SECA 6th Annual Workshop, April 18, 2005

~~Application of Quantum Methods to High Temperature Fuel Cell Materials~~

Use of first principles based modeling and simulation to characterize, design, and optimize new strategies for fuel cell technologies

applications to solid oxide, solid acid, and PEM fuel cells, cathode catalysts, anode catalysts, 3-phase interface

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Types of Fuel Cells we are studying with first principles

Proton Exchange Membrane Fuel Cells – Nafion – Pt, Pt_3Co

PEM FC with new membranes 100-200C

Solid Acid Fuel Cells – $RbHSeO_4$

Proton Ceramic Fuel Cells – $Ba(ZrY)O_3$

Solid Oxide Fuel Cells – $Ni/YZrO_2$

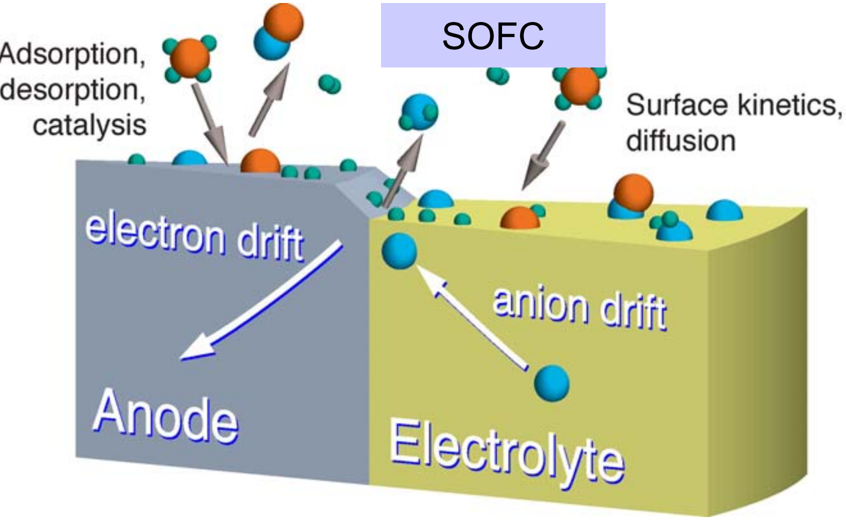
Low-temperature Fuel Cells

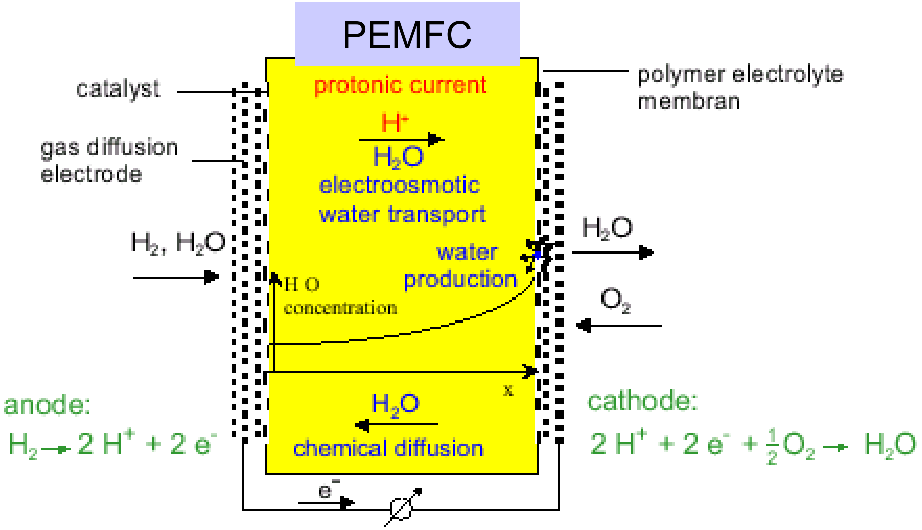
Medium-temperature Fuel Cells

High-temperature Fuel Cells

Why use first principles in modeling?

Probably everyone in fuel cell technologies uses some sort of modeling to estimate changes of performance expected from changes in design





Problem: even for well studied FC there remain **tremendous uncertainties in fundamental rates** and how they depend on materials and processing. Often even the **fundamental mechanisms are uncertain**; processes involved with aging are generally unknown

Solution: To develop optimum materials and processes and to maintain optimum performance as conditions change, it is essential to determine the fundamental mechanisms and to determine how these steps control the macro level performance. This requires **first principles (no use of empirical data)**

Is the use of first principles for practical fuel cell problems possible?

First principles ➔ quantum mechanics (~100 atoms) → 1 day to do 1 picosecond (10^{-12} sec) of dynamics

Fuel cell $(1\text{mm})^3$ ➔ ~ 10^{20} atoms → 10^{48} days to do one second of dynamics

Obviously, this is NOT practical

Solution? Multiple paradigms with overlapping scales

QM up to 10^2 atoms; use to derive force field for MD

MD up to 10^6 atoms; use to derive coarse grain (bead) description for mesoscale

Mesoscale dynamics up to 10^6 beads or 10^9 atoms; use to derive constitutive equations, rate constants, conductivities, diffusion rates required for macro modeling

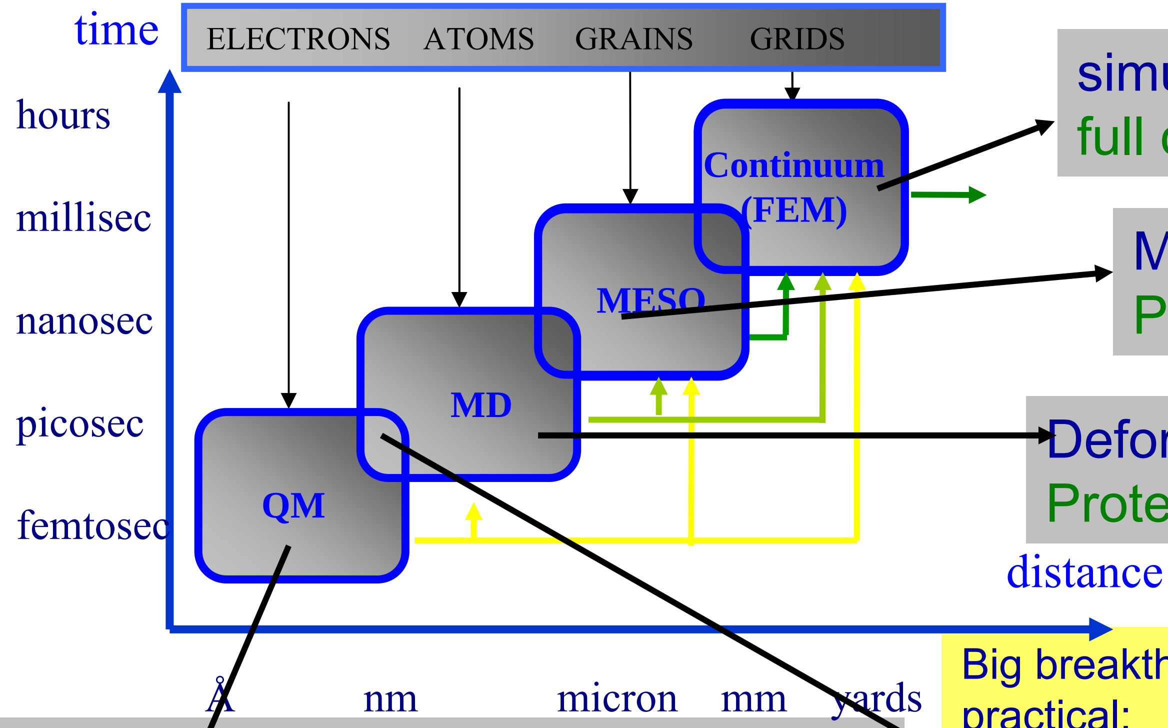
Continuum simulations using parameters from meso dynamics to describe device performance

1st Principles Design of Materials, Pharma, Catalysts

Need simulations of macroscale systems to be of 1st Principles quality, so can predict NEW materials never before synthesized and optimize them

1st Principles→ connect Macro to QM. Strategy use an overlapping hierarchy of methods (paradigms) (fine scale to coarse)

Allows Design of new materials and drugs (predict hard to measure properties)



simulations real devices and full cell (systems biology)

Micromechanical modeling
Protein clusters

Deformation and Failure
Protein Structure and Function

Accurate calculations for bulk phases and molecules (EOS, bond dissociation)
Chemical Reactions (P-450 oxidation)

Big breakthrough making FC simulations practical:
reactive force fields based on QM
Describes: chemistry,charge transfer, etc. For metals, oxides, organics.

Applications using a hierarchical multiparadigm strategy

BIOTECHNOLGY: Membrane Proteins (GPCR), non-natural Amino Acids, Pharma (VLS)

NANOSYSTEMS: Nanoelectronics, Devices based on Carbon Nanotubes or DNA

CATALYSTS: Methane Activation, Selective Oxidation, ElectroCat (O_2), Polar Olefins

SEMICONDUCTORS: Dielectric Breakdown, $Si/SiO_2/Si_3N_4$ interfaces, B diffusion

CERAMICS: Ferroelectrics, Zeolites, Exfoliation Clays

POLYMERS: PEM (Nafion), Dendrimers, Gas diffusion, Surface Tension, Biobased

METAL ALLOYS: Glass Formation, Plasticity (dislocations, crack propagation, spall)

ENVIRONMENTAL: Dendrimers for Selective Encapsulation, Humic acid

INDUSTRIAL APPLICATIONS (SonafiAventis, ChevronTexaco, Berlex Biopharma, Nissan, Intel)

- Polymers: Gas Diffusion, Surface Tension Modification, Water solubility
- Polymerization Catalysts for Polar Monomers
- Catalysts: CH_4 activation, Alkylation phenols, zeolites (Acid sites/templates)
- Semiconductors: Dielectric Breakdown nanometer oxides, nitrides, B Diffusion in Si
- Automobile Engines: Wear Inhibitors (iron and aluminum based engines)
- Oil Pipelines: Inhibitors for Corrosion , Scale, Wax; Hydrates, Demulsifiers
- Oil Fields: Surfactants for low water/oil interface energy, Basin models
- Electronics: Carbon nanotube interconnects
- Catalysts: ammoxidation of propane
- Fuel Cells: H_2 Storage, Polymer Electrolyte Membranes, Electrocatalysis

MultiParadigm Strategy enables application of 1st principles to complex systems

Collaborations with Industry
Stimulation to Solve Impossible Problems

- Aventis Pharma: Structures and Function of GPCRs
- Berlex Biopharma: Structures and Function of CCR1 and CCR5 (GPCRs)
- Chevron Corporation: CH_4 to CH_3OH, Wax Inhibition/oil pipelines
- GM advanced propulsion: Fuel Cells (H_2 storage, membranes, cathode)
- Nissan Motor Co: Wear Inhibition in Automobile Engines (DLC)
- Intel Corp: Carbon Nanotube Interconnects

Previous

- Asahi Glass: Fluorinated Polymers and Ceramics
- Asahi Kasei: Ammoxidation Catalysis, polymer properties
- Avery-Dennison: Nanocomposites for computer screens Adhesives, Catalysis
- BP: Heterogeneous Catalysis (alkanes to chemicals, EO)
- Dow Chemical: Microstructure copolymers, Catalysis polymerize polar olefins
- Exxon Corporation: Catalysis (Reforming to obtain High cetane diesel fuel)
- General Motors - Wear inhibition in Aluminum engines
- Hughes Satellites/Raytheon: Carbon Based MEMS
- Hughes Research Labs: Hg Compounds for HgCdTe from MOMBE
- Kellogg: Carbohydrates/sugars (corn flakes) Structures, water content
- 3M: Surface Tension and structure of polymers
- Nippon Steel: $CO + H_2$ to CH_3OH over metal catalysts
- Owens-Corning: Fiberglas (coupling of matrix to fiber)
- Saudi Aramco: Up-Stream additives (Demulsifiers, Asphaltenes)

Each project (3 Years) supports full time postdoc and part of a senior scientist

Multiscale simulation essential for industrial applications

Role of Computation and Theory in Fuel Cell Technology

We contend that **computational** chemistry and computational materials science are **essential** for developing **new solutions to fuel cell technologies**

Use theory to **postulate novel** combinations of **materials** with improved properties

Use computation to **test and optimize the designs** by predicting structures and performance.

Use **experiment to test optimized designs** by synthesis and characterization of materials and designs most likely to succeed

To enable this approach we are developing new theory, new methods, and new software that can finesse from first principles a sufficiently clear idea about mechanisms and new designs that the development of new materials can be focused on the most promising designs

Track record of computation ➔ new materials for fuel cells?

Darn little, but current applications include:

- **High-temperature Fuel Cells**
  - ✓ Solid Oxide Fuel Cell (based on Y-stabilized zirconia)
    - YSZ electrolyte (O diffusion, surface properties)
    - Ni anode (mechanisms, decarbonylation, coking
  - ✓Proton Ceramic Fuel Cells (based on Y-doped BaZrO**3)**
    - (proton diffusion, surface properties)
- **Low-temperature Fuel Cells**
  - ✓ Nafion membrane (nanostructure, proton and water transport)
  - ✓ Pt electrode (chemical mechanisms at anode and cathode, alloys)
  - ✓ Pt/Nafion interface (coupling of protons with O_2 to form water)
- **Alternative Solid Electrolytes for Low- and Medium-temperature Fuel Cells**
  - ✓ Solid acids ($RbHSeO_4$)
  - ✓ Imidazole (fluorinated to avoid catalyst poisoning, good proton transport 100-200 C)
  - ✓ Dendrimers (carry acids groups, reduce H_2O content, retain nanosegration)
  - ✓Zeolites (provide sulfonate or phosphate character but impede fuel, water, gas transport)

Breakthrough enabling first principles applications to fuel cell technologies

The ReaxFF: first principles force field

ReaxFF bridges the Gap between QM and MD

ReaxFF is capable of describing reactive processes

ranging from oxidation to combustion to catalysis to shock induced chemistry but for systems with 1000s to millions of atoms instead of 100

This allows us to use ReaxFF to prepare the structures of complex heterogeneous systems by processes similar to experimental synthesis

ReaxFF references:

1: van Duin, A.C.T.; Dasgupta, S.; Lorant, F.; Goddard III, W.A. *J. Phys. Chem. A* **2001**, *105*, 9396.

2: van Duin, A.C.T.; Strachan, A.; Stewman, S; Zhang, Q.; Goddard III, W.A., *J. Phys. Chem. A* **2003**, *107*, 3803.

3: Strachan, A.; van Duin, A.C.T.; Chakraborty, D.; Dasgupta, S.;Goddard III, W.A. *Phys. Rev. Letters*. **2003**, *91,* 098301.

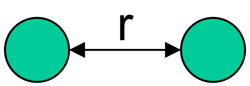
4. Zhang. Q.; Cagin, T.; van Duin, A.C.T.; Goddard III, W.A. *Phys. Rev. B*, **in press**

Many others published or in the process of being written and submitted

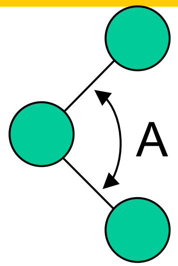
Ordinary Force Fields

Bonds, angles, torsions described as elastic springs

Fixed charges, Empirical vdW nonbond terms



$E = k_r(r\text{-}r0)$



$E = k_A(A\text{-}A_0)$

Examples: MM3, Dreiding, Amber, Charmm, Gromos, UFF

Problem: bonds cannot be broken, making the model unsuitable for modeling reactions.

ReaxFF:

Allow bonds to break and form and describe barriers for reactions.

All parameters from quantum mechanics, no empirical data

First Principles Reactive force fields: strategy

- **Describe Chemistry (i.e., reactions) of molecules**

-Fit QM Bond dissociation curves for breaking every type of bond (X_nA-BY_m), $(X_nA=BY_m)$, $(X_nA\equiv BY_m)$

-Fit angle bending and torsional potentials from QM

-Fit QM Surfaces for Chemical reactions (uni- and bi-molecular)

-Fit *Ab initio* charges and polarizabilities of molecules

•**Pauli Principle: Fit QM equation of state for all coordinations**

  •Metals: fcc, hcp, bcc, a15, sc, diamond (coord 12,12,8,mixed, 6,4)

  •Defects (vacancies, dislocations, surfaces)

  •cover high pressure (to 50% compression or 500GPa)

•**Generic: use SAME parameters for all systems**

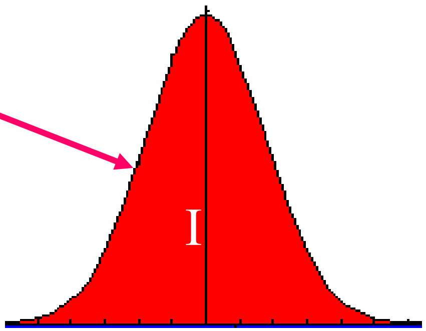
•(same O in O_3, SiO_2, H_2CO, HbO_2, $BaTiO_3$)

Require that One FF reproduces ***all*** the ab-initio data (ReaxFF)

No one (including me) thought that this would not be possible, but we have achieved and validated it for many systems

Critical element of ReaxFF: charges flow as the geometries change

- Self-consistent Charge Equilibration (QEq)
- Describe charges as distributed (Gaussian)
- Thus charges on adjacent atoms shielded (interactions → constant as R→0) and include interactions over ALL atoms, even if bonded (no exclusions)
- Allow charge transfer (QEq method)

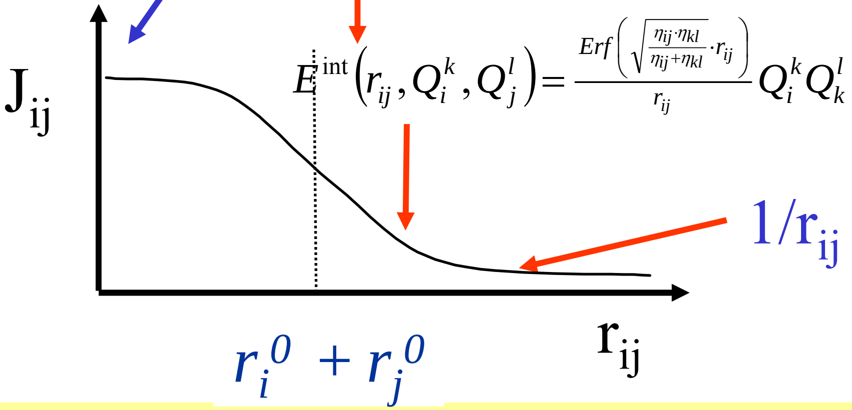


$$E(\{q_i\}) = \overset{\text{interactions}}{\sum_{i<j} J_{ij}(q_i, q_j, r_{ij})} + \sum_i \overset{\text{atomic}}{\left(\chi_i q_i + \frac{1}{2} J_i q_i^2 \right)}$$

Keeping: $\sum_i q_i = Q$

Hardness (IP-EA)

Electronegativity (IP+EA)/2



$$E^{\text{int}}(r_{ij}, Q_i^k, Q_j^l) = \frac{Erf\left(\sqrt{\frac{\eta_{ij}\cdot\eta_{kl}}{\eta_{ij}+\eta_{kl}}}\cdot r_{ij}\right)}{r_{ij}} Q_i^k Q_k^l$$

Three universal parameters for each element: χ_i^o, J_i^o, R_i

1991: use experimental IP, EA, R_i; ReaxFF get from fitting QM

Reactive Force Field - ReaxFF

$$E = E^{Val} + E^{Coul} + E^{VdW}$$

Valence energy

Electrostatic energy

short distance Pauli Repulsion + long range dispersion
(pairwise Morse function)

- •Based completely on First Principles QM (no empirical parameters)
- •Valence Terms (E^{Val}) based on Bond Order: dissociates smoothly
  - Bond distance → Bond order → Bond energy
  - •Forces depend only on geometry (no assigned bond types)
  - •Allows angle, torsion, and inversion terms (where needed)
  - •Describes resonance (benzene, allyl)
  - •Describes forbidden ($2_s + 2_s$) and allowed (Diels-Alder) reactions
  - •Atomic Valence Term (sum of Bond Orders gives valency)
- •Pair-wise Nonbond Terms between **all** atoms (no “bond” exclusions)
  - •Short range Pauli Repulsion plus Dispersion (E^{vdW})
  - •Electrostatics: charges flow depending on environment and fields (QEq)

Applications of ReaxFF

- Catalysts: PtRu Fuel cell anode, Pt_3Co cathode, HC reforming
- Ni catalyzed growth of bucky tubes
- MoO_x catalysts: selective oxidations of hydrocarbons

- $Si\text{-}SiO_2$ and $Si\text{-}SiO_xN_y$ interfaces: structures and dielectric breakdown
- Metal alloy phase transformations (crystal-amorphous)
- Zeolites, $MoVNbTaTeO_x$ (Mitsubishi) ammoxidation catalysts
- Enzyme Proteolysis

- Reaction Kinetics from MD simulations
- Ferroelectric oxides ($BaTiO_3$) domain structure,
- Pz/Ez Hysteresis Loop of $BaTiO_3$ at 300K, 25GHz by MD

- Decomposition of High Energy (HE) Density Materials (HEDM)
- MD simulations of shock decomposition and of cook-off

ReaxFF current development status

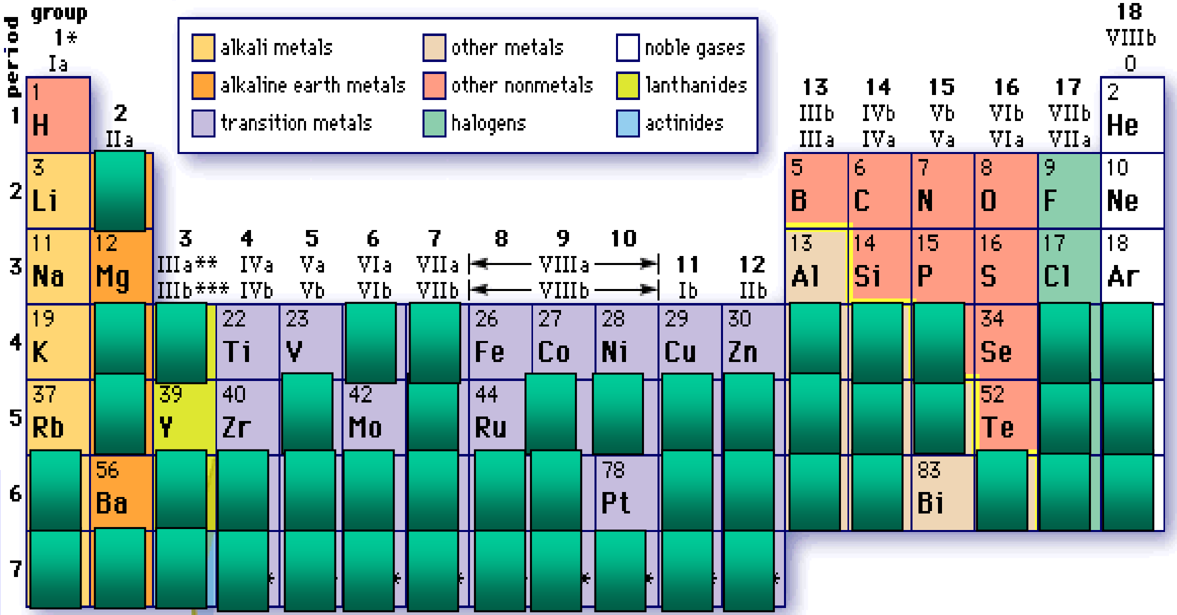
Published ReaxFF force fields for:

- Hydrocarbons (van Duin, Dasgupta, Lorant and Goddard, JPC-A 2001, **105**, 9396)
(van Duin and Sinninghe Damste, Org. Geochem.2003, **34**, 515
- Si/SiO_2 (van Duin, Strachan, Stewman, Zhang, Xu and Goddard, JPC-A 2003, **107**, 3803)
- **Nitramines/RDX/TATP** (Strachan, van Duin, Chakraborty, Dasupta and Goddard, PRL 2003,**91**,09301; Strachan, van Duin, Kober and Goddard, JCP 2005,**122**,054502; Han, Strachan, van Duin and Goddard, in preparation; van Duin, Dubnikova, Zeiri, Kosloff and Goddard, submitted to JACS)
- **Al/Al_2O_3** (Zhang, Cagin, van Duin, Goddard, Qi and Hector, PRB 2004,**69**,045423)
- Ni/Cu/Co/C (Nielson, van Duin, Oxgaard, Deng and Goddard, JPC-A 2005, **109**, 493)
- Pt/PtH (Jacob, van Duin, Niemer and Goddard, submitted to JPC-A; Chen, Lusk, Kee, van Duin and Goddard, submitted to J.Chem.Phys)
- Mg/MgH (Cheung, Deng, van Duin and Goddard, JPC-A 2005, **109**, 851)

Force fields in development:

Other transition metals,
metal alloys and
metals interacting
with first row elements
Proteins

🟩 : not currently described by ReaxFF



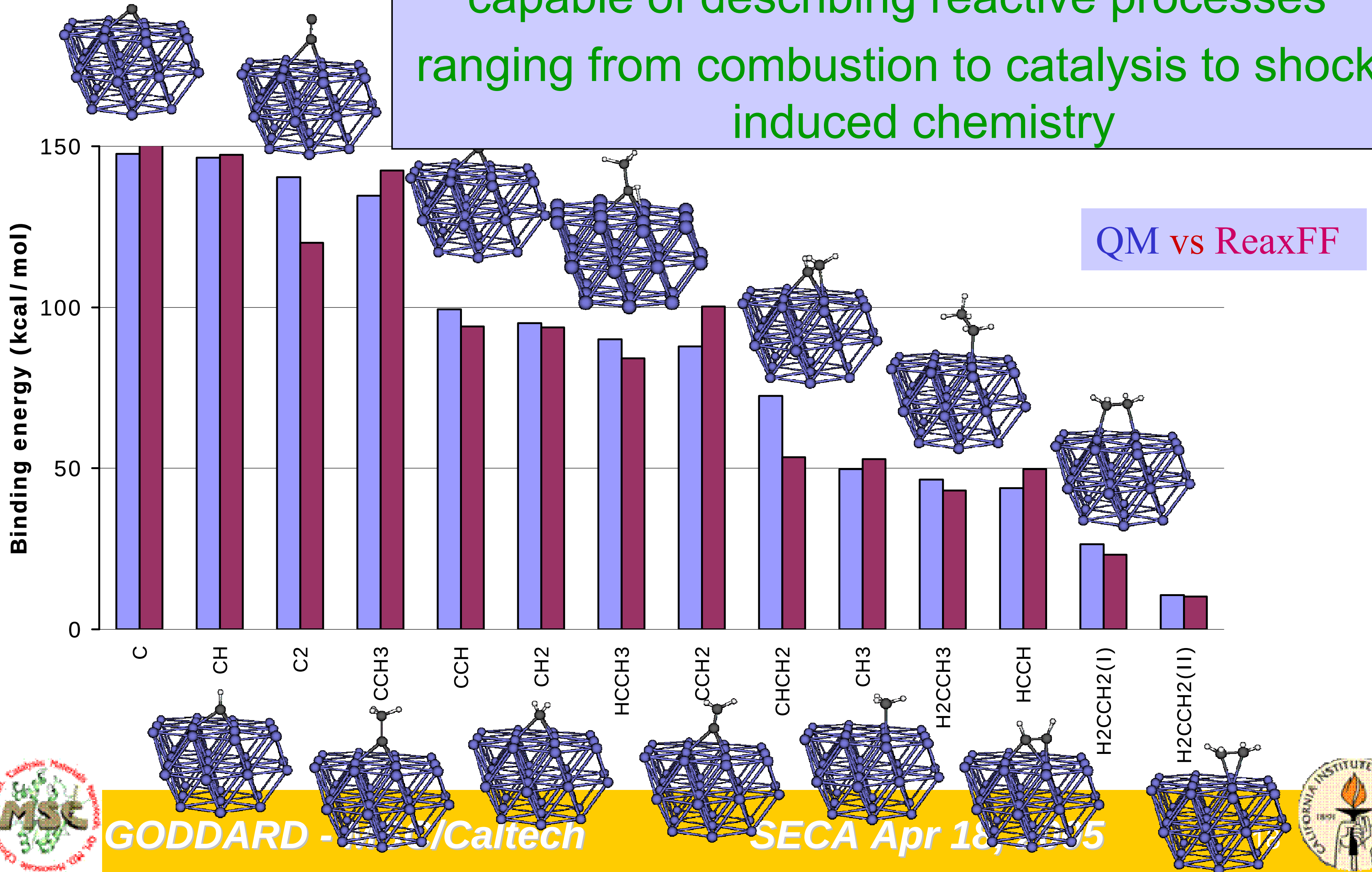
QM + ReaxFF opens door to Complex Reactions

- Use QM to Extend and develop the detailed reaction mechanism for reactions of organics, organometallics
  - Unimolecular and bimolecular reactions
- Extend ReaxFF to fit all possible unimolecular and bimolecular reactions.
- Use ReaxFF in computational experiments to describe fundamental processes as function temperature and pressure including uni-,bi-,ter, -tetra-molecular reactions
- Include defects, finite grain size, binder, plasticizer in these simulations to determine models for their effect on microstructure and performance of materials


Adri van Duin

ReaxFF: first principles force field

capable of describing reactive processes ranging from combustion to catalysis to shock induced chemistry

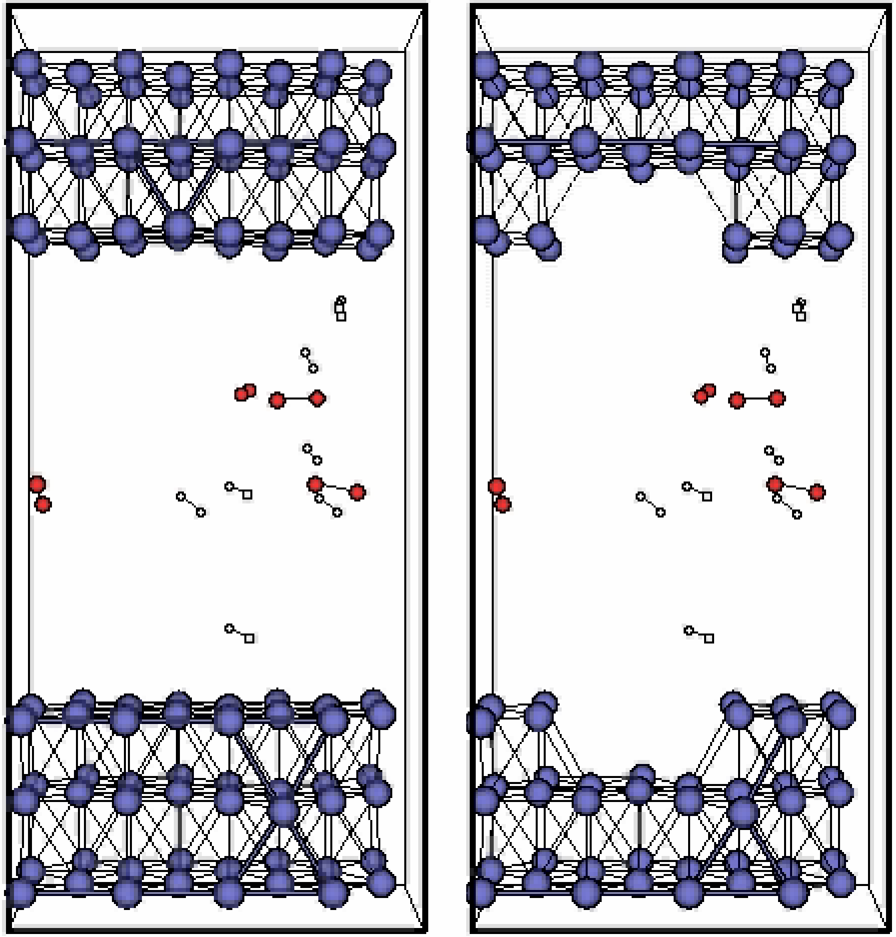


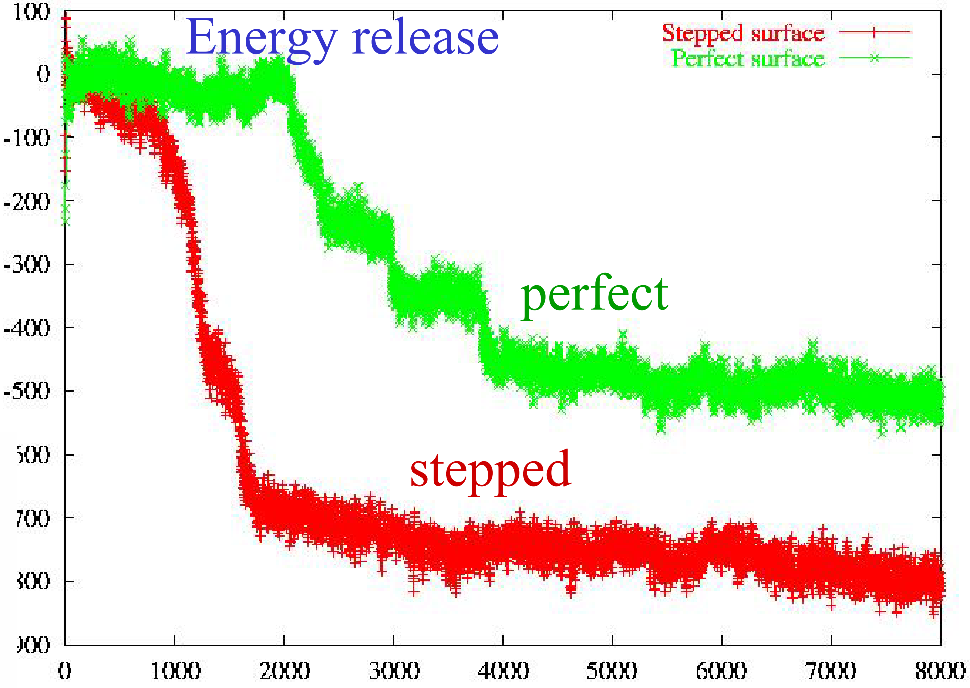
Reactions of H_2 and O_2 over Pt(111) surfaces

$8\ H_2 + 4\ O_2$
Pt(111) perfect
96 atoms

$8\ H_2 + 4\ O_2$
Pt (111) stepped
84 atoms

MD simulation at 1000K





Perfect surface generates H_2O
stepped surface gets oxidized

Energy profile for perfect surface shows H_2O generation events

Have not yet done QM with stepped surface to compare with ReaxFF

Applications of ReaxFF

- Decomposition of High Energy (HE) Density Materials (HEDM)
- MD simulations of shock decomposition and of cook-off
- Reaction Kinetics from MD simulations
- Ferroelectric oxides ($BaTiO_3$) domain structure,
- Pz/Ez Hysteresis Loop of $BaTiO_3$ at 300K, 25GHz by MD

- Catalysts: Pt Fuel cell anode, cathode, CH transformations
- Ni catalyzed growth of bucky tubes
- MoO_x catalysts: catalyzed growth of bucky tubes

- $Si\text{-}SiO_2$ and $Si\text{-}SiO_xN_y$ interfaces
- Metal alloy phase transformations (crystal-amorphous)
- Enzyme Proteolysis
- Si-Al-Mg oxides: Zeolites, clays, mica, intercolation with polymers
- $MoVNbTaTeO_x$ (Mitsubishi) ammoxidation catalysts

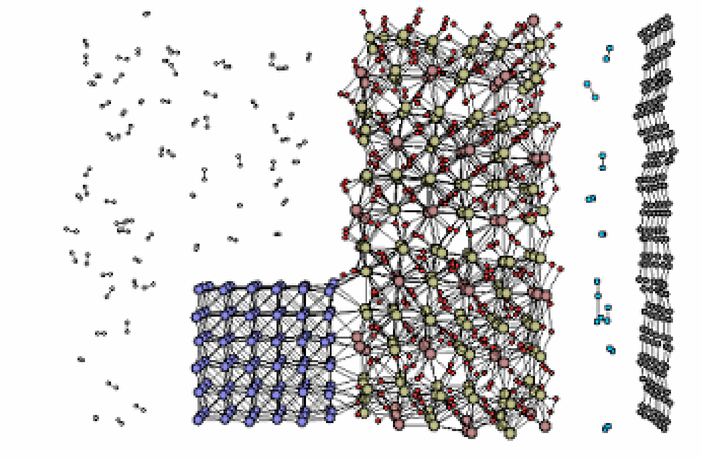
Fundamental Chemistry and Physics of Direct-Electrochemical Oxidation in Solid Oxide Fuel Cells

William Goddard III, Boris Merinov and Adri van Duin

Collab: Sossina Haile (MS), David Goodwin (ME)

DECO MURI **Colorado School of Mines** **University of Maryland** **California Institute of Technology**

Model for simulation of electrode(Pt)/electrolyte(YSZ) interface



S&T OBJECTIVES

- Understand fundamental chemical processes
  - Elementary charge-exchange kinetics
  - Internal CPOX/reform/shift chemistry
  - Ion and species transport
  - Homogeneous chemistry and deposit formation
- Develop and validate predictive models
  - New theory (e.g., mixed-potential charge exchange)
  - Software implementation of modeling tools
  - Provide tools to assist system development

APPROACH

- Apply first-principles QM calculations using DFT theory with PBE GGA to study the reaction mechanisms and rate constants for the various catalytic and diffusion processes
- Develop Reactive Force Field (ReaxFF) based on QM data obtained. ReaxFF allows chemical reactions, phase transformations, and diffusion processes to be modeled
- ReaxFF molecular dynamic simulations of the YSZ electrolyte and electrode/electrolyte interface
- Develop new electrochemical models

ACCOMPLISHMENTS

- Models incorporate elementary chemistry
  - Homogeneous chemistry leading to deposits
  - Heterogeneous shift/reform/CPOX at anode
  - Mixed-potential charge-exchange (e.g., H2 and CO)
- Processes characterized at the atomic scale
  - Ion transport in YSZ, gas-surface interactions
  - ReaxFF used in molecular dynamics
- Predicted Ni/H and Ni/C interactions to deposits

PLAN

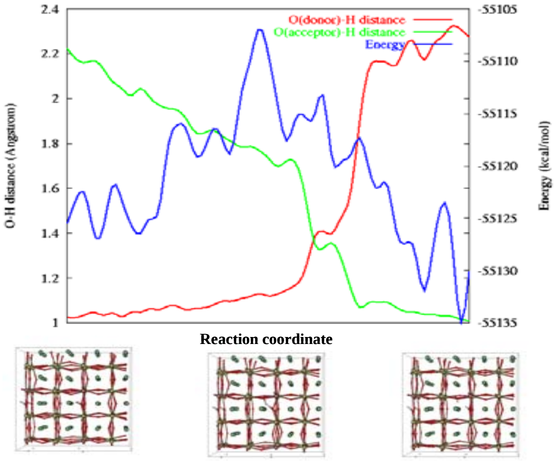
- Extend ReaxFF for more complex electrochemistry
- Extensions for higher hydrocarbons
- Deposit formation and removal processes

Enhanced Power Stability for Proton Conducting Solid Oxide Fuel Cells

William Goddard III, Boris Merinov, Adri van Duin, and Sossina Haile (MS)

DOE, California Institute of Technology, Materials and Process Simulation Center, Materials Science Department

ReaxFF MD simulation of the proton diffusion through Y-doped $BaZrO_3$ electrolyte



APPROACH

- Apply first-principles QM calculations using DFT theory to study the reaction mechanisms and rate constants for the various catalytic and diffusion processes
- Develop Reactive Force Field (ReaxFF) based on QM data obtained. ReaxFF allows chemical reactions, phase transformations, and diffusion processes to be modeled
- Perform ReaxFF molecular dynamics (MD) simulations on large systems to investigate physico-chemical processes in the Y-doped $BaZrO_3$ (BYZ) electrolyte and electrode/electrolyte interfaces

S&T OBJECTIVES

- Develop a fundamental understanding of the mechanisms and barriers for proton transport in SOFC fuel cells
- Develop modified electrolytes that exhibit both high proton conductivity and excellent chemical and mechanical stability.
- Develop highly efficient electrocatalysts for the anodes and cathodes of a SOFC based on this relatively new BYZ electrolyte
- Provide computational tools to assist system development

ACCOMPLISHMENTS

- A series of QM calculations has been performed on relevant clusters, bulk metals, metal alloys and oxides.
- ReaxFF for the above-mentioned materials and for BYZ has been developed.
- ReaxFF MD simulations have been applied to model the proton diffusion in the BYZ electrolyte.

PLAN

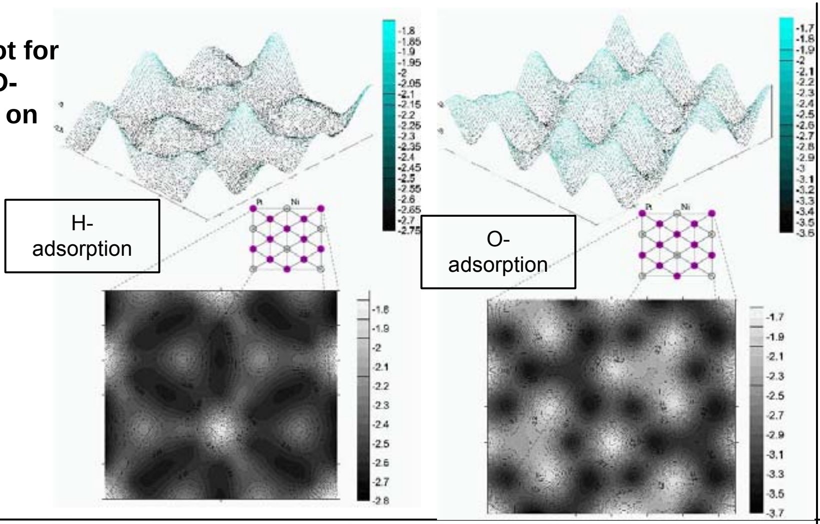
- Continue developing ReaxFF based on the interaction between QM and ReaxFF results.
- Perform QM calculations on stable $BaZrO_3$ surfaces for further modeling grain boundaries.
- Start applying ReaxFF on realistic electrolyte structures and interfaces.

Cathode Alloy Catalysts: Pt_3Ni, Pt_3Co

T. Jacob and W. A. Goddard III

General Motors-GAPC **California Institute of Technology** **Materials and Process Simulation Center**

Contour plot for H- and O-asorption on Pt_3Ni

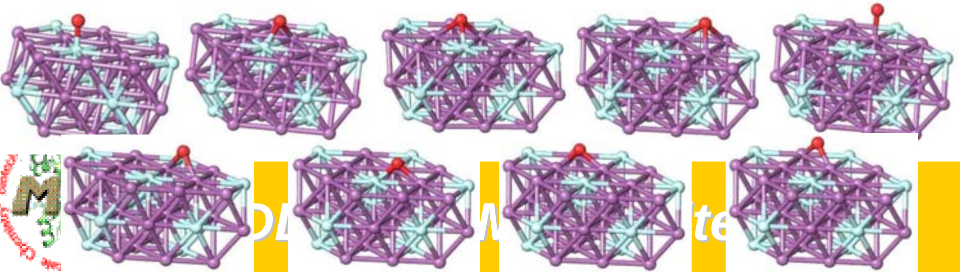


S&T OBJECTIVES

- Understand the influence of alloying transition metals
  - structure
  - composition
  - electronic characteristics
  - influence on the adsorption of molecules (stronger or weaker binding, different preferred surface sites, different adsorption structure)
  - study influence of electrode potential on reaction
  - apply kinetic simulations for large scale modeling

APPROACH

- First study the composition and structure of Pt/Ni alloy nanoparticles
- Then use the best cluster with the correct structure and composition to repeat similar studies as for pure Pt clusters
- Due to the complex composition much more surface sites can be distinguished



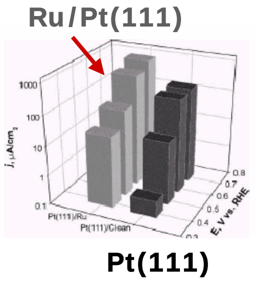
ACCOMPLISHMENTS and OUTLOOK

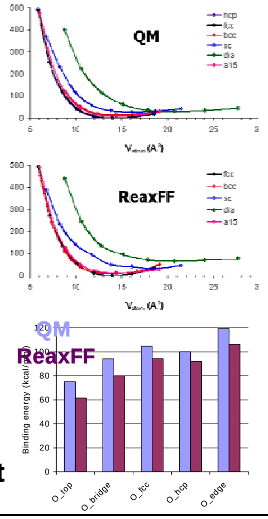
- Influence of alloying on entire reaction mechanisms
- Extract parameters to be tuned for improving reaction kinetics and generating better catalysts
- Study Quantum Size Effects:
  - Why and how nanoparticles behave different than infinite crystals or surfaces?
  - Can this size-dependent behavior be rationalized and be used as an tool?
  - Where (at which size and shape) is the transition from nanoparticle to infinite system?
- How the supporting material (mostly Carbon) changes the shape of the nanoparticle, which then due to QSE shows different characteristics

Pt-Ru Alloy Catalyst for Fuel Cell: Reactive Force Field Study

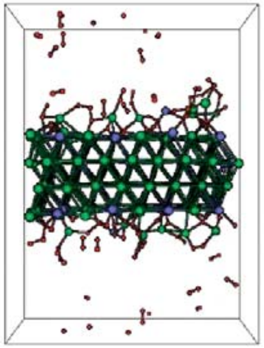
Yun Hee Jang, Adri van Duin, Timo Jacobs, William A. Goddard III
support GM-GAPC

Current density





ReaxFF development



Oxidized Ru_3Pt_1 Surface from ReaxFF

APPROACH

- Perform quantum mechanics (QM; DFT) calculations on relevant simple model systems of Pt, Ru, O, C, H (bulk metal, metal oxide, surface adsorption, composite clusters of various oxidation states, etc.; training set)
- Refine the ReaxFF based on the training set QM data
- Start ReaxFF simulation with a clean PtRu surface, then
  - Add O_2 (or O_3) to see the oxide formation/distribution
  - Add H_2O to see the hydroxide formation/distribution
  - Add CO or CH_3OH to see the reaction site, rate, etc.
- Compare the above steps done with clean Pt surfaces or other compositions/distributions of Pt-Ru surfaces to see the cooperation effect of various surface sites

S&T OBJECTIVES

- Realistic description of fuel cell catalyst surfaces, which often involves metal, metal oxide, and metal hydroxide
- Fundamental understanding of the reaction mechanism of $H_2/H_2O/CO$ (H_2 fuel cell) and H_2O/CH_3OH (DMFC) on Pt-Ru alloy surfaces, especially the cooperation between Pt, Ru, RuO_x and RuO_xH_y
- Mechanism-based design of plausible alternatives of fuel cells (fuel, catalyst composition, reaction condition, etc.)
- Developing a tool (e.g. reactive force field; ReaxFF) for a realistic simulation of complex catalytic processes

ACCOMPLISHMENTS

- The ReaxFF for Pt, Ru, O, C, H was developed based on a series of QM calculations on relevant models.
- Stronger affinity toward oxygen of Ru (compared to Pt) was demonstrated: An oxide layers is formed dominantly for Ru (RuO_x) from RuPt surfaces in oxidizing conditions.

PLAN

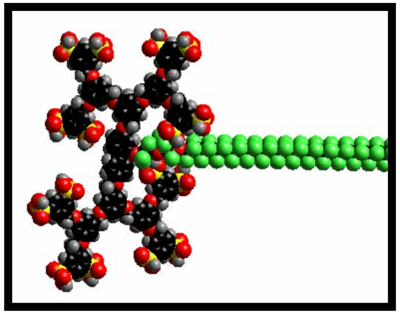
- ReaxFF simulations in the presence of H_2O to study the hydroxide formation (RuO_xH_y), the distribution of $Pt/Ru/RuO_x/RuO_xH_y$ at various conditions, and its effect on the reaction mechanism and rate when CO or CH_3OH is added later on (or together).

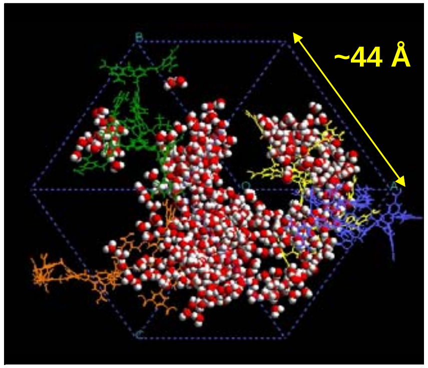
Dendrion: Water-soluble Fréchet-type Dendrimer-Linear PTFE Block Copolymer for Polymer Electrolyte Membrane Fuel Cell

Seung Soon Jang and William Goddard III

California Institute of Technology **General Motors-GAPC**

Model for the Dendrion polymer and its hydrated membrane





APPROACH

1. Apply first-principles QM calculations using DFT theory with B3LYP/6-31G**

1.1 to optimize the force field for atomistic simulation

1.2 to determine the energy barrier for proton hopping in water phase

2. Apply molecular dynamics simulation method to construct the nanophase-segregated structure

S&T OBJECTIVES

Understand atomistic details in the nanophase-segregation of hydrated Dendrion membrane

1. Develop the procedure to obtain the most probable configuration of nanophase-segregation
2. Develop tools to analyze the simulated morphologies
3. Develop tools to evaluate the transport properties of water/proton in this membrane

ACCOMPLISHMENTS

1. Morphology predicted using MD simulation

1.1 Hydrated Dendrion membrane has a well-developed nanophase-segregated structure between hydrophobic PTFE and hydrophilic dendrimer in the presence of water.

1.2 Water molecules form a percolated phase with the hydrophilic dendrimer block.

2. Predicted performances such as proton diffusion are better than the given Nafion-based membrane

PLAN

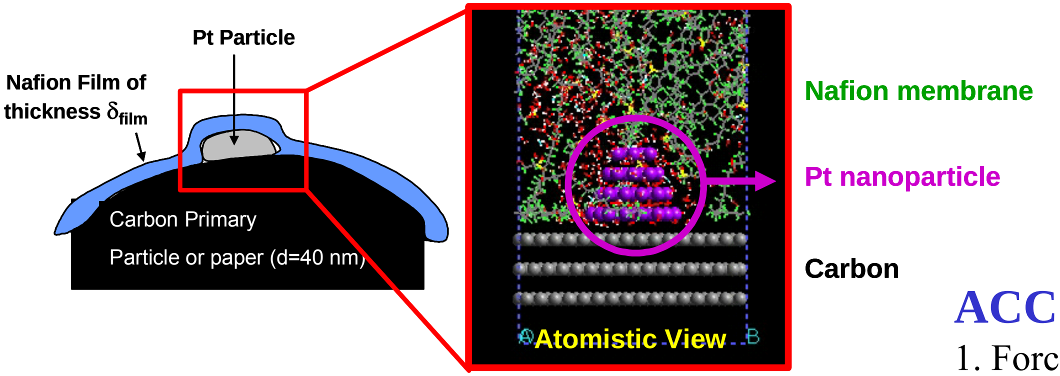
Investigate the temperature effect on various properties of Dendrion membrane

Nanoconfiguration of Interface between Polymer Electrolyte and Electrode in Polymer Electrolyte Membrane Fuel Cells

Seung Soon Jang, Boris Merinov, Timo Jacob
and William Goddard III

California Institute of Technology

Model for the interface between polymer electrolyte and electrode



APPROACH

1. Apply first-principles QM calculations using DFT theory with B3LYP/6-31G** to optimize the force field for atomistic simulation

2. Apply molecular dynamics simulation method to construct the interface between polymer electrolyte and electrode

S&T OBJECTIVES

Understand atomistic details in morphology of nanophase-segregation at the interface between polymer electrolyte and electrode.

1. Optimize the force field for atomistic simulation
2. Develop the procedure to simulate interface
3. Develop tools to analyze the simulated morphologies

ACCOMPLISHMENTS

1. Force field optimized to describe the interatomic interaction in atomistic simulation using DFT quantum chemistry (B3LYP/6-31G**)
2. Morphology predicted using MD simulation
2.1 Water distribution is predicted to have a percolated structure among the Nafion matrix.
2.2 Pt catalyst nanoparticle is solvated by water molecules on carbon support.

PLAN

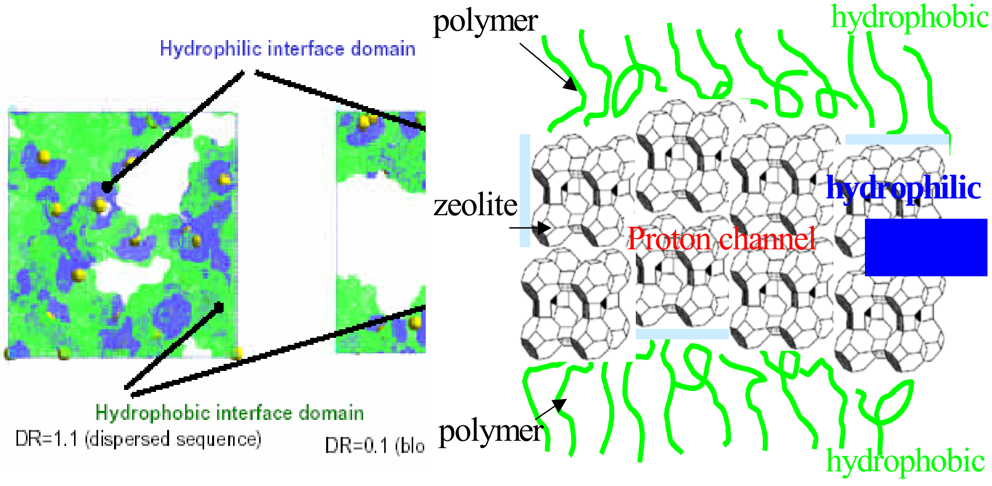
1. Understand the dynamics of water/proton/O_2 molecule at the interface
2. Develop ReaxFF to predict the electrochemical reaction at the interface.

Polymer Functionalized Zeolite Proton Exchange Membrane (PFZ-PEM) for Medium Temperature Fuel Cell

William A. Goddard III, Mark E. Davis (Caltech) and Yushan Yan (UC Riverside)

With support from DOE (pending)

Concept



Objectives

- Simulate, design, and fabricate a novel proton exchange membrane that can operate at a broader temperature range, i.e., from –30 °C to 200 °C
- Investigate the properties of novel membranes, evaluating the properties computationally to select the most reasonable candidates
- Carry out experiments on the more promising cases while also validating the theory on specific cases.

Accomplishments and Impact

- **Demonstrated proof-of-concept high temperature proton exchange membrane.**
- **Developed simulation methodology to be able to predict reasonable proton conductivity.**
- **Potentially leads to important discoveries of broader temperature fuel cell membrane.**
- **Possibility to deeply understand self-assemble, nano-structured channel etc. processes.**

Project coordinator: W.Q. Deng (Caltech)
Key Personals: X. Zhang, V. Molinero (Caltech)
Z.W. Chen, X. Wang (UC Riverside)

Expected Results

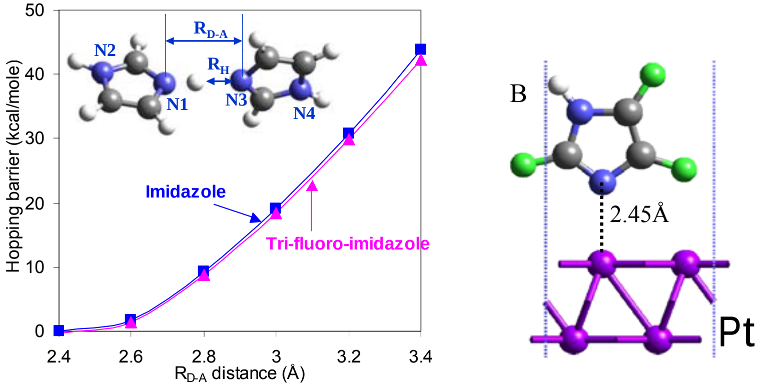
Dec 2005	**Design a functionalized zeolite with high proton conductivity**
Dec 2006	**Design a novel organic/inorganic hybridized membrane impregnated or copolymerized with functionalized zeolites**
Dec 2007	**Implement polymer/zeolite membrane into fuel cell device and obtain broader temperature fuel cell.**

Fluorinated Imidazoles as proton carriers for water-free fuel cell membranes.

Weiqiao Deng, William Goddard III, and Valeria Molinero.

General Motors-GAPC **California Institute of Technology**

The proton transfer barrier does not depend significantly on the degree of fluorination of imidazole, but the adsorption to the electrode does.



S&T OBJECTIVES

•Water-free membranes are desirable because although water is a good proton carrier its volatility limits its use to T < 100°C, where CO traces poison the Pt electrode.

•Develop new fuel cell membrane materials that

 -have high proton conductivity at T > 120°C,

 -are chemically stable and does not evaporate

 -do not poison the Pt electrode.

•Develop methods to evaluate proton diffusion with low computational cost, for the use in new membrane design.

APPROACH

• Develop atomistic force fields from QM data, for the modeling of (fluorinated) imidazole/Nafion membranes.

•Extract structural (rdf) and dynamical information (MSD and rotational tacf) from MD trajectories.

•Development of a mean field methodology for the fast evaluation of proton transfer in the membranes using a QM evaluation of the hopping probabilities on configurations extracted from the MD trajectory.

• QM Paramterization of proton hopping probabilities.

•Evaluate adsorption energies of (fluorinated) imidazole to Pt using QM.

•Compute pka of carriers to predict ionization of PEM.

ACCOMPLISHMENTS

• Proposed new family of high temperature PEM materials based on fluorinated imidazoles and Nafion.

• Predict the conductivity of ImF3/Nafion to be comparable to Im/Nafion without the drawback of the electrode poisoning.

•Develop a fast new methodology to evaluate proton diffusion using a combination of classical MD trajectories and proton hopping parameters obtained from QM calculations.

•PLAN

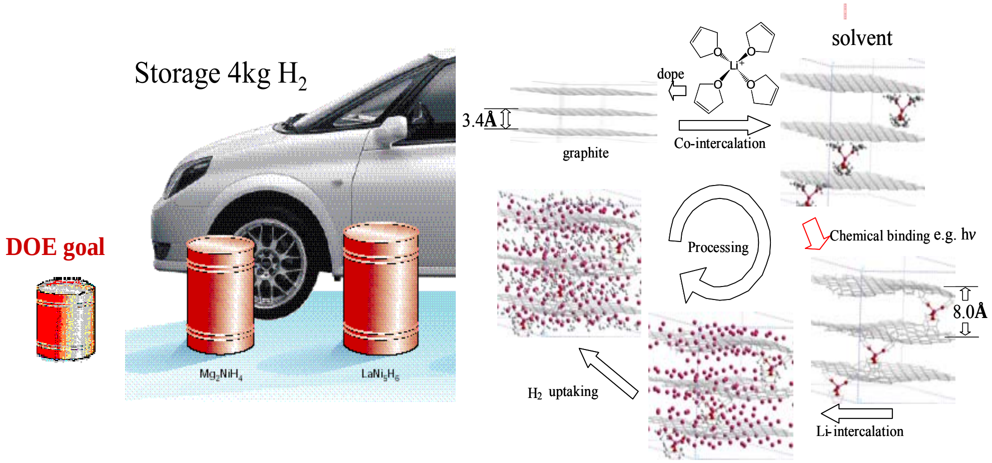
 •Use this methodology to predict the proton conductivity of new fuel cell materials.

•Synthesize the material and test its use in fuel cells.

Carbon-based Compositions for Reversible Hydrogen Storage Applied in Transportation

Weiqiao Deng and William A. Goddard III; Support GM-GAPC

Concept



Objectives

- **Understand hydrogen storage in carbon based materials.**
- **Understand fundamental science of adsorption/desorption procedure**
- **Simulation-aided design of novel composite that may satisfy DOE target.**

Our Approach

- **Used newly developed X3LYP to describe Van der Waals interaction accurately.**
- **Developed accurate force field to describe the interactions in the carbon based materials.**
- **Computer aided designed a novel composite and optimize the material structure to obtain best storage properties.**

Accomplishments and Impact

- **Computation-aided design a novel composite: Li doped pillared carbon materials that may reach DOE goal of hydrogen storage materials.**
- **Provide a basis to understand interaction of hydrogen in carbon based materials and its derivatives.**
- **Proposed a strategy to synthesis designed composite.**
- **Potentially lead to important discovery for next generation hydrogen storage materials.**

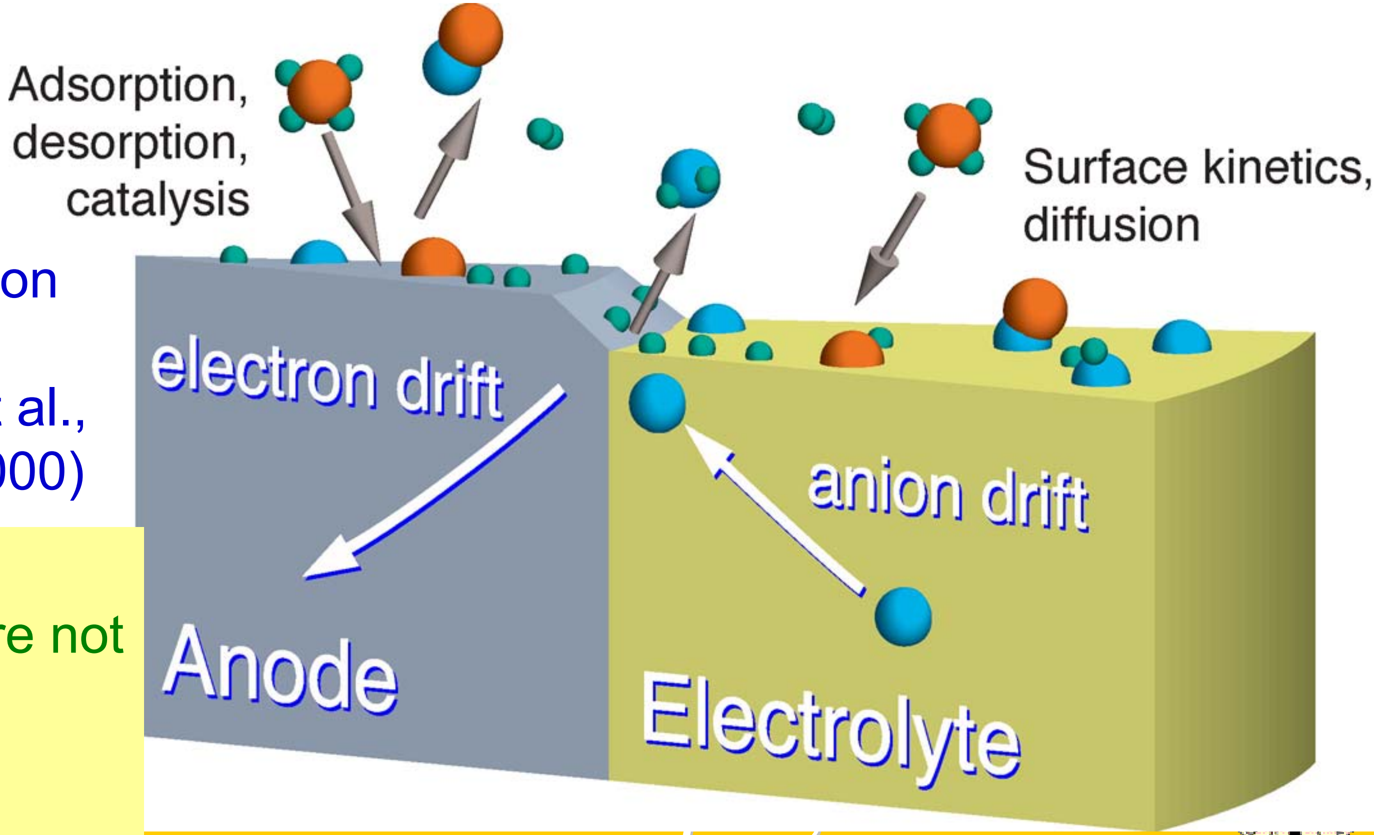
Selected Publications:

1. W.Q. Deng, X. Xu Muller, W.A. Goddard III; *Phys. Rev. Lett*. 2004, 92, 166103

High-temperature Fuel Cells

- Solid Oxide Fuel Cell based on Y-stabilized zirconia
  - YSZ electrolyte
  - Ni anode
- Proton Ceramic Fuel Cells based on Y-doped $BaZrO_3$

Triple phase boundary in SOFC



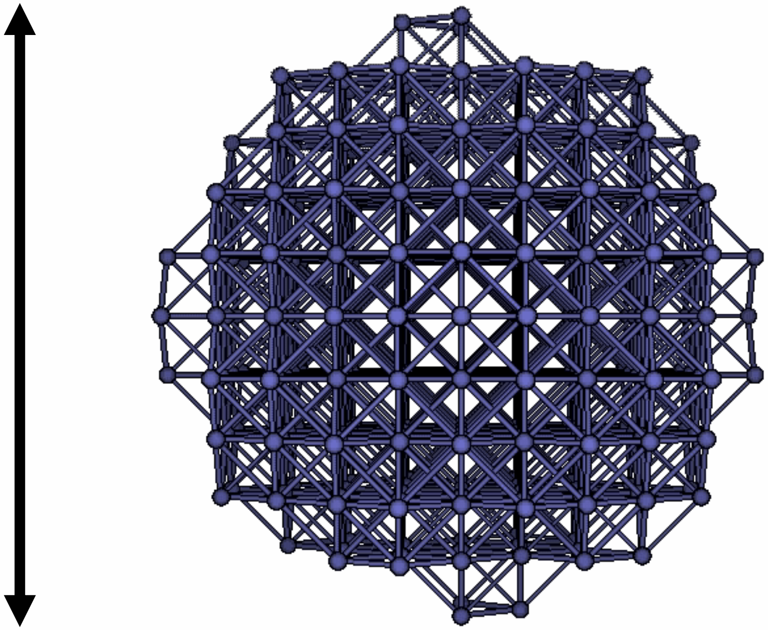
Direct electrochemical oxidation of hydrocarbon fuels has been demonstrated (Park et al., 1999; Murray et al., 2000)

But the physical and chemical processes are not understood and characterized at a fundamental level.

Generate catalyst cluster and examine the chemistry

Generate structure of a Pt cluster

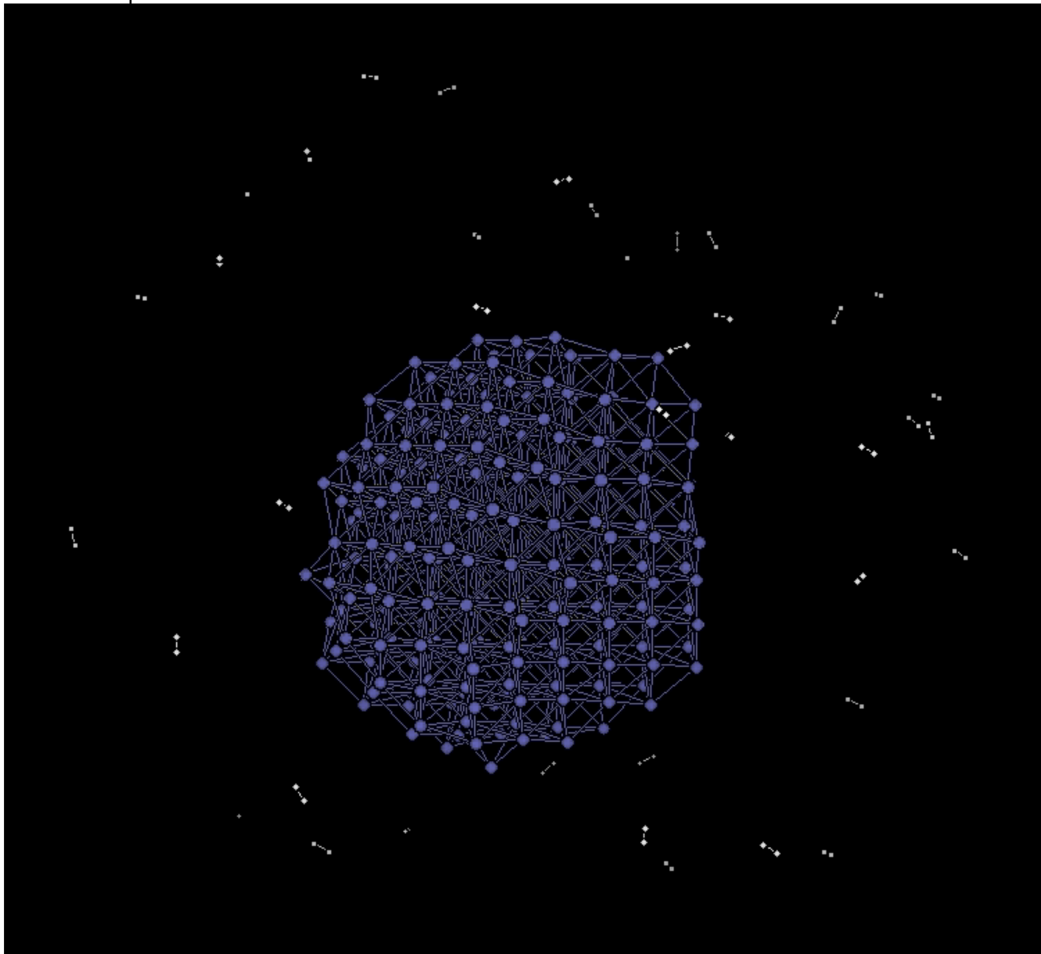
- Initial configuration 307 atom sphere fcc packing
- Heat up to 1600K, surfaces melt
- Cool slowly to 300K to form equilibrium surface
- dominated by [111] surfaces
- Core retains ordered fcc-configuration



27 A = 2.7 nm

React with fuel (e.g., H_2)

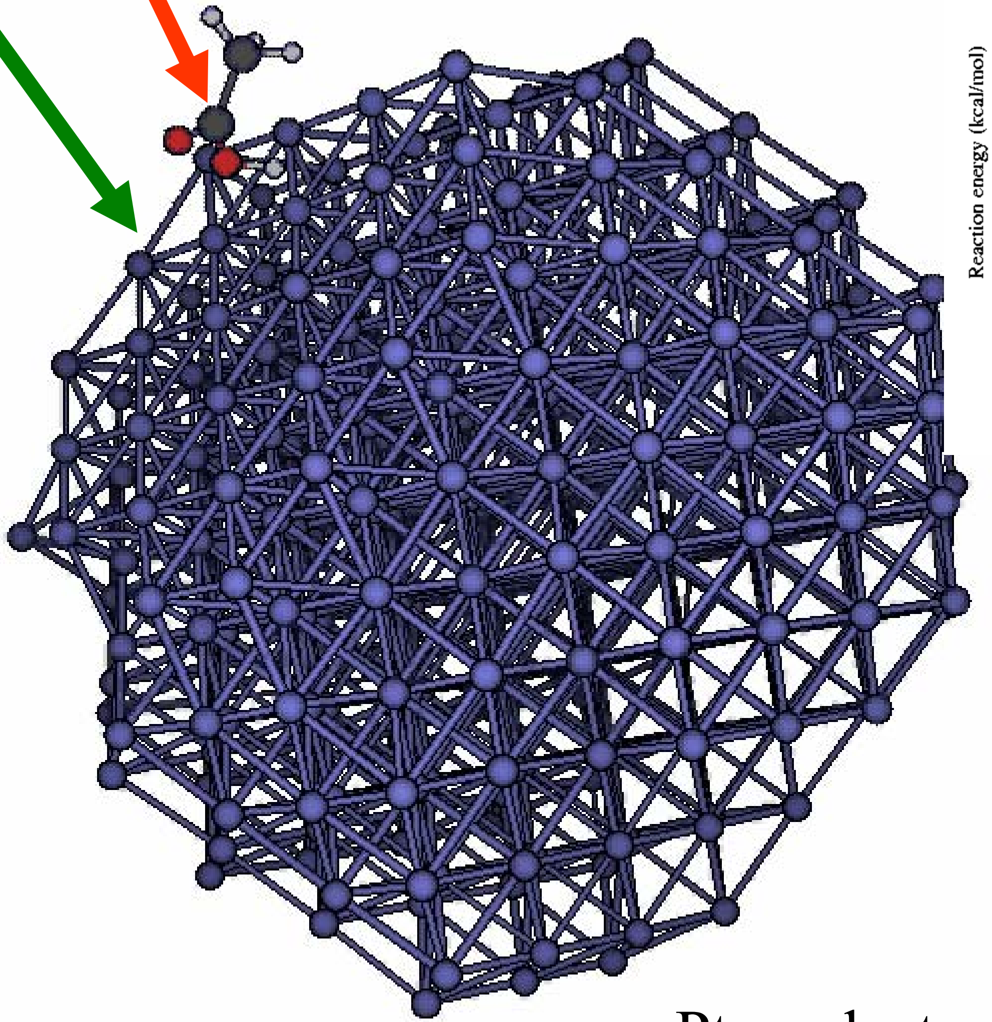
- MD simulation
- T=100K, H_2 dissociates on edge-sites and does NOT migrate to [111] surface facets



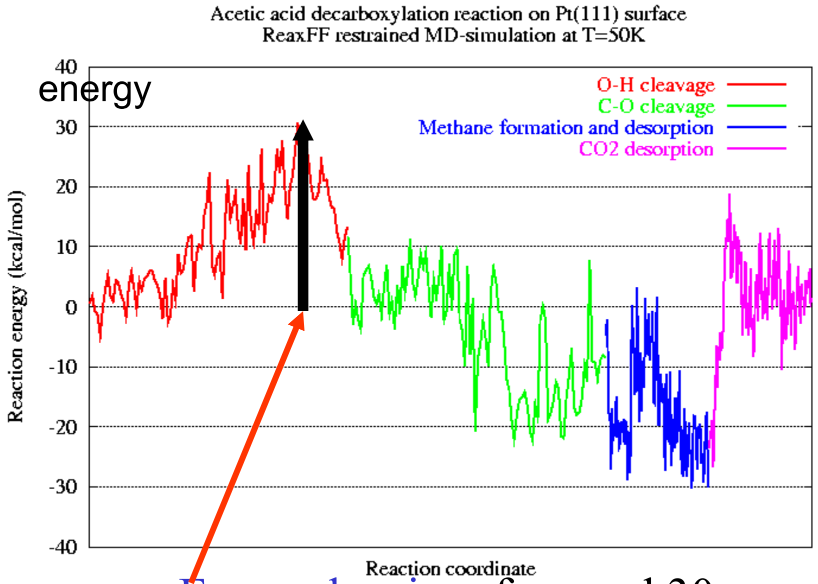
Decarboxylation of acetic acid on Pt cluster

Acetic acid (CH3COOH)

[111]facet



Pt_{307}-cluster

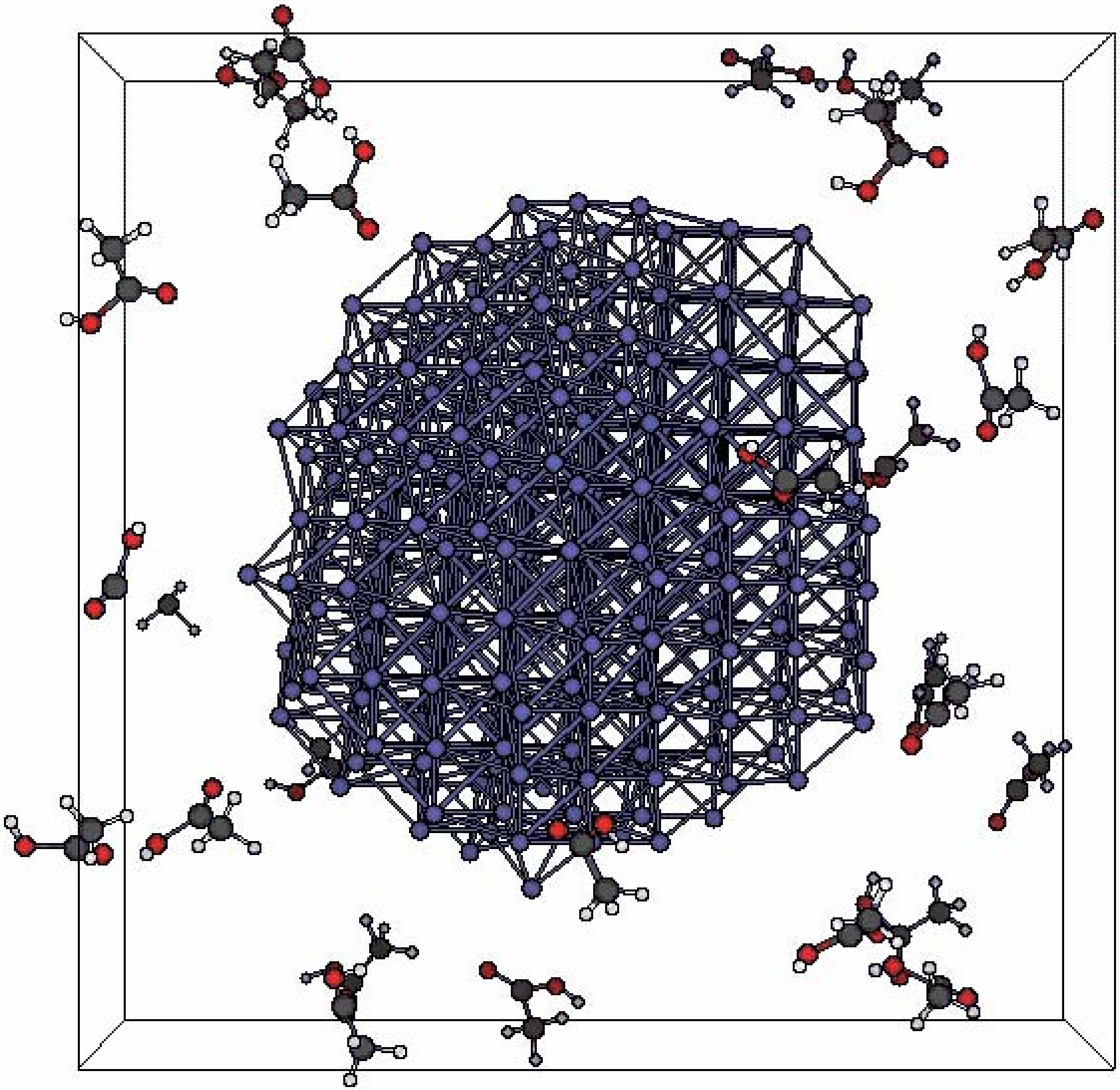


-Energy barrier of around 30 kcal/mol to break O-H bond; no higher barriers after that

- Overall reaction is marginally endothermic; entropy gain will favor products
- ReaxFF predicts that the Pt[111] surface will catalyze this reaction at temperatures slightly above room temperature

ReaxFF MD/NVT simulation at T=50K with restraints to drive reactions

Decarboxylation at T=800K

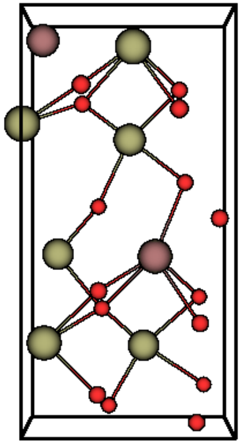


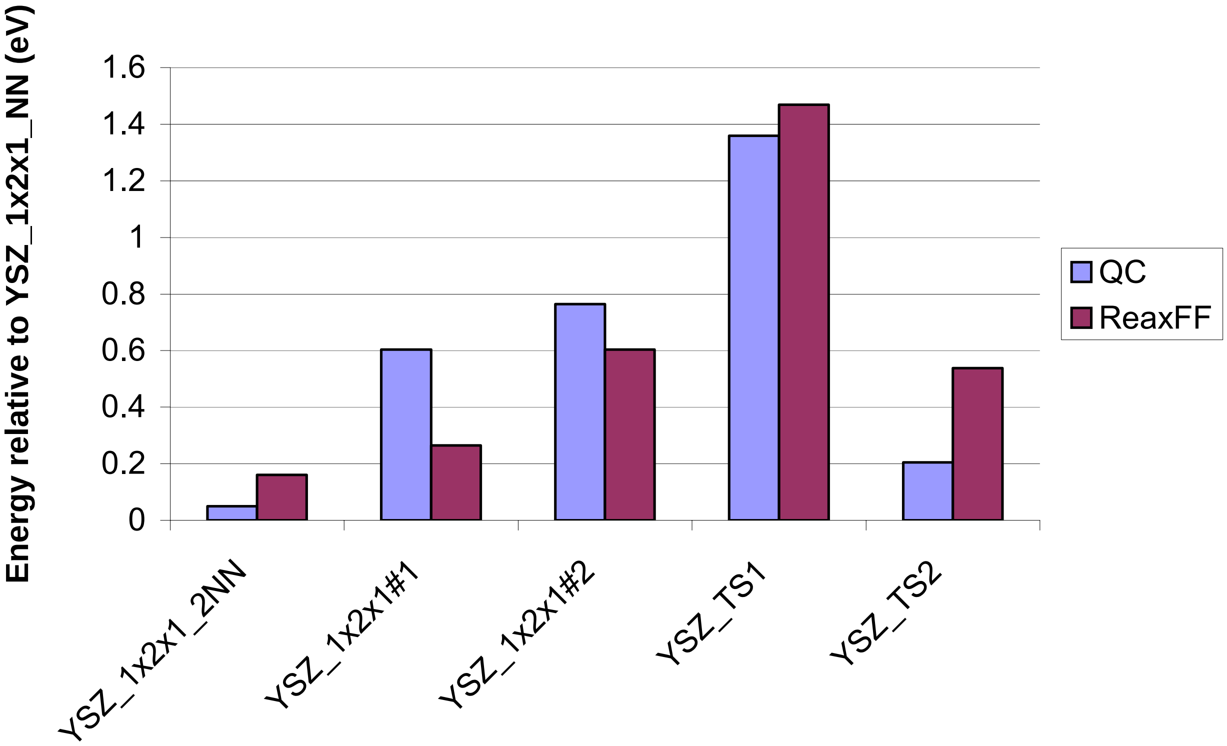
- Unrestrained MD
- All reactions happen at the surface
- Generate chemisorbed H, CH_3, and CO
- Final composition:

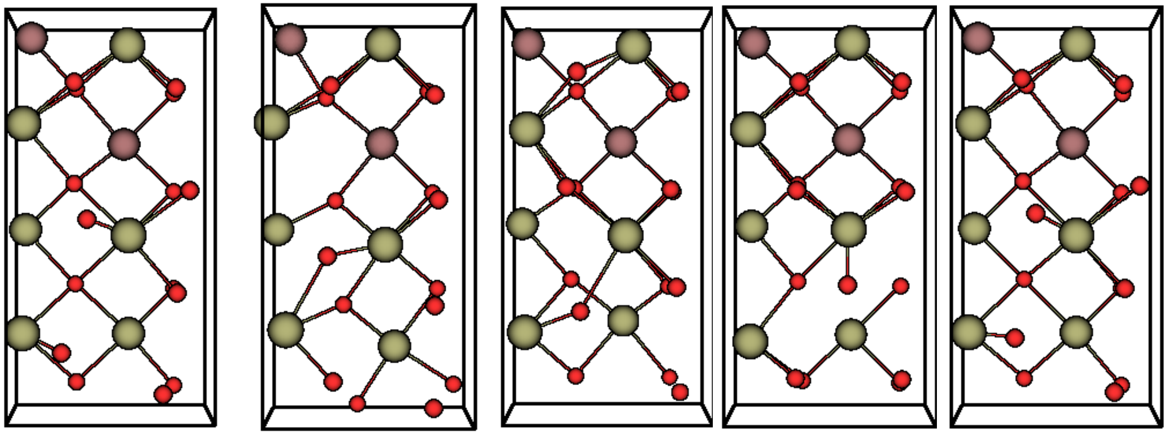
2 gas phase acetic acid
1 adsorbed acetic acid
17 adsorbed H
11 adsorbed O=C-OH
1 gas phase O=C-OH
13 adsorbed CH_3
5 adsorbed CH_2
6 adsorbed CO_2
2 adsorbed CH
2 adsorbed CO
2 adsorbed OH

- ReaxFF might provide a useful computational tool for studying surface reactions

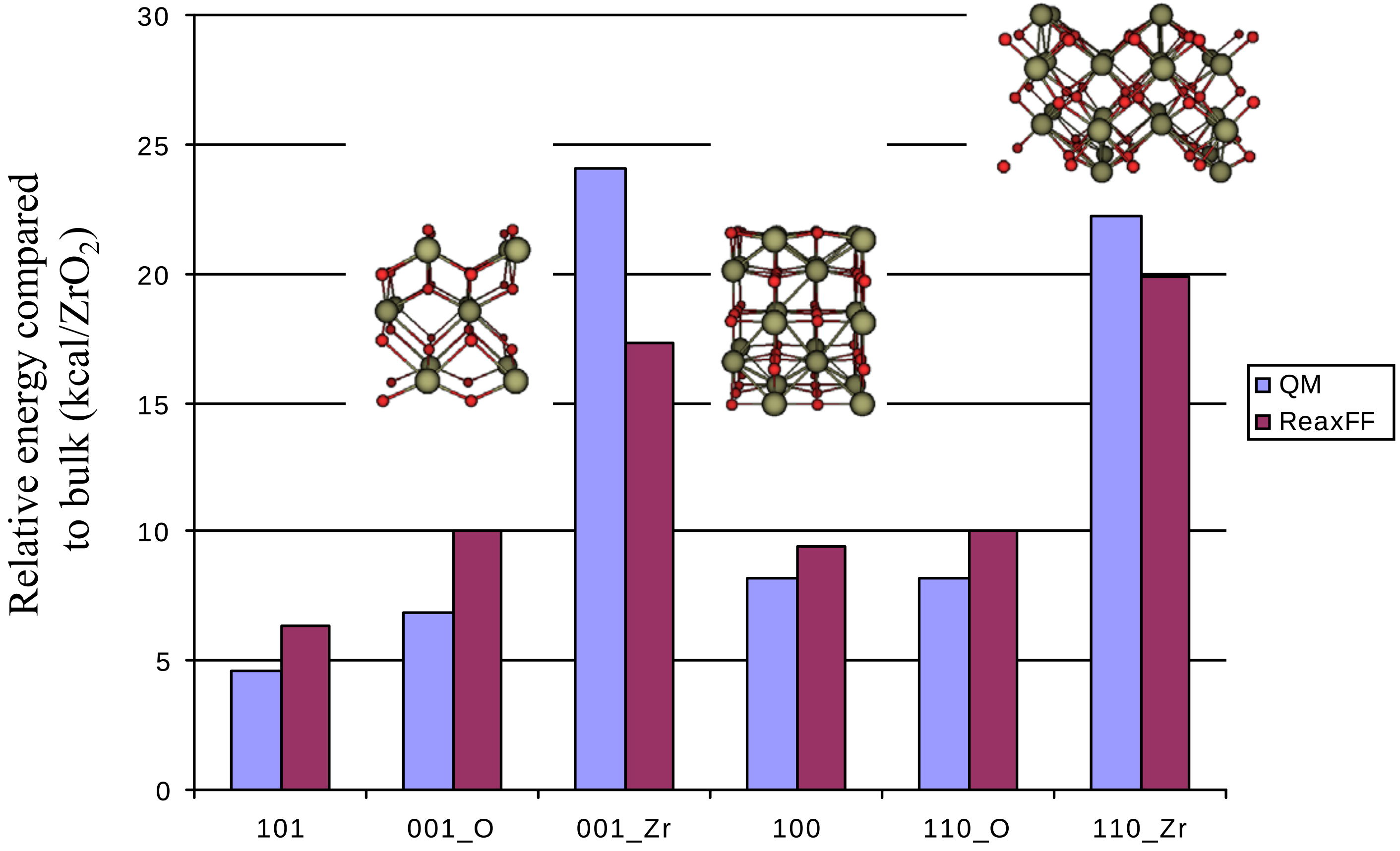
Y-stabilized ZrO2: use QM to determine energies for various locations of the O vacancies and fit ReaxFF

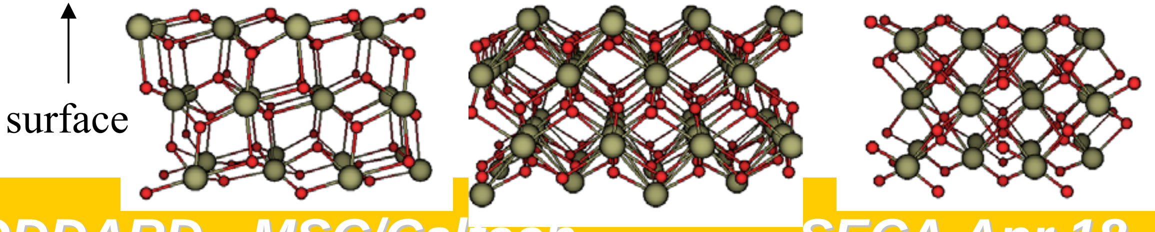




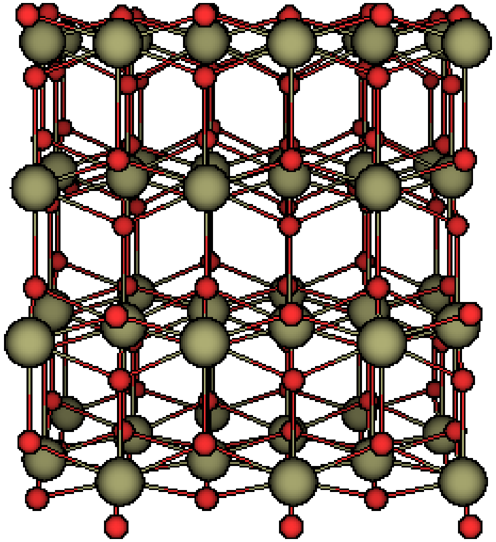


Use QM to determine energies for various ZrO2-surfaces and fit ReaxFF



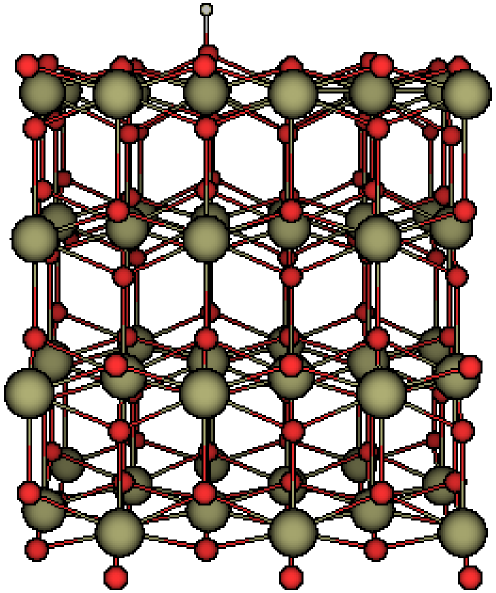


Use QM to determine energies for surface affinity for hydrogen to various ZrO2-surfaces and fit ReaxFF



ZrO_2(tetragonal)
101-surface

+ H(radical) ⟶



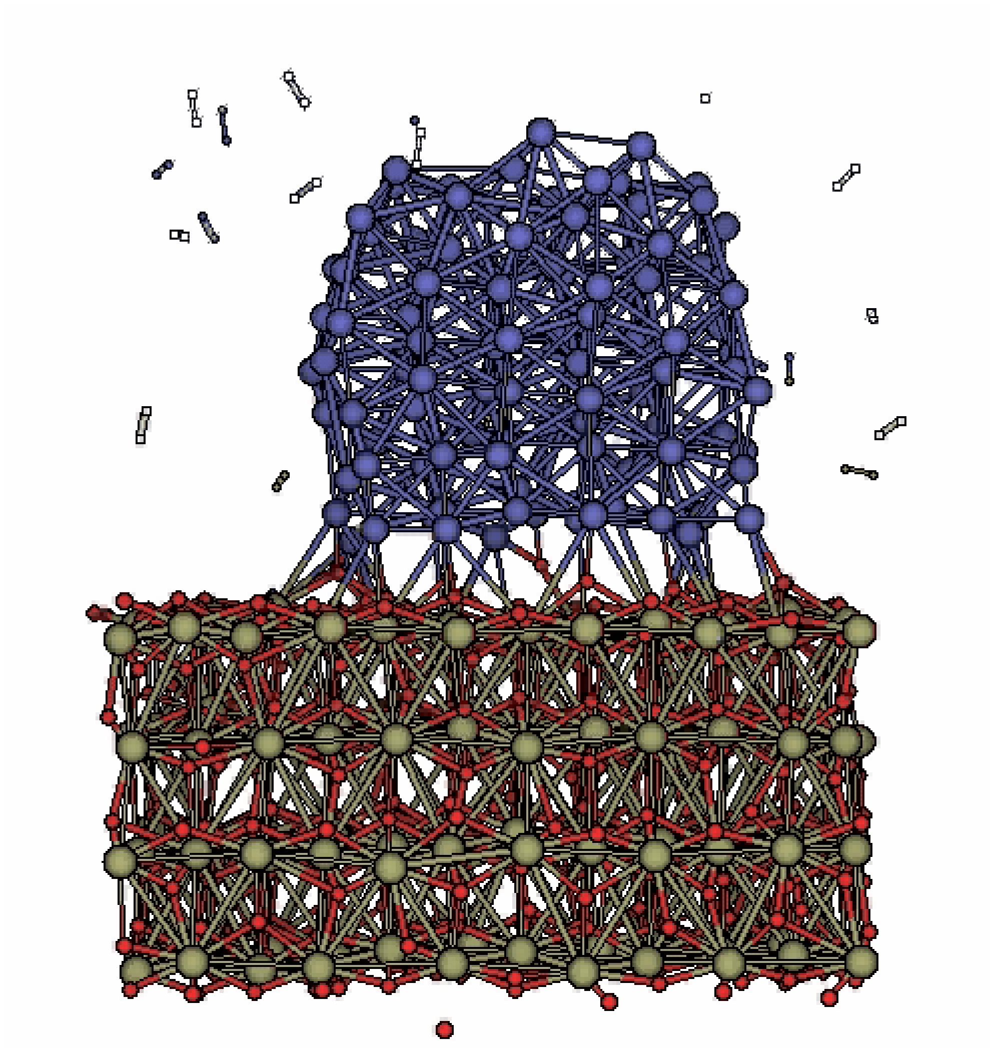
QM-data from Hofmann et al., PCCP 2002

DE(QM):-47.8 kcal/mol
DE(ReaxFF):-52.2 kcal/mol

- ReaxFF gives a good description of ZrO_2-surface energies and surface affinity to hydrogen
- H has higher affinity for Pt (111) than for ZrO_2(101) surface; H_2 should dissociate on Pt-surface and not migrate to ZrO_2(101) without defects

Simulation on H_2 interaction with Pt/ZrO_2 interface

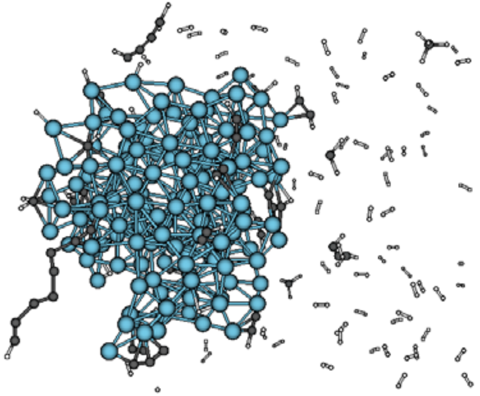
ReaxFF MD/NVT-simulation at 800K



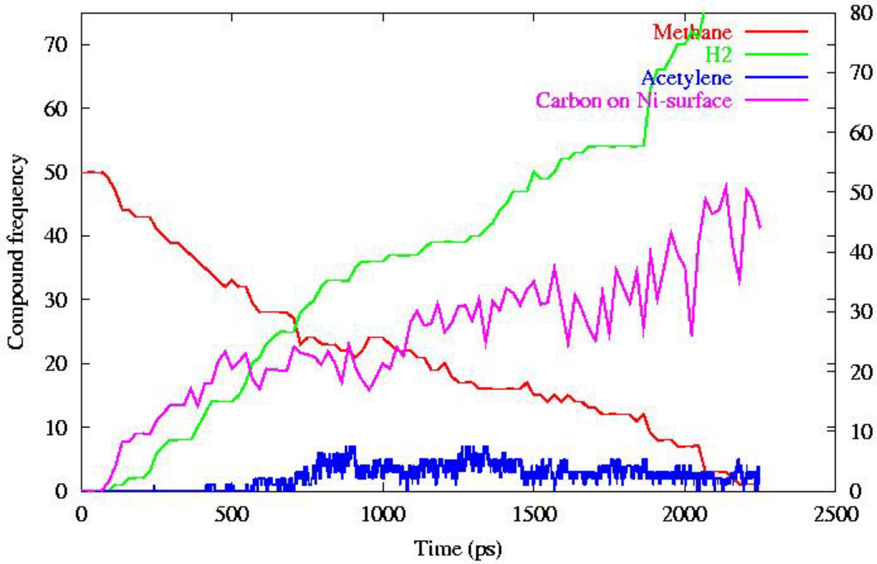
- H_2 dissociates on Pt-surface, but not on ZrO_2-surface
- No hydrogen transport from Pt to ZrO_2-surface observed; this requires surface defects (like in YSZ).
- ZrO_2-surface remains stable during the simulations

Influence of oxygen on CH4-reaction rate for Ni particle

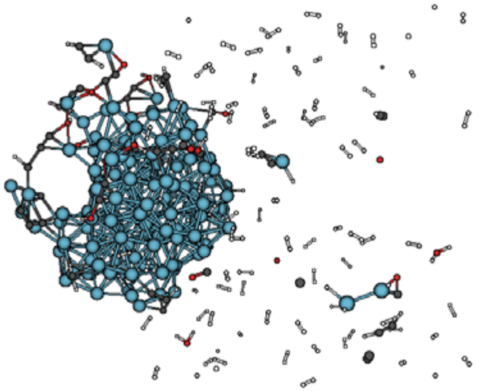
no O_2



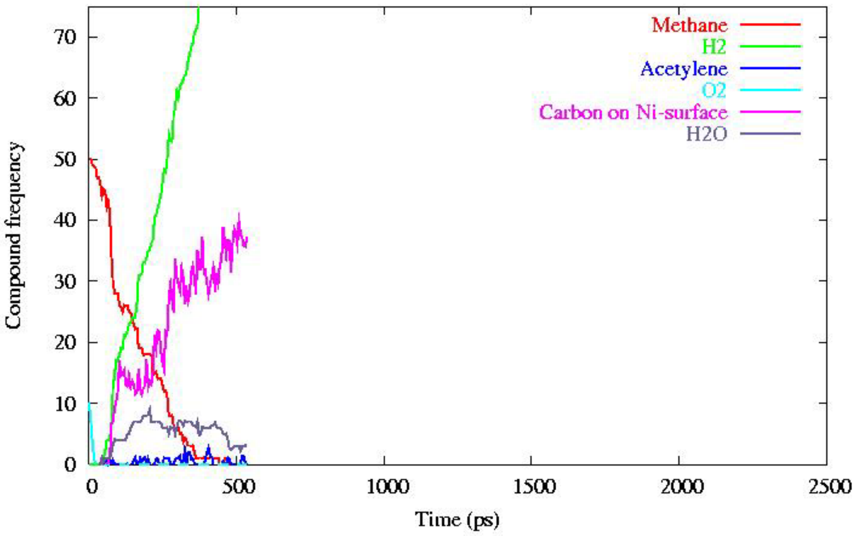
ReaxFF MD/NVT simulation on Ni144+50 methane at T=1500K
Weakened C-H bond by 20 kcal/mol



O_2



ReaxFF simulation on Ni144+50 methane + 10 O2 at T=1500K
Weakened C-H bond by 20 kcal/mol



- CH_4 conversion is substantially increased in the presence of oxygen
- Surface oxygens seem to activate the Ni-particle
- Need to test ReaxFF against more QM-cases to validate this result

Influence of O2 on hydrogen production and carbon deposition

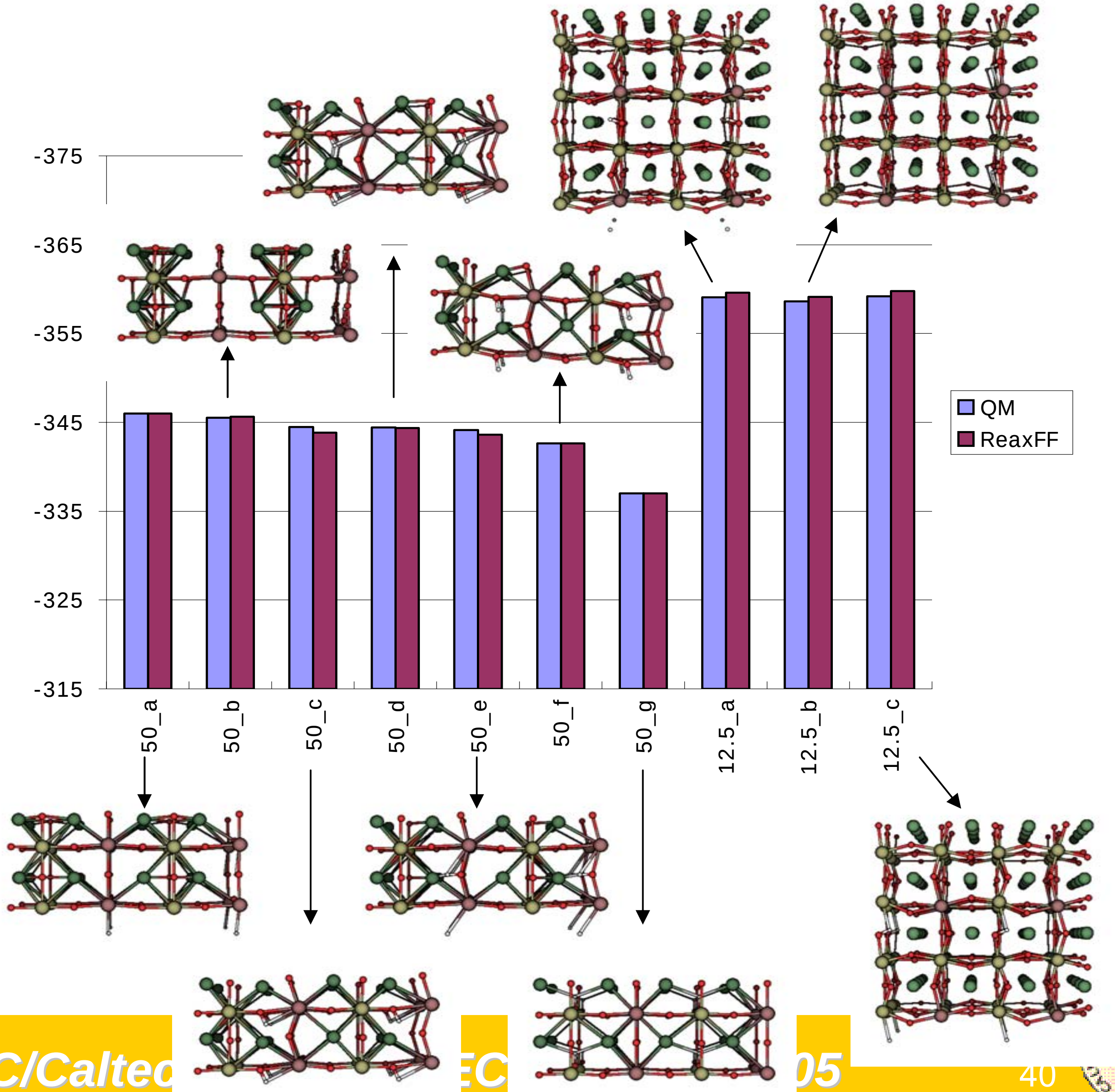
System	CH_4	O_2	H_2	H_2O	CO_2/CO	$C_xH_yO_z$	C_n on Ni surf.
Ni + CH_4	45	0	2	0	0/0	5	0
Ni + 50CH_4 + 10O Radicals	25	0	17	3	0/0	15	0
50CH_4 + 5O_2	50	5	0	0	0	0	0
Ni + 50CH_4 +1O_2	45	1	0	0	0/0	5	0
Ni + 50CH_4 + 5O_2	44	3	4	1	0	3	0
Ni + 50CH_4 + 10O_2	38	5	7	5	0/0	8	0
Ni + 50CH_4 + 25O_2	23	7	23	3	2/0	15	3
Ni + 50CH_4 + 50O_2	2	5	39	34	4/3	20	6

- Tabulated numbers are molecule numbers of the last point simulation results in the gas phase.

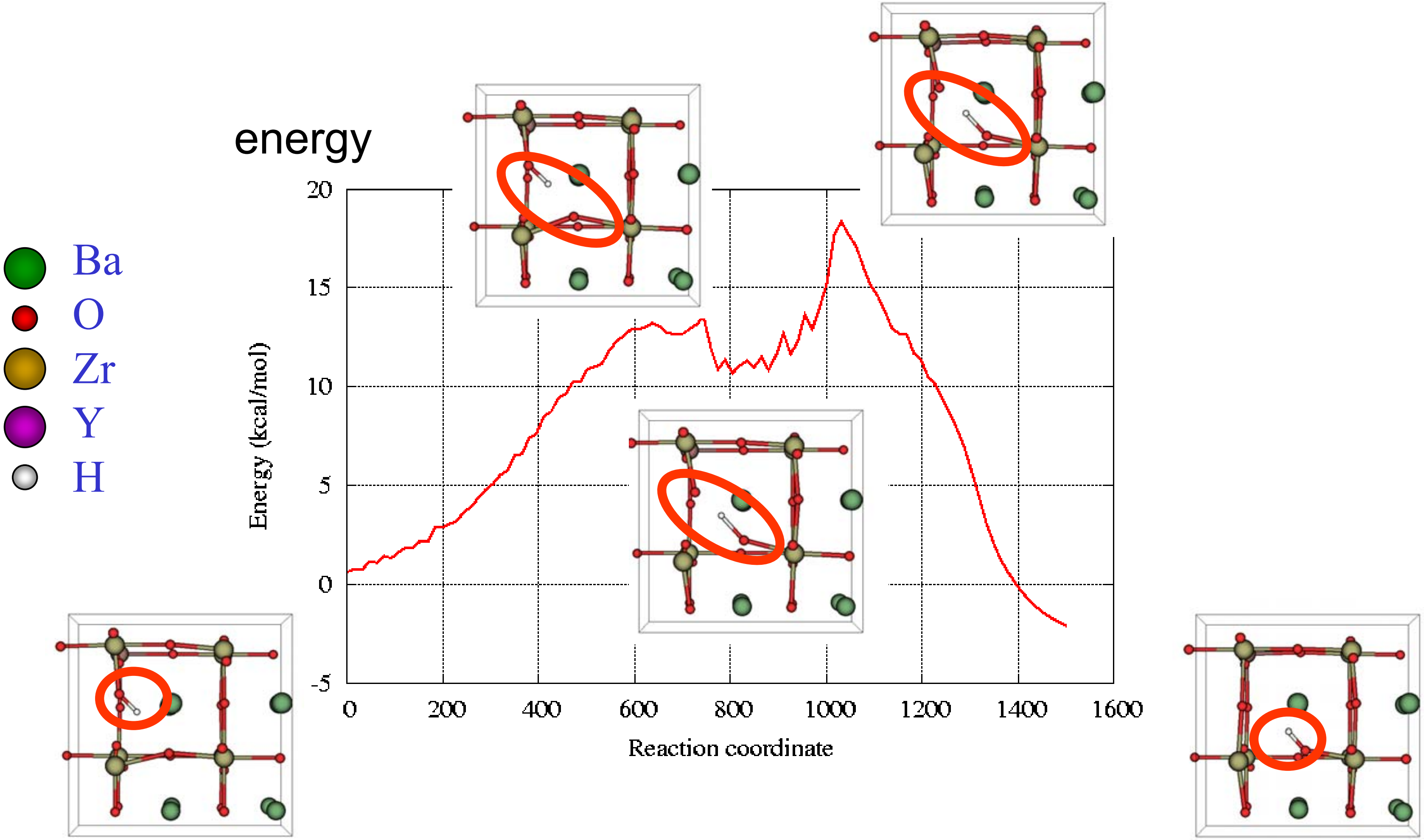
- Simulation time 0.625ns, C-H bond energy 85.83kcal/mol, 1500K

Heats of formation (in kcal/Ba) for Y-doped $BaZrO_3$-phases

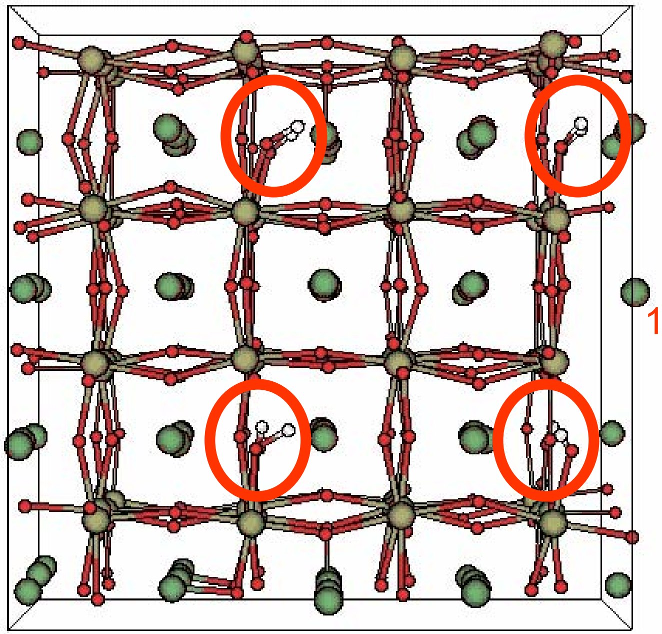
● Ba
● O
● Zr
● Y
○ H

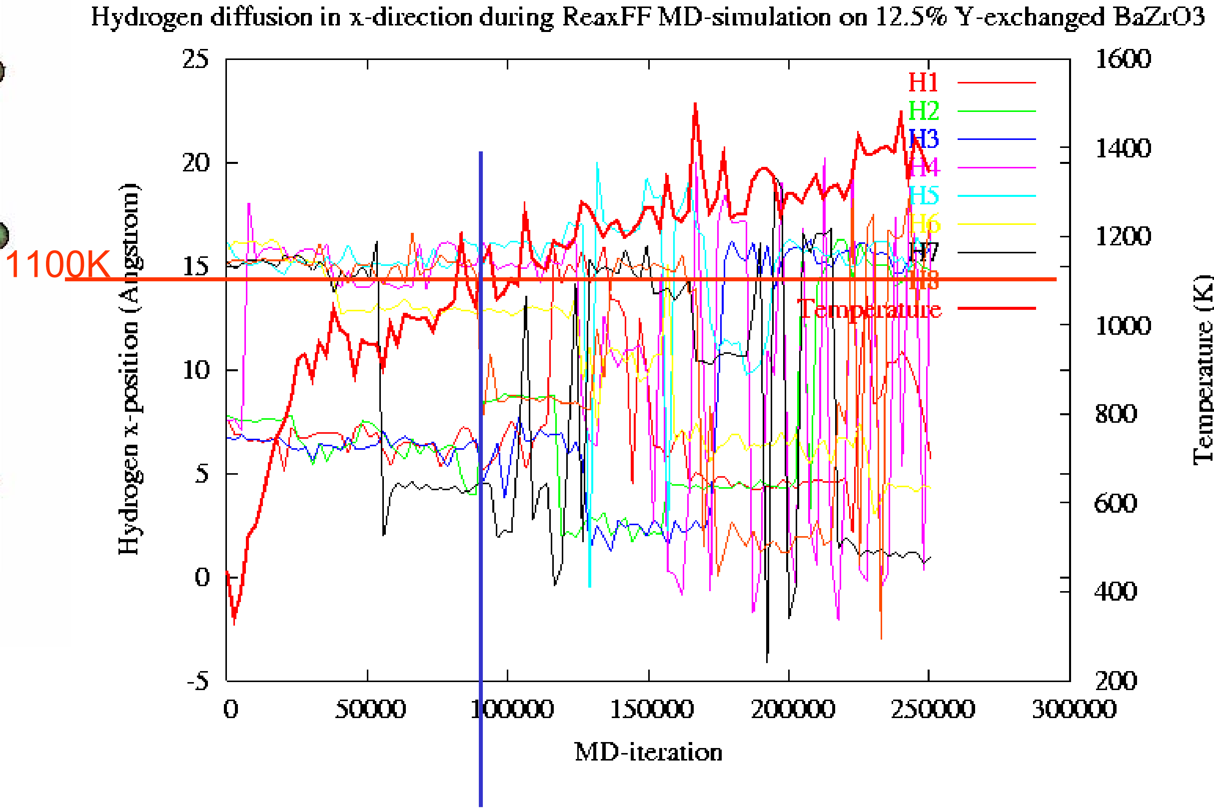


Use ReaxFF to determine Hydrogen diffusion pathways and barriers in Y-doped (25%) BaZrO3



Use ReaxFF MD as function of Temperature to follow H diffusion in Y-doped (12.5%) BaZrO3





Hydrogen becomes mobile at around 1100K

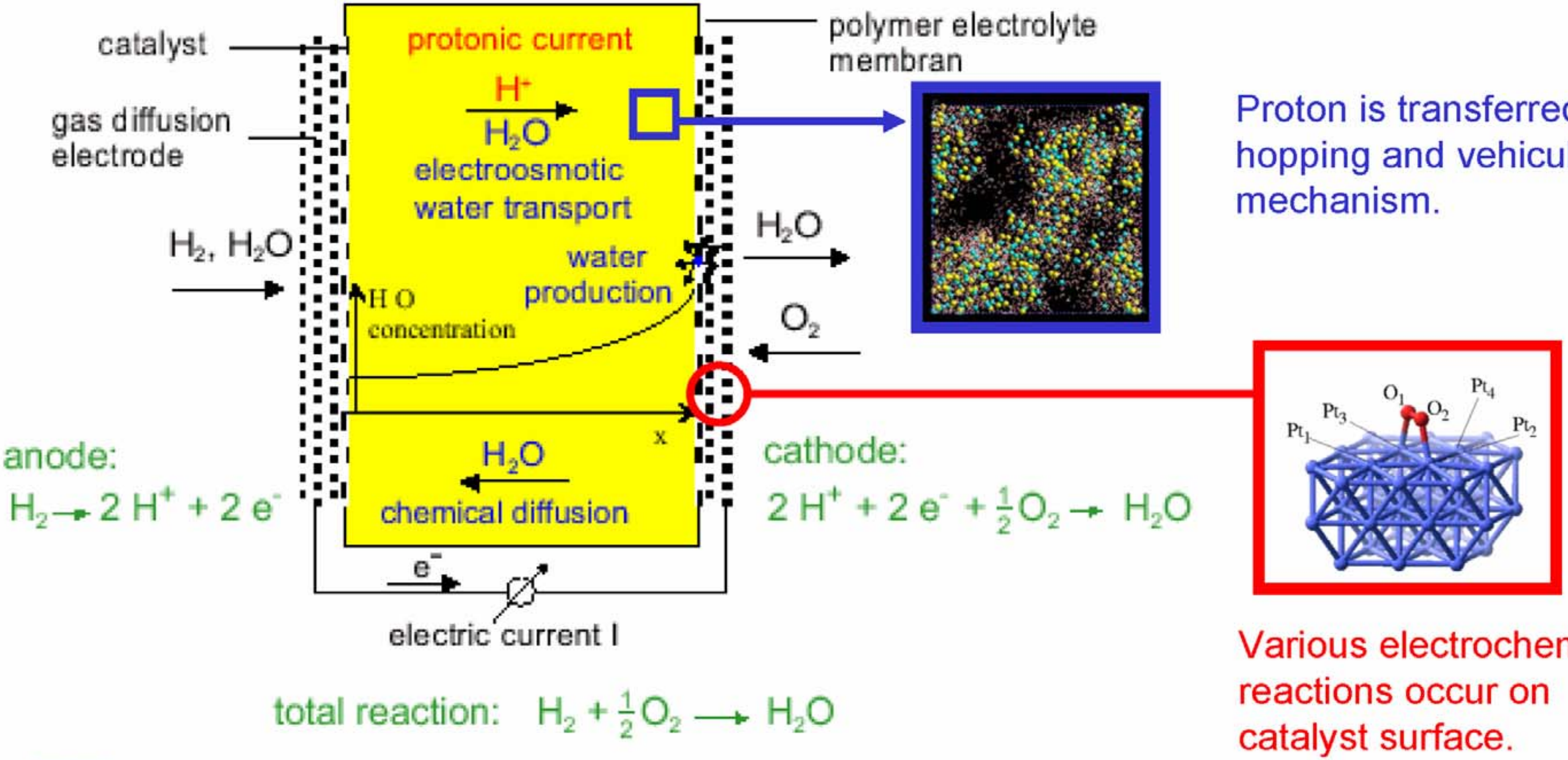
- ● Ba
- ● O
- ● Zr
- ● Y
- ○ H

Polymer Electrolyte Membrane Fuel Cell

Nafion-based PEMFC → the most successful & practical PEMFC

It is due to 1. high proton conductivity and
2. electrochemical and mechanical stability.

We have studied **membrane** and **catalyst**.



anode:
$H_2 \rightarrow 2H^+ + 2e^-$

cathode:
$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$

total reaction: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

Proton is transferred by hopping and vehicular mechanism.

Various electrochemical reactions occur on catalyst surface.

Now, INTERFACE

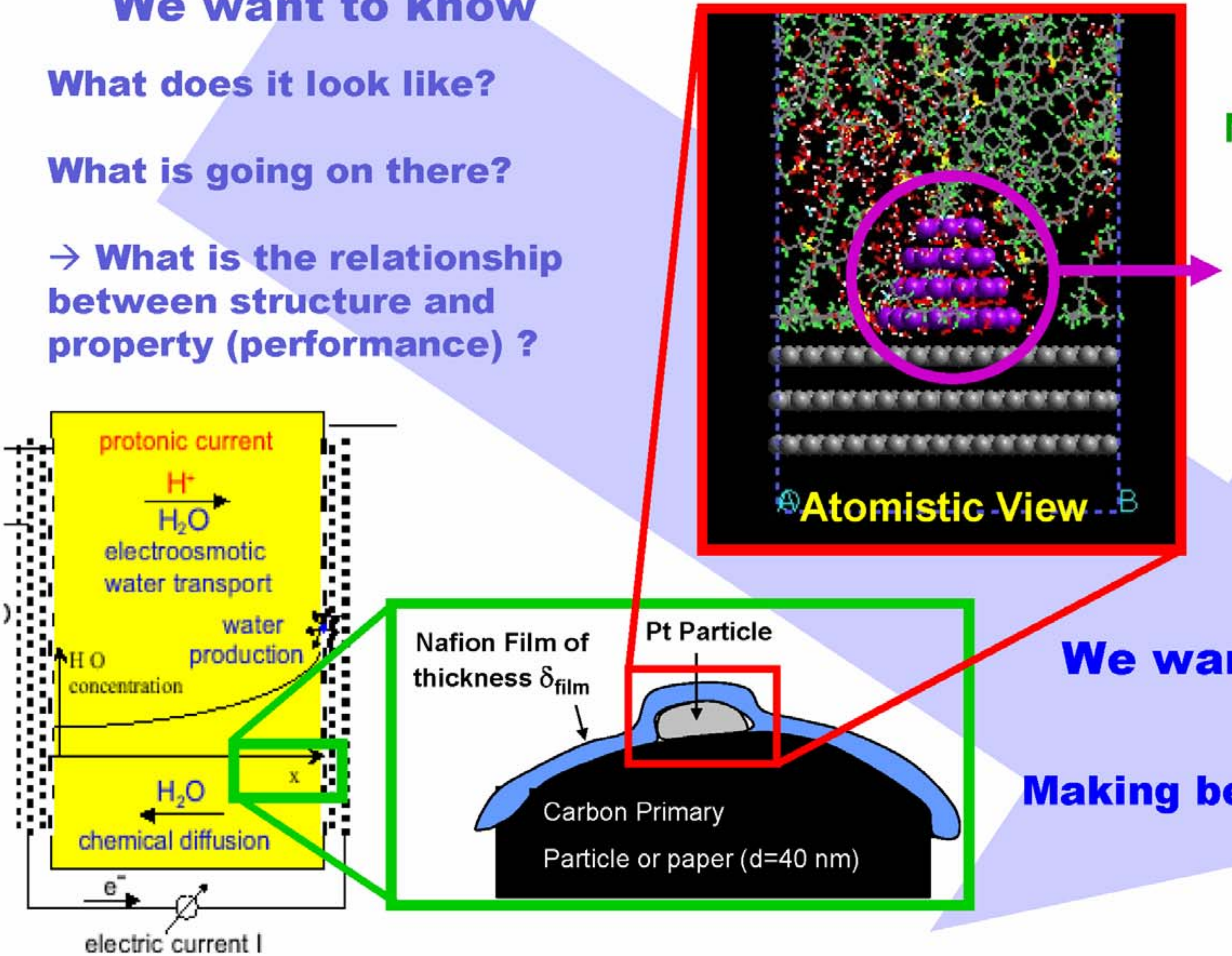
Good Membrane + Good Catalyst…… Is this enough?

We want to know

What does it look like?

What is going on there?

→ What is the relationship between structure and property (performance) ?

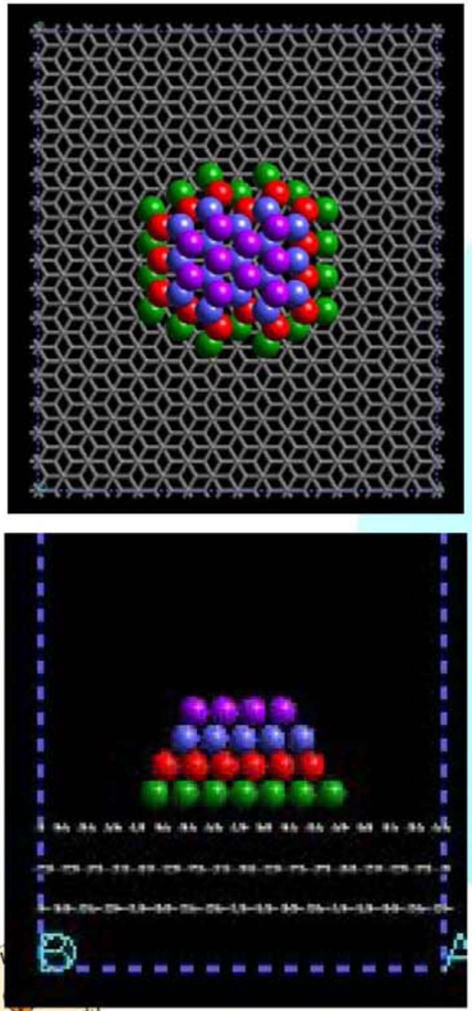


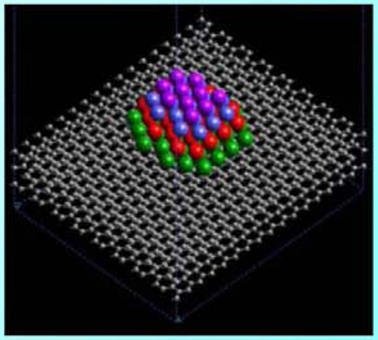
We want to do

Making better FUEL CELL

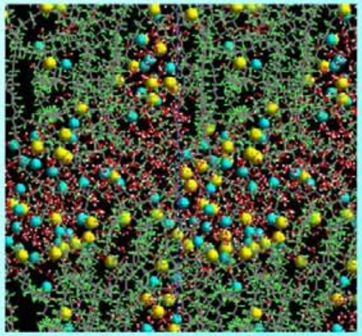
Building-up Interface: Integration with Membrane

Electrode Assembly
(Pt_{87} (111) on Graphite)



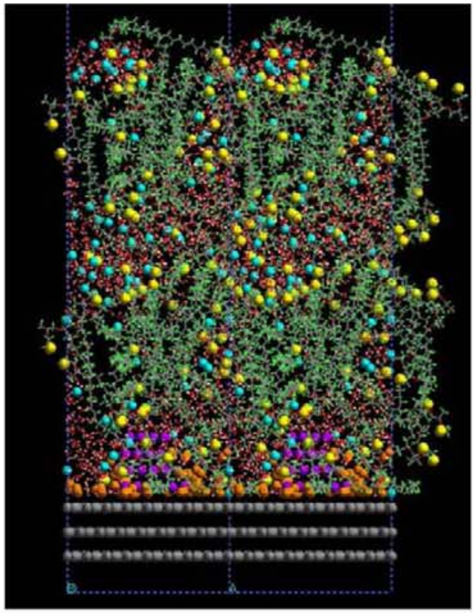


Hydrate Nafion
(20 wt % water)



+

Integrated System



NVT MD simulation of Interface

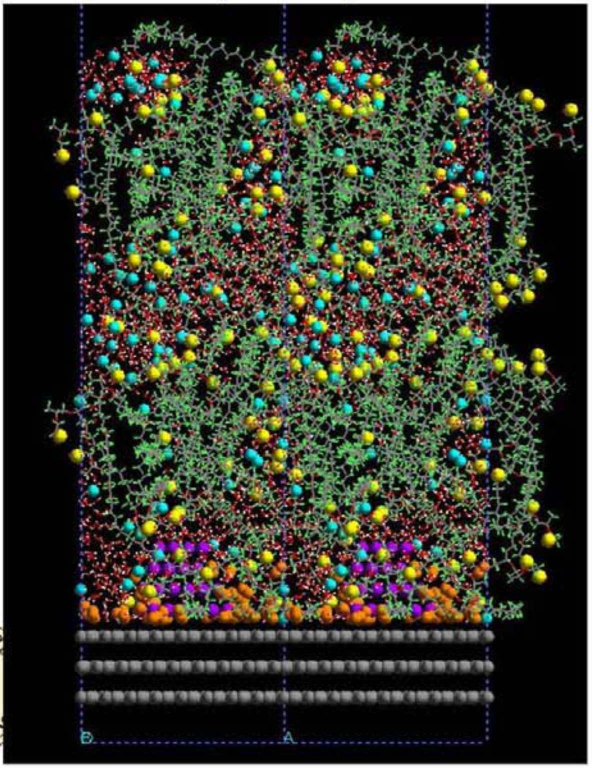
Water content	**~20 wt % (15 H_2O/-SO_3H)**
Total no. of atom	10839
No. of chain	8
No. of sulfonic acid	80
No. of water	1200
Temperature	353.15 K

Modeling software

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator)

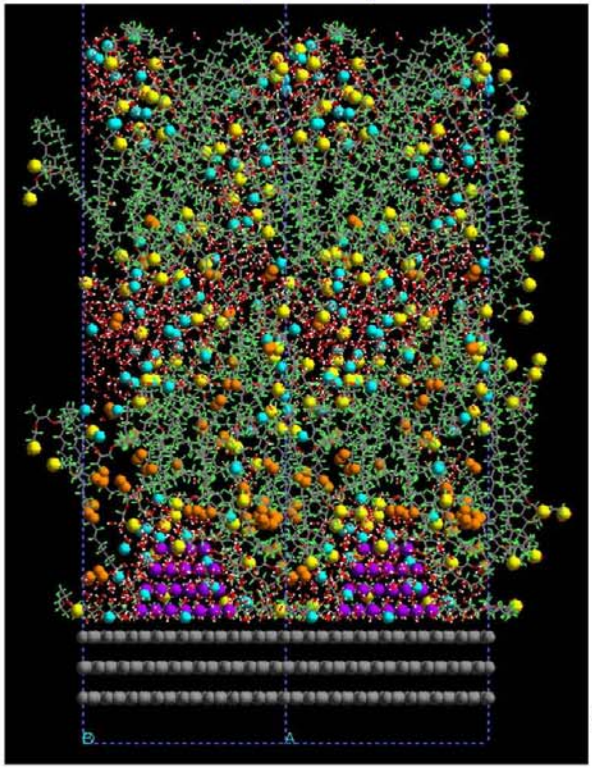
Plimpton, S. J. *J. Comp. Phys.* **1995**, *117*, 1.

Initial configuration
(t=0 ns)



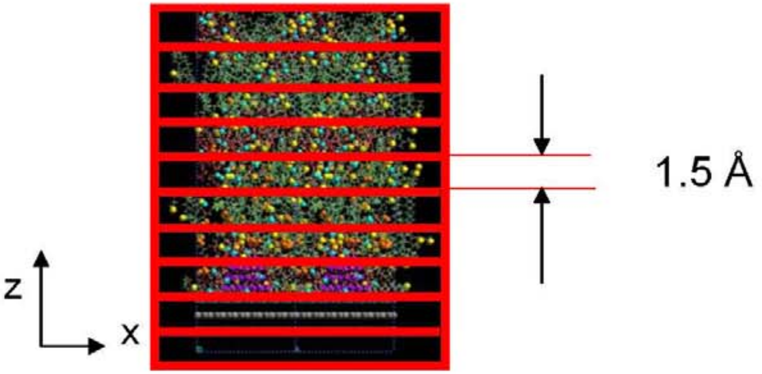
NVT MD simulation
3 ns

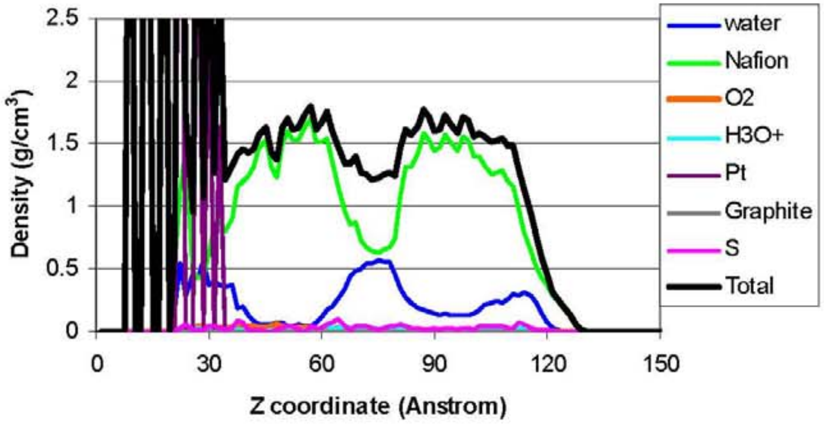
Final configuration
(t=3 ns)

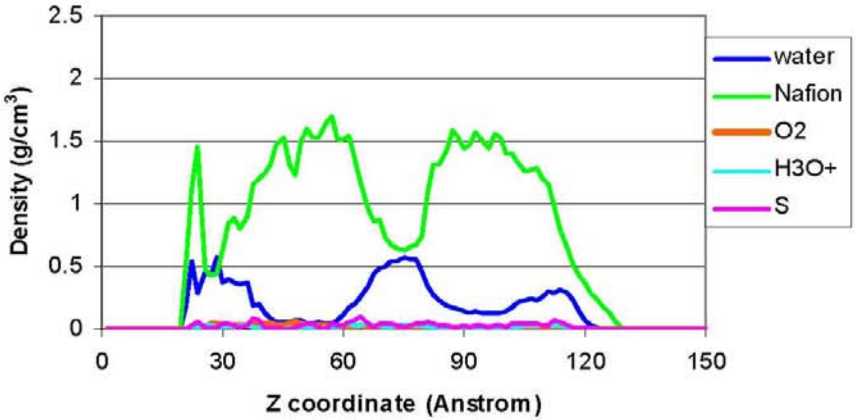


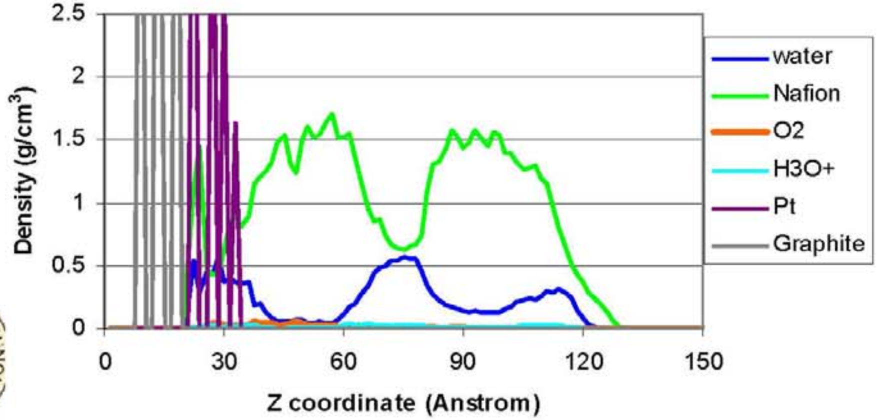
NVT MD simulation of Interface

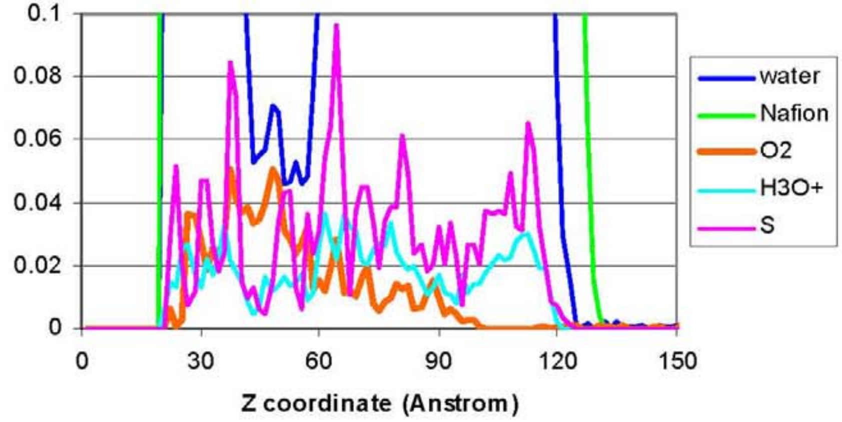
Density Profile











NVT MD simulation of Interface

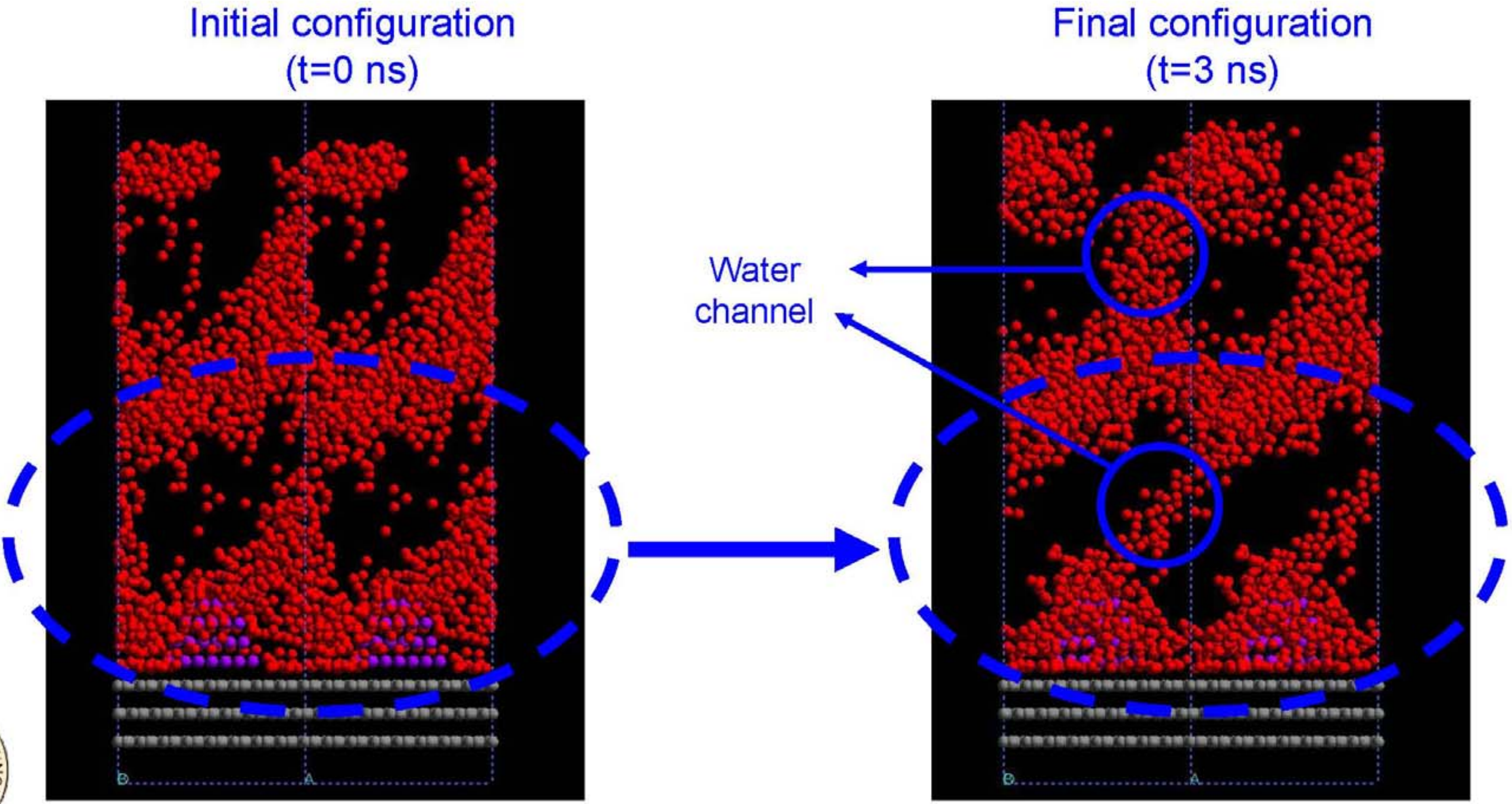
Water distribution

1. Membrane has percolated water phase.

→ critical for the proton transport

2. Pt nanoparticle is solvated by water.

→ critical for the reduction reaction in cathode



NVT MD simulation of Interface

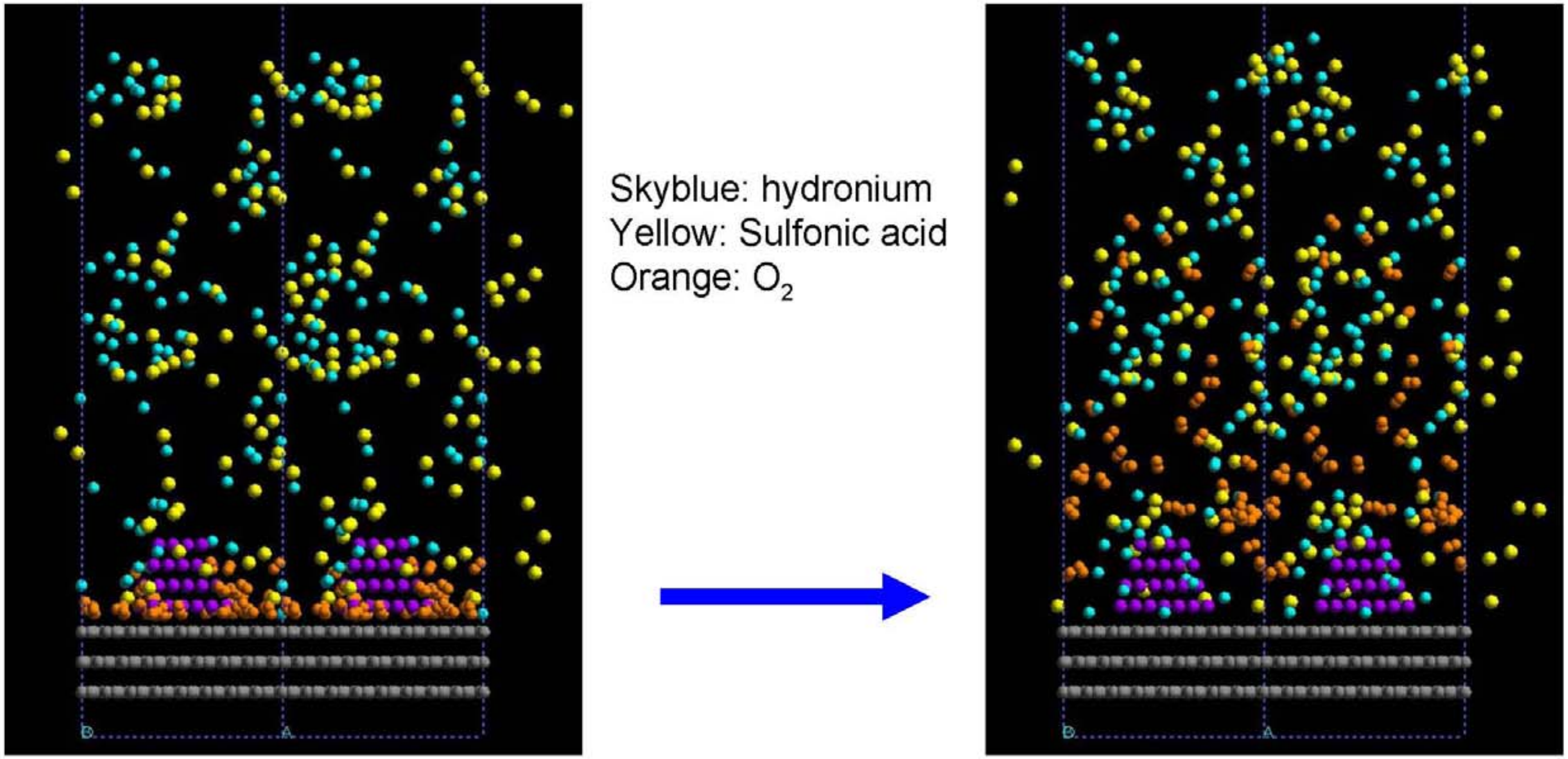
Distribution of H_3O^+, O_2 and ionized sulfonic acid

1. O_2 molecules diffuse into hydrophobic PTFE backbone phase.

→ Binding Energy: $E(O_2–Pt) < E(H_2O–Pt)$

2. H_3O^+ and ionized sulfonic acid group approaches Pt nanoparticle.

→ Attraction with Pt surface



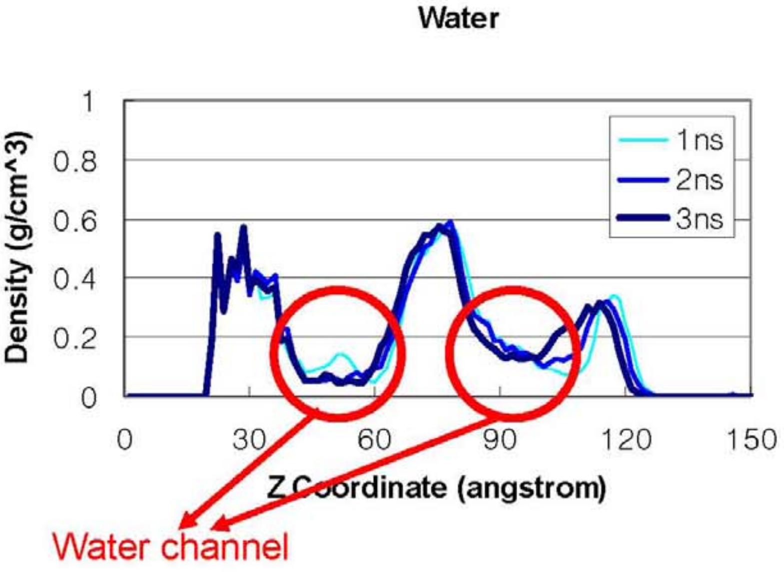
Initial configuration
(t=0 ns)

Final configuration
(t=3 ns)

Skyblue: hydronium
Yellow: Sulfonic acid
Orange: O_2

NVT MD simulation of Interface

Water distribution

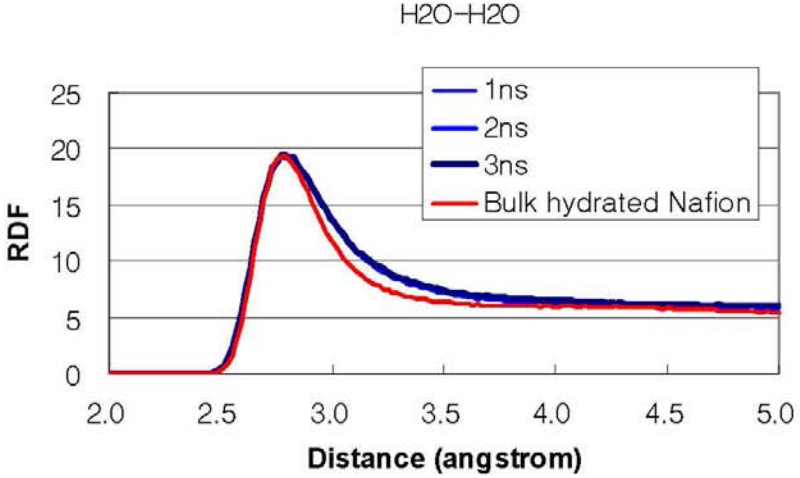


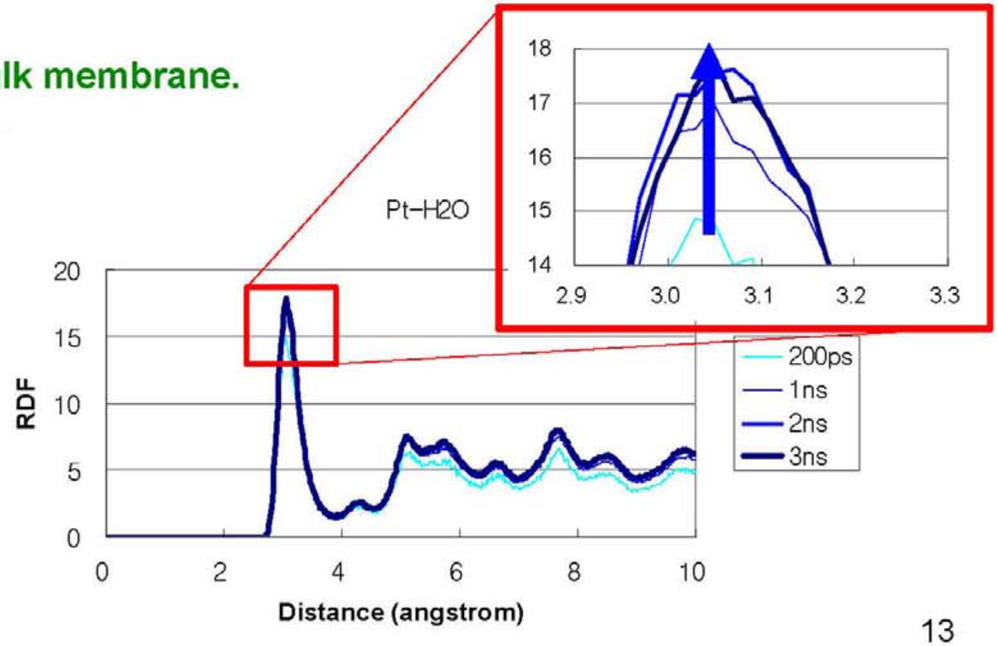
After 1ns MD, the system nearly reach its equilibrium.

Water domains are connected via water channel up to Pt nanoparticle.

Pt nanoparticle is well solvated by water.

Water structure is comparable to that in bulk membrane.
Water has more neighbors in the interface.



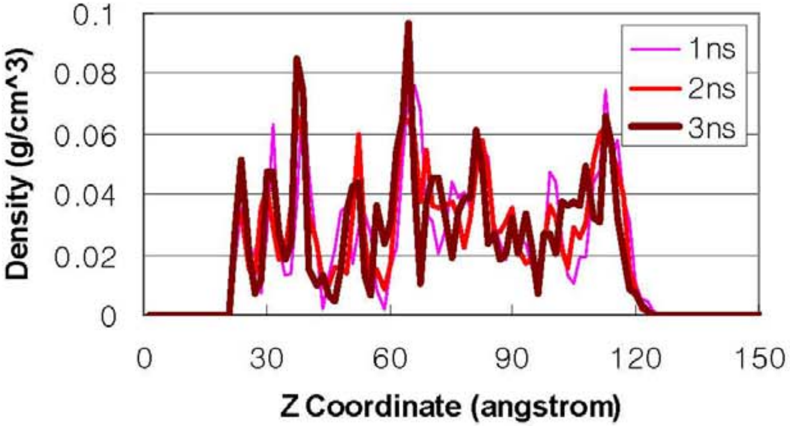


NVT MD simulation of Interface

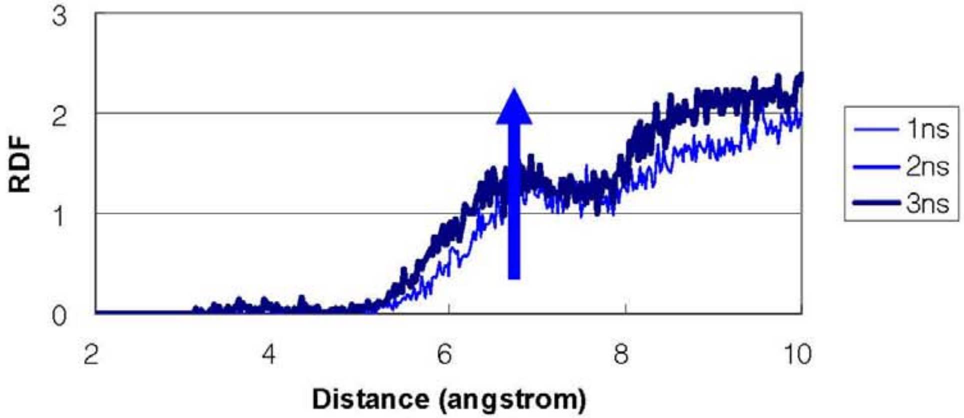
Distribution of ionized Sulfonic acid

Ionized Sulfonic acid group approaches Pt nanoparticle

S

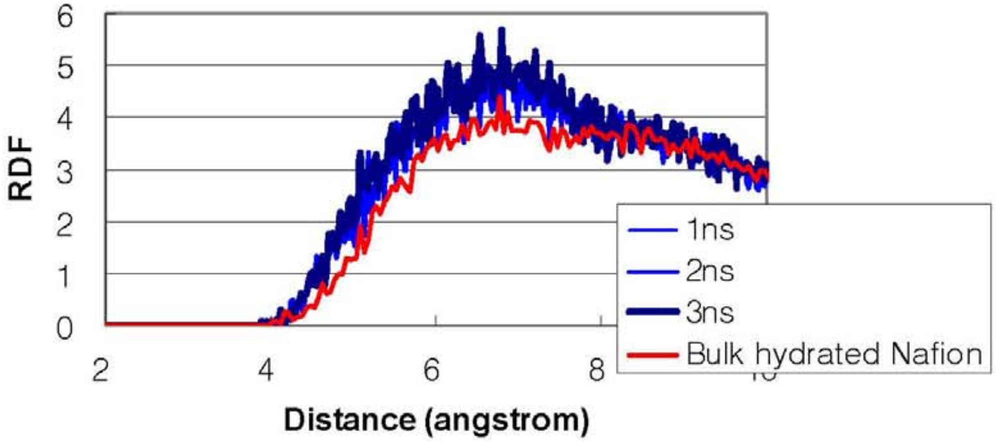


Pt–S



S–S

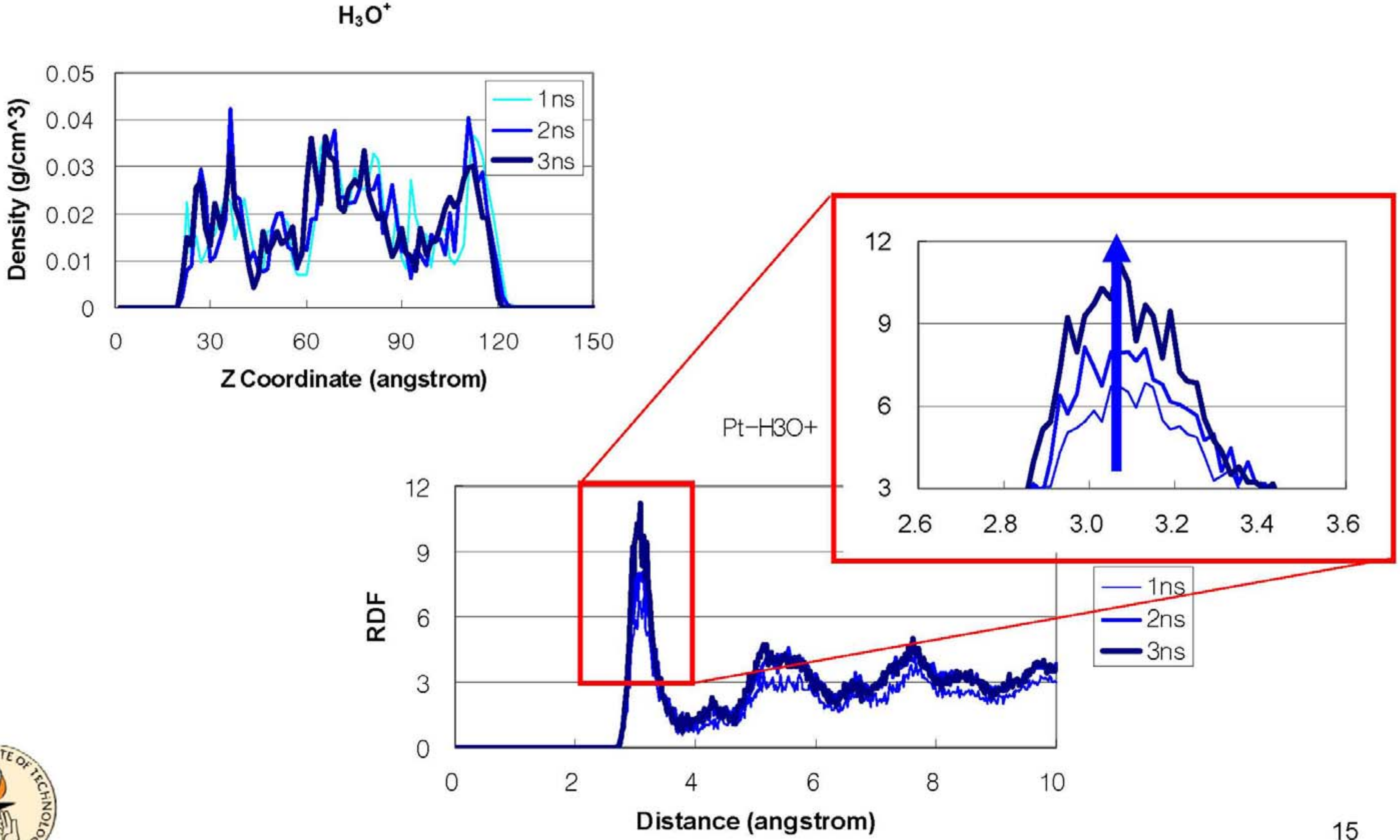
Avg. S-S distance is nearly comparable to that in the bulk hydrated Nafion.



NVT MD simulation of Interface

Distribution of H_3O^+

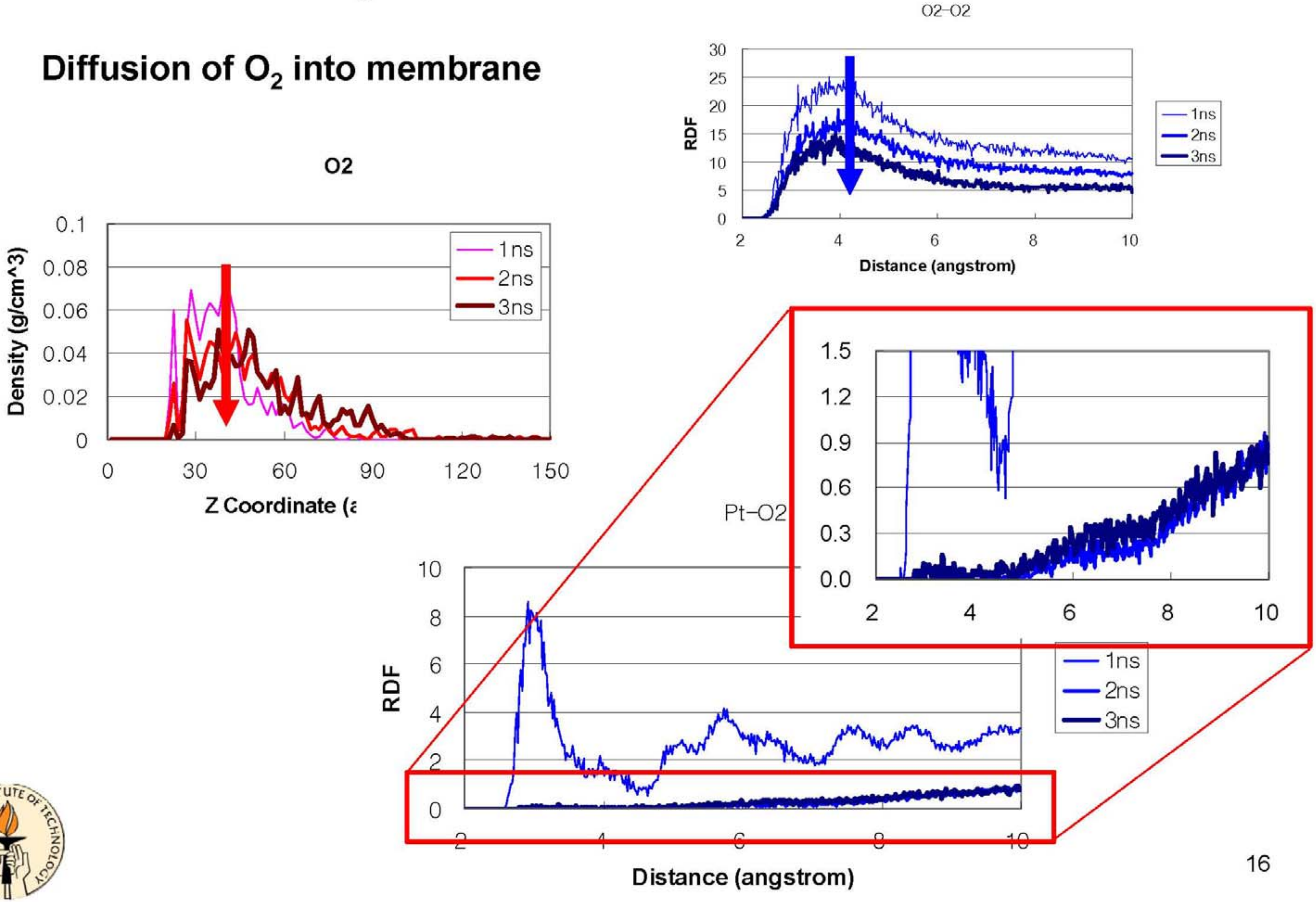
Hydronium approaches Pt nanoparticle.



NVT MD simulation of Interface

Distribution of O_2

Diffusion of O_2 into membrane



Summary

We simulate the hydrated Nafion membrane-electrode Interface using MD method with classical FFs.

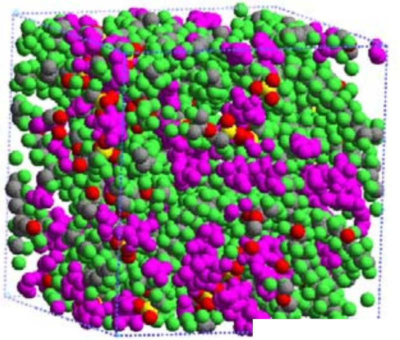
The interface has a well-developed nanophase-segregated configuration.

1. In such configuration, we found that the water phase is percolated where the water structure is comparable to that in the bulk membrane.
2. The distribution of ionized sulfonic acid group is also comparable to that of the bulk membrane.
3. The hydronium particles diffuse to the Pt nanoparticle whereas the O_2 molecules diffuse into the hydrophobic PTFE backbone phase.

Future

1. Analyze the dynamic transport of water, proton, and O_2
2. Consider the effect of electric field
3. Apply the reactive FF to describe the reduction reaction at cathode.

Fluorinated imidazoles as proton carriers for water-free fuel cell membranes

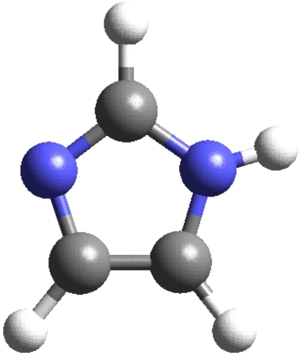


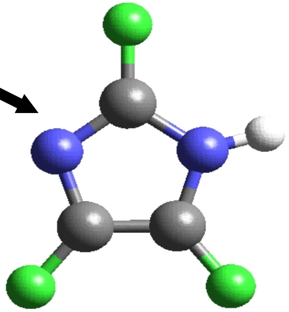
CHALLENGE

- Pt poisoning by CO (T < 120°C)
- Evaporation limits use of water

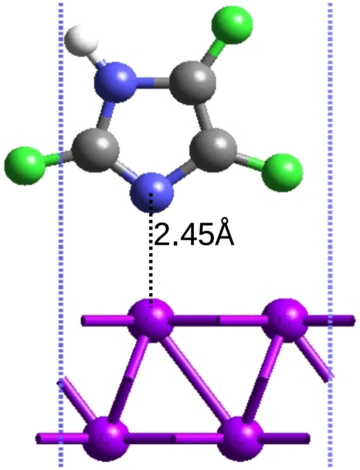
CONCEPT

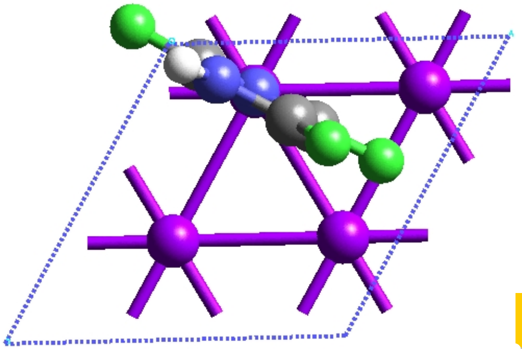
- Replace water by other proton carrier in Nafion.
- Imidazole/Nafion 0.1S/cm 177°C
- Problem: Imidazole poisons the Pt catalyst
- Solution: use Fluorinated imidazoles?
- Design and test computationally

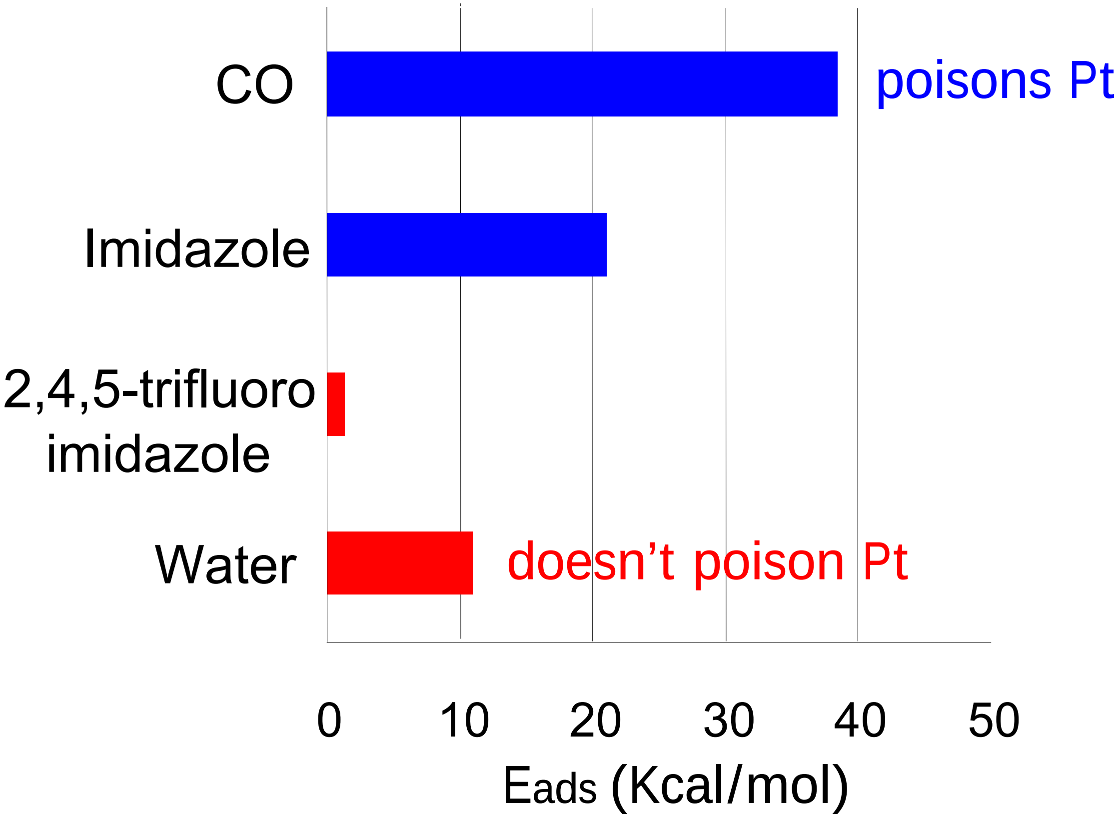




Using QM show that Fluorinated imidazole does not adsorb on Pt

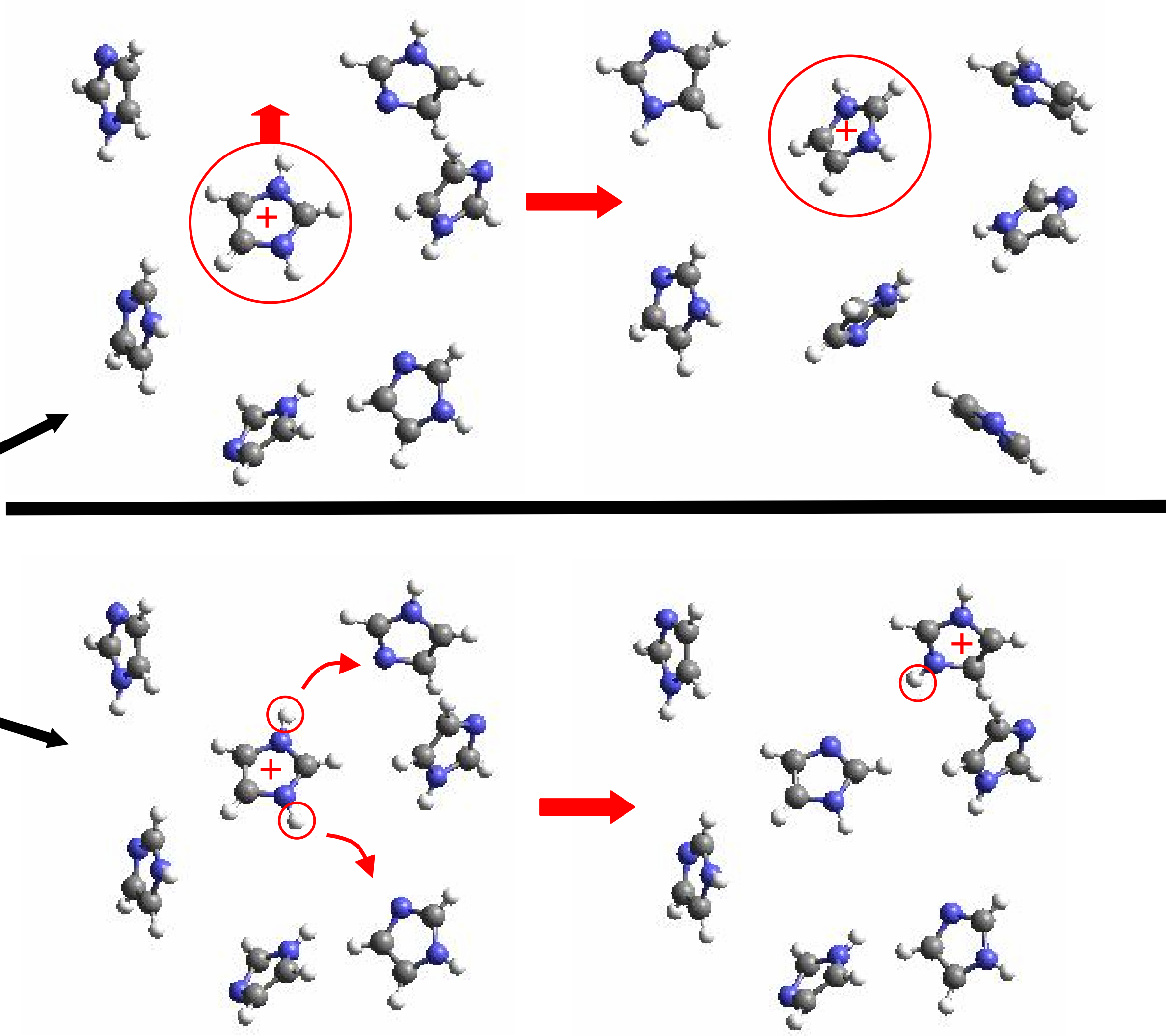






(GGA/PW91)

How good is fluorinated Imidazole for proton transport?



Compute proton diffusion using theory:

Two mechanisms

Vehicular Diffusion

Proton Hopping

Two contributions to H^+ diffusion

$$D = D_H + D_V$$

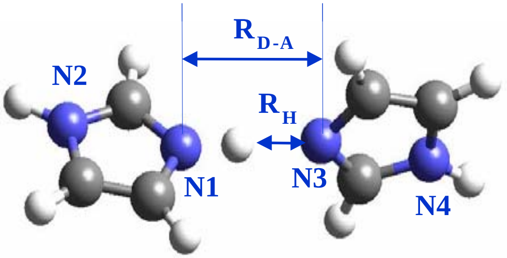
- Vehicular diffusion from MD: $\langle r^2(t)\rangle = 6\, D_V\, t$
- Hopping diffusion parameterized from QM & evaluated over MD trajectory

$$D_H = k(\underline{r})\underline{r}^2$$

$$D_H = \frac{1}{6Nt}\int_0^{t\to\infty}\sum_i^N\sum_j^M k(\underline{r_{ij}})\underline{r_{ij}}^2 P_{ij}(\underline{r_{ij}})dt \qquad P_{ij} = \frac{k_{ij}}{\sum_j^M k_{ij}}$$

Ingredients to compute H^+ transfer

$$k(r) = \kappa(T,r)\frac{k_B T}{2\pi\hbar}\exp\left(-\frac{E_b(r) - \hbar\omega_1(r)/2}{k_B T}\right)$$

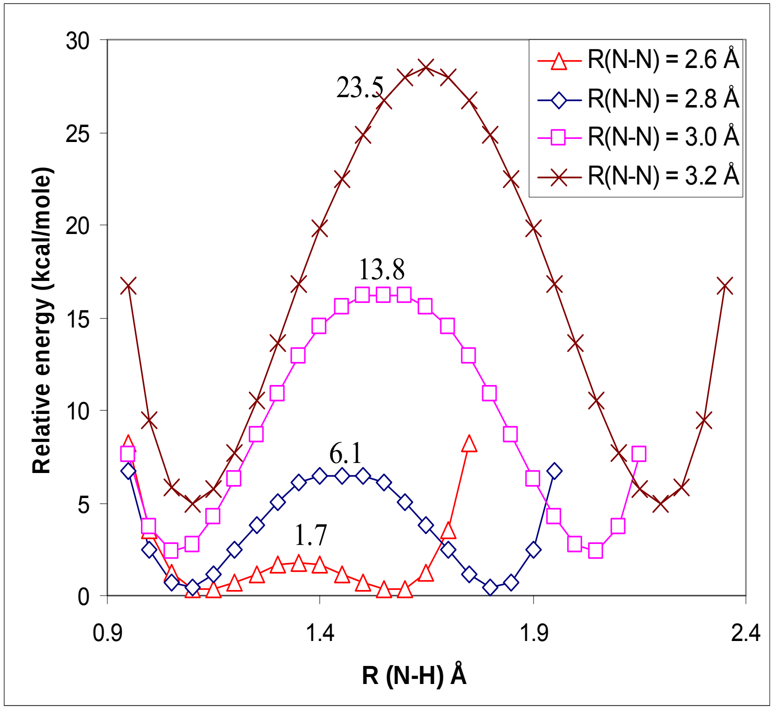


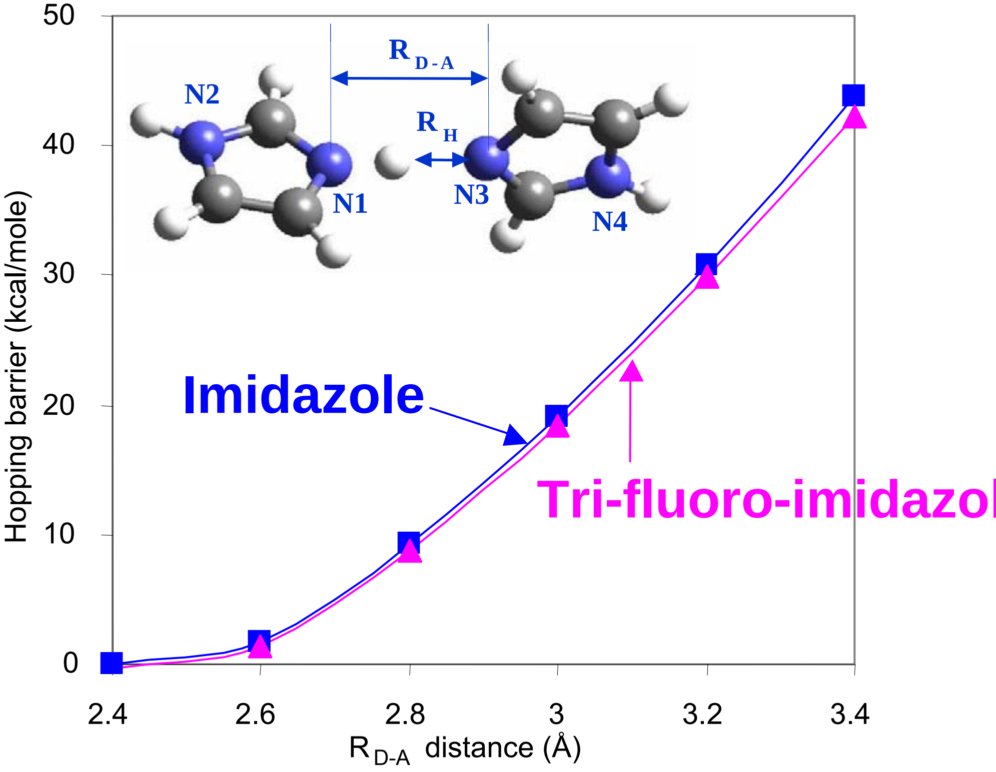
- Tunneling
- barriers E_b (solvation effect)

- distribution of pairs r_{ij}
- vehicular mobility

QM shows that the barrier for proton transfer does not depend on fluorination

- QM (B3LYP/6-311G**++)
- PBRF solvation





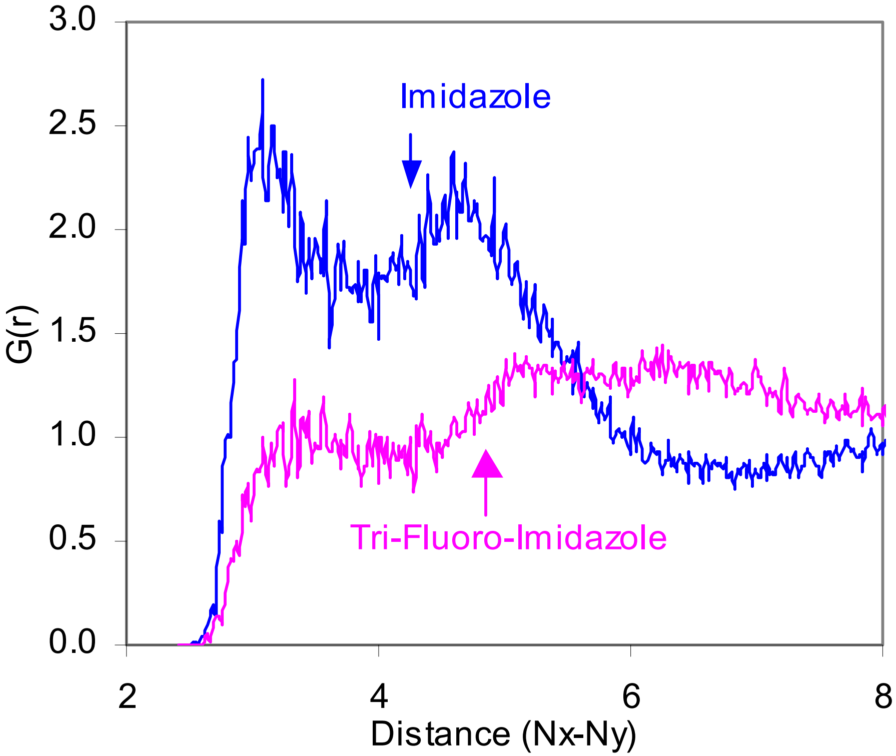
The distribution of carrier in the membrane depends on fluorination

Radial distribution function

Trifluoroimidazole in Nafion is more dispersed.

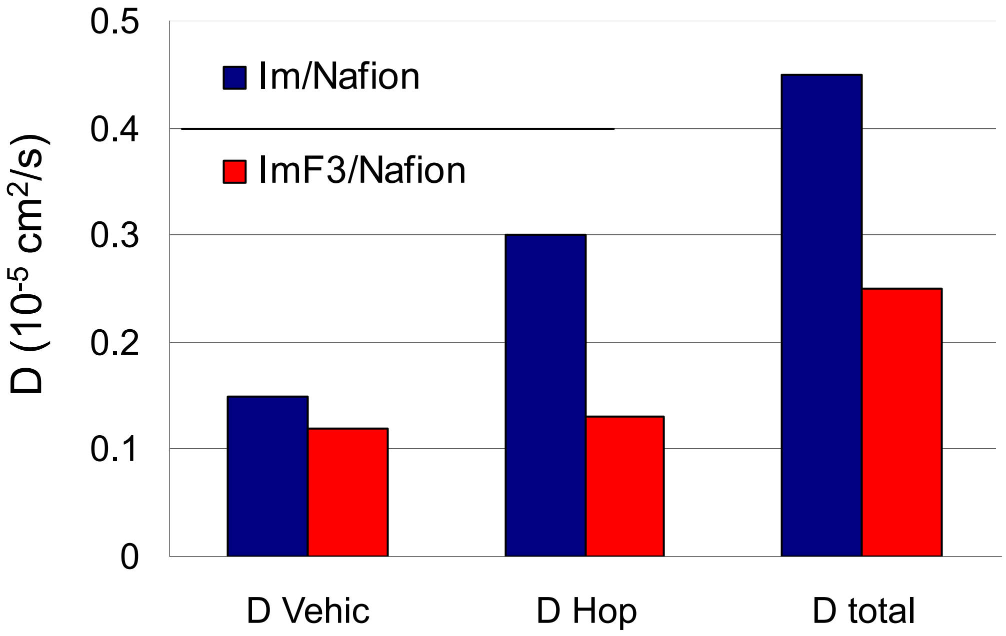
↓

Imidazole has higher hopping probability



Computed proton diffusion

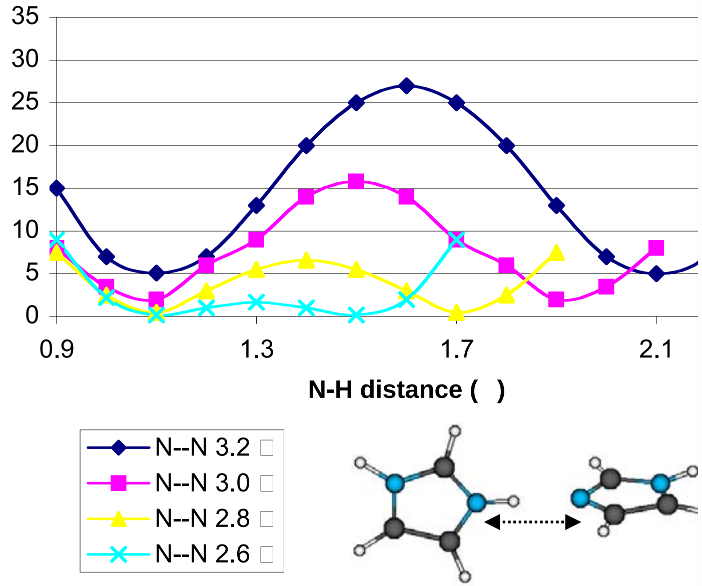
Im/Nafion &
ImF3/Nafion



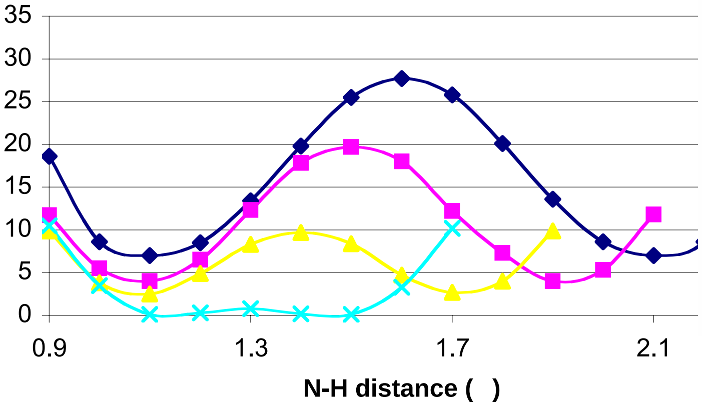
- Diffusion in ImF3/Nafion is ~60% of Im/Nafion.
- Experimental value Im/Fafion is **0.06 S/cm at 177°C.**
- **We predict conductivity of ImF3/Nafion 0.06 S/cm at 177°C.**

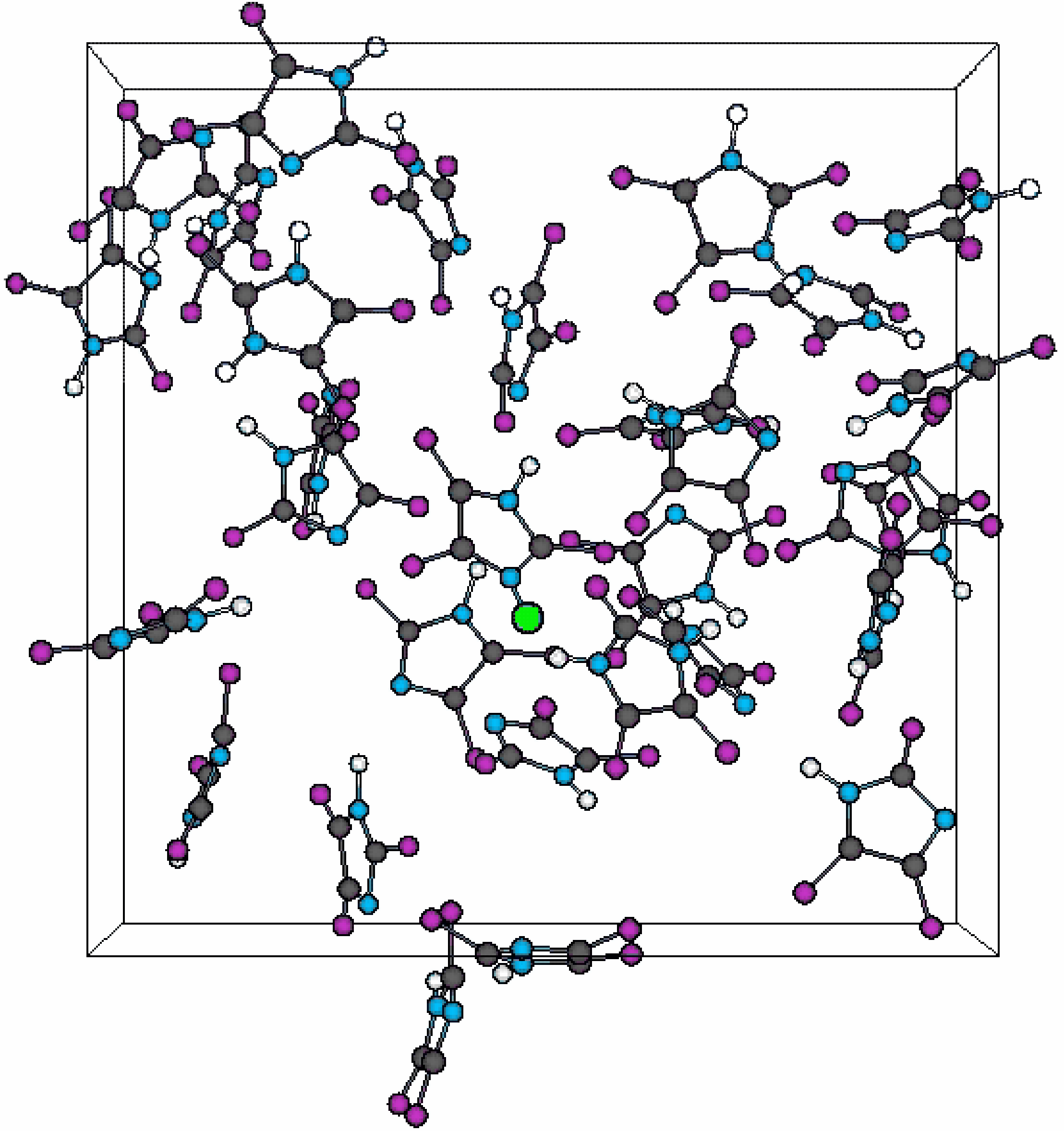
Proton migration through imidazole/imidazolium cation phases

H-transfer in [Im-Im]+: QM-data



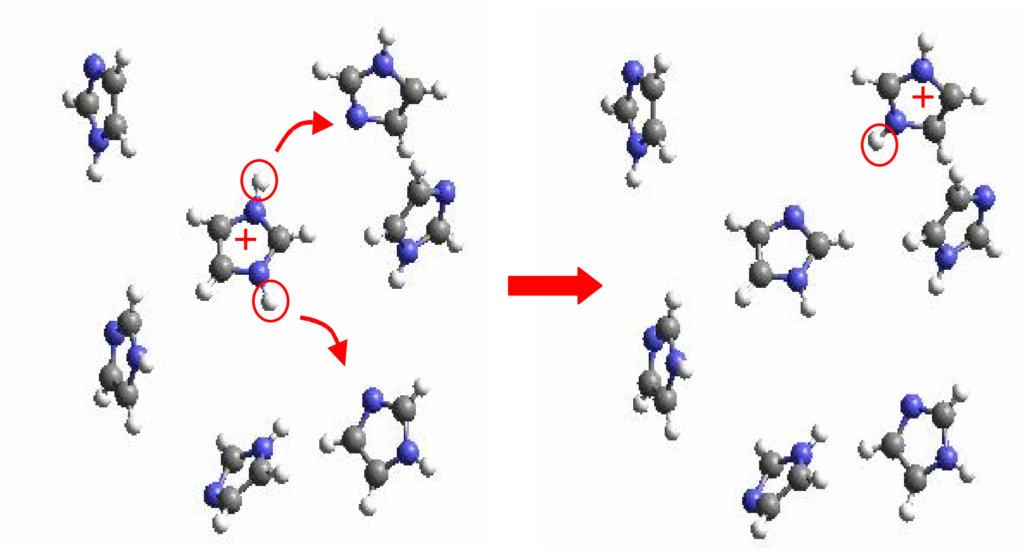
H-transfer in [Im-Im]+: ReaxFF-da

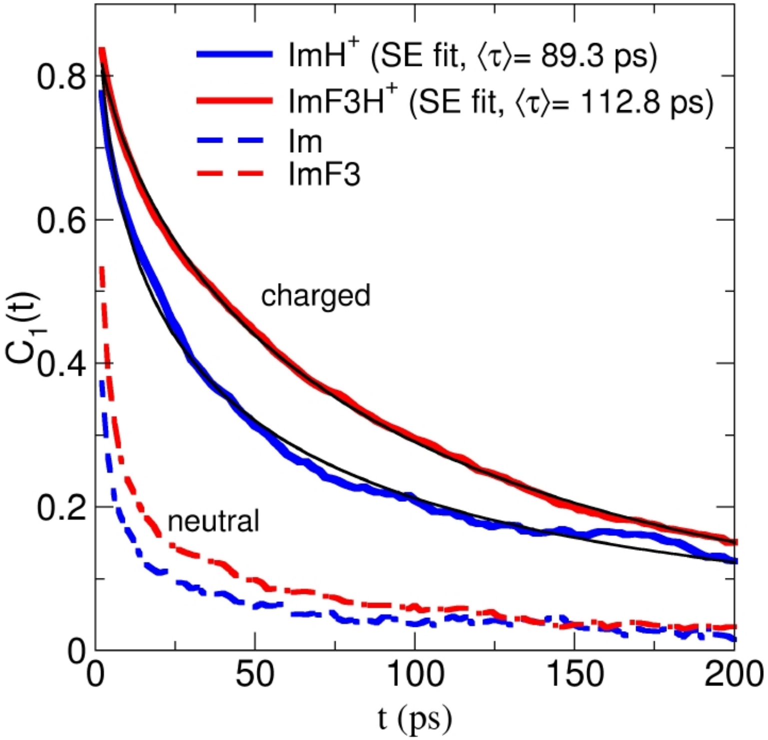




at T=300K

If rotation of proton carrier were limiting…





$$C_1(t) = \frac{1}{N}\sum_{i=1}^{N}\langle\cos(\theta_i(t))\rangle \longrightarrow C_1(t) = Ae^{-(t/\tau)^{\beta}}$$

Difference in conductivity of Im/Nafion and ImF3/Nafion would be only 20%

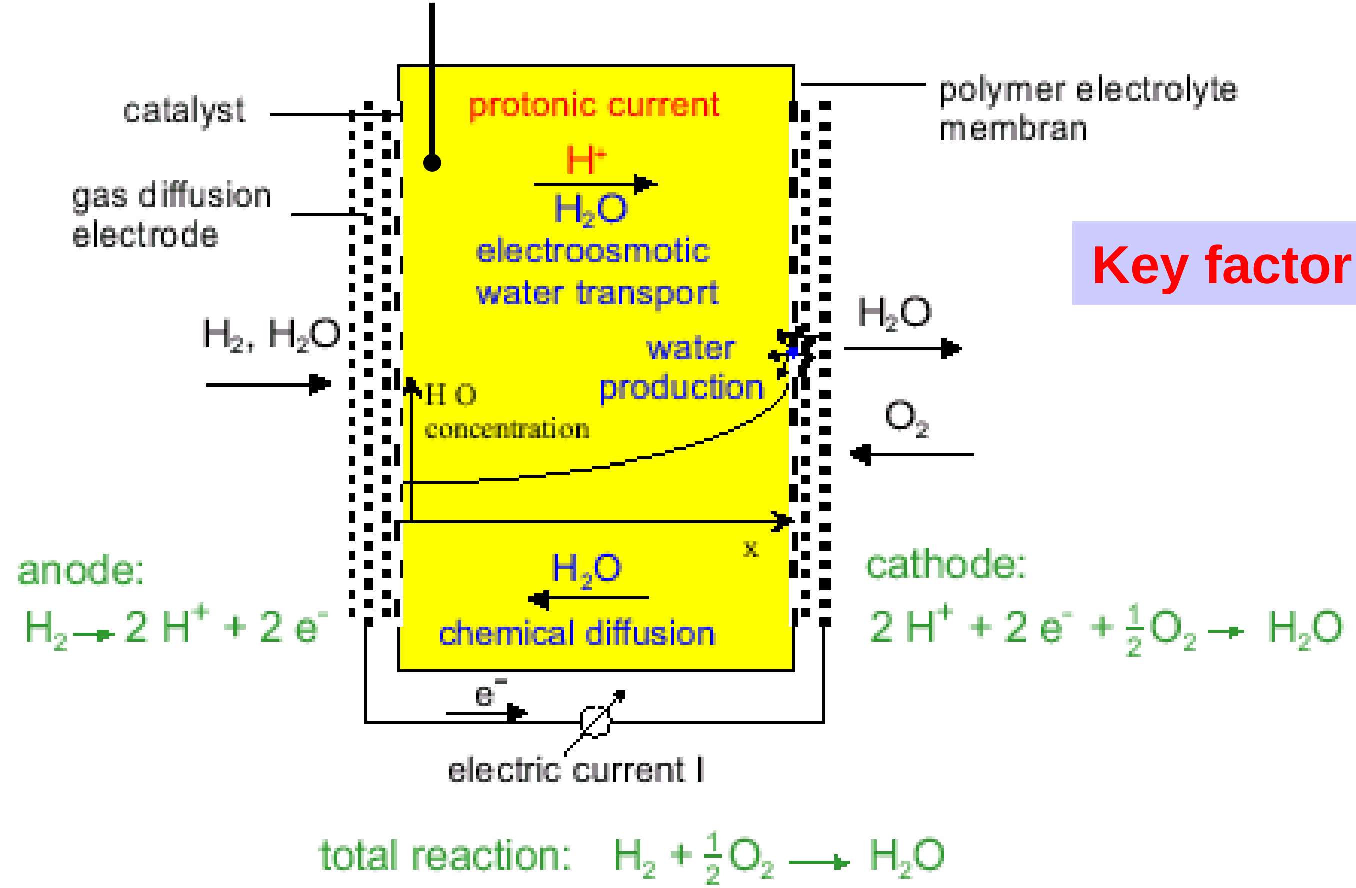
Conclusions

- New for proton transport, allows temperatures up to 200C
- Does Not poison Pt
- Conductivity comparable to imidazole

New Molecular Architecture for PEMFC: Dendrimer-PTFE copolymer

Current state-of-the-art PEMFCs are based on **Nafion** due to its high proton conductivity as well as electrochemical and mechanical stability.

We want to improve this membrane part for better performance.



Key factor: water management

New polymeric material for PEMFC

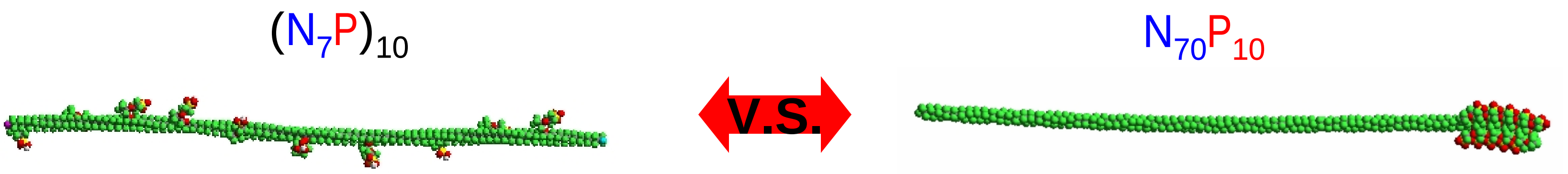
How to improve the performance? Make better structure !

Summary of our previous study on Nafion 117

We investigated the effect of monomeric sequence on nanostructure of hydrated Nafion 117.

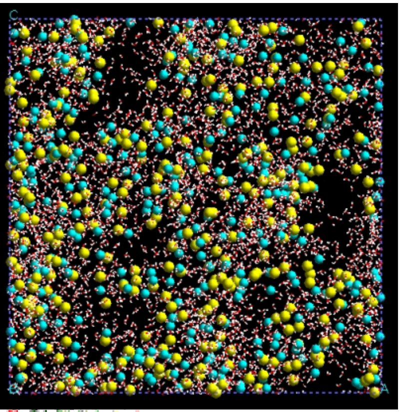
DR (degree of randomness)=1.1

DR (degree of randomness)=0.1

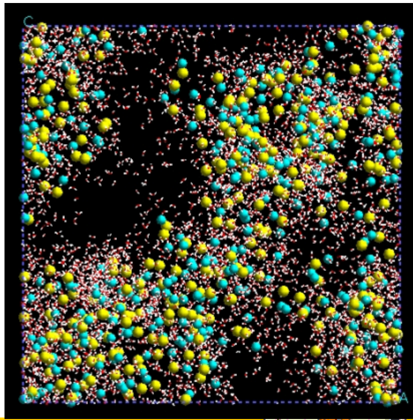


dispersed monomeric sequence

More blocky monomeric sequence



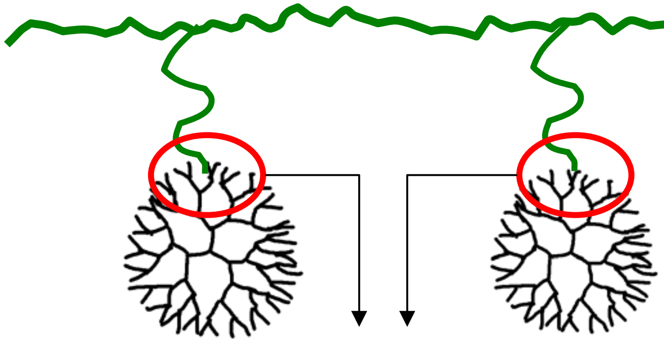
We found
the more blocky Nafion has
1. the larger phase-segregated structure
2. more diffusion of water



New Dendrimer-PTFE copolymer for PEMFC: DENDRION

Basic concept of Dendrion material

Combine a hydrophilic dendrimer with a hydrophobic linear polymer



Teflon (PTFE): Hydrophobic linear polymer backbone

Fréchet type dendrimer: Hydrophilic dendrimer whose surface is covered by acidic moieties such as carboxylic acid

Covalent junctions are required to prevent the structure from macroscopic phase-segregation.

Why is the dendritic architecture interesting?

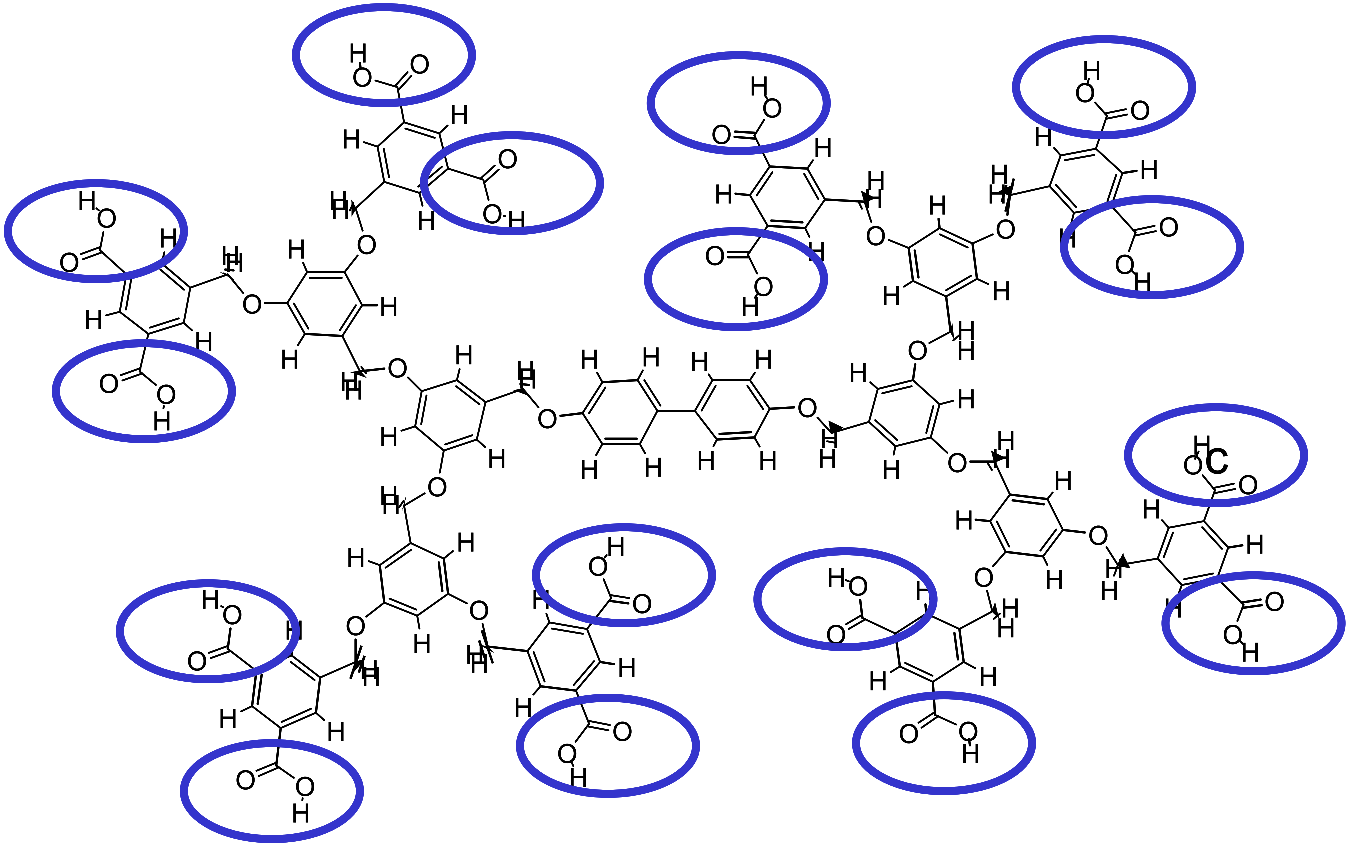
Many acidic groups are concentrated in small local space.

→ We expect that the phase-segregated structure is intrinsically endowed by its architecture.

How can we utilize this feature?

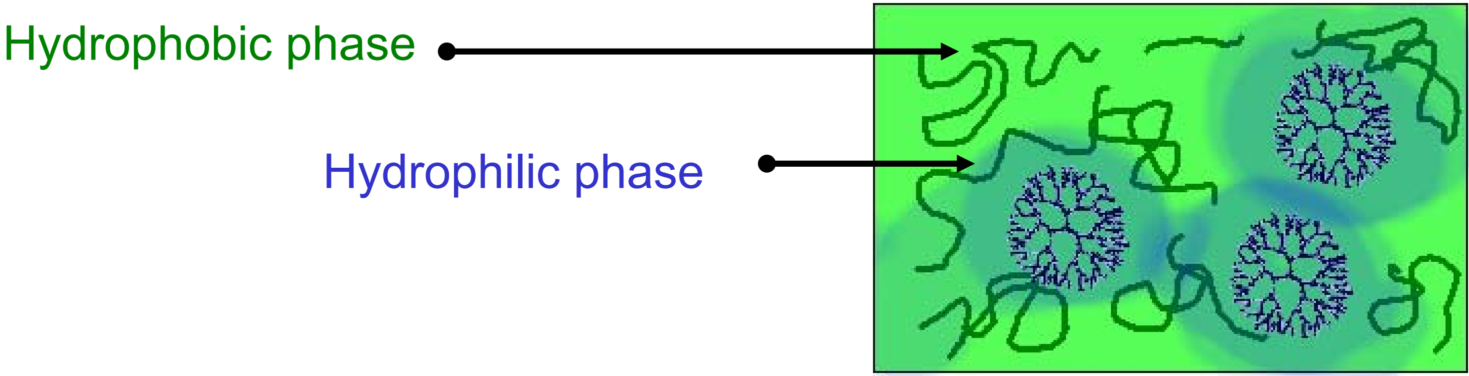
Use Fréchet type dendrimer:
water-soluble polyaryl ethereal dendrimer

Case study: 2nd generation (266 atoms) → 16 carboxylic acid groups



Unimolecular Micelles And Globular Amphiphiles - Dendritic Macromolecules As Novel Recyclable Solubilization Agents; Hawker Cj, Wooley Kl, Frechet Jmj
Journal Of The Chemical Society-perkin Transactions 1 (**12**): 1287-1297 Jun 21 1993

nanostructure of **Dendrimer-PTFE copolymer**



Target properties to be controlled

<u>Water distribution & structure</u>

<u>Water/proton transport</u>

Water cluster size

Via Nanophase-segregation

Relevant variables

<u>Water content</u>

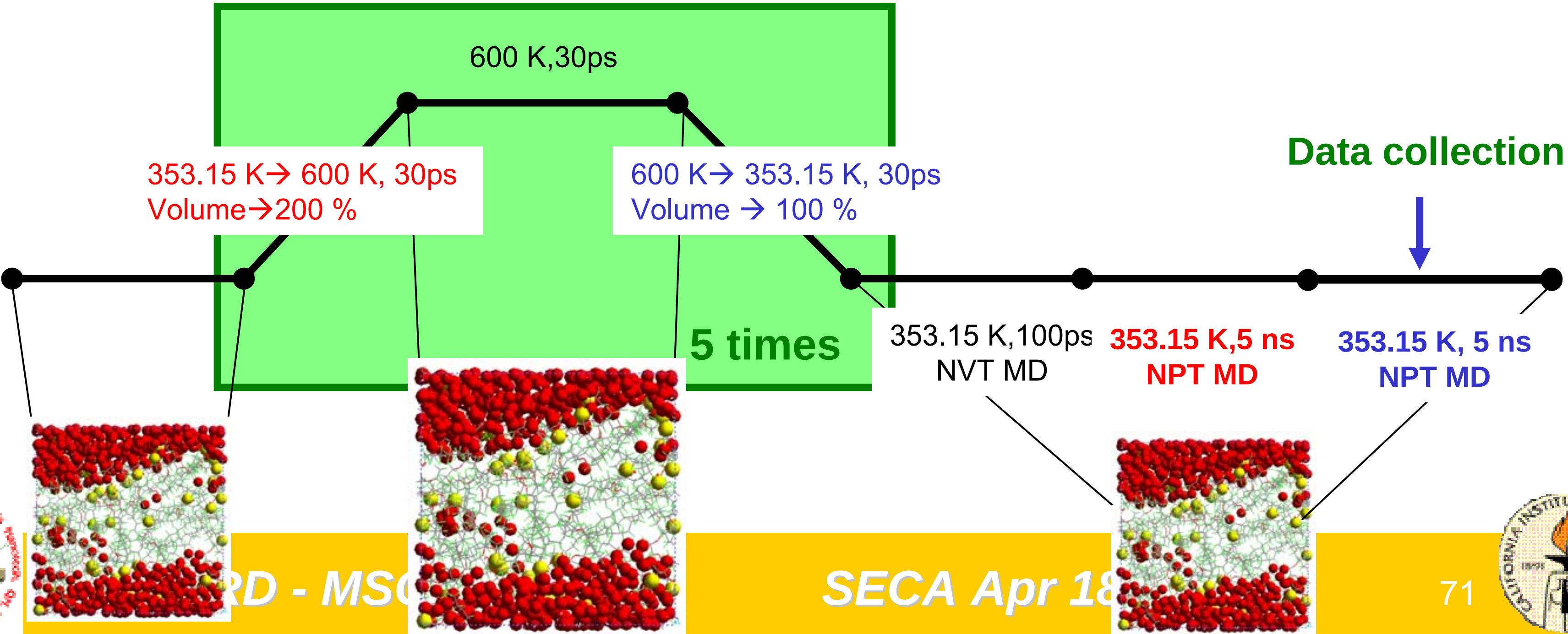
Type of acidic group (carboxylic acid or phosphoric acid?)

Size of dendrimer (generation of dendrimer)

Composition of dendrimer in polymer (equivalent weight)

Synthesis and equilibration

Water content	**~10 wt %** **(7 H_2O/-COOH)**	**~5 wt %** **(3 H_2O/-COOH)**
Total no. of atom	6080	5312
No. of chain	4	4
No. of carboxylic groups	64	64
No. of water molecules	448	192
Temperature	353.15 K	353.15 K



600 K,30ps

353.15 K→ 600 K, 30ps
Volume→200 %

600 K→ 353.15 K, 30ps
Volume → 100 %

5 times

Data collection

353.15 K,100ps
NVT MD

353.15 K,5 ns
NPT MD

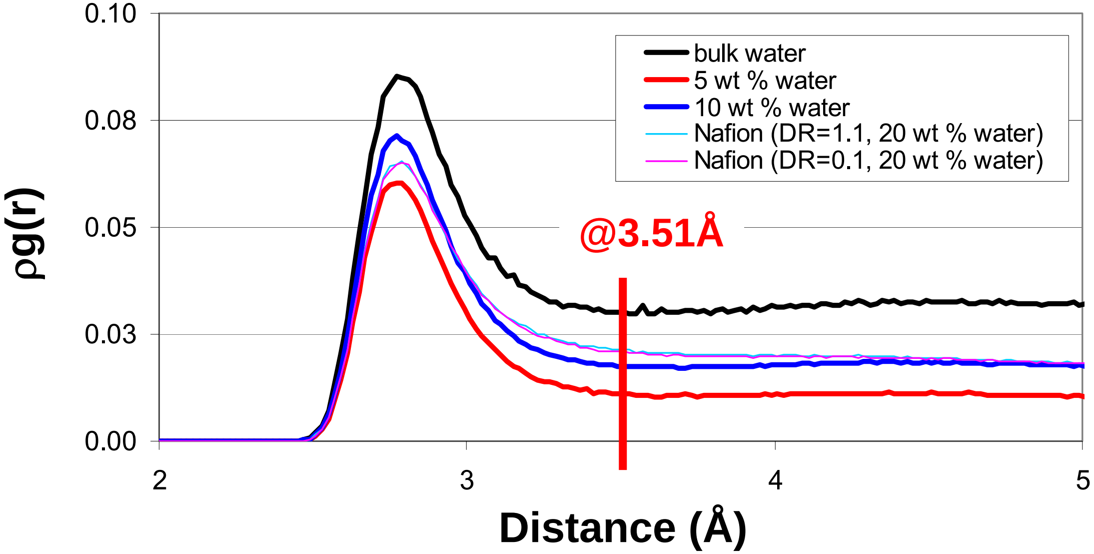
353.15 K, 5 ns
NPT MD

Water structure Hydrated membrane

(5 wt % and 10 wt % water content)

For the better performance of fuel cell, we want
1. Percolated water distribution at lower water content
2. Bulk-water-like structure at lower water content

RDF of O(water)-O(water)



System	Water Coord. No.
Pure water	5.14
Dendrion (5 wt % water)	**2.93**
Dendrion (10 wt % water)	**3.75**
Nafion DR=1.1 (20 wt % water)	3.85
Nafion DR=0.1 (20 wt % water)	3.82

The water in Dendrion membrane retains a bulk-like structure more efficiently than the given Nafion membrane.
What if the water content becomes 20 wt % in this new polymer?

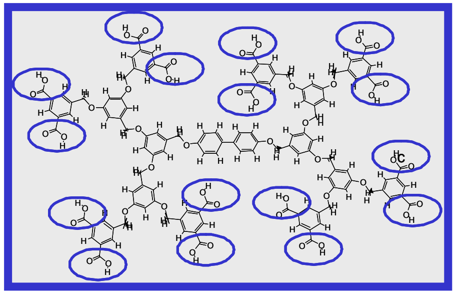
Water diffusion Hydrated membrane

(5 wt % and 10 wt % water content during 5 ns simulation)

$$\left\langle \left(r(t)-r(0)\right)^2 \right\rangle = 6Dt^{\nu}$$

System	$D_{linear}(\nu = 1)$ (10^{-5} cm^2/s)
Pure water (300 K)	**2.90 (exp. 2.46[a])**
Dendrimer-PTFE (5 wt % water @ 353.15K)	**0.21**
Dendrimer-PTFE (10 wt % water @ 353.15K)	**0.37**
Nafion DR=1.1 (20 wt % water @ 353.15 K)	**1.43 (exp. 1.25[b])**
Nafion DR=0.1 (20 wt % water @ 353.15 K)	**1.62 (exp. 1.25[b])**

Water diffusion in our new membrane is smaller than in the Nafion membrane.
→ It can reduce the electro-osmotic drag coefficient.



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[a] Mills, R. *J. Phys. Chem.* **1973**, 77, 685.

[b] Okada, T.; Xie, G.; Meeg, M. *Electrochim. Acta* **1998**, *14*, 2141.

Summary

We suggest a new molecular architecture for the fuel cell membrane technology by combining the hydrophilic, water-soluble **Fréchet type dendrimer** with the hydrophobic **PTFE**.

1. The dendrimer structure has very well-defined feature in terms of the size and the distribution of acid groups.

→ The size and distribution of acid groups are not affected by the water content.

2. The new polymer has a well-developed phase-segregated structure.

→ The different water content has the different intensity of structure factor. However, we need larger system to see the possibility of the structural development in larger scale.

3. <u>More bulk-water-like structure & smaller water diffus</u>

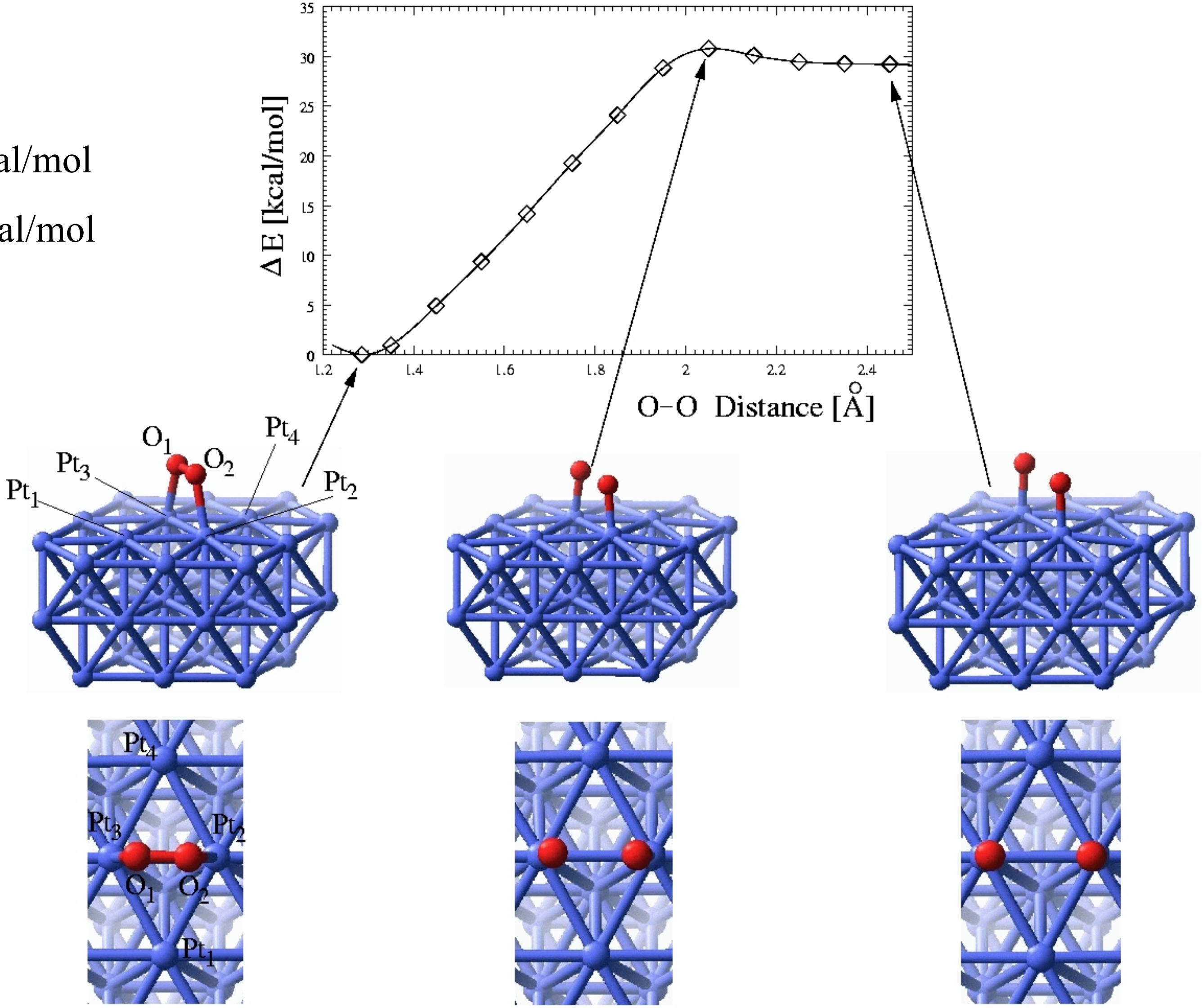
→ <u>promising!!!</u>

Seung Sung Jang

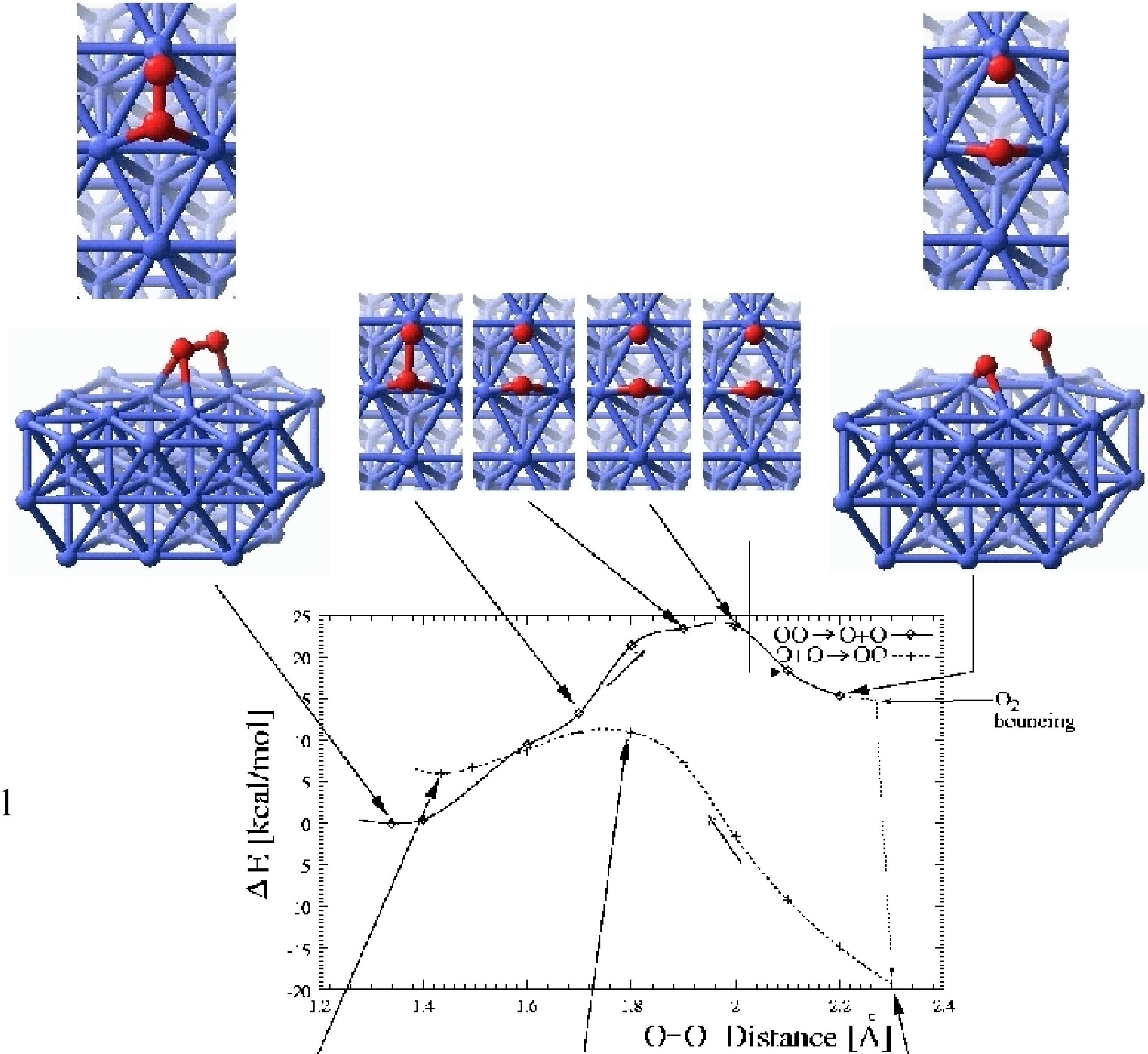
Mechanism of Cathode chemistry
Dissociation of O_2 at bridge position

E_{bind}=11.29kcal/mol

E_{diss}=30.80 kcal/mol



O_2 fcc position (1)



E_{bind}=7.21 kcal/mol

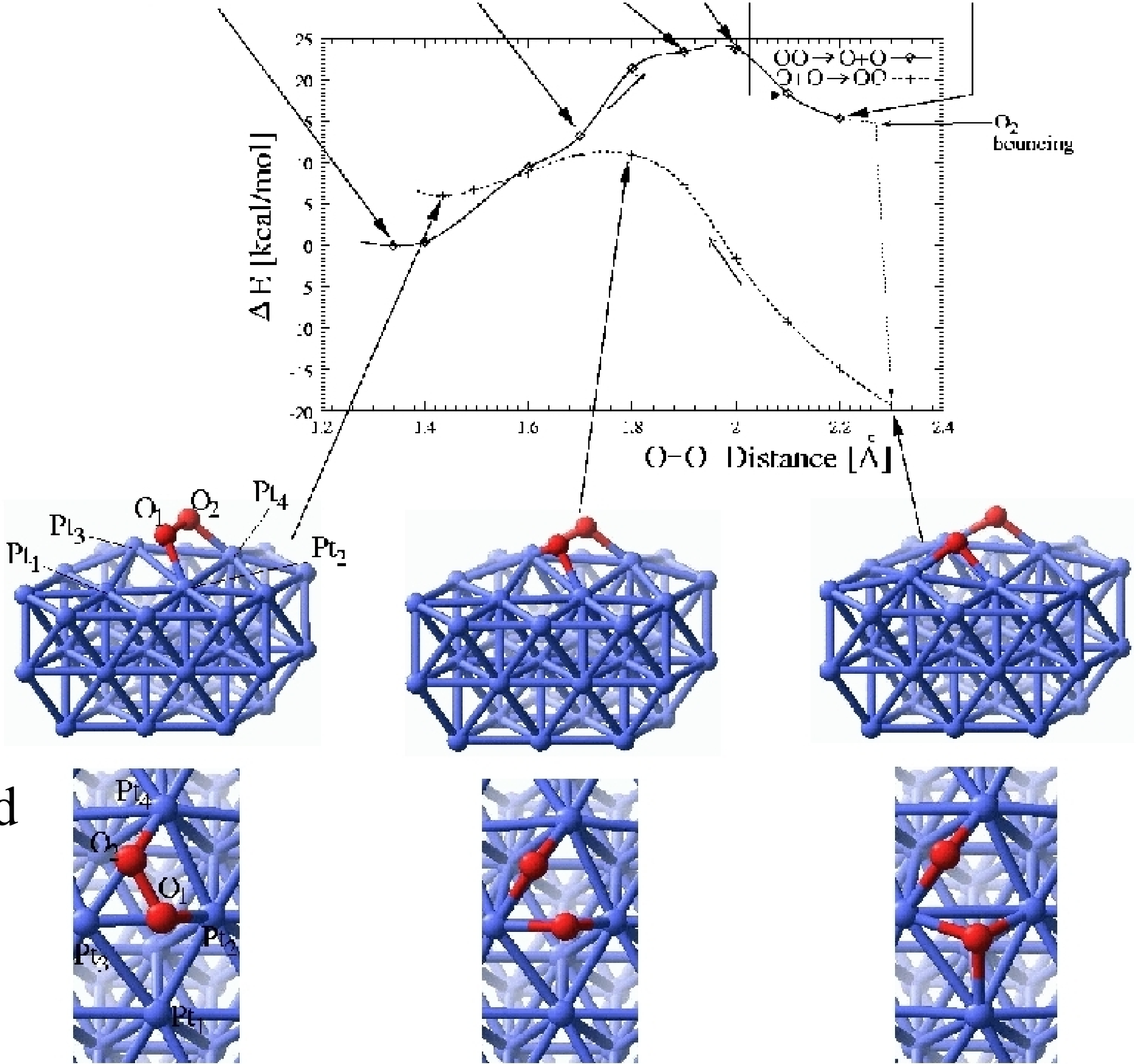
E_{diss}=23.86 kcal/mol

O_2 fcc position (2)

E_{bind}=1.33 kcal/mol

E_{diss}=5.06 kcal/mol

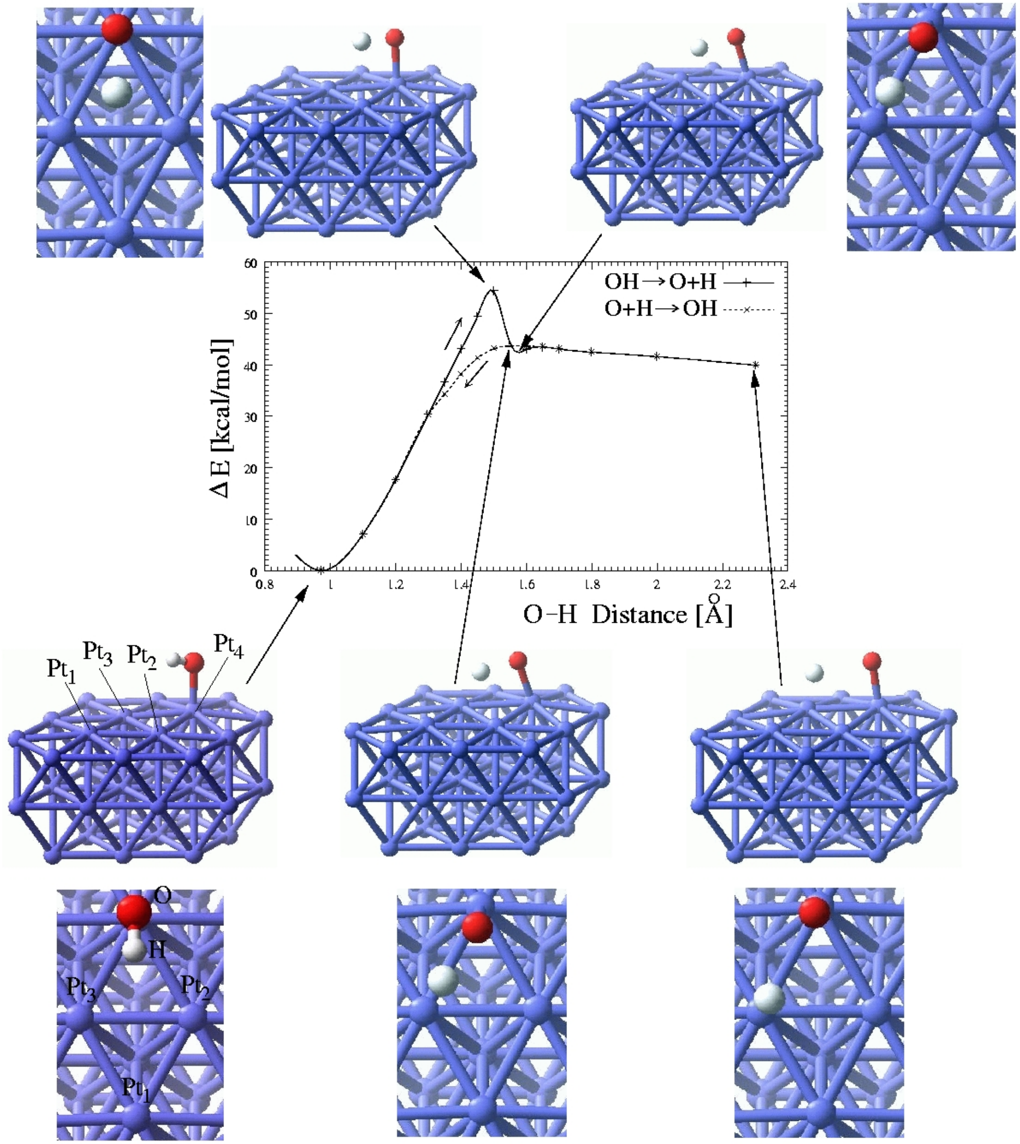
O_2 tilted



OH dissociation

E_{bind}=47.45 kcal/mol

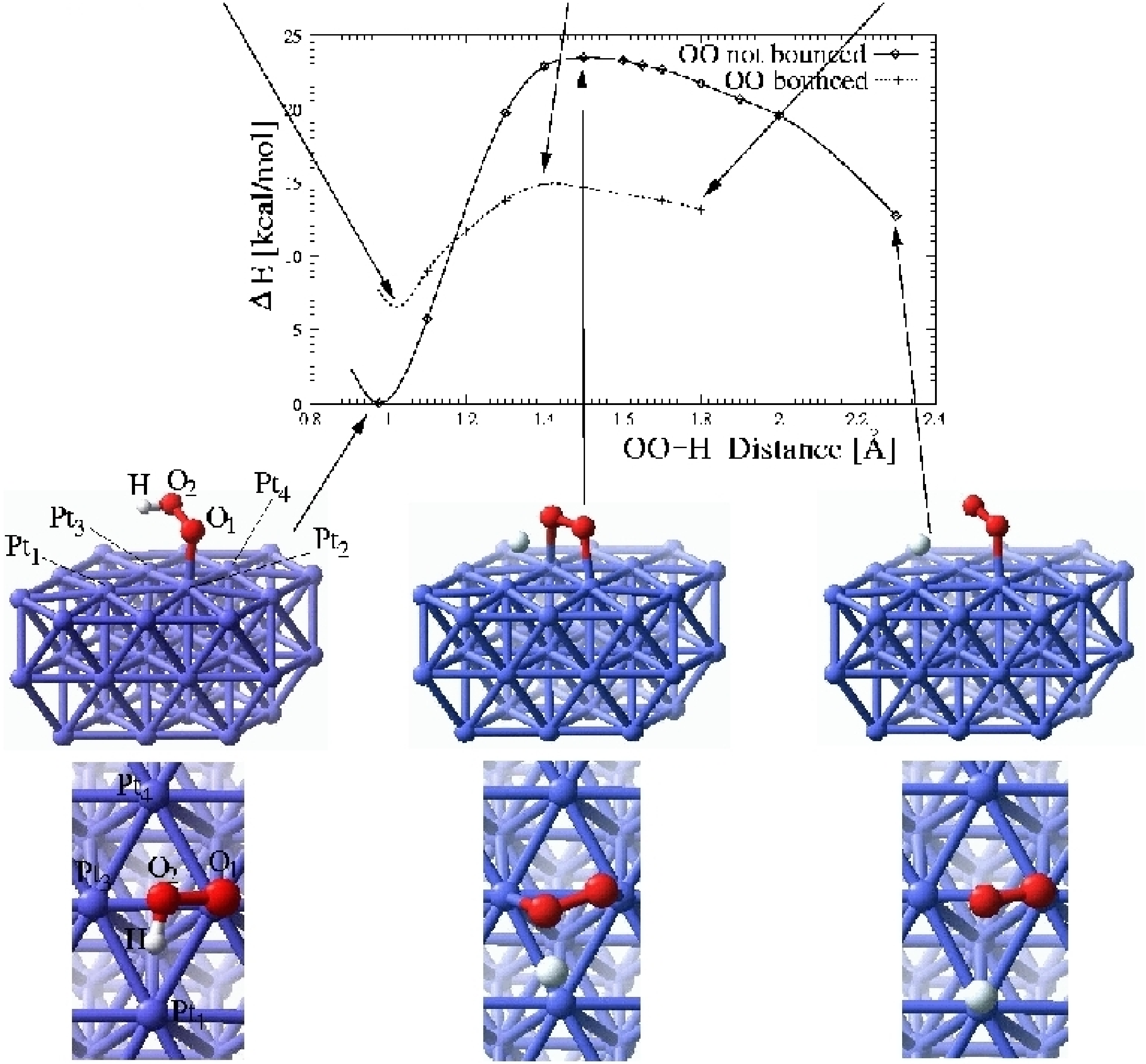
E_{diss}=54.33 kcal/mol
E_{diss}=43.70 kcal/mol



OO-H dissociation of OOH (1)

E_{bind}=23.85 kcal/mol

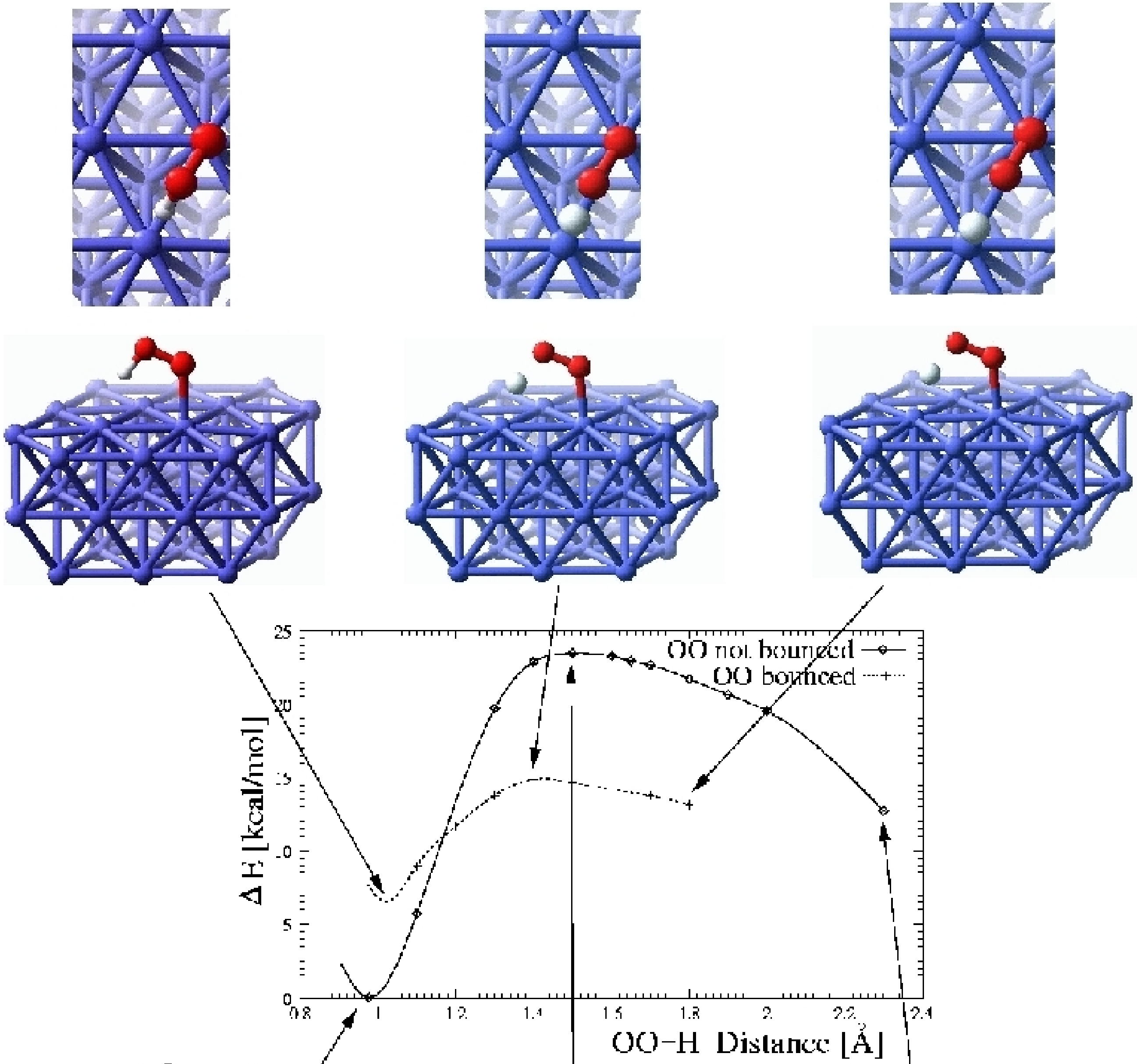
E_{diss}=23.45 kcal/mol



OO-H dissociation of OOH (2)

E_{bind}=17.30 kcal/mol

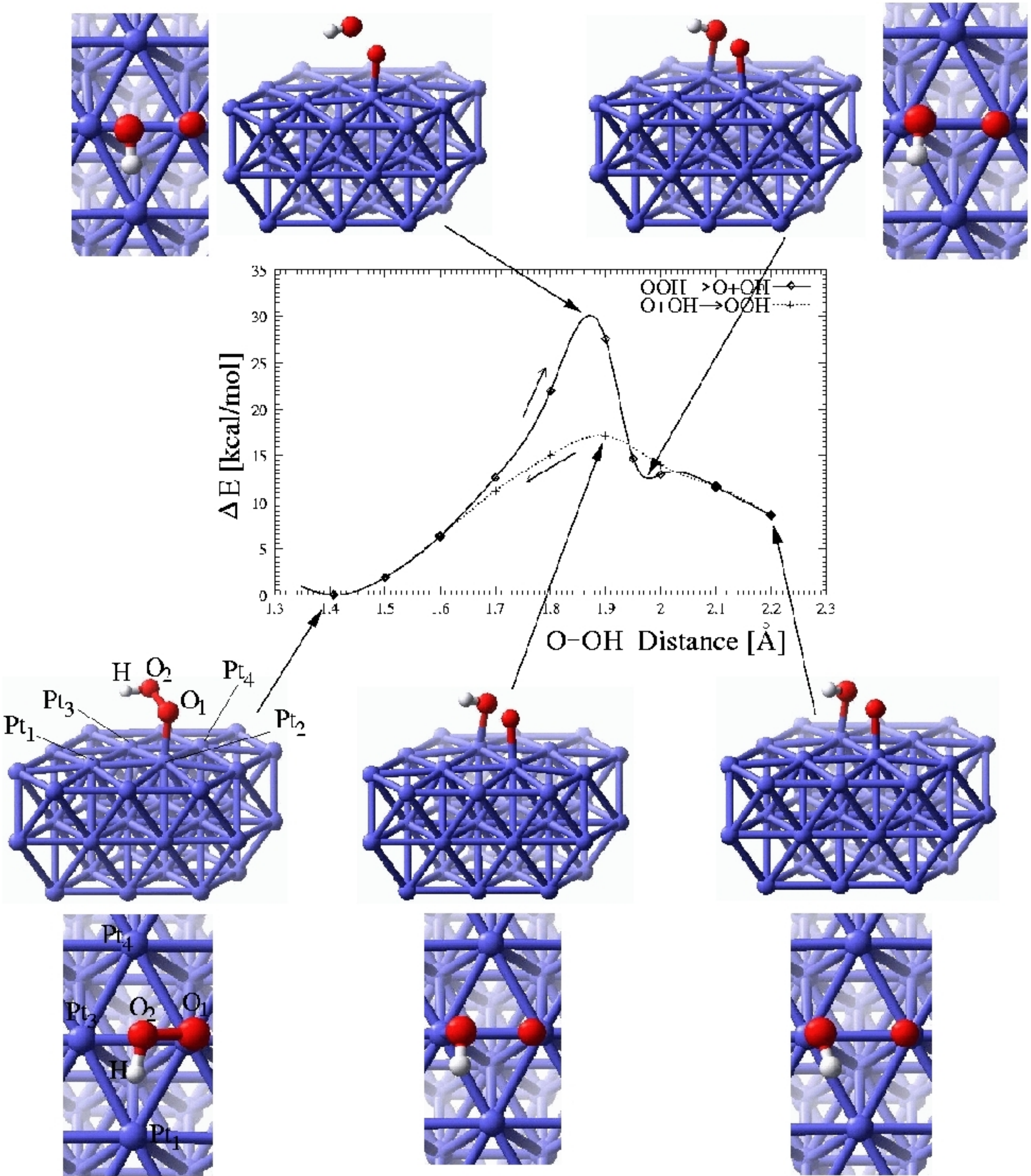
E_{diss}=8.29 kcal/mol



GODDARD

E_{bind}=23.85 kcal/mol

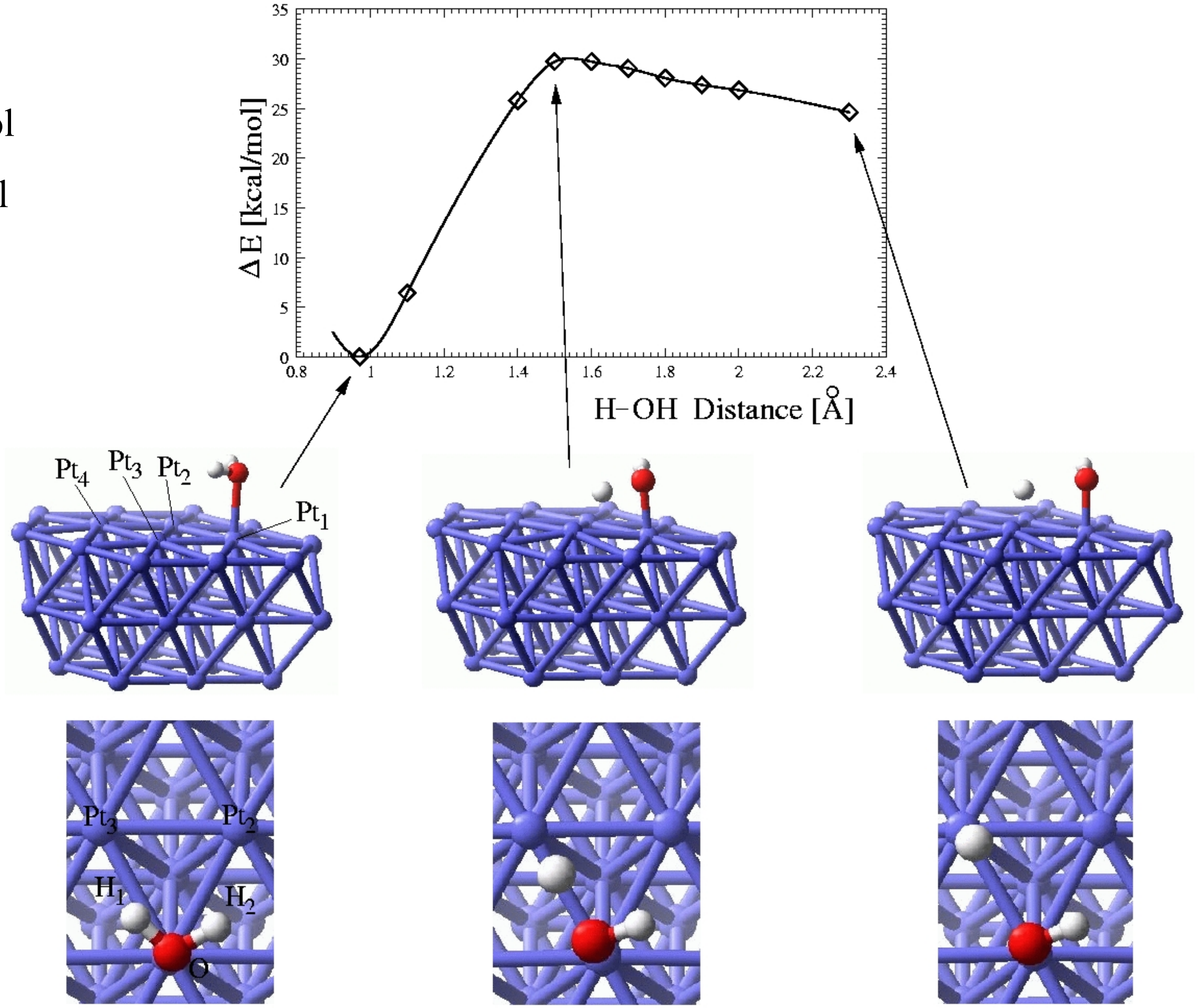
E_{diss}=30.01 kcal/mol
E_{diss}=17.13 kcal/mol



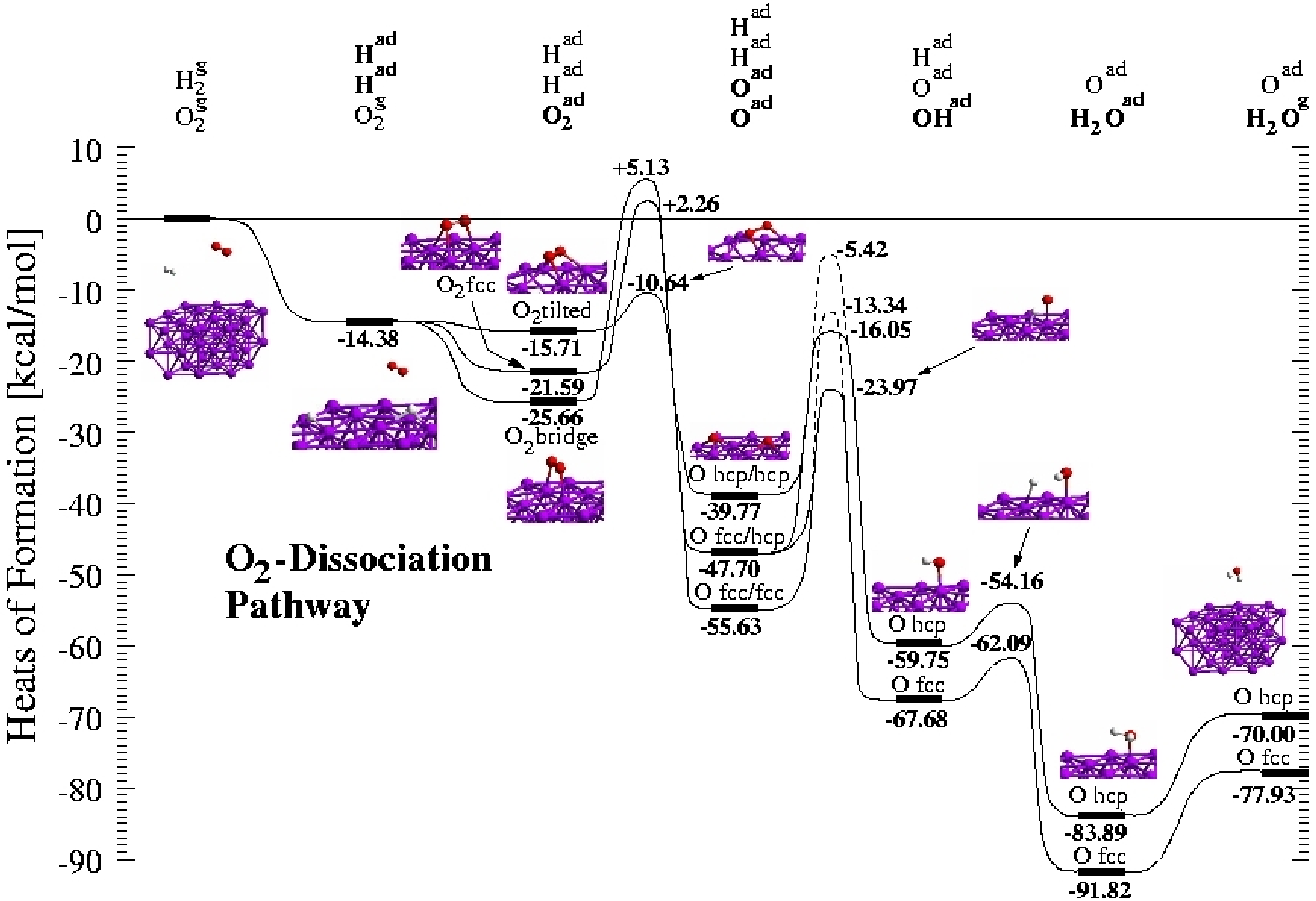
H-OH dissociation of water

E_{bind}=13.90 kcal/mol

E_{diss}=29.73 kcal/mol



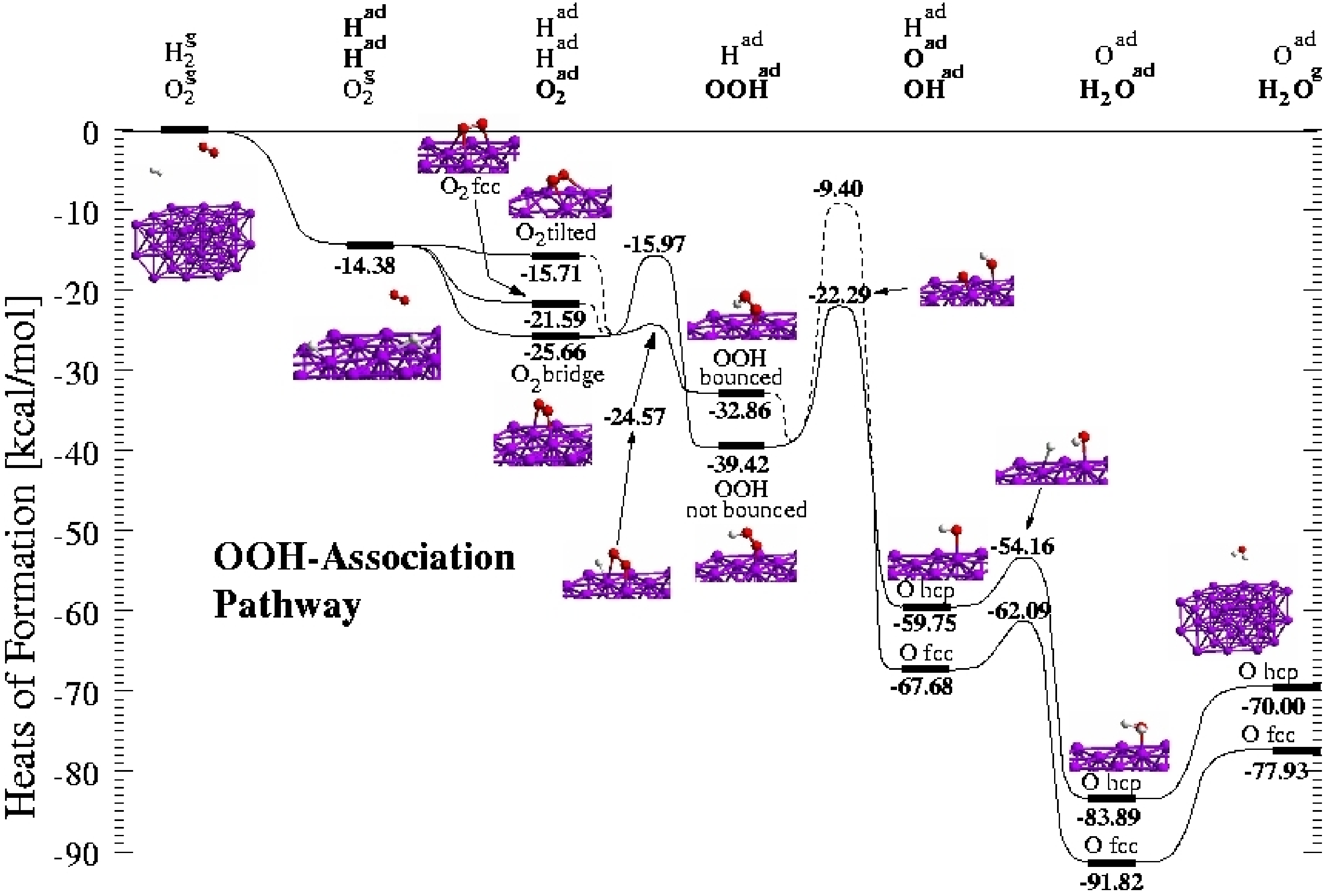
Mechanism (1) gas-phase



$$H_2^g + O_2^g \xrightarrow{-14.38} 2H^{ad} + O_2^g \xrightarrow{-11.28} 2H^{ad} + O_2^{ad} \xrightarrow[15.02]{-29.97} 2H^{ad} + 2O^{ad} \xrightarrow[31.66]{-12.05} H^{ad} + O^{ad} + OH^{ad}$$

$$\xrightarrow[5.59]{-24.14} O^{ad} + H_2O^{ad} \xrightarrow{+13.89} O^{ad} + H_2O^g$$

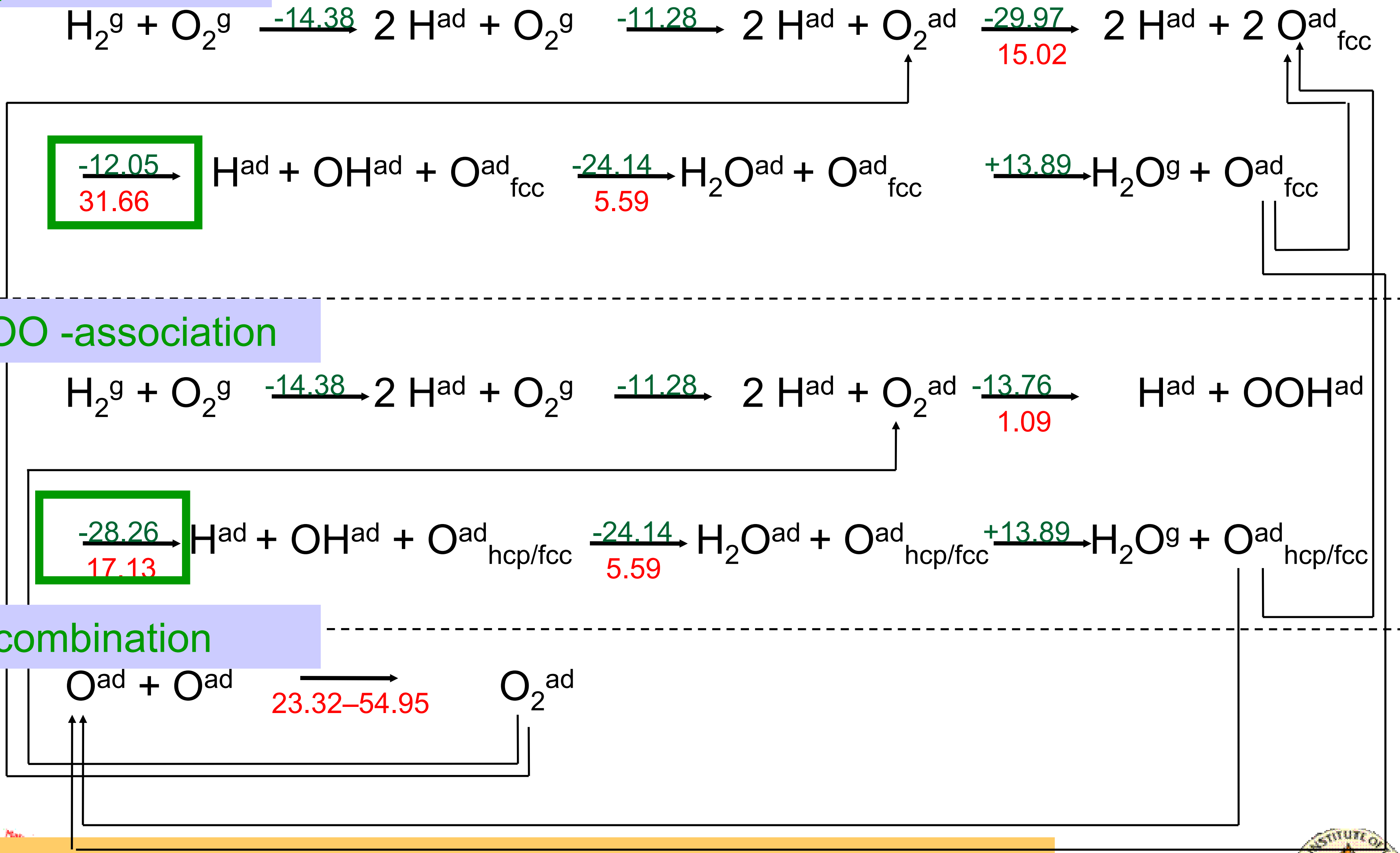
Mechanism (2) gas-phase



$$H_2^g + O_2^g \xrightarrow{-14.38} 2\,H^{ad} + O_2^g \xrightarrow{-11.28} 2\,H^{ad} + O_2^{ad} \xrightarrow[1.09]{-13.76} H^{ad} + OOH^{ad} \xrightarrow[17.13]{-28.26} H^{ad} + O^{ad} + OH^{ad}$$

$$\xrightarrow[5.59]{-24.14} O^{ad} + H_2O^{ad} \xrightarrow{+13.89} O^{ad} + H_2O^g$$

Energetics for Both Reaction Mechanisma



O_2 -dissociation

$H_2^g + O_2^g \xrightarrow{-14.38} 2\,H^{ad} + O_2^g \xrightarrow{-11.28} 2\,H^{ad} + O_2^{ad} \xrightarrow[15.02]{-29.97} 2\,H^{ad} + 2\,O^{ad}_{fcc}$

$\boxed{\xrightarrow[31.66]{-12.05}} H^{ad} + OH^{ad} + O^{ad}_{fcc} \xrightarrow[5.59]{-24.14} H_2O^{ad} + O^{ad}_{fcc} \xrightarrow{+13.89} H_2O^g + O^{ad}_{fcc}$

HOO -association

$H_2^g + O_2^g \xrightarrow{-14.38} 2\,H^{ad} + O_2^g \xrightarrow{-11.28} 2\,H^{ad} + O_2^{ad} \xrightarrow[1.09]{-13.76} H^{ad} + OOH^{ad}$

$\boxed{\xrightarrow[17.13]{-28.26}} H^{ad} + OH^{ad} + O^{ad}_{hcp/fcc} \xrightarrow[5.59]{-24.14} H_2O^{ad} + O^{ad}_{hcp/fcc} \xrightarrow{+13.89} H_2O^g + O^{ad}_{hcp/fcc}$

recombination

$O^{ad} + O^{ad} \xrightarrow[23.32–54.95]{} O_2^{ad}$

Critical barrier is 32 kcal/mol for O_2 dissociation mechanism and 17 kcal/mol for HO_2 dissociation mechanism

Realistic description I (of VII)

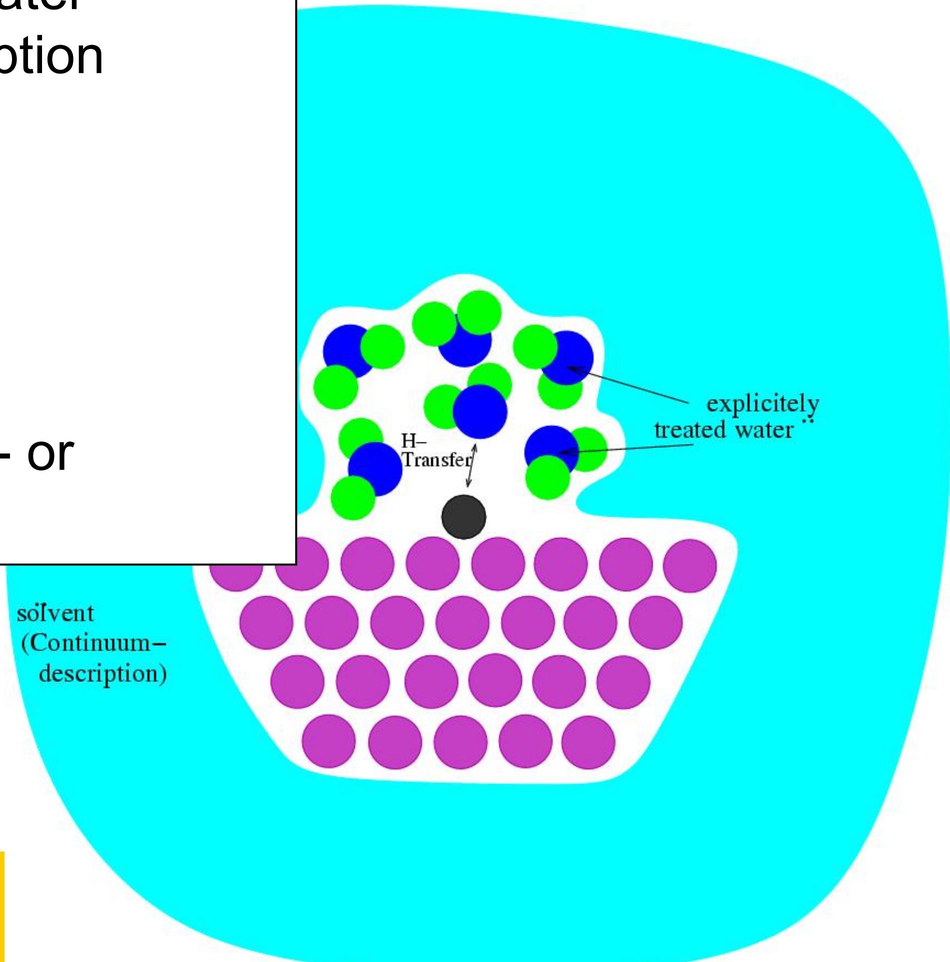
- Solvation effects due to solvent in the electrolyte

  In case of PEM-FCs the electrolyte is hydrated

  At the cathode water is generated

  → The electrode is surrounded by water molecules, which influence adsorption energies and structures.
  This might change the reaction mechanism, but also stabilize or destabilize certain structures (e.g. electrode, adsorbates)

  → Solvation can be treated by a two- or three-shell model



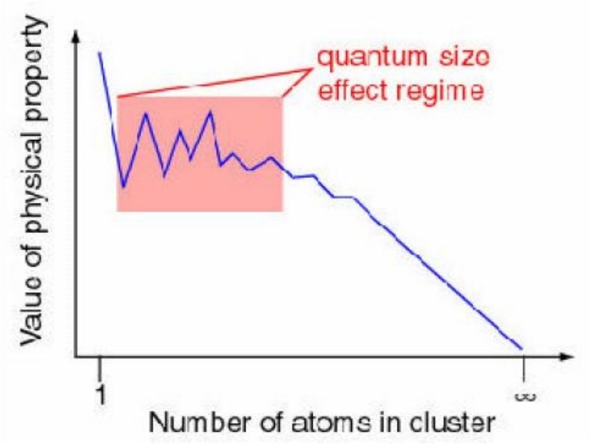
Realistic description II (of VII)

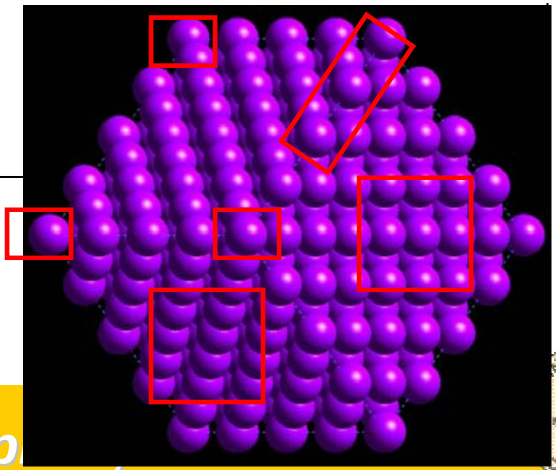
- Morphology of the catalyst

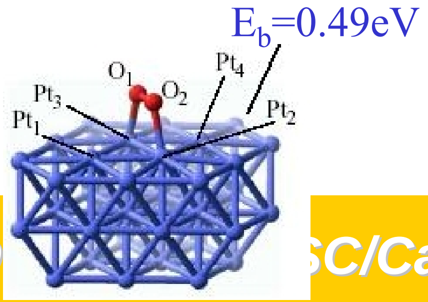
  In order to provide a large surface area for simultaneous catalysis Pt nanoparticles are used instead of (semi-) infinite systems

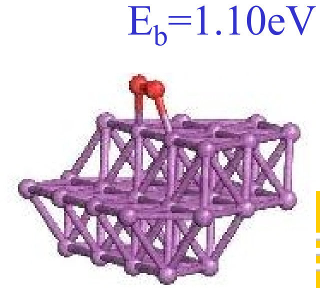
  However:

  - Nanoparticles have structural and electronical properties, which might strongly depend on size and shape (e.g. Quantum Size Effects)
  - Nanoparticles combine a variety of different functional groups: different surfaces, steps, kinks, tips, vacancies, ...), having different properties



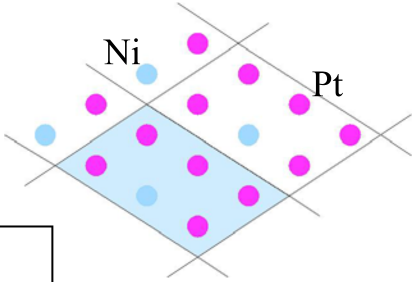






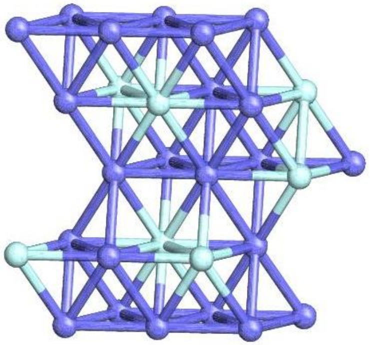
Pt_3Ni segregation

- 2x3 unit cell with 5-layers



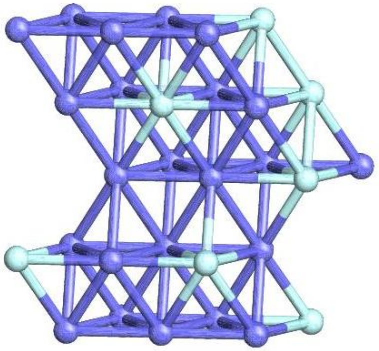
Exp:
(100-48-89)

100-50-83-50-100



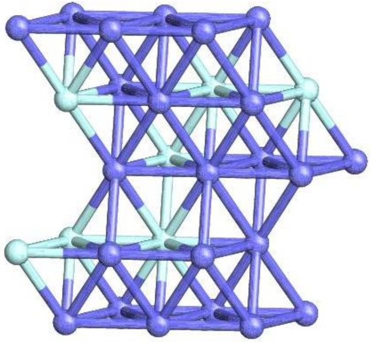
E=0 eV

83-66-83-66-83



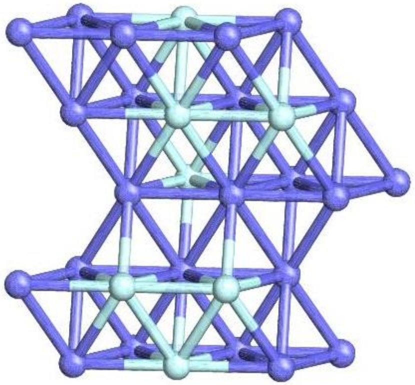
ΔE=1.09eV

100-50-83-50-100



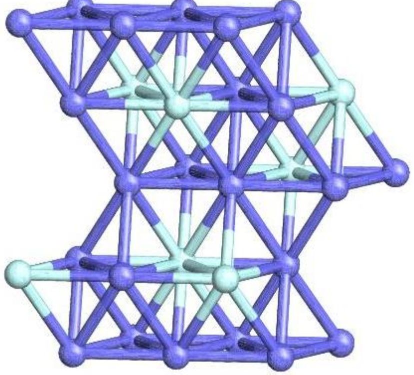
ΔE=0.52eV

83-66-83-66-83



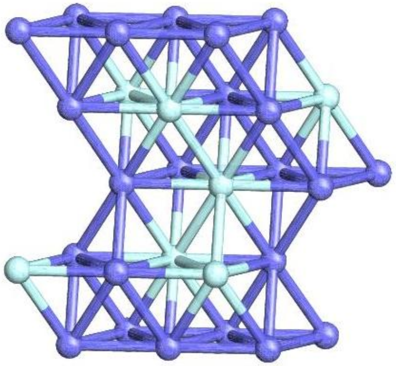
ΔE=1.27eV

100-50-83-50-100



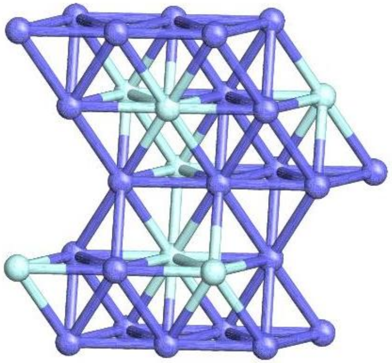
ΔE=0.17eV

100-50-83-50-100



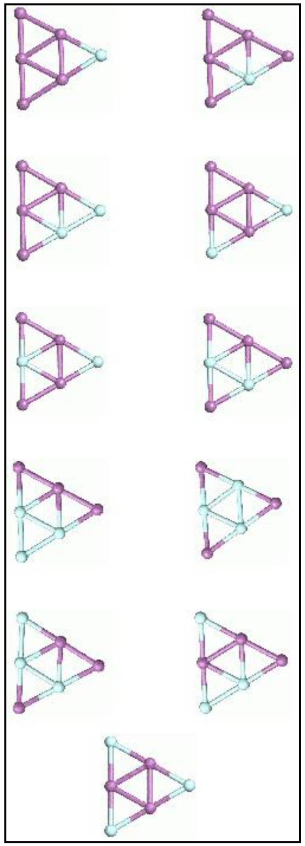
ΔE=0.16eV

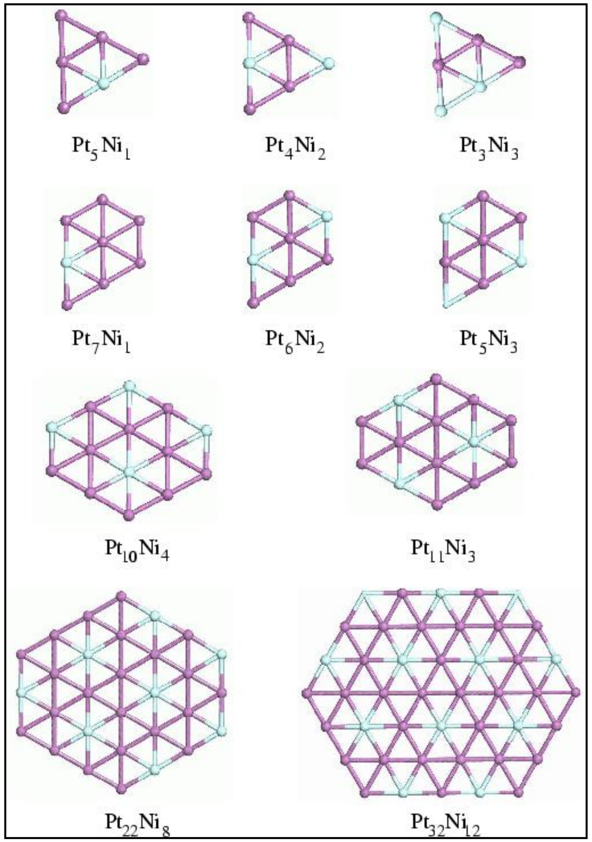
100-50-83-50-100

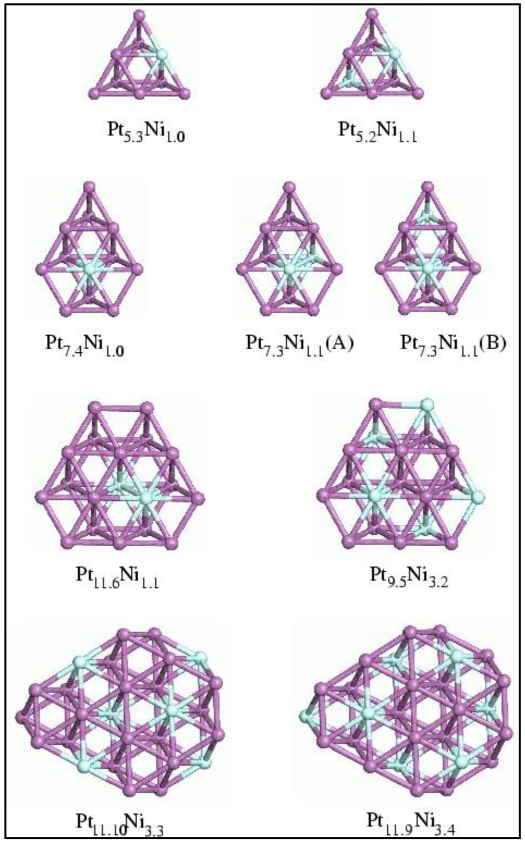


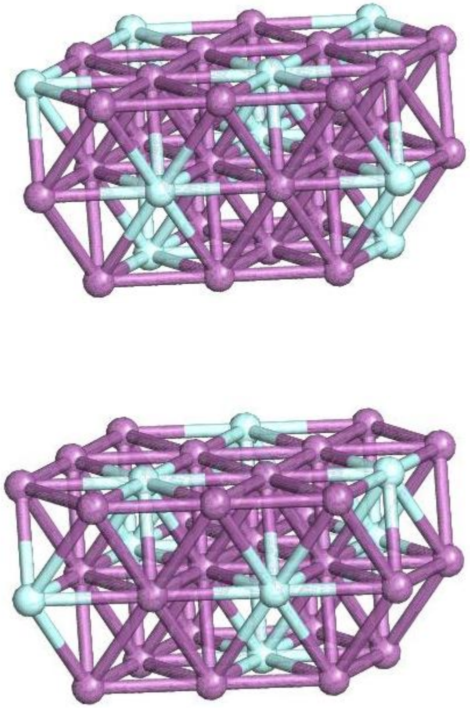
ΔE=0.18eV

Bimetallic Alloy-systems Pt_3Ni





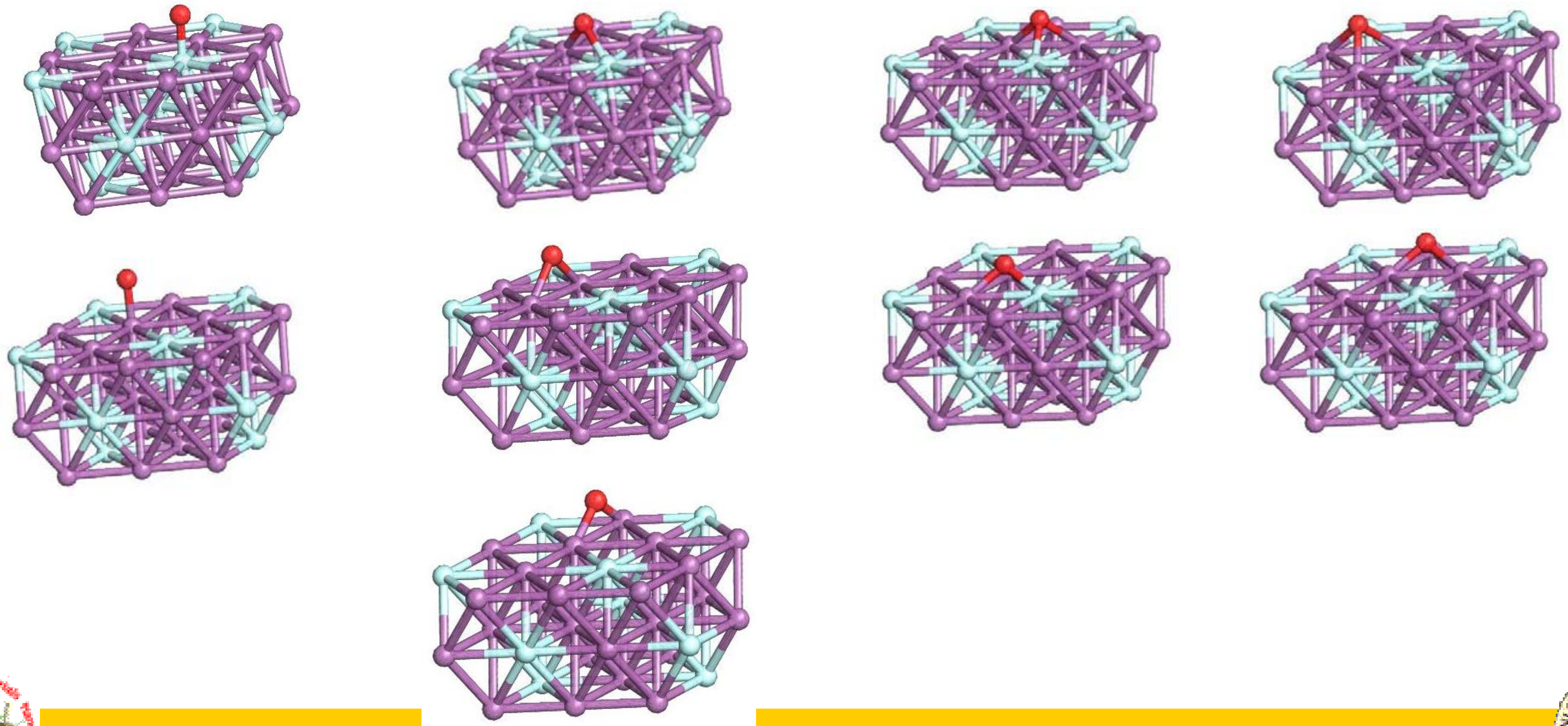




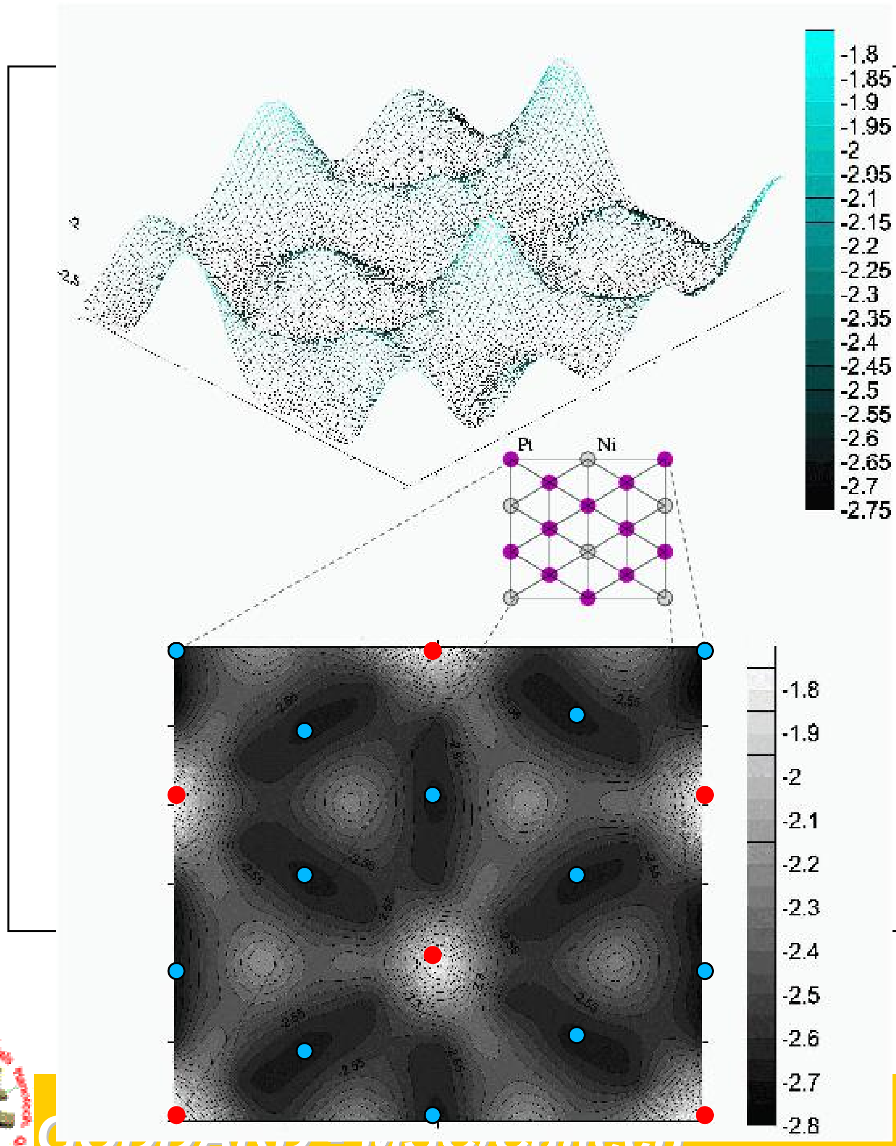
Change the composition in the first layers, while keeping bulk structure for the second and third layer

Adsorption of O and H on Pt_3Ni

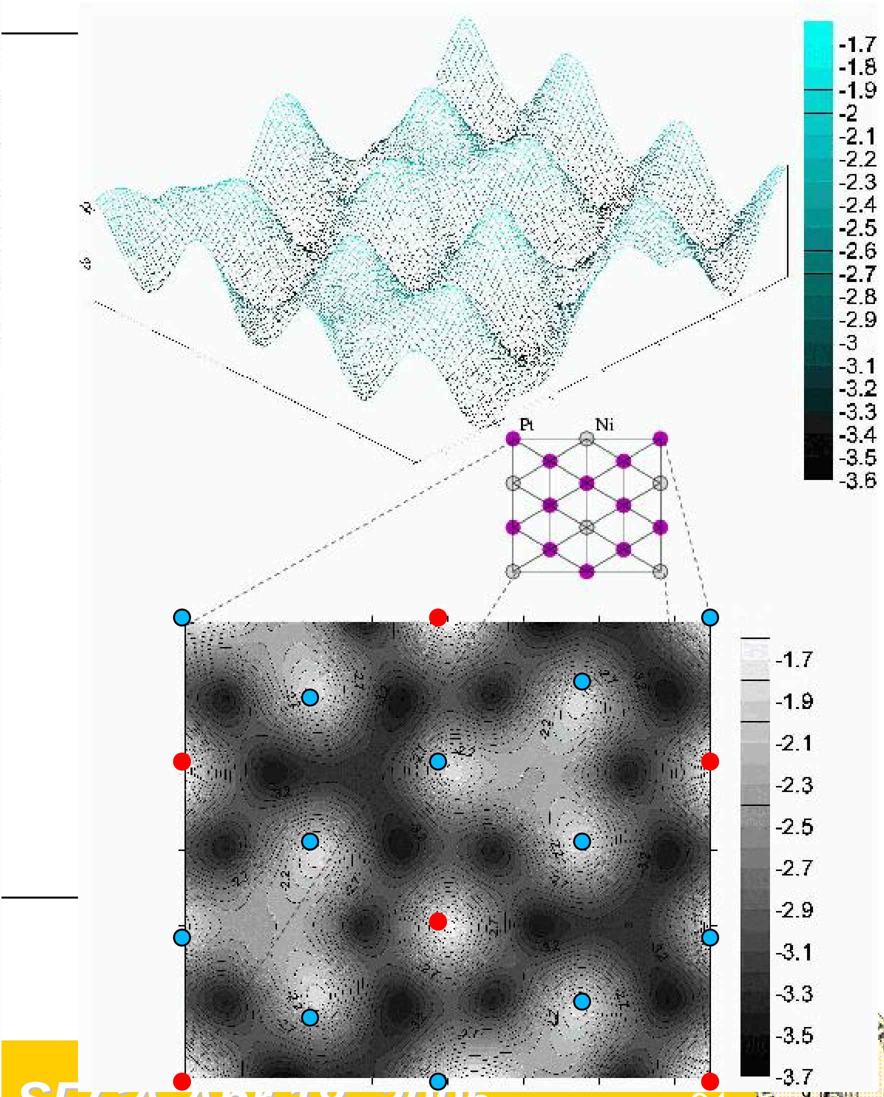
- Adsorption on 1 layer and 3 layer clusters at all different sites (bonds to only Pt or bonds to Pt and Ni)



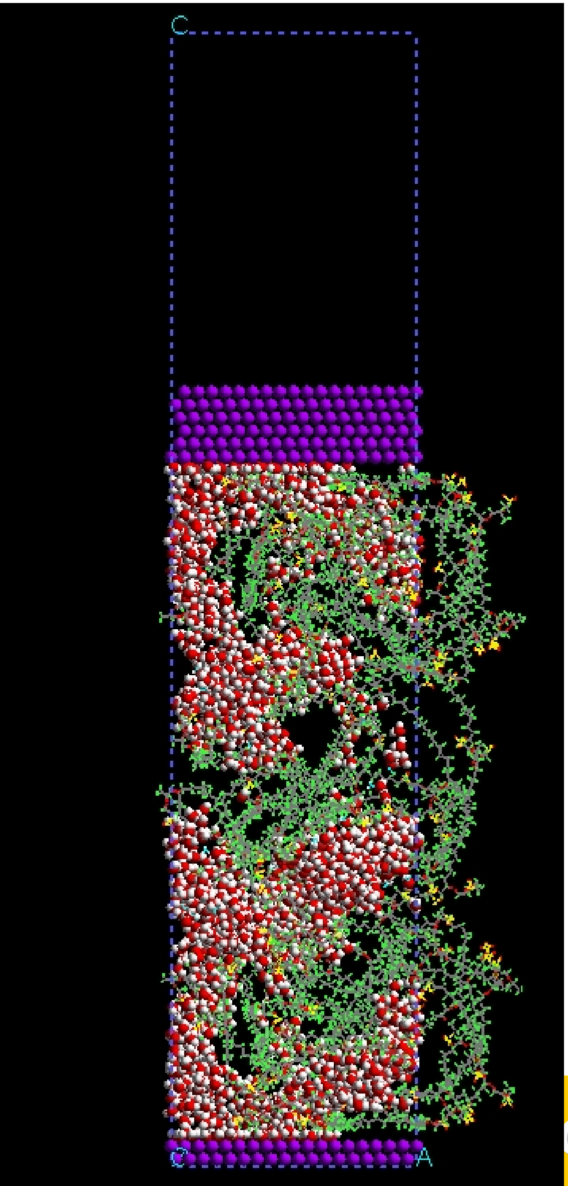
H adsorption



O adsorption



Realistic description IV (of VII)

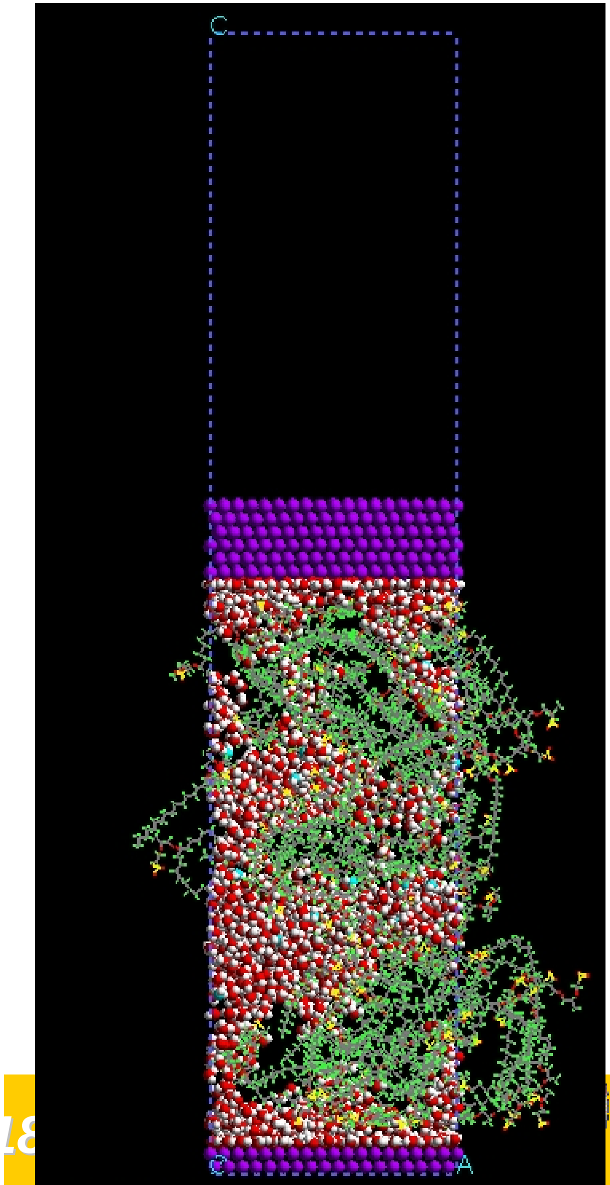


- Bulk region should have structural properties (density, distribution, …) of bulk Nafion, otherwise system need to be expanded

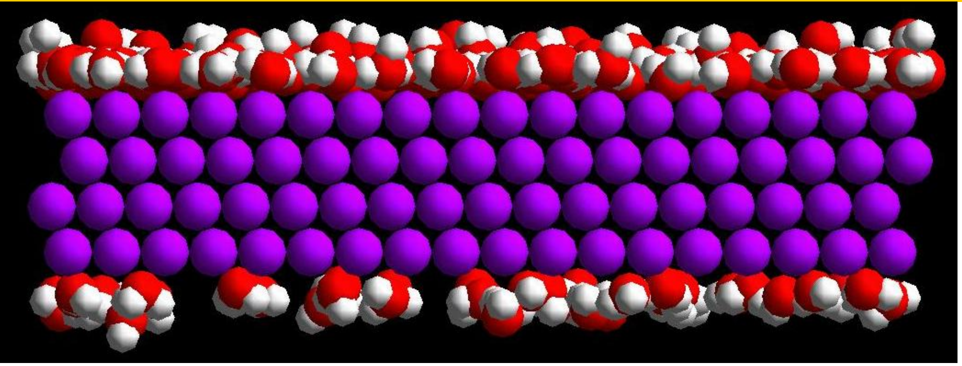
- Water layer forms between electrode and membrane (will be different in presence of E-field)

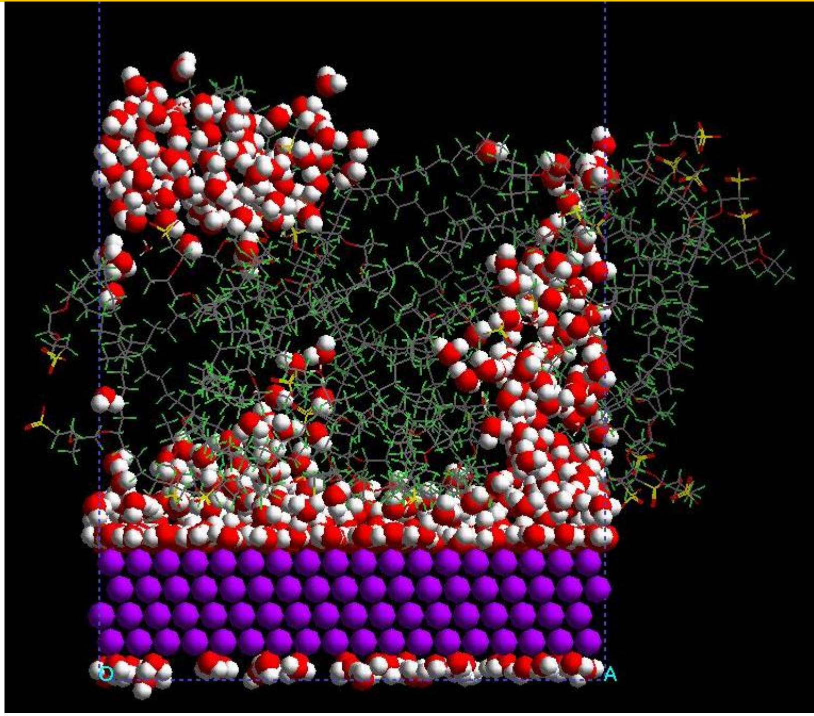
after 2ns

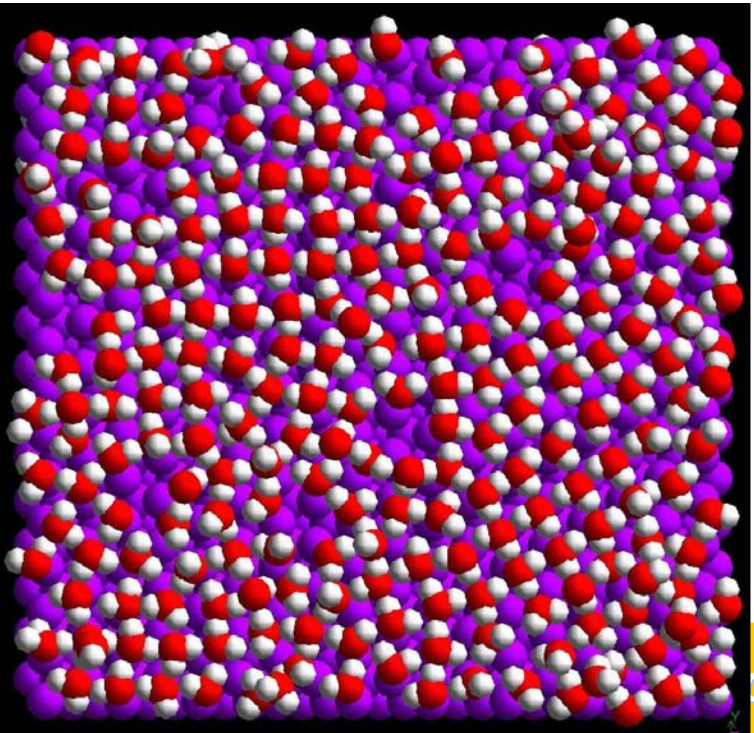
- 20ps equilibration
- 2ns simulation time
- Temperature 80°C
- NPT dynamics
- Simulations at **5, 10, and 15** waters per sulfonate
  (180 waters / 360 waters / 540 waters)



15 Waters per Sulfonate (corresponds to fuel cell operation at 60% humidity and 85C)







- a bilayer structure is established On top of the Pt surface

- Coverage is ~0.85 ML
  270 Pt – ~229 waters
  → some water molecules start
  to form second (Ice_h-like) layer

Realistic description V (of VII)

- Reactive Environment
  - Cathode is surrounded by a variety of different compounds:
    - *H_2O of the electrolyte, and reaction product*
    - *H_3O^+ as proton carrier (surrounded by water molecules)*
    - *O_2 gas as reaction component*
    - *Different reaction intermediates (e.g. O, H, OH, OOH, HOOH,...)*
    - *Impurities in the fuel (e.g. CO, NO_x, ...)*

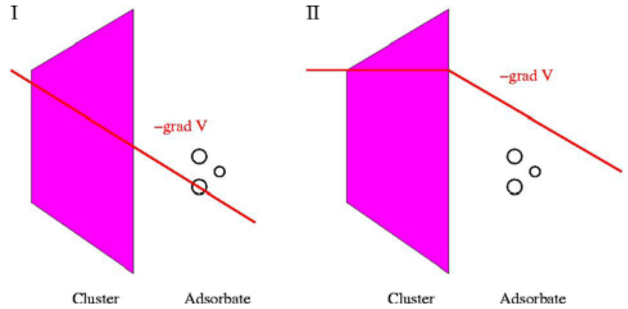
→ The environment might influence the structure, stability, and composition of the Pt nanoparticles (or certain functional groups).

→ This may vary for different *T* and *p* conditions

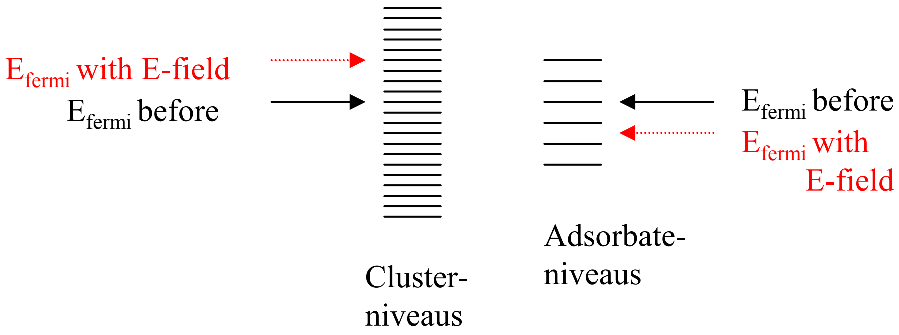
Problem: Is a surface-oxide formed?

Realistic description VI: Electrode Potential
Different ideas to model the electrode potential

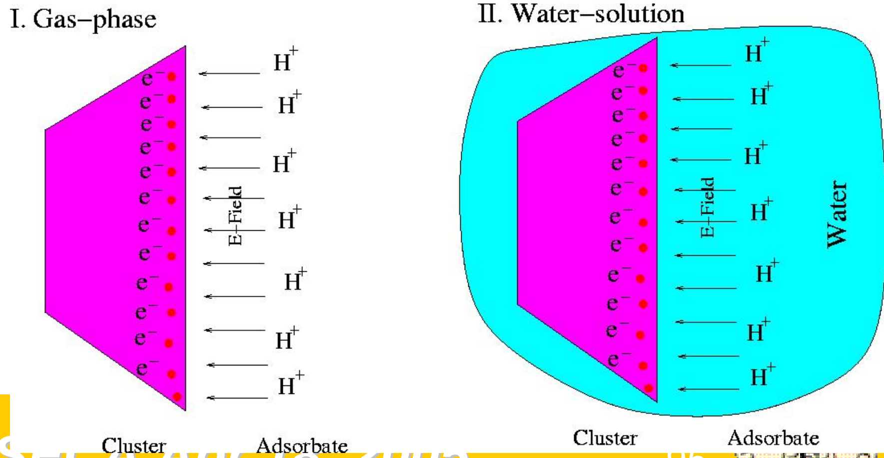
A: Apply an external electric field through the entire system



B: Change the Pseudopotentials or Fermi-level of the surface and the adsorbate with respect to their distance



C: Put additional or take electrons from the cluster to model the bahavior in the E-field. The water solvent is treated either by a solvation calculation (self-consistent reaction field SCRF method) or including water molecules explicitely.



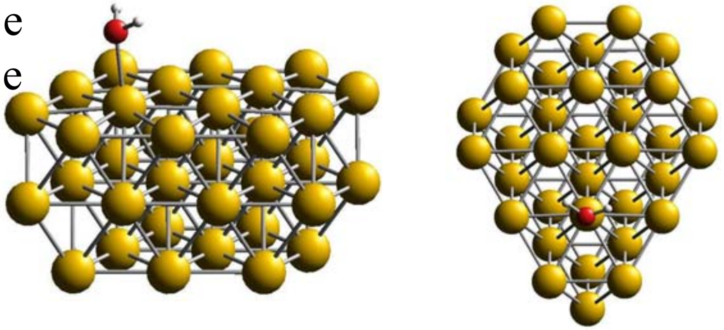
Example I

Structure of H_2O as a function of electrode potential φ

Adsorption of H_2O was studied as a function of the cluster charge (electrode potential):

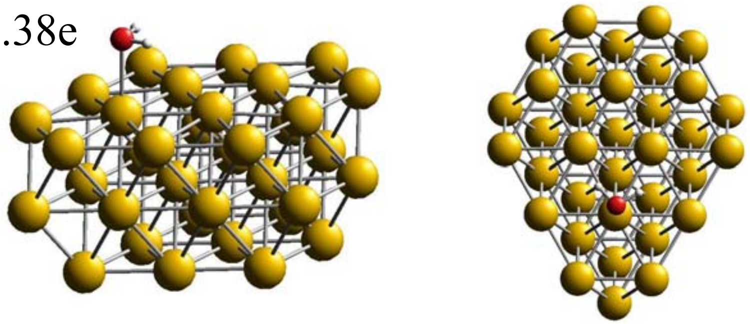
- +3e: Water is bound on top of an Pt atom, but both H atoms are oriented away from the surface

O: -0.45e
H:+0.38e



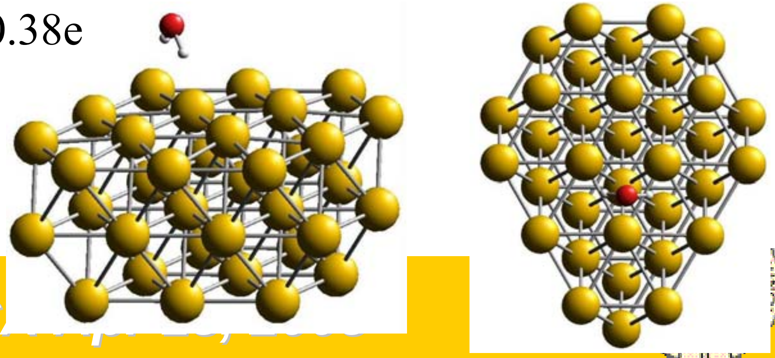
- neutral: Water is also bound on top of an Pt atom with both H atoms oriented parallel to the surface above three-fold sites

O: -0.50e
H:+0.38e



- -3e: As a result of the additional partial negative charge on the cluster surface, O is facing away from the surface and both H atoms are attracted. This causes water being adsorbed on top of a three-fold site

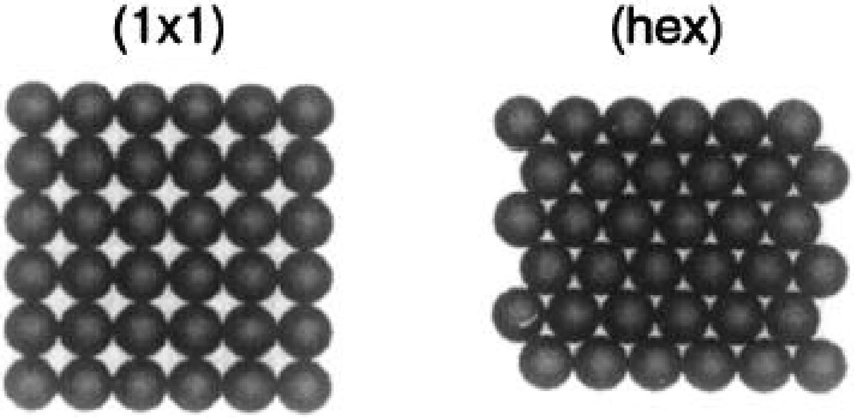
O: -0.61e
H:+0.38e

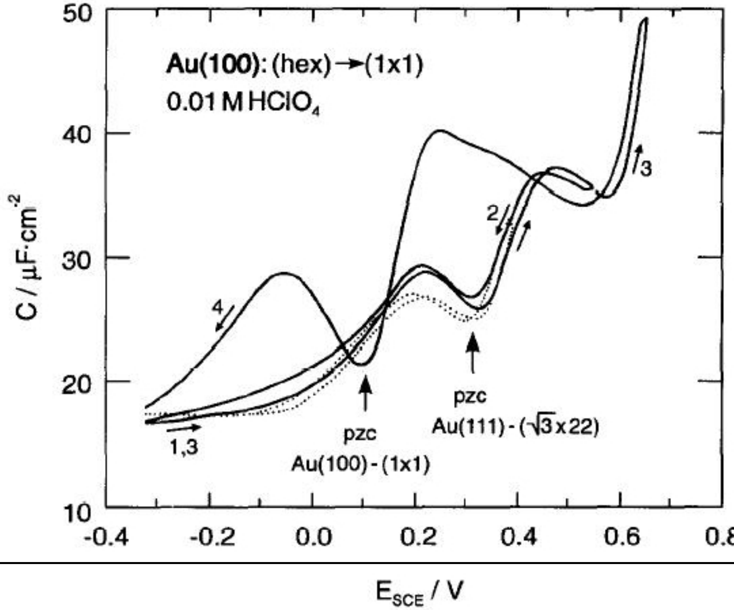


Example II

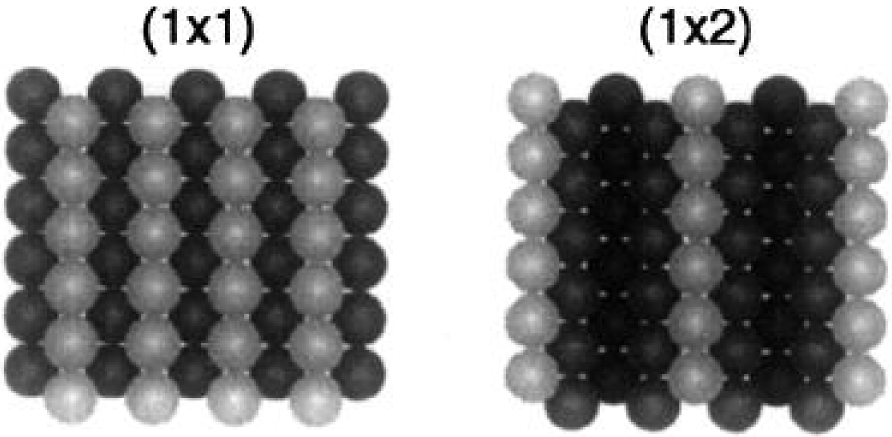
Au surface reconstruction

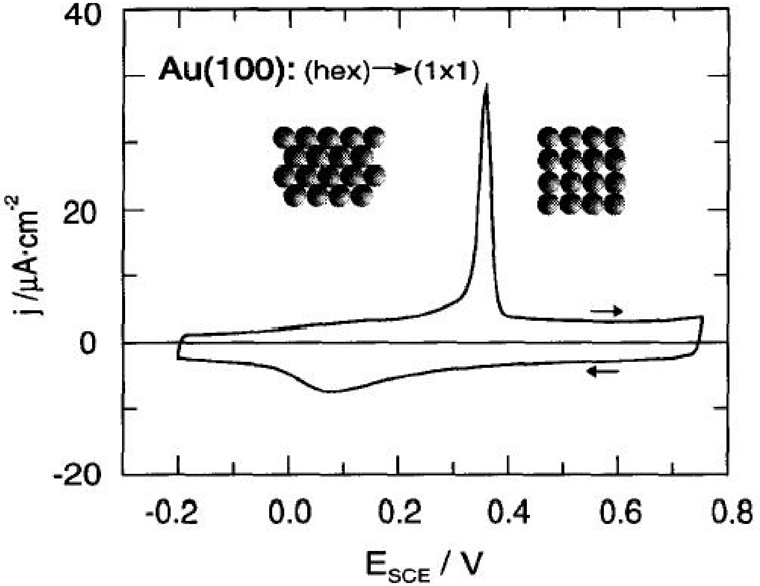
Au(100)





Au(110)

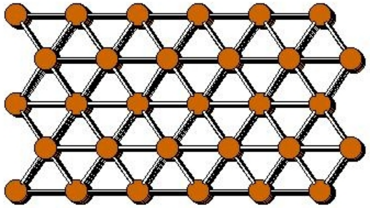


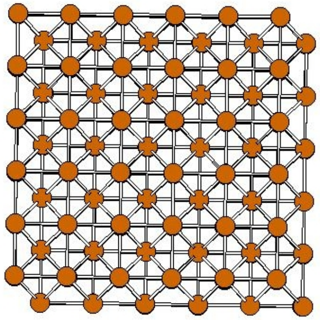


Example II

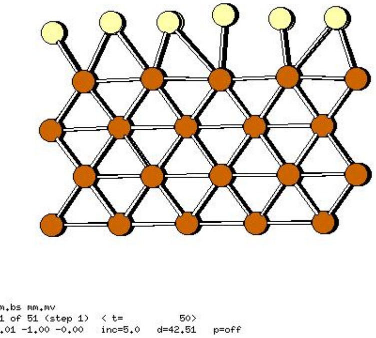
Au surface reconstruction

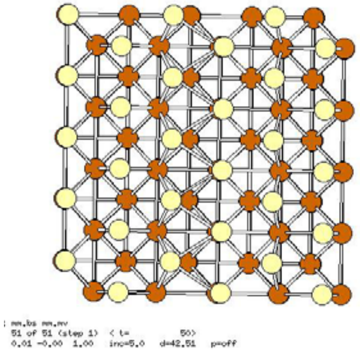
1x1 non-reconstructed



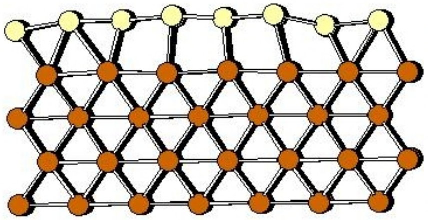


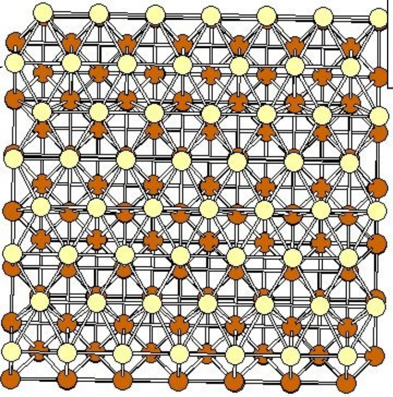
5x1 hex-reconstructed





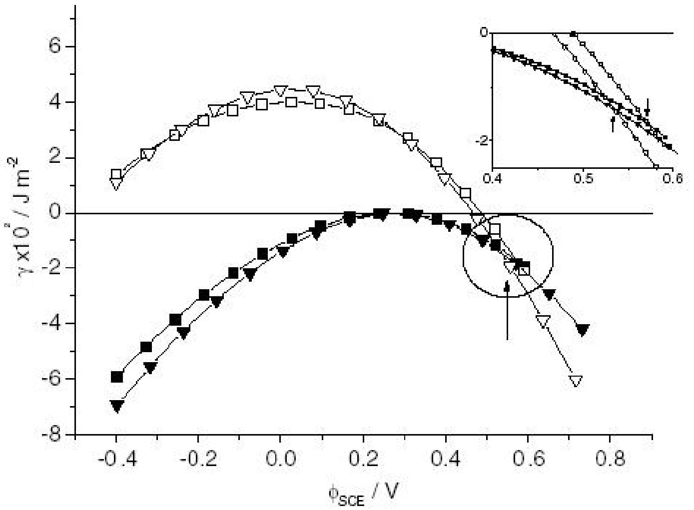
7x1 hex-reconstructed



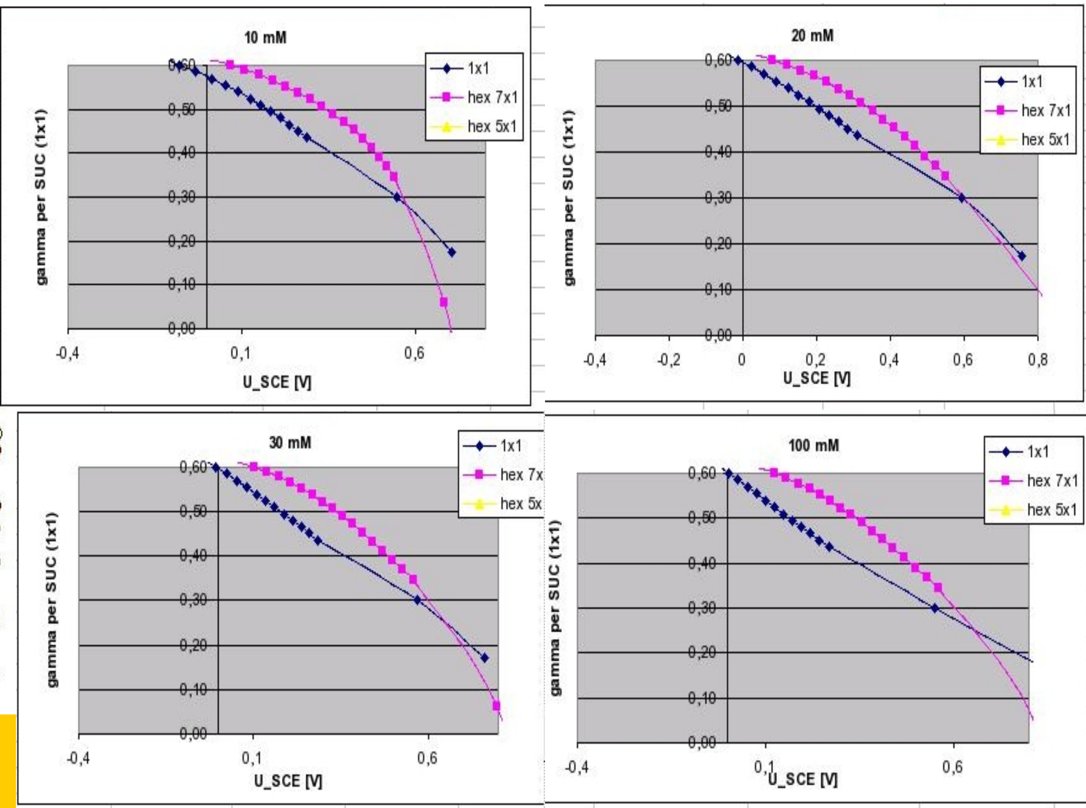


Experiment

KPF$_6$ solvent



DFT Calculation



Realistic description VII (of VII)

- All previous problems deal with the system in equilibrium.
  However, under ***steady state conditions*** structures, compositions, and reaction mechanisms might be significantly different?

→ Use ***kinetic simulations*** to study exactly these influences.

However, in order to get reliable results ***all significant processes*** need to be studied and the corresponding parameters extracted:

Adsorptions, desorptions, diffusions, reactions, …

Contributors to Fuel Cell Applications


Timo Jacob


Seung Sung Jang


Valeria Molinero

Yun Hee Jang
Tahir Cagin
Mario Blanco


Weiqiao Deng


Boris Merin

H_2 storage in carbon materials

Goal: Dept. Transportion
- H_2 weight percent : 6.5%
- H_2 density: 62kg H_2/m^3

At conditions of
- Pressure: 1-10bar,
- Temperature: 0-100^0C

Many wild claims (over 100% reversible by weight at 300K) have been made of very high reversible H_2 storage in carbon formed in special ways. These have not been reproduced

Validated experiments
- 6-8% 1bar 77K in single wall nanotube
  Heben etc. Nature 386, 377-379, 1997
- 6.5% 120bar 298K in carbon nanofibers
  Turpin etc. Nano Lett. A-E 2001
- 6.3% 148bar 298K in multi wall nanotube
  Cheng etc. J. Chem. Phys. 106, 963-966, 2002

None of these experiments come close to the pressure and temperature range attractive for mobile storage

Question what is the best possible performance for reversible H2 storage in carbon based materials? Use theory and computioanl chemistry to find out

Weiqiao Deng

Strategy

- Use First principles Quantum Mechanics to develop an accurate force field using in simulating the maximum possible reversible H_2 storage performance for candidate materials

- Current Focus: Determine maximum performance from carbon based system

- Assumptions: graphitic or fullerene type systems likely to be best (high electron affinity, stable against reactions with H_2

- Initial Tests: Determine maximum H_2 bonding for pure carbon and carbon doped with Li.

Strategy: H2 storage

Determine maximum performance from candidate systems

- carbon based systems
- metal hydride systems

If maximum performance not satisfactory, don’t bother with experiments

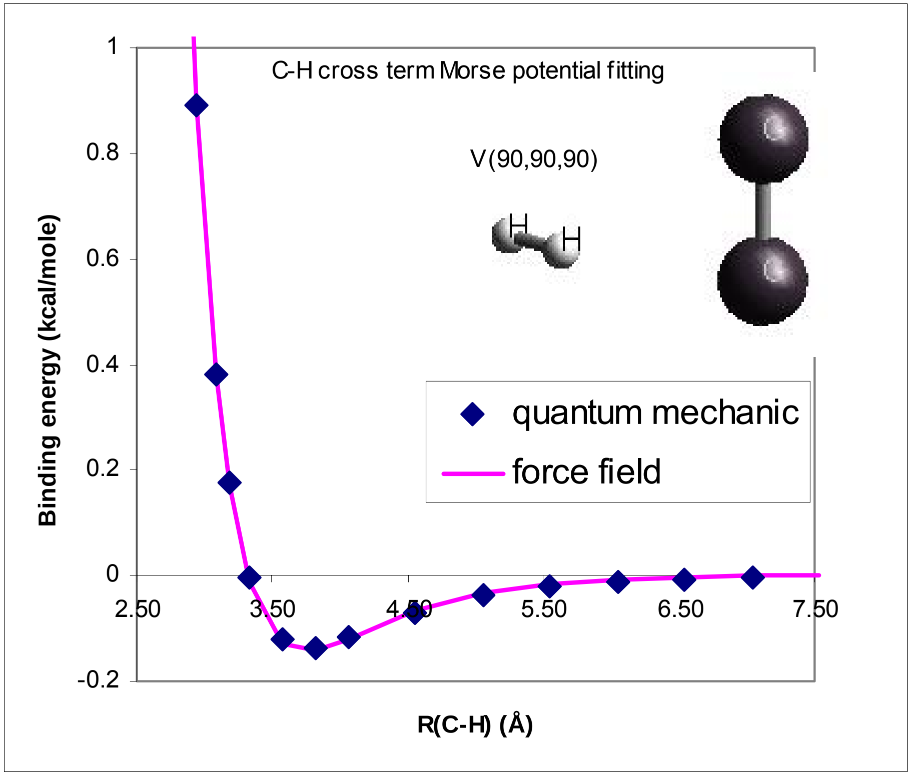
If maximum performance is satisfactory, first validate theory with experiment and then optimize experimentally

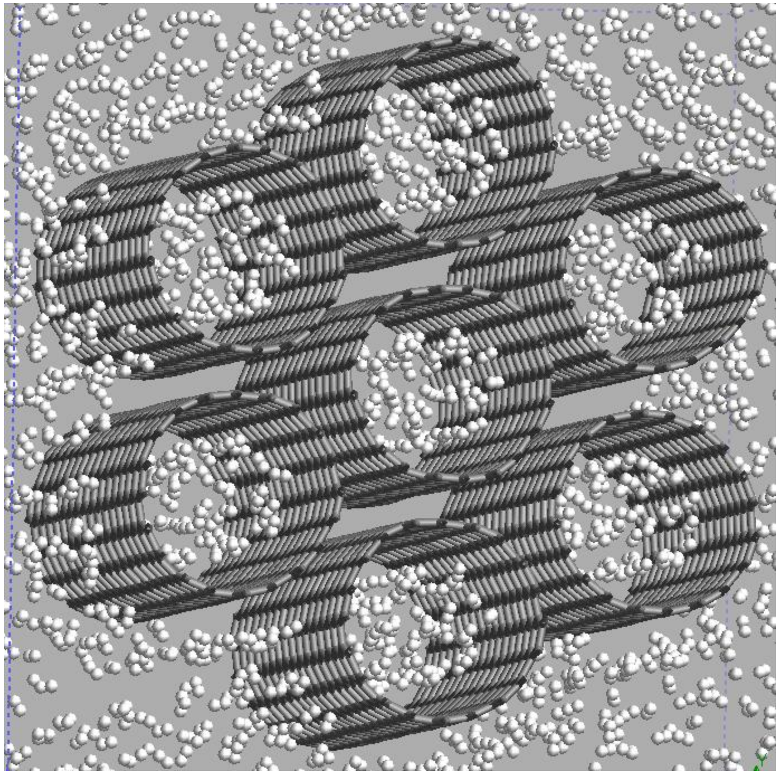
1st Stop: Develop Force Fields Accurate for H_2 binding to C and Li systems

- Developed new H-H vdW FF based on QM calculations on H_2-H_2 cluster.
- Developed new C-H vdW FF based on QM calculations on C_2-H_2 cluster
- Developed new Li-H vdW FF based on QM calculations on Li doped graphite cluster interaction with H_2
- For Valence parameters:
  - H-H fit to experimental R_e, D_e, ω_e
  - C-C Fix at known values

FF makes accurate fit to QM C-H Vdw interactions

C_2-H_2 vdw interaction





MP4/cc-pvtz++ with mid point function

7 (10,10) tube theoretical surface: 157.6 m^2/g

Experimental BET surface: 285 m^2/g

Binding of H_2 as function of Temperature and Pressure

Use Grand Canonical Monte Carlo (GCMC) method to predict the amount of H_2 bound at various pressures and temperatures

GC-MC method:

In GC-MC the chemical potential (μ) is fixed while the number of molecules fluctuates. Equilibrium is achieved when the temperature and chemical potential of the gas inside the framework are equal to free gas outside.

We start with the pure framework (no H_2) as the starting configuration, each subsequent configuration is generated by one of four moves:

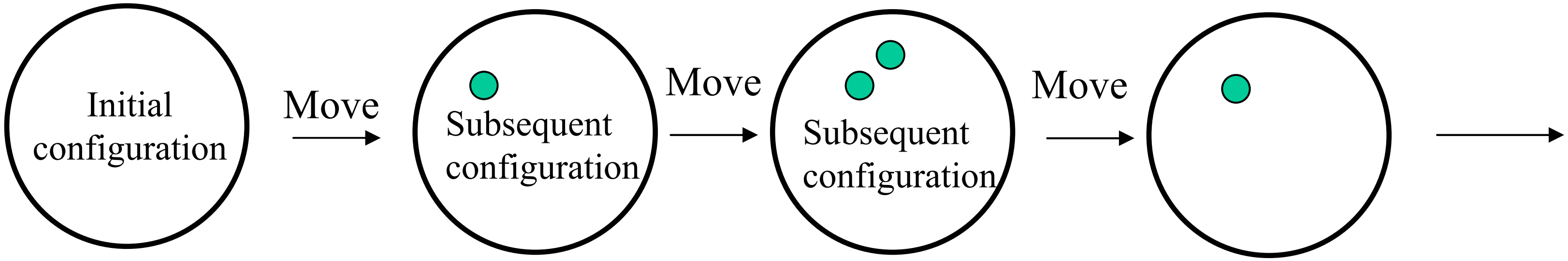
1. A molecule is created at a random position. The new configuration is accepted with probability P

$$P = \min\left[1; \exp\left(-\frac{\Delta E}{kT} - \ln\frac{(N_i+1)kT}{V}\right]\right.$$

2. A random molecule is destroyed.
3. A random molecule is translated a random amount and kept with probability P
4. A random molecule is Rotated a random amount and kept with probability P

When converged have a Grand Canonical Ensemble of structures for the given μ, T, p

Simulation method to predict H2 storage as function T and p: Grand Canonical Monte Carlo



Each subsequent configuration is generated by one of four moves:

1.A molecule is created. New configuration is accepted with probability:

$$P = \min\left[1; \exp(-\frac{\Delta E}{kT} - \ln\frac{(N_i + 1)kT}{V} \right]$$

2.A molecule is destroyed with probability:

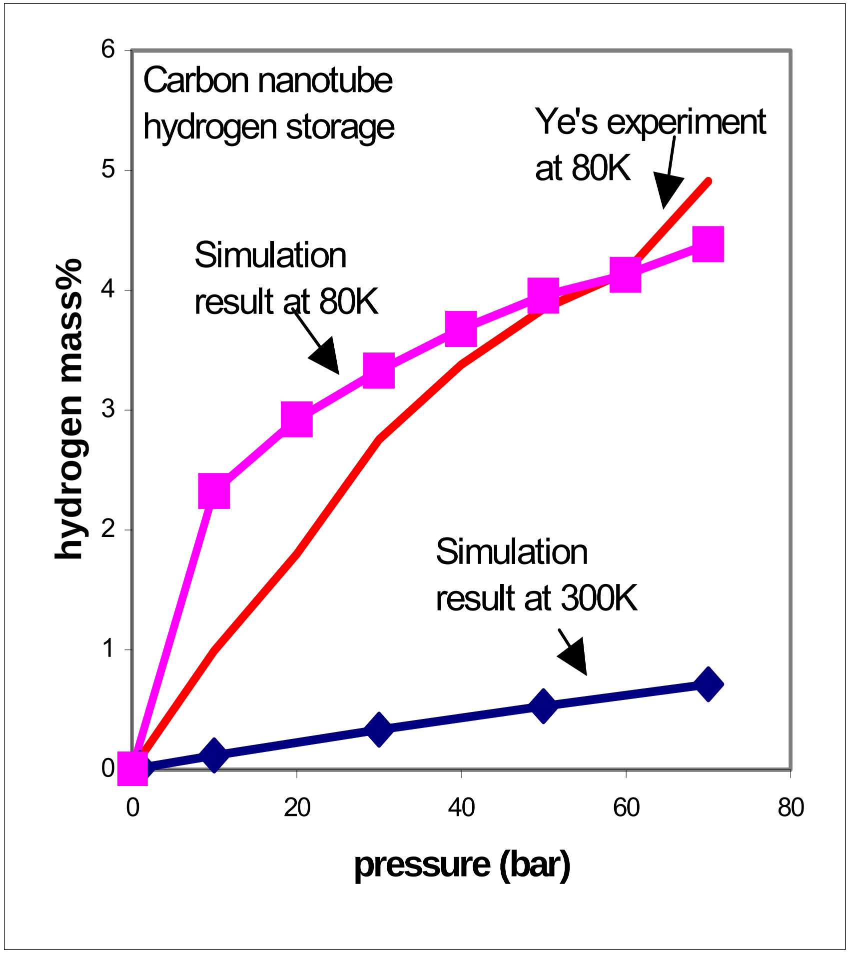
$$P = \min\left[1; \exp(-\frac{\Delta E}{kT} - \ln\frac{N_i kT}{V} \right]$$

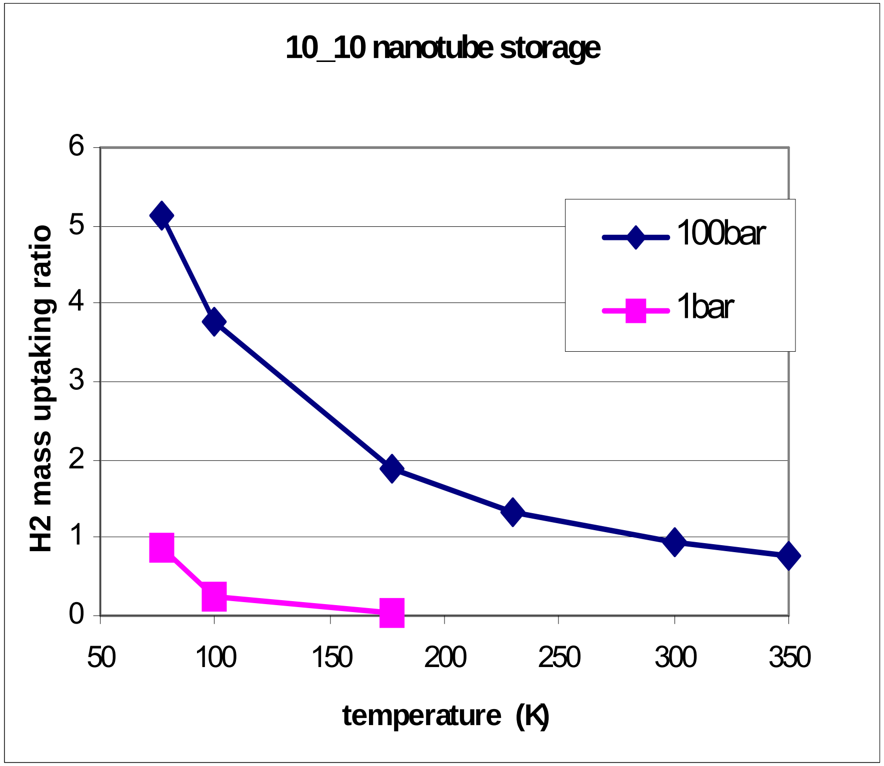
Chemical potential is kept fixed during the procedure

3. Molecule translate

4. Molecule Rotate.

Validation with experiment
uptake of hydrogen by carbon nanotubes



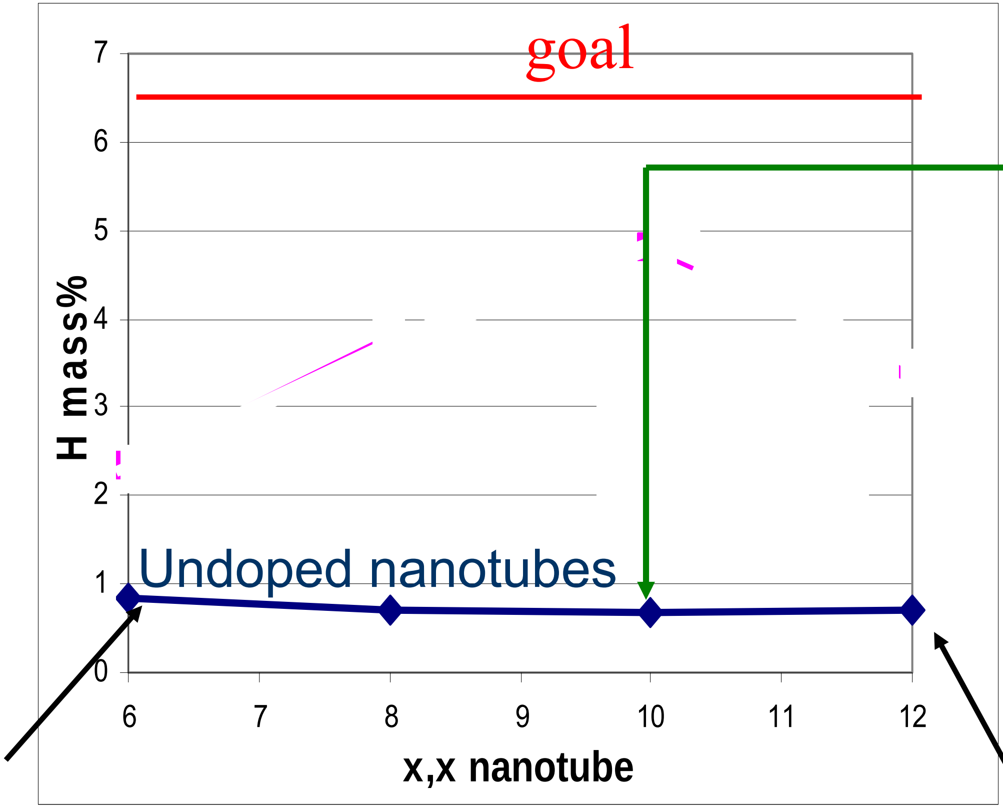


Bucky tubes Not practical:
at 20 bar and 80K only 3%,
at 100 bar and 300K only 1%

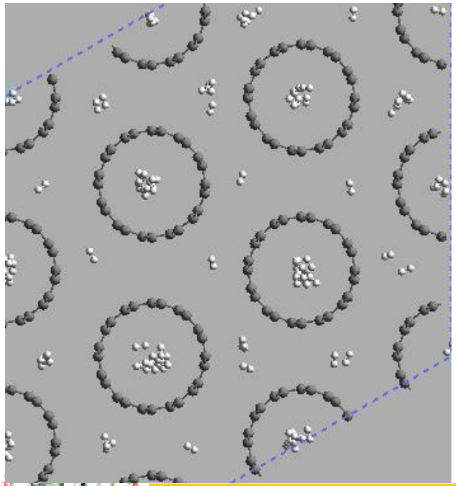
Predicted H_2 storage in bucky tubes
In good agreement with experiment
Ye, Y.; Ahn, C.C.; Witham, C.; Fultz, B.
and et al. *Appl. Phys. Lett.* **1999**, *74*, 2307

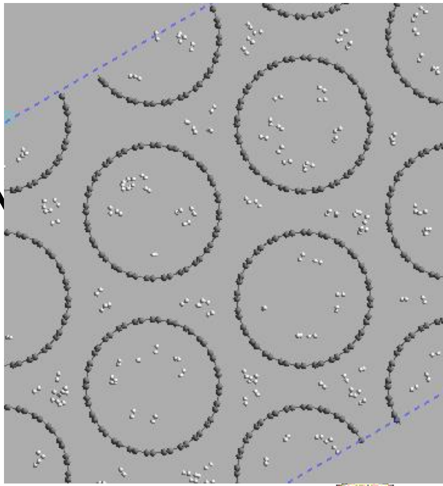
Adsorb H_2 into Carbon nanotube systems

298K
50bar



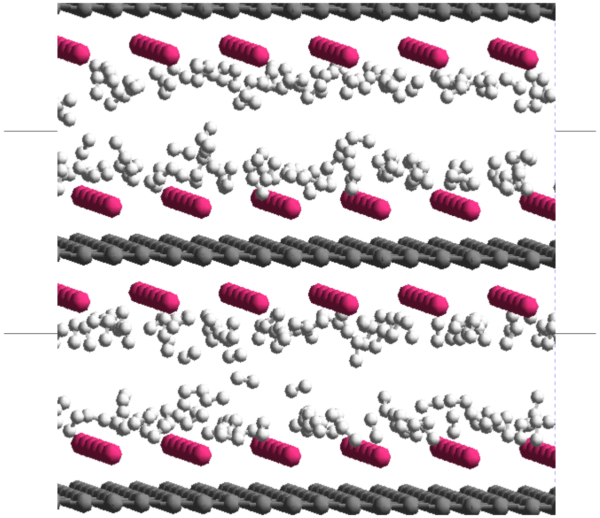
(10,10) most common bucky tube by normal catalysts



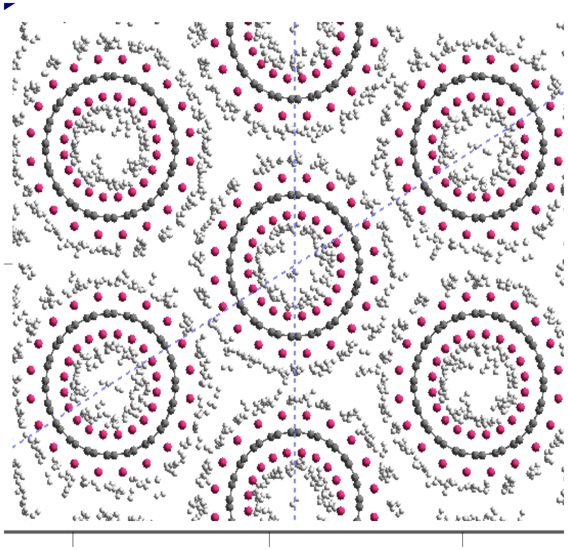


Conclusion: Pure bucky tube systems not adequate

New Design: Pillared Aromatic carbon framework loaded with alkali



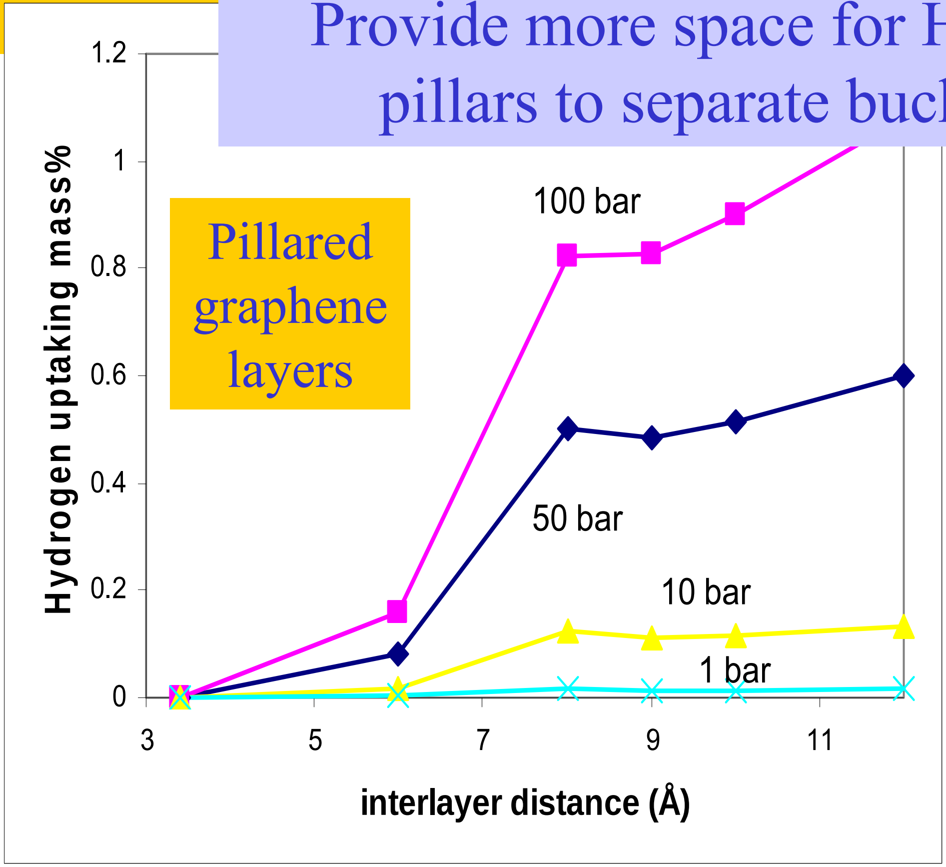
Pillared Graphene sheets, separated by 9A with Li:C=1:3 doping achieves 6.5% H2 at 300K and 10 bar

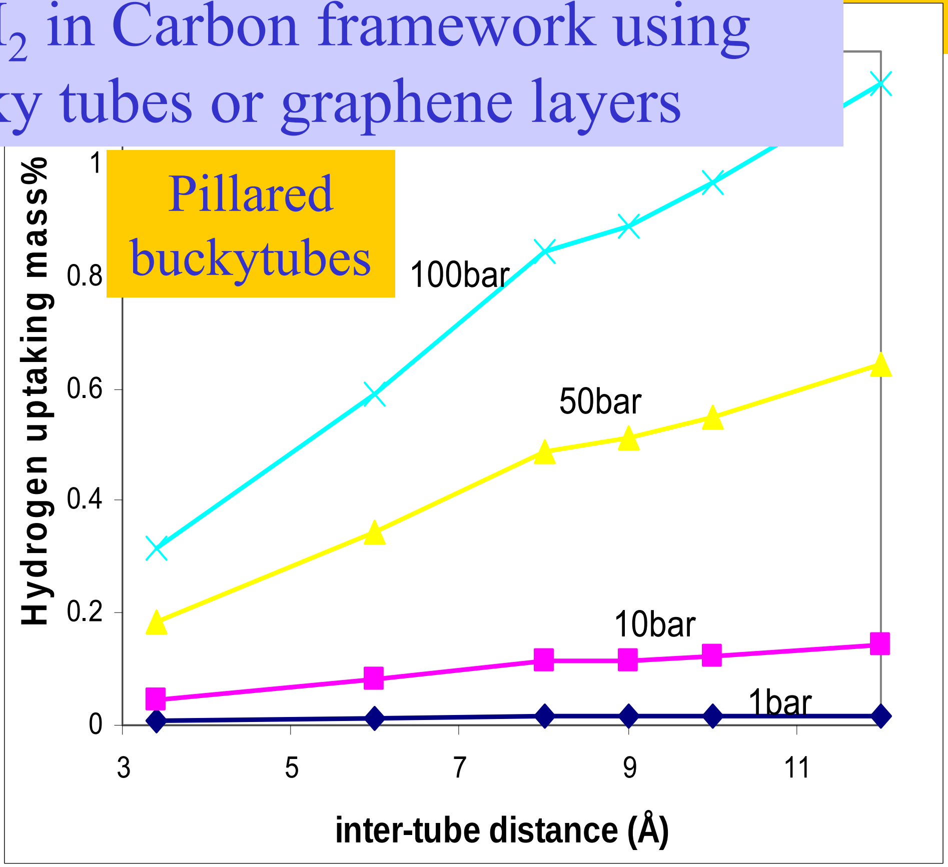


Pillared (10,10) bucky tubes, separated by 10A with Li:C=1:3 doping achieves 5.5% H2 at 300K and 10 bar

Pillared graphite and nanotube

Provide more space for H_2 in Carbon framework using pillars to separate bucky tubes or graphene layers





Experiments used Ball milling

M. Hirscher , M. Becher , M. Haluska , A. Quintel , V. Skakalova , Y.-M. Choi , et al. Journal of Alloys and Compounds 330–332 (2002) 654–658

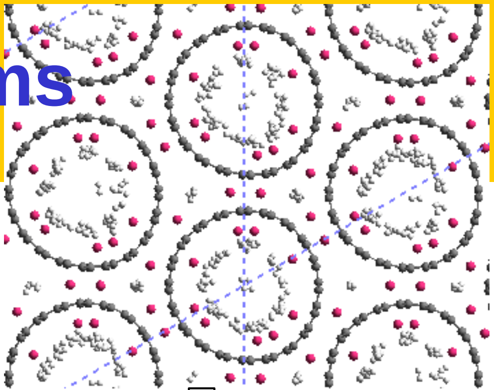
hydrogen storage capacity 90 bar

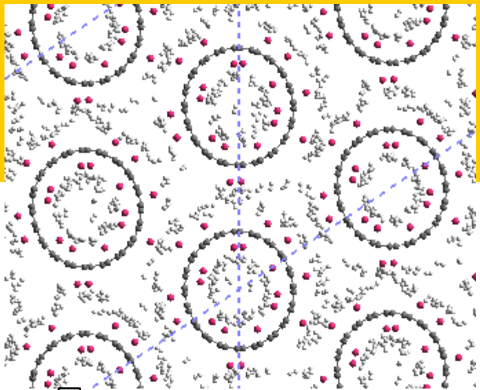
SWNTs 1.0 wt.%; GNFs 0.5 wt.% and for graphite 0.3wt.%

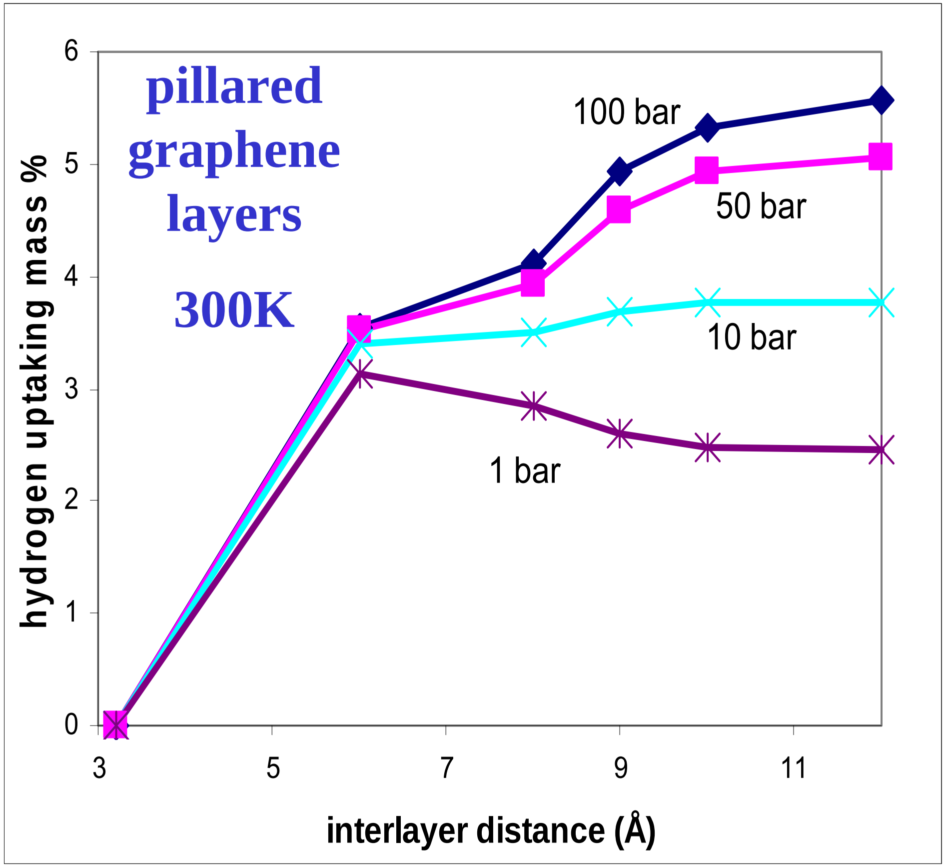
Pillared graphite and nanotube lead to Little improvement

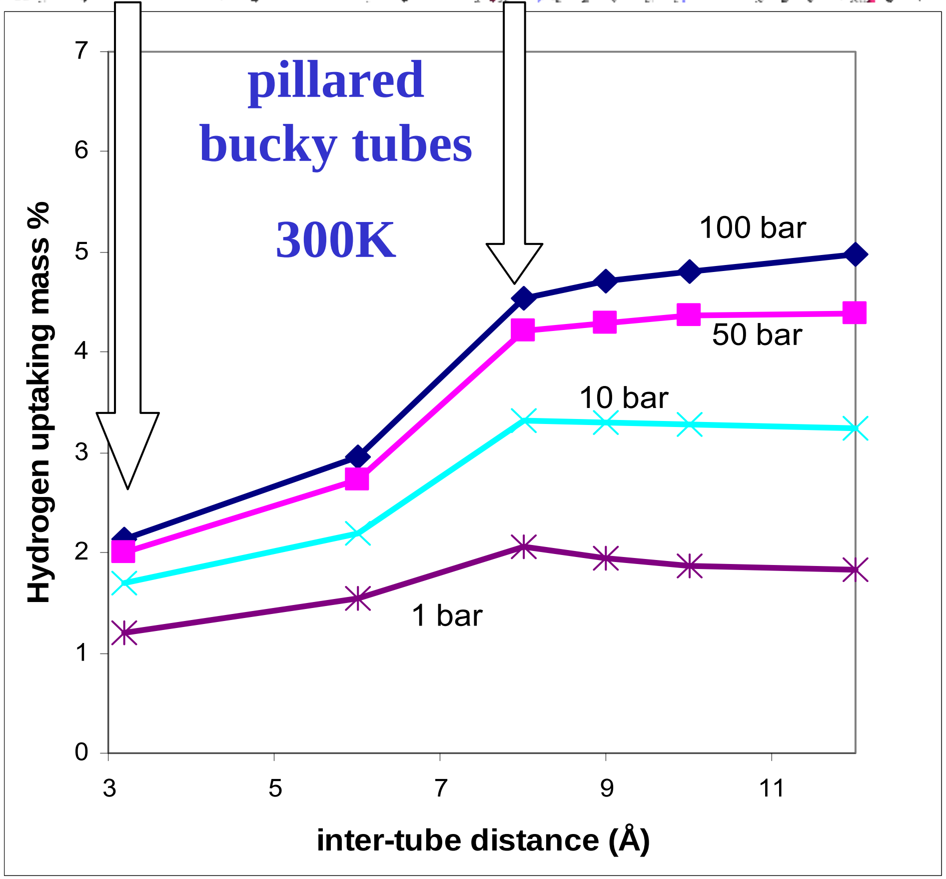
Add Li to Pillared Systems

Li:C (1:6) doped pillared graphite and nanotube









Conclusion: substantial improvement (4 to 6 %)

Find maximum reasonable Li doping level

Method for the synthesis of Li:C (1:3) doped graphite:

Ball milling: a new route for the synthesis of super-dense Lithium GICs

Janot R, Conard J, Guerard D;

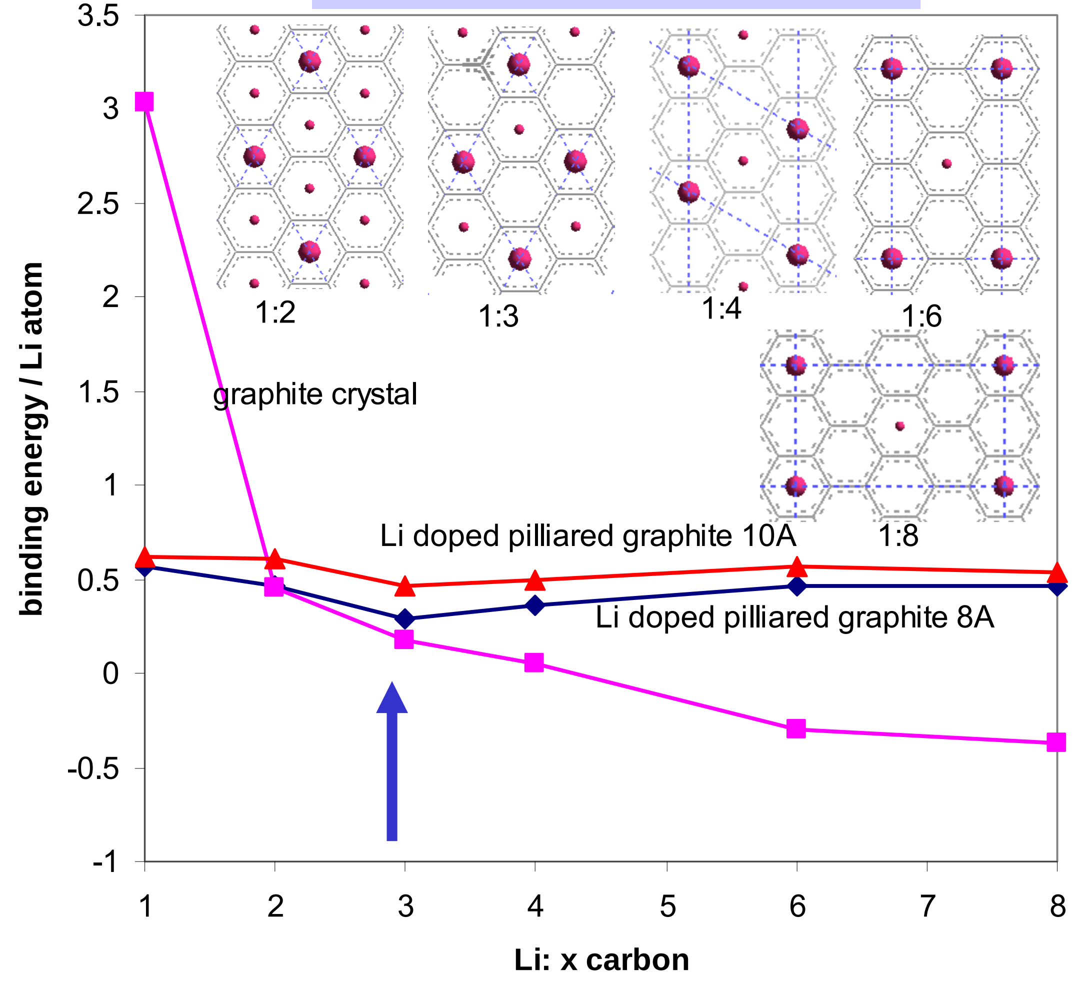
CARBON 39, (2001) 1931

Method for the synthesis of Li:C (1:3) doped nanotube:

H. Shimoda, B. Gao, X.P. Tang, A. Kleinhammes, L. Fleming, Y. Wu and O. Zhou,

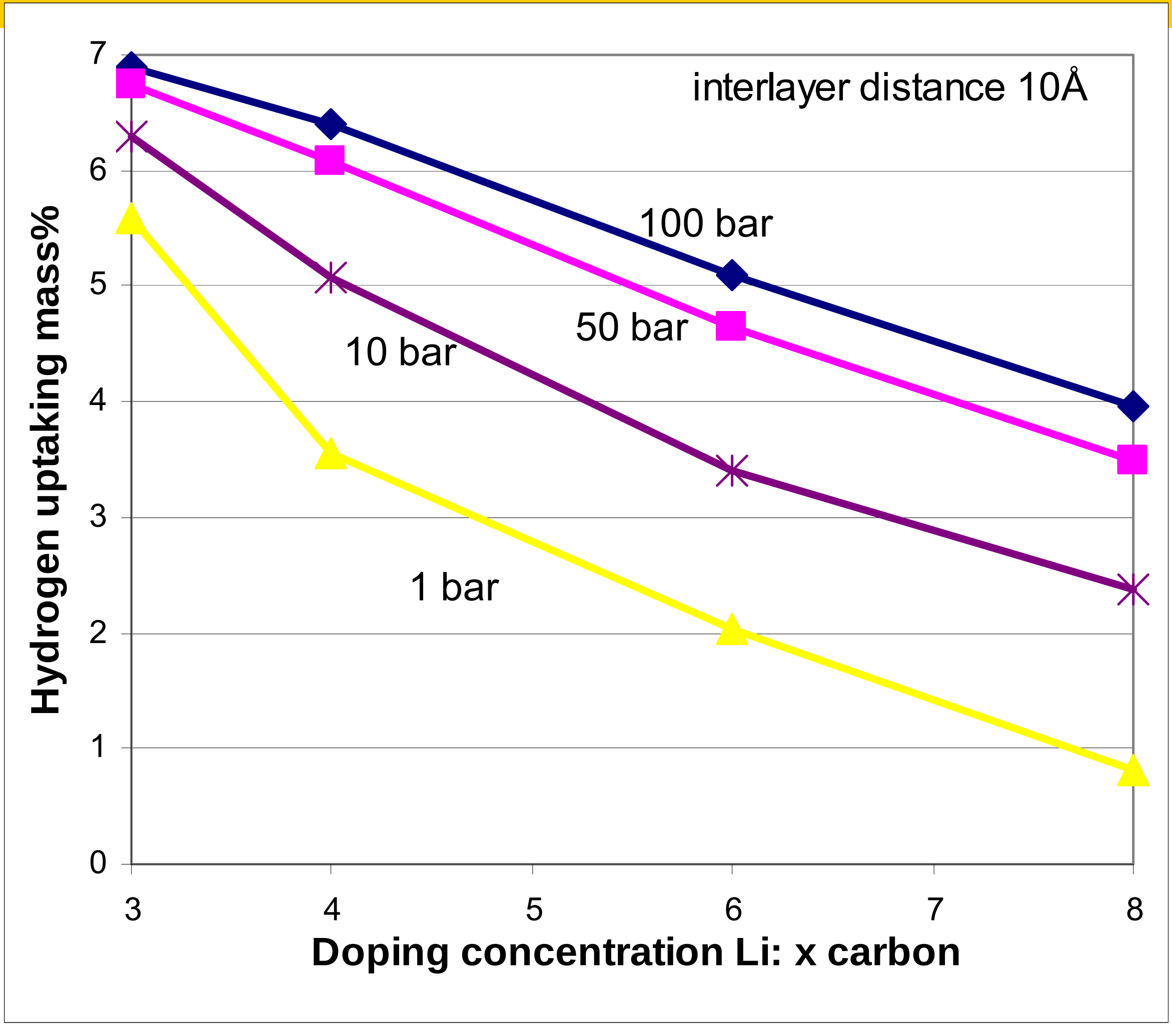
Phys. Rev. Lett. 88, 0155021 (2002)

PBE DFT calculations



Conclusion: QM → Li:C = 1:3 is achievable
Experiments demonstrate this level

Effect of doping concentration on H_2 Storage



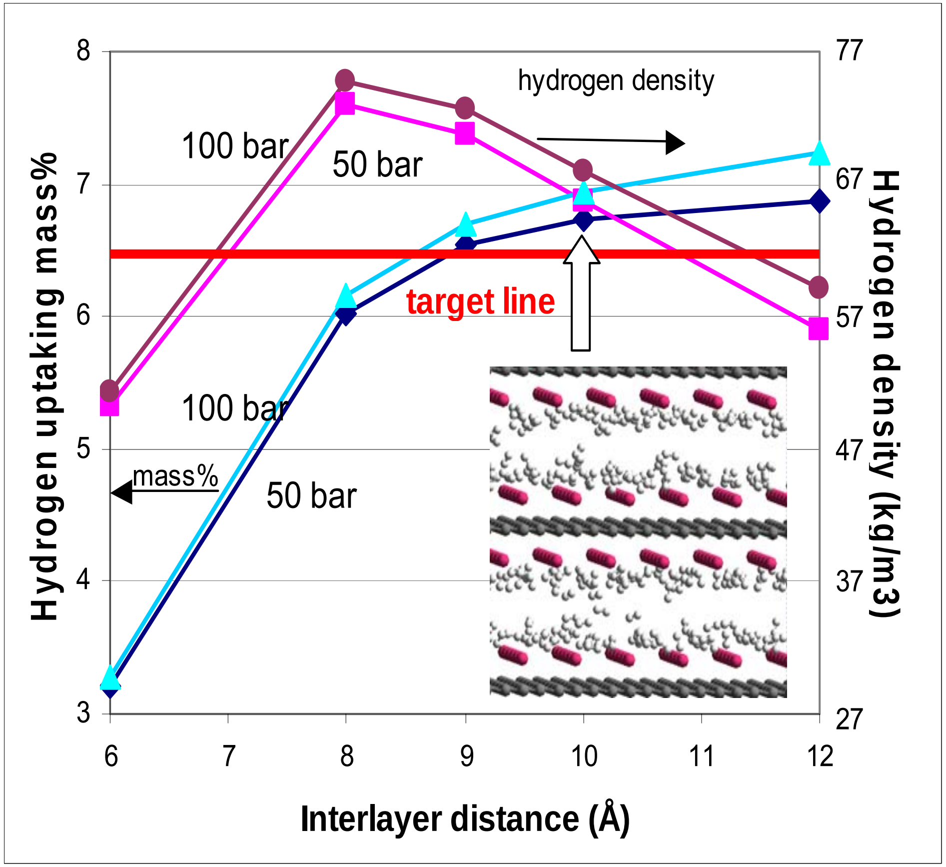
DOE target

Use of 1:3 doping concentration dramatically improves hydrogen storage

Hitting the storage goal

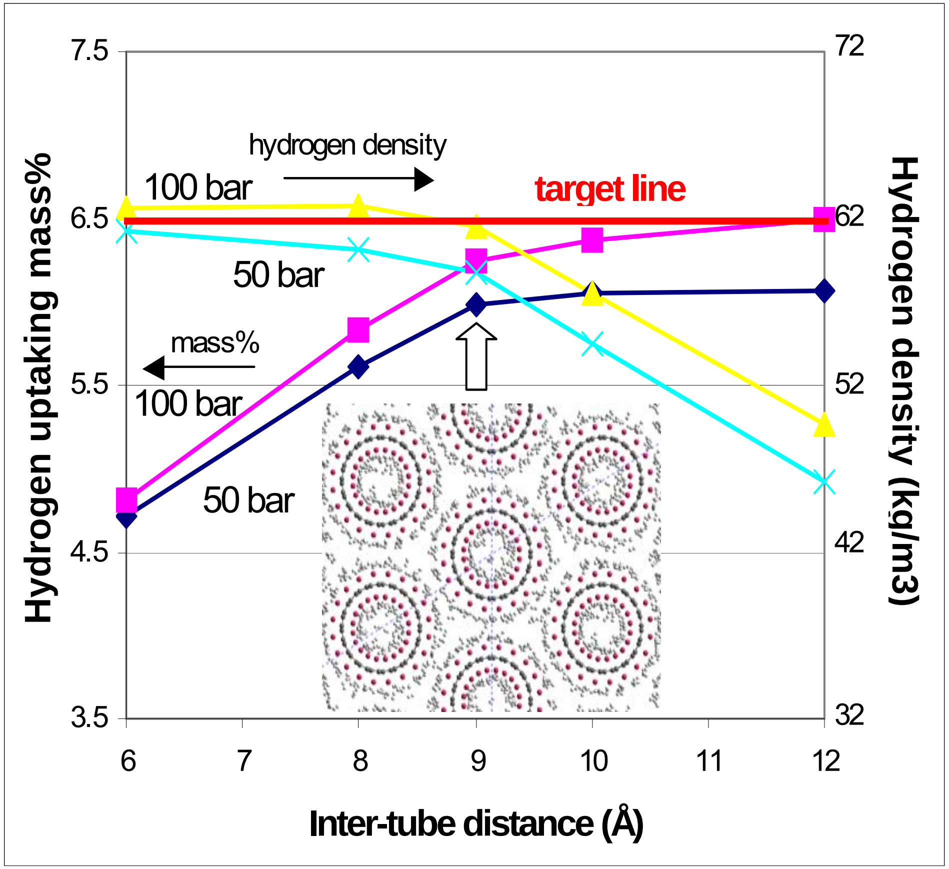
pillared graphene layers

300K



pillared bucky tubes

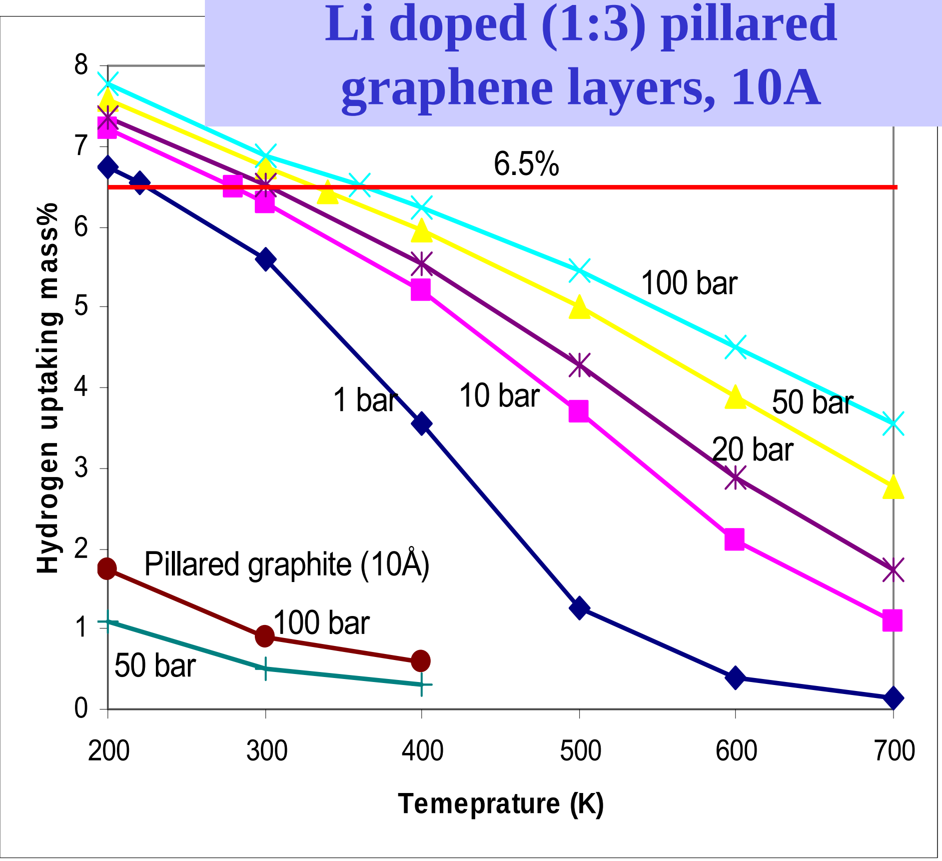
300K



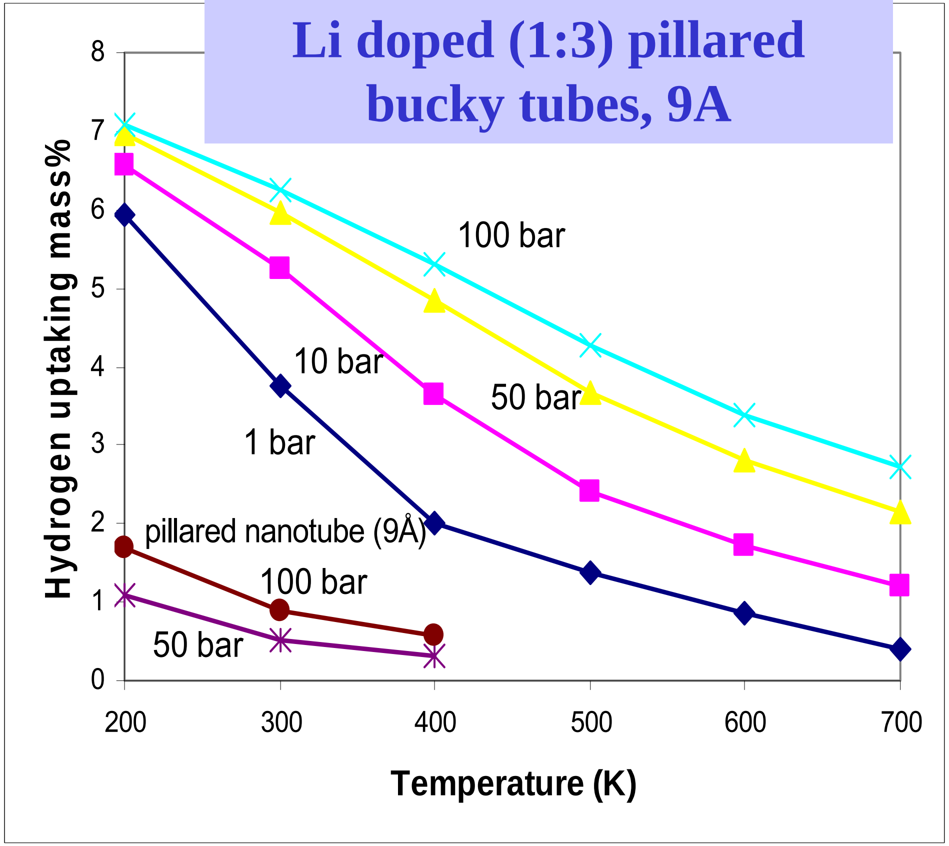
Pillared graphene 10A ➔ 6.7% at 50 bar

Pillared bucky tubes: 9A ➔ 5.9% at 50 bar

Use temperature and pressure to control hydrogen uptake



Li doped (1:3) pillared graphene layers, 10A



Li doped (1:3) pillared bucky tubes, 9A

1 bar, 700K: 0.12% **20 bar, 300K: 6.51%**

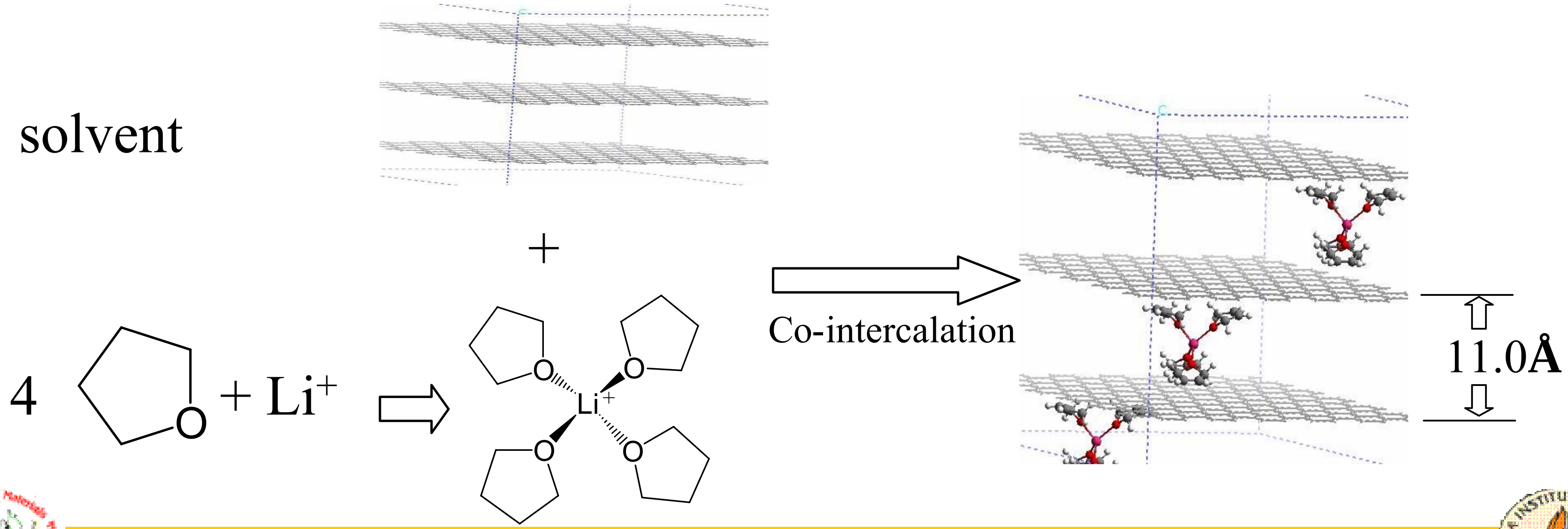
At fixed volume conditions cycle from 20bar at 300K to 1bar at 500K
Li-Pillared graphene: 5% reversible
Li-Pillared bucky tube: 4% reversible

Allowing volume changes for cycle from 20bar at 300K to 1bar at 400K expect
Li-Pillared graphene: 6.5% reversible
Li-Pillared bucky tube: 5.5% reversible

Strategy to pillar the graphite containing Li ions

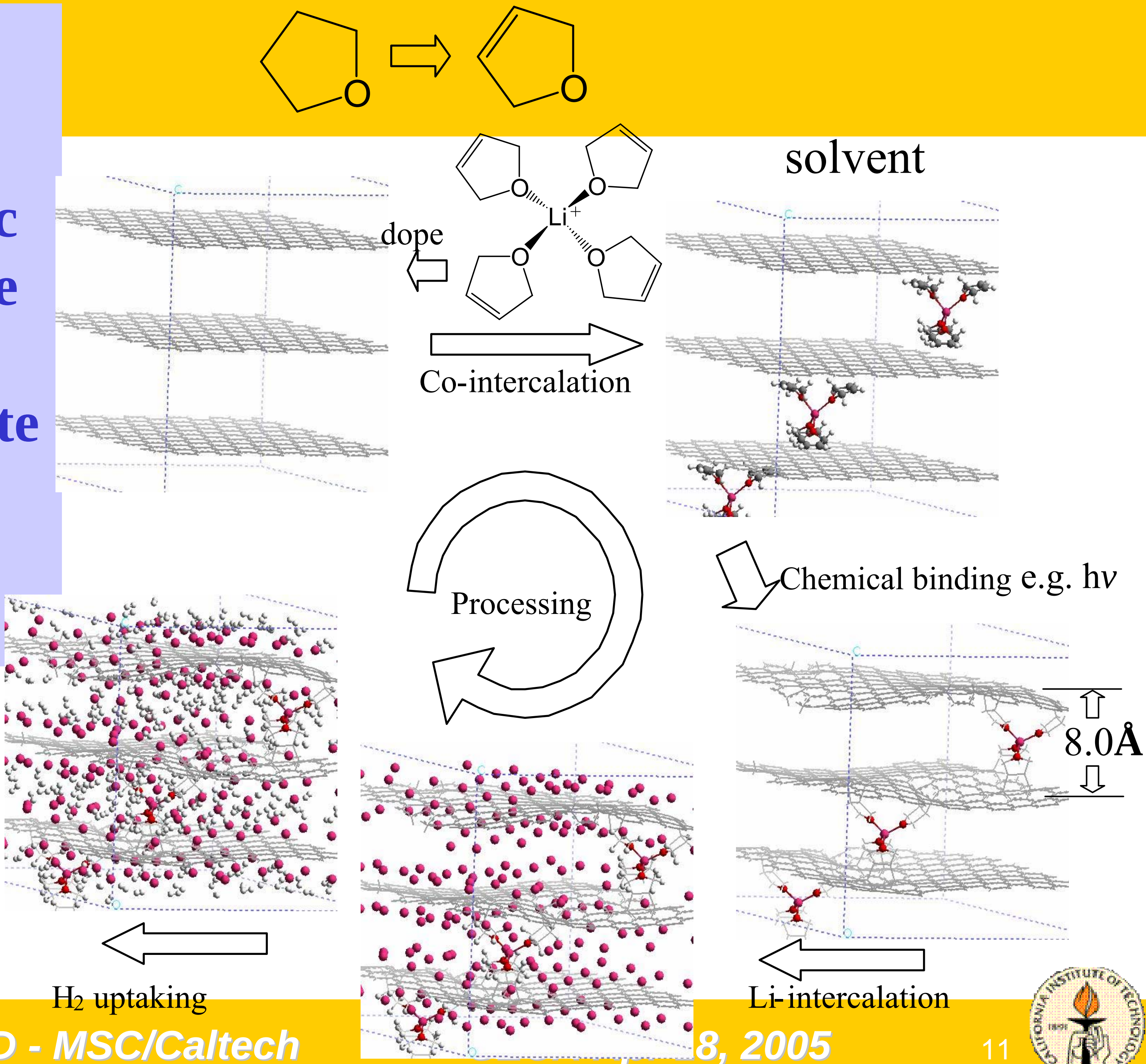
Co-intercalate Li+ and organic into GICs

T. Abe, Y. Mizutani, N. Kawabata, M. Inaba, Z. Ogumi, Syn. Metals 125, 249 (2002)
M. Inagaki, O. Tanaike, Carbon 39, 1083 (2001)



Better procedure

Use organic with double bond and photoactivate to form covalent linkages



solvent

dope

Co-intercalation

Processing

Chemical binding e.g. hν

8.0Å

H₂ uptaking

Li-intercalation

Summary

- Used Multiscale de novo Simulations to design a practical H_2 storage medium capable of meeting Transportation Fuel Cell goals.
- Find two possible systems
  - Li doped and pillared graphene
  - Li doped and pillared nanotube.

- Developed new QM based force field for Li-doped carbon based system and interactions with H_2.
- Use grand canonical Monte Carlo to simulate performance and optimize hydrogen uptake parameters of the new materials
- Design procedures to synthesis the new materials.
- Now ready for experimental validation

Deng, Xu, Goddard; Physical Review Letters, **92** (16): art. no. 166103 (**2004**)

Theory and Computation are providing valuable information about:

- Structure and properties of new Materials
- Design strategies for new materials

Discussion

"Goddard is in medical research"

William Goddard PhD (Engineering Science 1965,Caltech) advisor: Pol Duwez
Pol Duwez DSc (Physics, 1933, Brussels) advisor: Emile Henriot
Emile Henriot DSc (Physics 1912, Sorbonne, Paris) advisor: Marie Curie
Marie Curie DSc (1903, Ecole Phys. Chim. Ind, Paris) advisor: Henri Becquerel