触媒層内液水飽和モデルの開発

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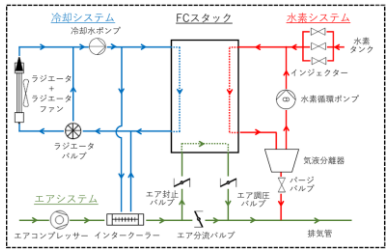
シミュレーションGr(京都大学 河瀬GL)事業内容説明会

2025年1月29日　NEDO川崎23F 2304会議室

固体高分子形燃料電池内の物質輸送解析

Multi-physics

FC-DynaMo



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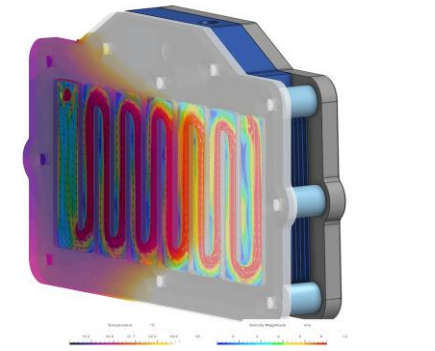

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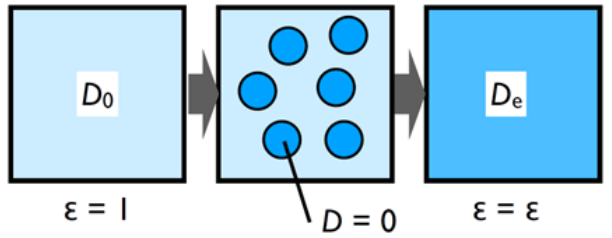


Bruggeman correlation

[V. D. Bruggeman, *Ann. Phys.*, 1935]

$$\frac{\varepsilon}{\tau} = \frac{D_e}{D_0} = \varepsilon^a$$

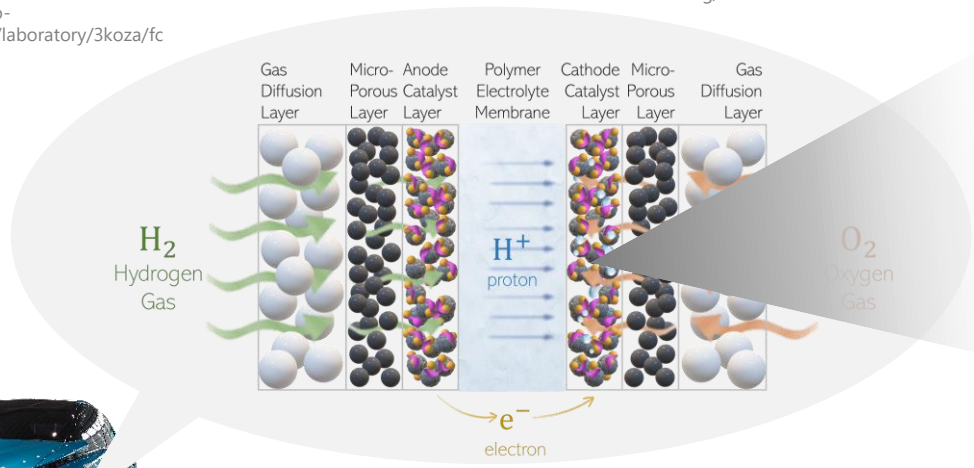
a=1.5 (spheres)
a=2 (cylinders)

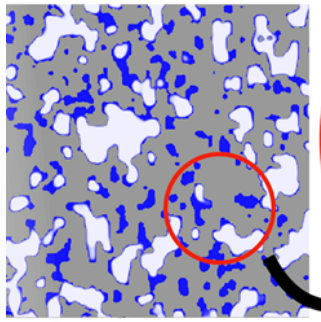
$$\Omega(\{\rho\}) = k_B T \sum_i [\rho_i \ln \rho_i + (1-\rho_i)\ln(1-\rho_i)]V_i$$ Ideal Gas Contribution

$$- \frac{\varepsilon_{ff}}{2} \sum_i \sum_{a \le r_c} \rho_{i+a}\rho_i V_i$$ Fluid-Fluid Interaction

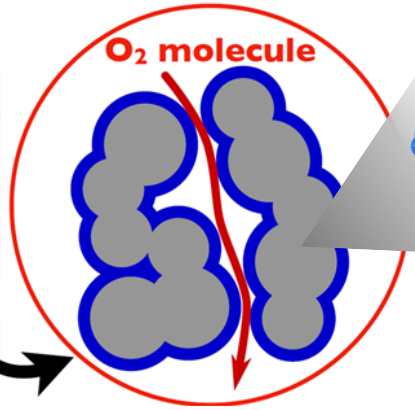
$$- \varepsilon_{sf} \sum_i \sum_{|a| \le r_c} \chi(i,a)\rho_i V_i$$ Solid-Fluid Interaction

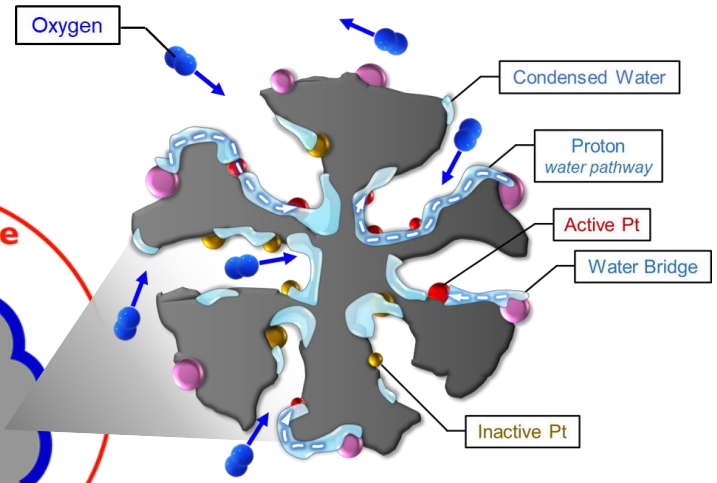
$$- \sum_i \mu \rho_i V_i$$ Chemical Potential





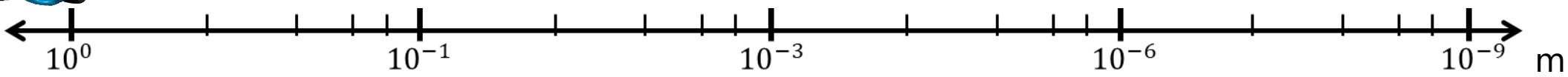
Secondary Pores



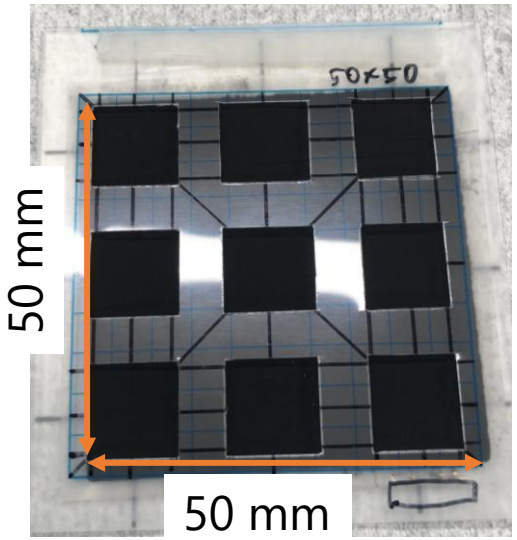


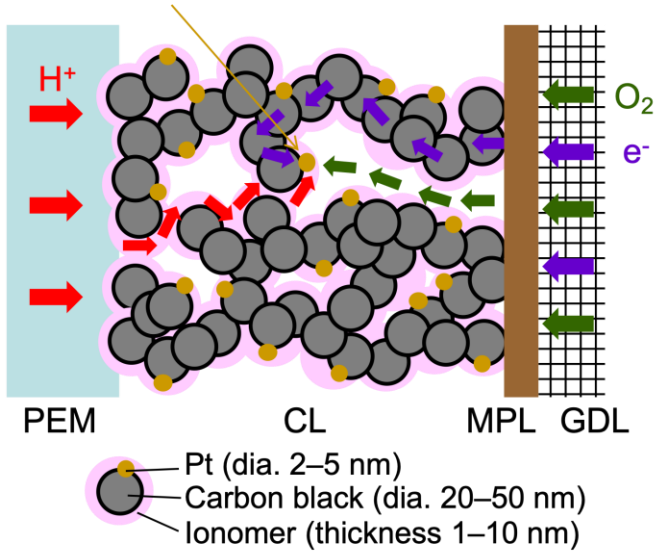
Primary Pores

Multi-scale

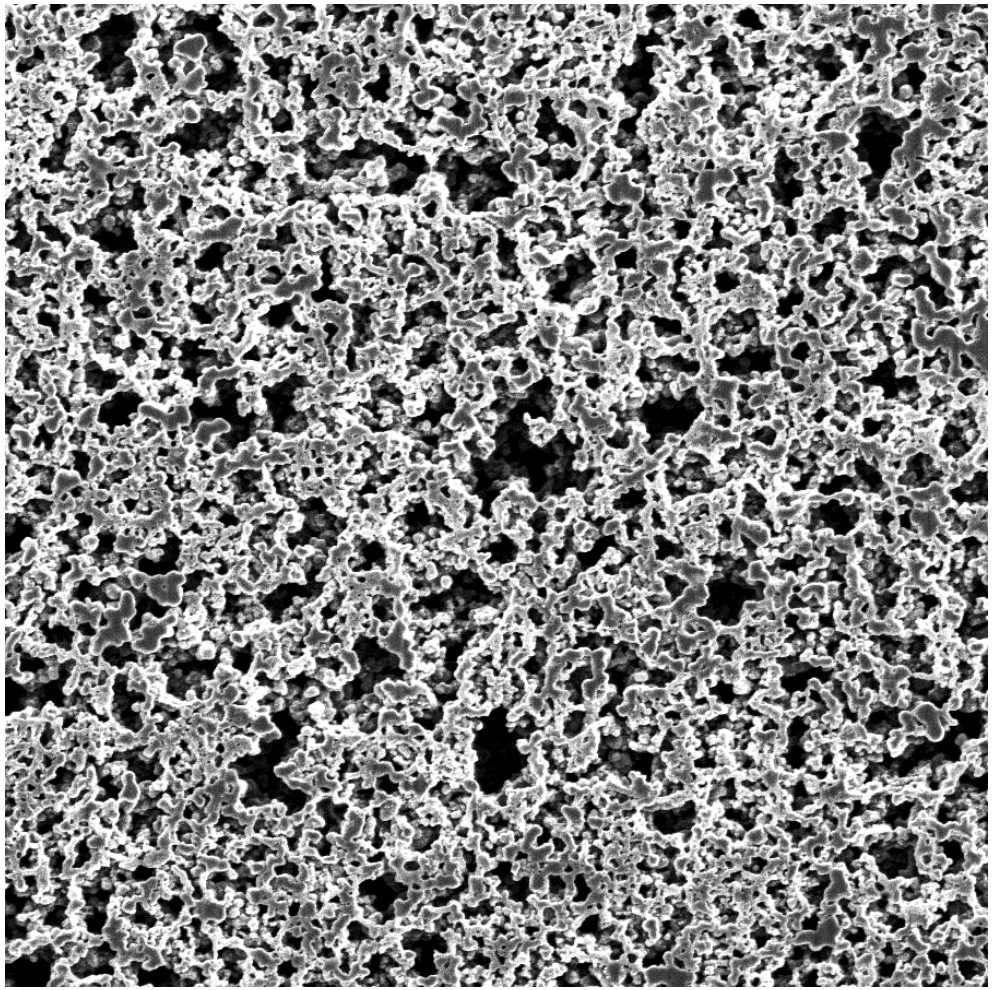


カソード触媒層

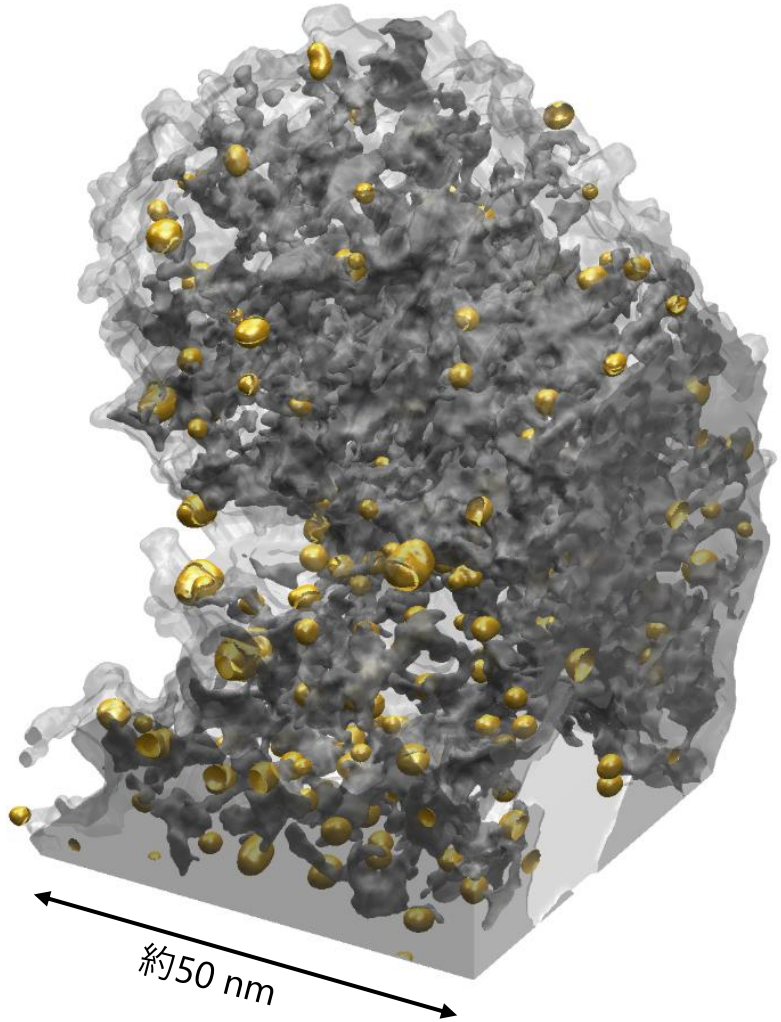




● **FIB-SEM連続断面像（二次細孔構造）**

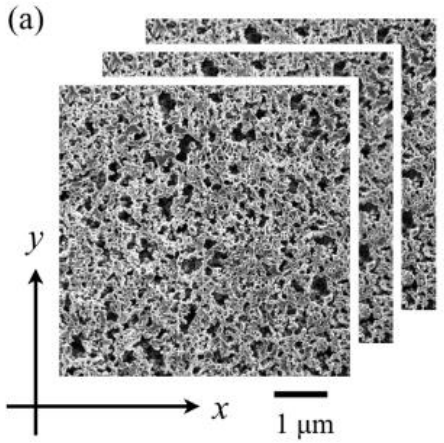


● **3D TEM像**
（触媒担体粒子）

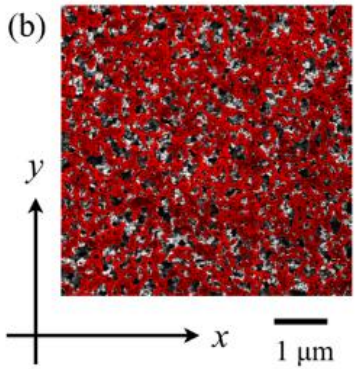


触媒層三次元構造モデルの作成

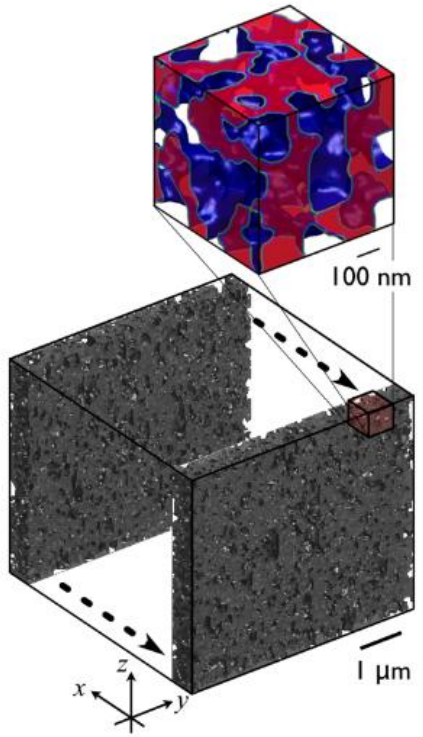
触媒層の**クライオFIB-SEM連続断面画像**から
高精度な三次元構造モデルを構築



低温集束イオンビーム－走査電子顕微鏡
（cryo-FIB-SEM）装置により
新共通MEA 触媒層の連続断面画像を取得

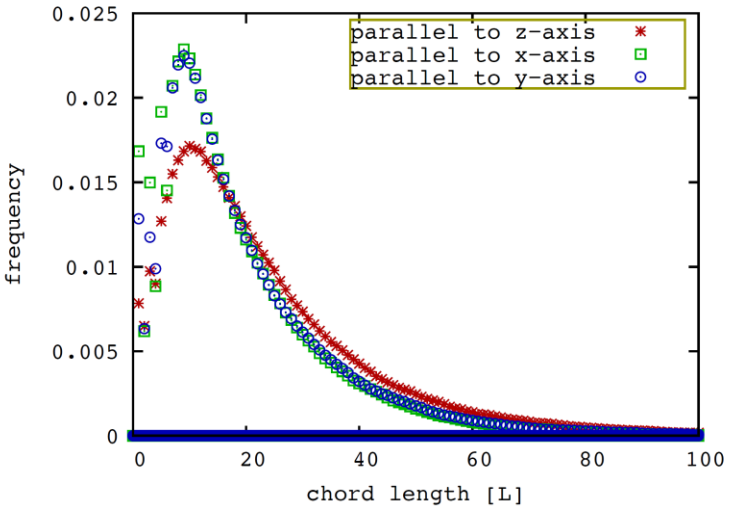


画像間の比較を取り入れた
断面抽出アルゴリズムにより
各面内の固体部(炭素，アイオノマー，Pt粒子)を特定(赤色)



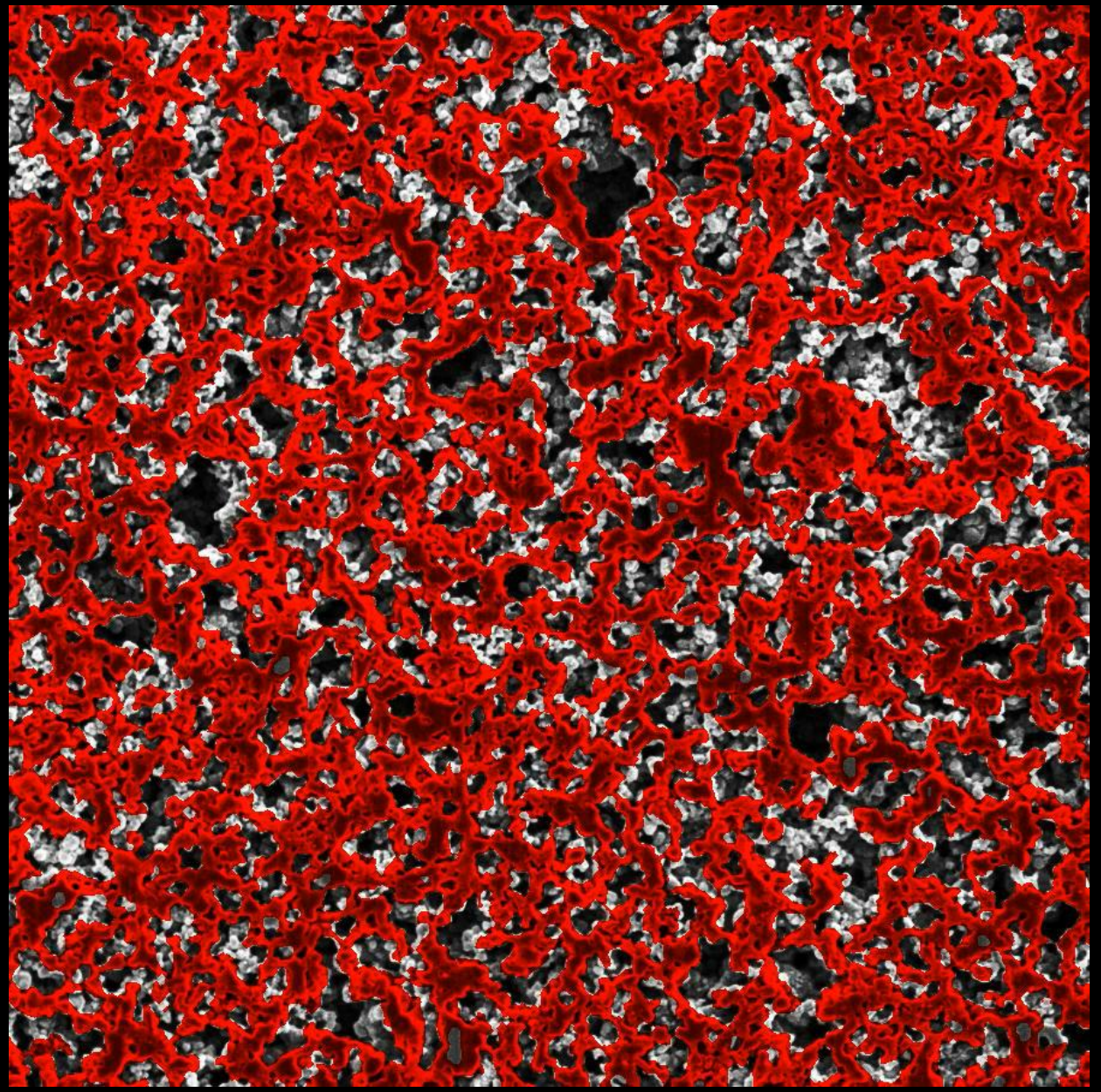
触媒層の三次元構造数値モデル
（TEC10V30E・解像度 6 nm）

コード長分布



課題

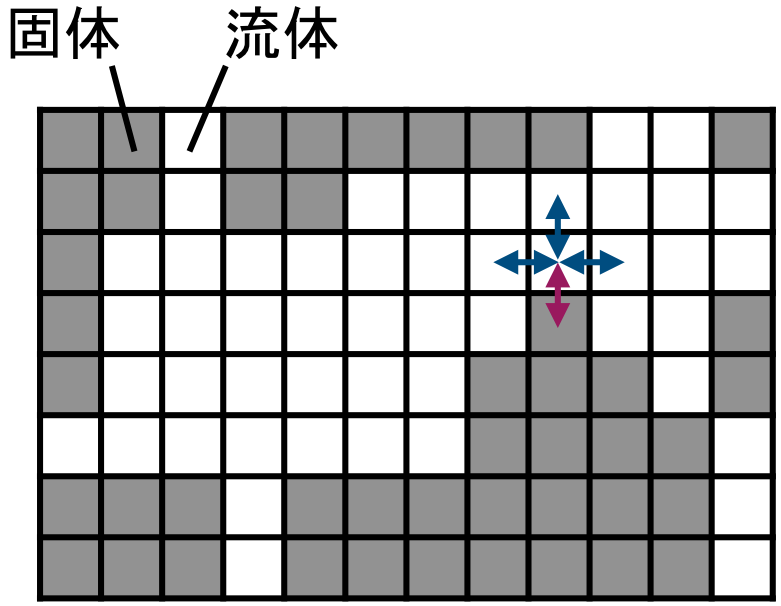
- FIB加工およびSEM観察方向に起因する構造異方性の低減
- アイオノマー被覆分布を含む構造モデルの生成方法の確立


1 µm

格子密度汎関数法による相変化解析

Y. Yoshimoto, T. Hori, I. Kinefuchi, and S. Takagi, *Phys. Rev. E* **96**, 043112 (2017).

- 格子密度汎関数理論に基くメソ細孔内の相変化解析



↔ 流体–流体間の相互作用 ε **ff**

↔ 固体–流体間の相互作用 ε **sf**

Helmholtz 自由エネルギーの理想気体成分

$$\Omega(\{\rho\}) = k_B T \sum_i [\rho_i \ln \rho_i + (1 - \rho_i) \ln(1 - \rho_i)]$$

$$- \frac{\varepsilon_{ff}}{2} \sum_i \sum_a (1 - \chi(i, a)) \rho_i \rho_{i+a} - \varepsilon_{sf} \sum_i \chi(i, a) \rho_i$$

流体–流体間の相互作用　　固体–流体間の相互作用

$$- \sum_i \rho_i \mu$$

化学ポテンシャル

$a = (\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)$

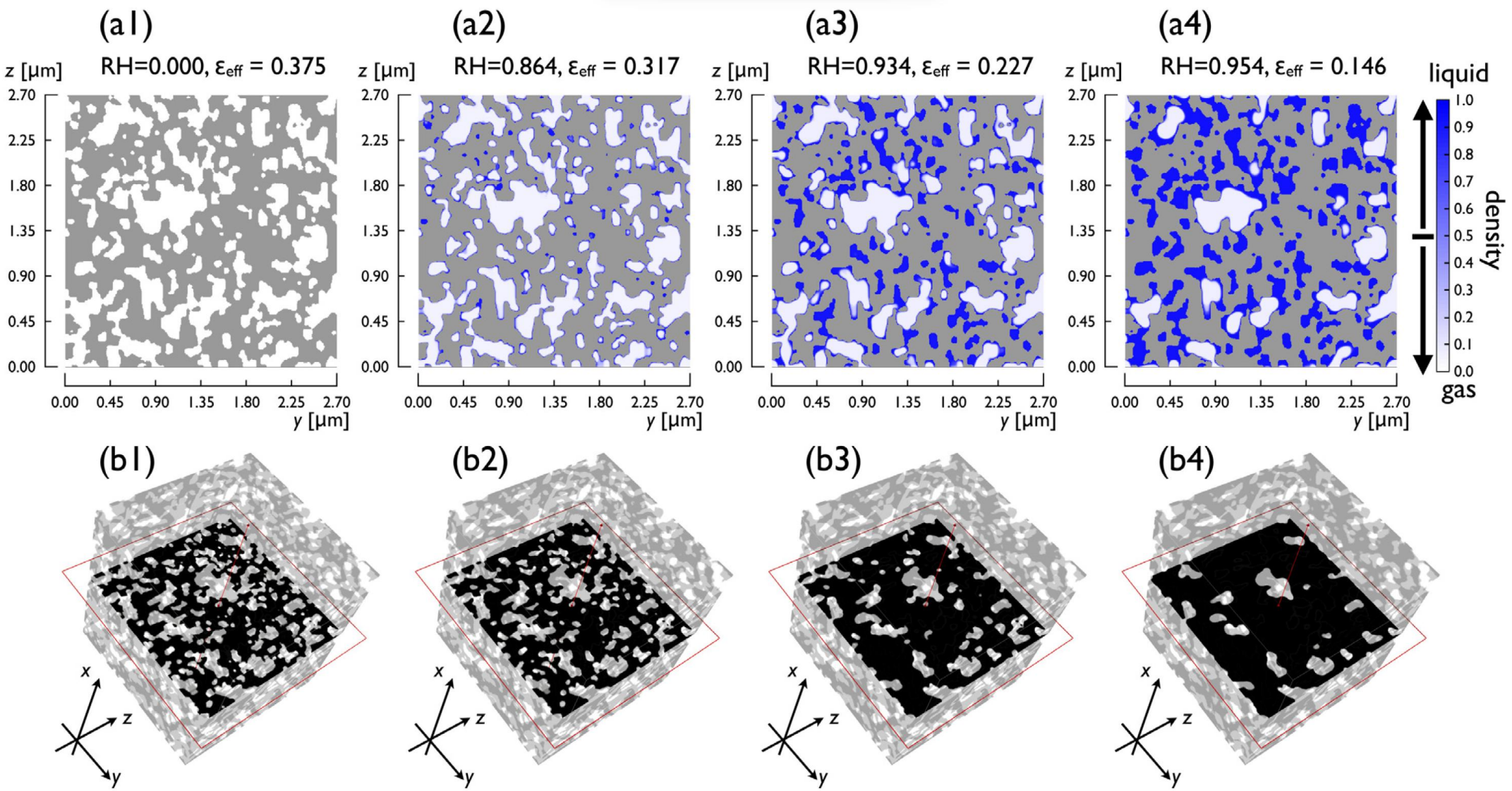
ただし $\chi(i, a) = \begin{cases} 1 & i + a \text{ が固体のとき} \\ 0 & i + a \text{ が流体のとき} \end{cases}$

$\left(\frac{\partial \Omega}{\partial \rho_i}\right)_{\mu, T} = 0$ for $\forall i$　となる密度分布が平衡状態に対応

Kelvin式に基づく毛管凝縮モデルが適用できない複雑形状に適用可能

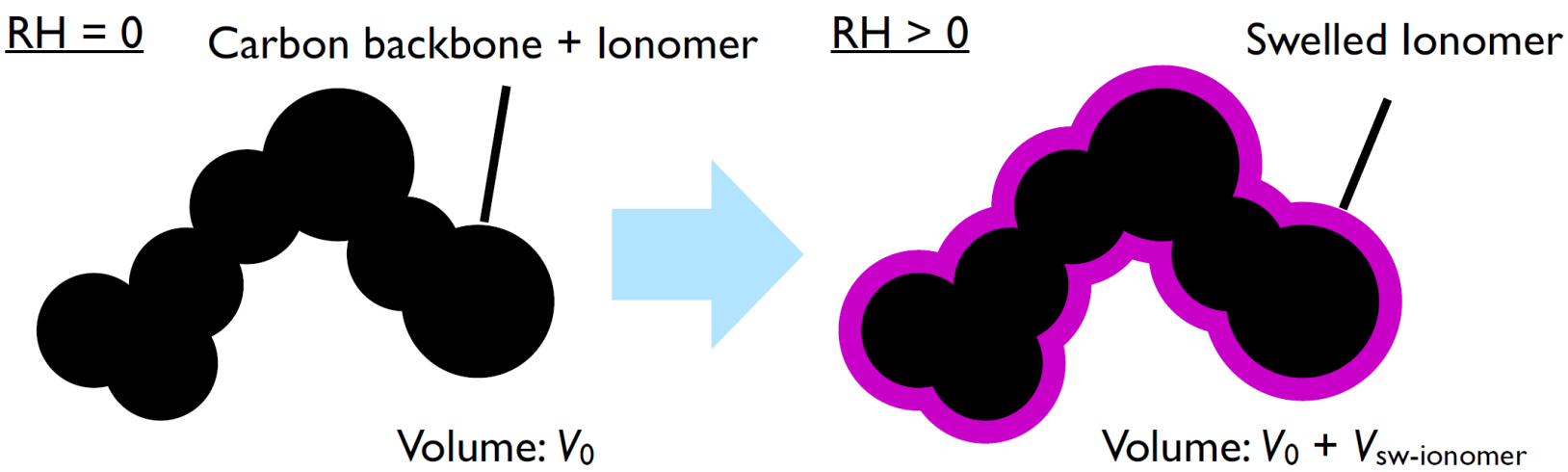
- モンテカルロ法による酸素輸送解析（液水生成構造に対する拡散性評価）

計算例（アイオノマー膨潤無し）



T. Kaneko, Y. Yoshimoto, T. Hori, S. Takagi, J. Ooyama, T. Terao, I. Kinefuchi, *Int. J. Heat Mass Transf.* **150**, 119277 (2020).

触媒層構造およびアイオノマー膨潤モデル

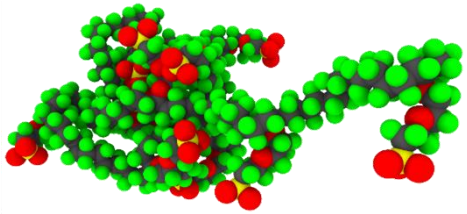


アイオノマーに関する仮定

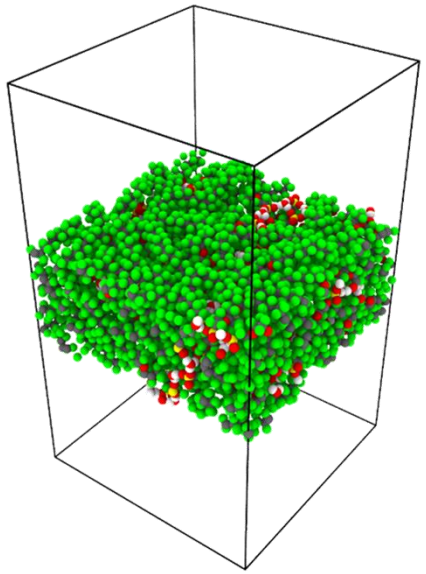
- アイオノマーの被覆が均一
- 固体表面から法線方向に均一に膨潤する
- 膨潤体積はRHに比例

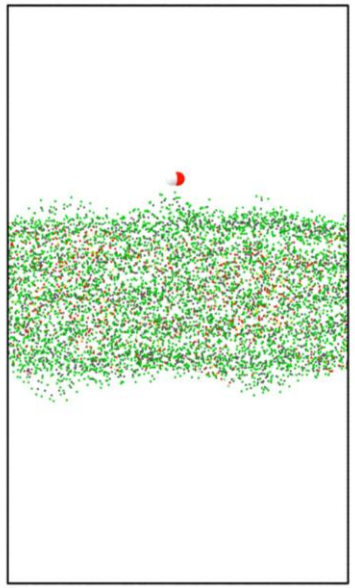
→ RH = 100%において膨潤体積を0%～40%の範囲で変化させて，酸素輸送特性への影響を評価

● **ナフィオン膨潤のGCMC/MD解析**



ナフィオン分子
（重合度100）





触媒層構造

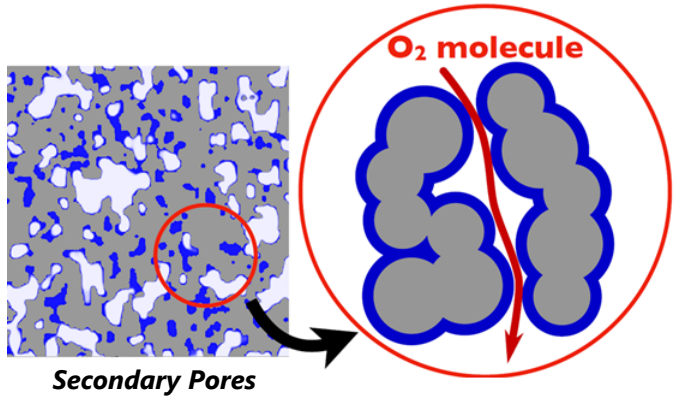
- TEC10V30E, I/C = 1.0

多孔体内の気体拡散解析

空隙率

有効拡散係数 $D_e = \frac{\varepsilon_{eff}}{\tau} D_0$

屈曲度



$$\frac{\varepsilon_{eff}}{\tau} = \frac{D_e(\mathrm{Kn}=\infty)}{D_0(\mathrm{Kn}=\infty)} = \frac{D_e^{\infty}}{D_K}$$ } **Monte-Carlo Simulations**

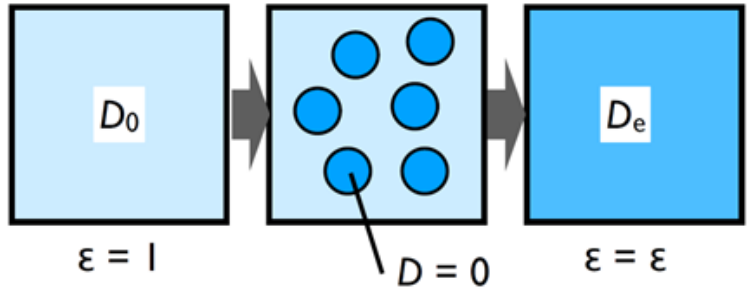
Knudsen Diffusion and Monte Carlo Simulation

D_e^{∞}, the effective diffusion coefficient in the Knudsen regime can be evaluated using mean-square displacement (MSD):

$$D_e^{\infty} = \varepsilon_{eff} \lim_{t\to\infty} \frac{\langle |\boldsymbol{r}(t) - \boldsymbol{r}(0)|^2 \rangle}{6t}$$

D_K, the Knudsen diffusion coefficient can be evaluated from

$$D_K = \frac{v}{3}\left(\frac{\langle l^2 \rangle}{2\langle l \rangle^2} - \beta\right)\langle l \rangle$$



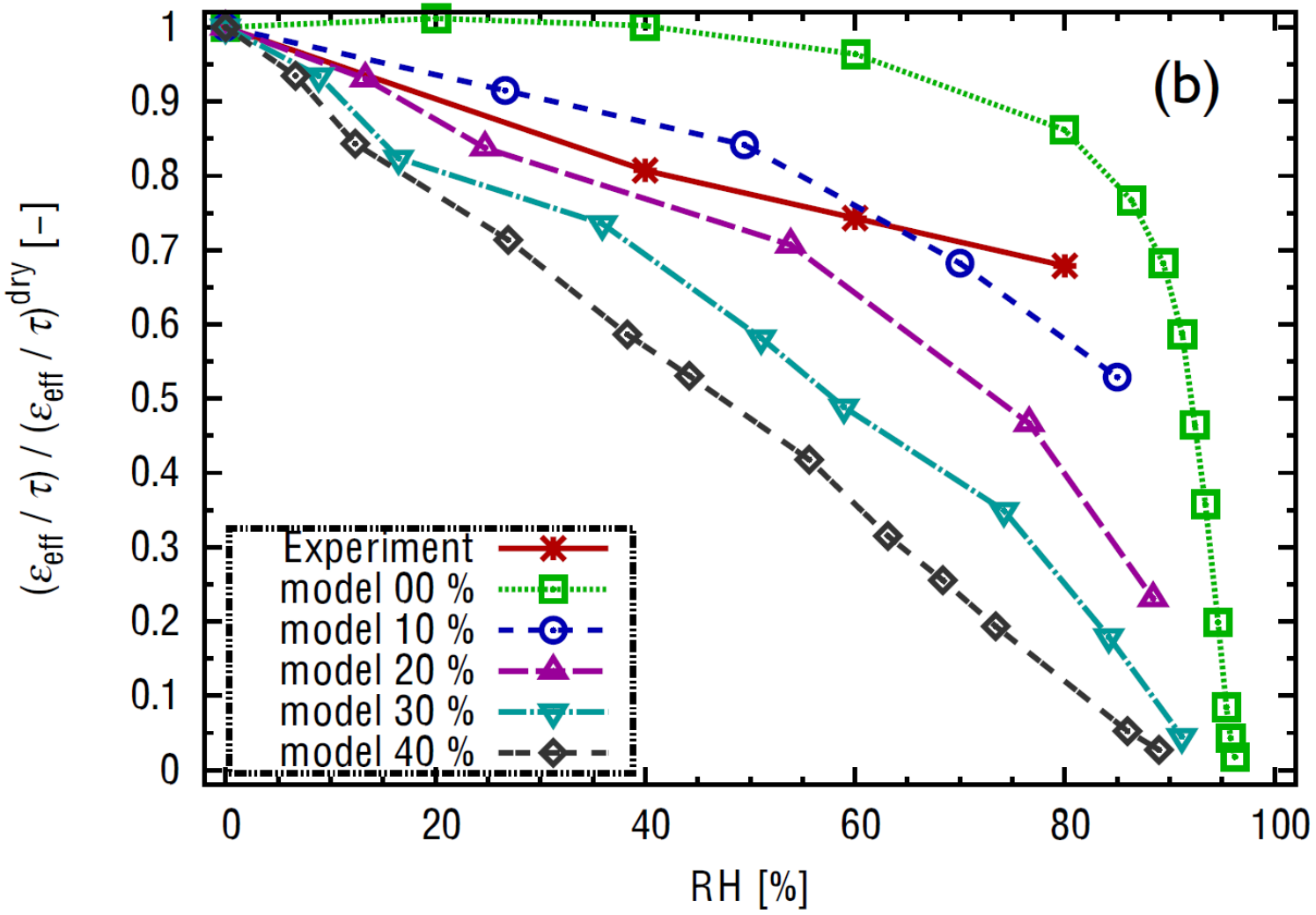
Bruggeman correlation

[V. D. Bruggeman, *Ann. Phys.*, 1935]

$$\frac{\varepsilon}{\tau} = \frac{D_e}{D_0} = \varepsilon^a$$

a=1.5 (spheres)
a=2 (cylinders)

$\varepsilon_{\mathrm{eff}}/\tau$ （空隙率／屈曲度）の相対湿度依存性



- 乾燥条件（RH=0%）の$\varepsilon_{\mathrm{eff}}/\tau$からの相対変化で評価
- アイオノマー膨潤体積 10% @RH=100% のモデルが実験結果と比較的良く一致

固体高分子形燃料電池内の物質輸送解析（再掲）

Multi-physics

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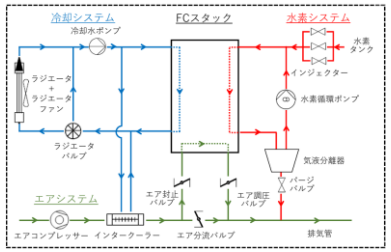

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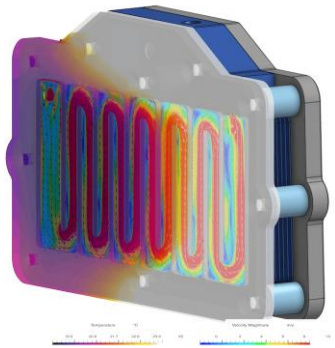

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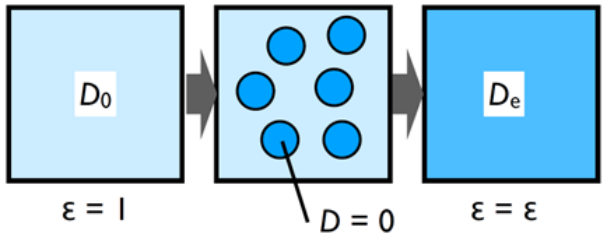

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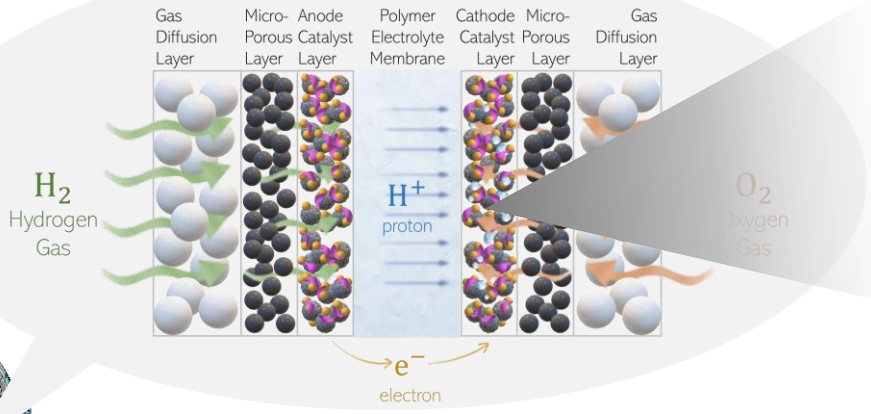
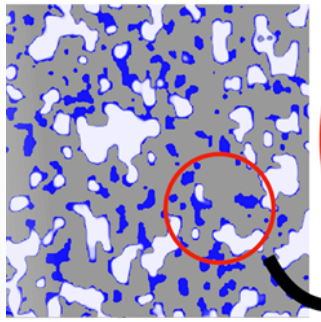
$$- \sum_i \mu \rho_i V_i$$ Chemical Potential





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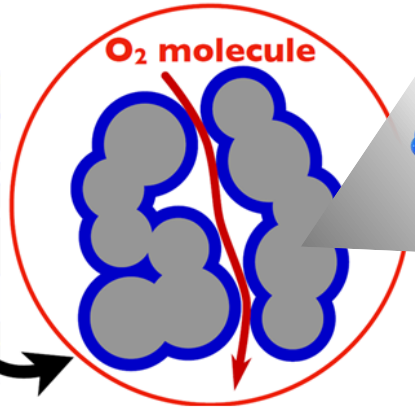
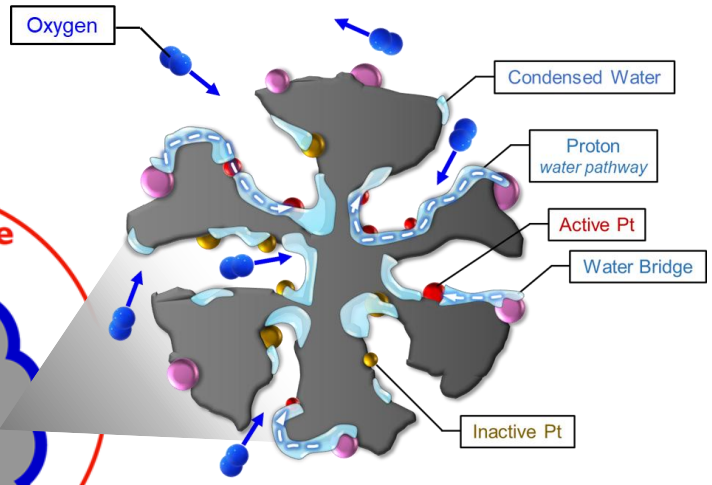
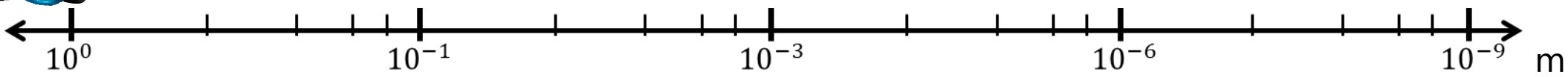




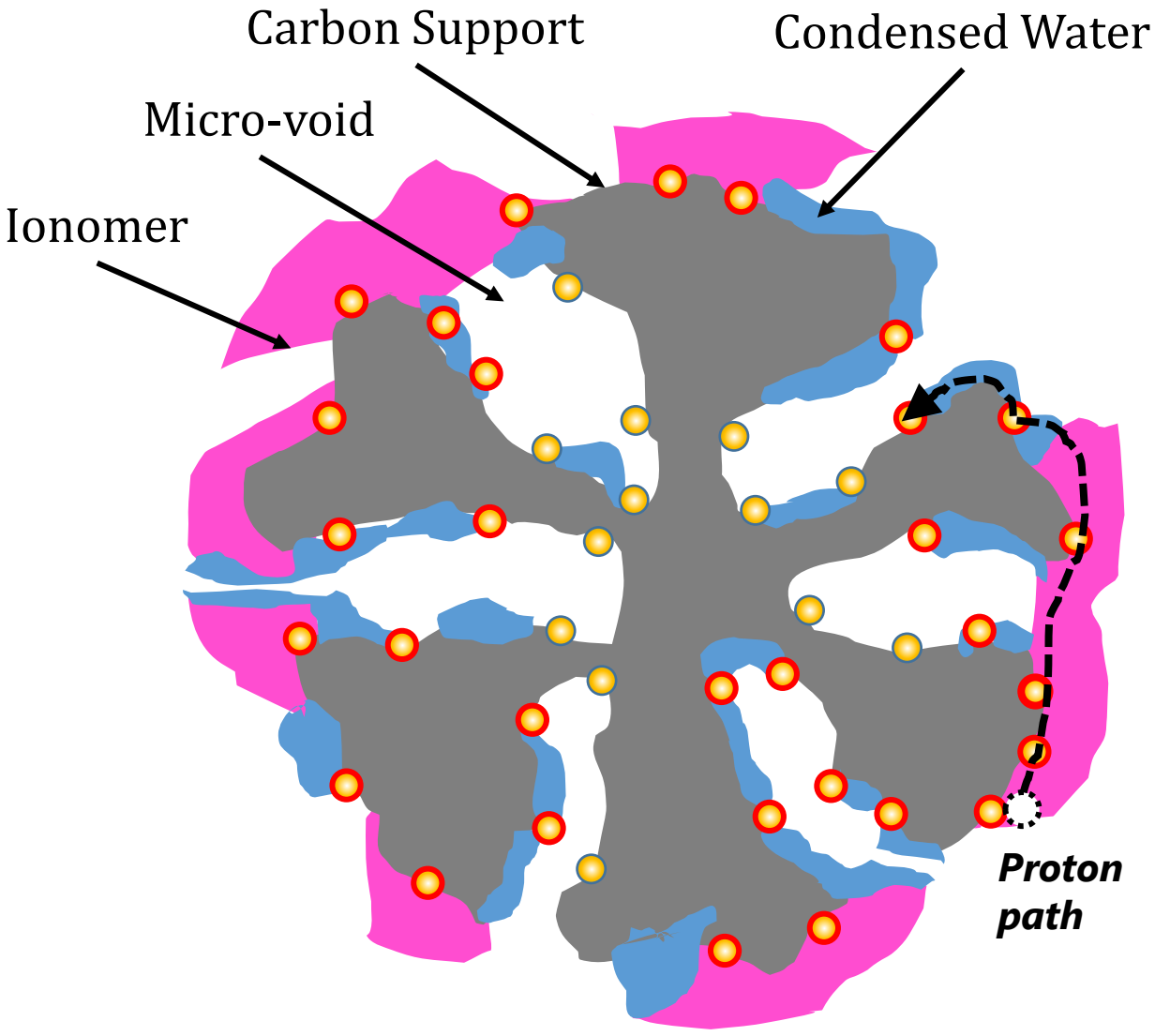
Primary Pores

Multi-scale



多孔性触媒担体内部の白金利用率の変化

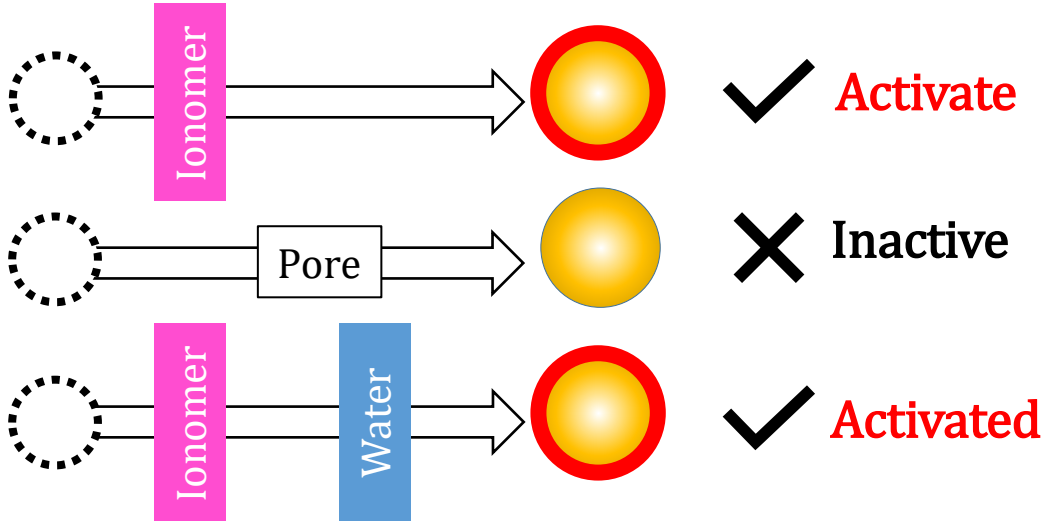
電気化学的表面積（ECSA：Electrochemical surface area）



Platinum Particle **(Active)**
in-contact with ionomer

Platinum Particle **(Inactive)**
no contact with ionomer

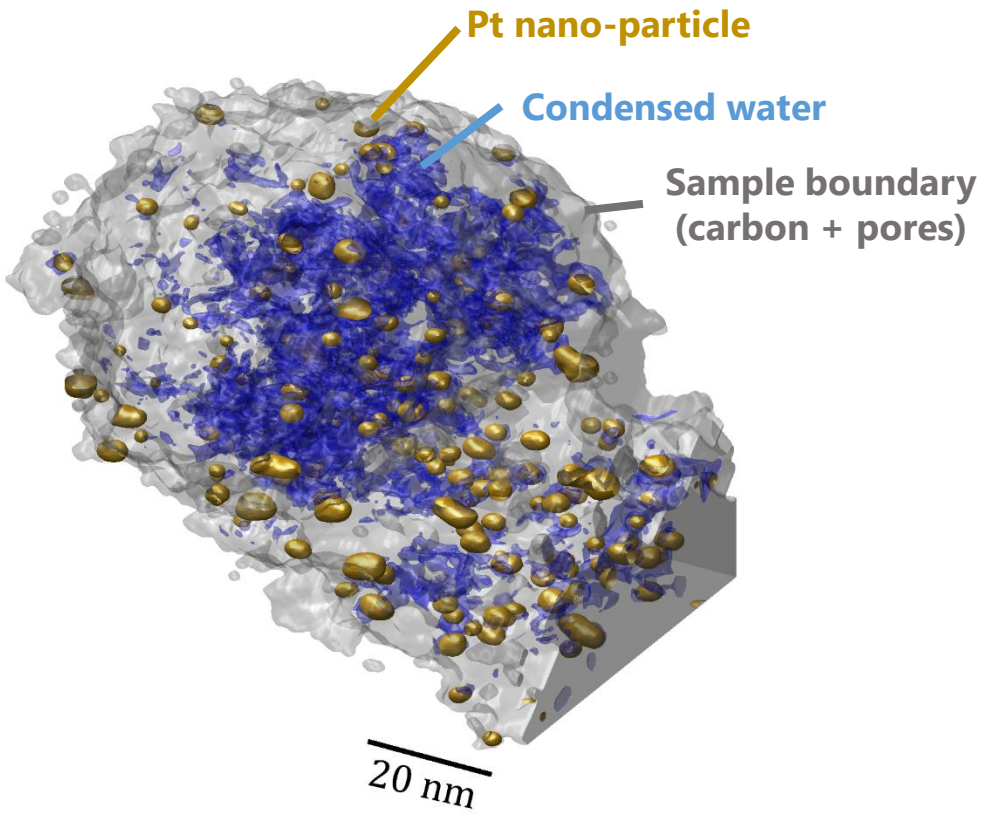
Proton Pathway

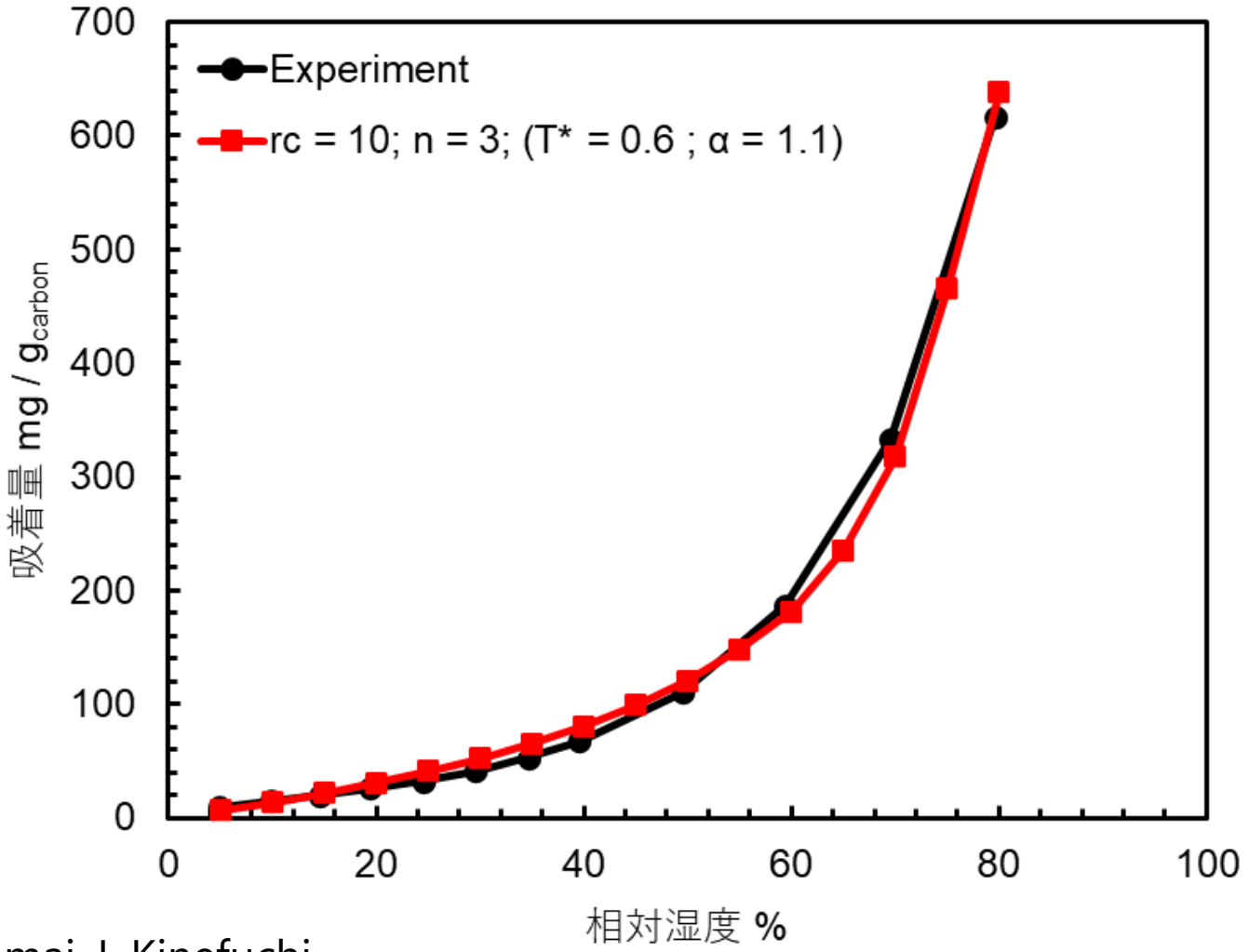


多孔性触媒担体の吸着等温線の再現

LDFT Simulation

トヨタMIRAI（第2世代）のカソード触媒層材料を対象





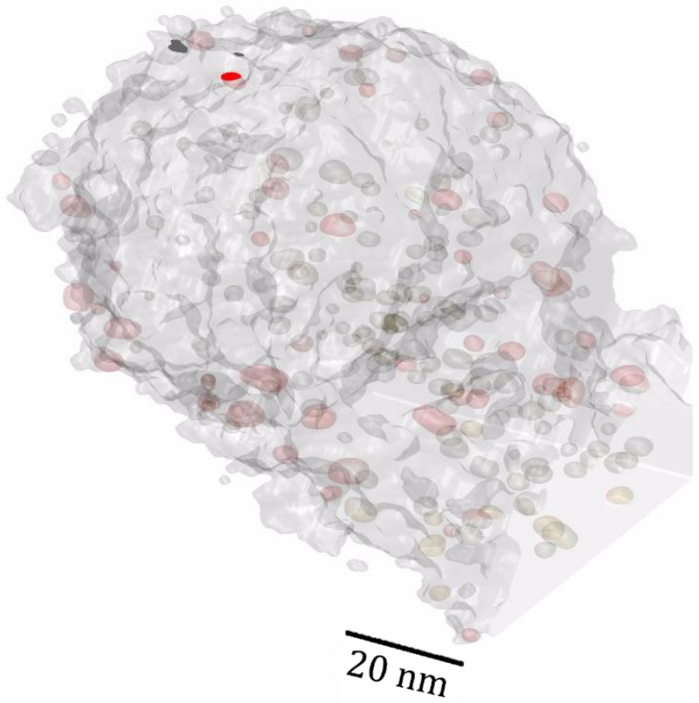
C. Otic, S. Katayama, M. Arao, M. Matsumoto, H. Imai, I. Kinefuchi,
ACS Applied Materials & Interfaces **16** (16), 20375 (2024).

多孔性触媒担体内の液水分布

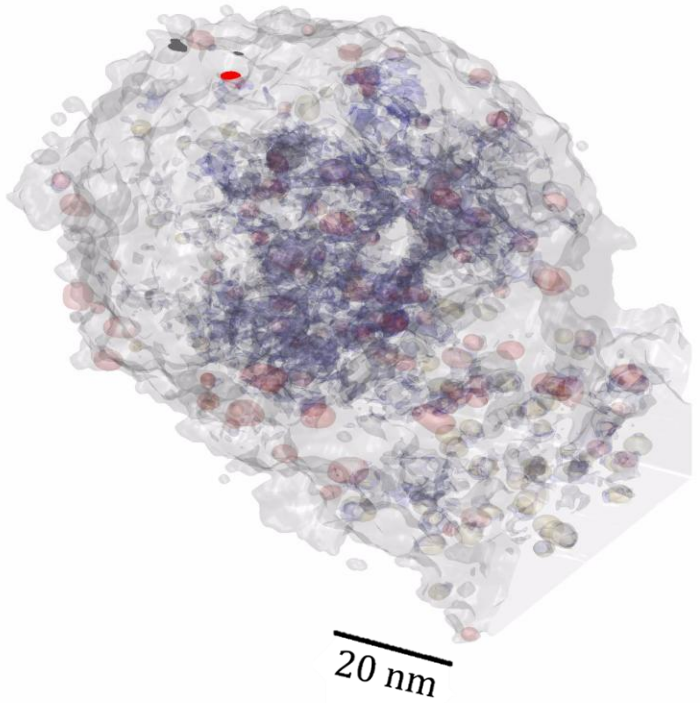
Pt utilization based on LDFT simulation (Wet)

*The goal is to evaluate whether Pt nanoparticles **"have access"** to the surface of the particle through **"water bridges"**.*

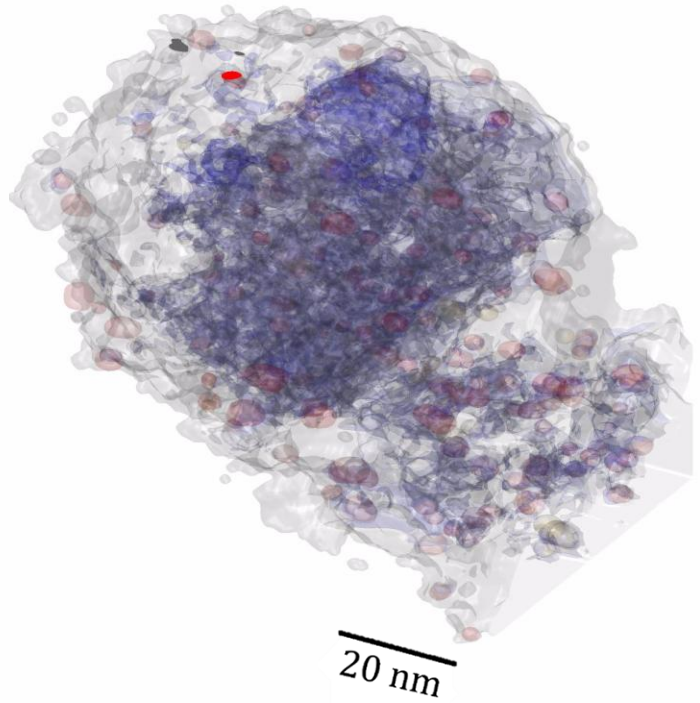
Inactive Platinum
Active Platinum
Sample Boundary (Carbon + Pore)
Condensed Water



RH = 00%
Active Pt = 28%



RH = 60%
Active Pt = 62%



RH = 80%
Active Pt = 87%

白金利用率

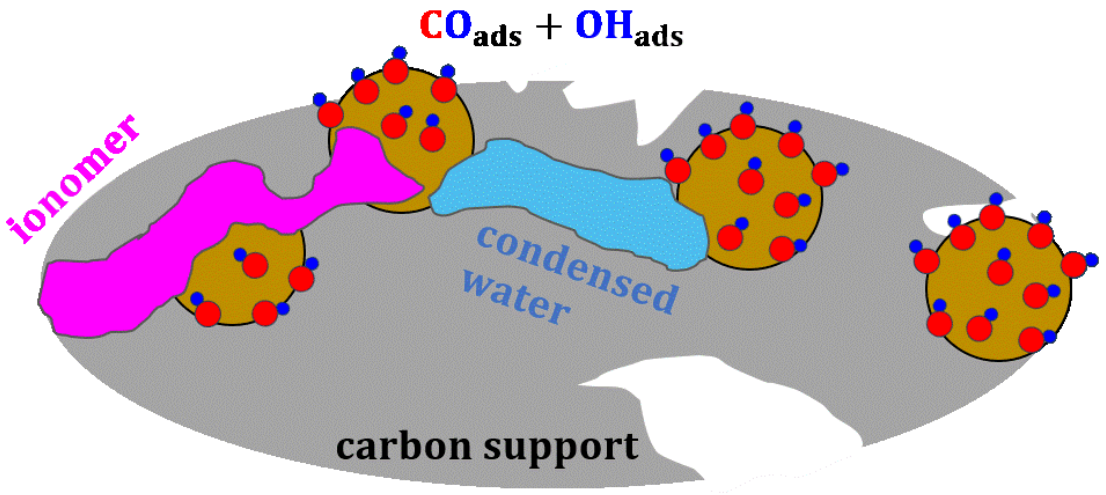
多孔性触媒担体「内部」の白金利用率の湿度依存性の説明に成功

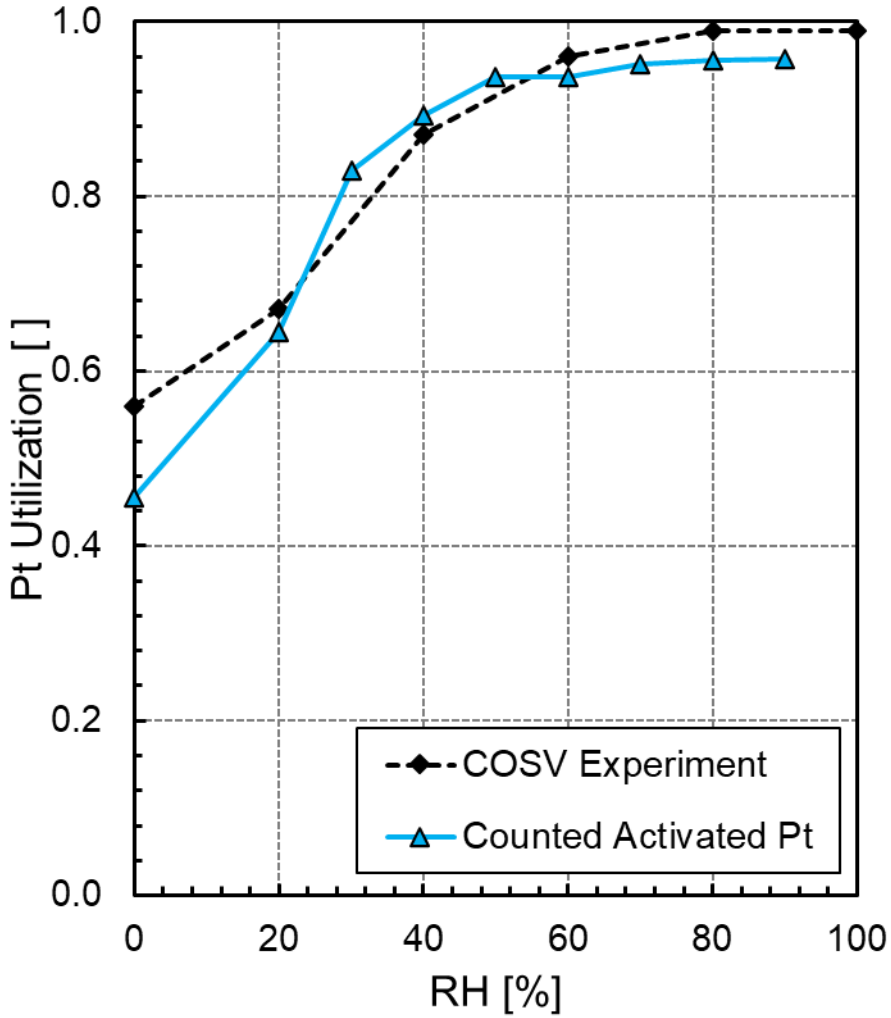
Comparison with
Carbon Monoxide Stripping Voltammetry (COSV)

ECSA by electrooxidation of adsorbed CO monolayer on the catalyst surface.

$$H_2O + * \Longleftrightarrow OH_{ads} + H^+ + e^- \qquad (1)$$

$$CO_{ads} + OH_{ads} \longrightarrow CO_2 + H^+ + e^- + 2^* \qquad (2)$$





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まとめ

実材料の三次元構造データを用いて，カソード触媒層内の水の相変化，酸素拡散，プロトン伝導を評価するシミュレーションツールを構築

対象：触媒担体粒子内の細孔（数nm），二次細孔（数十nm～数μm）
手法：格子密度汎関数法 (相変化), 気体拡散 (希薄気体力学), 画像処理 (断面抽出)

実験結果の理解，材料設計指針の提示

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