# Pulse Current Electrodeposition of Nanocatalysts Using Different Waveforms for use in PEMFCs

Shahram Karimi
Alternative Energy Engineering, Lambton College
1457 London Rd, Sarnia, ON, N7S 6K4 Canada

Traditional deposition techniques such as spraying, brushing and rolling have been shown to be unsuitable for fabrication of MEAs with low catalyst loading and high catalytic activity [1,2]. Accordingly, non-traditional methods have been devised and utilized to attain better results. One such method is pulsed electrodeposition in which nanoparticles are selectively deposited where they are needed. Although the superiority of the above technique has been proven in other applications such as nickel and copper electrodeposition, its use in fuel cells has been limited to conventional square-pulse waveform [3,4]. The influence of other types of waveforms on size, distribution and catalytic activity of nano-catalysts has not been reported in the literature.

In the present study, an attempt was made to fabricate MEAs using pulse current electrodeposition employing four different pulse waveforms—ramp-up, ramp-down, triangular and square—to examine their influence on the quality of electrodeposits in terms of catalytic activity, dispersion and size. Electrodeposition was carried out at 25 °C in a flow cell using an aqueous platinum solution containing 0.05 M tetraamineplatinum (II) chloride. A galvanostat (PAR 263A, Princeton Applied Research) was employed to control both the pulse waveform and the deposition current density. A thin layer of the catalyst 0.35 ± 0.02 mg Pt $cm^{-2}$ was electrodeposited on wet-proofed carbon substrates and was then compared with commercial electrodes with platinum loadings of 1.0 mg $cm^{-2}$. Electrodeposited catalyst layers were characterized using SEM, TEM, XRD and CV.

Figure 1 compares the performance of a commercial E-TEK MEA with those prepared by pulse current electrodeposition. The best performance was delivered by the MEAs prepared with a ramp-down waveform. The MEAs fabricated using a triangular waveform performed equally well. This is primarily attributed to the deposition of smaller platinum crystallites with higher effective area for catalyzation. When a rectangular waveform is utilized, the deposition current density is instantaneously increased to its maximum and then kept constant for the duration of the pulse on-time. The continuous high cathodic current encourages crystal growth, leading to formation of fewer nuclei and, subsequently, a marked decrease in the effective surface area of the deposited platinum [5]. On the other hand, when a ramp-down waveform is applied, the peak deposition current density is sharply increased to promote nucleation, followed by a gradual decrease to inhibit crystal growth, while new nuclei can still be formed. Similar to ramp-up, the application of a triangular waveform results in a sharp increase at the beginning of the pulse, leading to the creation of high concentration overvoltage at the electrolyte-electrode interface, causing the electrodeposition process to be dominated by nucleation. As the electrodeposition continues, however, the concentration of the electroactive species at the interface begins to decrease, resulting in a system that is now dominated by crystal growth. However, as soon as the peak deposition current density is reached, it changes direction and nucleation becomes the dominant process. This ensures a well-dispersed catalyst layer with high active surface area [5].

Figure 2 presents TEM images and their corresponding histograms of platinum particles deposited using three different pulse current waveforms all with a peak current density of 400 mA $cm^{-2}$, a duty cycle of 4% and a catalyst loading of 0.35±0.02 mg Pt $cm^{-2}$. Catalyst layers prepared by ramp-down and triangular waveforms exhibited a more uniform distribution as well as smaller particle size compared with those obtained by the conventional square pulse waveforms [5].

In summary, MEAS prepared by pulse current electrodeposition using a ramp-down waveform deliver a better performance than the commercial MEAs, but only with one-third of the catalyst. This is attributed to the deposition of smaller, better-dispersed and more effective nano-catalysts.

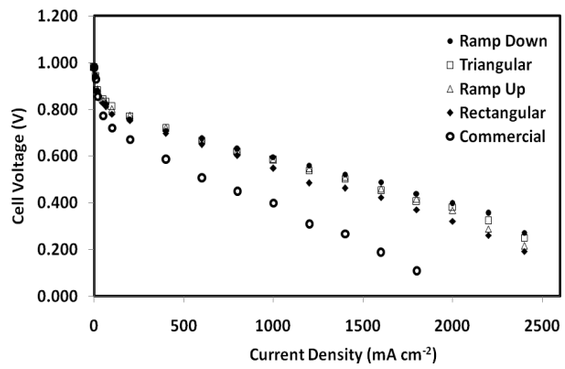


Figure 1 – Cell performance as a function of electrodeposition waveform ($H_2/O_2$, cell temperature of 80 °C and fully humidified fuel and oxidant)

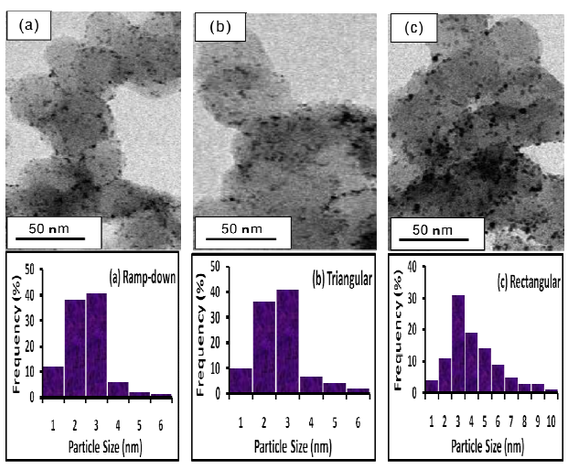


Figure 2 – TEM imgaes and histograms of platinum catalyst electrodeposited using different pulse waveforms (peak deposition current density of 400 mA $cm^{-2}$, 4% duty cycle and 0.35 ± 0.02 mg Pt $cm^{-2}$ per electrode)

## References

1. N. Rajalakshmi & K.S. Dhathathreyan, *Chem. Eng. J.* **129** (2007) 31-40
2. B.M. Koraishy, J.P. Meyers, K.L. Wood, *J. Electrochem. Soc.* **158** (2011) B1459-1471
3. W. Zhu, J.P. Zheng, R. Liang, B. Wang, C. Zhang, G. Au, E.J. Plichta, *Electrochem. Commun.* **12** (2010) 1654-1657
4. W.-J. Beom, R.S. Kalubarme, K.-S. Yun, C.-J. Park, *Appl. Surf. Sci.* **257** (2011) 9694-9702
5. S. Karimi & F.R. Foulkes, *Electrochem. Commun*. **19** (2012) 17-20