Electrochemical Deposition of Nanoparticles on Metallic and Carbonaceous Substrates: A Mathematical Model

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A simple method based on pulse current electrodeposition utilizing different waveforms was developed for fabricating membrane-electrode assemblies (MEAs) with low platinum loading for use in proton exchange membrane fuel cells. It was found that both peak deposition current density and duty cycle control the nucleation rate and the growth of platinum crystallites. Based on the combination of parameters used in this study, the optimum conditions for pulse electrodeposition were found to be a peak deposition current density of 400 mA cm^{-2}, a duty cycle of 4%, and a pulse generated and delivered in the microsecond range using a ramp-down waveform (Figs 1 and 2). MEAs prepared by the above method using the ramp-down waveform show performance comparable with commercial MEAs that employ several times the loading of platinum catalyst. The thickness of the pulse electrodeposited catalyst layer is about 5-7 µm, which is ten times thinner than that of commercial state-of-the-art electrodes. Electrodeposition of Nickel from a modified Watt's bath onto metallic substrates also was carried out to show the generality of the aforementioned technique.

A comprehensive mathematical model based on the works reported by Molina et al. [1] and Milchev [2] was developed to predict the influence of different electroplating parameters, including peak deposition current density, pulse waveform, pulse on-time and pulse off-time, on the size and catalytic activity of the resulting catalyst layers. The model is based on progressive nucleation and considers contributions from both nucleation and growth currents [3]. A comparison between the model and experimental results revealed a reasonably good agreement at peak deposition current densities of 400 mA cm^{-2} or lower, where the average grain size of platinum nanoparticles was greater than 50 nm. However, at higher peak deposition current densities, the difference between the model and experimental results became more pronounced. According to the model, at high peak deposition current densities and low duty cycles, the ramp-down waveform yielded the highest nucleation rates (Fig. 3), confirming the experimental findings in which platinum nanoparticles generated with the above waveform produced the smallest average grain size.

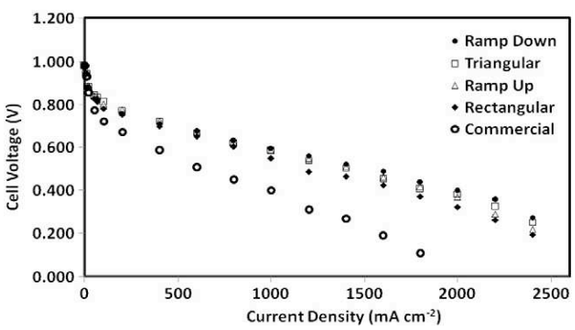

Figure 1 Fuel cell performance as a function of electrodeposition waveform (running on fully humidified hydrogen and oxygen at a cell temperature of 80 °C)

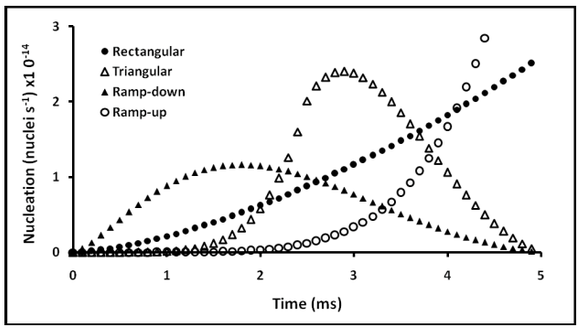

Figure 2 Nucleation rate for different waveforms with a peak deposition current density of 400 mA cm^{-2}, pulse on-time of 5 ms and 100 Hz (showing the first half-cycle)

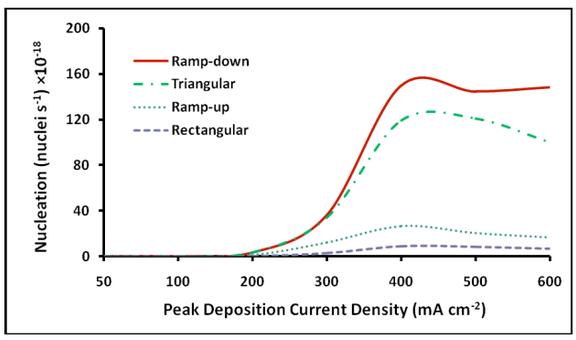

Figure 3 Nucleation rate for various waveforms with a pulse on-time of 1.0 ms, pulse off-time of 49 ms, and 200 pulse cycles at different peak deposition current densities

References

1. J. Molina, B.A. Hoyos, *Electrochim. Acta*, 54 (2009) 1784-1790
2. A. Milchev, "Electrocrystallization: Fundamentals of Nucleation and Growth" 2002, Kluwer Academic Publisher, 189-215
3. S. Karimi, F.R. Foulkes, *Journal of the Electrochemical Society* **159** (11) (2012) D659-D670