燃料電池・蓄電池の
電気化学界面シミュレーションのこれまで
の発展とこれから

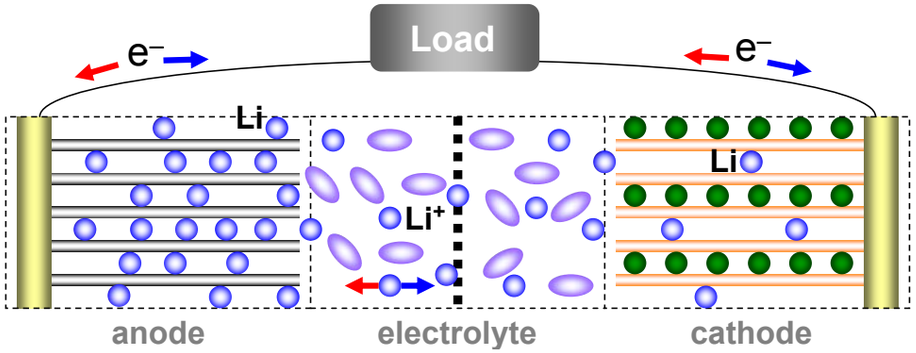
国立研究開発法人　産業技術総合研究所
機能材料コンピュテーショナルデザイン研究センター
大谷　実

Outline

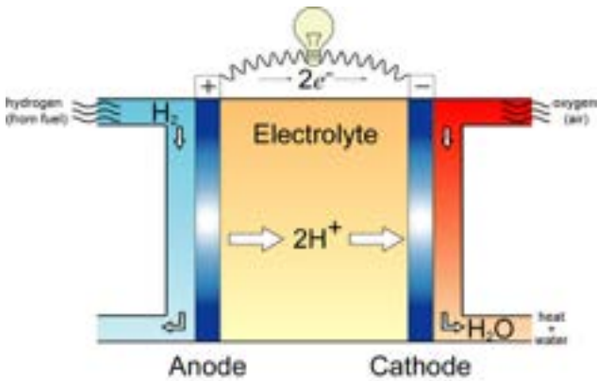
- バックグラウンド・シミュレーション技術の発展
- 電気化学界面シミュレーション事例
  （スーパーキャパシター、燃料電池）
- 現状と今後の展望

Target devices

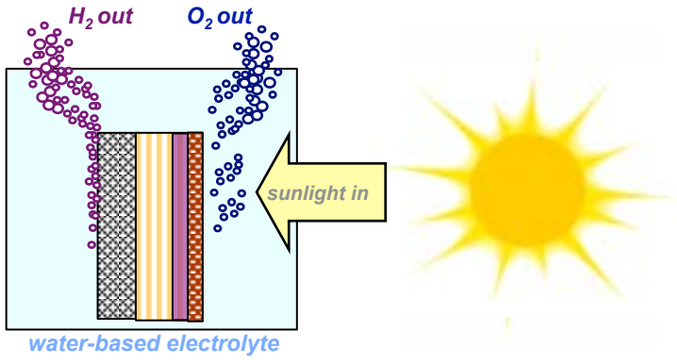
Energy storage



Energy generation



Energy harvesting



Electrochemical devices

<u>Battery</u>
- Manganese dry cell
- Lead battery
- NiCd, NiH secondary battery
- Fuel cell
- Lithium secondary battery

<u>Capacitor</u>
- Electrolytic condenser
- Double layer condenser
- Supercapacitor

<u>Photovoltaic cell</u>
- c-Si, a-Si solar cell
- Dye sensitized solar cell
- photoelectrochemical hydrogen production

<u>Sensor</u>
- pH meter
- ion selective concentration meter
- glucose, etc. (using enzyme)
- gas (oxygen, etc.)

<u>Electroplating</u>

<u>Cathodic protection</u>
- $Fe \rightarrow Fe_2O_3$

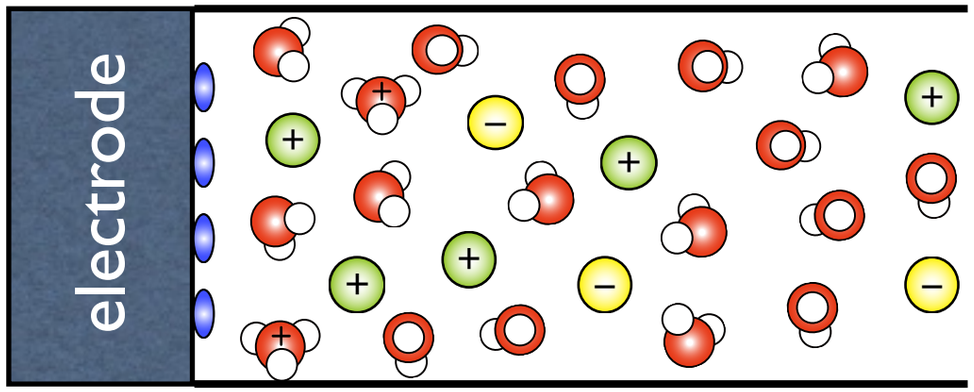
<u>Electrolysis</u>
- Aluminum, Copper, etc.
- Water, salt, etc.
- Organic chemicals
- tetraethyl lead

Challenges in modelling an electrochemical reaction

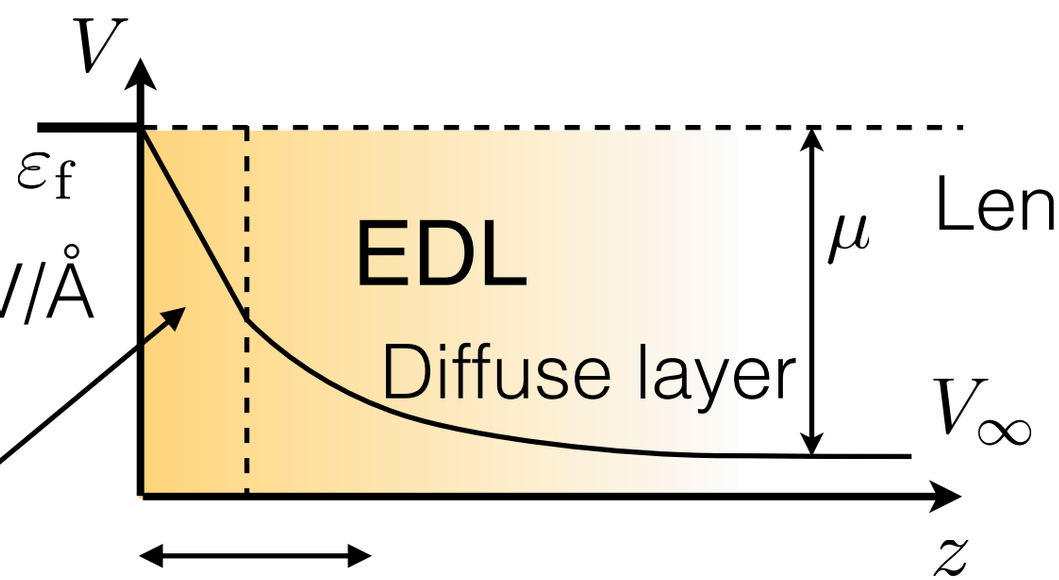
25°C, 1.0M NaCl, Electrode: Pt

4 nm^2 surface area

3-layer Pt(111):
460Pt atoms



1 NaCl / 50 H_2O



Length scale of EDL:
nm ~ μm

Electric field: 0.1~0.5 V/Å

Helmholtz layer: ~Å

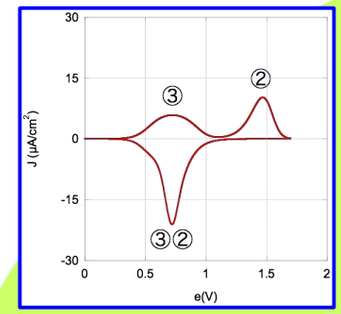
Depth

2 nm: 800 atoms (264 H_2O, 5 NaCl)
10 nm: 5000 atoms (1320 H_2O, 25 NaCl)
0.1 μm: 50000 atoms (13200 H_2O, 250 NaCl)

目標

化学電池性能評価シミュレータ

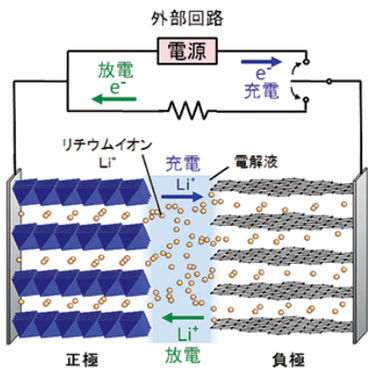
劣化診断・寿命予測

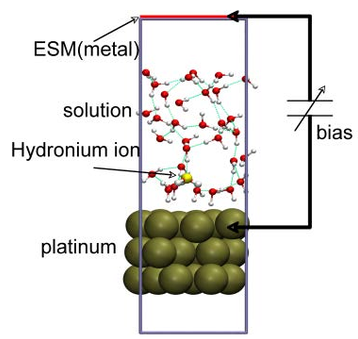


I-V曲線

- CV、LSV曲線
- 充放電曲線
- 交流インピーダンス解析

電気化学反応シミュレーション



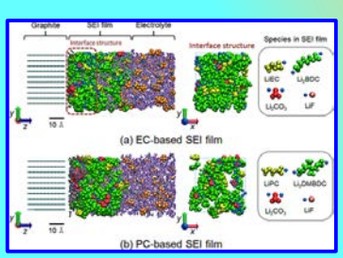


フェーズフィールド法

古典分子動力学法

計算物理、計算化学

電極界面近傍の電気化学反応の量子化学シミュレーション



電池反応

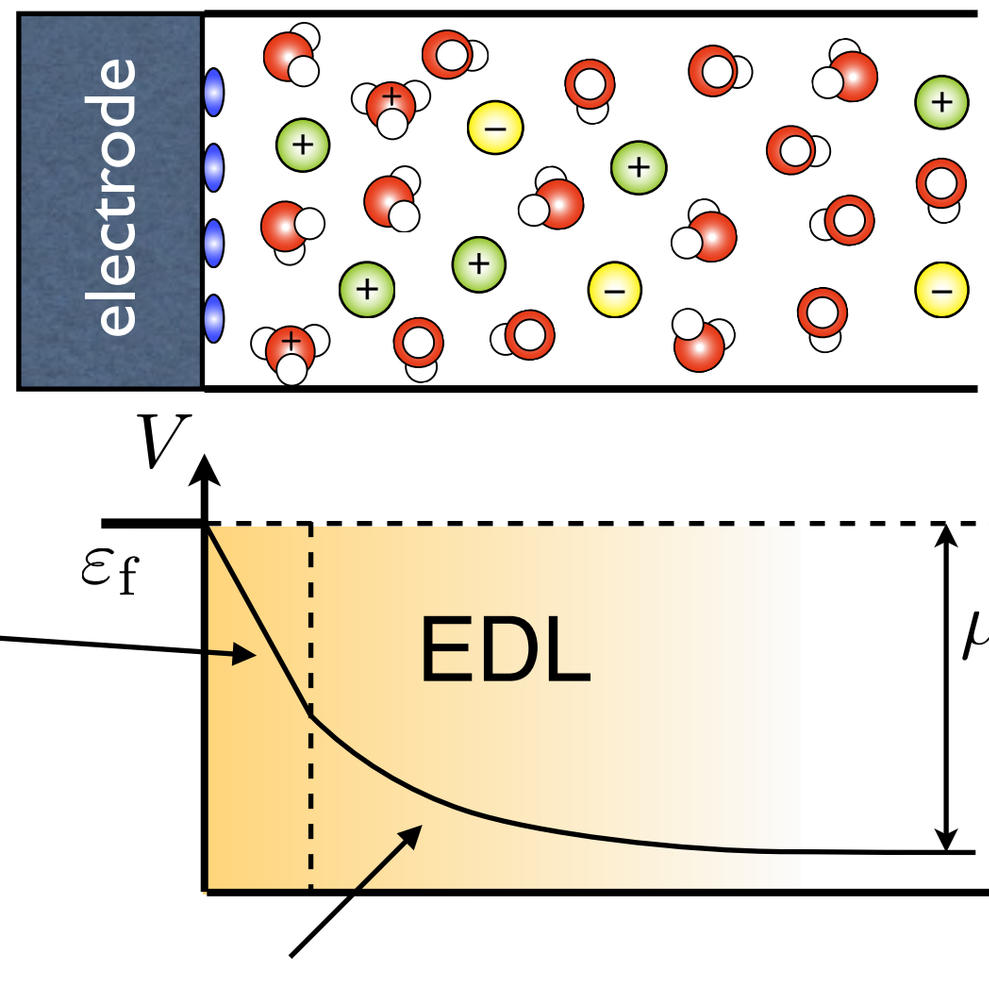
- 自由エネルギー計算
- スペクトロスコピー（XES/XAS・IR）

時間スケール

nm　μm　mm

長さスケール

4 Challenges in modelling an electrochemical reaction for DFT-MD



1. Strong electric field in Helmholtz layer

2. Screening in diffuse layer

3. Origin of electrostatic potential

4. Bias potential control

電気化学界面シミュレーションの課題

1. Strong electric field in Helmholtz layer

Effective Screening Medium method

Phys. Rev. B **73**, 115407 (2006)

2. Screening in diffuse layer

3. Origin of electrostatic potential

Smooth ESM method

Phys. Rev. B **88**, 155427 (2013)

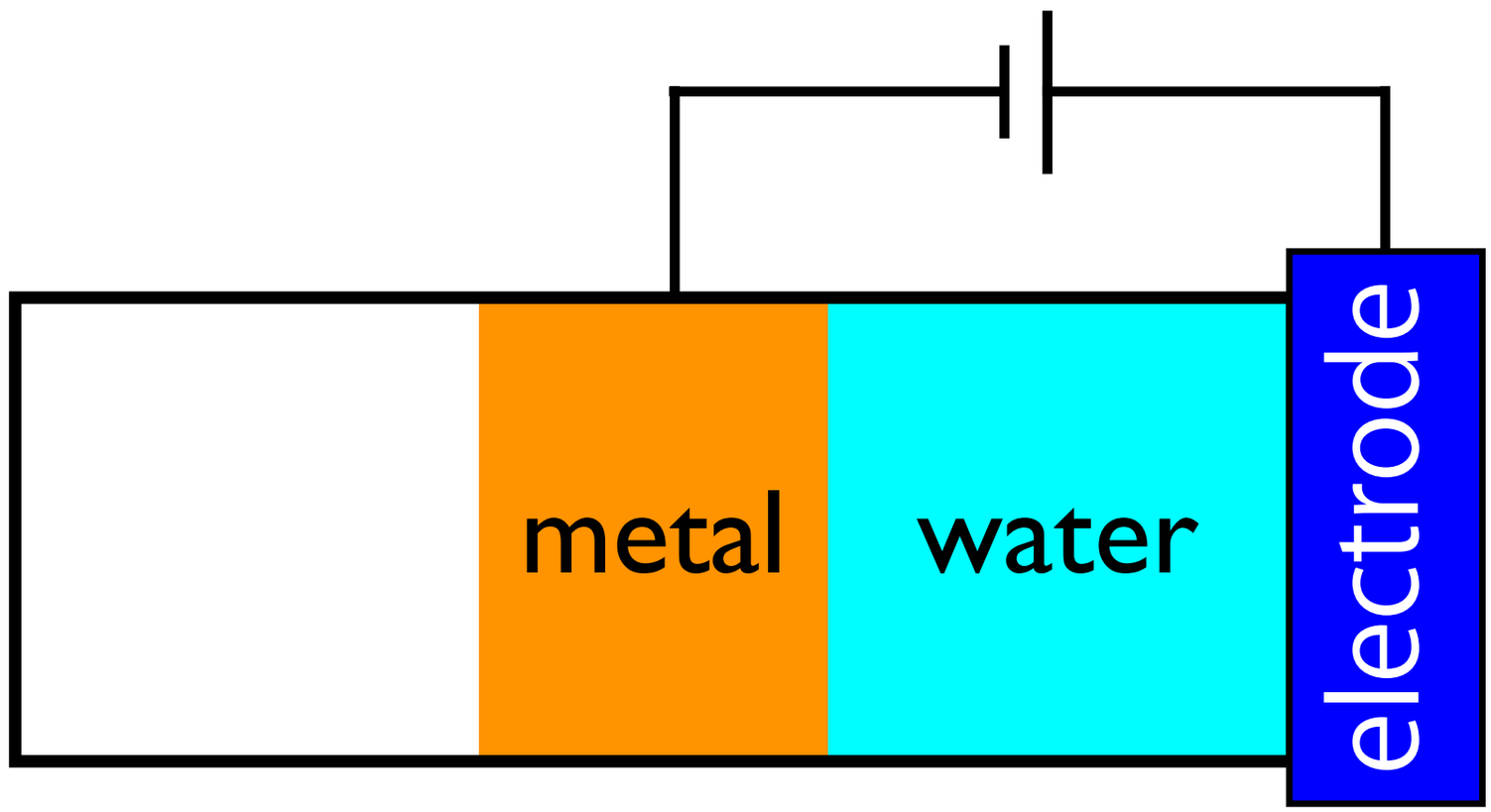
4. Bias potential control

Constant-μ method

Phys. Rev. Lett. **109**, 266101 (2012)

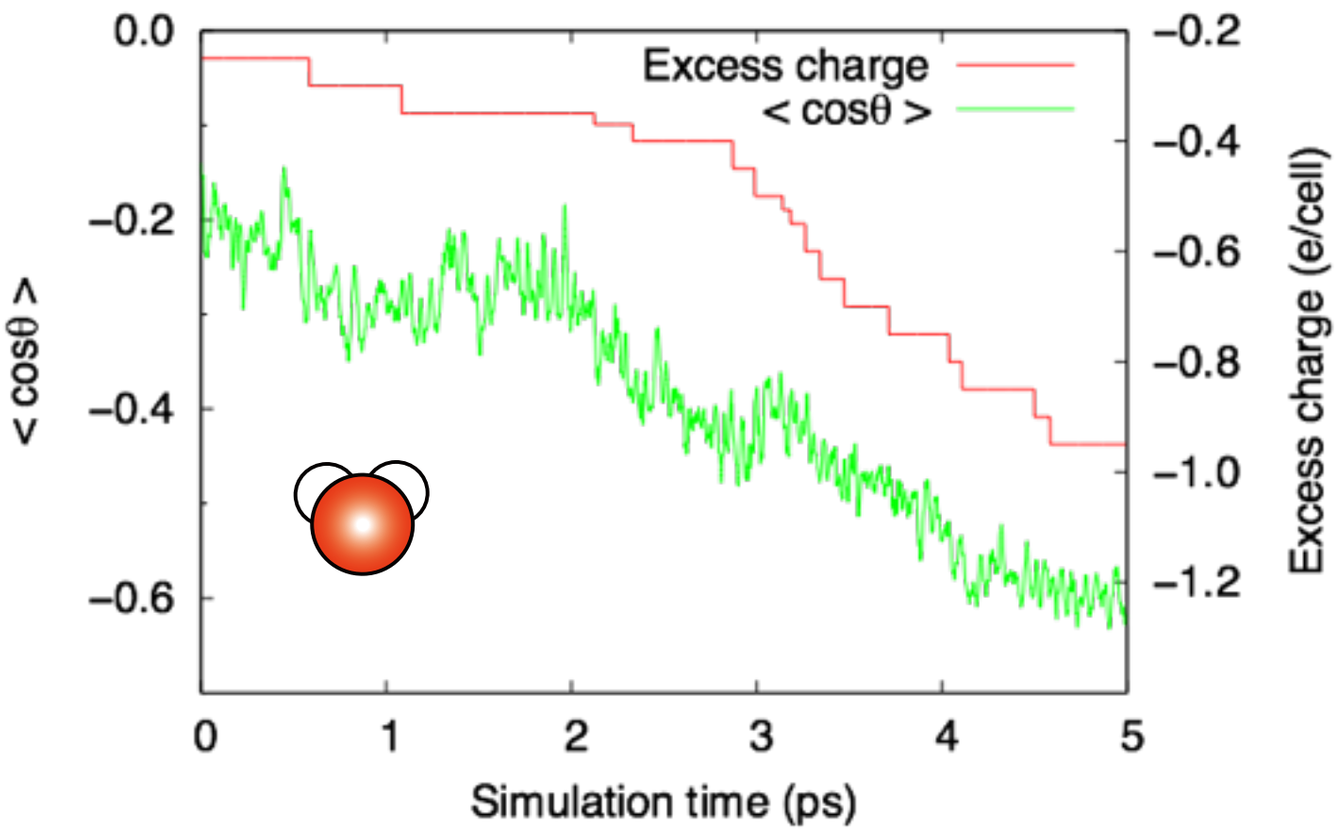
ESMとは？

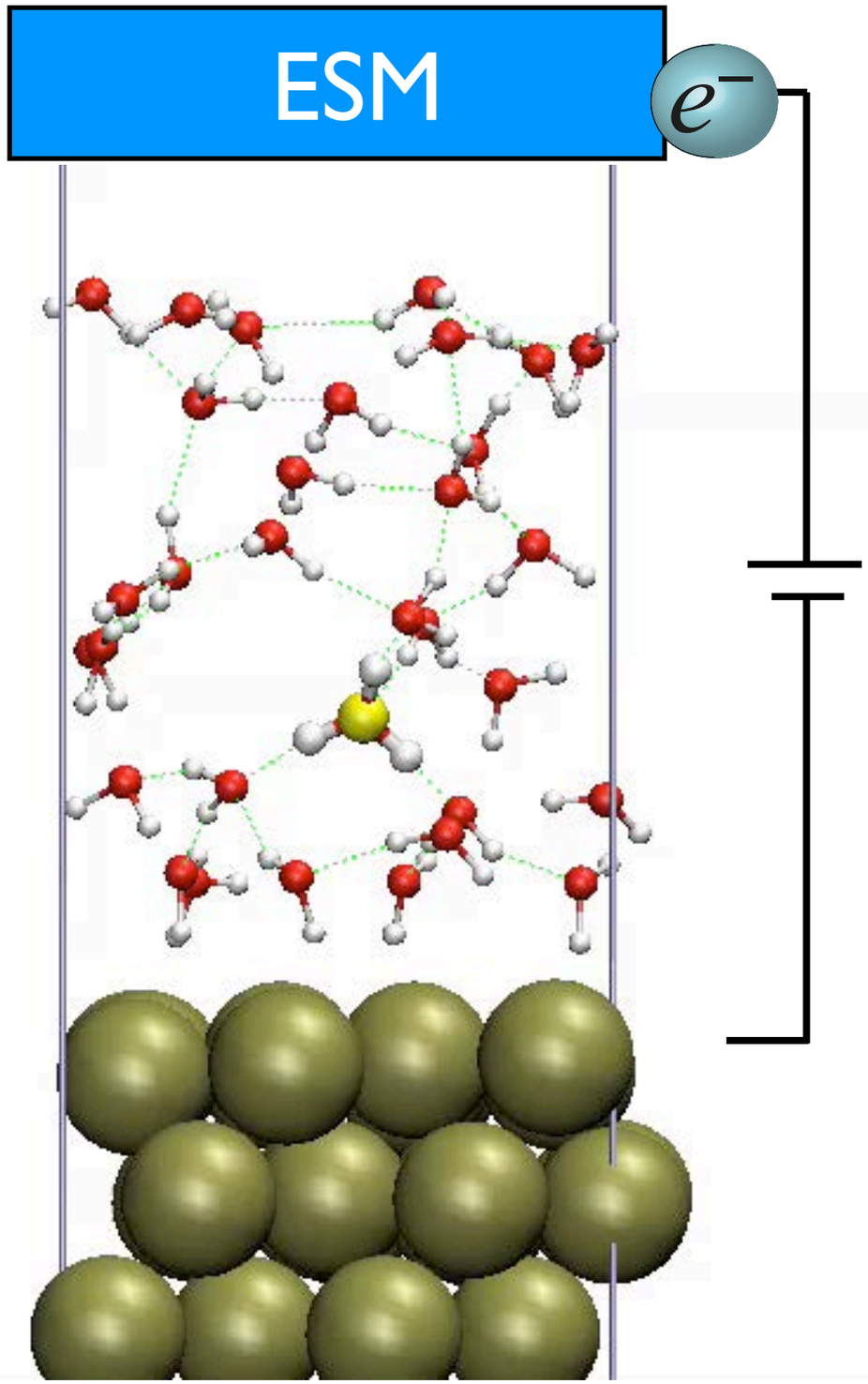
従来のDFT計算のプログラムを用いて電池・キャパシタ構造の電子状態計算を可能になる



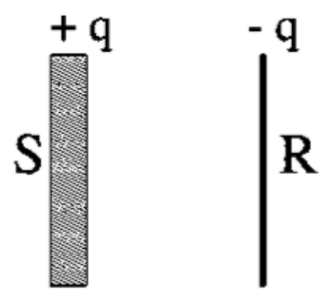
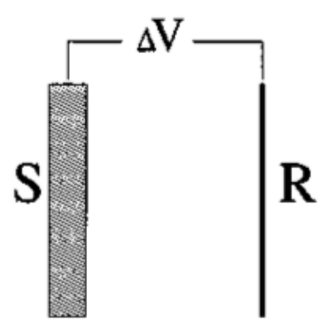
従来の方法では周期境界を課すので、外側に電極を置くような計算はできなかった

ESM法を用いたシミュレーションの様子





Limitation of the original conventional DFT-MD

Mode	Scheme	Thermodynamic potential	Experimental realization
$N_e = \text{const}$		$F(T, V, N_e)$	Isolated capacitor
$\mu = \text{const}$		$\Omega(T, V, \mu)$	Electrochemistry (STM)

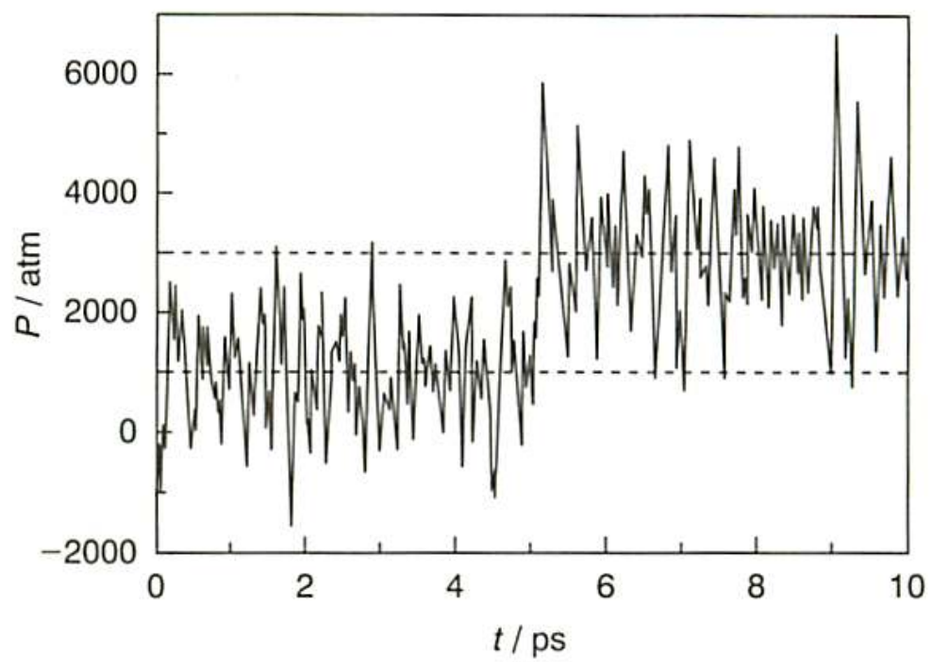
conventional simulation

experimental simulation

A. Lozovoi et al., JCP 115, 1661 (2001)

電子系のグランドカノニカルアンサンブル法

Conventional NPT MD simulation



v_{cell} : Cell volume

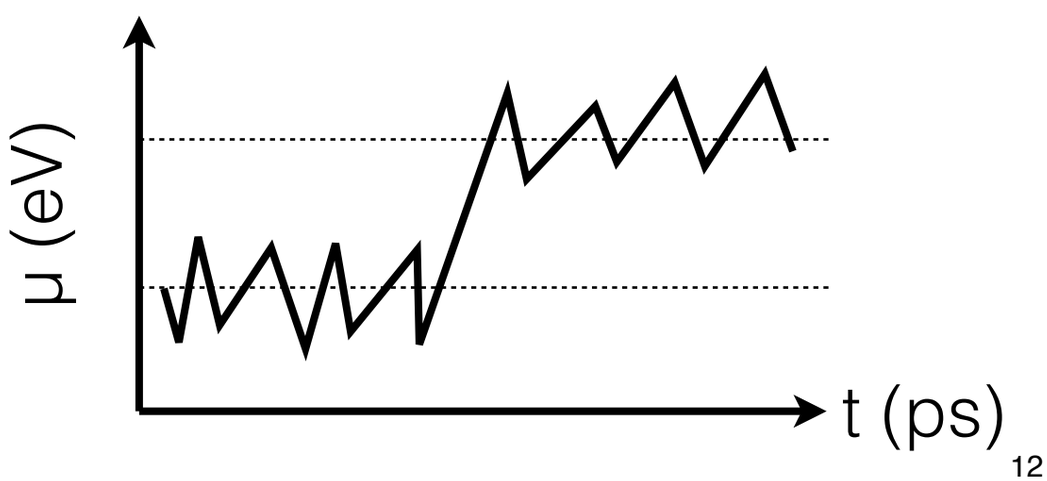
$M_{v_{\mathrm{cell}}}$: Fictitious mass for variable cell

$$\dot{v}_{\mathrm{cell}} = \frac{P_{v_{\mathrm{cell}}}}{M_{v_{\mathrm{cell}}}}$$

$$\dot{P}_{v_{\mathrm{cell}}} = P - P_{\mathrm{ext}}$$

from Virial theorem

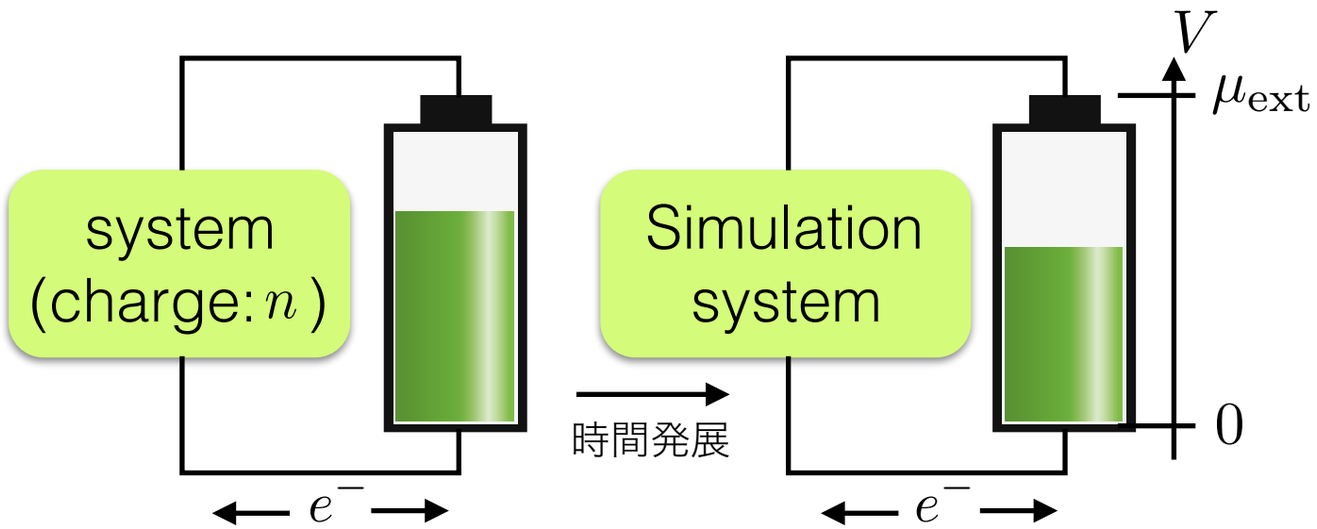
If we can introduce a fictitious motion for amount of charge n_e, we can realize NVTμe MD simulation



$$\dot{n}_{\mathrm{cell}} = \frac{P_{n_{\mathrm{cell}}}}{M_{n_{\mathrm{cell}}}}$$

$$\dot{P}_{n_{\mathrm{cell}}} = \mu - \mu_{\mathrm{ext}}$$

定電位手法



- 系の電荷量（n）を運動の変数とする
- Potentiostatを接続し、systemの電位を $\mu_{\rm ext}$ に保つ

仮想的なLagrangianを導入

$$L_\mu = \frac{1}{2}\sum_i^N m_i \dot{\boldsymbol{r}}_i^2 - E(\{\boldsymbol{r}\};\psi) + \frac{1}{2}M\dot{n}^2 - (-\mu_{\rm ext} n)$$

ここで、 M は電荷量の仮想的な重さを表す。Euler-Lagrange方程式は

$$\begin{cases} m_i \ddot{\boldsymbol{r}}_i = -\dfrac{\partial E(\{\boldsymbol{r}_i\};\psi)}{\partial \boldsymbol{r}_i} \\ M\ddot{n} = -\left(\boxed{\dfrac{\partial E(\{\boldsymbol{r}_i\};\psi)}{\partial n}} - \mu_{\rm ext}\right) \end{cases}$$

瞬間的な電子系の電位 $\mu_{\rm in}$

となる。

N. Bonnet et al., Phys. Rev. Lett. 109, 266101 (2012)

Test calculation (Pt-H_2O interface)

constant-N

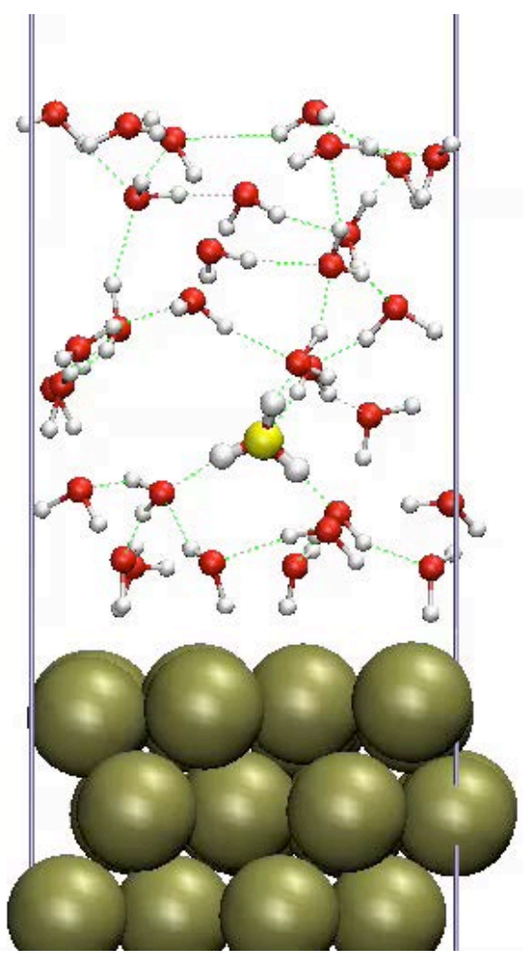
$T_{\mathrm{atom}} = 353$ K
$Q = 0.35$ (e/cell)

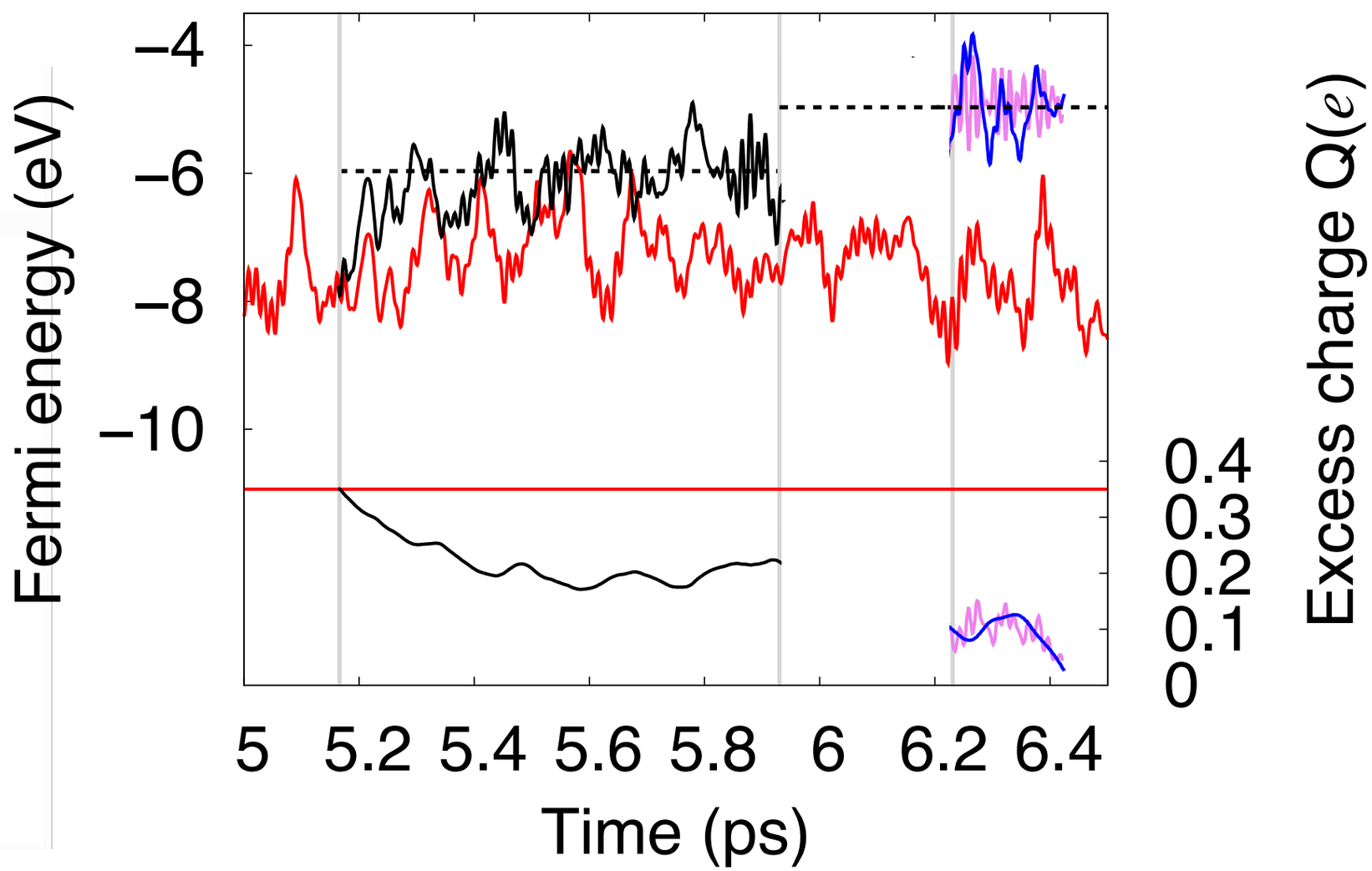
constant-μ

$\mu_{\mathrm{ext}} = -6.0 \rightarrow -4.9$ eV
$T = 3$ K
$M_{n_e} = 300$ cm^{-1}
$M_{\xi_c} = 100$ cm^{-1}

$\mu_{\mathrm{ext}} = -4.9$ eV
$T = 3$ K
$M_{n_e} = 2500$ cm^{-1}
$M_{\xi_c} = 100$ cm^{-1}

$\mu_{\mathrm{ext}} = -4.9$ eV
$T = 300$ K
$M_{n_e} = 300$ cm^{-1}
$M_{\xi_c} = 100$ cm^{-1}





Experimental technique on electrochemical devices

in situ spectroscopy

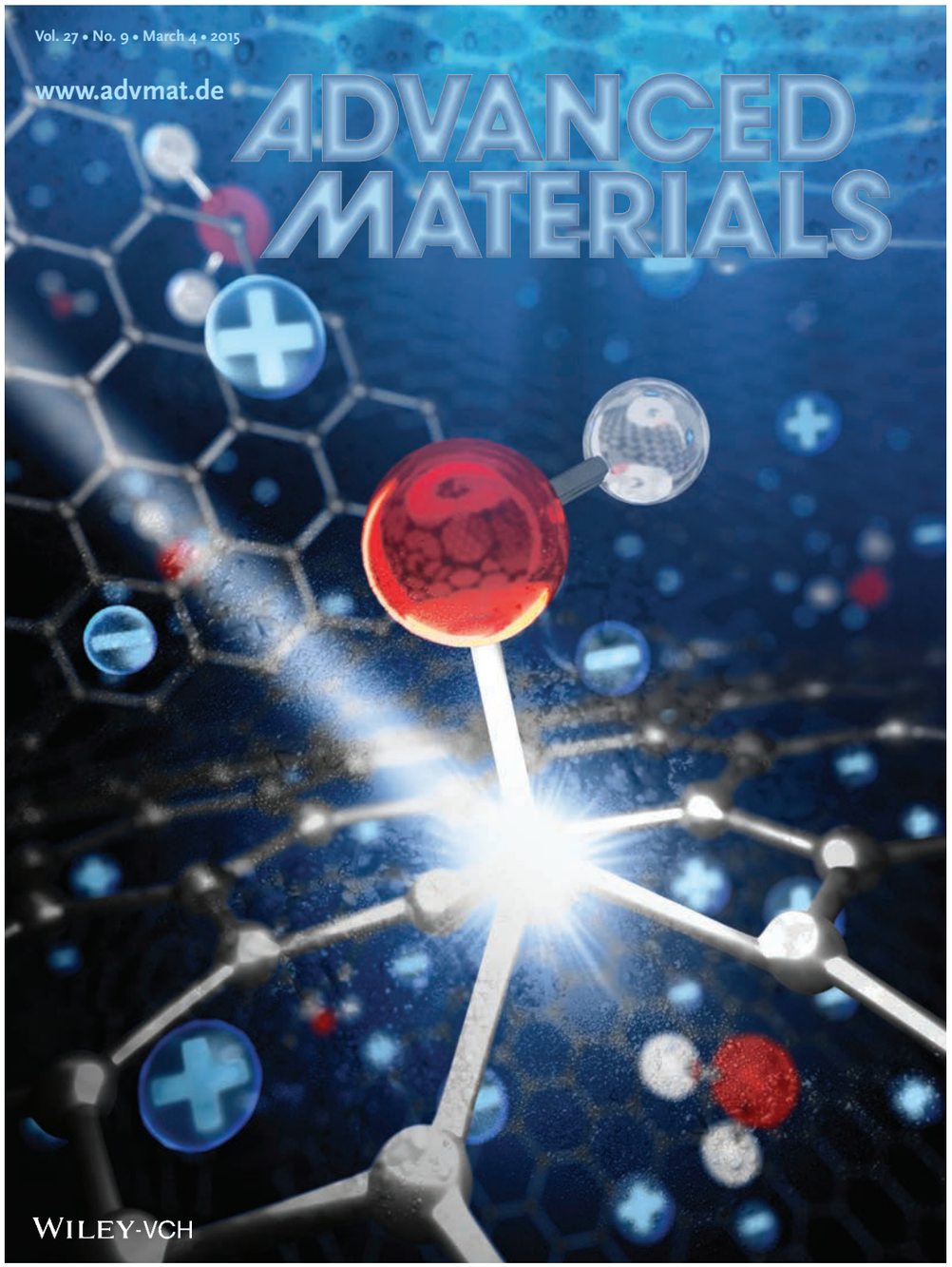
- X-ray emission/absorption spectroscopy (XES/XAS)
- Raman spectroscopy
- Infrared spectroscopy (IR)
- Auger electron spectroscopy (AES)
- etc…

I-V characteristic

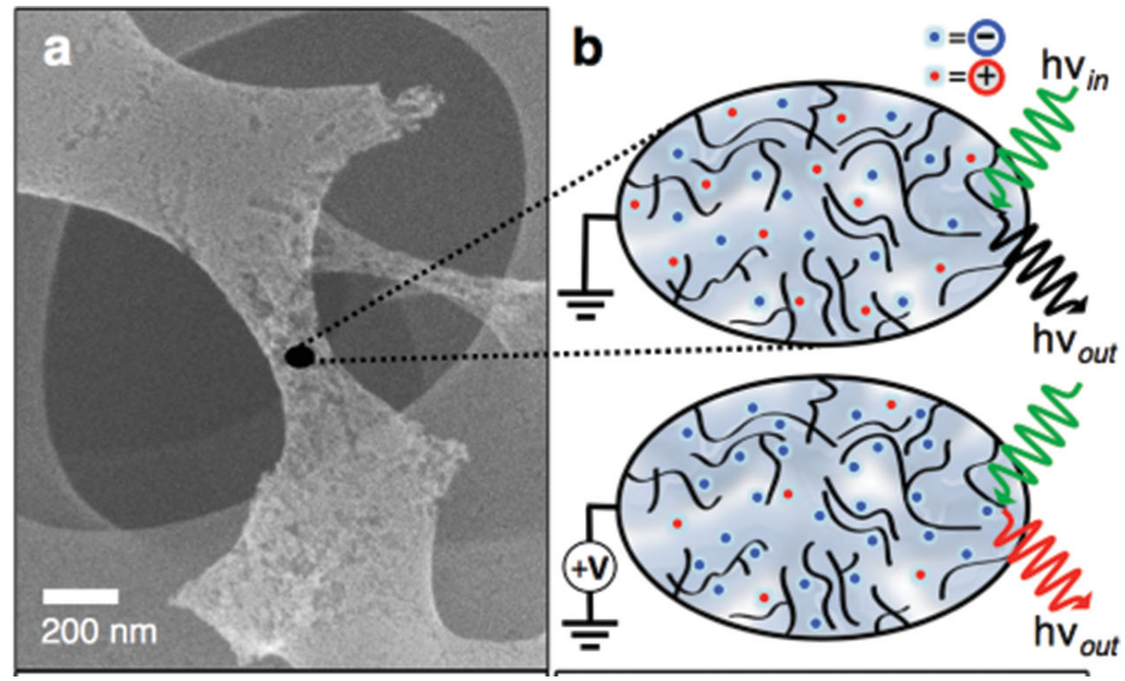
- Cyclic voltammetry (CV)
- Linear sweep voltammetry (LSV)
- Charge/discharge characteristic
- Impedance spectroscopy
- etc…

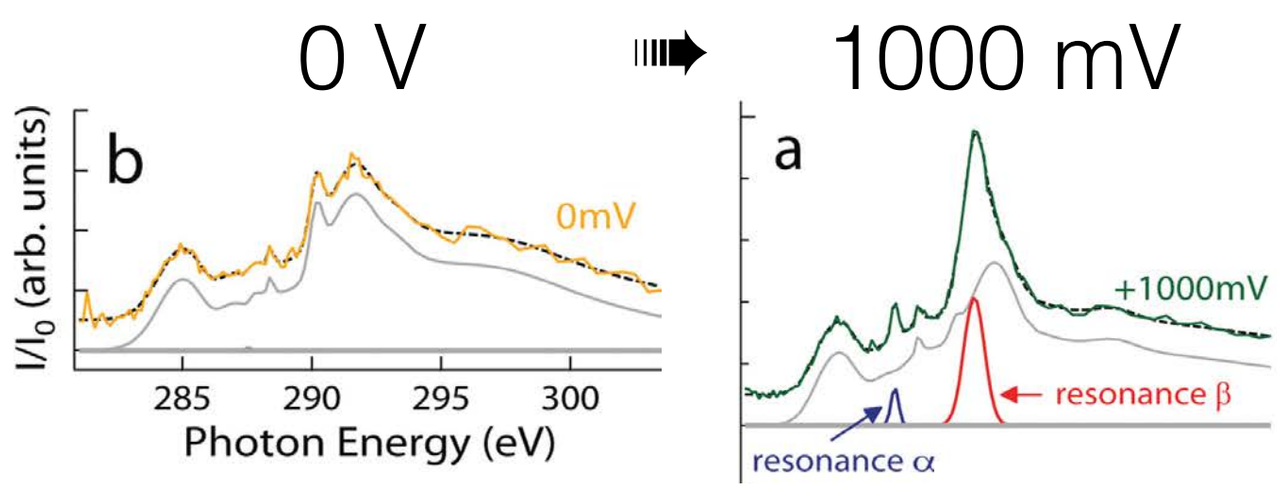
動作環境下における第一原理
シミュレーションが可能に

XAS analysis of carbon aerogel super capacitor



Advanced Materials **27**, 1512 (2015)





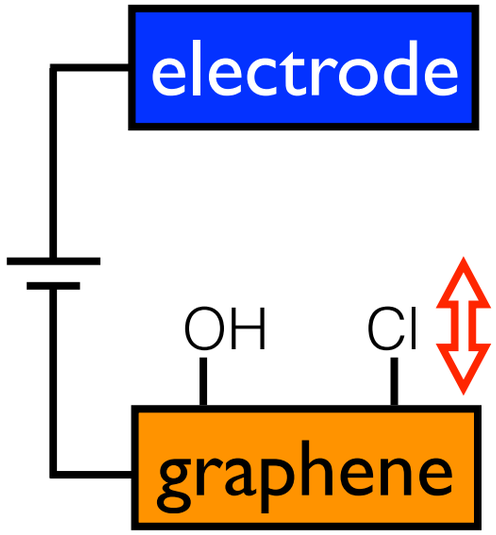
Newly developed XAS technique reveals the bias induced changes of the electronic structure of the electrode.

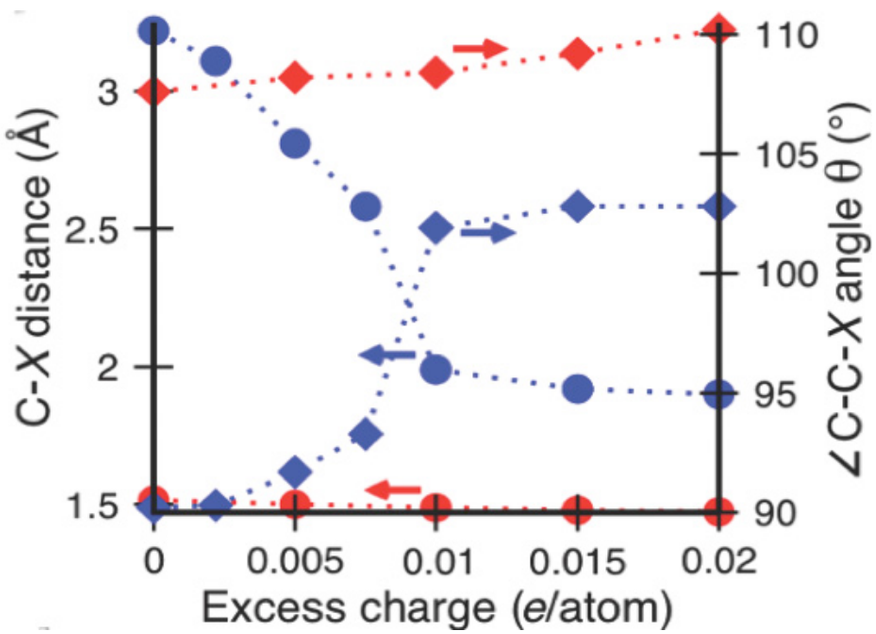
XAS analysis of carbon aerogel super capacitor

Advanced Materials **27**, 1512 (2015)

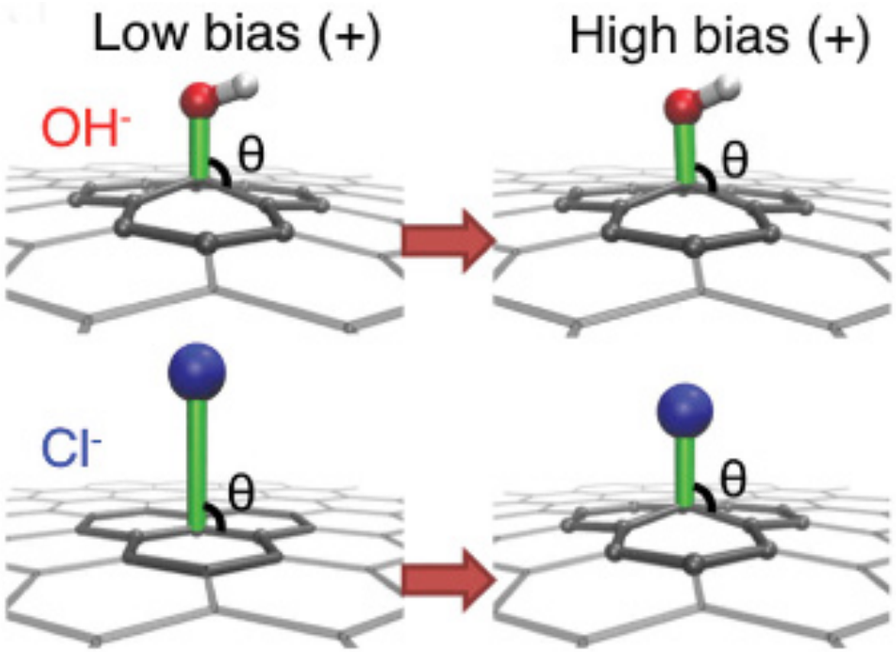
XAS spectral calculation with quantum espresso package

http://www.quantum-espresso.org





Low bias High bias



Cl^-は印可電圧による表面状態変化を誘発しやすい

Experimental technique on electrochemical devices

in situ spectroscopy

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I-V characteristic

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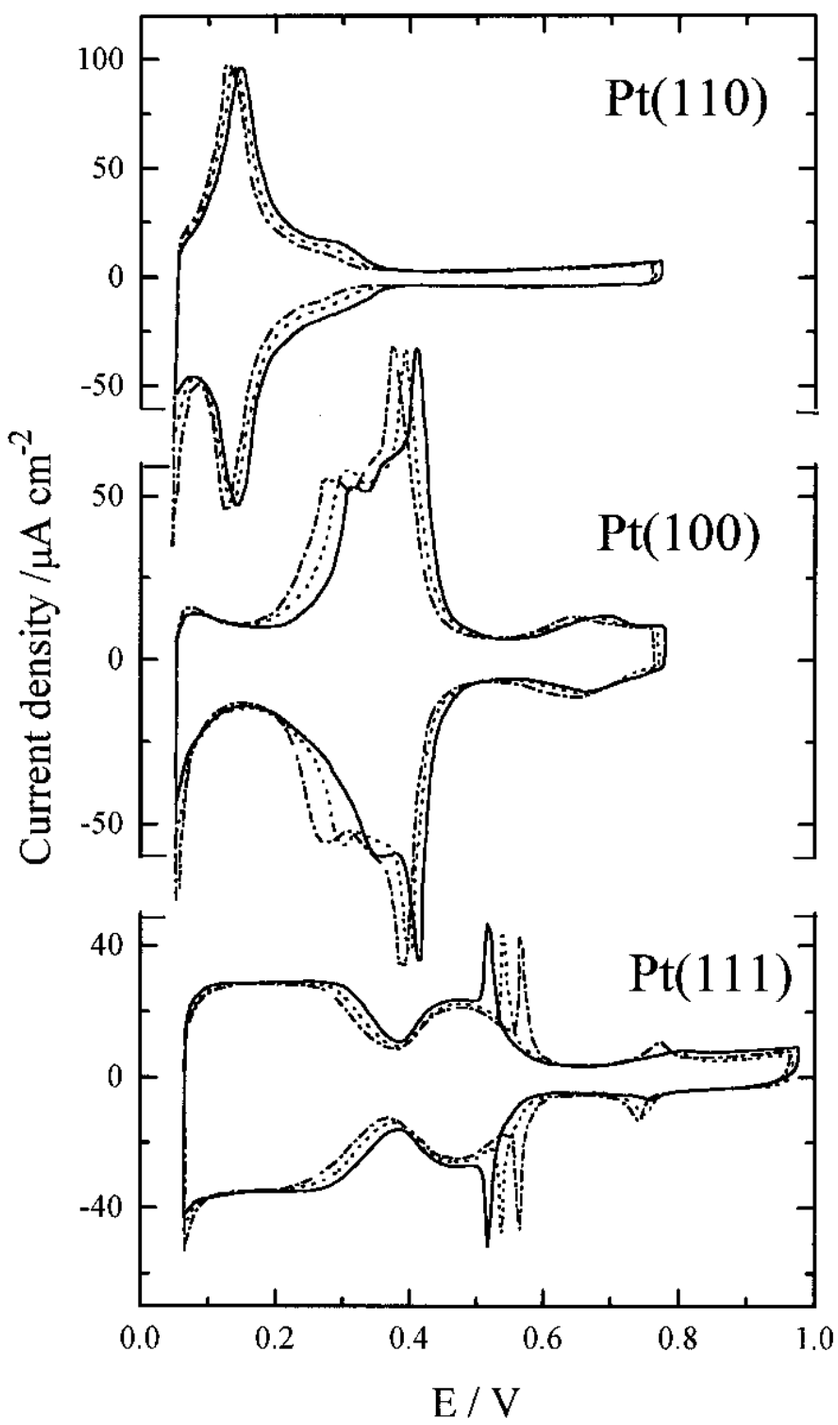
動作環境下における第一原理
シミュレーションが可能に

面方位で異なる反応



水の電気分解／燃料電池反応

$$2H_2O \rightarrow O_2 + 2H_2$$

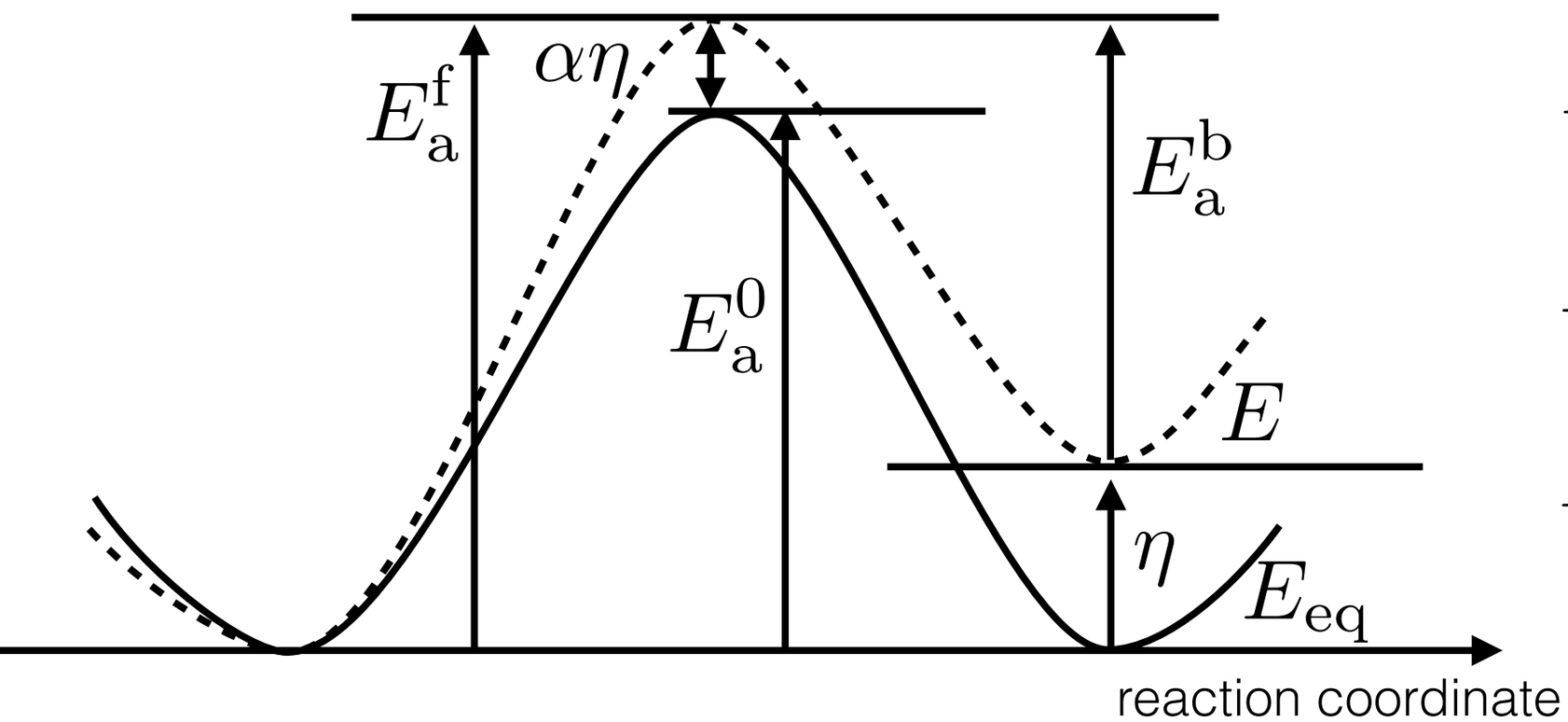
- 陰極
  $$4H^+ + 4e^- \rightarrow 2H_2$$
- 陽極
  $$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$$

Pt(*hkl*)	mechanism **rds**
Pt(110)	**Tafel**−Volmer
Pt(100)	**Heyrovsky**−Volmer
Pt(111)	Tafel−Volmer, Heyrovsky−Volmer

Markovic et.al., J. Phys. Chem. B 101, 5405 (1997)

Kinetic analysis

Energy profile of an electrochemical reaction



E : electrode potential

E_{eq} : equilibrium potential

E_{a}^{0} : activation energy at equilibrium

$E_{\mathrm{a}}^{\mathrm{f}}$: activation energy of forward reaction

$E_{\mathrm{a}}^{\mathrm{b}}$: activation energy of backward reaction

η : over potential

α : symmetry factor

I-V characteristic

✓What do we need to simulate the I-V characteristic:

- Nernst equation

$$E_{\mathrm{eq}} = \boxed{E_0} + \frac{RT}{nF} \log\left(\frac{c_{\mathrm{ox}}}{c_{\mathrm{red}}}\right)$$

First principles molecular dynamics simulation

- Butler-Volmer equation

$$j = j_0 \left\{ \exp\left(\frac{(1-\alpha)(E-E_{\mathrm{eq}})}{RT}\right) - \exp\left(-\frac{\alpha(E-E_{\mathrm{eq}})}{RT}\right) \right\} \quad j_0 = \boxed{k} \exp\left(-\frac{\boxed{E_a}}{RT}\right)$$

$$\frac{k_{\mathrm{B}}T}{h} \sim 245\ \mathrm{cm}^{-1}$$

from Eyring theory

- Diffusion equation

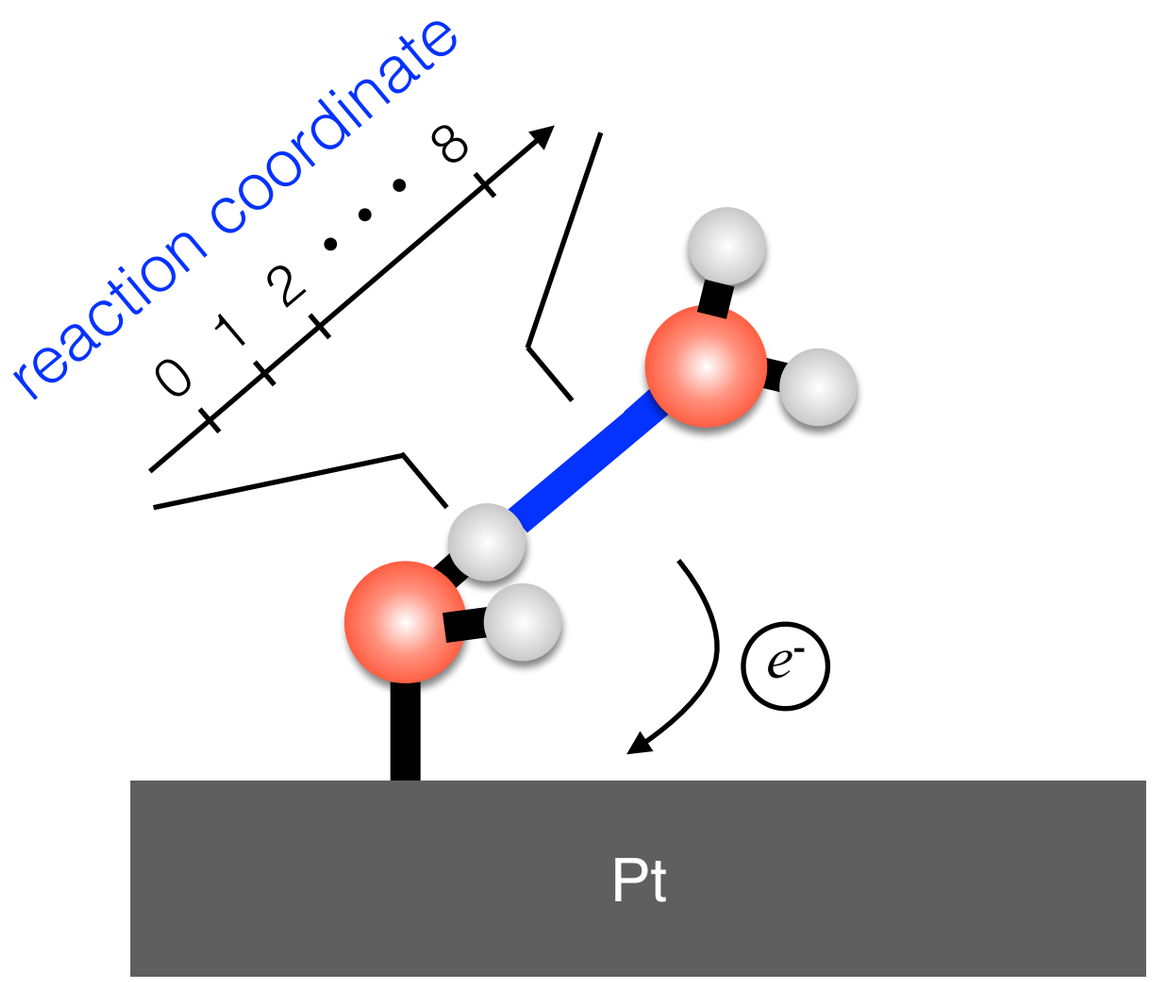
$$\frac{\partial c}{\partial x} = -\boxed{D}\frac{\partial^2 c}{\partial x^2}$$

from experiment, classical MD, FPMD,…

Free energy profile

① $\mathrm{Pt} + \mathrm{H_2O} \leftrightharpoons \mathrm{PtOH} + \mathrm{H^+} + e^-$

Free energy & charge



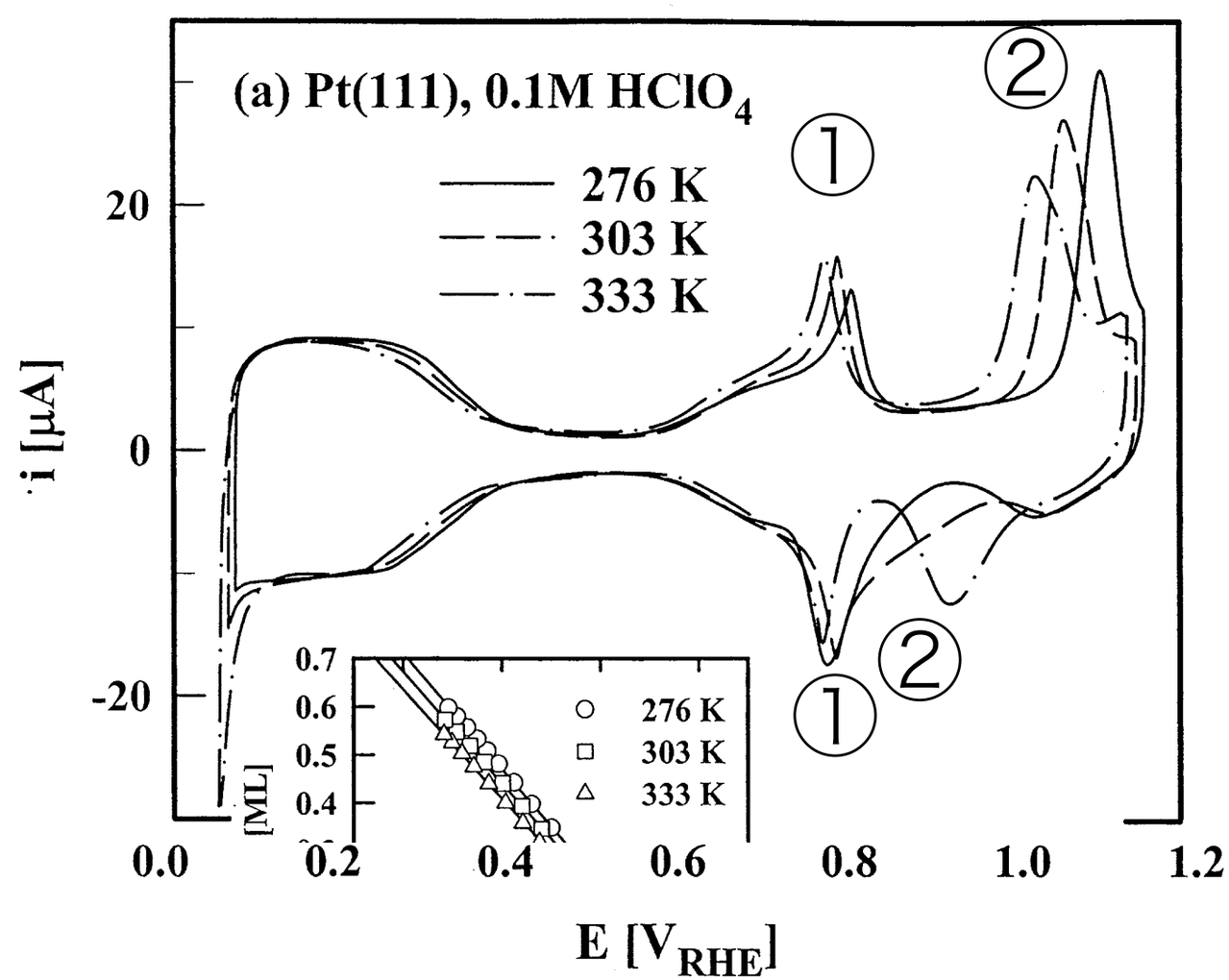
OH distance (Å)

$E_a^f = 0.14$ eV $\quad E_a^b = 0.12$ eV

μ_{ext}=-7.08eV

CV curve of Pt(111)

- ESM+BM calculation can reproduce the CV curve

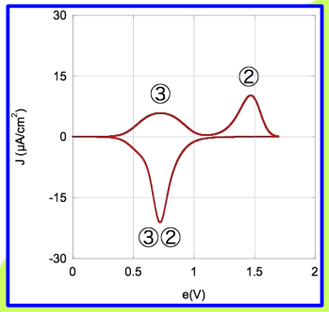


T. Ikeshoji, et al., in preparation

現状

化学電池性能評価シミュレータ

劣化診断・寿命予測



I-V曲線

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- 充放電曲線
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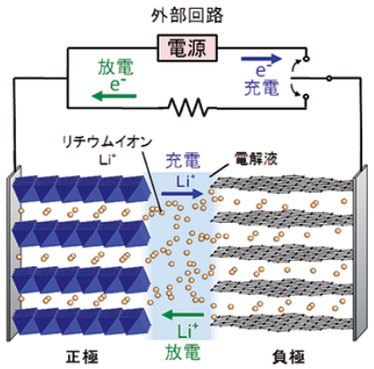
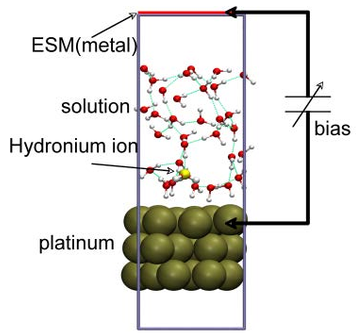
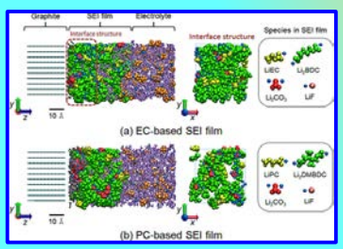
電気化学反応シミュレーション





計算物理、計算化学

電極界面近傍の電気化学反応の量子化学シミュレーション



電池反応

- 自由エネルギー計算
- スペクトロスコピー（XES/XAS・IR）

フェーズフィールド法

古典分子動力学法

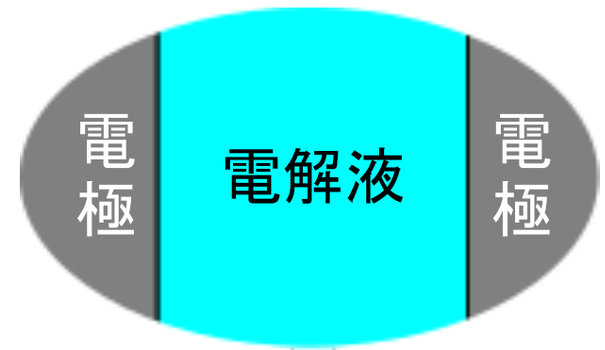
速度論を用いてバイパス

時間スケール

nm　μm　mm

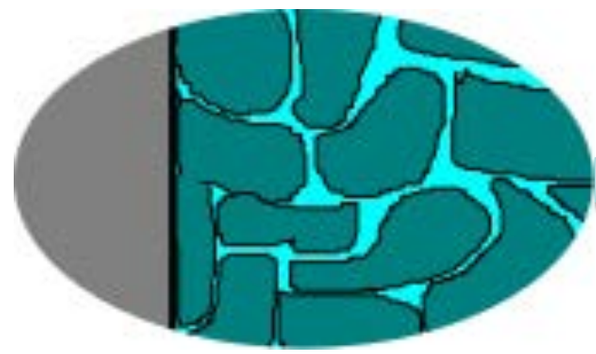
長さスケール

将来



SEI中のイオン拡散をシミュレーション。アモルファス・ポリマー中の反応解析及び、拡散経路探索。電位依存性も考慮

電池特性や劣化の支配因子を明らかにし、性能改善のための設計指針を提示する



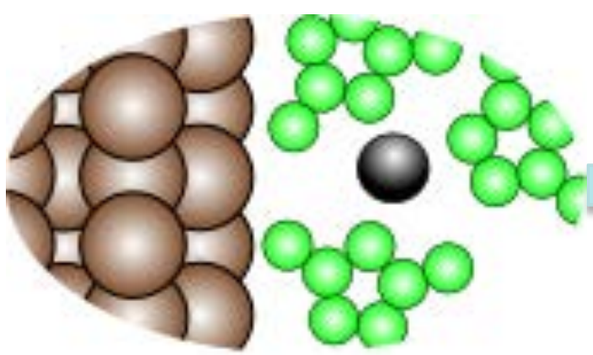
マクロ界面

~sub-μm

・実験データ
・古典分子動力学データ

電池シミュレータ

電位を制御しながら第一原理計算を行い、電極界面における電気化学反応を正確にシミュレーション



ミクロ界面

~nm

未知材料及び実験データ取得が困難なパラメータを第一原理計算をベースに計算する

・CV、LSV曲線
・充放電曲線
・交流インピーダンス解析

Collaborators

Method development

- Osamu Sugino (ISSP)
- Nicephore Bonnet
- Tetsuya Morishita (AIST)
- Ikutaro Hamada (NIMS)
- Hu Chunping (AIST)

Fuel cell

- Tamio Ikeshoji (FC-Cubic)
- Yoshitada Morikawa (Osaka U.)

Lithium ion battery

- Tsukuru Ohwaki (NISSAN ARC)
- Taisuke Ozaki (U. Tokyo)

Super capacitor

- Tadashi Ogitsu (LLNL)
- Brandon Wood (LLNL)
- David Prendergast (LBNL)

Computer resources

- KEI-computer
- ISSP (U Tokyo)
- ITC (U Tokyo)