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Theoretical study of electrochemical processes on novel platinum group metal catalysts

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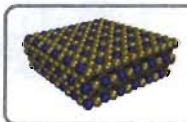
ECS, Boston, October 2011

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Overview

Introduction & Motivation



Oxygen Reduction Reaction on Pt-Ni alloys

Oxygen Reduction Reaction on Pt nanotubes

Introduction

- theory plays a crucial role in the design of ***new materials*** used in heterogeneous catalysis

- the engineering of metal catalysts with targeted performance requires a detailed understanding of the elemental processes on solid surfaces

  - **structure of materials (surfaces, nanostructures)**
  - **elucidate reaction mechanisms**
  - **models for screening of new catalysts**

Introduction

Motivation - slow kinetics of the oxygen reduction reaction (ORR) in acidic environment

$$O_2(g,1atm) + 4e^- + 4H^+(aq,1M) \rightarrow 2H_2O \quad E^0_{half\_cell} = 1.23V$$

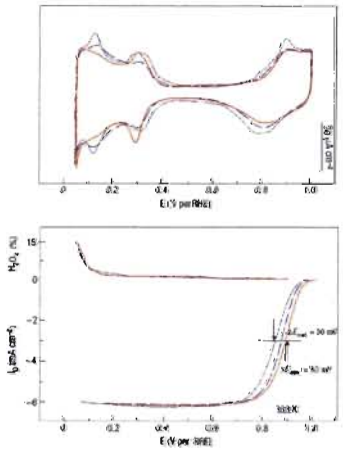


Figure: Cyclic voltammograms and polarization curve of ORR on Pt$_x$Fe

- significant cathode overpotential decreases the fuel cell electrical efficiency:

overpotential of 500-600 meV - efficiency of 45-55 % compared to the theoretical thermodynamic efficiency of 93 % at 25 ℃.

$$\Delta_r G_{cell} = -nF\Delta E_{cell}$$

Motivation

Reducing the ORR overpotential/cost:

(1) alloying platinum with platinum group metals

(2) nanostructures: nanotubes and nanoparticles

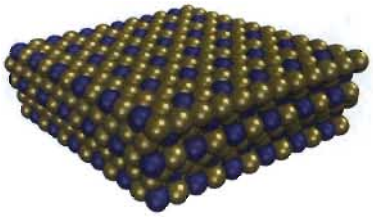


Figure: $Pt_3Ni(111)$ surface

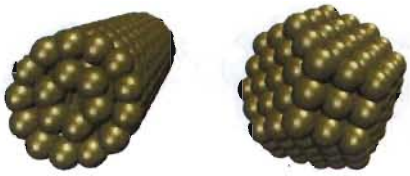
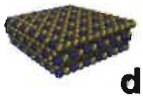


Figure: (6,6)@(13,13) MWPtNT nanotube and 2nm Pt_{201} cluster

Motivation

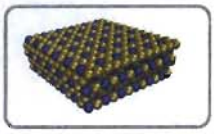


study the influence of alloying component **concentration and distribution** on stability and ORR activity in aqueous environment

study the effect of **size and structure** of a nanomaterial on the ORR activity and stability in aqueous environment

Overview

Introduction & Motivation



Oxygen Reduction Reaction on Pt-Ni alloys

Oxygen Reduction Reaction on Pt nanotubes

Methodology - study of ORR mechanism

Reactions connecting different states of the metal surface(*) in the ORR mechanism

$$\frac{1}{2}O_2 + * \rightarrow O*$$
$$O* + e^- + H^+ \rightarrow OH*$$
$$OH* + e^- + H^+ \rightarrow * + H_2O(l)$$

relative to the standard hydrogen electrode

$e^- + H^+(aq) = 1/2H_2(g)$

Free gibbs energy of the reactions (Norskov et al. J. Phys. Chem. B 2006, 110, 21833)

$$\Delta G_{w,water} = \Delta E_{w,water} + \Delta ZPE + T\Delta S$$

$$\Delta G(U, pH, T = 298K) = \Delta G_{w,water} \underbrace{- eU}_{\text{bias effect}} + \underbrace{kT \ln(10) pH}_{\text{correction for the free energy of H+}}$$

Models of different states of the metal surface

water layer 1	water layer 2	OH + water	O + water	H + water
2/3 coverage	2/3 coverage	1/3 coverage	1/3 coverage	1/3 coverage

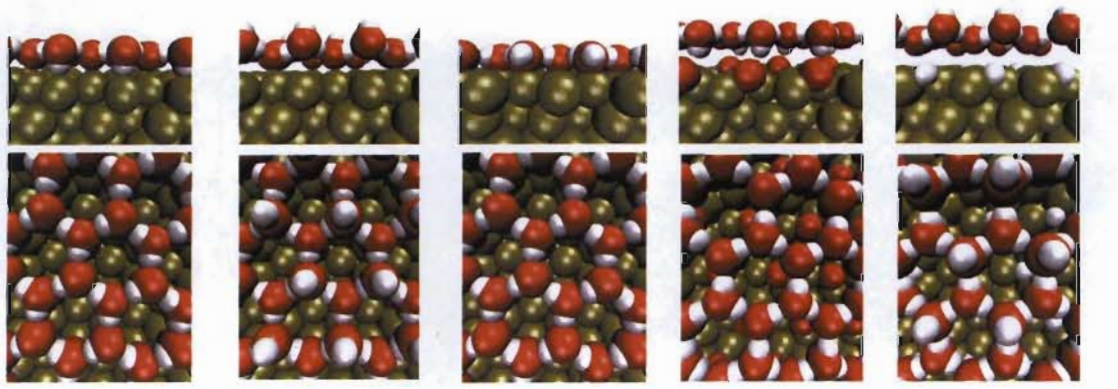
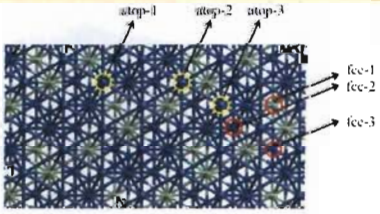


Figure: Pt(111) surface with different ORR intermediates + water environment

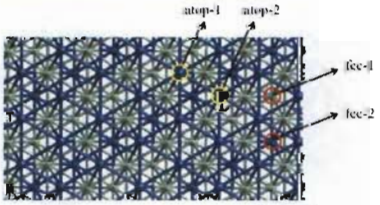
Models of the structure of alloys – Pt/Ni atom distribution

$Pt_3Ni(111)$, seg



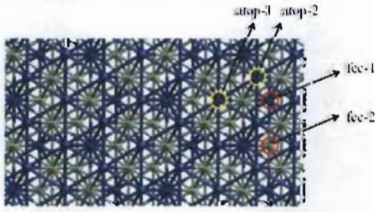
50 % Ni in second layer

PtNi(111), seg



100 % Ni in second layer

$PtNi_3(111)$,seg



75 % Ni in second layer

Figure: Structures od $Pt_3Ni(111)$, PtNi(111) and $PtNi_3(111)$ surfaces with a Pt monolayer on surface

Stability of the surfaces

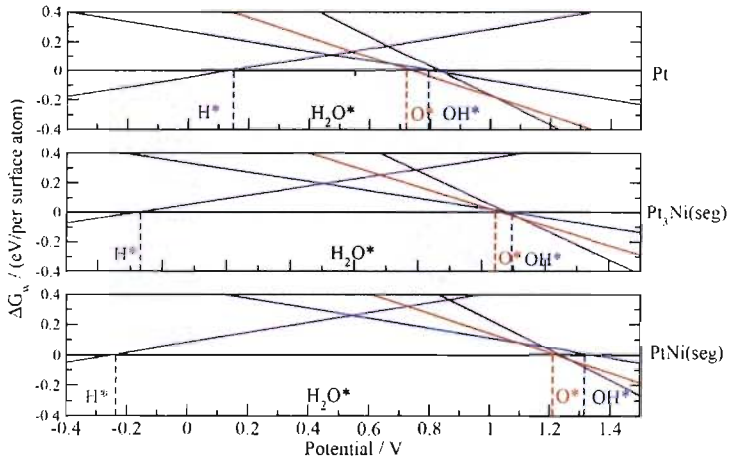
Estimate of the shift in *the electrochemical dissolution potential*

Table: surface cohesive energy and the estimate of the shift in the electrochemical dissolution potential relative to Pt(111)

reaction	M_N(surface) → M_{N-1} + M	ΔE/eV	ΔU_{corr}/V	$\Delta U_{corr}{}^{b}$/V
Pt(111)		5.79	0.00	0.00
$Pt_3Ni(111)$	site 1	6.11		
	site 2	6.23		
	site 3	6.04	+0.13	+0.10
PtNi(111)	site 1	6.41		
	site 2	6.38	+0.30	+0.30
$PtNi_3(111)$	site 1	5.69		
	site 2	5.58	−0.11	−0.23
Ni(111)		5.26	−0.27	−0.30

$PtNi_3$ has worse corrosive properties then Pt

Phase diagrams



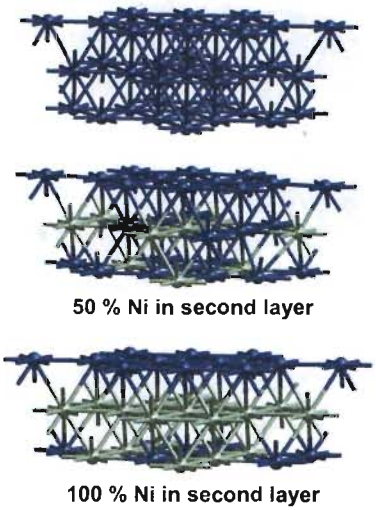


Figure: Phase diagram showing the free energy as a function of the potential for different surface structures at pH=0

Surface Pourbaix diagrams

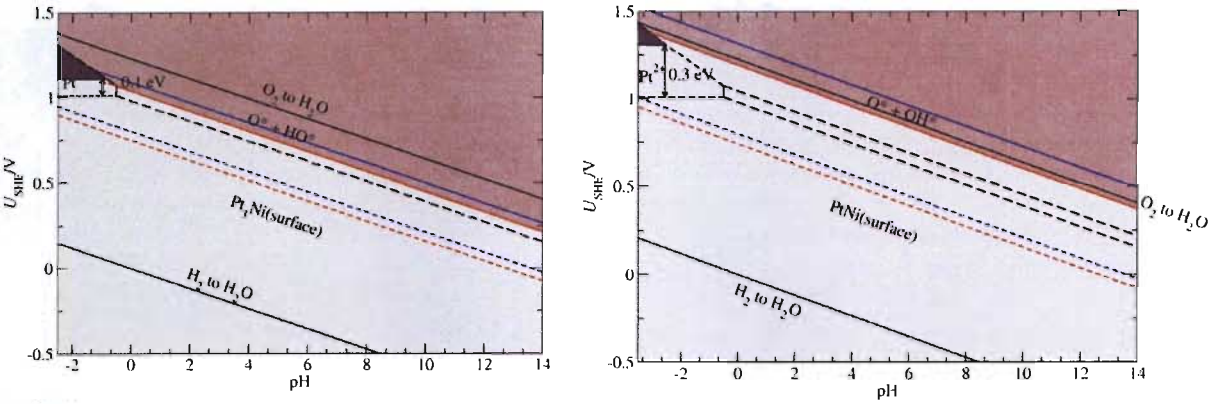


Figure: Calculated surface Pourbaix diagrams for a) Pt_3Ni and b) PtNi compared to a bulk Pourbaix diagrams (black dashed lines)

Pt_3Ni, PtNi and $PtNi_3$ bind O and OH less stronger then Pt

This is reflected on the ORR mechanism!

Dissociative oxygen reduction reaction (ORR) mechanism

$$\frac{1}{2}O_2 + * \rightarrow O* \quad (1)$$

$$O* + e^- + H^+ \rightarrow OH* \quad (2)$$

$$OH* + e^- + H^+ \rightarrow * + H_2O(l) \quad (3)$$

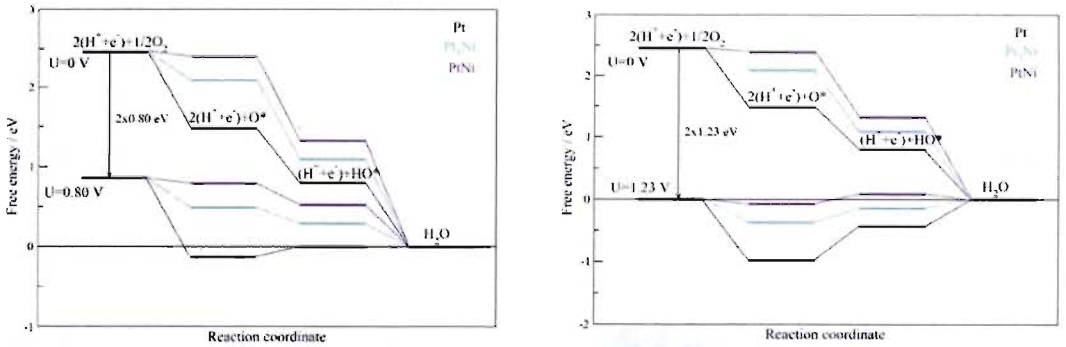
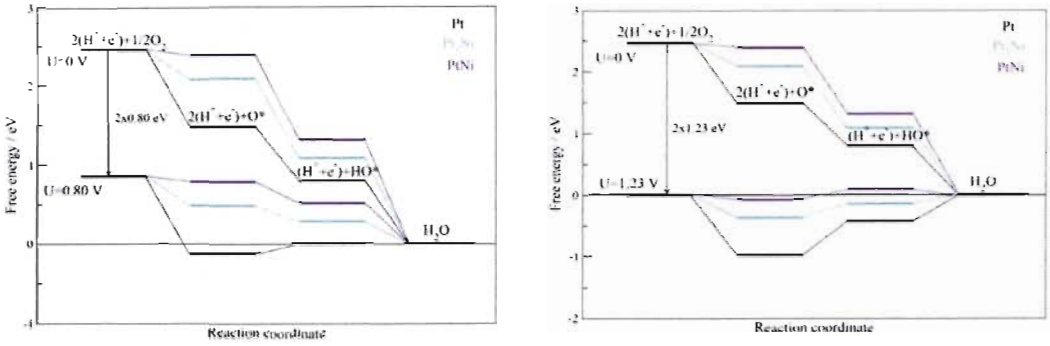


Figure: Free-energy diagrams for ORR over Pt(111) surfaces with different Ni concentration in the second layer, for cell potentials U=0.80 V and U=1.23 V

Dissociative oxygen reduction reaction (ORR) mechanism

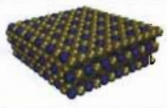


The ORR overpotential was found to decrease :

$$Pt < Pt_3Ni < PtNi_3 < PtNi$$

Overview

Introduction & Motivation



Oxygen Reduction Reaction on Pt-Ni alloys

Oxygen Reduction Reaction on Pt nanotubes

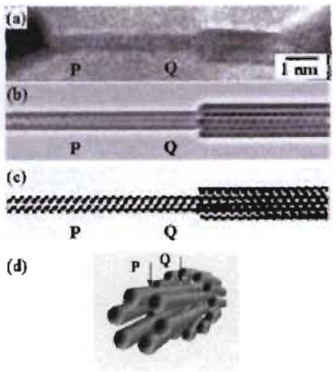
Pt nanotubes

Oxygen-Reduction Catalysts

DOI: 10.1002/anie.200700689

Supportless Pt and PtPd Nanotubes as Electrocatalysts for Oxygen-Reduction Reactions**

*Zhongwei Chen, Mahesh Waje, Wenzhen Li, and Yushan Yan**



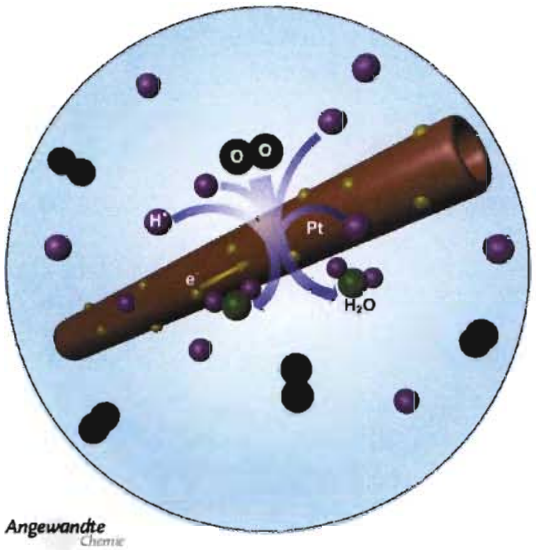
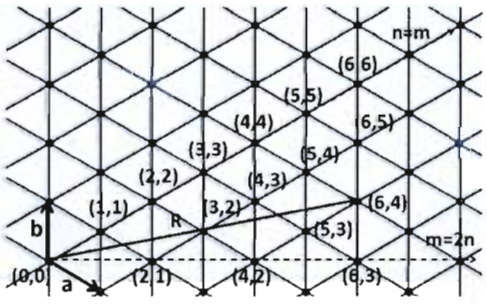


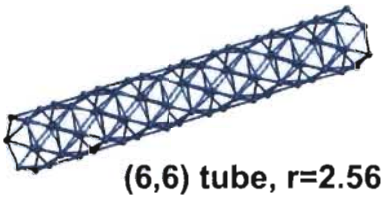
Figure: HR-TEM image of platinum nanotube
Y. Oshima et. al, Phys. Rev. B, 65, 121401 (2002)

Pt nanotubes

PtNT: Rolling-up Pt(111) sheet to form a tube



roll-up



(6,6) tube, r=2.56 Å

(6,4) tube, r=2.28 Å

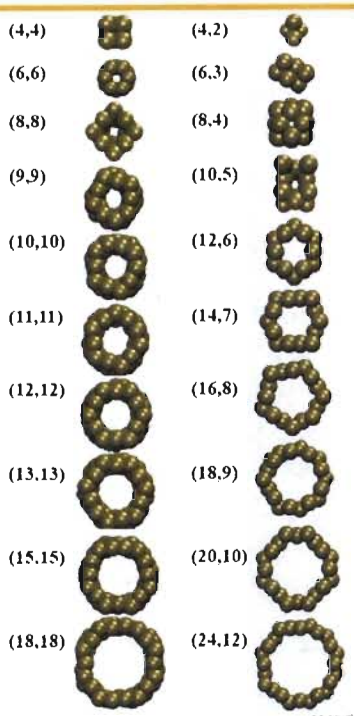
(6,3) tube, r=2.23 Å

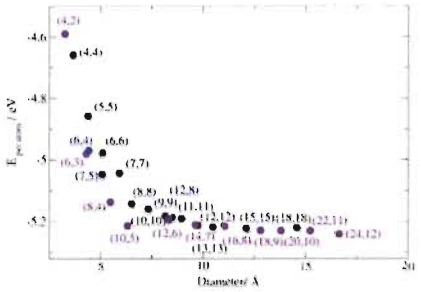
a_c = 3.70- 3.85 Å
R is the rolling up vector

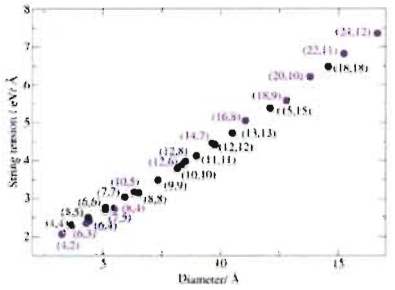
$$R = na + mb$$

$$r = \frac{\sqrt{2}a_c}{4\pi}\sqrt{n^2 + m^2 - nm}$$

Pt nanotubes







(*n*,*n*) Pt nanotubes + oxygen/ hydroxyl

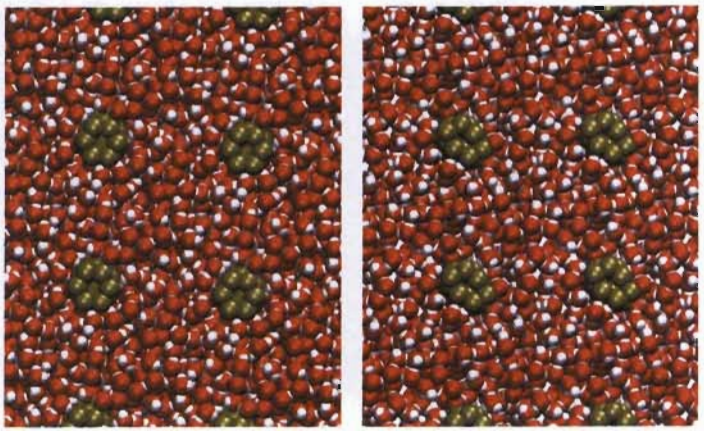
Table. Adsorption energies in eV and a shift in equilibrium adsorption potential in V for oxygen/hydroxyl for different nanotubes and coverages

	Pt(111)	(6,6)SWNT		(13,13)SWNT		(6,6)@(13,13)DWNT	
		E_{ad}	ΔU_f	E_{ad}	ΔU_f	E_{ad}	ΔU_f
1/4	-4.42	-4.72	-0.15	-4.14	+0.14	-4.05	+0.19
1/3	-4.25	-4.41	-0.08	-3.90	+0.17	-4.21	+0.02
1/2	-4.07	-4.46	-0.20	-3.92	+0.08	-4.06	+0.05
2/3	-3.79	-4.34	-0.28	-3.75	+0.02	-4.00	-0.11

	Pt(111)	(6,6)SWNT		(13,13)SWNT		(6,6)@(13,13)DWNT	
		E_{ad}	ΔU_f	E_{ad}	ΔU_f	E_{ad}	ΔU_f
1/4	-2.88	-3.54	-0.66	-2.83	+0.03	-3.07	-0.19
1/3	-2.92	-3.54	-0.62	-2.87	+0.03	-3.13	-0.21
1/2	-3.09	-3.52	-0.43	-2.85	+0.24	-3.20	-0.11
2/3	-3.12	-3.24	-0.12	-2.77	+0.35	-3.14	-0.02

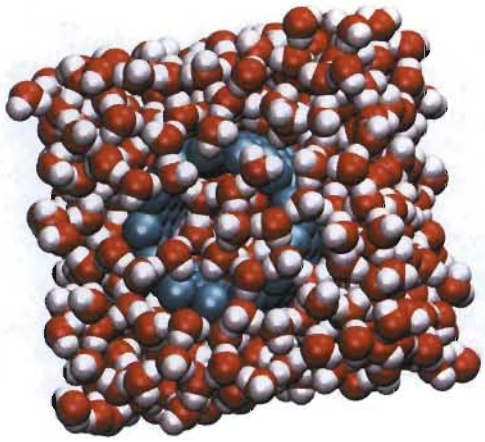
Pt nanotubes – ab initio MD simulations in water

Aim (1) characterize change of atomic and electronic structure on solvation
(2) structure of water around curved surfaces - develop models for water-surface interface



~700 atom cell, 1300 MD steps in 24h, 480 processors, average ~1min/step

Pt nanotubes – ab initio MD simulations in water



20 Å length tube, d=10.9 Å in a 30 Å length simulation box

bigger tubes accommodate water – increased stability?

Conclusions (1)

The ORR overpotential was found to decrease :

$$Pt < Pt_3Ni < PtNi_3 < PtNi$$

- Decrease in the d-band center position in Pt,Ni alloys
→ decrease in adsorption energy of oxygen and hydroxyl
→ increase in the equilibrium adsorption potentials
→ decrease in the ORR overpotential

- shifts in the electrochemical dissolution potentials relative to Pt indicate that PtNi is the least susceptible to corrosion

I. Matanovic et al. J. Phys. Chem. C, 115, 10640–10650 (2011)

Conclusions (2)

- (6,6) Pt nanotube binds oxygen more strongly then Pt(111)
- (13,13) Pt nanotube binds oxygen comparable or weaker then Pt(111)

- (6,6) Pt nanotube unstable in water – collapses to a non-hollow structure

Acknowledgements

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