Average particle size, size distribution and electrocatalytic activity of bimetallic PdxPt1-x nanoparticles

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Average particle size, size distribution and electrocatalytic activity of bimetallic Pd_xPt_{1-x} nanoparticles

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Outline

- Introduction – Direct Formic Acid Fuel Cells
  - mechanism of formic acid oxidation

- Synthesis of Pd_xPt_{1-x} nanoparticles supported on carbon

- Average particle size and size distribution of Pd_xPt_{1-x} nanoparticles from X-ray diffraction patterns
  - New approach to the analysis of XRD patterns through Debye's formula

- Formic acid electrooxidation on Pd_xPt_{1-x}

- Conclusions

Direct Formic Acid Fuel Cells (DFAFC's)

Direct Formic Acid Fuel Cell is convinient energy source for micropower energy devices

Advantages of Formic acid as fuel:

- is non-explosive liquid
- shows negligible fuel crossover and cathode poisoning
- is good electrolyte demonstrating less contact resistance
- has high theoretical open circuit potential (1.43V)
- DFAFC's use less water, reducing the need to store or recycle water

Dual path mechanism for electrooxidation of formic acid:

Dehydration mechanism

$HCOOH + Pt \rightarrow Pt\text{-}CO + H_2O$ (1)

$H_2O + Pt \rightarrow Pt\text{-}OH + H^+ + e^-$ (2)

$Pt\text{-}CO + Pt\text{-}OH \rightarrow 2Pt + CO_2 + H^+ + e^-$ (3)

Dehydrogenation mechanism

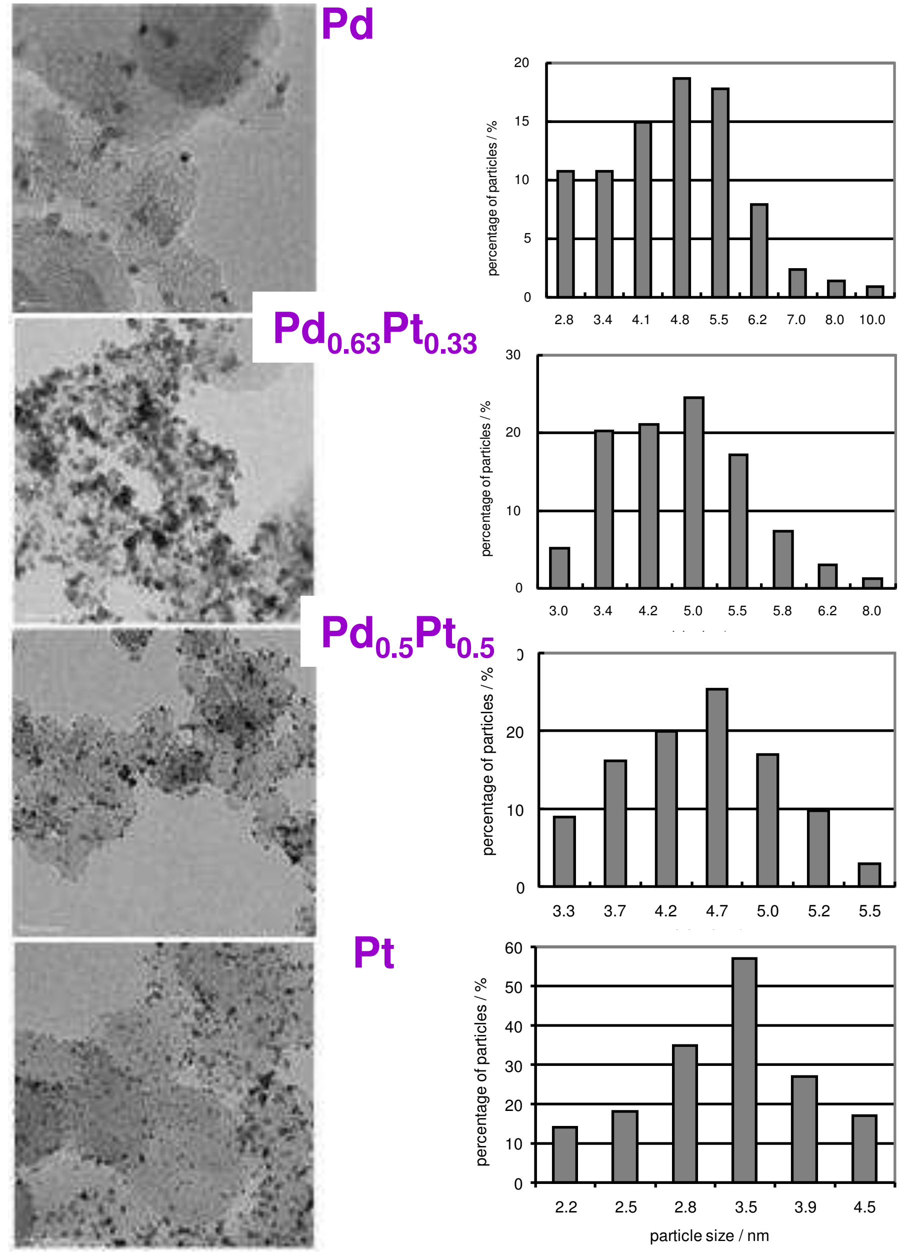
$HCOOH + Pt \rightarrow X \rightarrow CO_2 + Pt + 2H+ + 2e^-$ (4)

Synthesis of Pd_xPt_{1-x} carbon supported nanoparticles

- Nanoparticle synthesis in ethylene glycol + PVP stabilizer + carbon Vulcan XC-72 support

- Resulting particles:
  Pd,
  $Pd_{0.67}Pt_{0.33}$,
  $Pd_{0.5}Pt_{0.5}$,
  $Pd_{0.33}Pt_{0.67}$
  Pt

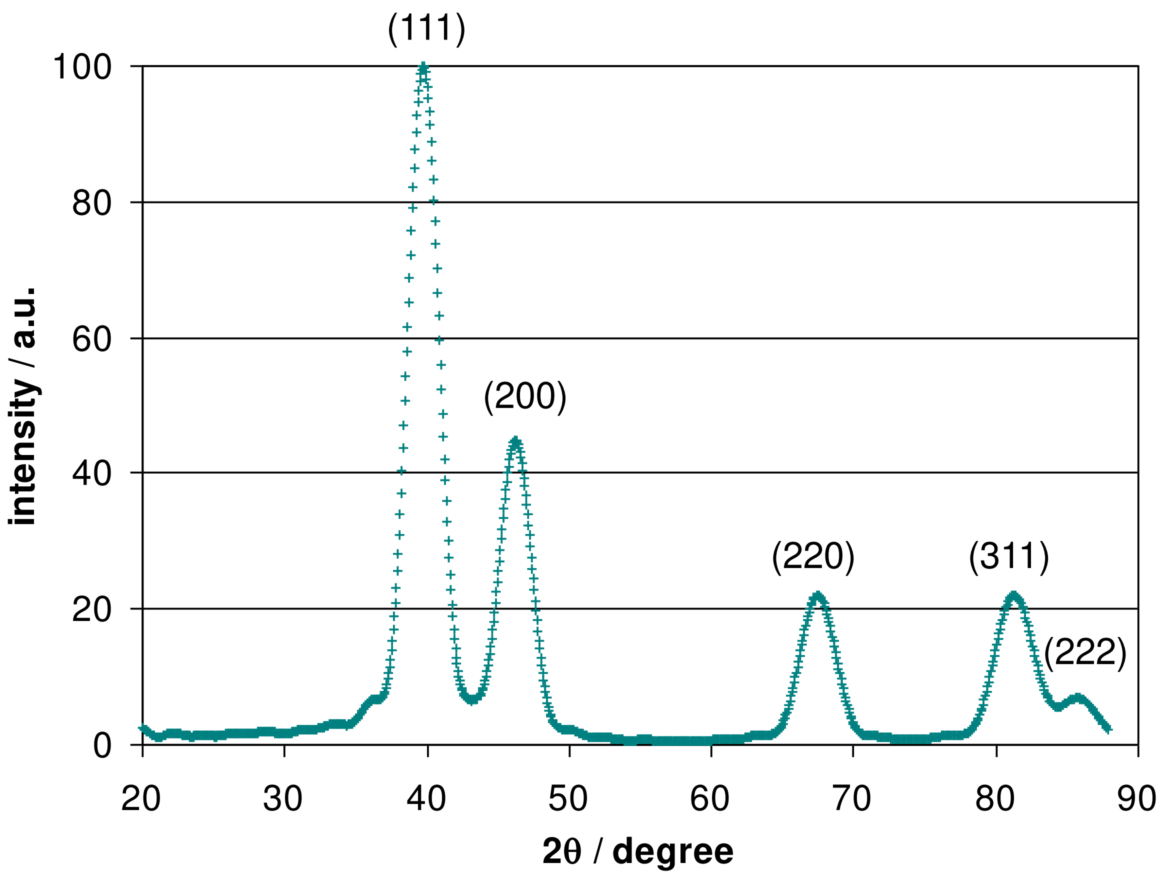
- 20 wt% of metal loading on carbon



TEM and histograms of carbon supported Pd_xPt_{1-x}

Size of Pt nanoparticles from XRD patterns

XRD pattern of Pt nanoparticles of 4 nm size.



Particle size is found from either 111/200 or 220 Pt peaks using full-width at half-maximum (FWHM) in combination with the well-known Scherrer formula:

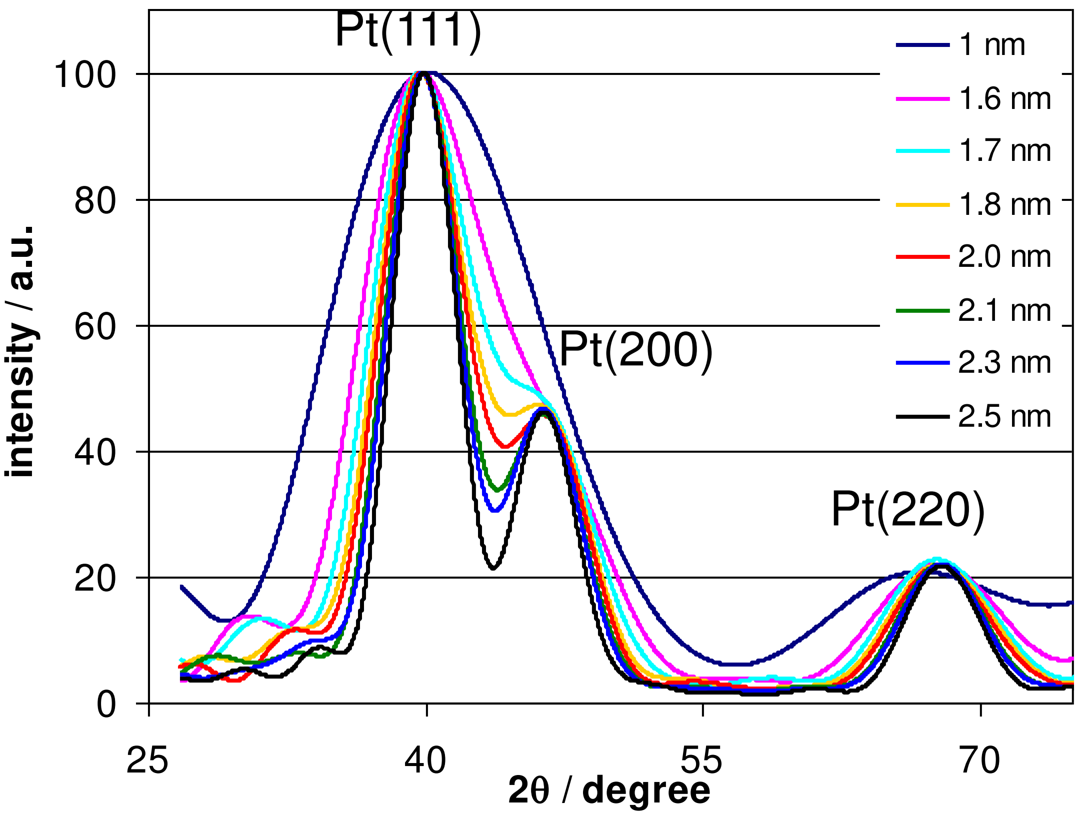
$$D = \frac{K\lambda}{FWHM \ \cos\theta}$$

where λ is the wavelength and K is a numerical constant with value close to 0.88.

Both Bulk Pt and Pd have face-centered cubic structures

Inadequacy of Scherrer formula for estimation of nanoparticles sizes

Simulated XRD patterns of Pt nano-particles using *Materials Toolkit Program [1]*



For particles smaller than 6 nm diffraction effects shift Bragg peaks and reflection 111 and 200 overlaps

Overlapping powder peaks cannot be deconvoluted in a regular way using Scherer formula

Our approach is analysis of XRD patterns with Debye's formula for scattering by randomly oriented molecules [2, 3]

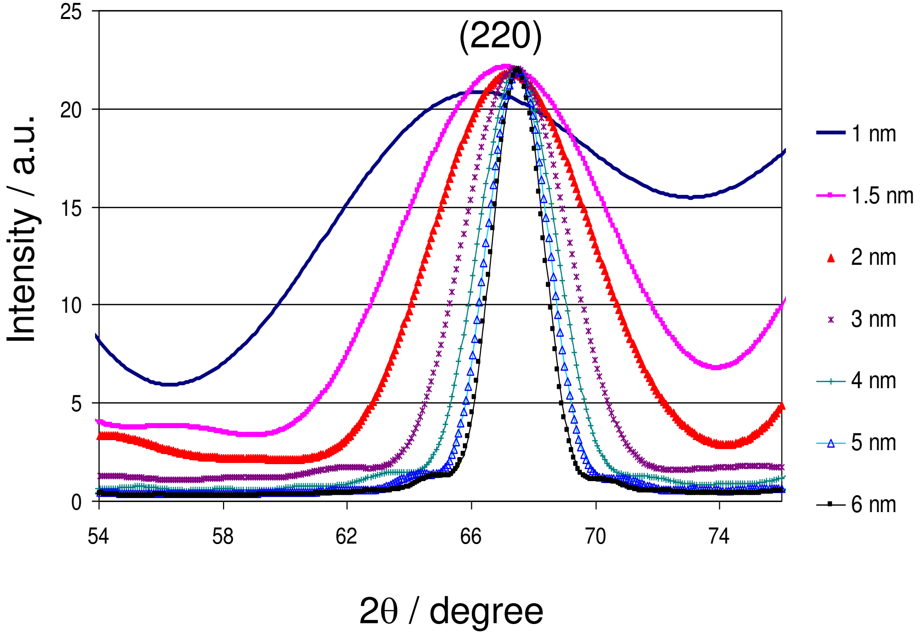
Y. Le Page, J.R. Rodgers, *J. Appl. Crystallogr*. 38, (2005) 697

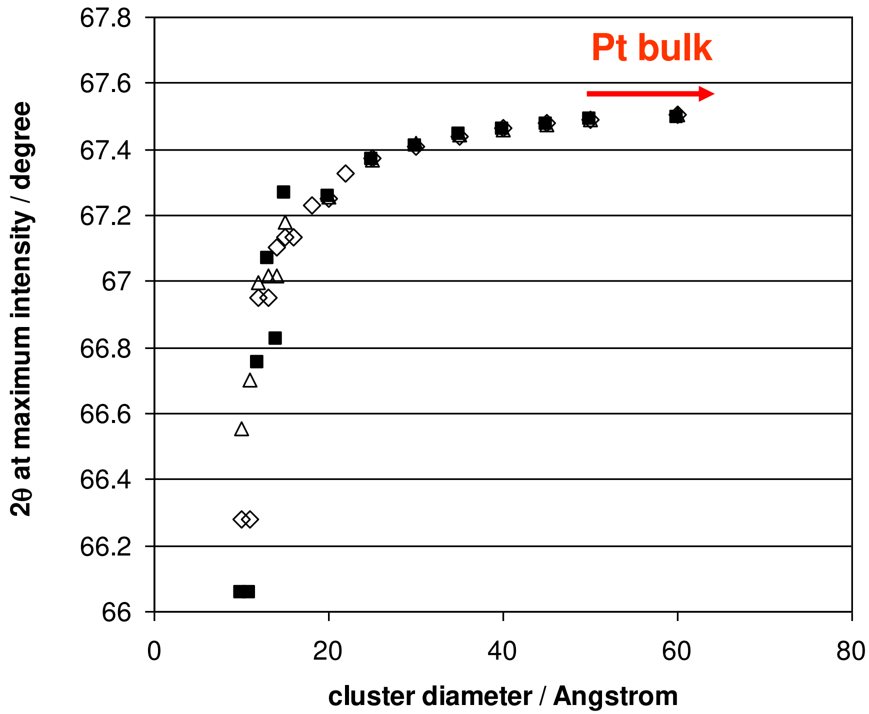
P. Debye, *Ann Phys. (Leipzig)* 46, (1915) 809.

E.A. Baranova, Y. Le Page, D. Ilin, C. Bock, B. MacDougall, P.J.H. Mercier. *J. Alloys and Comp*. 471 (2009) 387

Analysis of (220) *fcc* peak using Debye's formula

- Carbon reflection around 25 and 45 °2θ overlaps with main Pt peaks (111) and (200)
- Analysis of (220) *fcc* peak using Debye's formula

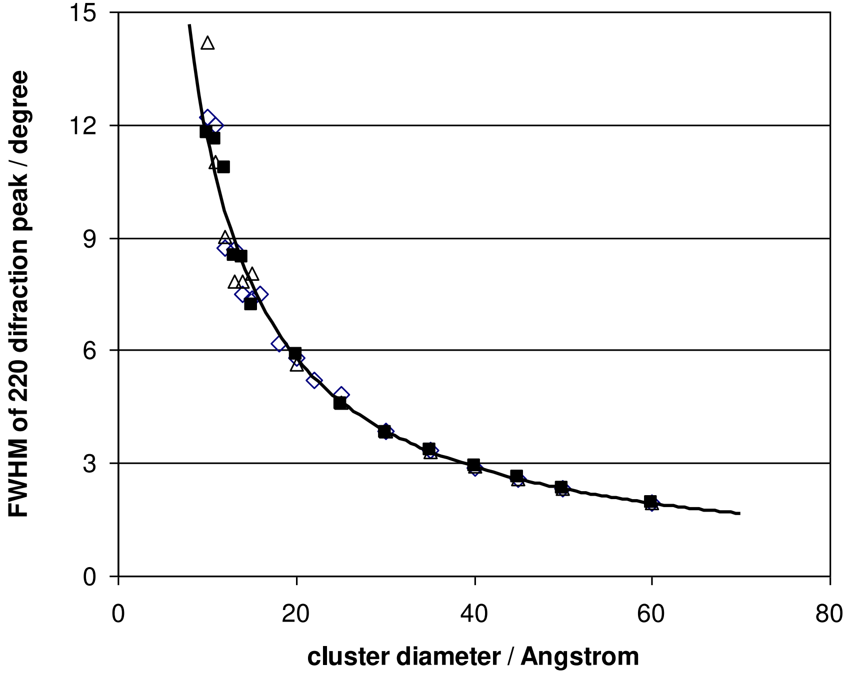




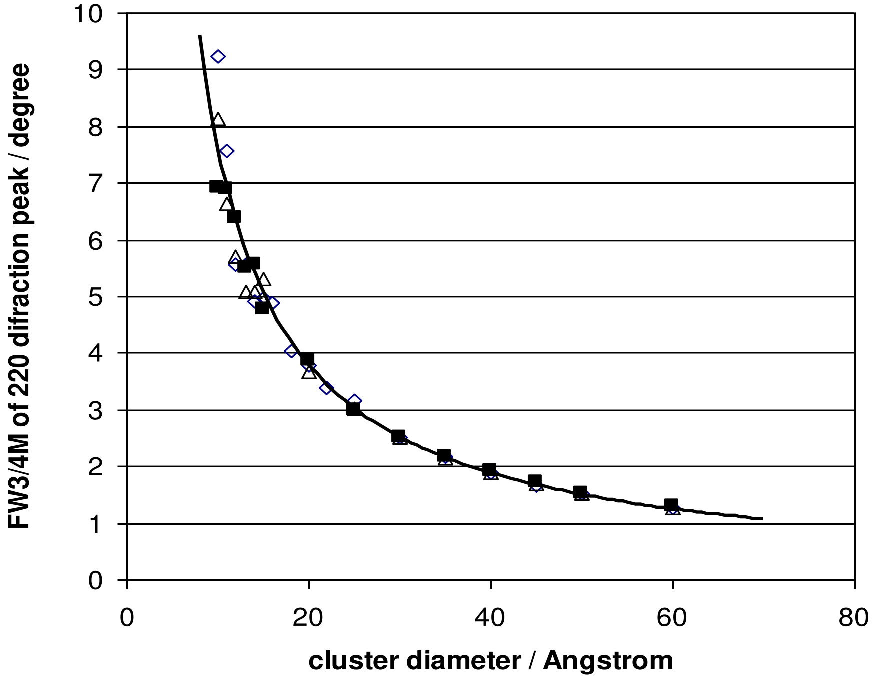
Cu Kα 2θ angle at maximum peak intensity for Pt nanoparticles vs. nanoparticle diameter in Angstroms.

E.A. Baranova, P.H.J. Mercier, Y. Le Page, B. Patarachao. J. Nanoscie. and Nanotech. (2009)

Calculated FWHM and FW3/4M for particle size estimation



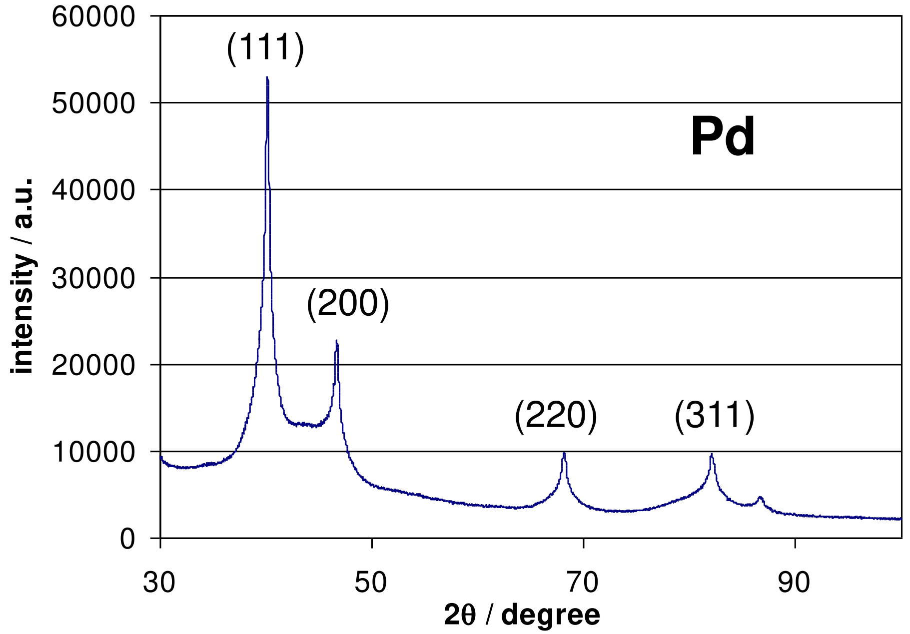
Cu Kα full-width at half-maximum for Pt nanoparticles vs. nanoparticle diameter

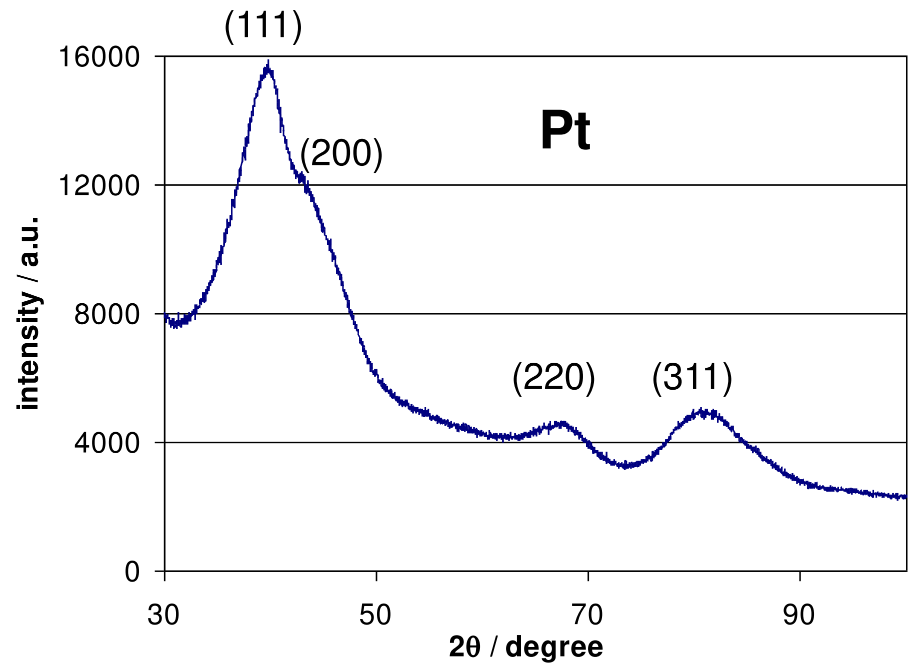


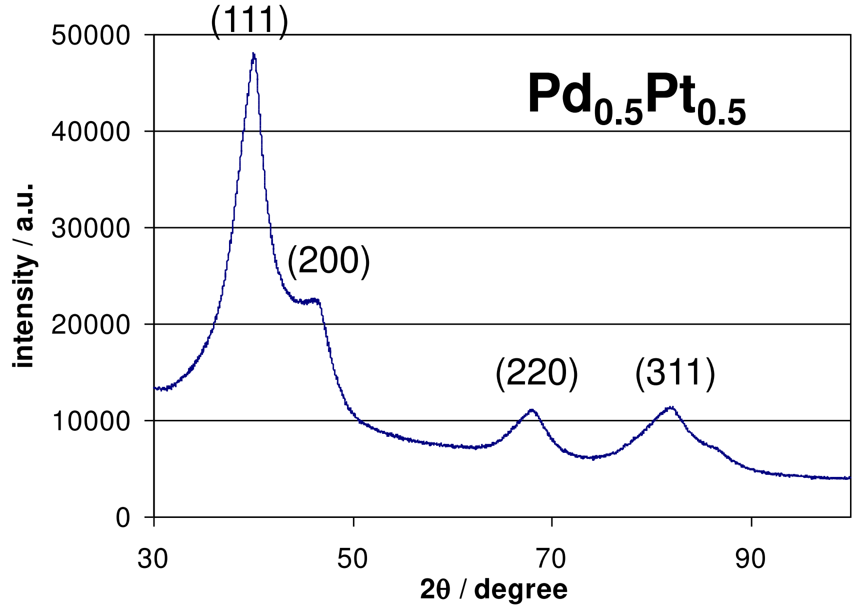
Cu Kα full-width at 3/4 maximum for Pt nanoparticles vs. nanoparticle diameter

Symbols correspond to calculations: at Pt nanoparticle center, at tetrahedral sites Δ at octahedral sites.

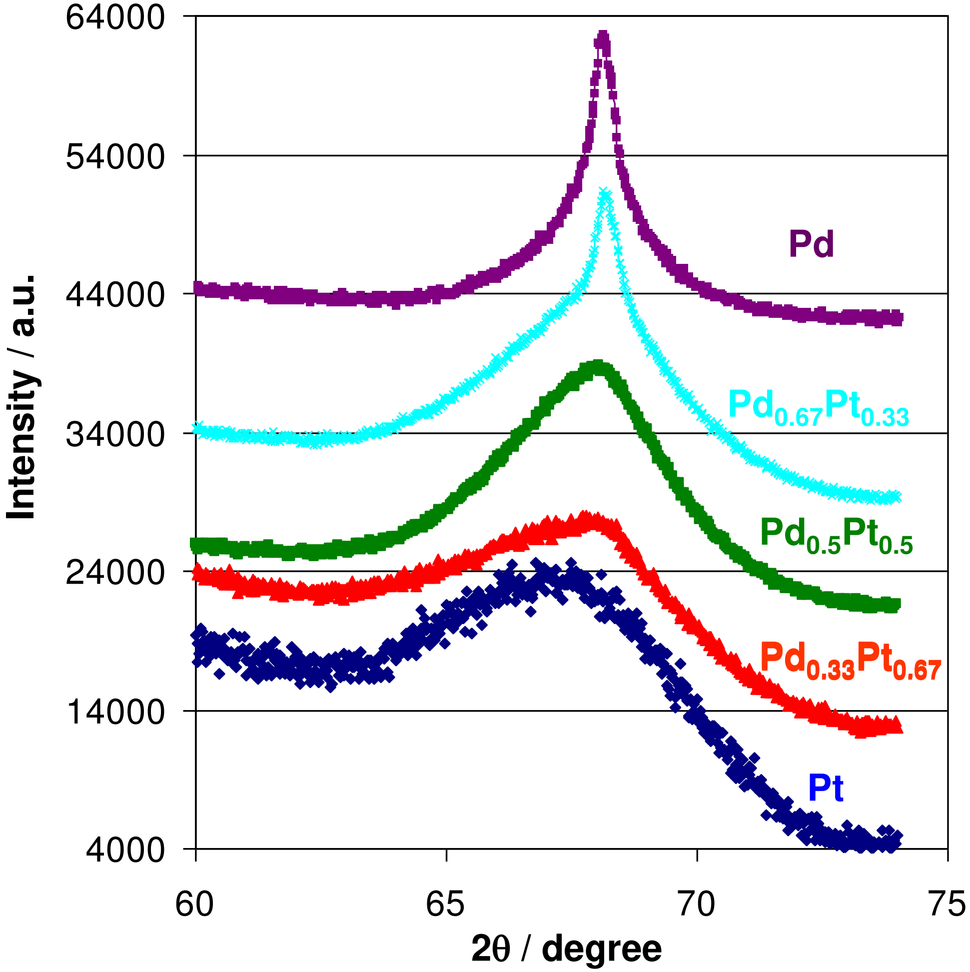
Experimental XRD patterns







Experimental XRD patterns for carbon supported Pd_xPt_{1-x} nanoparticles



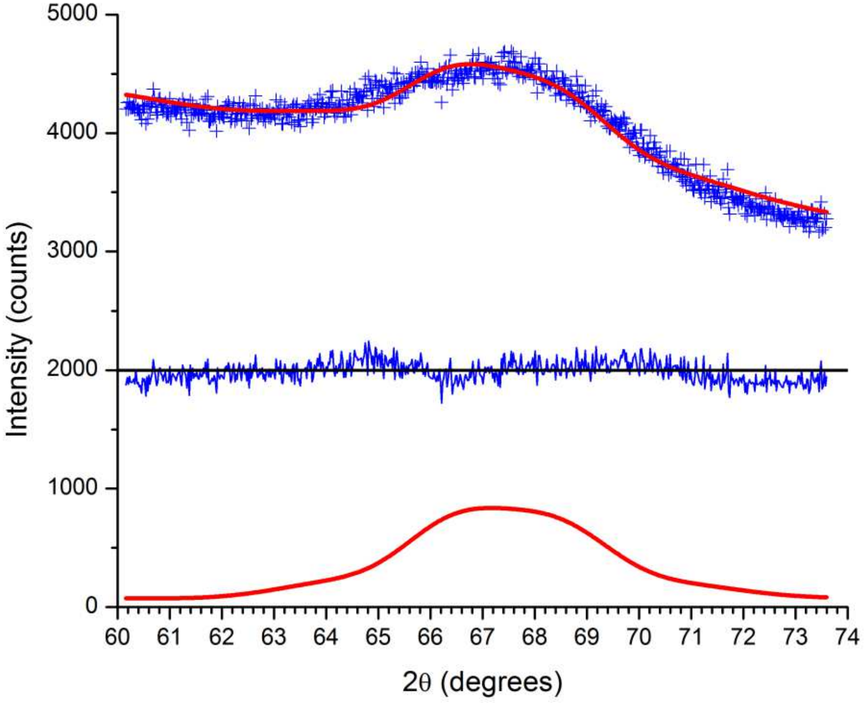
Precise Bragg angles are derived from a third-order polynomial fit to the top of fcc 220 peak

Particle diameters calculated from FWHM and FW3/4M of fcc 220 peak and using Debye formula

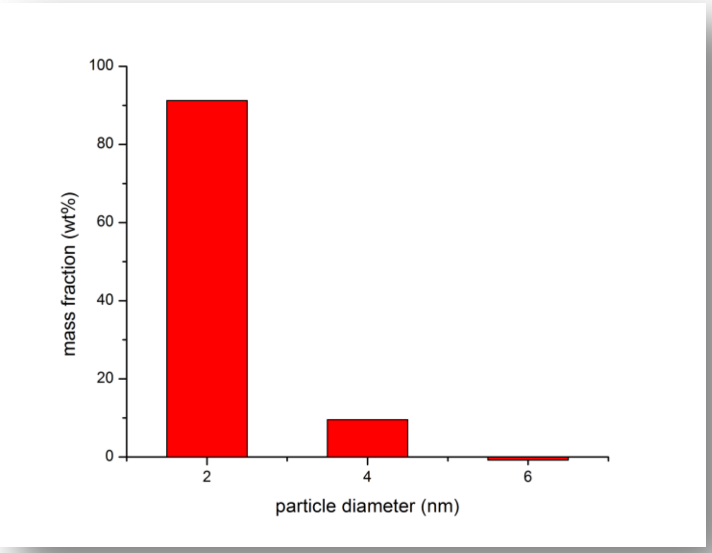
Experimental profiles are affected by the non-uniformity of the particle sizes

Least-squares analysis of XRD powder patterns for particle size distribution

Particle size distribution for Pt/C nanoparticles



Histograms of particle sizes from XRD

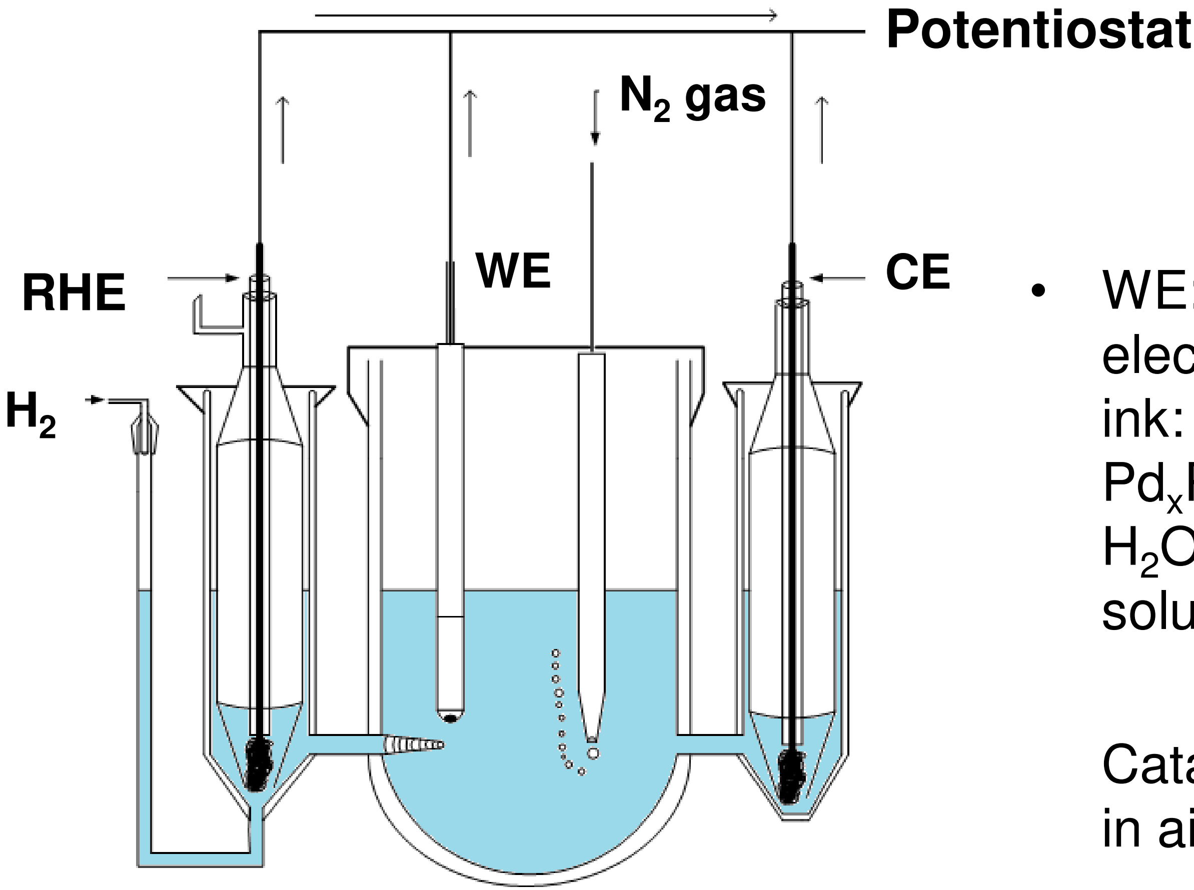


Summary of experimental XRD and TEM results of Pd_xPt_{1-x} nanoparticles

Nanoparticle	Average size from XRD / nm	Average size from TEM / nm	$2\theta_{max}$ of (220)/ ° nanoparticles	$2\theta_{max}$ of (220) bulk metals	Particle structure
Pd/C	10	4.8 +agglomerates	68.11	68.1	Pd
$Pd_{0.67}Pt_{0.33}$/C	7	5.0 +agglomerates	68.10		Pd + Pt
$Pd_{0.5}Pt_{0.5}$/C	4	4.7	68.02		PdPt alloy
$Pd_{0.33}Pt_{0.67}$/C	3.8	-	67.85		PdPt alloy
Pt/C	3.0	3.5	67.04	67.6	Pt

Pd-rich particles display a broad range of crystallite sizes, while Pt-rich particles have more homogeneous size distributions, with dominant sizes around 3-4 nm.

Electrochemistry



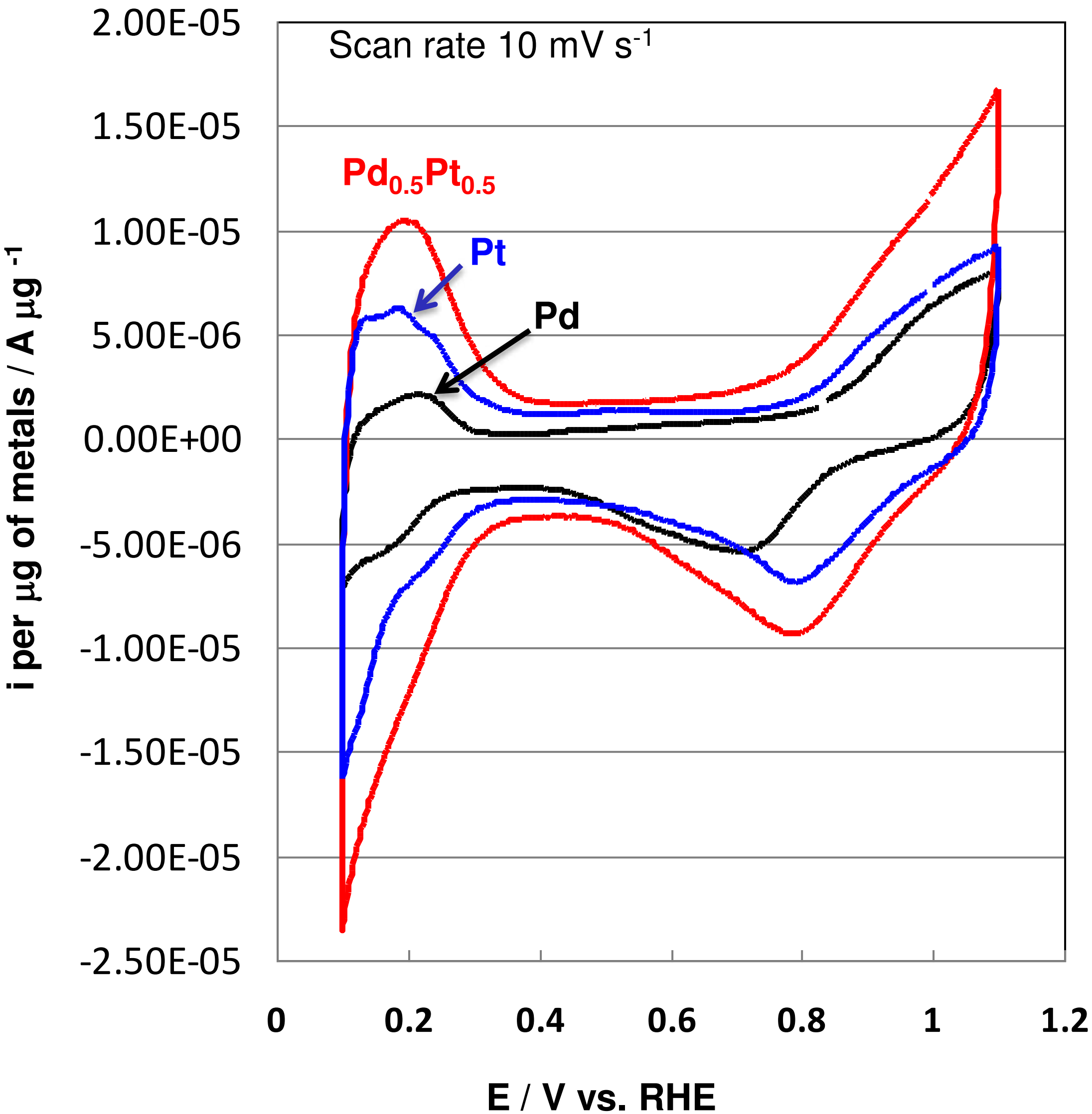
Three-compartment electrochemical cell

- WE: Glassy carbon disc electrode + 2.5 μL catalyst ink: 13 mg of the 20wt% Pd_xPt_{1-x} on carbon in 1 mL of H_2O and 300 mL of the Nafion solution.

  Catalyst layer was then dried in air at 80 ^oC for 30 min.

- CE is Pt gauze
- RE is RHE

Cyclic voltammetry in 0.5 M H_2SO_4

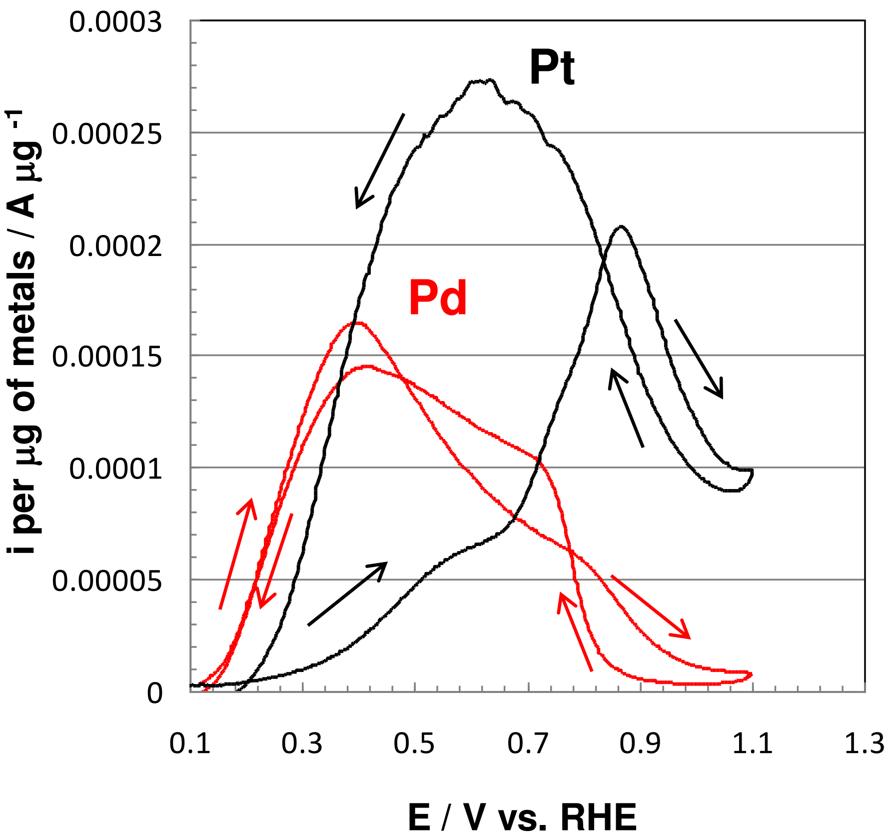


Pd shows the smallest voltammetric charge and largest particles

Electrochemical active surface are increases with decreasing particle size

Formic acid electrooxidation

Cyclic voltammetry of Pd and Pt in 0.01M HCOOH + 0.01M H_2SO_4

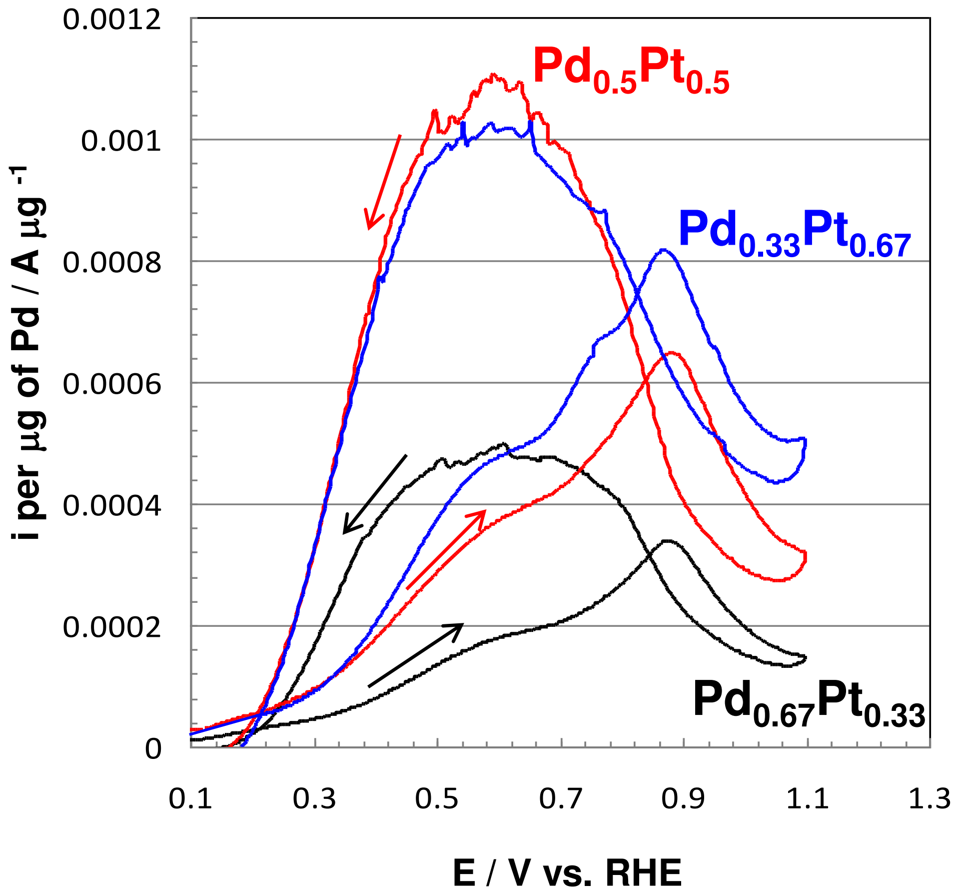


Scan rate 10 mV s^{-1}

- No clear inhibition of HCOOH oxidation can be observed on Pd
- Onset potential is much lower on Pd nanoparticles and current maximum occurs at 0.3V
- CO poisoning is not observed on Pd or this process is very slow
- Oxidation of HCOOH proceeds through formation and oxidation of CO_{ads} on Pt nanoparticles

Formic acid electrooxidation

Cyclic voltammetry in 0.01M HCOOH + 0.01M H_2SO_4

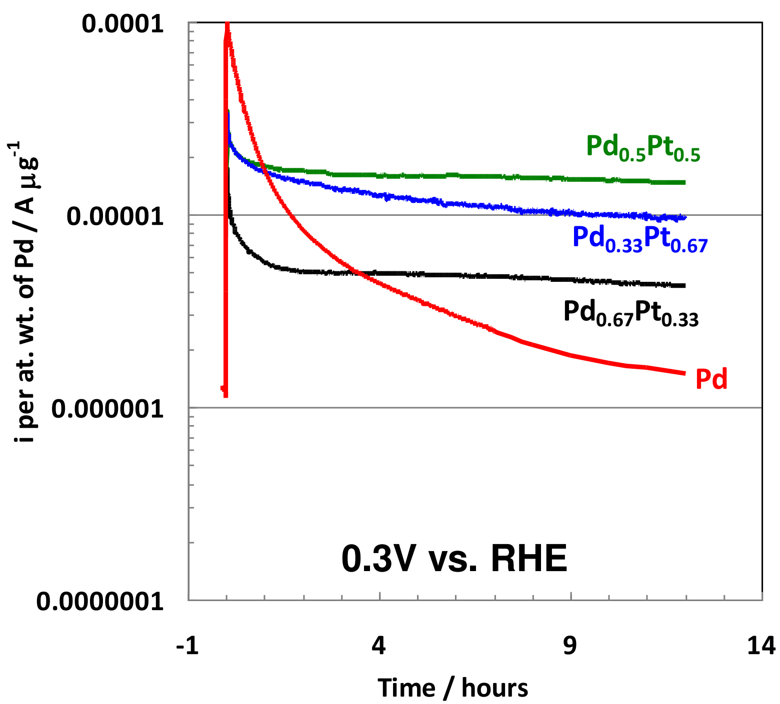


Scan rate 10 mV s^{-1}

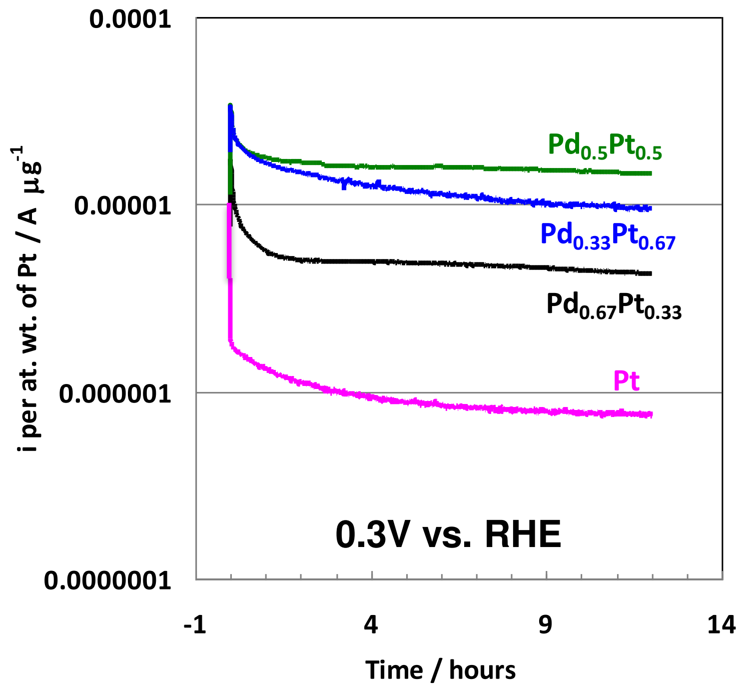
Oxidation of formic acid on Pd_xPt_{1-x} bimetallic particles occures through the formation of inactive intermediates such as CO_{ads} similar to Pt

Chronoamperograms in 0.01M HCOOH + 0.01M H_2SO_4

Current densities per atomic weight of Pd



Current densities per atomic weight of Pt



Pd shows very high initial activity, however its stability decreases rapidly without reaching a steady-state even after 12 hours

$Pd_{0.5}Pt_{0.5}$ shows the best electrocatalytic activity per mass of Pd or Pt and good stability among the investigated electrocatalysts

Conclusions

- Pd_xPt_{1-x} nanoparticles supported on carbon were synthesized using modified polyol method
- We proposed a novel approach to find particle size and size distributions of carbon supported nanoparticles
- The analysis method is based on Debye’s formula for scattering by molecules and it was applied for the analysis of carbon supported nanoparticles using Pt (220) diffraction peak
- Least-squares analysis of the XRD powder profile of the 220 reflection based on Debye's formula also allows calculation of particle-size distributions

Conclusions

- Pt-rich nanoparticles show homogeneouse size distrubutions with dominant size around 3-4 nm

- Pd has the highest initial catalytic activity due to the oxidation of formic acid through the direct dehydrogenation pass way mechanism, however low stability

- $Pd_{0.5}Pt_{0.5}$ shows the best catalytic activity and stability among the investigated electrocatalysts. Narrow size distribution and alloyed structure may be responsible for the observed improvement

Acknowledgement

NSERC Discovery Grant

Centre for Catalysis Research and Innovation

Dr. Dashan Wang for TEM measurements
Bussaraporn Patarachao for XRD measurments
Neil Miles for electrochemical measurements