

Preparation of Bimetallic Materials using Atomic Layer Electroless Deposition

SAND2017-4614C

Sita Gurung^a, April A. Munro^a, David B. Robinson^b, Joshua D. Sugar^b and Patrick J Cappillino^a



a. Department of Biochemistry and Chemistry, University of Massachusetts Dartmouth, MA

b. Energy Nanomaterials Department, Sandia National Laboratories, Livermore, CA



Motivation and Significance

Multimetallic materials often exhibit enhanced functional properties compared to their parent metals alone. They have a wide range of applications in areas such as hydrogen storage, catalysis, and electrocatalysis. Examples include a dramatic increase in the oxygen reduction activity of Pt catalysts in the presence of subsurface alloy layers¹, surface-poisoning resistance in formic acid oxidation catalysts², and improved kinetics in hydrogen storage materials³. Further, the topology (e.g., particle size, morphology, porosity) exhibited by metal materials plays an important role in determining functional properties. Despite much recent effort to develop approaches to synthesize multimetallic materials, **simultaneous control of both surface morphology and composition remains a challenge**. This is particularly true at large scale, and with high surface area powders and nanomaterial substrates. We have developed means of preparing these materials that addresses these issues known as Atomic Layer Electroless Deposition (ALED).

Objectives

- Elucidate details of ALED process with noble metals
 - Stoichiometry of galvanic replacement
 - Growth rate per cycle
 - Growth mechanism
- Expand the scope for different substrates and adlayers other than noble metals
 - Nanoporous metal
 - Adlayer metals other than noble metals
 - Substrate other than Pd

Introduction

What is Atomic Layer Electroless Deposition (ALED)?

ALED is a scalable approach to surface-modified metal powders in which deposition of adlayer elements on substrate metals is carried out. In this method, elements more noble than the surface hydrides of the substrate metal are deposited layer-by-layer in surface-limited fashion. The substrate is first charged with a controlled partial pressure of H₂ gas to chemically form a surface hydride. After terminating the flow of reagent gas, surface-limited reduction of an adlayer of a different metal is carried out by galvanic exchange of the surface hydride.

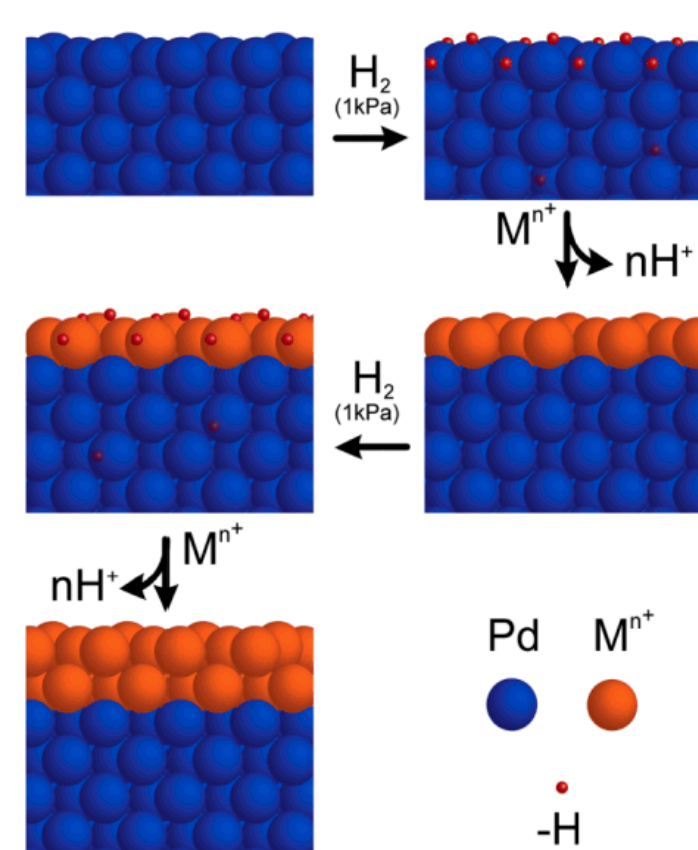


Fig. 1. ALED scheme on Pd metal⁴

Results and Discussion

One pot preparation of Bimetallic materials

ALED is a one pot approach containing reference (Ag/AgCl), counter (Pt) and working electrodes (Pd), and a stir bar as shown in Fig. 2. Working electrode is exposed 2cm, to ensure that a consistent surface area is in contact with electrolyte (0.1M H₂SO₄) before and after deposition. The cell is filled with 35 ml of electrolyte and purged with N₂ prior to initial and final CV.

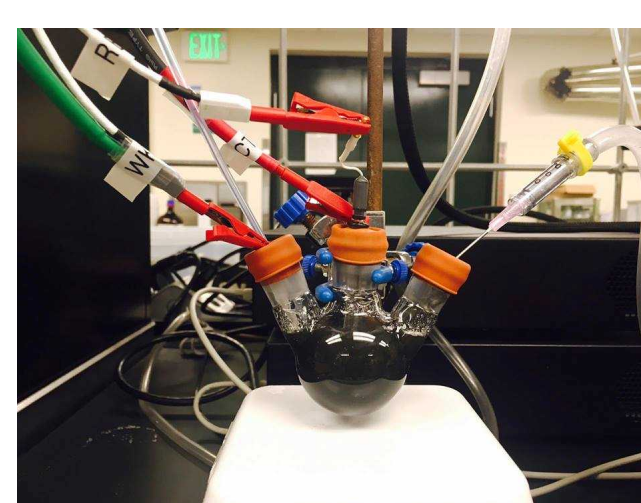


Fig. 2. ALED apparatus

The Open Circuit Potential (OCP) is the potential of the working electrode relative to the reference electrode when no potential or current is being applied to the cell. The cell is introduced with known amount of Pd powder and reagent gas (1% H₂ in N₂) is bubbled through. The OCP is monitored with time. The details of ALED is shown in Fig. 3, which involves:

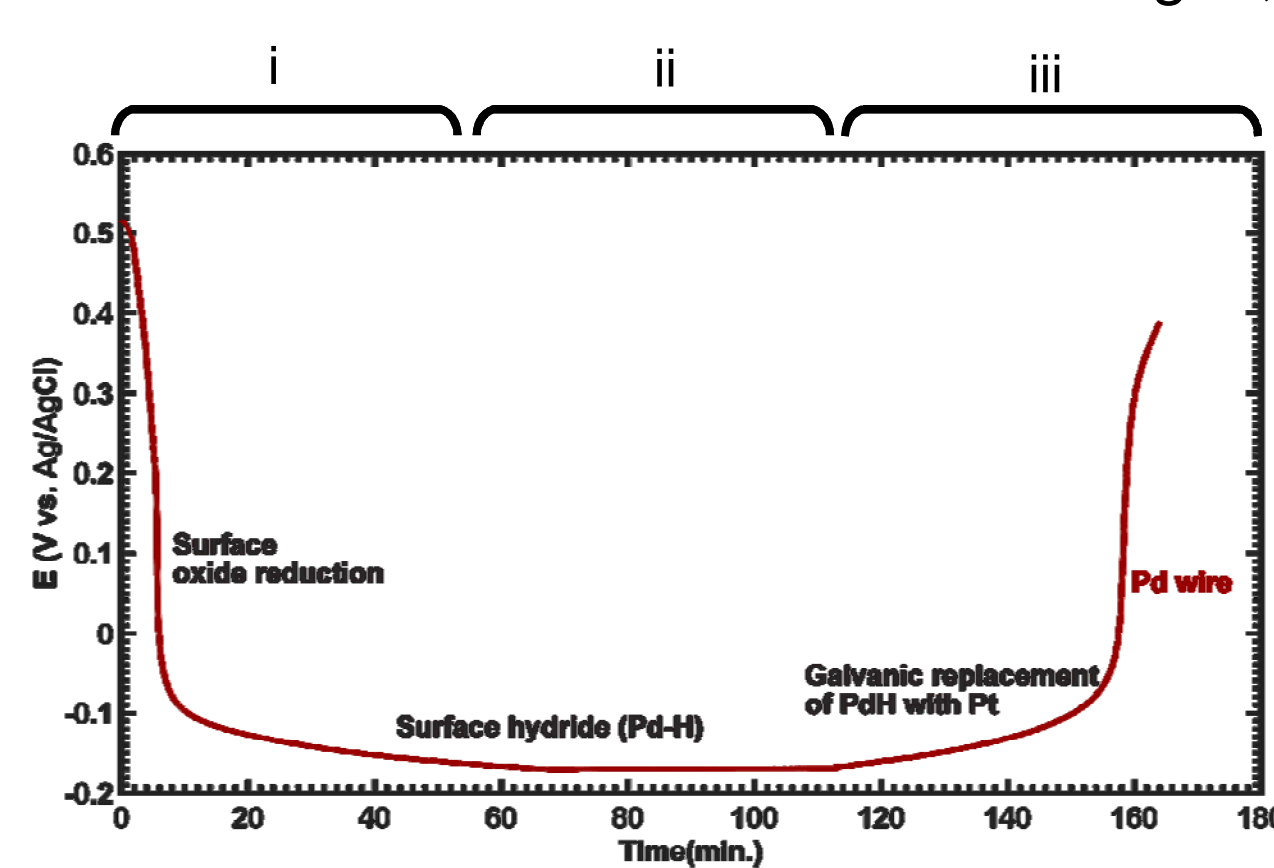


Fig. 3. OCP of Pd wire (inset: initial and final CV)

- The surface oxides are reduced
- Formation of Surface Hydrides
- Galvanic replacement of surface hydrides by adlayer metal

ALED of Pt on Pd powder (PdPt)

The OCP between the Pd working electrode and Ag/AgCl reference electrode shows the changes at the surface of the Pd WE. The OCP stabilizes at -0.2 V which is the value for Pd hydride electrode. Small aliquots of adlayer salt H₂PtCl₆ increases OCP. This accounts for the galvanic replacement of PdH at the surface with Pt.

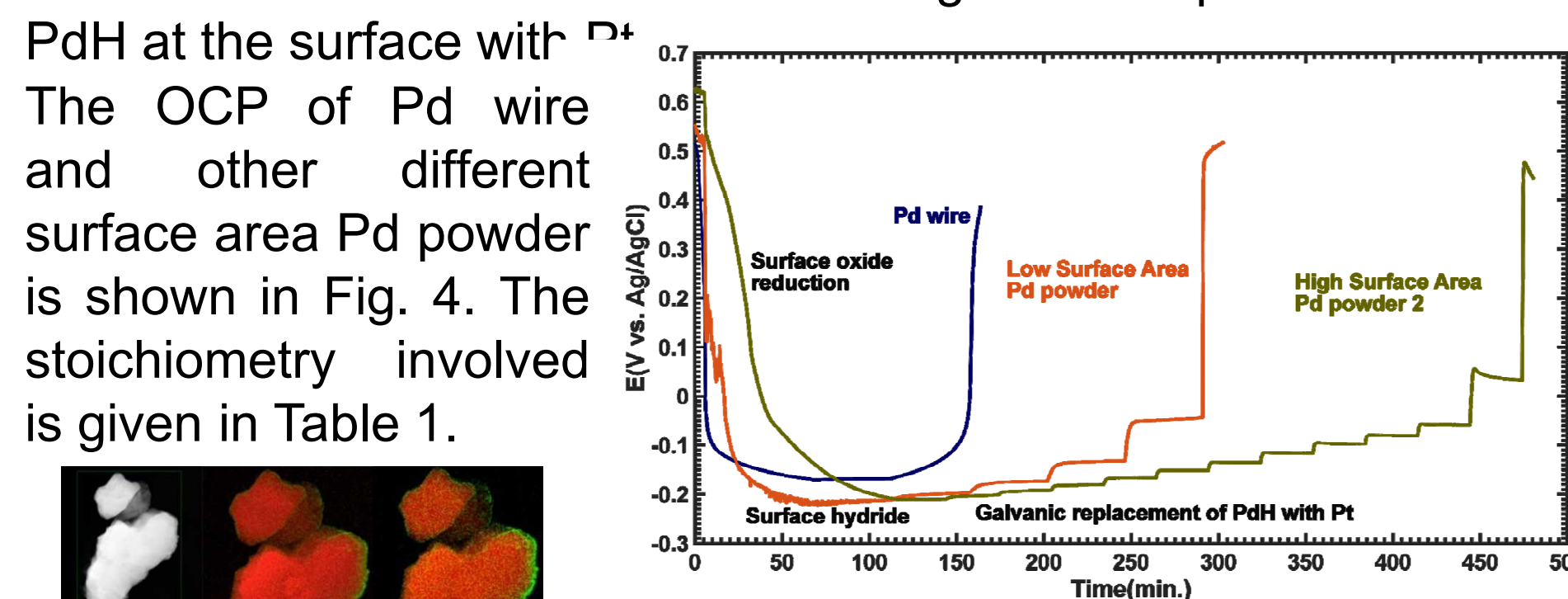


Fig.4. TEM image of PdPt (left) and OCP of Pd wire and Pd powder (right)

	Pd wire	Low Surface Area Pd powder	High Surface Area Pd powder
Surface Area (m ² /g) from N ₂ porosimetry	3.15×10 ⁻⁵	1.00	3.00
Sample size	2 cm × 0.04 cm	0.10 g	0.10 g
Moles of surface atoms (111)	8.01×10 ⁻¹⁰	2.45×10 ⁻⁶	7.37×10 ⁻⁶
Reducing equivalents (Pt ⁴⁺ Theoretical)	2.00×10 ⁻¹⁰	6.14×10 ⁻⁷	1.84×10 ⁻⁶
Added Pt ⁴⁺ reducing equivalents (Observed)	6.15×10 ⁻⁷	3.08×10 ⁻⁶	7.38×10 ⁻⁶
Observed / Theoretical	3.07×10 ²	5.00	4.00

Table 1. Stoichiometry of Pt ALED on Pd (PdPt)

XPS data of Pt on Pd (PdPt) from previous study⁴ suggested 3D growth concluding each cycle was not strictly confined to a single atomic layer.

ALED of Pd on Pt powder (PtPd)

Similar ALED approach is used on Pt powder and the amount deposition is quantified by X-ray Photoelectron Spectroscopy (XPS). The OCP and XPS spectra is shown in Fig. 5 and Fig. 6 respectively.

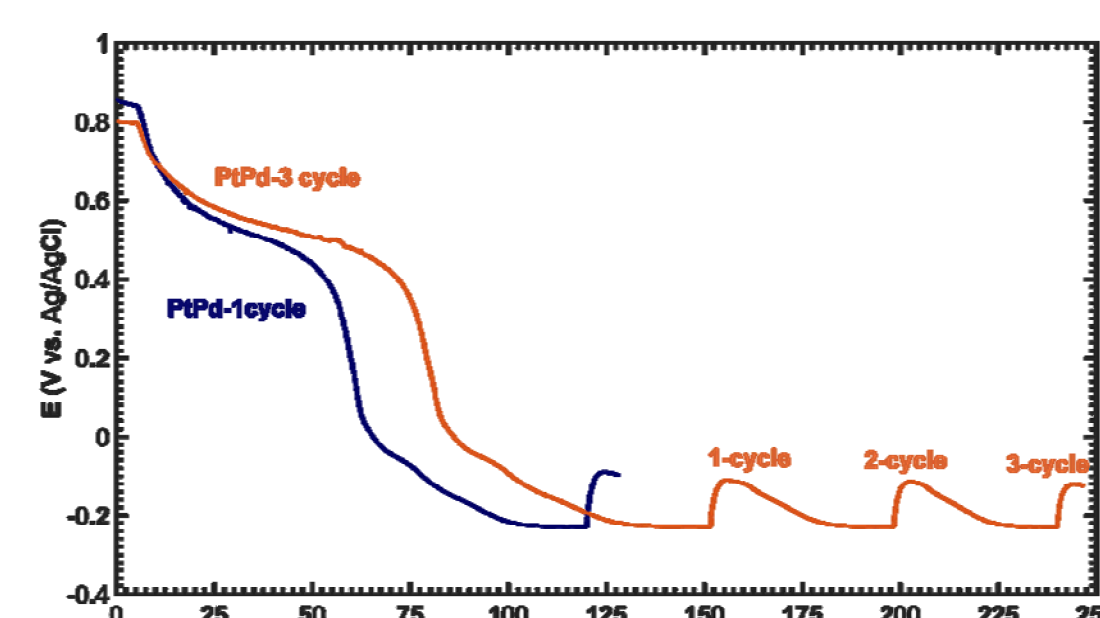


Fig. 5. Change in OCP over time Pd

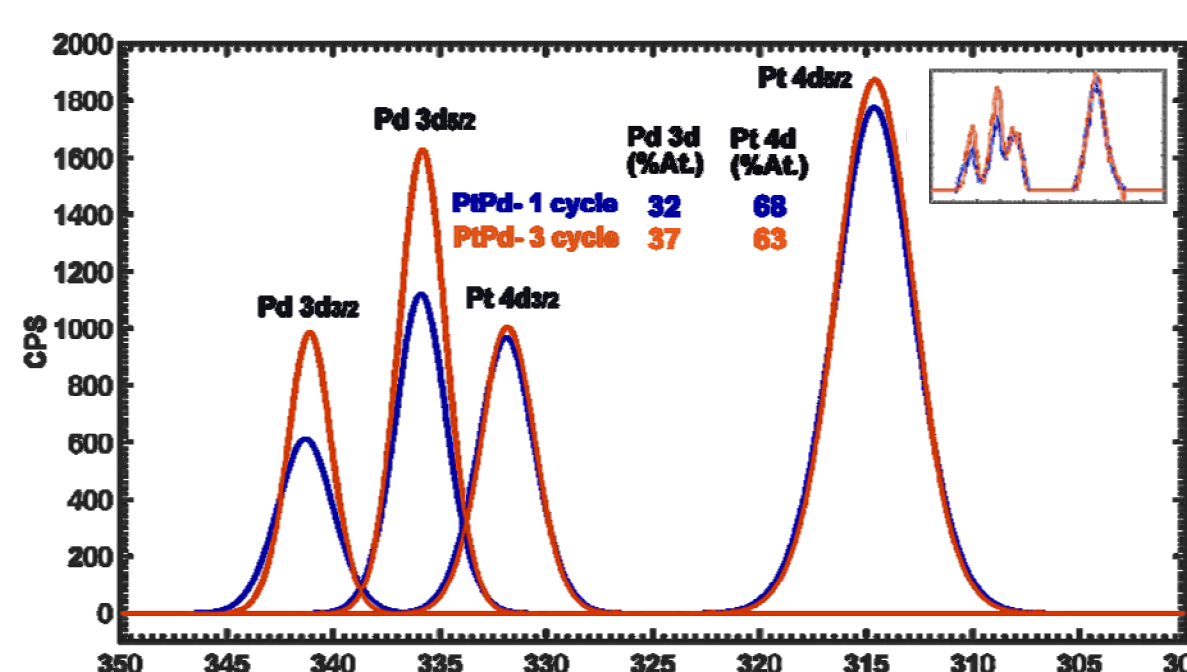


Fig. 6. Fitted XPS spectra of PtPd after 1 and 3 cycle (inset: raw data).

	Pt wire	Pt powder	NP _{Pt}
Surface Area (m ² /g) from N ₂ porosimetry	2.55×10 ⁻⁵	5.20	26.21
Sample size	2 cm × 0.04 cm	0.10 g	0.10 g
Moles of surface atoms (111)	6.37×10 ⁻¹⁰	1.31×10 ⁻⁵	5.79×10 ⁻⁵
Reducing equivalents (Pd ²⁺ Theoretical)	3.18×10 ⁻¹⁰	4.91×10 ⁻⁶	2.17×10 ⁻⁵
Added Pd ²⁺ reducing equivalents (Observed)	2.46×10 ⁻⁷	4.88×10 ⁻⁶	2.45×10 ⁻⁵
Observed / Theoretical	7.73×10 ²	0.99	1.12

Table 2. Stoichiometry of Pd ALED on Pt (PtPd)

ALED on Nanoporous Platinum powder NP_{Pt} (PtPd)

The OCP on NP_{Pt}, one cycle and three cycle are shown in Fig. 7 and Quantification of elements on surface by XPS is shown in Fig. 8.

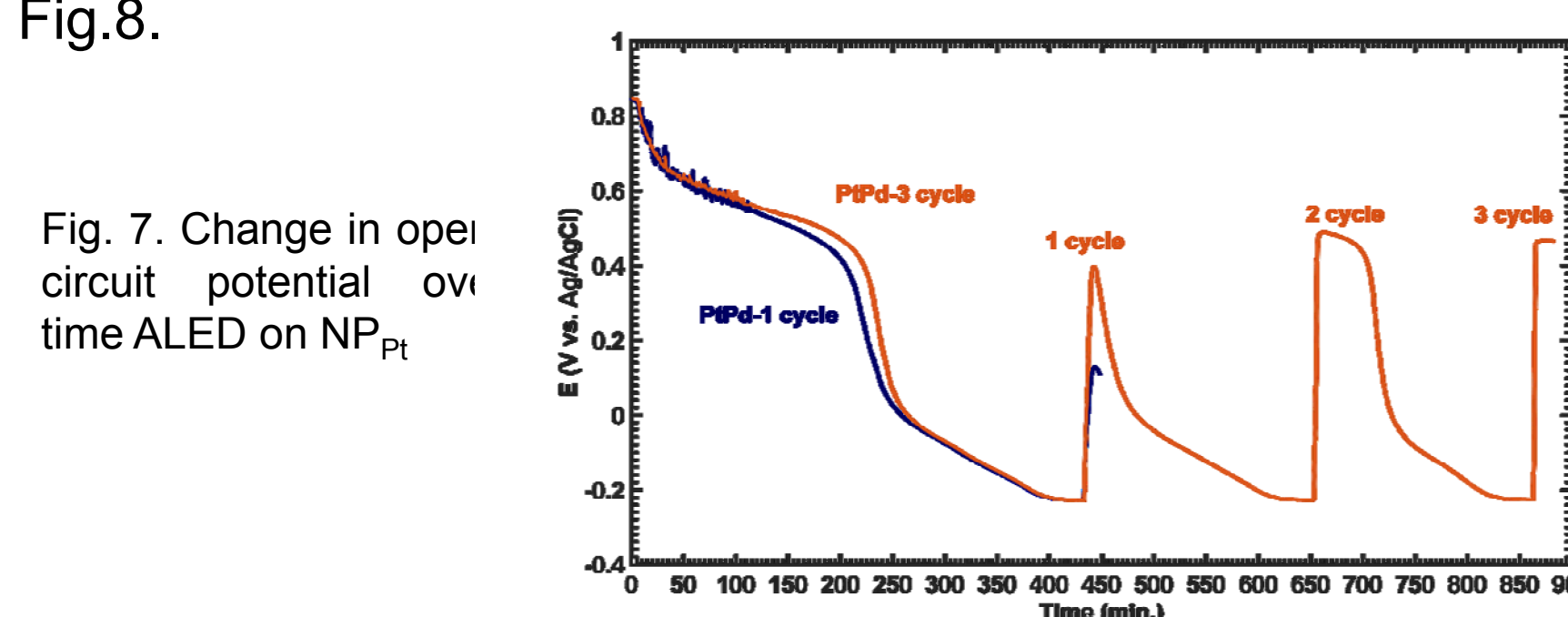
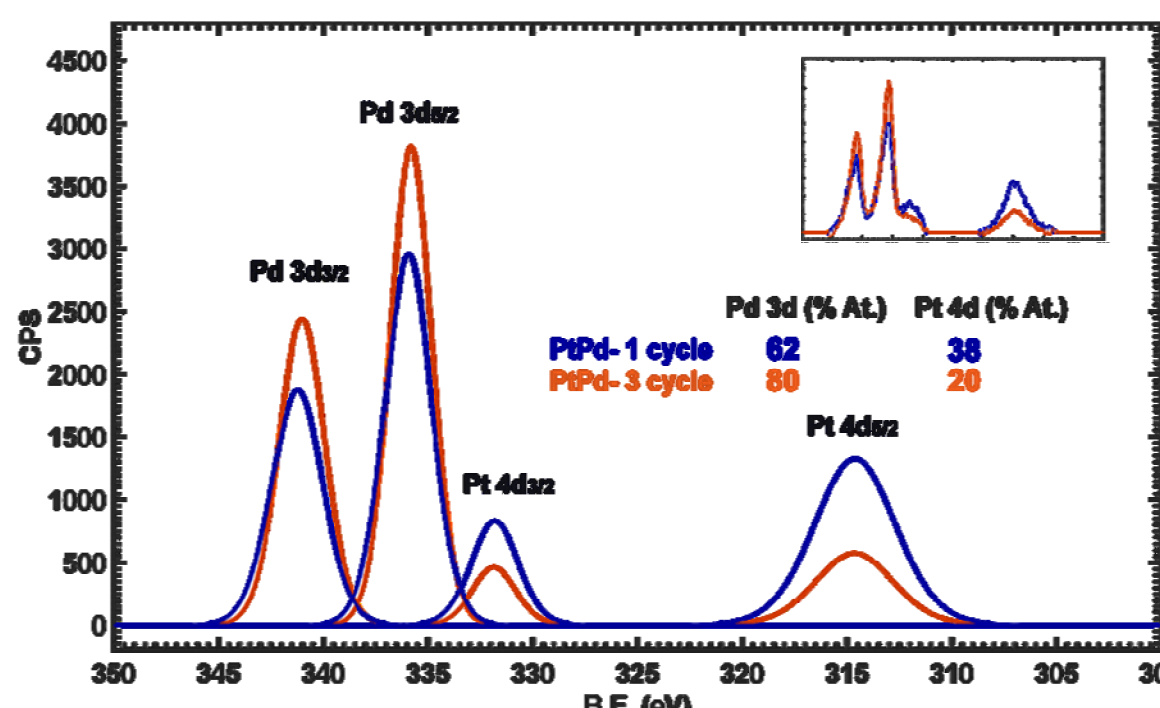


Fig. 7. Change in open circuit potential over time ALED on NP_{Pt}



NP_{Pt} forming more surface hydrides shows higher % Pd deposition compare to less surface area Pt powder

8. Fitted XPS spectra of Pd on NP_{Pt} PtPd (inset: raw data)

How do we prepare Nanoporous Platinum?

Nanoporous Metals (NPM) are nanostructured materials with pore diameter less than 100nm, they possess superior properties of high surface to volume ratio, uniform pore size distribution, unique physical, chemical and mechanical properties different from their bulk counter part.

The nanoporous metals are synthesized by chemical reduction of metal salt in soft templates in the presence of a nonionic surfactant oligo (ethylene glycol) hexadecyl ether (Brij 56)⁵. This soft template is washed by a 3:1 ratio of ethanol and water. The synthesized nanoporous metals are characterized by porosimeter.

Characterization of Nanoporous Platinum

BET Surface Area of Nanoporous Pt from (NH₄)₂PtCl₆ is found to be 30 m²/g and Pore width is found to be less than 4nm as shown in Fig. 8.

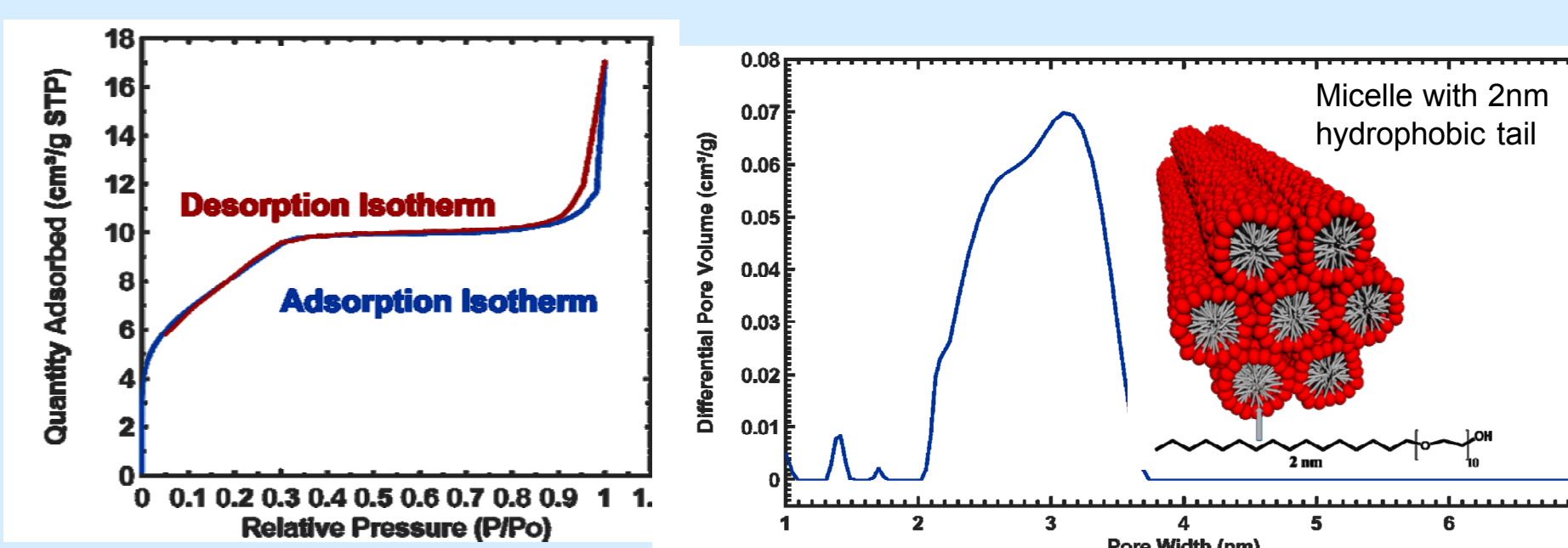


Fig. 8. Isotherm from nanoporous Pt (left) and Pore size distribution (right). Inset shows diagram of micelle which self assembles itself.

(<http://www.biomedcentral.com/content/figures/1757-5036-2-3-3-1.jpg>)

Analysis using 1,4 Phenylene Diisocyanide

Vibrational spectroscopy of phenylene diisocyanide (PDI) adsorbed on metals has been investigated in the context of research on Self-Assembled-Monolayer (SAMs)⁶. We plan to use this technique to study the surface composition of ALED-prepared materials. PDI is adsorbed on the metal surface by soaking in a THF solution of PDI.

The sample is then

washed with THF and dried in a N₂ purge.

It is then pressed into a titanium grid

and subjected to transmission IR

spectroscopy (Fig. 9). The IR

shows a PDI stretch around

2130 cm⁻¹ but when

PDI adsorbs on platinum

and palladium the stretch shifts in a manner that is dependent upon the metal to which it is bound. From these data we plan to determine the amount of coverage from ALED.^{7,8}

Conclusions

- ALED approach is studied in detail using different substrates
- NP_{Pt} is used as potential substrate to form bimetallic PtPd
- Quantification of prepared bimetallic is done by using XPS.
- Important preliminary data suggests that IR spectroscopy of PDI adsorbed on metal particles will be useful in determining surface coverage.

References

- V. R. Stamenkovic, B. Fowler, B. S. Mun, G. Wang, P. N. Ross, C. A. Lucas and N. M. Markovic, *Science*, 315 (5811), (2007), 493-497
- H. Lee, S. E. Somorjai and P. Yang, *J. Am. Chem. Soc.*, 130 (16) (2008) 5406-5407
- J. Greeley and M. Mavrikakis, *J. Phys. Chem. B*, 109 (8) (2005) 3460-3471
- P. J. Cappillino, J. D. Sugar, F. El Gabaly, T. Y. Cai, Z. Liu, J. L. Stickney, D. B. Robinson, *Langmuir*, 30(16) (2014) 4820-4829
- D.B. Robinson, M. E. Langham, S. J. Fares, M. D. Ong, B. W. Jacobs, W. M. Clift, J. K. Murton, R. P. Hjelm and M. S. Kent, *Int. J. Hydrogen Energy*, 35 (2010) 5423-5433
- M. Lazar and R.J. Angelici, *Modern Surface Organometallic Chemistry*, (2009) 513-556
- S. A. Swanson, R. McClain, K. S. Lovejoy, N. B. Alamdari, and J. S. Hamilton, *Langmuir*, 21 (2005) 5034-39.
- T. H. Ballinger, J.C.Wong and J. T. Yates, *Langmuir* 8 (1992) 1676-78

Acknowledgements

- We gratefully acknowledge Professor David Manke for access to the ASAP 2020 nitrogen porosimeter, and University of Massachusetts Dartmouth for providing opportunities to explore.
- Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
- Research was sponsored by the Army Research Laboratory and was accomplished under Grant Number W911NF-16-1-0438. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.
- We are also thankful to Northeastern Section of the American Chemical Society for the support and the Gesellschaft Deutscher Chemiker and Jung Chemiker Forum for the hospitality.