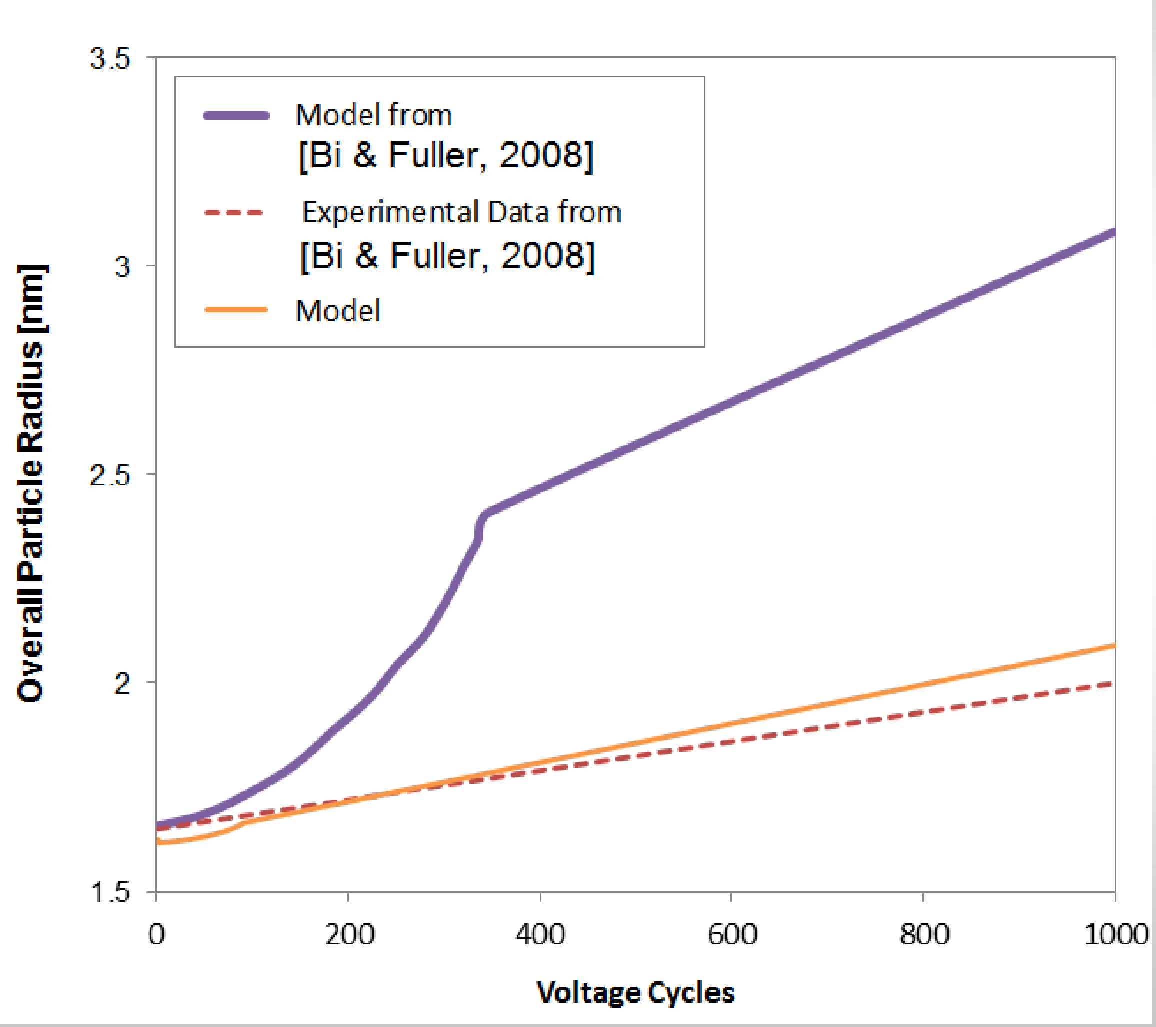
Effect of Migration



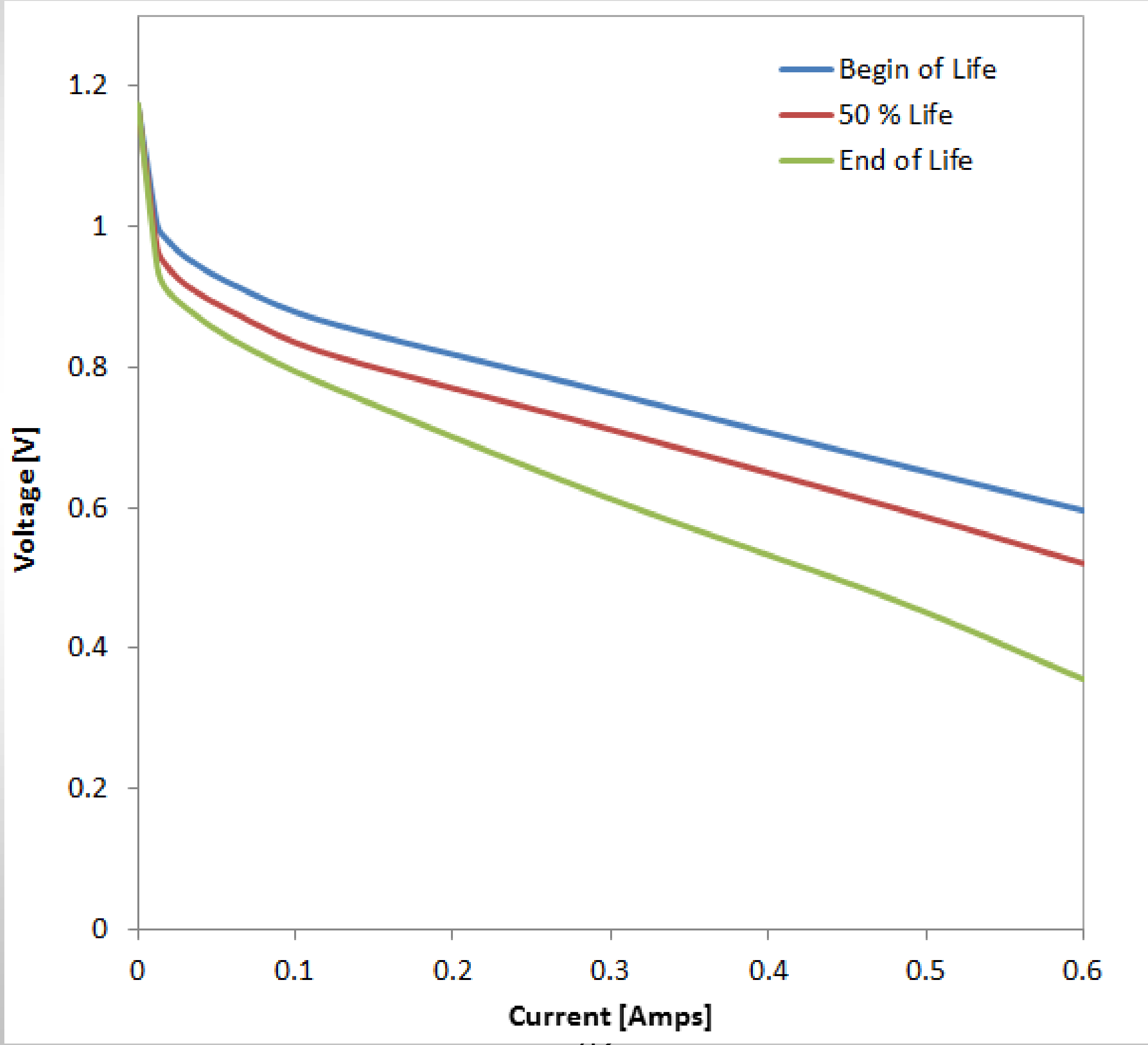
Models vs. Data



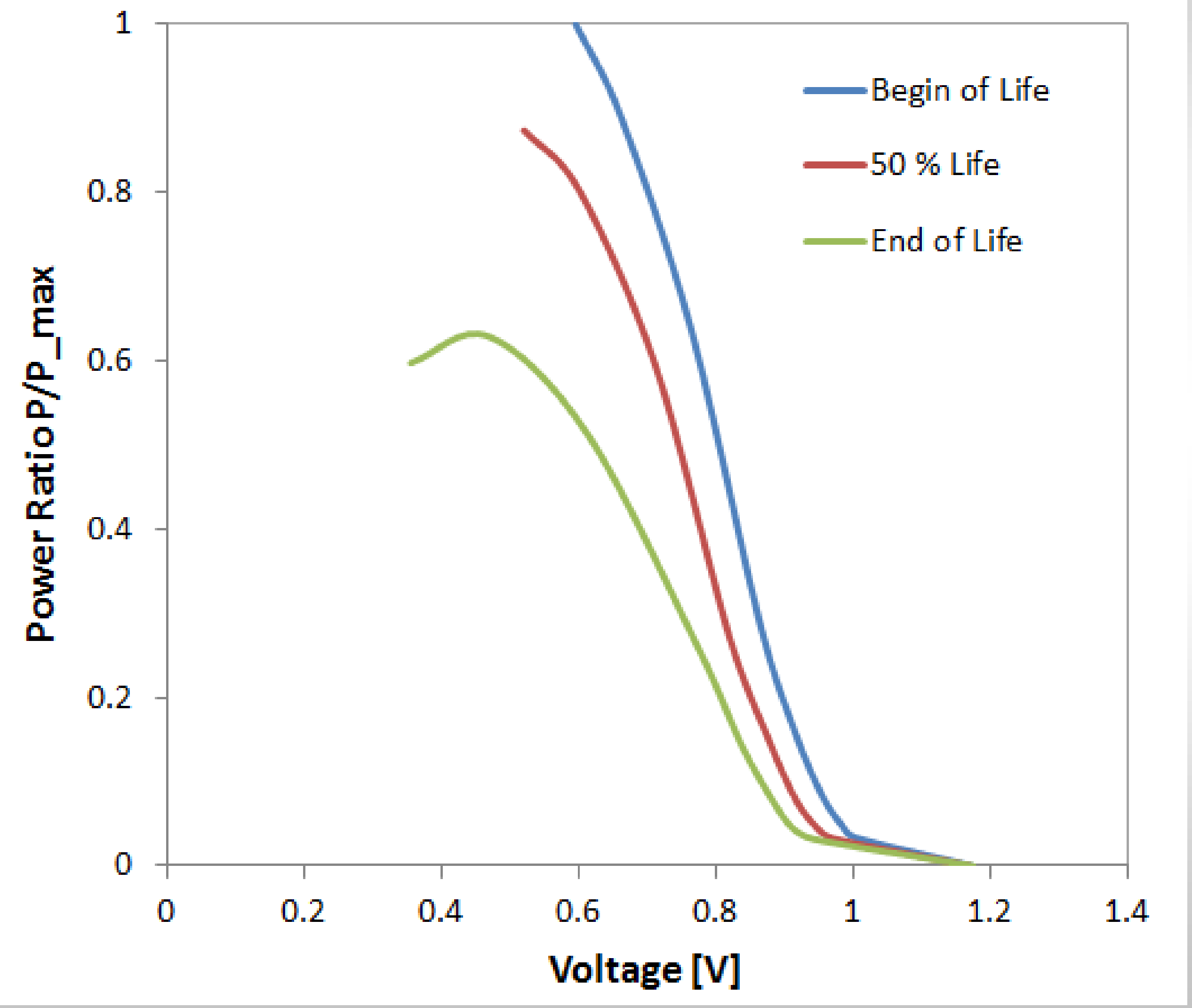
Models vs. Data



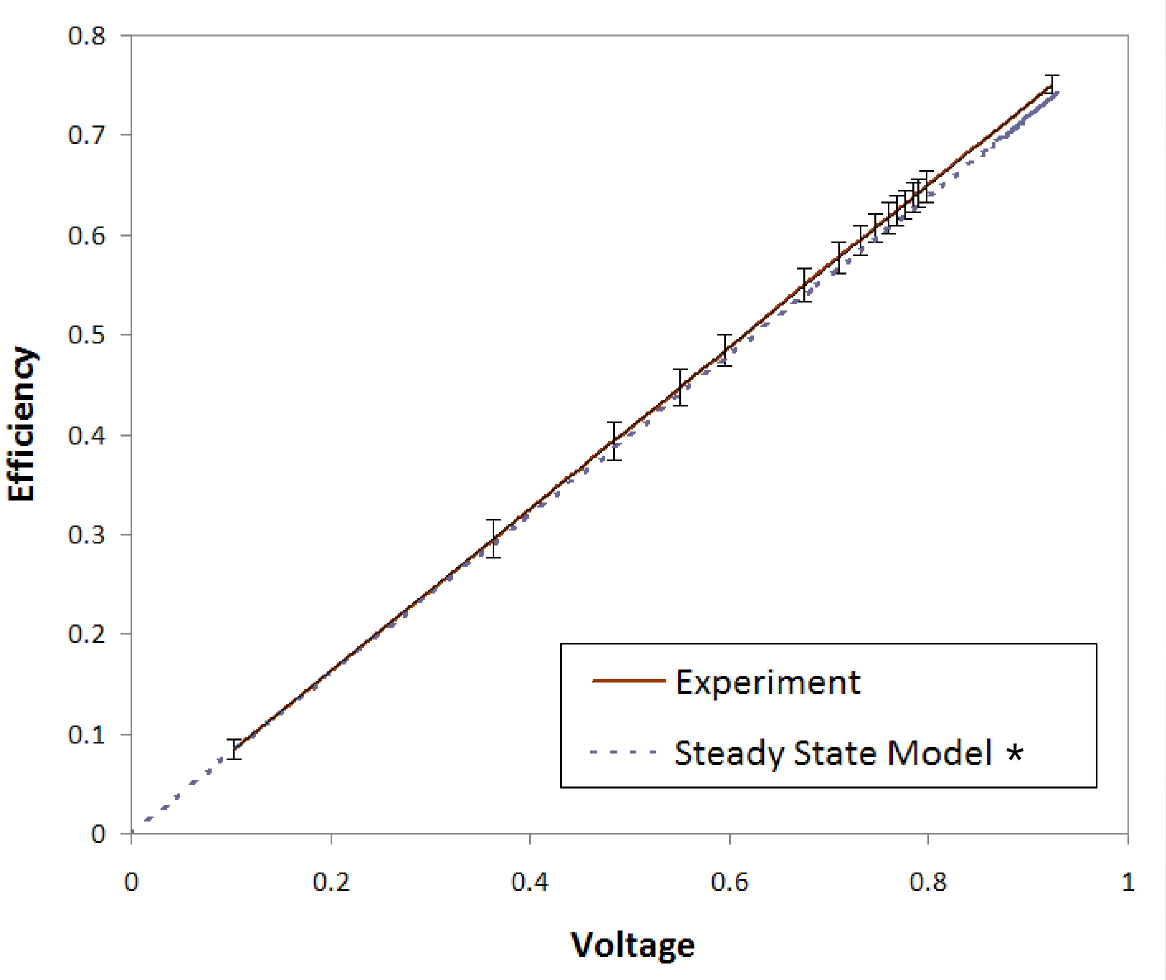
FC Degradation – Polarization Curve



FC Degradation – Power Performance

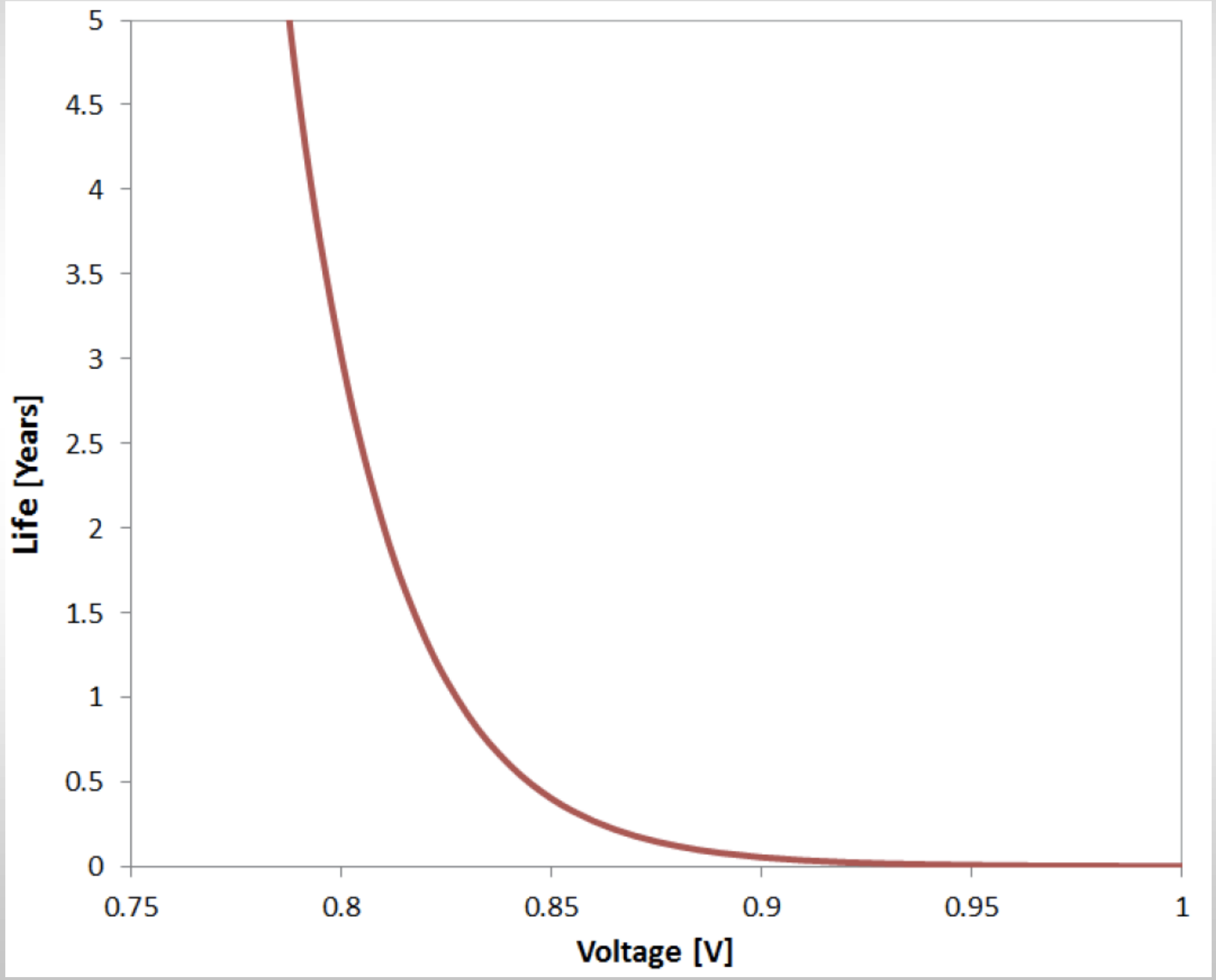


Fuel Cell Efficiency

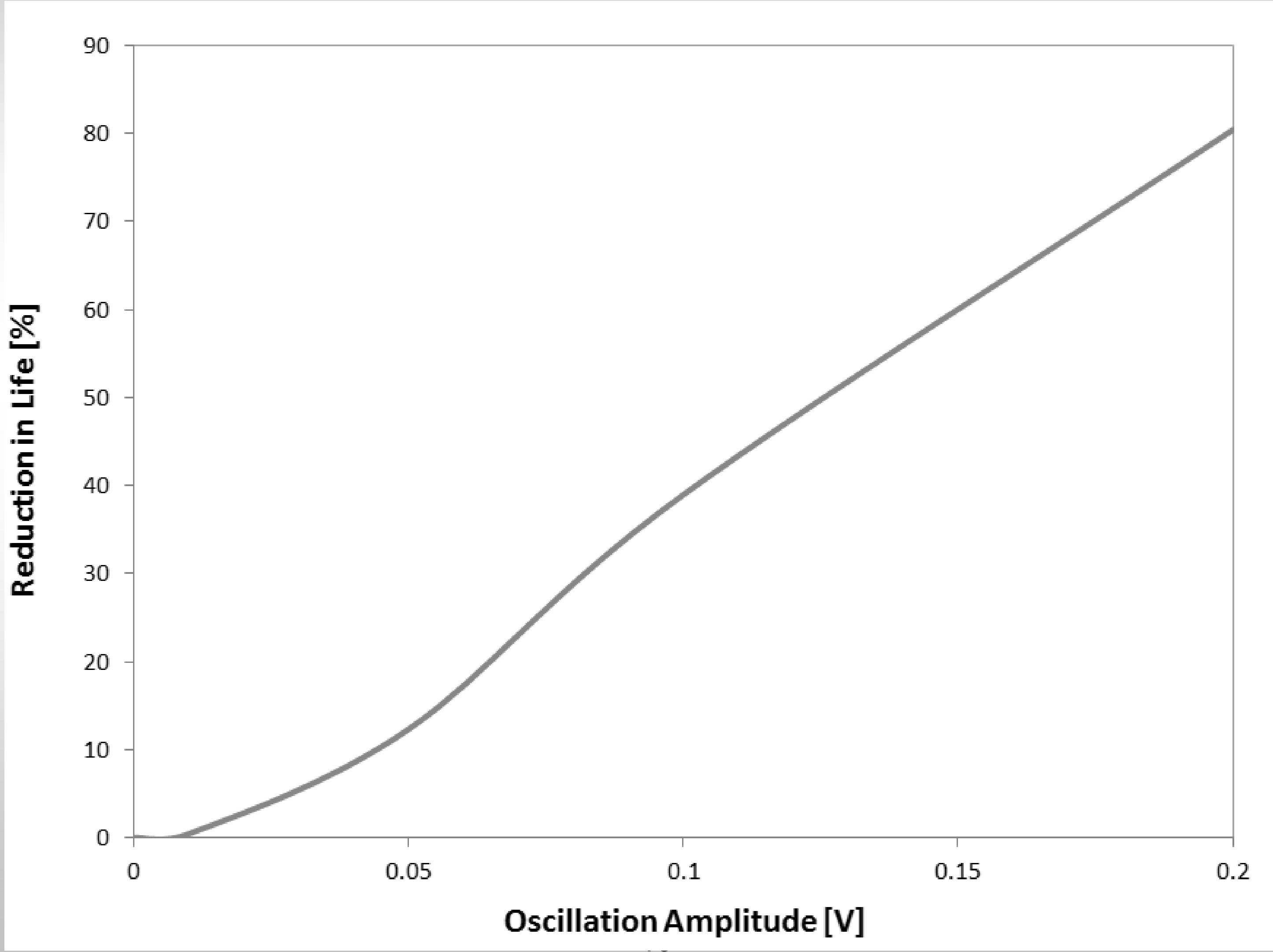


* Manyapu, K., Chapter 3: PEM Fuel Cell Steady State Model SM Thesis, 2010

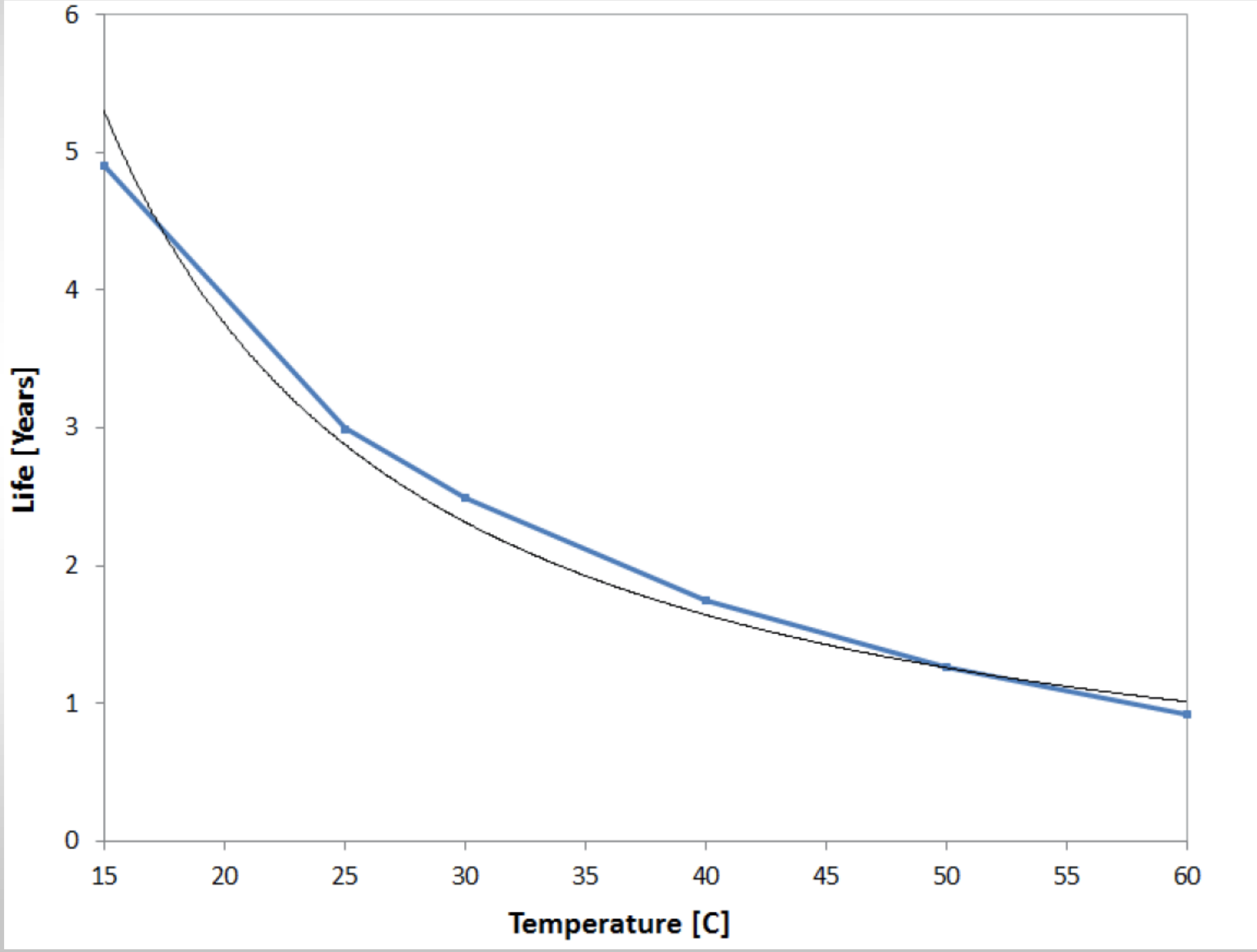
Effect of Voltage on Life



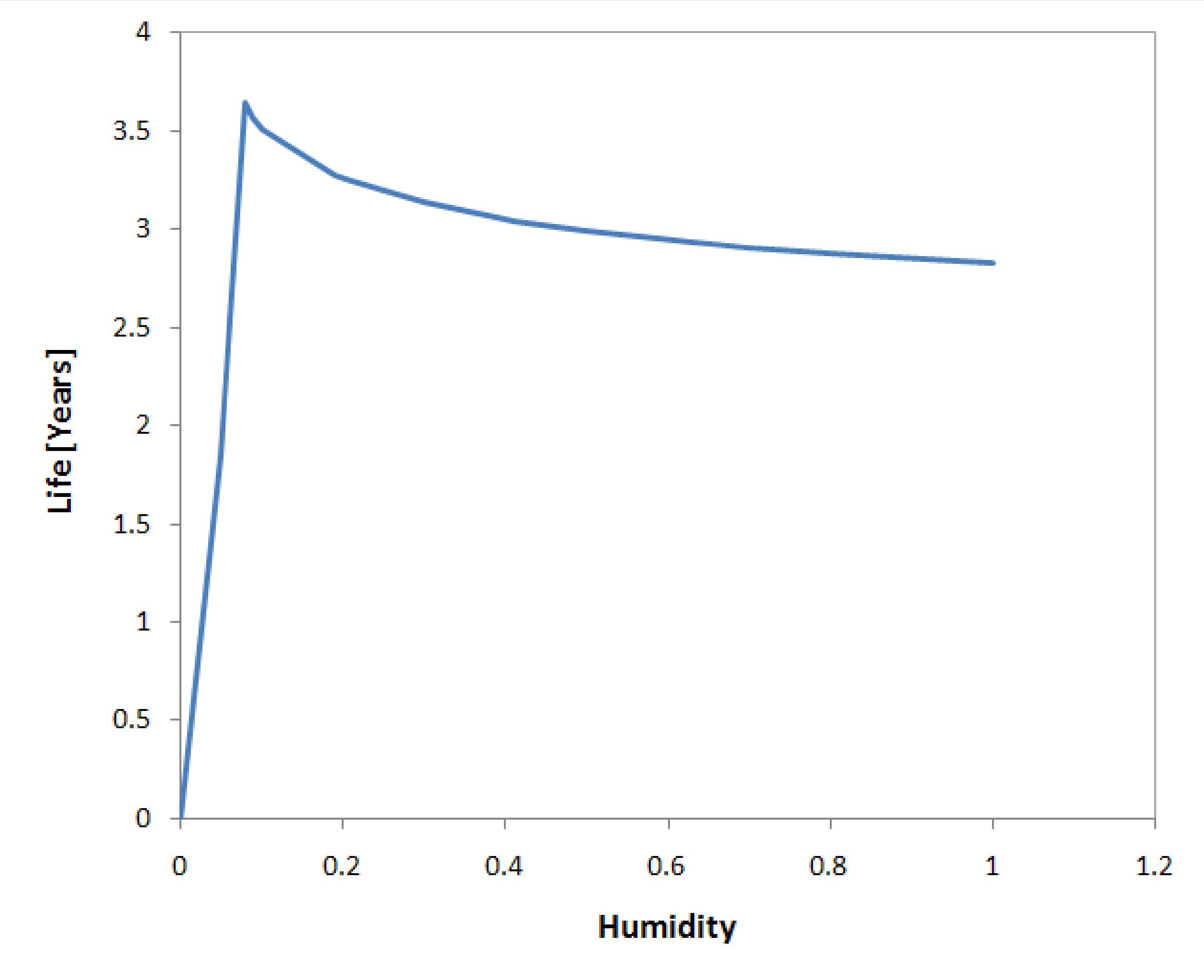
Effect of Voltage Oscillation



Effect of Temperature on Life



Effect of Relative Humidity



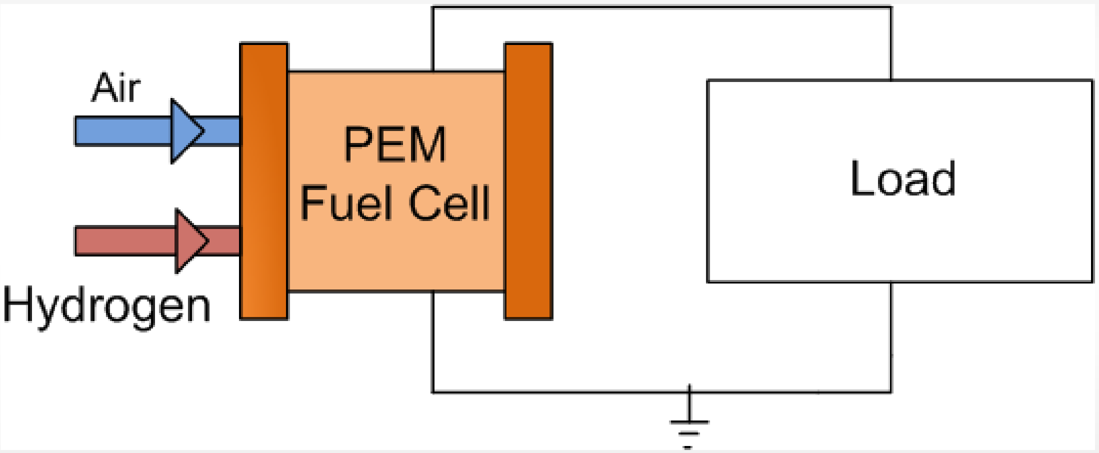
Kinetic Model: Conclusions

- Avg. degradation rate under ideal conditions between 1-9 μV/hr
  - Agrees with compiled experimental evidence [Wu et al., 2008]
- Catalyst degradation simulations highlight the severe effects of temperature and operating voltage
- Operating at high voltage increase fuel cell efficiency but drastically shortens life
- Very low humidity also found to shorten life.

The Effects of Degradation on Control

- For the field sensor network, we consider the effect of degradation, when the fuel cell is directly connected to a load
- We also analyze other suitable configurations to connect a fuel cell to a load.
- Point of comparison is expected life.
- End of life is when catalyst surface area decrease 25 % from original.

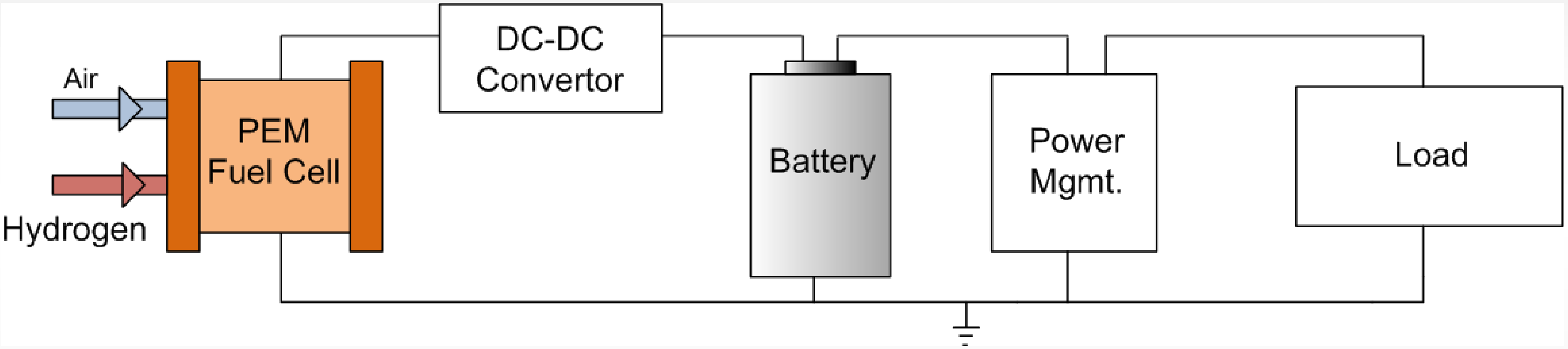
Fuel Cell Power Configuration 1



Feasibility of Degradation Control

Fuel Cell System Configuration	Operating Voltage	Power Output [w]	Fuel Cell Ambient Environment	Life [Months]
Config. 1 Fuel Cell Direct	1.0 – 0.75	0.003 – 0.1	15 – 40 °C, RH 15 – 75 %	**0.5**

Fuel Cell Power Configuration 2



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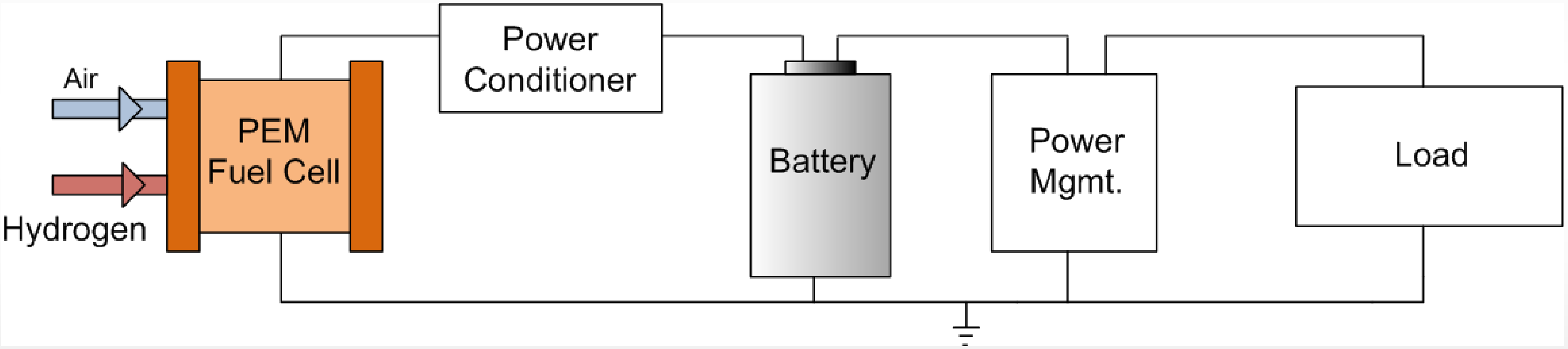
Config. 2 **Fuel Cell Battery Hybrid**	0.8 – 0.9	0.05 avg.	15 – 40 ^{o}C, RH 15 – 75 %	2.0

Fuel Cell Power Configuration 3



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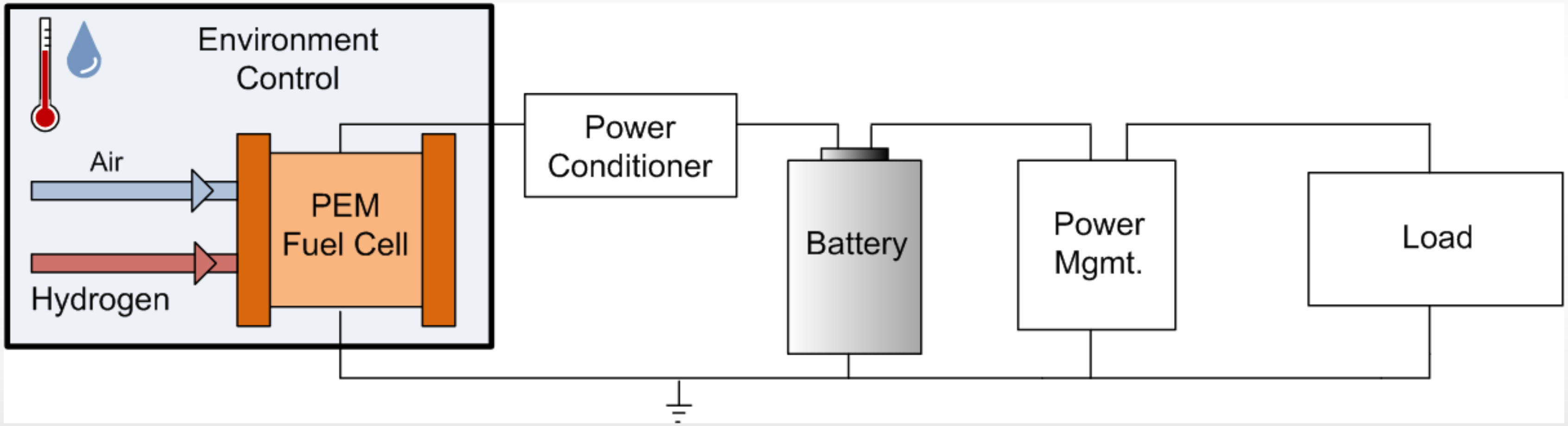
Config. 3 **Fuel Cell Hybrid + Power Conditioning**	0.8	0.05 avg.	15 – 40 ^{o}C, RH 15 – 75 %	**30**

Fuel Cell Power Configuration 4



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Config. 3 **Fuel Cell Hybrid + Power Conditioning**	0.8	0.05 avg.	15 – 40 ^{o}C, RH 15 – 75 %	**30**
Config. 4 **Fuel Cell Hybrid + Power Conditioning + Environment Control**	0.8	0.05 avg.	20 – 25 ^{o}C, RH 30 – 50 %	**40**

Discussion

- Our models shows fuel cells directly connected to typical loads in the field have short lives
  - High Operating Voltage
  - High Temperature
  - Extremely Low/High Humidity
- Use of fuel cells in direct configuration suggest short lives. This reinforces the notion the devices are unreliable.
- The key is to prevent high voltages, off nominal temperatures, humidity and oscillations,

Discussion

- Introducing voltage oscillations using DC-DC convertor is expected not do much better [Gallardo, 2010].
- Hybrid fuel cell-battery combination is a solution that significantly increases life.
  - Requires power conditioning that suppresses any oscillation from the fuel cell.
- Use of environmental control system to control humidity and temperature results in further increase in life

Control of Fuel Cell Degradation

- Catalyst Degradation can be substantially reduced through effective control
- Need to avoid deep cycling/fluctuation of voltage, temperature, humidity to maximize life and
  - Balance conditions to maximize efficiency

Expected Lifetime with Control

Scenario	Efficiency	Voltage	Humidity	Temp.	Life [years]
1	65 %	0.8	0.3-0.5	20-25 ^{o}C	3.3
2	65 %	0.8	0.3-0.5	18-35 ^{o}C	2.8
3	65 %	0.78-0.82	0.3-0.5	18-35 ^{o}C	2.4
4	66 %	0.8-0.82	0.3-0.5	18-35 ^{o}C	1.9

FC Operating Condition for Long Life

- Life: 3+ years
- Anode Pressure: 1.1 Bar
- Cathode Pressure: 1 Bar
- Voltage: $\leq$ 0.8 V ($\leq$ 65 %)
- Temperature: 15 – 40 ^{o}C
- Relative Humidity: 30 – 50 %

- Further increase in life expected if temperature and humidity is held constant within stated range.

Conclusion

- Our fuel cell degradation research suggests that to achieve long life the operating and environmental conditions for the fuel cell must be carefully controlled.

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