

In-situ Transmission Electron Microscopy for Characterizing Electrochemical Deposition of Nanostructured Materials

Jie Yang¹, Carmen M. Andrei², Gianluigi A. Botton^{2,3} and Leyla Soleymani^{1,4}

¹ School of Biomedical Engineering, McMaster University, Hamilton, Canada

² Canadian Centre for Electron Microscopy, McMaster University, Hamilton, Canada

³ Department of Materials Science and Engineering, McMaster University, Hamilton, Canada

⁴ Department of Engineering Physics, McMaster University, Hamilton, Canada

In-situ electron microscopy of liquid samples has been under intense investigation over the past few years due to the advantages that it offers for imaging samples in their native environments. Real-time observation of processes such as electrodeposition [1], Lithium battery cycling [2], and biomaterials and biological molecule interactions [3] is possible through in-situ electron microscopy of liquid samples, and has the potential to significantly improve our understanding in these areas.

In the field of biosensing, improving the analytical sensitivity of devices is critical for moving these platforms from the research lab to clinical applications. This can be achieved by increasing the capture efficiency of biosensors by tuning the structure of biosensing surfaces [4]. In order to develop these nanostructures with optimal capture efficiency, a detailed understanding of the growth mechanism is of great importance. In-situ electron microscopy of liquid samples provides the opportunity to observe the electrodeposition process in real time with nanometer resolution; however, electron beam damage remains a critical obstacle in using in-situ electron microscopy for better understanding electrodeposition in liquid [5].

We have applied an in-situ transmission electron microscopy (TEM) system to observe the electrodeposition process of noble metals (gold and palladium) on carbon electrodes. The TEM compatible holder (Poseidon 500, Protochips Inc., Raleigh, NC, USA) has a miniaturized liquid cell, which confines the samples in between two silicon nitride membranes, through which the samples were imaged. This holder, with built-in electrical and fluidic circuitry, enables us to simultaneously collect electrical signals and electron micrographs during the deposition process [6]. We firstly evaluated the effect of electron beam dose on homogenous nucleation and growth of gold nanoparticles under different beam doses to identify suitable dose for the in-situ studies. The system was further evaluated by studying the electrochemical growth kinetics of gold nanoparticles in-situ and comparing this with theoretical calculations based on current transients. We further extended this study to the electrodeposition of palladium and studied the effect of hydrogen chloride, used as the supporting electrolyte, on the structural evolution of the deposits.

Both of the electrodeposition of gold and palladium on carbon demonstrate the typical structures obtained under ex-situ electrochemical deposition conditions. In the palladium deposition experiments, the hydrogen chloride reduces the growth rate of palladium nanostructures by showing lower current and less dense deposition compared to that from electrolytes without hydrogen chloride. In addition, the morphology of the deposition in hydrogen chloride appeared more spike-like whereas the palladium deposited without hydrogen chloride was more smooth and spherical.

In conclusion, we have applied in-situ electron microscopy to investigate processes of noble metal

electrodeposition by properly tuning the beam dose. The electrodeposition of gold on carbon demonstrates an instantaneous nucleation and followed by a three dimensional diffusion limited growth until coalescence. The hydrogen chloride as supporting electrolyte plays an essential role on the final morphology and distribution of the palladium deposition.

References:

- [1] M J Williamson *et al*, Nature Materials, 2 (2013), p. 532.
- [2] M Gu, *et al*, Nano Letters, 13 (2013), p. 6106.
- [3] S M Hoppe, *et al*, Langmuir, 29 (2013), p. 9958.
- [4] L Soleymani *et al*, Nature Nanotechnology 4 (2009), p. 844.
- [5] T J Woehl *et al*, Ultramicroscopy, 127 (2013), p. 53.
- [6] R R Unocic *et al*, Microscopy and Microanalysis, 20 (2014), p. 452.
- [7] The authors acknowledge funding from NSERC under the Discovery Program. Dr. G. Silveira, Dr. A. Korinek and A. Duft are thanked for their helpful contributions to this work.

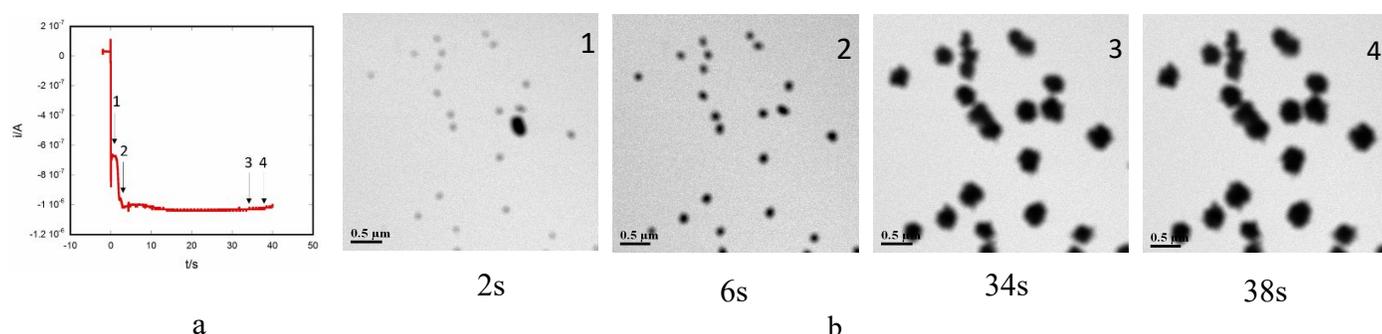


Figure 1. Current transient curve and corresponding bright-field STEM images showing the in-situ electrodeposition of Au on carbon under a fixed potential of -0.6V for 200s. Images 1, 2, 3, 4 in b are related to the time points indicated by the arrows in the current vs. time curve in a.

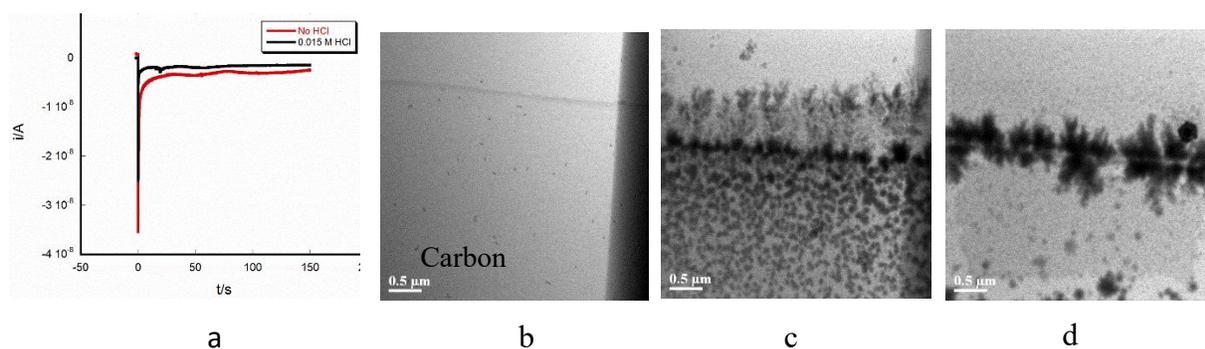


Figure 2. Current transient curve and bright-field STEM images showing the in-situ electrodeposition of palladium on carbon in electrolyte with and without hydrogen chloride (HCl). b. The initial carbon electrode in electrolyte before electrodeposition. c. Morphology of the palladium structure after in-situ electrodeposition in electrolyte without HCl; d. Morphology of the palladium structure after in-situ electrodeposition in electrolyte with HCl.