Modeling Hydrogen Permeation through a Thin TiO_2 Film Deposited on Pd Using COMSOL Multiphysics

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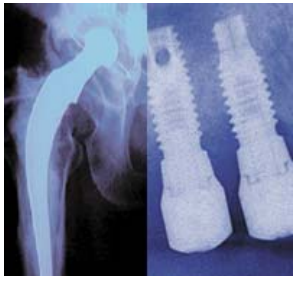
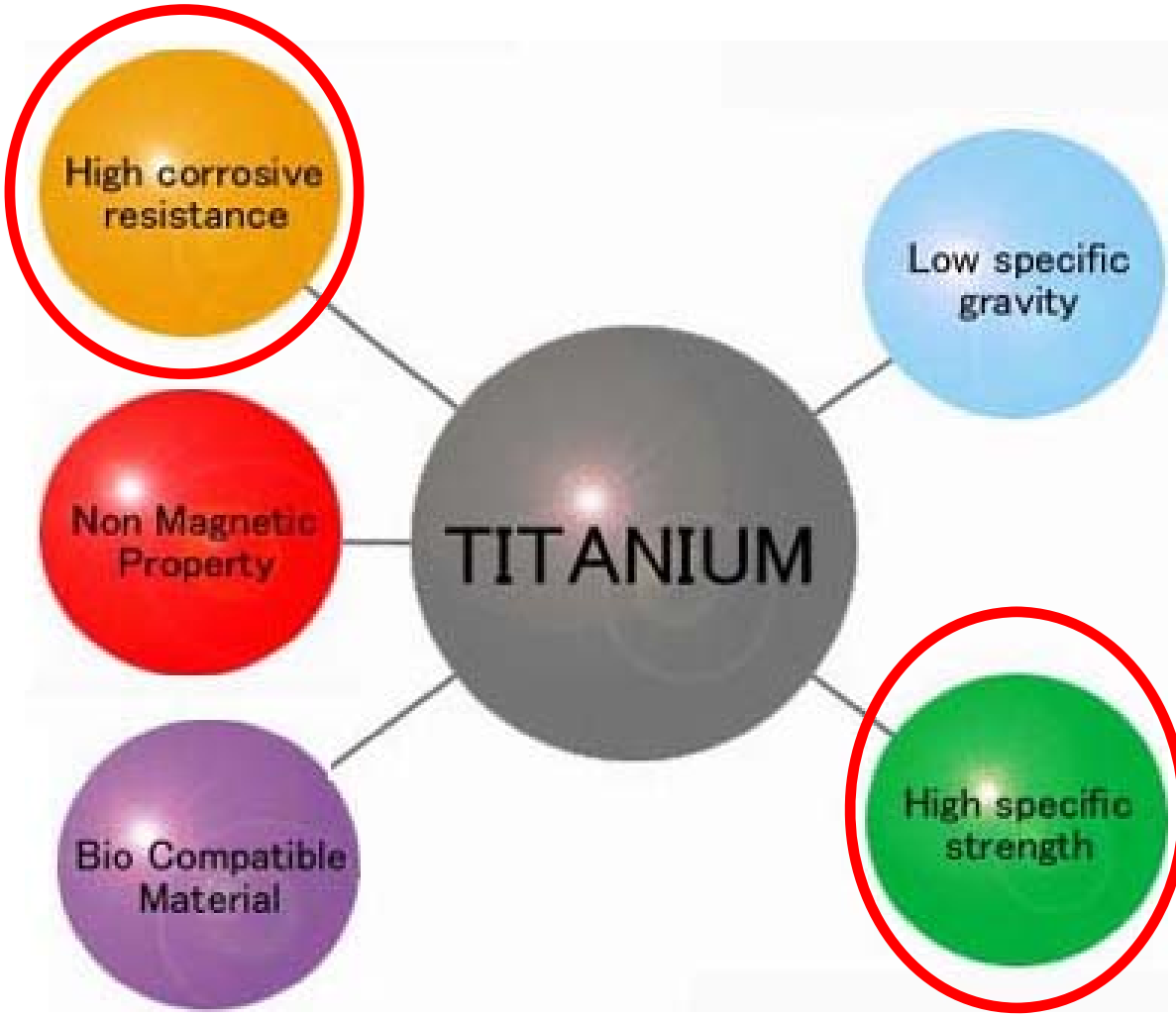
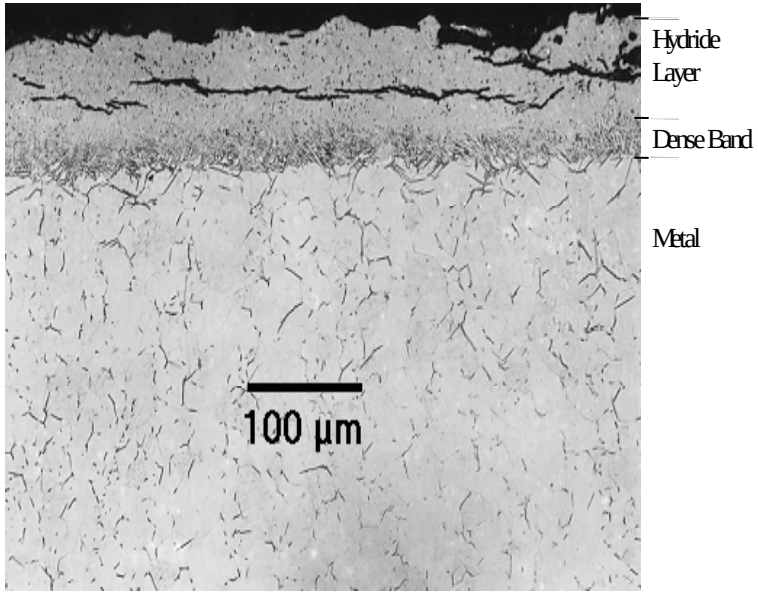
Titanium and Its Alloys



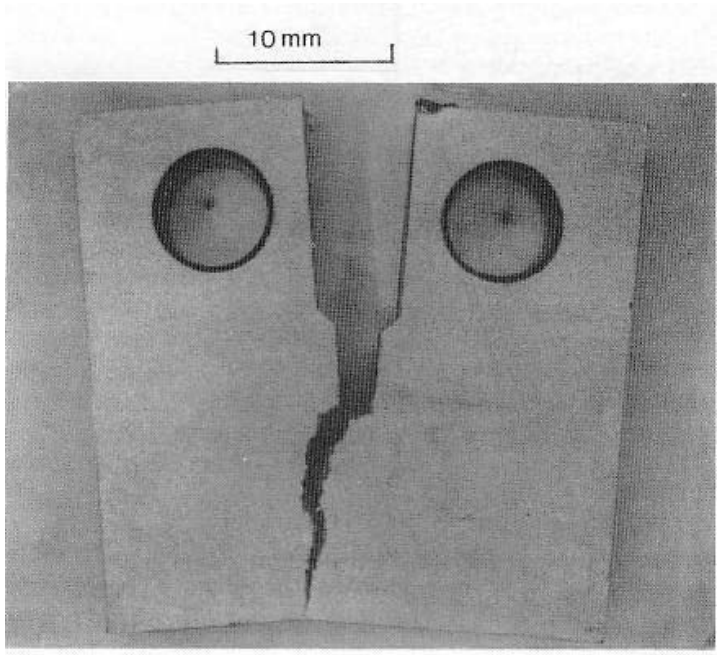


Hydrogen-Induced Cracking (HIC)

- Potentially susceptible to HIC as a consequence of H absorption
- Absorbed hydrogen results in hydride formation and fast crack growth leading to the cracking of Ti and its alloys.



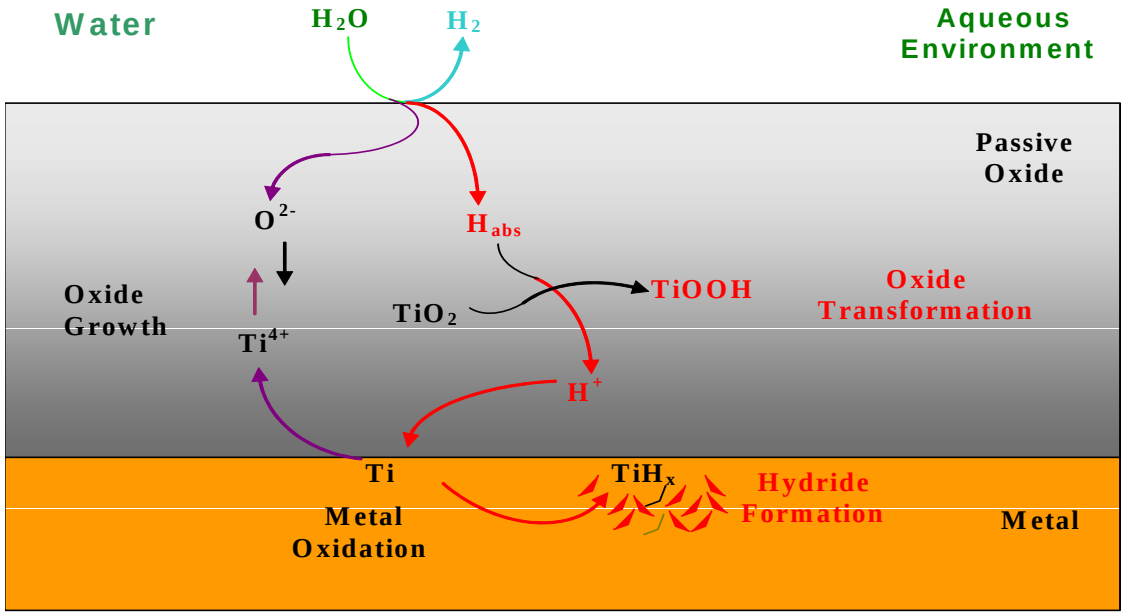
From AECL report 11608



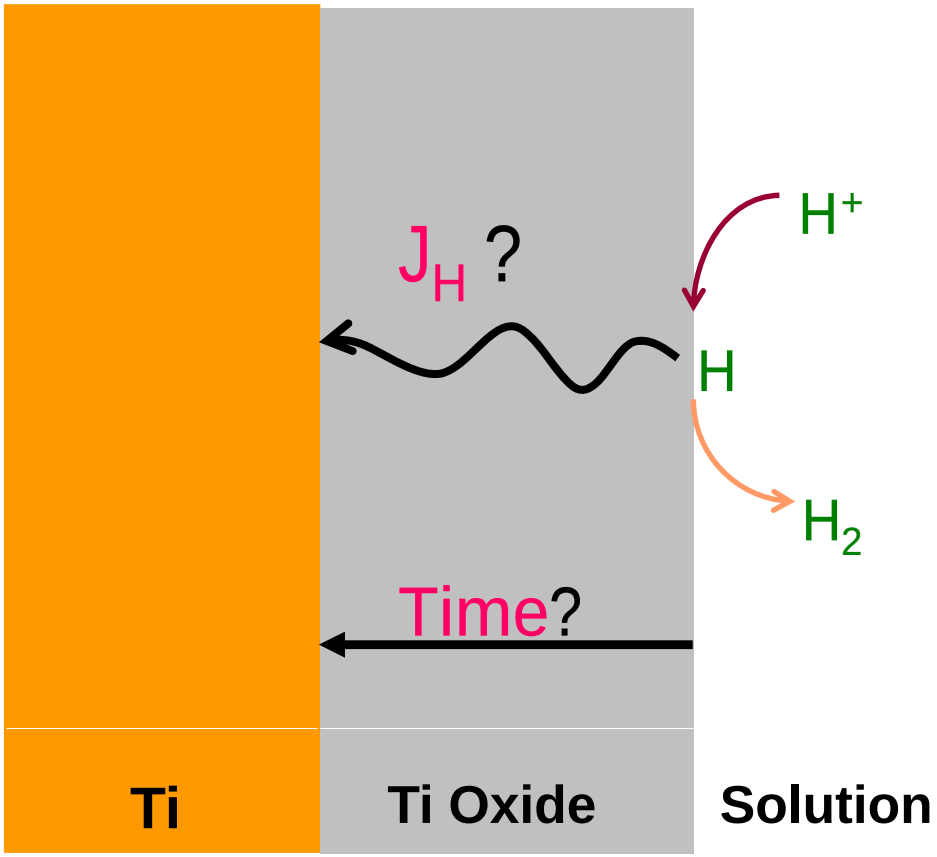
From AECL report 11284

Influence of Oxide Films

- Ti is generally covered by a thin passive oxide (TiO_2) film.
- The impermeability of this film is the limiting feature preventing HIC in Ti-alloys.
- The mechanism by which TiO_2 influences H permeation is complicated and still not well established.



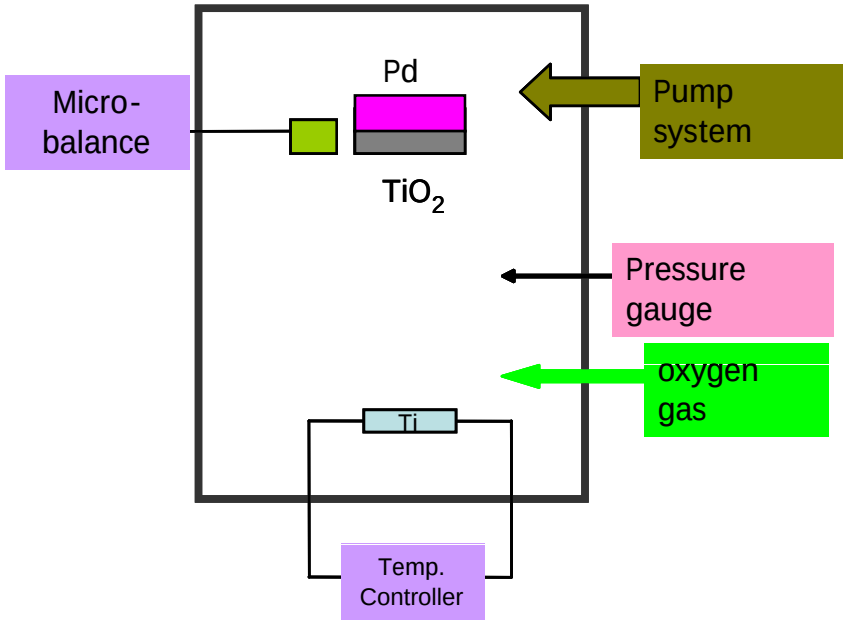
Critical Questions

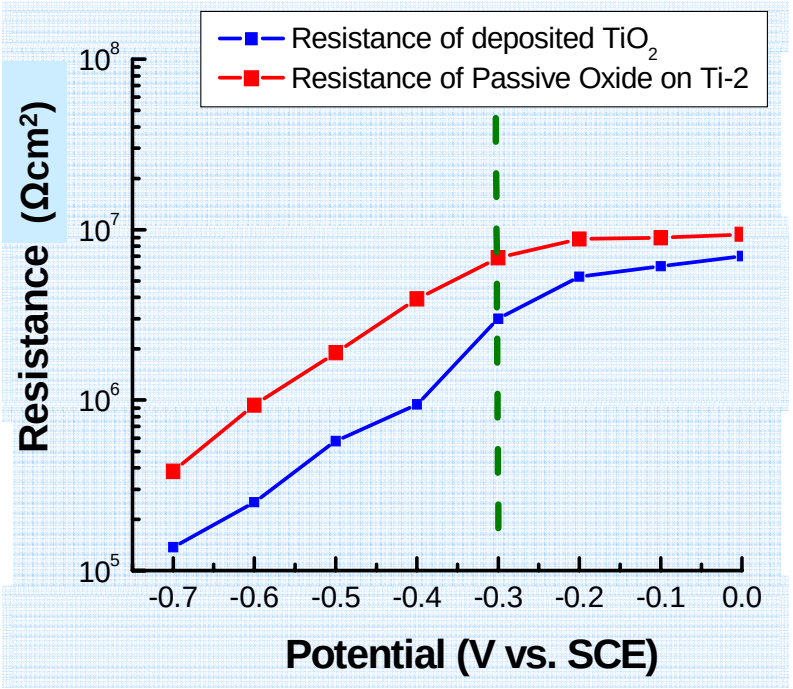


- Can hydrogen permeate the oxide film?
- How much the hydrogen entering the oxide can reach the underlying metal?
- How long does it take for the absorbed hydrogen to permeate through the oxide?

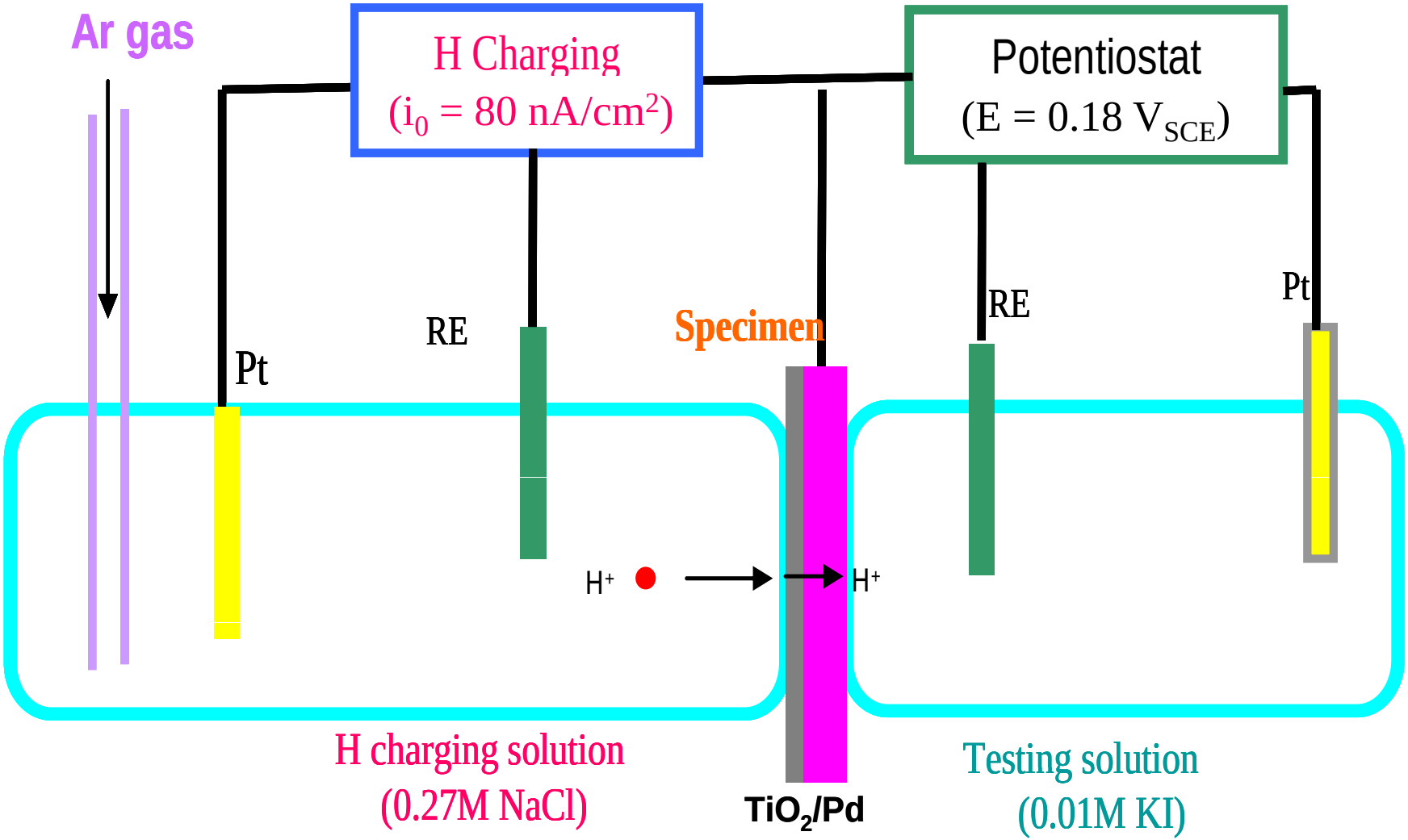
TiO_2 Deposited on Pd

- Due to complications caused by formation of hydrides in Ti metal, a thin TiO_2 film deposited on a Pd foil was used.
- Pd was selected because of its high hydrogen solubility and rapid kinetics for hydrogen absorption and transport.

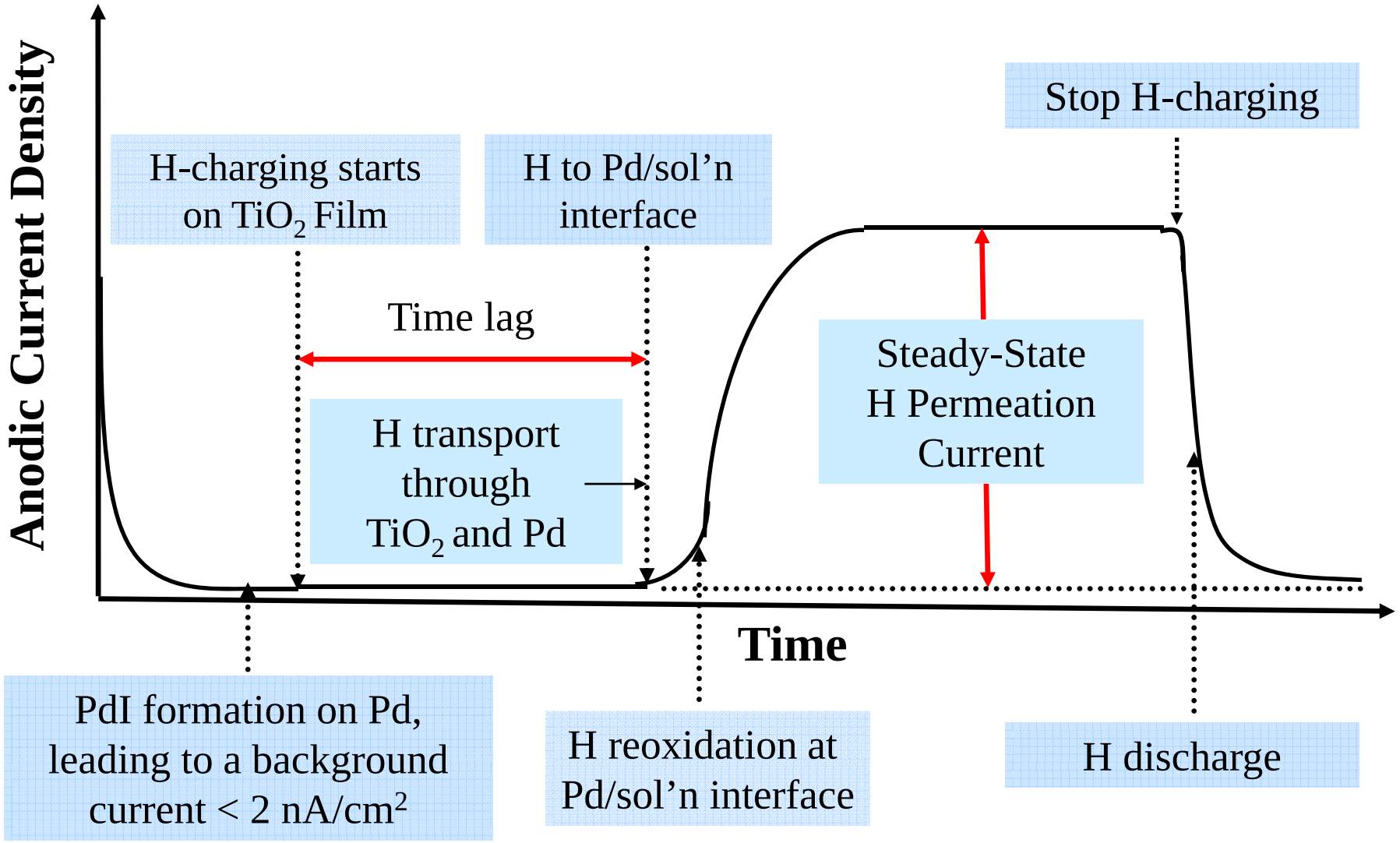




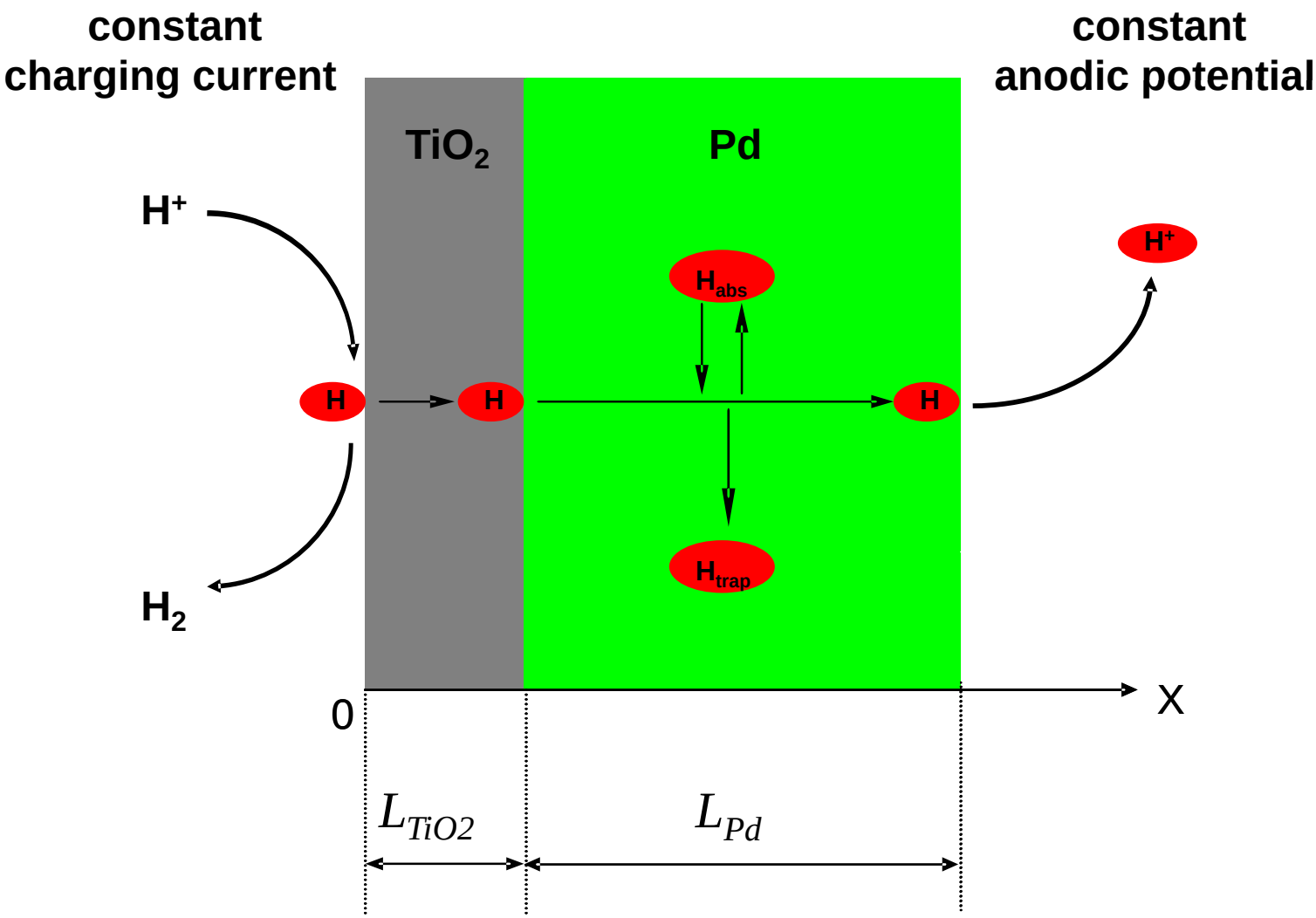
Hydrogen Permeation Measurements



Hydrogen Permeation Curve



Hydrogen Permeation Model



Hydrogen Permeation in Pd

$$\frac{\partial}{\partial t}C_D^{Pd}(x,t) = D_H^{Pd}\frac{\partial^2}{\partial x^2}C_D^{Pd}(x,t) - \frac{\partial}{\partial t}\left[C_A^{Pd}(x,t) + C_T^{Pd}(x,t)\right]$$

reversible absorption:

$$\frac{\partial}{\partial t}C_A^{Pd}(x,t) = k_A^{Pd}C_D^{Pd}(x,t) - k_D^{Pd}C_A^{Pd}(x,t)$$

irreversible trapping:

$$\frac{\partial}{\partial t}C_T^{Pd}(x,t) = k_T^{Pd}\left(1 - \frac{C_T^{Pd}(x,t)}{C_T^S}\right)C_D^{Pd}(x,t)$$

boundary conditions:

$$-D_H^{Pd}\frac{\partial}{\partial x}C_D^{Pd}(x=0, t \le t_{off}) = f_H\frac{i_0}{F}$$

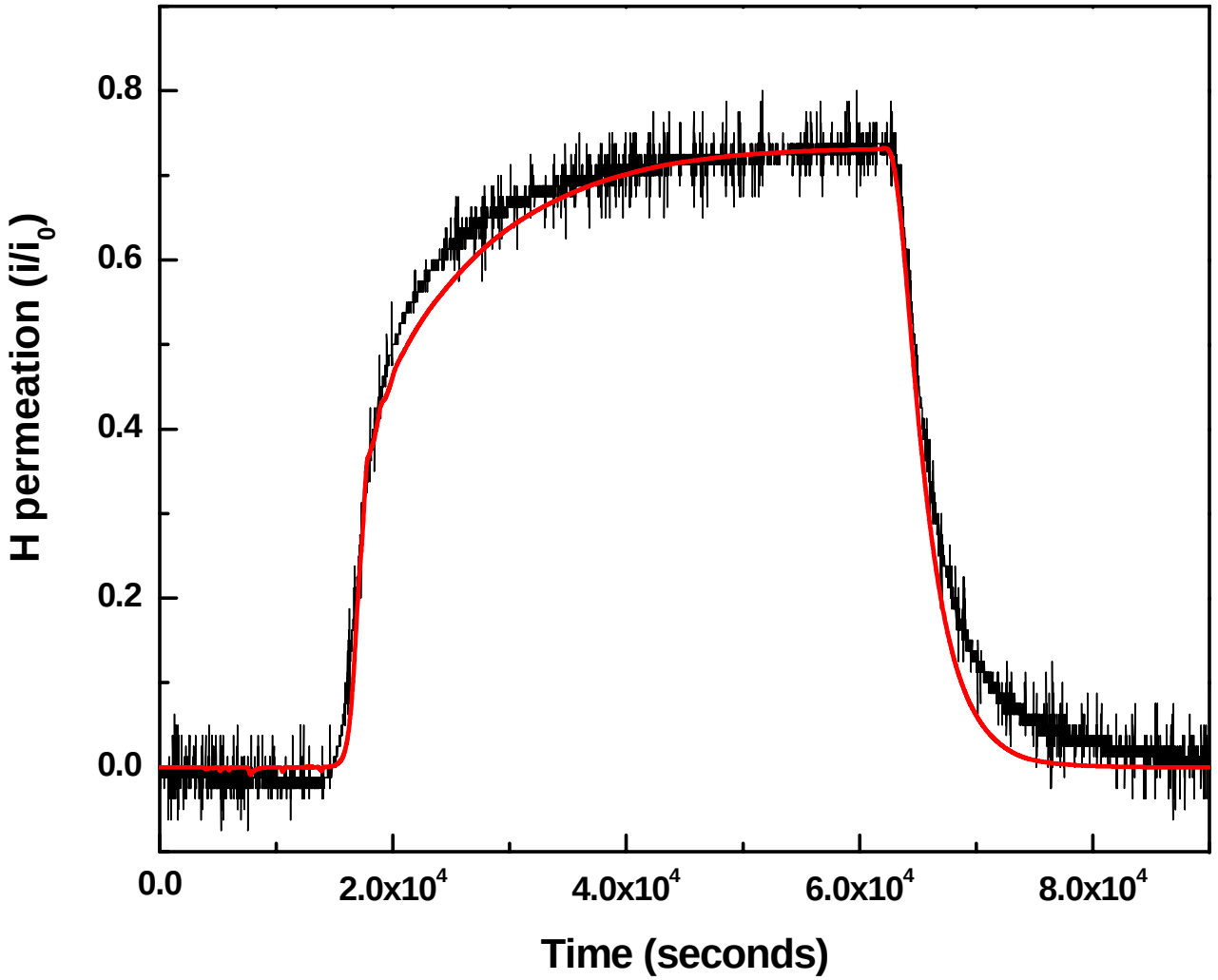
$$C_D^{Pd}(x=0, t > t_{off}) = 0$$

$$C_D^{Pd}(x=L_{Pd}, t) = 0$$

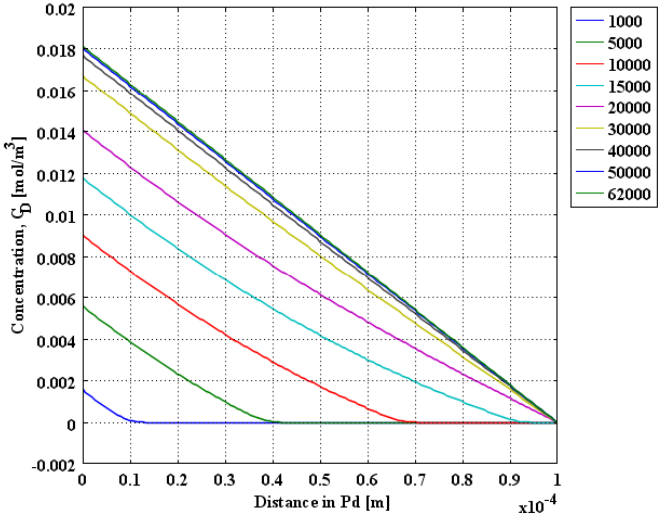
initial conditions:

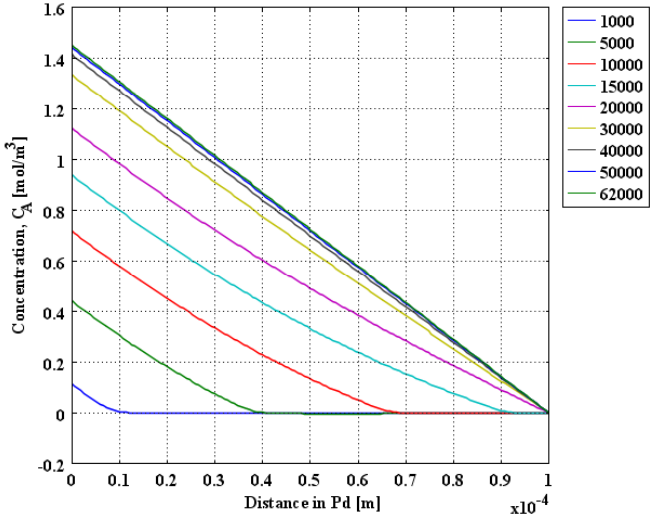
$$C_D(x, t=0) = C_A(x, t=0) = C_T(x, t=0) = 0$$

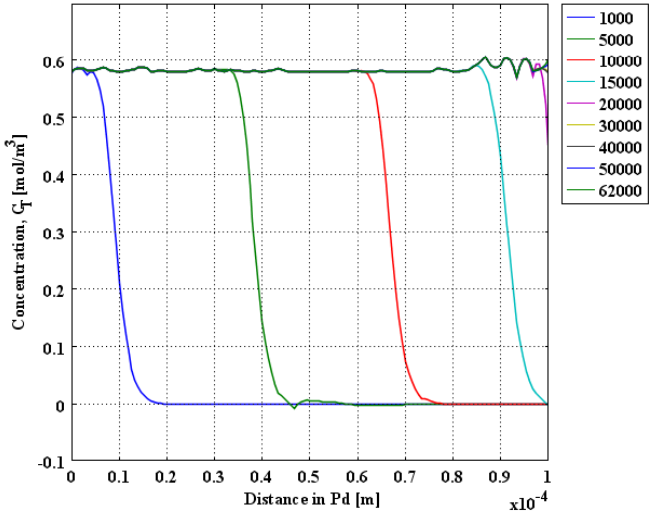
Simulation vs Experiment for Pd



Evolution of H Profiles in Pd







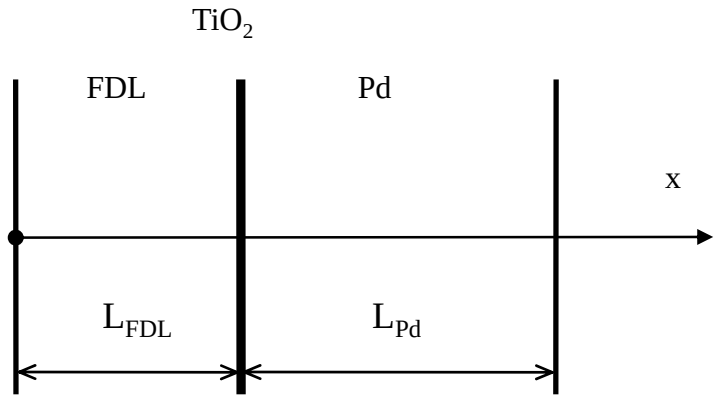
- Steady-state achieved in >14 hrs.
- Reversible absorption is fast, and, hence, always at equilibrium.
- Irreversible trapping sites are saturated after ~ 6 hrs.

TiO_2 Deposited on Pd

- Large geometric scale variations in TiO_2 and Pd (24nm:0.1mm)

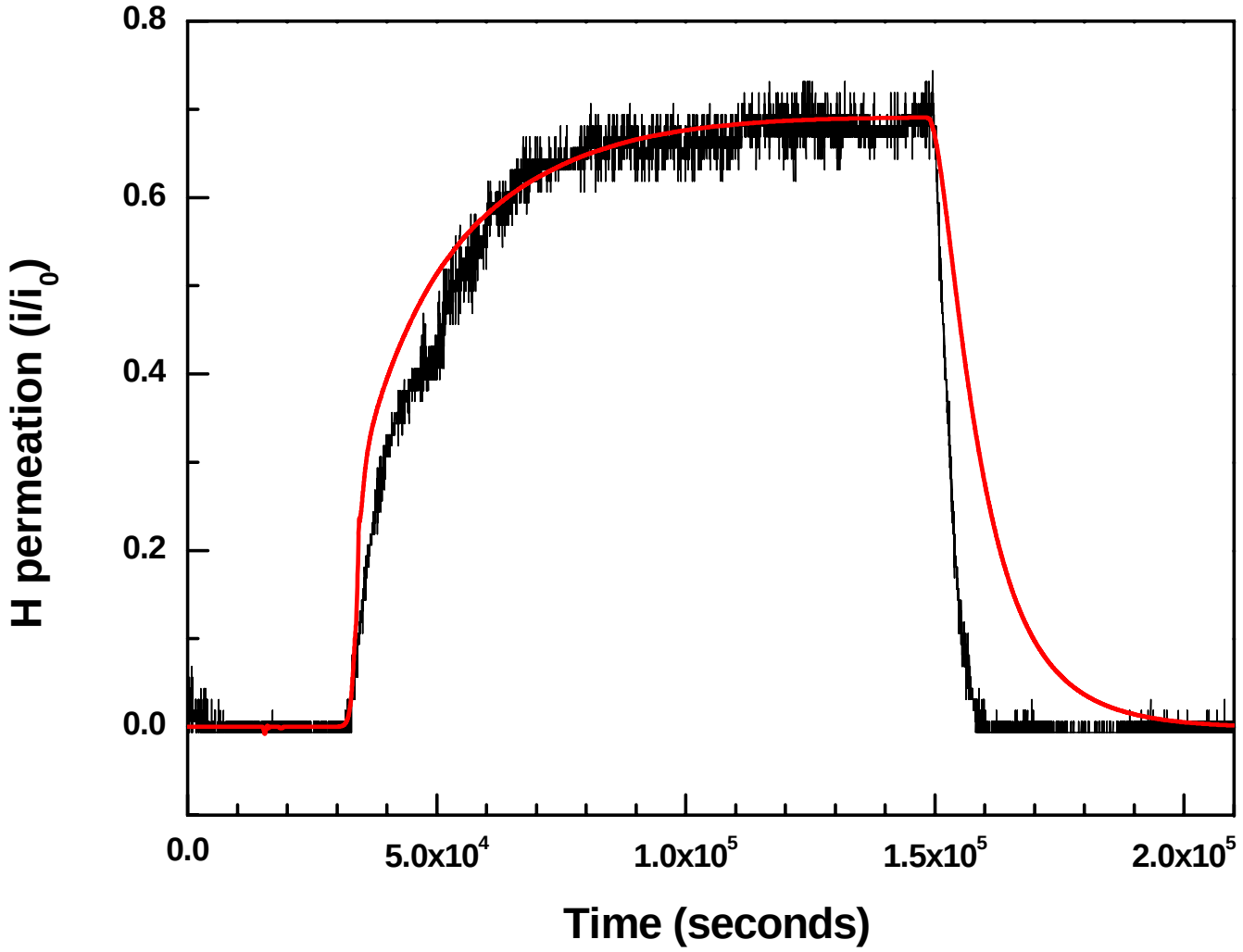
- Three approaches:
- ☒ Actual dimensions but different mesh densities – simulations appear to yield reasonable results for certain parameter values but not for others.
- ☒ Different length scales in the TiO_2 and Pd – the diffusion and absorption parameters are normalized accordingly. However, normalization of the flux is ambiguous at the TiO_2/Pd interface.
- ☑ Thin layer approximation (Sandwich model) – the thin TiO_2 film is replaced by a boundary layer sandwiched between a hypothetical fast diffusion layer (FDL) and the Pd.

Sandwich Model

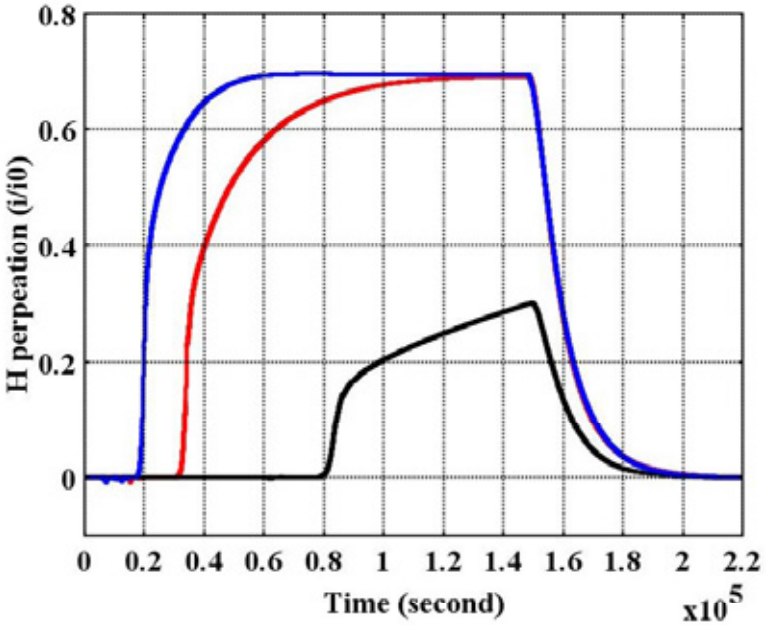


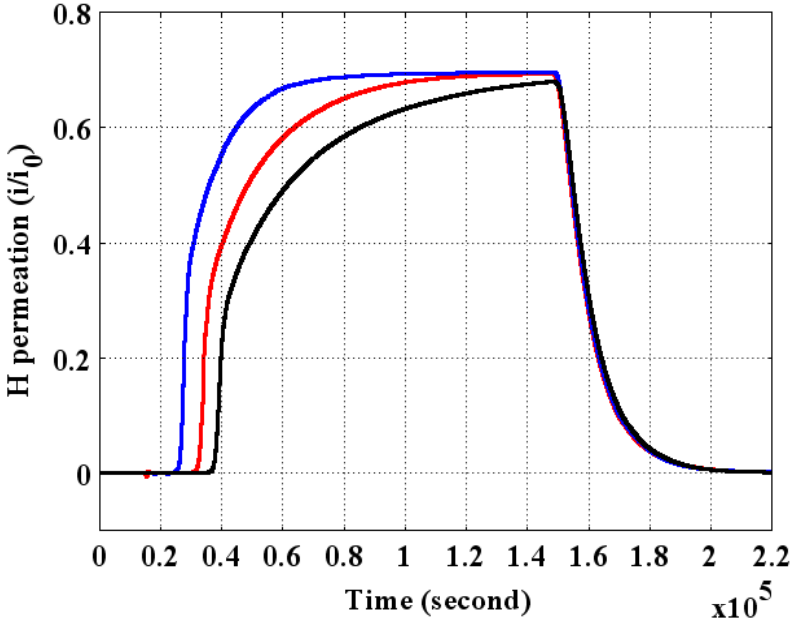
- The FDL is a hypothetical layer in which diffusion is so fast that it has a little effect on the subsequent TiO_2 and Pd.
- The thin TiO_2 film is replaced by an interior boundary layer between the FDL and the Pd. Diffusion in TiO_2 is incorporated as interior boundary conditions.
- The Pd is governed by the mass balance equations as stated.

Simulation vs Experiment for TiO_2/Pd



Sensitivity to Model Parameters





Effect of H diffusion in TiO_2:

- $D_H^{TiO2} = 10^{-16}$ m^2/s
- $D_H^{TiO2} = 10^{-17}$ m^2/s
- $D_H^{TiO2} = 10^{-18}$ m^2/s

Effect of TiO_2 thickness:

- $L_{TiO2} = 12$ nm
- $L_{TiO2} = 24$ nm
- $L_{TiO2} = 36$ nm

Conclusions

- Models describing hydrogen permeation through a thin TiO_2 film deposited on Pd were developed and solved using COMSOL Multiphysics.
- The model simulation reproduced the experimental permeation curves and yielded values of the permeation parameters required to predict hydrogen absorption into Ti-alloys.
- The value of D in TiO_2 is three orders of magnitude lower than that in Ti metal, indicating that hydrogen transport through the oxide is responsible for the strong retardation of TiO_2 films on hydrogen permeation.

Electrochemical and Corrosion Studies at Western

Acknowledgements

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Simulation Parameters

	Value	Description
i_0	8×10^{-4} A/m^2	charging current density
f_H	0.7325 / 0.6935	charging efficiency (Pd / TiO_2+Pd)
t_0	62000 / 149000 s	charging time (Pd / TiO_2+Pd)
L_0	1×10^{-5} m	FDL thickness
L_1	2.4×10^{-8} m	TiO_2 thickness
L_2	0.0001 m	Pd thickness
D_0	1×10^{-5} m^2/s	diffusion coefficient in FDL
D_1	1×10^{-17} m^2/s	diffusion coefficient in TiO_2
D_2	3.34×10^{-11} m^2/s	diffusion coefficient in Pd
k_A	1 s^{-1}	absorption rate constant in Pd
k_D	0.0125 s^{-1}	desorption rate constant in Pd
k_T	10 s^{-1}	trapping rate constant in Pd
C_T^S	0.58 mol/m^3	trapping saturation in Pd

Sandwich Model Equations

FDL:

$$\frac{\partial}{\partial t}C_0(x,t) = D_0\frac{\partial^2}{\partial x^2}C_0(x,t) \qquad (D_0 >> D_1, D_2)$$

TiO_2 interface condition:

$$J_1(t) = -\frac{D_1}{L_1}\left(C_2(L_0^+,t) - C_0(L_0^-,t)\right)$$

Steady-state concentrations:

$$C_0^{ss}(x) = \frac{f_H i_0}{F\cdot D_0}(L_0 - x) + \frac{f_H i_0}{F}\left(\frac{L_1}{D_1} + \frac{L_2}{D_2}\right)$$

$$C_2^{ss}(x) = \frac{f_H i_0}{F\cdot D_2}(L_0 + L_2 - x)$$

$$C_A^{ss}(x) = \frac{k_A}{k_D}C_2^{ss}(x); \quad C_T^{ss}(x) = C_T^S$$

Discharge boundary conditions:

$$D_1\frac{\partial}{\partial x}C_1(x = L_0, t > t_{off}) = 0$$

$$C_2(x = L_0 + L_2, t > t_{off}) = 0$$