Catalytic Performance Enhancement by Low Temperature Plasma Treatment

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ABSTRACT

Increasing the performance of fuel cell electrocatalysts can help make fuel cell technology economically viable. One way to improve the catalytic activity of fuel cell electrocatalysts is through plasma treatment of the surfaces of such catalyst to create defects which can serve as possible catalytic reaction sites. The focus of this plasma modification process is on fuel cell electrocatalysts. The purpose of the plasma treatment process is to increase the catalytic performance of the fuel cell electrocatalysts possibly making fuel cells a commercially viable product.

Keywords: plasma, heterogeneous catalysts, fuel cell electrocatalysts, plasma treatment / modification / irradiation

1 INTRODUCTION

In this paper we emphasize the application of the plasma treatment method to improve PEM fuel cell catalysts, however in a closely related paper at this meeting we stress broader use for a variety of commercial processes involving catalysts [1]. Heterogeneous catalysts which produce good reaction rates are sometimes composed of noble metals (e.g. platinum, palladium, etc.) which are scarce and expensive [2]. Such noble metals are used as electrocatalysts in PEM fuel cell technology. There are a variety ways to try to circumvent the use of these scarce and costly catalysts [3] [4], but none have been fully successful to date. The process under study here uses a low temperature plasma to enhance catalytic performance of fuel cell electrocatalysts.

2 BACKGROUND

In surface "structure-sensitive" catalysts, certain sites on the surface of the catalysts enhance the rate of the chemical reactions [4] [5] [6] [7]. The reaction rate of these structure-sensitive catalyst greatly increases with the number of surface defects (e.g. steps, kinks, etc.) [6] [7] [8]. This observation is based on experiments comparing reaction rates of catalyst with single-crystal surfaces and catalyst containing many surface defects [7]. Other factors that enhance catalytic activity include increasing the surface area of the heterogeneous catalyst [9]. Furthermore catalytic activity of materials with equal surface areas may also differ depending on their actual form [9]. For example, materials that are normally inert in macroscopic solid form (e.g. gold), demonstrate high catalytic activity in submicron solid form [10].

In the semiconductor manufacturing industry low temperature plasmas are used to manipulate the surfaces of solid materials. Plasma ions can damage the surfaces of materials through ion bombardment which can eject surface atoms; this process is called sputtering. Plasmas can also induce the formation of submicron structures on the surfaces of solid materials. The effects caused by plasma-surface interaction (notably surface damage and defects, as well as the formation of submicron structures) are utilized to possibly alter PEM fuel cell electrocatalysts surface so the catalytic activity can be enhanced. The plasma-catalysts treatment process has been studied for some time [11].

Polymer electrolyte membrane (PEM) fuel cells have been proposed as one of the technologies that can displace the use of fossil fuels in the transportation sector. The issues that hold back PEM fuel cells from being commonplace are: (1) the membrane, (2) the catalyst, (3) the bipolar plate, and (4) water management [12] [13] [14] [15] [16] [17] [18] [19] [20] [21]. The membrane is a thin layer of electrolyte which has high ionic conductivity, but prevents the transport of electrons. The membrane accounts for ~6% of the PEM fuel cell cost; additionally the membrane suffers from degradation due to mechanical stress and chemical attack. Thus the membrane suffers from low lifetimes [13] [18]. The electrocatalysts are where the electrochemical reactions in the fuel cell take place. In PEM fuel cells the electrocatalyst is ~77% of the fuel cell cost, making it the key factor causing the high cost for fuel cell. The catalysts also plays a key role in the durability of a fuel cell; catalyst degradation is common and causes gradual loss of fuel cell performance [13] [18]. The bipolar plate separates fuel and oxidants in a fuel cell. The bipolar plates also conducts electrons and diffuses heat [13] [18]. There are two types of bipolar plate materials, they are metal or carbon. Carbon (bipolar) plates are thicker, more massive, and are structurally weaker than metal plates, however metal plates especially less expensive metal plates suffer from corrosion in the fuel cell environment [13] [16]. Water management involves damage to PEM fuel cell due to freezing and thawing of water. The freezing and thawing of water in fuel cells significantly lower fuel cell component lifetimes [13].

3 EXPERIMENT

The focus of the present work is on the electrocatalysts, because the electrocatalyst represents the majority of the cost in PEM fuel cells. Electrocatalysts are a subcategory of catalysts and incorporate similar characteristics as regular heterogeneous catalysts. Characteristics that affect electrocatalysts performance include crystal orientation and structural defects at the surface [22] analogous to regular heterogeneous catalyst. PEM fuel cell electrocatalysts are shown to be structure-sensitive; this is because experiments have shown that the catalytic activity of platinum and platinum-nickel alloys change with crystal structure and surface form [13]. This indicates that certain sites on the surface of PEM fuel cell electrocatalysts allow for more reactions to take place. The goal is to demonstrate that plasma-surface treatment of electrocatalysts in PEM fuel cells can enhance catalytic performance. Figure 1 shows a schematic of a DC plasma discharge system with the cathode (exposed to the plasma) made out of an electrocatalysts. Electrocatalysts as the name suggest are electrically conducting.

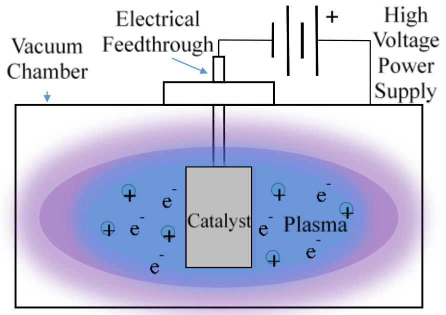

Figure 1: Schematic of DC plasma source modifying the surface of a conducting heterogeneous catalysts.

A simple plasma-surface modification method is being studied to treat PEM fuel cell catalytic material (e.g. platinum, etc.). The plasma-surface treatment modifies the surface of the catalytic material creating very pack submicron structures and defects [23] [24] [25] [26] [27] [28]. These submicron formations and defects on the catalytic material can serve as reactant adsorption and reaction sites [4] [5] [6] [7] [29] [30] [31]. The plasma modification can potentially increase the number reaction sites this can greatly improve the performance of the fuel cell catalytic material which would therefore improve the economic viability of fuel cells technology. Furthermore plasma irradiating some of the more expensive catalysts can also increase their catalytic activity, thereby increasing reaction rates and ultimately improving the economics without changing the catalysts employed in the process.

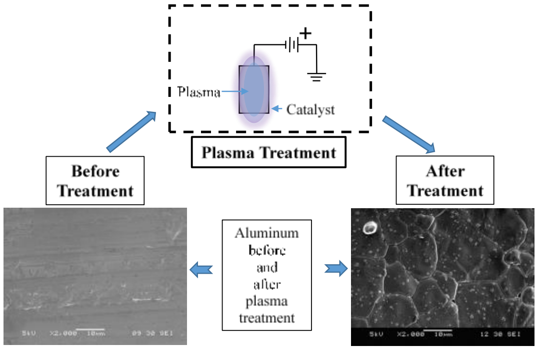

Figure 2: Plasma treatment of aluminum foil showing the effects of plasma on material surfaces.

Figure 2 shows a plasma treatment system currently set up to study and optimize the PEM fuel cell electrocatalysts treatment process. As shown, before and after measurements using SEM of the surfaces of conducting materials. The case shown is for an aluminum foil, but this work will eventually cover catalysts for interest for fuel cells. In addition to SEM scans, changes in the catalysts activity will be measured. To do that for fuel cell electrocatalysts an electrochemical test setup is being constructed.

4 CONCLUSION

A successful outcome can lead to economic fuel cell applications in automobile transportation or distributed stationary power generation. This plasma treatment technique can also be applied to other electrochemical systems that use electrocatalysts. Catalysts are ubiquitous in chemistry and enhancing the activity of fuel cell electrocatalyst through simple plasma treatment can ripple through the automotive and distributed stationary power sector. This should accelerate the use of less polluting fuel cell vehicles in the transportation industry.

REFERENCES

[1] G. H. Miley, S. Srivastava and K.-J. C. G. Kim, "Low Temperature Plasma Surface Treatment of Catalytic Material," in *TechConnect World 2015*, Washington, DC, 2015.

[2] M. Armbruster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, P. Gille, L. Szentmiklosi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlogl and Y. Grin, "Al13Fe4 as a low-cost alternative for palladium in heterogeneous hydrogenation," *Nature Materials*, vol. 11, pp. 690-693, 2012.

[3] M. P. de Almeida and S. A. C. Carabineiro, "The Best of Two Worlds from the Gold Catalysis Universe Making Homogeneous Heterogeneous," *CHEMCATCHEM*, vol. 4, pp. 18-29, 2012.

[4] S. He, C. Li, H. Chen, D. Su, B. Zhang, X. Cao, B. Wang, M. Wei, D. G. Evans and X. Duan, "A Surface Defect-Promoted Ni Nanocatalyst with Simultaneously Enhanced Activity and Stability," *Chemistry of Materials*, vol. 25, pp. 1040-1046, 2013.

[5] M. Boudart, "Heterogeneous Catalysis By Metals," *Journal of Molecular Catalysis*, vol. 30, pp. 27-38, 1985.

[6] T. Zambelli, J. Wintterlin, J. Trost and G. Ertl, "Identification of the "Active Sites" of a Surface-Catalyzed Reaction," *Science*, vol. 273, pp. 1688-1690, 1996.

[7] Z.-P. Liu and P. Hu, "General Rules for Predicting Where a Catalytic Reaction Should Occur on Metal Surfaces: A Density Functional Theory Study of C-H and C-O Bond Breaking/Making on Flat, Stepped, And Kinked Metal Surfaces," *Journal of the American Chemical Society*, vol. 125, pp. 1958-1967, 2003.

[8] R. T. Vang, K. Honkala, S. Dahl, E. K. Vestergaard, J. Schnadt, E. Laegsgaard, B. S. Clasusen, J. K. Norskov and F. Besenbacher, "Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking," *Nature Materials*, vol. 4, pp. 160-162, 2005.

[9] U. Heiz, F. Vanolli, A. Sanchez and W. D. Schneider, "Size Dependent Molecular Dissociation on Mass-Selected, Supported Metal Clusters," *Journal of the American Chemical Society*, vol. 120, pp. 9668-9671, 1998.

[10] A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett and U. Landman, "When Gold Is Not Noble: Nanoscale Gold Catalysts," *Journal of Physical Chemistry A*, vol. 103, pp. 9573-9578, 1999.

[11] C.-j. Liu, G. P. Vissokov and B. W.-L. Jang, "Catalyst preparation using plasma technologies," *Catalysis Today*, vol. 72, pp. 173-184, 2002.

[12] B. R. Limoges, R. J. Stanis, J. A. Turner and A. M. Herring, "Electrocatalyst materials for fuel cells based on the polyoxometalates," *Electrochimica Acta*, vol. 50, pp. 1169-1179, 2005.

[13] J. Macinkoski, J. P. Kopasz and T. G. Benjamin, "Progress in the US DOE fuel cell subprogram efforts in polymer electrolyte fuel cells," *International Journal of Hydrogen Energy*, vol. 33, pp. 3894-3902, 2008.

[14] J. J. Zhang, PEM Fuel Cell Electrocatalysts and Catalyst Layers, London: Springer-Verlag, 2008.

[15] S. Zhang, X.-Z. Yuan, J. N. C. Hin, H. Wang, K. A. Friedrich and M. Schulze, "A review of platinum-based catalyst layer degradation in proton exchange membrane fuel cells," *Journal of Power Sources*, vol. 194, pp. 588-600, 2009.

[16] R. A. Antunes, M. C. L. Oliveira, G. Ett and V. Ett, "Corrosion of metal bipolar plates for PEM fuel cells: A review," *International Journal of Hydrogen Energy*, vol. 35, pp. 3632-3647, 2010.

[17] Z. Chen, D. Higgins, A. Yu, L. Zhang and J. Zhang, "A review on non-precious metal electrocatalyst for PEM fuel cells," *Energy & Environmental Science*, vol. 4, pp. 3167-3192, 2011.

[18] Y. Wang, K. S. Chen, J. Mishler, S. C. Cho and X. C. Adroher, "A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research," *Applied Energy*, vol. 88, pp. 981-1007, 2011.

[19] R. Othman, A. L. Dicks and Z. Zhu, "Non precious metal catalysts for the PEM fuel cell cathode," *International Journal of Hydrogen Energy*, vol. 37, pp. 357-372, 2012.

[20] D. C. Higgins and Z. Chen, "Recent Progress In Non-Precious Metal Catalysts For PEM Fuel Cell Applications," *The Canadian Journal of*

Chemical Engineering, vol. 91, pp. 1881-1895, 2013.

[21] P. Pei and H. Chen, "Main factors affecting the lifetime of Proton Exchange Membrane fuel cells in vehicle applications: A review," *Applied Energy,* vol. 125, pp. 60-75, 2014.

[22] V. S. Bagotsky, "Fundamentals of Electrochemistry," in *Fundamentals of Electrochemistry*, Hoboken, John Wiley & Sons, Inc., 2006, pp. 530-531.

[23] Y. Zayachuk, A. Manhard, M. H. J. 't Hoen, W. Jacob, P. A. Zeijlmans can Emmichoven and G. van Oost, "Depth profiling of the modification induced by high-flux deuterium plasma in tungsten and tungsten-tantalum alloys," *Nuclear Fusion,* vol. 54, no. 123013, 2014.

[24] H. Y. Xu, G. N. Luo, H. Schut, Y. Yuan, B. Q. Fu, A. Godfrey, W. Liu and G. D. Temmerman, "Enhanced modification of tungsten surface by nanostructure formation during high flux deuterium plasma exposure," *Journal of Nuclear Materials*, vol. 447, pp. 22-27, 2014.

[25] M. Laurent-Brocq, N. Job, D. Eskenazi and J.-J. Pireaux, "Pt/C catalyst for PEM fuel cells: Control of Pt nanoparticles characteristics through a novel plasma deposition method," *Applied Catalysis B: Environmental,* vol. 147, pp. 453-463, 2014.

[26] S. M. M. Coelho, F. D. Auret, P. J. Janse van Rensburg and J. M. Nel, "Unexpected properties of the inductively coupled plasma induced defect in germanium," *Physica B,* vol. 439, pp. 97-100, 2014.

[27] O. V. Ogorodnikova, J. Roth and M. Mayer, "Deuterium retention in tungsten in dependence of the surface conditions," *Journal of Nuclear Materials,* Vols. 313-316, pp. 469-477, 2003.

[28] T. Takimoto, K. Takeshita, S. Nakamura and T. Okumura, "Effects of plasma-induced defects on electrical characteristics of AlGaN/BaN heterostructure before and after low-temperature annealing," *Thin Solid Films,* vol. 557, pp. 212-215, 2014.

[29] R. C. Egeberg, S. Ullmann, I. Alstrup, C. B. Mullins and I. Chorkendorff, "Dissociation of CH4 on Ni(1 1 1) and Ru(0 0 0 1)," *Surface Science,* vol. 497, pp. 183-193, 2002.

[30] H. Uetsuka, K. Watanabe, H. Kimpara and K. Kunimori, "Structure Sensitivity in the Kinetics and the Dynamics of CO Oxidation over Stepped Pd(335) Studied by the Molecular Beam Infrared Chemiluminescence Technique: Determination of Working Sites during the Steady-State Reaction," *Langmuir,* vol. 15, pp. 5795-5799, 1999.

[31] B. Hammer, "Bond Activation at Monatomic Steps: NO Dissociation at Corrugated Ru(0001)," *Physical Review Letters,* vol. 83, no. 18, pp. 3681-3684, 1999.