Argonne NATIONAL LABORATORY

... for a brighter future

Fuel Cells

Just a Dream - or Future Reality

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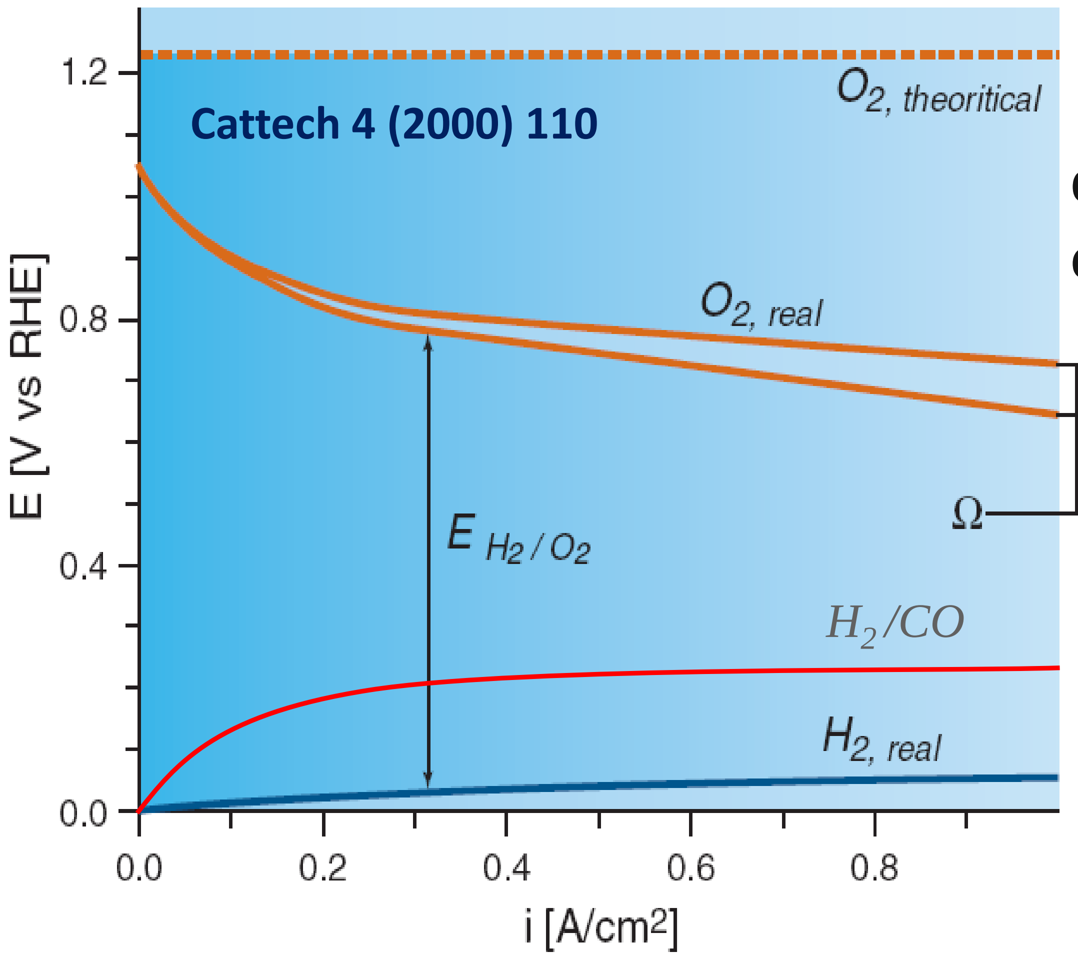
UChicago Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Fuel Cells and Electrocatalysis

➢**More than just devise for energy conversion - the development of fuel cell catalysts in the last three decades has transformed electrocatalysis from art to science**



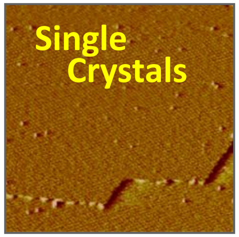
ORR/OER: a key for the development of alternative energies

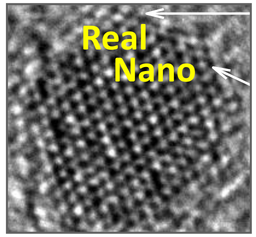
CO: a key "test molecule"

HOR/HER : the mother of all electrochemical reactions

Surface Science Approach

MATERIALS-BY-DESIGN





METALS

M -OXIDES

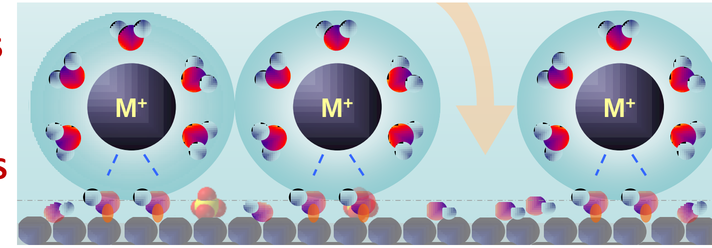
OXIDES

DOUBLE-LAYER-BY-DESIGN

ANIONS

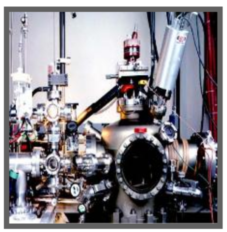
WATER

CATIONS

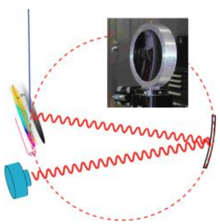


DESIGN — SYNTHESIZE — CHARACTERIZE — UNDERSTAND — APPLY

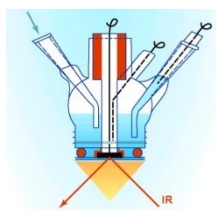
CHARACTIZATION METHODS



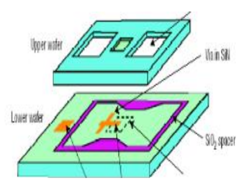
UHV



SXS
STM/AFM

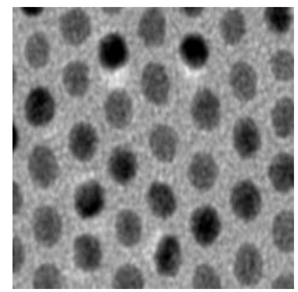


FTIR
RAMAN

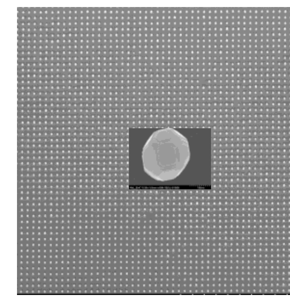


HRTEM

SYNTHESIS METHODS

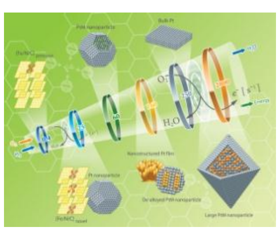


CHEMICAL

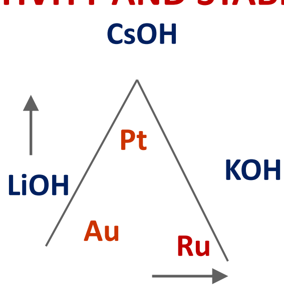


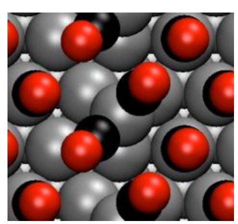
PHYSICAL

ACTIVITY, SELECTIVITY AND STABILITY MAPPING



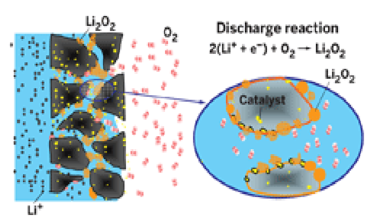
Experiment



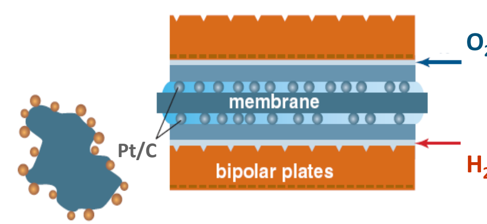


Theory/Modeling

REAL SYSTEM

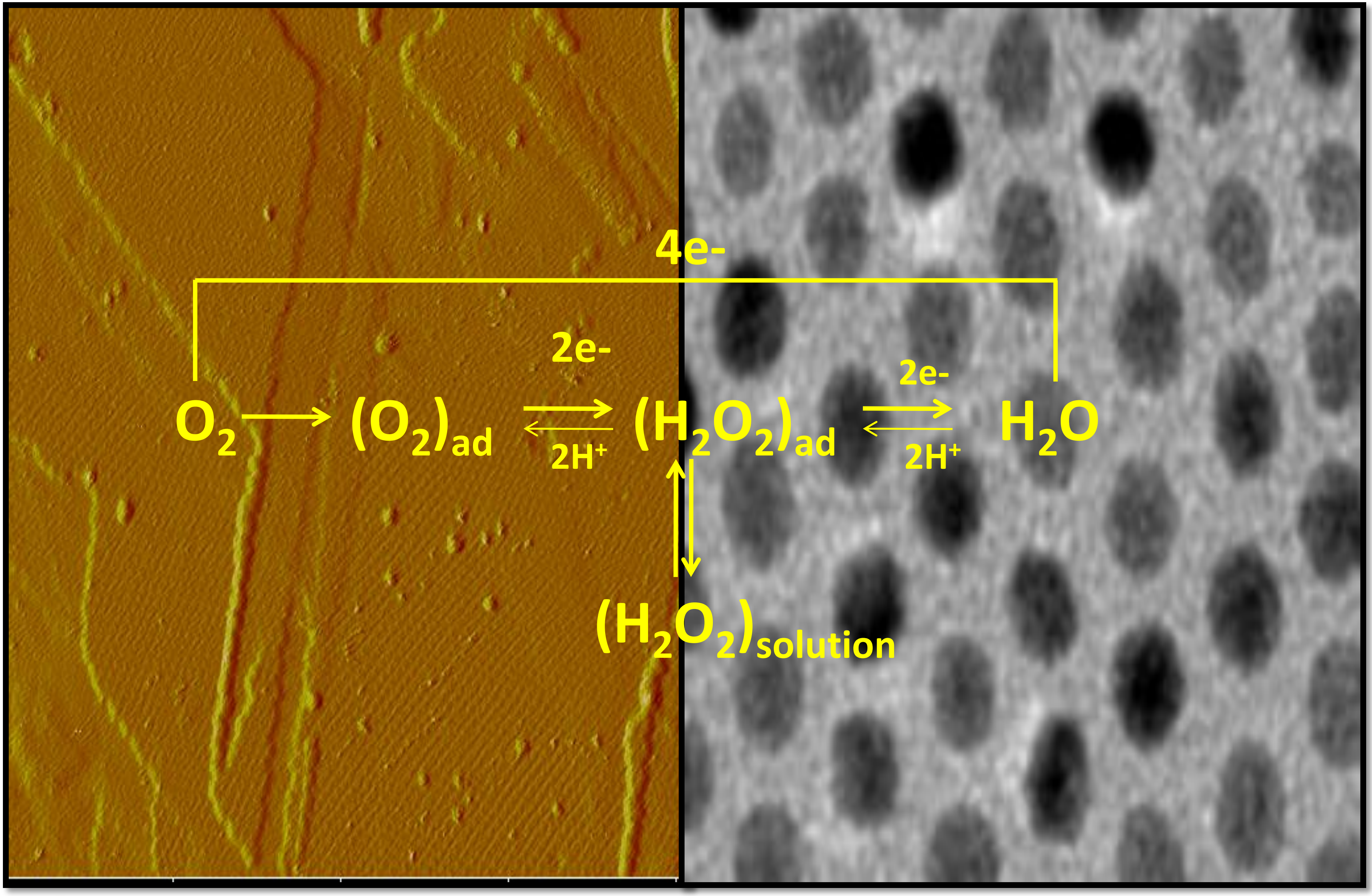


Metal-Air Batteries



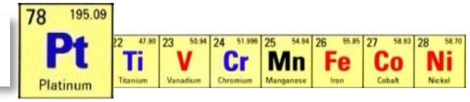
Fuel Cell ↔ Electrolyzer

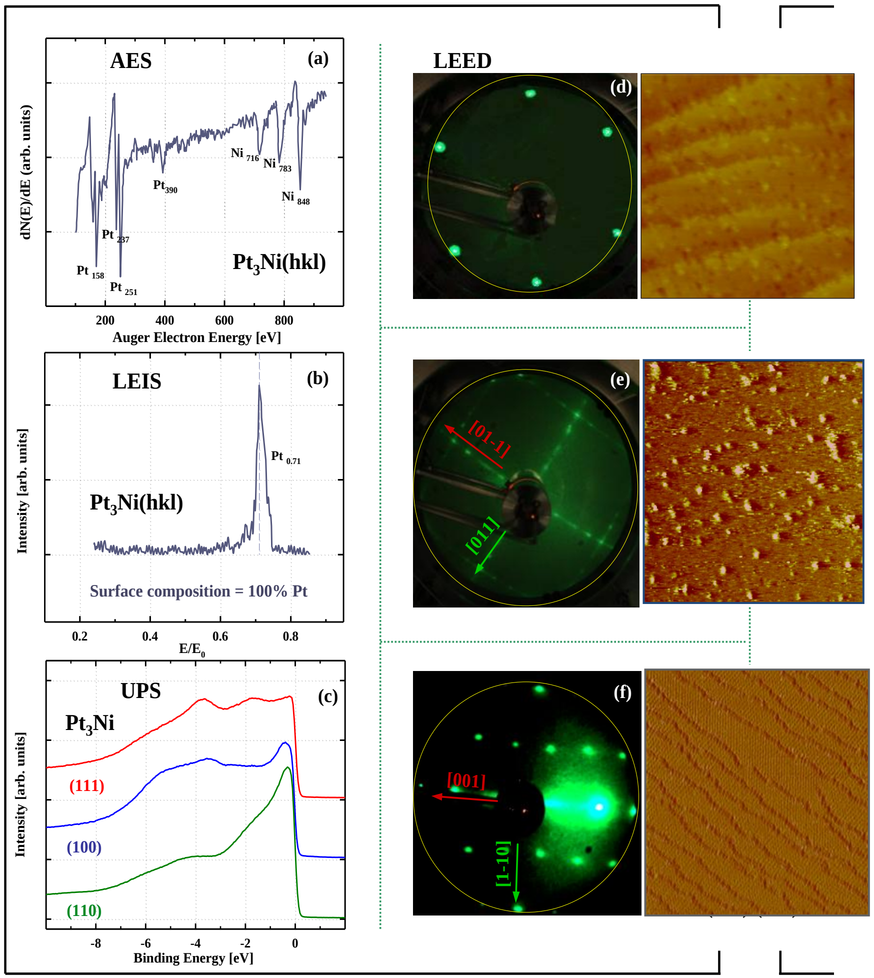
ORR- The reaction pathway

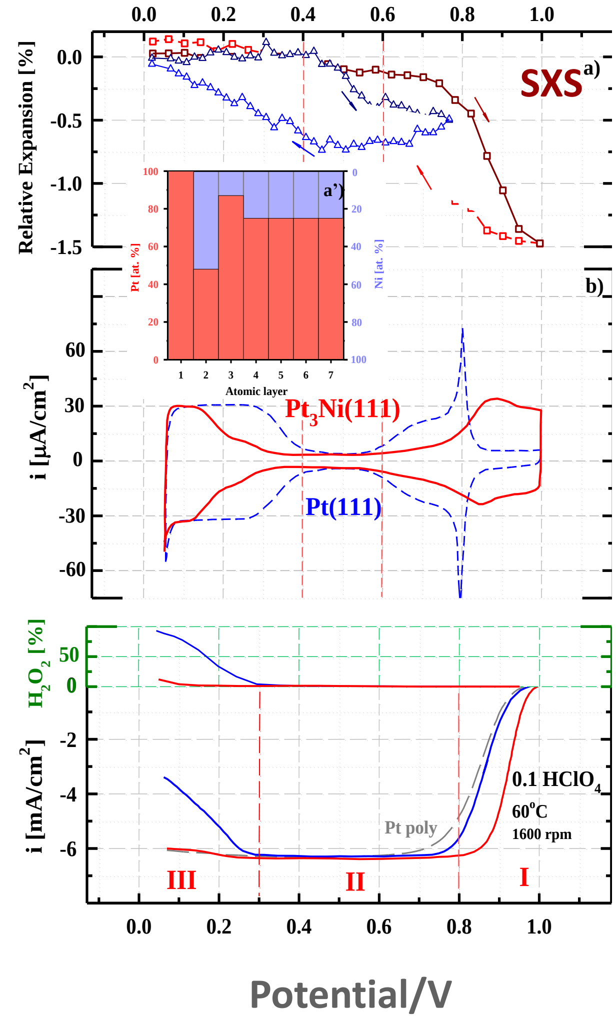


Tailoring Electronic Properties

Metal Alloys(Pt_3M)





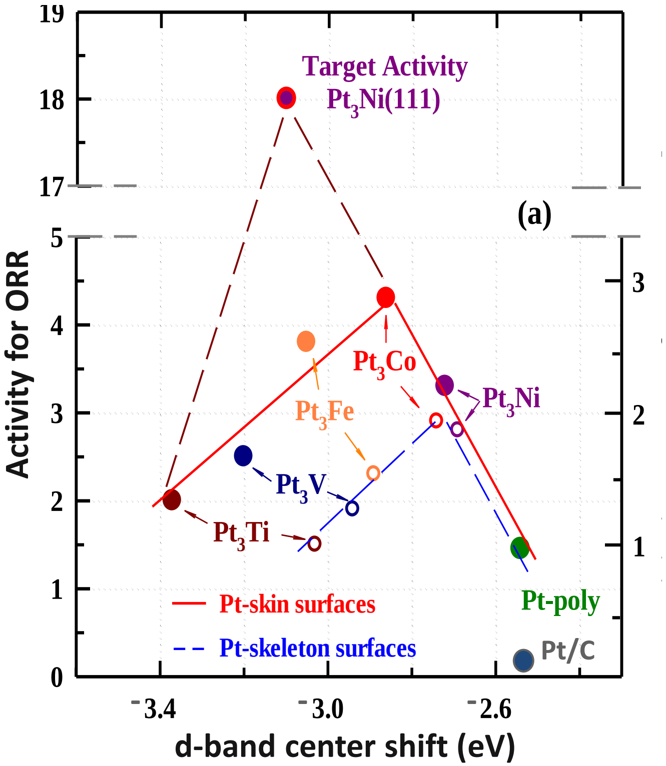


Science, 315(2007)493

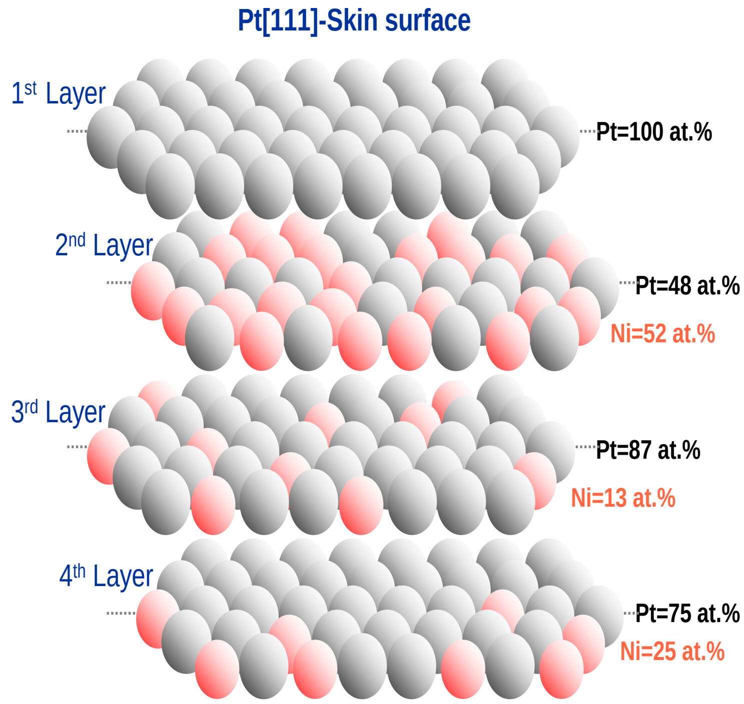
$$i = n F K(1-\Theta_s) \exp(-\gamma \Delta G_i / RT)$$

Tailoring Activity by Electronic Properties

Activity mapping



Nanosegregated Profile



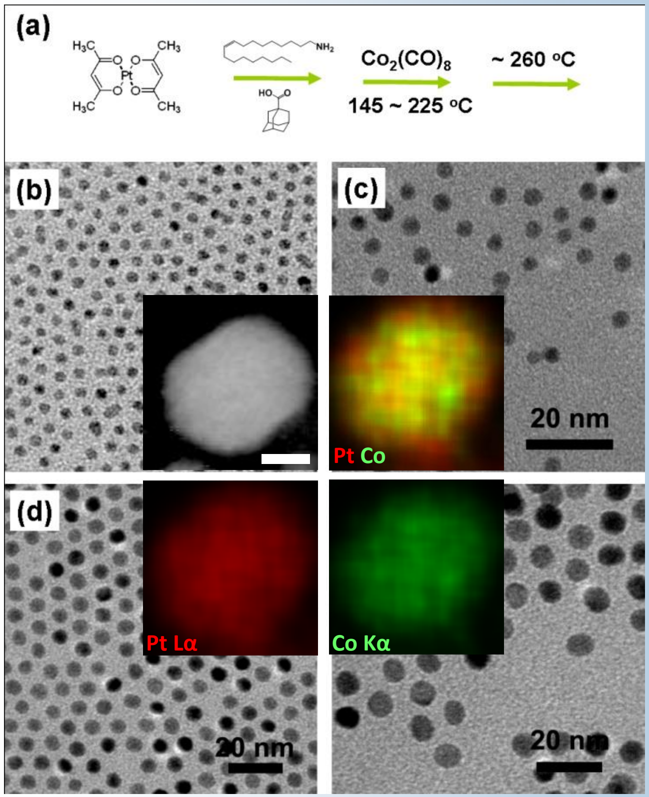
Nature Materials, 6(2007)241

Guiding Principles:

- Maximize activity by minimizing surface coverage of spectators
- Without compromising activity protect 3d elements by additional Pt layer

Tailoring Electronic Properties

Colloidal solvo - thermal approach for monodispersed PtM NPs with controlled size and composition



Efficient surfactant removal

1° Particle size effect applies to Pt-bimetallic NPs

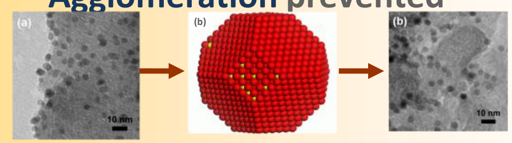
Specific Activity increases with particle size: 3 < 4.5 < 6 < 9nm

Mass Activity decreases with particle size

Optimal size particle size ~5nm

2° Temperature induced segregation in Pt-bimetallic NPs

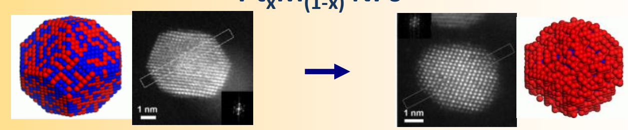
Agglomeration prevented



Optimized annealing temperature 400-500°C

3° Surface chemistry of homogeneous Pt-bimetallic NPs

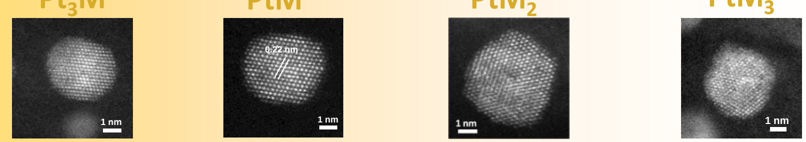
$Pt_xM_{(1-x)}$ NPs



Dissolution of non Pt surface atoms leads to **Pt-skeleton** formation

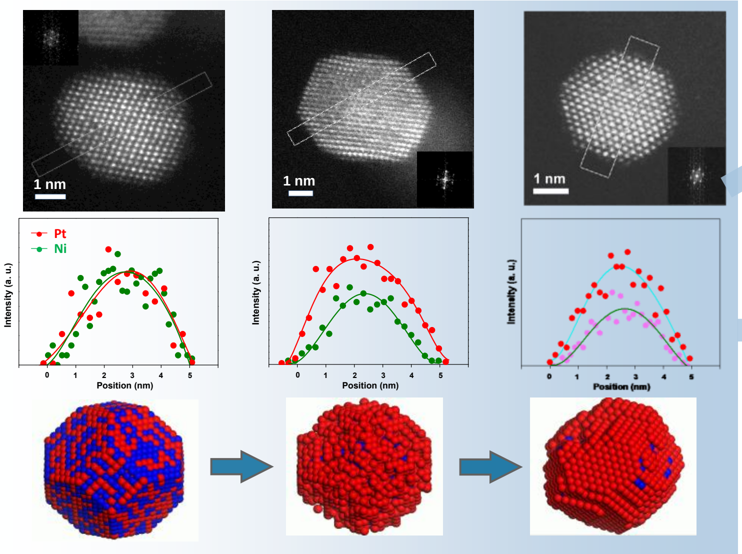
4° Composition effect in Pt-bimetallic NPs

Pt_3M | PtM | PtM_2 | PtM_3

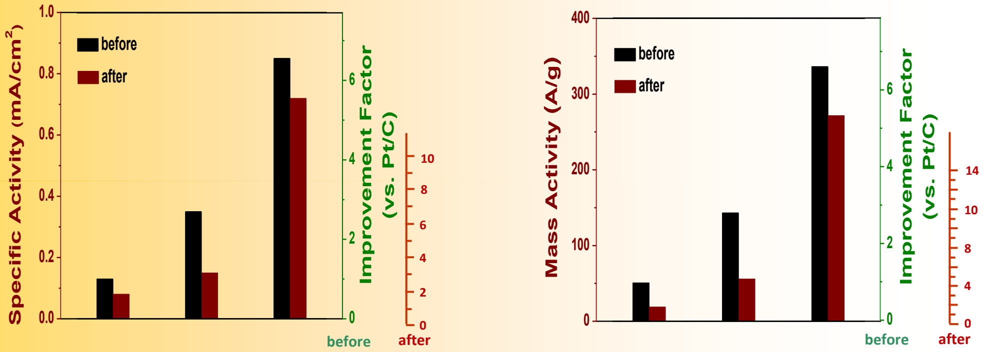


Optimal composition of Pt-bimetallic NPs is PtM

From Model to Real Catalysts



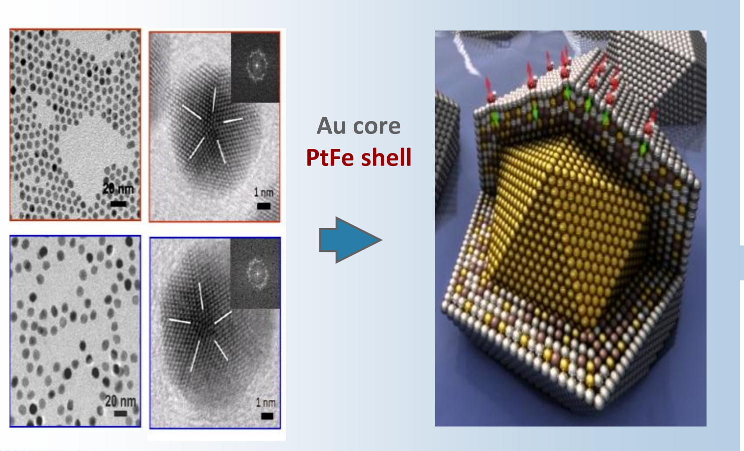
5° Pt-bimetallic catalysts with mutilayered Pt-skin surfaces



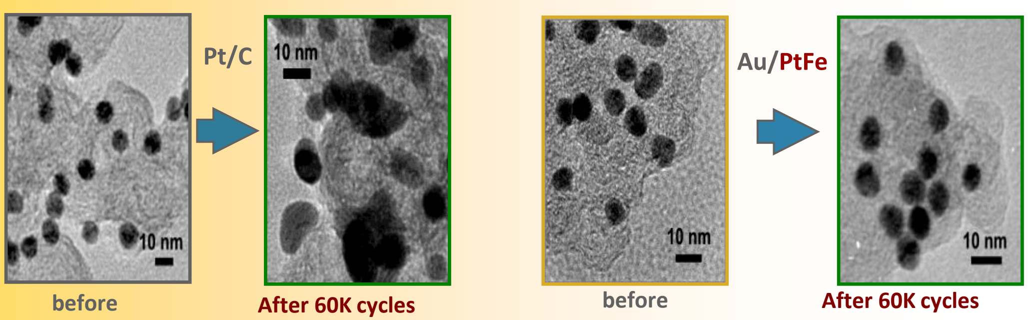
RDE after 4K cycles @60°C (0.6-1.05V vs. RHE):

8-fold specific and 10-fold mass activity improvements over Pt/C

Advanced Functional Materials, 21(2011)147



6° Multimetallic NPs can further improve activity and durability



Nano Letters, 11(2011)919-928

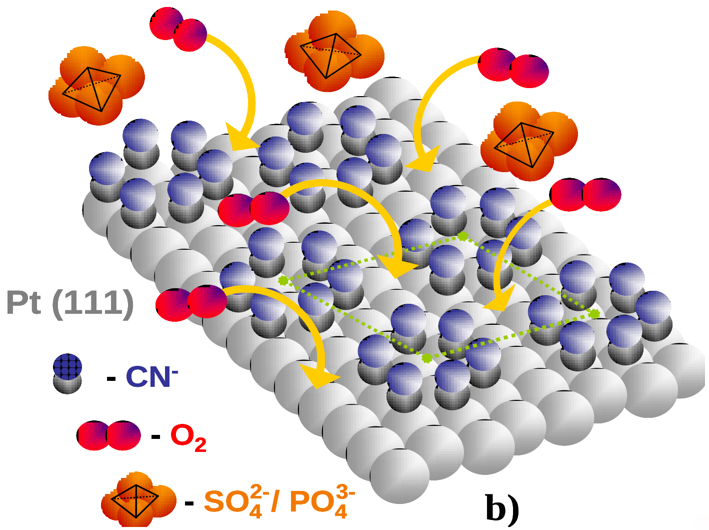
Beyond electronic effects

Keep electronic properties constant

Maximize activity and selectivity by inert self assembled monolayer

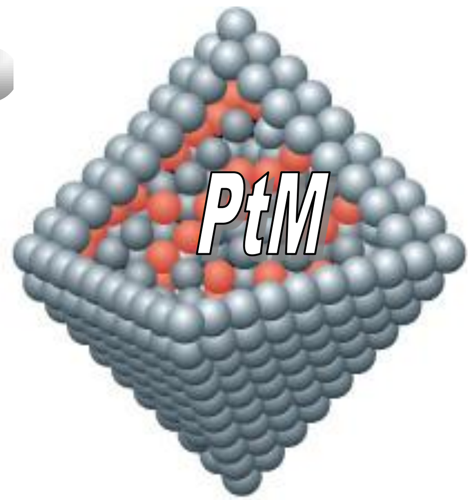
Molecular patterning

Inorganic

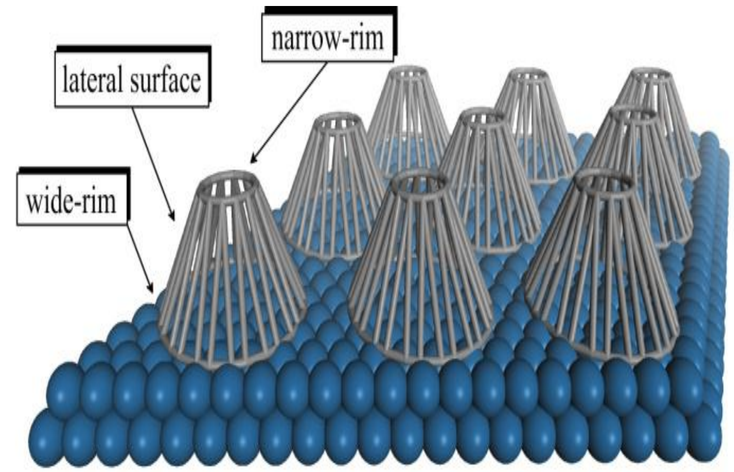


Inert Pt-CN_{ad} adlayer

Nature Chemistry 2 (2010) 880



Organic

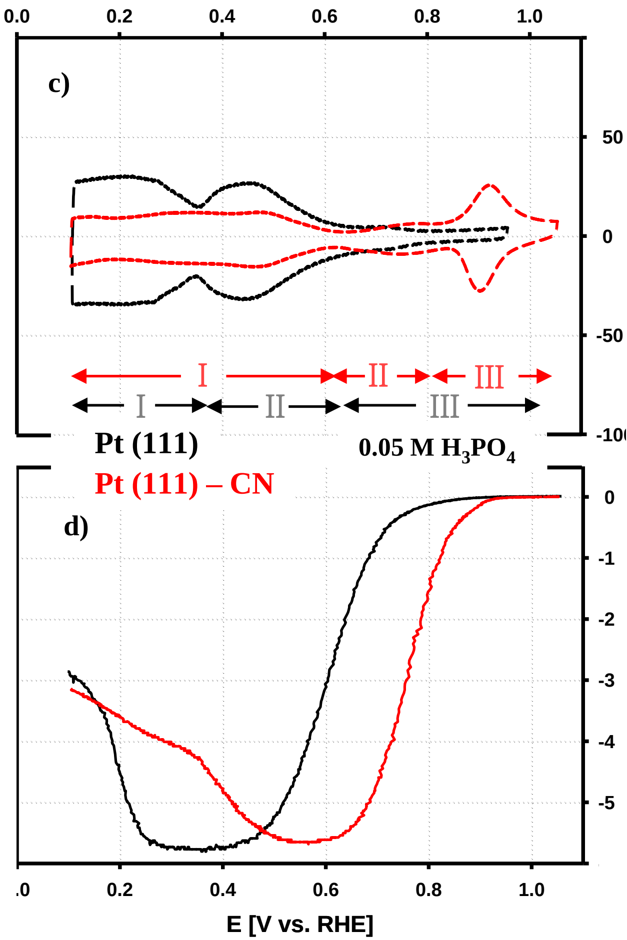


Inert Pt-Calix[4]arene adlayer

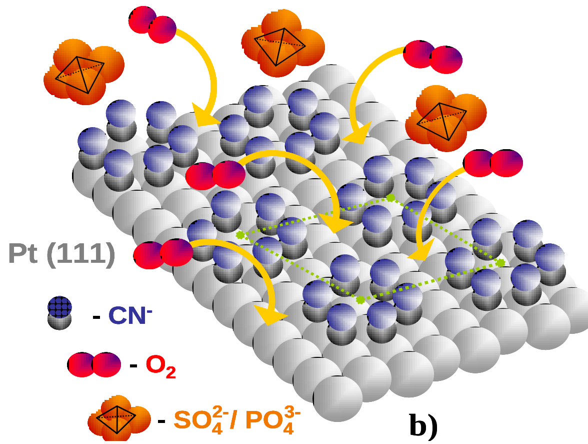
Nature Materials, 9, *2010,881*

Selectivity controlled activity

- **ORR is strongly inhibited by adsorbed phosphoric acid anions**



"Big vs. Small"



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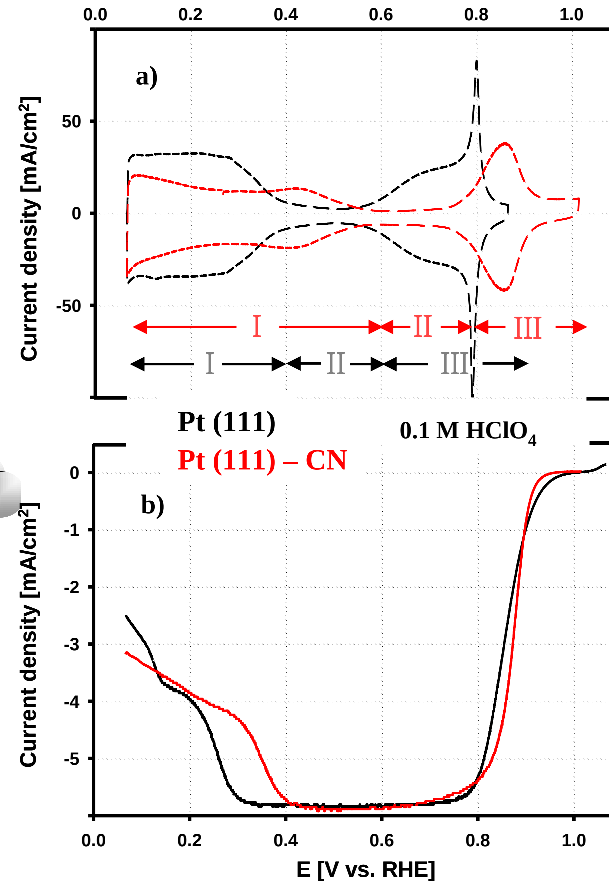
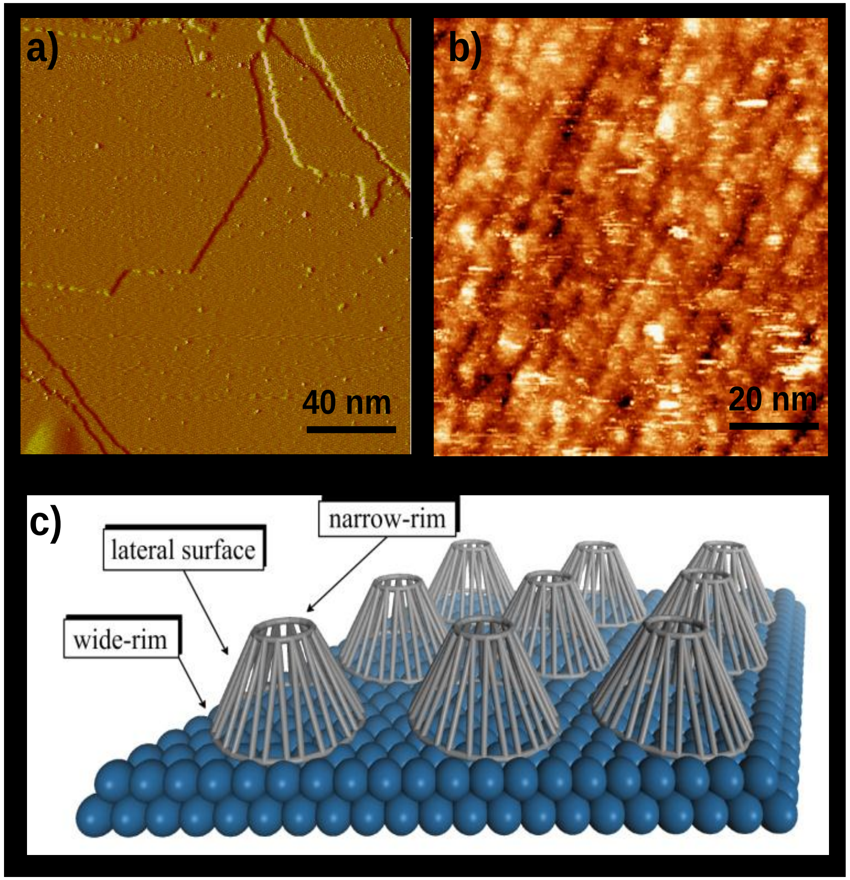


- **CN adlayer selectively blocks adsorption of anions**

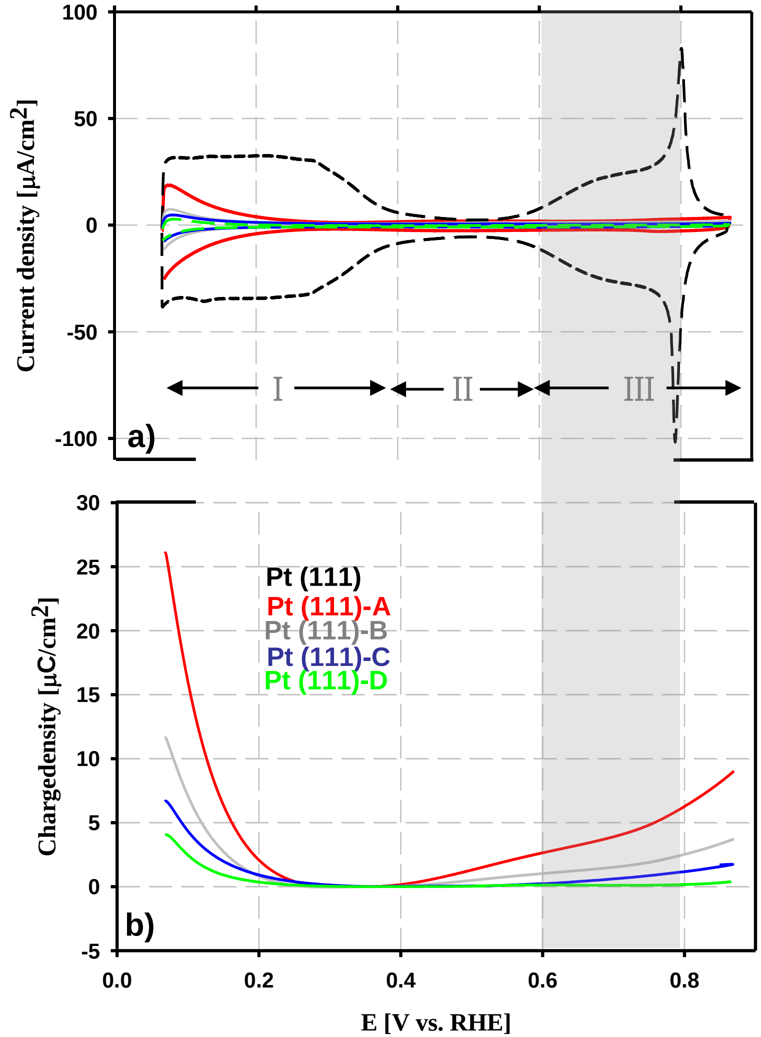
$$i = n F K (1-\Theta_s) \exp(-\gamma \Delta G_i / RT)$$

Selectivity controlled stability

Improving stability of cathode catalysts



2% of active sites

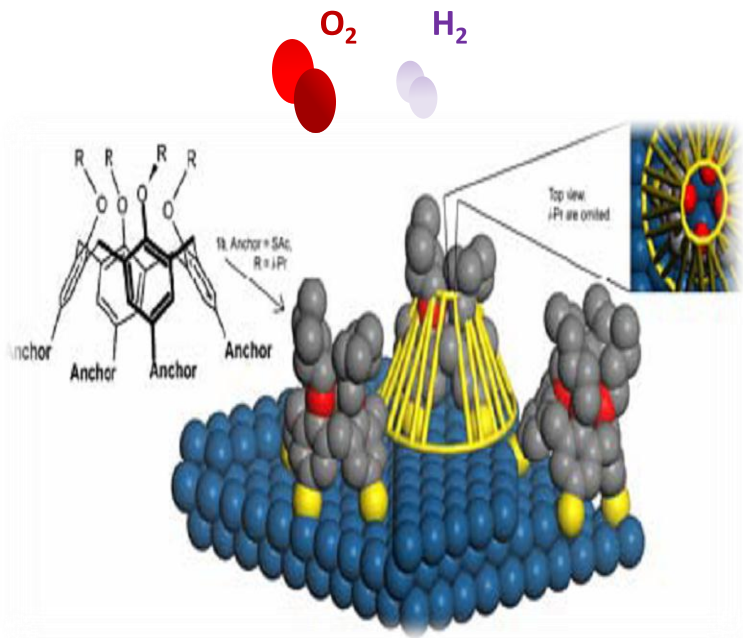


Nature Materials, 9, 2010,881

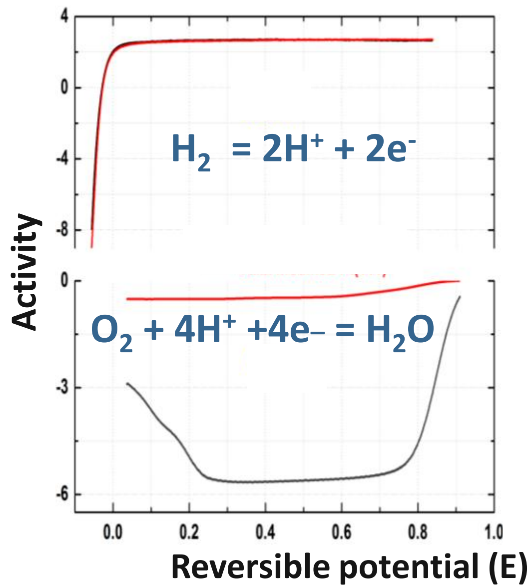
Tailoring Activity/Stability by Molecular Patterning

- Maintain electronic properties and optimize stability by molecular patterning

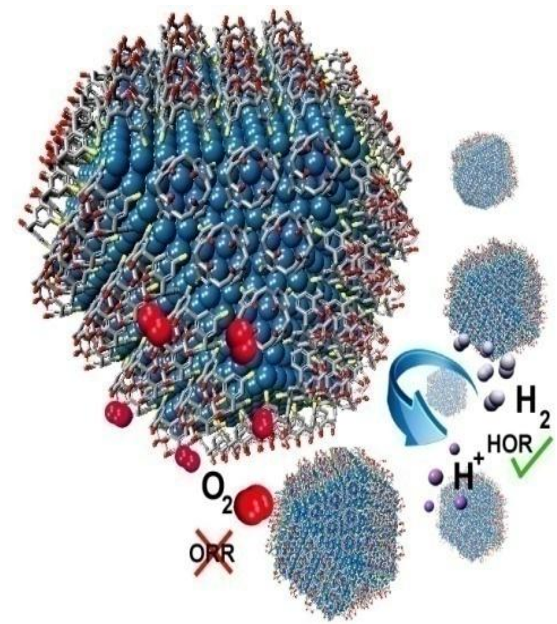
Extended



Pt(111)-Calix[4]arene



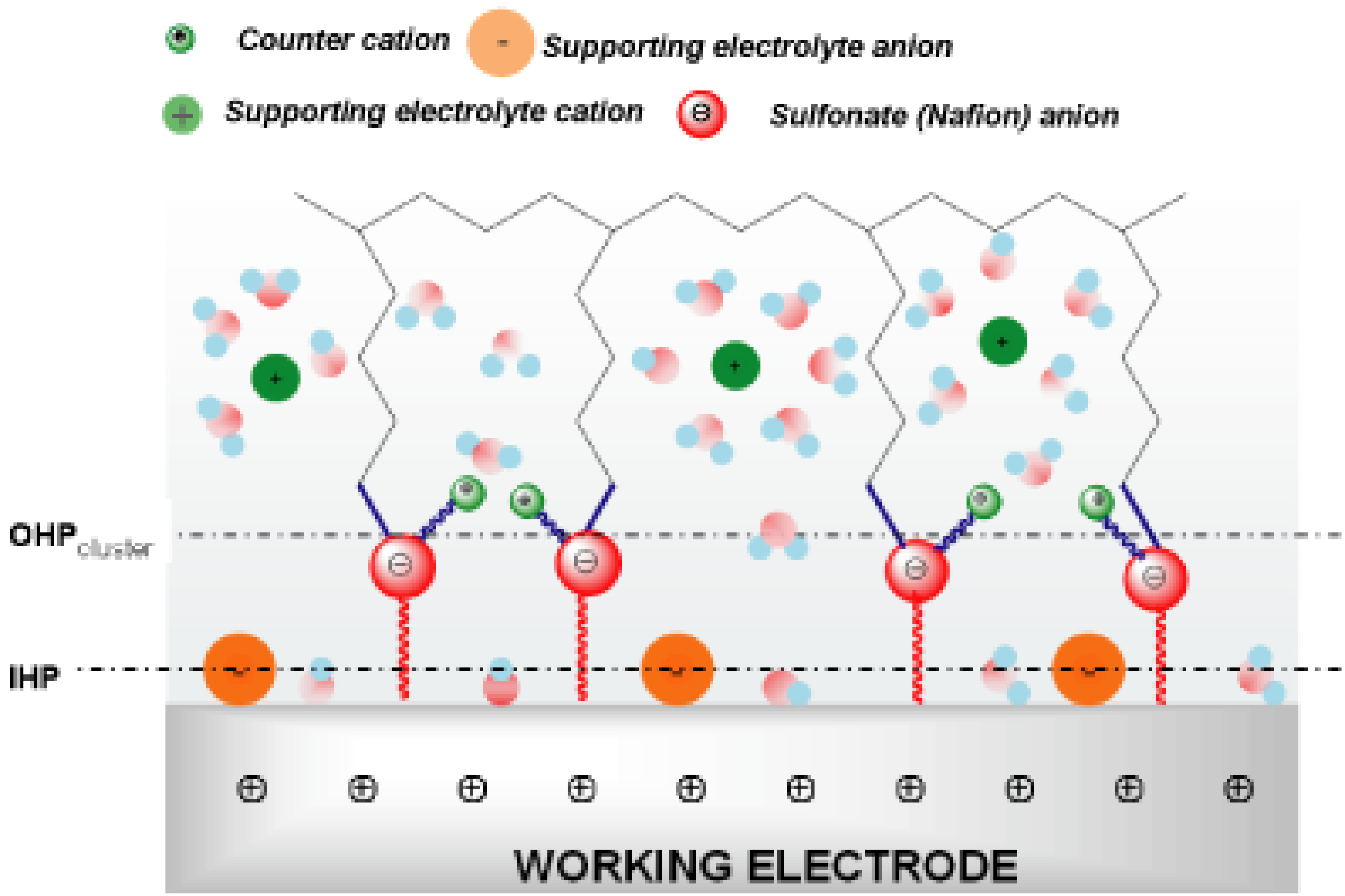
Nano



- Calix adlayer prevents adsorption of O_2 but not H_2

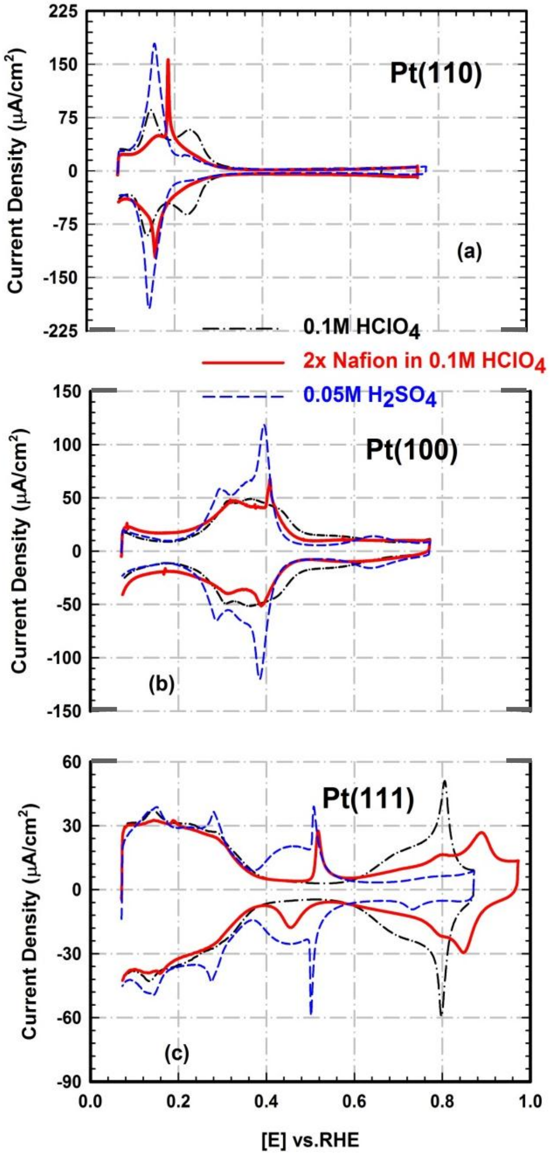
- Selective anode catalysts for the ORR and HOR are of grate importance for stability of cathode materials in Fuel Cells

Three Phase (Nafion) Interface



- **What type of interactions are possible at three phase interfaces ?**

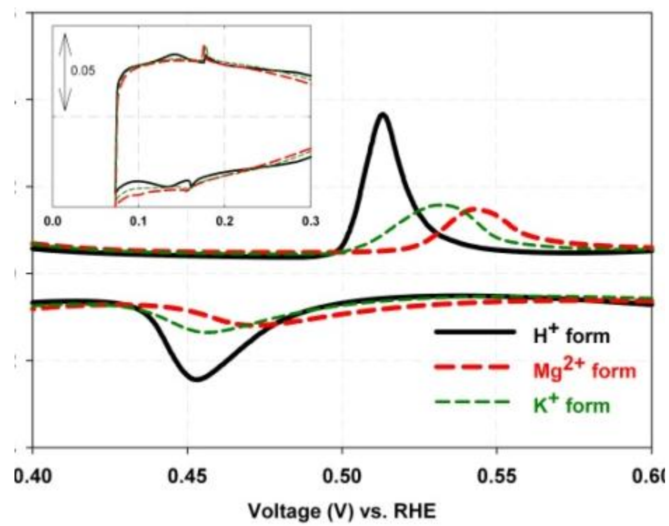
Interplay of Covalent, Electrostatic and Non-covalent Interactions



Sulfonate anions
are "specifically" adsorbed on Pt (covalent interactions)

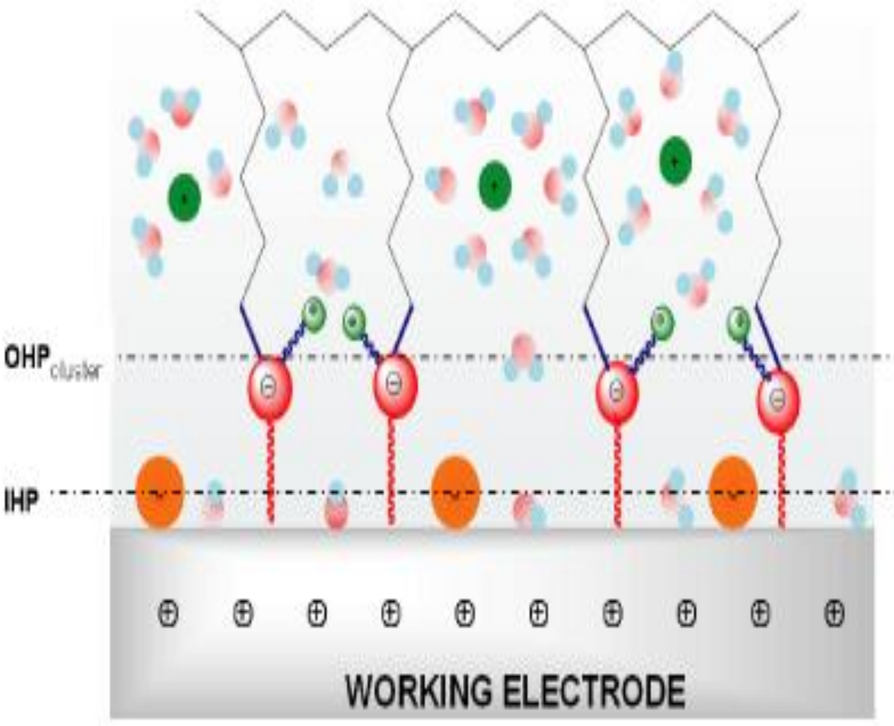
Pt-beckbone
interaction is very week (electrostatic forces)

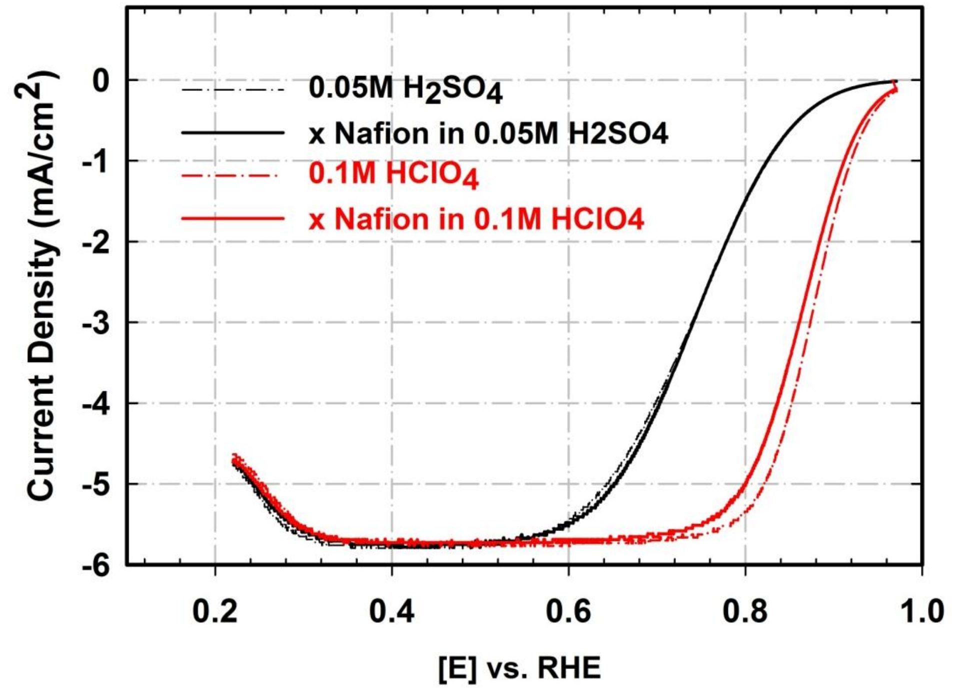
Non-covalent
cation-sulfonate interaction



J. Phys. Chem., C. (2010) .

The Spring Model





$$i = n\,F\,k\,(1-\Theta_{anions.})\,\exp(-\Delta G_i/RT)$$

J. Phys. Chem., C. (2010) .

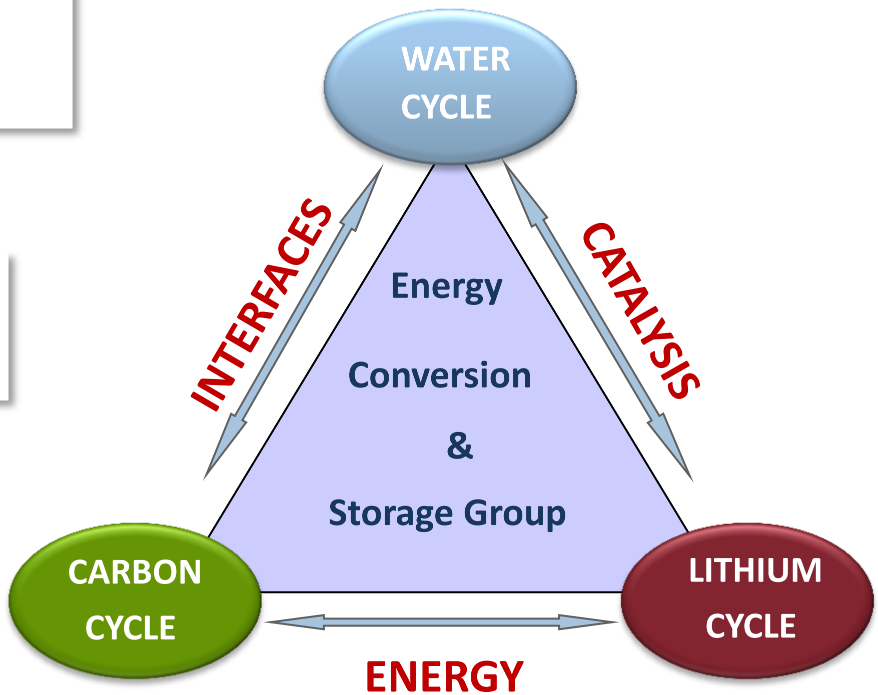
Perspectives

➢ Understanding complexity (simplicity) of electrochemical interfaces all the way down to molecular and atomic levels will pave the way to:

- Greatly improve our predictions for accelerating and directing chemical transformations

- Dramatic new energy production and storage technologies

- Enable new mitigation strategies for environmental damage



Fuel Cells

Just a Dream - or Future Reality

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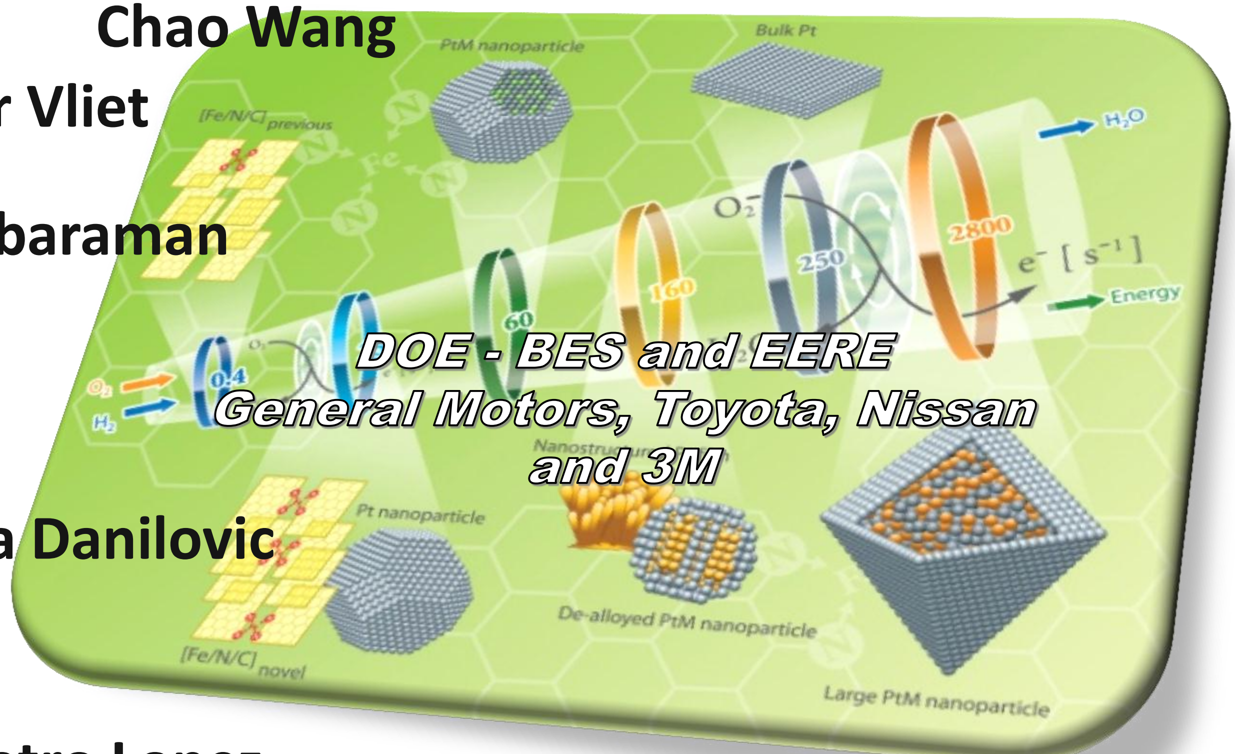

DOE - BES and EERE

General Motors, Toyota, Nissan and 3M

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