

Catalytic Nanoparticles for DMFC and DFAFC: Reaction Rates, Local Densities of States, and Oxygen Shuttling Pathways

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1 Overview

The object of this project has been to combine novel synthetic methods to produce much more active anode catalysts for fuel cells, and the use of spectroscopy to develop a molecular-level understanding of chemical physics principles of the fuel cell catalyst operation. We have made tremendous recent progress as evidenced by our 25 journal articles and 6 patents listed in Section 3.7 page 7. We have developed the most active catalysts for Direct Formic Acid Fuel Cells and discovered a correlation between spectroscopy (Pd 3d binding energy) and performance. We have observed the largest effect of particle size on fuel cell performance found to date where 3 nm palladium particles give an order of magnitude higher steady state current *per exposed metal atom* than 6 nm particles. We discovered a series of as yet unexplained support effects where Pd on V₂O₅ gives an order of magnitude more current than pure palladium. We have verified the results in operating fuel cells and are closing in on the DOE targets[1, 2] of anode catalysts for portable fuel cells (costing less than \$1/watt). Table 1 page 2 summarizes where these findings are described in the proposal for the reviewers reference.

Generally, our approach will be to correlate spectroscopy (XPS, NMR, and STM) to kinetic (CA, CV and VI) measurements as summarized in **Error! Reference source not found.** page **Error! Bookmark not defined.** in an attempt to better understand how differences in the particle size and support lead to differences in performance. We already have noticed a correlation between XPS binding energy and activity. We propose expanding this correlation to see if we can explain the effects of particle size and support on performance. We also propose expanding the effort using in situ STM, and EC-NMR to better characterize the changes in the catalysts as we change the support so that we can develop a fundamental understanding for catalyst design.

As a second thrust of the work, we will continue of our efforts to develop novel synthetic methods to prepare electrochemical catalysts. In particular we will extend the spontaneous deposition methodology developed in previous grant cycles [3-8] to the production of metal coated conducting oxide supports so we can turn the Pd on/metal oxide films that show high activity into practical catalysts.

Table 1 Our key results over the last three years	
Much more active catalysts for DFAFC's - 100 × previous ones	Section 3.1 page 4
An unexpected difference between nanoparticles and metal bulk:	
Reactivity and BE change	Section 3.1 page 5
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25 publications, 6 patents, and a startup company	Section 3.7 page 7

2 Introduction

This is a report for the project "Catalytic Nanoparticles for DMFC and DFAFC: Reaction Rates, Local Densities of States, and Oxygen Shuttling Pathways" by Andrzej Wieckowski and Richard Masel. The work combines *in situ* electrochemical spectroscopies (EC-NMR and XPS) and UHV measurements to provide a *rational basis for the anode catalyst development for PEM fuel cells*. The focus has been on using novel synthetic methods to produce much more active anode catalysts for fuel cells, and the use of spectroscopy to develop a molecular-level understanding of chemical physics principles of the fuel cell catalyst operation.

A continuing thrust of the work has been the use of spontaneous deposition to produce novel fuel cell catalysts. We start with a metal nanoparticle core and use spontaneous deposition to "decorate" the core with a second metal. This has produced catalysts with unique structure and activity. Ruthenium particles decorated with Pt (Figure 1) are currently one of the most active catalysts for direct methanol fuel cells (DMFC) [4] while palladium decorated with gold shows the highest stability for direct formic acid fuel cells (DFAFC) [8-10]. (The list of references is on page 13).

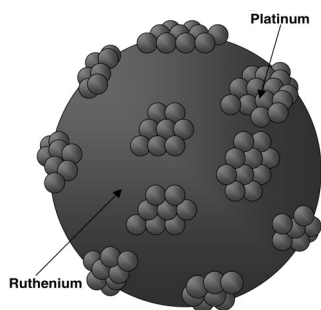


Figure 1 Schematic diagram of a Ru nanoparticle decorated with Pt atoms.

A second continuing thrust of the work has been to use spectroscopy to better

understand how fuel cells function. When we started the project, we predominantly used a combination of UHV and electrochemical measurements to understand the fuel cell performance. As the work has proceeded, while we still rely on the UHV measurements, we are now concentrating mainly on *in situ* measurements, such as electrochemical NMR and STM, plus measurements such as XPS where we rapidly transfer samples out of an electrochemical cell for the UHV-XPS assay.

In our work, we have concentrated on anode catalysts portable applications. When we started this work, the anode catalysts for portable electronics cost \$25/watt, while the DOE had set a target of \$1/watt. Thus there was a substantial need to improve the catalytic activity. In the last three years we have spent more time on formic acid fuel cells than on direct methanol fuel cells. Formic acid fuel cells are a new technology originally developed at UIUC, and now being commercialized by Renew Power and Motorola. The advantages of formic acid are:

- Low crossover: about 20 ma/cm² with 20 M solutions in operating fuel cells. This allows high concentrations to be used within the fuel cell simplifying the design.
- Much higher specific energy densities: over 80 W/liter in packaged devices. This is the only technology that has exceeded the DOE target of 30 w/lit for portable electronics. (DMFC is now at 6 w/l)
- Lower catalyst loadings: unlike methanol, formic acid seems to enhance rather than poison the cathode catalyst. In unpublished data we have produced 240 mW/cm² at 35 C with only 0.1 mg/cm² of Pt/C on the cathode. This should allow the DOE cost targets to be met.
- Much simpler regulatory situation. There are many regulatory hurdles than need to

be overcome before fuel cells can be sold to consumers. In particular, consumer electronics that contain class III flammable liquids need to be approved by the International Civil Aviation Organization (ICAO), and get a United Nations (UN) vote to allow an exception to the UN dangerous goods rules for transport. The ICAO vote is at least a year away. Then there is a two year delay to get approval by the UN. Formic acid, being non-flammable does not require UN approval. It does require approval by ICAO.

Given these advantages, particularly the regulatory advantages, it is likely that formic acid fuel cells will be the first to the market in consumer products.

Our DOE supported effort has been to use novel synthetic methods to produce more active catalysts for DMFC and DFAFC's, and to do detailed spectroscopy to understand how and why the catalysts function. In work in the prior grant period, we developed a novel method, **spontaneous deposition** [3-8] to create new catalysts. We have exploited that method and others in the present grant period, and have also continued developing NMR and XPS to understand how the catalysts function.

3 Results from DOE Support

We have 31 papers and patents over the last three years as listed in section 3.7. There is not room here to discuss all of the findings, but it is useful to list the highlights. Our key discoveries over the last three years include:

- Much more active catalysts for DFAFC's - $100 \times$ previous ones
- An unexpected difference between nanoparticles and metal bulk: Reactivity and BE change. A unexpected ligand effect, further enhancing the rate by a factor of 10.
- Unexpected reaction pathways
- Interesting anion and concentration effects

- New method of nanoparticle catalysts transfer to UHV for XPS study
- Reactivity enhancing heat treatment effect for Pt/Ru catalysis for methanol
- Coordinated EC-NMR – reactivity measurements

3.1 Much more active catalysts

One key discovery over the last three years was a series of palladium based catalysts for formic acid electrooxidation that are much more active than any catalyst considered previously. This discovery arose out of our attempt to understand why the Pt/Pd catalysts first synthesized in our previous grant cycle [3] showed unusual catalytic activity [8]. We did a number of studies [13-15] to understand the differences. We found that CO formation was inhibited by the addition of palladium; see Figure 2. The CO is normally a poison for the reaction, and so the suppression of the CO formation pathway by palladium leads to higher steady state catalytic activity.

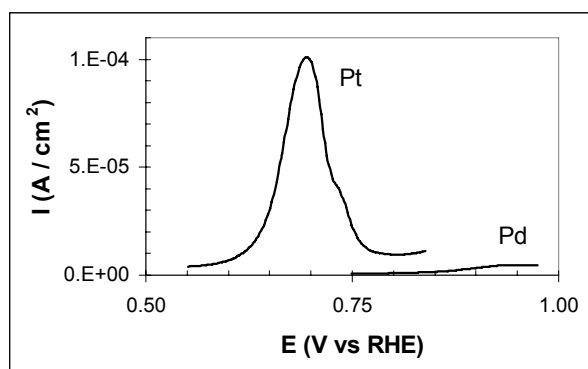


Figure 2 A comparison of the CO stripping peaks taken after oxidation for 1 hour in 5 M HPLC grade formic acid at 0.3 V vs RHE [8, 15].

The surprising feature in the data, though was that the catalytic activity increased

monotonically with the palladium coverage on the platinum surface, up to palladium coverages of 3 monolayers. This suggested that the palladium itself was the active catalyst and the platinum was merely a support.

Previously, Capon and Parsons [16] had compared formic acid electrooxidation on palladium and platinum foils, and found that palladium was less active than platinum, but given these results we decided to reexamine formic acid electrooxidation on palladium again. In particular, Capon and Parsons had only considered palladium foils. We decided to consider palladium particles, and to determine whether small palladium particles, would show unusual activity.

Figure 3 and Figure 4 shows some of the results of this work. We find that palladium nanoparticles are much more active than palladium foils, commercial platinum catalysts or commercial platinum ruthenium catalysts. The foils show some initial activity for formic acid electrooxidation, but they are quickly poisoned due to CO formation. Surprisingly, the poisoning is suppressed [8-12] on palladium nanoparticles. There is also an interesting effect of particle size, where smaller particles give superior poisoning resistance. At steady state, ***3 nm palladium particles are an order of magnitude more active per unit surface area than 6 nm particles.*** Clearly, we have found a new, more active class of catalysts for the proposed study, see below.

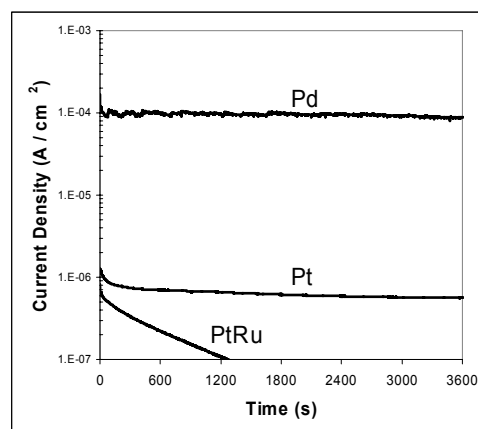


Figure 3 Chronoamperometric data taken during oxidation of formic acid in a solution of 5M formic acid and 0.1 N H₂SO₄ at 21 °C at 0.3V with respect to RHE. Notice that the palladium catalysts are more than 100 times as active as Johnson Matthey Pt or Pt/Ru. [10, 11]

In other work we have run these catalysts for 500 hours. There is some loss of activity due to buildup of impurities in our formic acid stream, but that can be eliminated by purifying the formic acid using a procedure we have developed [17-18] and/or by occasionally pulsing the anode to 1 V with respect to RHE to remove chemisorbed species formed from impurities in the formic acid feed.

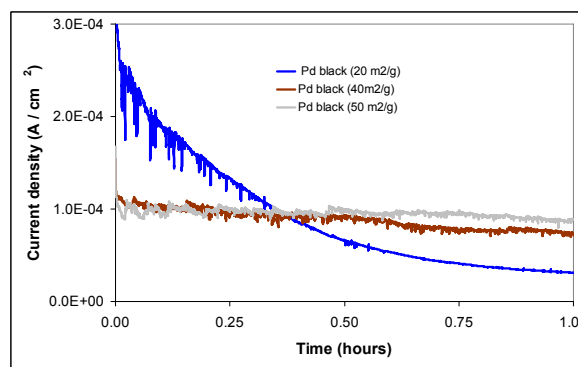


Figure 4 Chronoamperometric data taken during oxidation of formic acid in a solution of 5M formic acid and 0.1 N H₂SO₄ at 21 °C at 0.3V with respect to RHE formic acid and 0.1 H₂SO₄ at 21 °C. Palladium catalysts with 20 m²/gm show high initial activity but quickly poison. 40-50 m²/gm show lower initial activity but the activity is stable[10].

3.2 Unexpected ligand effects

Given our results above we also did a screening study to see if we could further enhance the activity by supporting the palladium particles on a conductive support that we expected to further shift the binding energy.

Figure 5 shows some of the results. In these experiments we grew a thin layer of metal oxide on top of a metal foil, deposited 0.6-1 monolayers of palladium onto the foil via spontaneous deposition or electrodeposition, and then used chronoamperometry to measure the catalytic activity. The results show that one can enhance the rate of formic acid electrooxidation by an additional factor of 20 by depositing the palladium on a vanadia support, even though vanadia is completely inactive for the reaction and vanadia is also inactive for CO oxidation in an electrochemical cell. High activity is seen even when there are 2 monolayers of Pd on the surface. Thus it appears that there is an interesting ligand effect that needs to be explored.

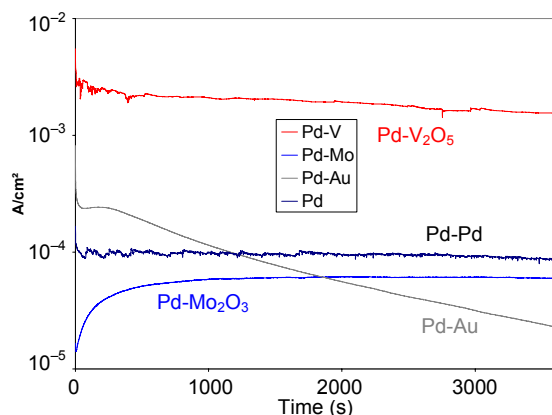
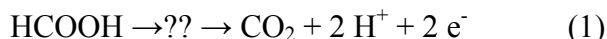


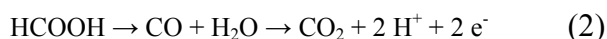
Figure 5 Chronoamperometric data taken at 0.3V with respect to RHE during oxidation of formic acid in a solution containing 5M formic acid and 0.1 M H₂SO₄ at 21 °C. The support exerts dramatic effects on the activity of the monolayer-level Pd metal, with the Pd-V₂O₅ catalyst exhibiting highest activity. [8]

3.3 Additional reaction pathways

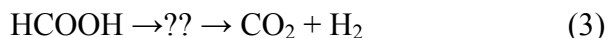
We also noticed that the reaction pathway for formic acid electrooxidation is not as reported previously. In the previous literature, people have said [19-23] that formic acid electrooxidation occurs via two reaction pathways: a “direct” pathway



And a pathway involving a CO intermediate



We have observed H₂ and formic anhydride formation during the reaction. Neither are formed in reactions 1 and 2. Therefore we believe that there are at least two other reaction pathways:



3.4 Applications in real devices

We have also verified that our enhanced activities seen in the electrochemical experiments carry over to real fuel cell conditions. Figure 6 compares the IV characteristics of our catalysts to commercial Pt/Ru. We observe 100 times as much current in the commercially useful range (i.e. 0.6 to 0.8) V. This allowed us to exceed the DOE targets for power density and anode catalyst cost in portable fuel cells. Clearly, the new catalysts are an important advance.

3.5 Anion and Concentration effects

Finally, we have characterized some unexpected anion and concentration effects. Generally we find that H₂SO₄ enhances the rate of reaction as shown in Figure 7. Such enhancement was also reported by Swamy et al. [24, 25]. We also find that the rate of formic acid oxidation is independent of concentration, at concentrations between 3 and 10 M, and then falls at high formic acid concentrations as shown in Figure 8. Such kinetics have not been reported previously.

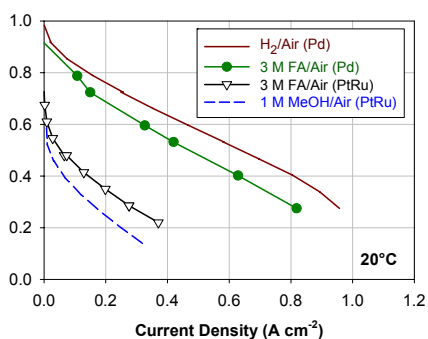


Figure 6 A comparison of the IV characteristics of a formic acid fuel cell with Pt/Ru and Pd catalysts[12]. Notice the large differences in current. The formic acid fuel cell is only slightly better than a methanol fuel cell when a commercial Pt/Ru is used. However, the current is 100 times larger when the new catalysts are used.

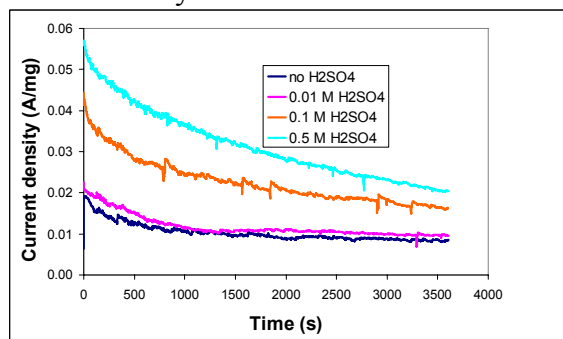


Figure 7 Chronoamperometric data taken during oxidation of formic acid in a solution of 5M formic acid and varying amounts of H₂SO₄ at 21 °C. Notice that the H₂SO₄ enhances the rate.

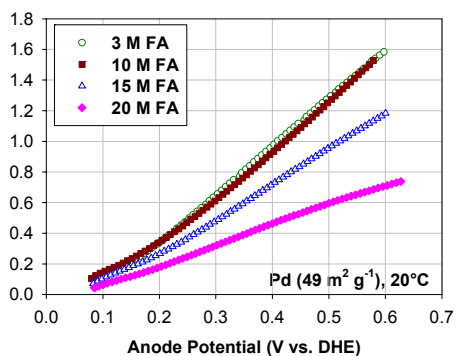


Figure 8 Anode polarization of the catalysts measured as a function of the formic acid concentration[12] at 20 °C. Notice that the rate decreases at high formic acid concentrations.

Table 2 The position of the Pt 4f XPS peak for Ru/Pt 1:1 alloy, Pt decorated Ru nanoparticles and Pt black.

Compound	Pt 4f _{7/2} peak BE /eV	BE shift vs. Pt (111)/ eV
Pt (111)	71.10	0.00
Pt black	71.33	0.23
Pt decorated Ru nanoparticles	71.47	0.37
Ru/Pt 1:1 alloy	71.62	0.52

3.6 XPS characterization of the catalysts

We have also used XPS to try to understand the difference between the reactivity of (bulk) single crystals and of nanoparticle electrodes for both methanol and formic acid oxidation, and to begin correlating the rate data to binding energy of electrodes of various particle size [26-30]. We have already taken some initial data on ruthenium nanoparticles enhanced by platinum and palladium nanoparticles, respectively to see if the idea has promise. To carry out this project, we developed a new method of immobilization of catalytic metal/alloy nanoparticles on an inert surface (of gold) for the noninvasive transfer from an electrochemical cell to ultra-high vacuum (UHV) for X-ray photoemission spectroscopy (XPS) measurements. Several Ru/Pt nanoparticle catalyst samples were examined: (i) the Pt decorated Ru nanoparticles prepared from Ru black onto which Pt was spontaneously deposited, (ii) the commercial Ru/Pt 1:1 alloy nanoparticles and (iii) pure Pt and Ru nanoparticle samples (Pt and Ru blacks). XPS Pt 4f spectra, measured from the decorated and alloy Ru/Pt nanoparticle samples show that the Pt 4f BE in the Ru/Pt 1:1 alloy nanoparticles is higher by 0.52 eV when compared to that of pure Pt (111) (and +0.37 eV for the Pt decorated Ru nanoparticles, see Table 2)). Additionally, the BE for pure platinum and ruthenium blacks is

shifted toward more positive BE value (0.23 and 0.15 eV, respectively) when compared to the single crystal BE benchmark. Notably, the Ru BE data show a smaller shift with an opposite trend. There is clearly a charge transfer from Pt to Ru due to Pt and Ru atoms intermixing, confirming previous NMR studies reported by this laboratory.[9]

These data show that there is large difference in BE between the bulk Pt and Ru samples and the nanoparticle samples. Rodriguez and Goodman demonstrated [26] a correlation between the CO adsorption energy on bimetallic surfaces to the BE shift due to the metal intermixing. The Hammer-Norskov model provides the state-of-the-art rationale for this behavior, namely, *changes* in the adsorbate chemisorption energies scale directly with the *changes* in the metal center of the d-band. In our work, the most active sample for methanol oxidation is the Ru/Pt 1:1 alloy that shows **the highest BE Pt 4f shift** (vs. Pt(111)), the pure Pt black shows the smallest shift, while the Pt decorated Ru nanoparticles are in between (Figure 9).

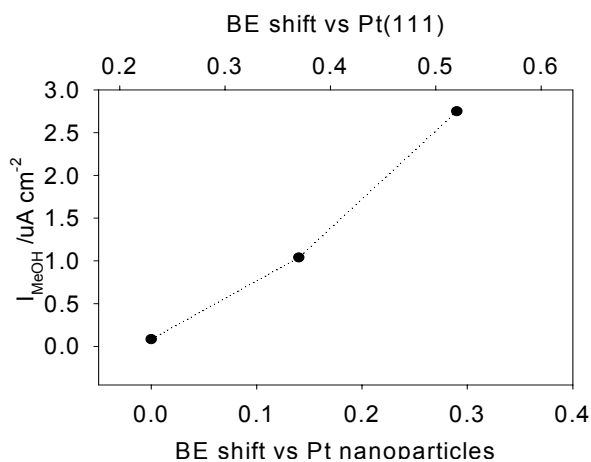


Figure 9 Methanol oxidation currents vs. BE shift for different nanoparticle catalysts: from left to right: Pt black, Pt decorated Ru and Ru/Pt 1:1 alloy nanoparticles.

Table 3 XPS spectra of Pd 3d core levels for a Pd nanoparticle sample: (A) as received (partially oxidized), (B) completely reduced, and for clean Pd(111) (C).

Binding Energy (Ev)	Pd(0)	BE Shift vs. Pd(111)
C: Pd(111)	335.10	0.00
B: reduced	335.31	0.21
A: received	335.33	0.23

XPS data of the Pd 3d core levels of Pd nanoparticles immobilized on Au disk and of Pd (111) are summarized in Table 3. XPS data of the Pd 3d core level were obtained for the as-received and oxidized Pd nanoparticles sample, directly after immobilization on the Au disk surface. The peak at 335.3 eV is assigned to metallic Pd. After electrochemical reduction only metallic Pd was detected. The Pd 3d_{5/2} peak at 335.1 eV was then obtained from a clean Pd (111) surface. Thus (Table 3), the binding energy in Pd nanoparticles is shifted by +0.2 eV compared to the BE in the bulk of Pd (in the Pd single crystal). Notably, the most active sample for formic acid oxidation is the Pd nanoparticle sample (Figure 4) that (again) shows the **highest BE for Pd 3d**. We are therefore beginning to establish the trend between particle size, binding energy and the reactivity that will be further explored in this project.

3.7 Publications Supported by Department of Energy grant DE-FG02-99ER14993 since 2002

The description above gave some of the highlights of our work. We have 31 publications as outlined below.

3.7.1 Journal Articles

1 K.-L. Chu, M. A. Shannon, and R. I. Masel, "Improved Miniature Direct Formic Acid Fuel Cells Based on Nanoporous Silicon Membranes for Portable Power Generation," J. Electrochem Soc., 153(8), A1554-A1561,

2006.

- 2 W. P. Zhou, A. Lewera, P. S. Bagus, R. Larsen, R. I. Masel, A. Wieckowski, "Size Effects in Electronic and Catalytic Properties of Unsupported Palladium Nanoparticles in Electrooxidation of Formic Acid," *Journal of Physical Chemistry B*, 110 (27), 13393-13398, 2006 .
- 3 S. Ha, Z. Dunbar, and R. I. Masel, "Characterization of a High Performing Passive Direct Formic Acid Fuel Cell," *Journal of Power Sources*, 158, 129-136, 2006.
- 4 P. K. Babu, H.-S. Kim, S. T. Kuk, J. Ho Chung, E. Oldfield, E. S. Smotkin (UPR) and A. Wieckowski, "Activation of Nanoparticle Pt/Ru Fuel Cell Catalysts by Heat Treatment: A ^{195}Pt NMR and Electrochemical Study", *J. Phys. Chem. B.*, submitted.
- 5 A. Lewera, W. P. Zhou, C. Vericat, J.H. Chung, R. Haasch, A. Wieckowski and P. S. Bagus "X-ray Photoemission Spectroscopy and Reactivity Measurements of Ru/Pt Nanoparticles Supported on a Gold Disk", *Analytical Chemistry*, in preparation.
- 6 M. S. McGovern, P. Waszczuk and A. Wieckowski, "Stability of Carbon Monoxide Adsorbed on Nanoparticle Pt and Pt/Ru Electrodes in Sulfuric Acid Media", *Electrochimica Acta*, in press.
- 7 R. Larsen, S. Ha, J. Zakzeski and R. I. Masel, "Unusually Active Palladium Based Catalysts for the Electrooxidation of Formic Acid," *Journal Power Sources*, 157(1):78-84, 2006.
- 8 179. S. Ha, R. Larsen and R. I. Masel, "Performance Characterization of Pd/C Nanocatalyst for Direct Formic Acid Fuel Cells," *J. Power Sources*, 144, 28-34, 2005.
- 9 174. R. Larsen, J. Zakzeski, Y. Zhu, and R. I. Masel, "Unexpected Activity of Palladium on Vanadia Catalysts for Formic Acid Electrooxidation," *Electrochemical and Solid-State Letters*, 8(6) A291-293, 2005.
- 10 Y. Zhu, Z. Khan and R. I. Masel, "Performance characterization of Pd nanocatalyst for direct formic acid fuel cells", *J. Power Sources*, 139 (2005) 15.
- 11 S. Ha, R. Larsen, Y. Zhu, and R. I. Masel, "Direct formic acid fuel cells with 600 mA/cm² at 0.4 V and 22 °C", *Fuel Cells*, 4(2004) 337-343.
- 12 J. Spendelow, G. Q. Lu, P. J. A. Kenis and A. Wieckowski, "Electrooxidation of Adsorbed CO on Pt(111)/Ru in Alkaline Media: Comparison with Results from Acidic Media", *J. Electroanal. Chem.*, 568, 215-224 (2004).
- 13 R. Larson and R. I. Masel, "Kinetic study of CO tolerance during electrooxidation of formic acid on spontaneously deposited Pt/Pd and Pt/Ru nanoparticles", *Electrochemical and Solid State Letters*, 7, A148-A150, 2004.
- 14 Y. Zhu, S. Ha, and R. I. Masel, "High Power Density Direct Formic Acid Fuel Cells", *J. Power Sources*, 130, 1-2, 8-14, 2004.
- 15 F. Thomas and R. I. Masel, "Formic Acid Decomposition on Palladium-Coated Pt(110)", *Surface Science*, 573(2004) 169-175.
- 16 B. Adams, S. Ha, Y. Zhu, R. Larsen, M. Shannon, A. Wieckowski, and R. I. Masel, "Formic Acid Fuel Cells: New Possibilities For Portable Power", *Proceedings Power Sources*, 41, 428-431, 2004.
- 17 S. Ha, B. Adams, and R. I. Masel, "A Miniature Air Breathing Direct Formic Acid Fuel Cell", *J. Power Sources*, 128, 2, 119-124, 2004.
- 18 M. Zhao, C. Rice, R. I. Masel, P. Waszczuk, and A. Wieckowski, "Kinetic Study of Electrooxidation of Formic Acid on Spontaneously-Deposited Pt/Pd Nanoparticles. CO Tolerant Fuel Cell Chemistry", *J. Electrochem. Soc.*, 151, A131-A136 (2004).
- 19 P. K. Babu, H.-S. Kim, E. Oldfield and A. Wieckowski, "Electronic Alterations Caused by Ruthenium in Pt/Ru Alloy Nanoparticles as

Revealed by Electrochemical NMR”, *J. Phys. Chem.* 107, 7595-7600 (2003).

20 C. Rice, S. Ha, R. I. Masel, A. Wieckowski, *J. Power Sources*, “Catalysts for Direct Formic Acid Fuel Cells”, 115, 229-235 (2003).

21 M. S. McGovern, E. C. Garnett, C. Rice, R. I. Masel, A. Wieckowski, “Effects of Nafion as a Binding Agent for Unsupported Nanoparticle Catalysts”, *J. Power Sources*, 115, 35-39 (2003).

22 S. Ha, C. A. Rice, R. I. Masel, A. Wieckowski, “Methanol conditioning for improved performance of formic acid fuel cells”, *J. Power Sources*, 112, 655-659 (2002).

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24 P. Waszczuk, G.-Q. Lu, A. Wieckowski, C. Lu, C. Rice, and R. I. Masel, “UHV and Electrochemical Studies of CO and Methanol Adsorbed at Platinum/Ruthenium Surfaces, and Reference to Fuel Cell Catalysis”, *Electrochimica Acta*, 47, 3637-3652 (2002).

25 C. Lu, C. Rice, R. I. Masel, P. K. Babu, P. Waszczuk, H.-S. Kim, E. Oldfield, A. Wieckowski, “UHV, Electrochemical NMR and Electrochemical Studies of Platinum/Ruthenium Fuel Cell Catalysts”, *J. Phys. Chem., B*, 106, 9581-9589 (2002).

26 C. Lu, I. C. Lee, R. I. Masel, A. Wieckowski and C. Rice, “Correlations between the heat of adsorption and the position of the center of the d-band: Differences between computation and experiment”, *J. Phys. Chem. B*, 106, 3084-3091 (2002).

27 C. Rice, S. Ha, R. I. Masel, P. Waszczuk and A. Wieckowski, “Characteristics Of Small Formic Acid Fuel Cells”, *Proceedings 40th Power Sources Conference*, 254-258, 2002.

28 P. Waszczuk, T. M. Barnard, C. Rice, R.

I. Masel and A. Wieckowski, “A Nanoparticle Catalyst With Superior Activity for Electrooxidation of Formic Acid”, *Electrochemistry Communications*, 4, 599-603, 2002.

29 P. Waszczuk, T. M. Barnard, C. Rice, A. Wieckowski* [addition] and R. I. Masel, “A Nanoparticle Catalyst with Superior Activity for Electrooxidation of Formic Acid,” *Electrochemistry Communications*, 4, 732, 2002.

30 C. Rice, S. Ha, R. I. Masel, P. Waszczuk, A. Wieckowski, “Direct Formic Acid Fuel Cells,” *J. Power Sources*, 111, 83-89, 2002.

31 C. Lu, C. Rice, P. K. Babu, P. Waszczuk, H.S. Kim, E. Oldfield, A. Wieckowski and R. I. Masel, “UHV, Electrochemical NMR and Electrochemical Studies of Platinum/Ruthenium Fuel Cell Catalysts,” *J. Physical Chemistry, B*, 106, 9581-9589, 2002.

32 I. C. Lee and R. I. Masel, “Measurement of the Metal Surface Acidity/Electronegativity of Pt(110),” *Catalysis Letters*, 83, 43-48, 2002.

3.7.2 Allowed patents

33 Masel, R.I. and C.A. Rice, “Solids Supporting Mass Transfer for Fuel Cells and Other Applications and Solutions and Methods for Forming,” US Patent US7,108,773, Sept. 2006

34 Masel, R.I., C.A. Rice, P. Waszczuk and A. Wieckowski, “Fuel Cells and Fuel Cells Catalysts,” US Patent US7,132,188, Nov, 2006.

35 Masel, R.I., C.A. Rice, P. Waszczuk and A. Wieckowski, “Fuel Cells and Fuel Cells Catalysts,” British Patent GB2401987, Mar, 2006.

36 Masel, R.I., C. Rice, P. Waszczuk and A. Wieckowski, “Fuel Cell and Fuel Cell Catalysts,” British Patent GB2420219, Oct 2006

37 Masel, R.I., Y. Zhu, Z. Kahn, M. Man, “Low contaminant formic acid fuel for direct

liquid fuel cell," British Patent, GB2424650B, May 2007

38 Masel, R.I., S. Ha, B. Adams, "Organic fuel cells conducting sheets and Fuel Cell Conduction " US patent submitted 10/664,772, US20040115518. Allowed

3.7.3 Pending Patent applications

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3.7.4 Startup company based on the findings

A new company, Renew Power/Tekion has been started to build formic acid fuel cells

using the catalysts discovered in this program. The company already has 50 employees and has received funding from Motorola.

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