

MINIATURE FUEL CELL WITH MONOLITHICALLY FABRICATED Si ELECTRODES - Au-Pd-Pt MULTILAYER CATALYST -

Ryo Shirai¹, N.Vasiljevic², and Masanori Hayase¹

¹Tokyo University of Science, Japan
2641 Yamazaki, Noda, Chiba 278-8510, Japan

²University of Bristol, United Kingdom
Tyndall Avenue, Bristol BS8 1TL, UK

E-mail: mhayase@rs.noda.tus.ac.jp

Abstract. A novel catalyst layer structure is proposed for our miniature fuel cells. In our fuel cells, conventionally porous Pt was used as a catalyst layer. In order to reduce the Pt amount, instead of porous Pt, porous Pd was formed on a Si chip and Pt was deposited atomically on the Pd by UPD-SLRR (Under Potential Deposition – Surface Limited Redox Replacement). The Pd-Pt catalyst showed satisfying performance, besides high CO tolerance was observed. Though the Pd-Pt catalyst is quite promising, Pd is also a rare metal and reduction of Pd amount is necessary. In this study, a novel Au-Pd-Pt catalyst formation strategy is proposed by UPD-SLRR, and the layered structure is preliminary fabricated.

1. Introduction

We have developed miniature fuel cells with monolithically fabricated Si electrodes (Fig.1). In the fuel cells, two Si electrodes with porous Pt catalyst layer, which Pt usage was $3.6\text{mg}/\text{cm}^2$, were hot-pressed onto either side of a PEM (polymer electrolyte membrane), and the prototype fuel cells showed promising performances of over $500\text{mW}/\text{cm}^2$ output at 313K with $\text{H}_2\text{-O}_2$ supply [1-3]. However, recent improvements of Li-ion battery are lowering expectation to the miniature fuel cells, and miniature fuel cell products are not available yet commonly. The advantage of the fuel cell, i.e. clean and efficient energy source, should be strengthened.

Bio-mass is an ultimate energy source, and effective utilization of the bio-mass is desired. Hydrogen can be produced by gasification of the bio-mass, but gasification is performed in reducing environment, and high CO concentration in the bio-mass derived hydrogen is inevitable. To utilize the bio-mass derived hydrogen, catalyst poisoning by CO is problematic. In the PowerMEMS 2013, we reported that our Pd-Pt catalyst had promising feature [3]. Though the catalyst layer used only $6\mu\text{g}/\text{cm}^2$ of Pt, high tolerance to CO was obtained. But the catalyst layer was based on the porous Pd, and more than $1.5\text{mg}/\text{cm}^2$ of Pd was used. Pd and Pt are rare metals, and both amounts should be minimized.

In this study, a novel Au-Pd-Pt multilayer catalyst is proposed as shown in figure 2. Though Au is also a precious metal, reserve of Au is much larger than Pd and Pt, and porous Au can be formed on a Si substrate by similar process to porous Pt [4].



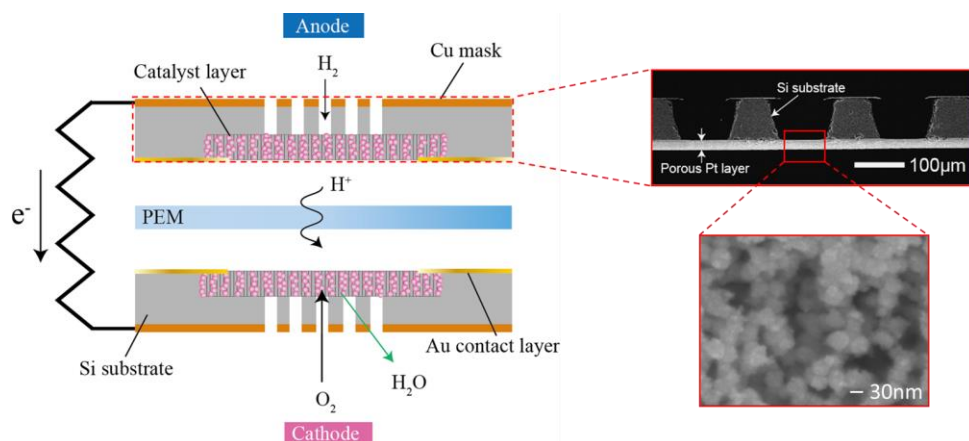


Figure 1. Miniature fuel cell with monolithically fabricated Si electrodes. Porous Pt catalyst layer was formed on a Si substrate, and fuel channels were opened by plasma etching.

2. Au-Pd-Pt Multilayer Catalyst

There is no clear evidence, but it is assumed that high CO tolerance of the Pd-Pt catalyst is realized with sub-monolayer Pt on Pd, and release of absorbed hydrogen from Pd has important role. Hydrogen absorption into Pd is sensitive to the number of atomic layer of Pd, and fine control of Pd and Pt deposition on Au is crucial. In our previous study, sub-monolayer Pt was deposited with Cu-UPD-SLRR (Cu – Under Potential Deposition - Surface Limited Redox Replacement). In this process, formation of a monoatomic layer of Cu on porous Pd was performed by UPD. Then, the deposited Cu was replaced to Pt galvanically, and a sub-monolayer Pt was expected to deposit on porous Pd. But we needed to separate Cu plating bath and Pt plating bath, because simultaneous deposition of Cu and Pt occurs. Because of the two baths limitation, it is difficult to repeat the Cu-UPD-SLRR for Pd multilayer formation. Recently, instead of Cu or Pb, it was reported that UPD hydrogen can be used for SLRR. Hydrogen also absorbs on some metal surfaces and form atomic monolayer at slightly under the equilibrium potential [5]. The H-UPD-SLRR can be performed just in an acidic plating bath containing Pd^{2+} or Pt^{4+} . There is no need to replace the plating bath, and repetition of the atomic layer deposition process will be easy. In this study, basic fabrication strategy of the Au-Pd-Pt multilayer catalyst using H-UPD-SLRR process was examined.

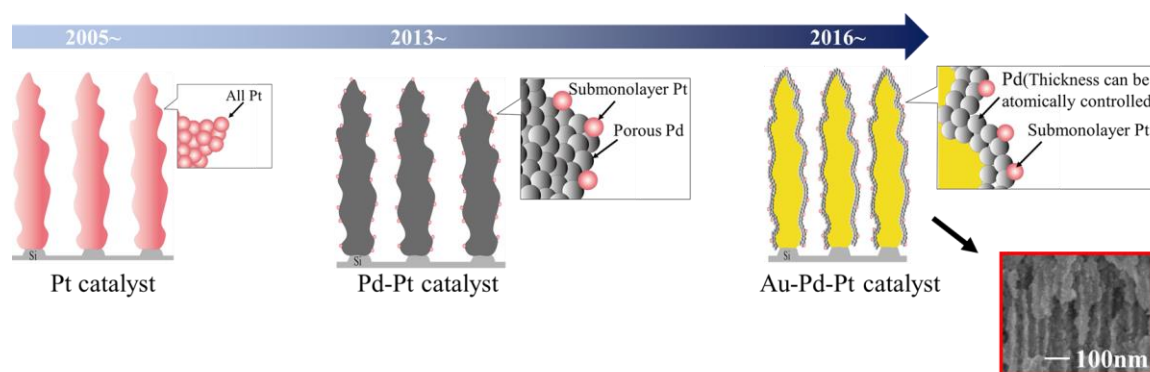


Figure 2. History of our catalyst layer.

Pt catalyst is original porous catalyst. Pt amount was 3.6 mg/cm^2 . Pd-Pt catalyst is sub-monolayer Pt deposited on porous Pd. Pt amount was reduced to $6 \mu\text{g/cm}^2$ and high CO tolerance was obtained. Au-Pd-Pt catalyst will realize that amount of platinum group can be reduced, while expected performance can be maintained. Porous Au can be formed on Si substrate by similar process to porous Pt.

3. Experimental

Conditions for the H-UPD-SLRR Au-Pd-Pt catalyst formation process are shown in Table 1. Figure 3 shows the experimental setup. Au wire was masked by polyester film tapes, and 1cm of Au wire was exposed to the solution. A mercury-mercurous sulfate electrode (MSE) and a Pt wire were used as the reference and the counter electrodes, respectively. An electrolyte solution of 0.1M HClO₄+10μM PdCl₂ was prepared, and the solution was bubbled with nitrogen gas for at least 30 min prior to the experiment to eliminate dissolved oxygen and carbon dioxide. Before the UPD process, the Au wire was cleaned by a piranha solution, then the Au wire was immersed in a 0.1M HClO₄ solution, and the electrode potential was cyclically varied from -1000 to 1500 mV vs. MSE more than 100 times. After the cleaning process, the wire was immersed into the electrolyte solution in a vessel filled with nitrogen gas.

Figure 4 shows the schematic of the H-UPD-SLRR process. H-UPD was performed by applying -600mV vs. MSE. Because the process bath contains Pd ions, bulk electrodeposition also proceeds during the UPD process. To minimize the Pd electrodeposition, UPD process was limited for 1 s. The amount of Pd electrodeposition for 1 s UPD period was estimated to be less than 1% of the electrode surface assuming a monolayer, and hydrogen UPD was assumed to be dominating. Then, the electrical circuit was opened until the electrode potential reached 0 mV vs. MSE. During the circuit was opened, adsorbed hydrogen was replaced by novel metals. This process is called as the SLRR, and sub-monolayer Pd or Pt deposition was expected. Pd multilayer formation was expected by repeating the H-UPD-SLRR process in the Pd process bath. Finally, Pt sub-monolayer deposition was performed by identical way in the Pt process bath.

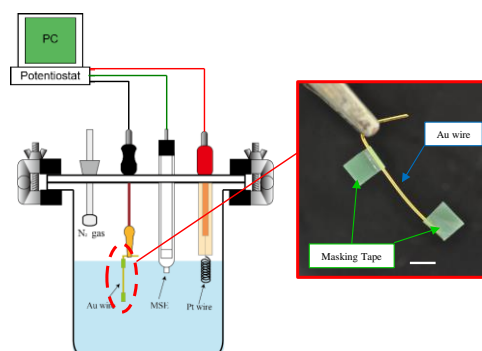


Figure 3. Experimental model of H-UPD-SLRR.

In this time, three-electrode cell was used, and during experiment, nitrogen gas was filled in a vessel because oxygen and carbon dioxide were concerned.

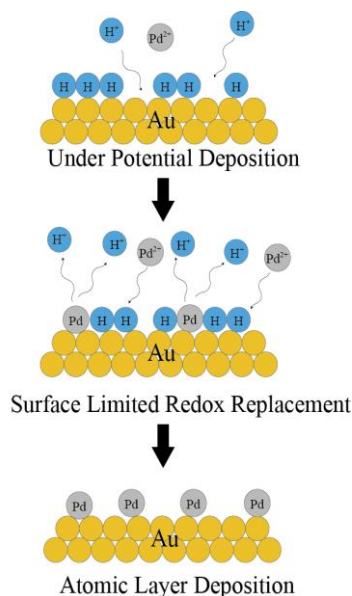


Figure 4. Schematic of the H-UPD-SLRR. In H-UPD-SLRR process, Electrochemical sub-monolayer metal is completed.

Table 1. Condition for atomic layer Pd or Pt deposition on Au wire by H-UPD-SLRR.

Experimental condition	
Pd deposition	
Working Electrode	Au wire
Counter Electrode	Pt
Composition of solution	0.1M HClO ₄ + 10μM PdCl ₂
Negative potential(E ₁)	-600mV vs. MSE
UPD time	1s
Positive potential(E ₂)	0mV vs. MSE
Pt deposition	
Working Electrode	50R Pd + Au wire
Counter Electrode	Pt
Composition of solution	0.1M HClO ₄ + 10μM H ₂ PtCl ₆
Negative potential(E ₁)	-600mV vs. MSE
UPD time	1s
Positive potential(E ₂)	0mV

4. Results and discussion

Figure 5 shows Pd film thickness estimated from H-UPD charges. Figure 6 shows variation of CV (cyclic voltammograms) along Pd deposition cycles. The CV was obtained in a solution of 0.1M HClO₄. The hysteresis became larger along the repetition of the deposition process. Negative current suggests hydrogen adsorption or absorption into Pd, and it is assumed that amount of hydrogen absorption can be modulated.

Figure 7 showed CVs after Pt deposition on the Au wire with 50 Pd deposition cycles. Surprisingly, the hysteresis loop became larger significantly with only one Pt deposition cycle, and Pt catalytic activity was expected. Typical Pt electrode behavior with several peaks was observed with increasing the Pt deposition cycles, but no significant enlargement of the hysteresis loop was obtained.

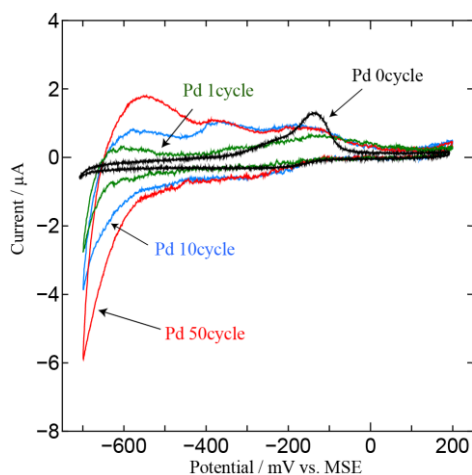


Figure 6. Variation of cyclic voltammogram along the Pd deposition cycles.

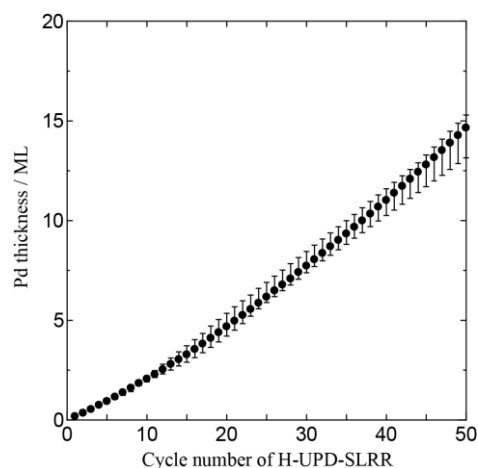


Figure 5. Estimated palladium thickness was evaluated by multiplying current and time during H-UPD.

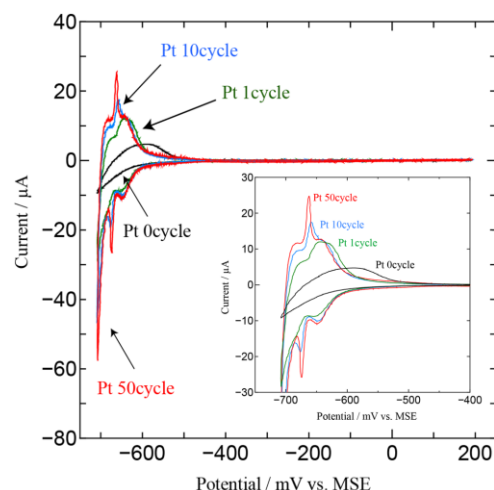


Figure 7. Cyclic Voltammogram after Pt deposition on Au-Pd wire.

5. Conclusion

In this study, we proposed a novel Au-Pd-Pt multilayer catalyst structure, and fabrication process using H-UPD-SLRR was preliminary examined with Au wire. Electrochemical analyses suggested that amount hydrogen absorption in the Pd layer, which associates to CO tolerance, can be controlled by the cycle of Pd deposition process. Pt catalytic activity was also observed with only one cycle of the H-UPD-SLRR deposition process. Further study with porous Au will be performed.

References

- [1] M. Hayase, K. Horikoshi, T.Tajima, *Proc. PowerMEMS2009*, pp. 13-16.
- [2] M. Kobayashi, T. Suzuki, M. Hayase, *J. Power Sources*, **267** (2104), pp. 622-628.
- [3] D.Ogura, T. Suzuki, N. Katayama, K. Dowaki, M. Hayase, *Proc. PowerMEMS2013*, 012066.
- [4] Jose. G. A. Brito-Neto, K.Kondo, and M.Hayase, *J. Electrochem. Soc.*, **155**(2008), pp. D78-D82.
- [5] J. Nutariya, M. Fayette, N. Dimitrov, N.Vasiljevic, *Electrochim. Acta*, **112** (2013), pp.813-823.