doi:10.1017/S143192761400926X
Microsc. Microanal. 20 (Suppl 3), 2014

Tuning Electrodeposition Parameters for Tailored Nanoparticle Size, Shape, and Morphology: An *In Situ* ec-STEM Investigation

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Advances in vacuum-tight *in situ* liquid cell TEM systems have attracted significant attention because of the ability to directly interpret chemical and electrochemical reactions within their native liquid environments [1]. Conducting quantitative *in situ* electrochemistry experiments within the S/TEM is feasible using the relatively new platform of *in situ* electrochemical S/TEM (ec-S/TEM). In this approach, microfabricated electrochemical cells are used to seal the liquid electrolyte between two silicon microchips with electron transparent SiN_x viewing membranes and micropatterned electrodes. The electrochemical microchip devices used in the present study have platinum reference and counter electrodes and a glassy-carbon working electrode (GC-WE) that are directly patterned on the microchip device. Figure 1a shows a schematic of the microfabricated electrochemical cell and vacuum-tight *in situ* TEM holder assembly. SEM images of the spacer microchip and electrochemical microchip are shown in Figure 1b and Figure 1c, respectively. The GC-WE is microfabricated onto the SiN_x viewing window, which permits the direct visualization of electrochemical reactions occurring directly on the electron transparent glassy-carbon (Figure 1d). Quantitative electrochemical measurements can be performed using these small-scale electrochemical devices via techniques such as cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy, with no adverse effects from the electron beam [2]. In the present study, this method is used to investigate the dynamics of crystal nucleation and growth mechanisms. Moreover, we demonstrate how electrodeposition parameters (CV scan rate) can be adjusted to tailor the size-scale and morphology of electrodeposited nanoparticles.

It has been previously shown that this approach can be use to reduce copper from a $CuSO_4$-based electrolyte onto a gold working electrode, the dynamics of which were captured with TEM imaging [3]. Aberration-corrected HAADF-STEM imaging (C_s corrected FEI Titan S/TEM operating at 300kV), with its increased spatial resolution and the benefits of Z-contrast STEM imaging, was used to characterize the electrodeposited Cu nanoparticle nucleation and growth events. As a result of the Cu nanoparticles having a higher atomic number (Z-29), as compared to the glassy-carbon working electrode (Z-6), HAADF-STEM imaging proves to be beneficial because Cu will have a more intense contrast as compared to the "low Z" glassy carbon background. Figure 2 shows a typical CV from a 0.2M $CuSO_4$ electrolyte acquired at sweep rates of 50 mV/s (blue) and 100 mV/s (red). The CV data shows several characteristic cathodic and anodic peaks that correlate with Cu electrodeposition and electrodissolution, respectively. During the CV experiments, HAADF-STEM imaging captured Cu nucleation on the GC-WE and at the glassy-carbon/SiN_x interface. The CV scan rate had a profound effect on the size scale and distribution of the electrodeposited nanoparticles, with higher scan rates resulting in smaller nanoparticles, as shown in Figures 3a-c and Figure 3d-f for scan rates of 50 mV/s and 100 mV/s, respectively. The low electron beam current (0.23 nA) and dose rate (6.67 e^-/nm^2-s) used in these experiments is below the threshold for Cu reduction by the electron beam, which is clearly evident by the lack of Cu nanoparticles on the SiN_x viewing window adjacent to the edge of the GC-WE interface. It is expected that under higher electron beam currents and higher electron dose rates, Cu can

readily be reduced on the SiN_x membranes from the $CuSO_4$ electrolyte [4]. This work provides the framework for directly interpreting the fundamental mechanisms of crystal nucleation and growth [5].

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[5] Research supported by Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

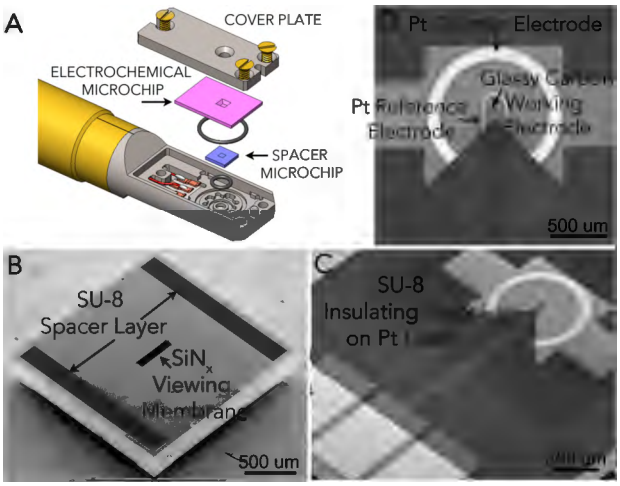

Figure 1. a) Schematic of the *in situ* ec-S/TEM system. SEM images of the b) spacer microchip and c-d) electrochemical microchip [2].

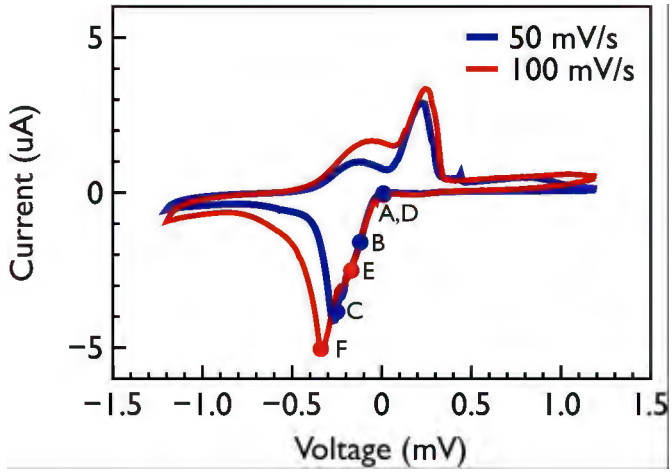

Figure 2. CV from a 0.2M $CuSO_4$ electrolyte acquired at scan rates of 50 mV/s (blue) and 100 mV/s scan rate (red).

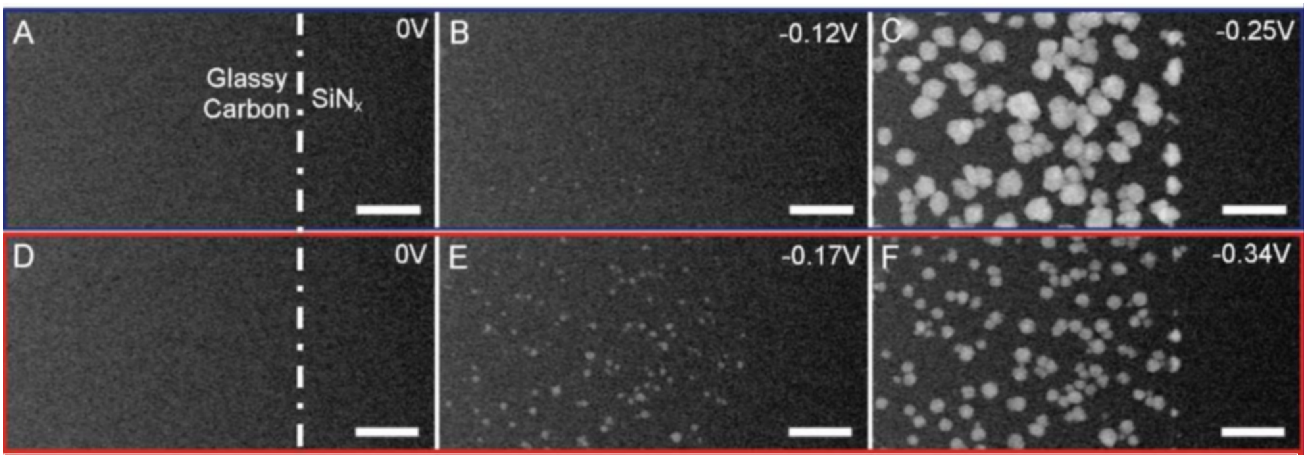

Figure 3. Series of HAADF-STEM images showing the electrodeposition of Cu on a glassy-carbon working electrode under different CV scan rates: a-c) 50 mV/s and d-f) and 100 mV/s. Scale bar is 2 μm.

https://doi.org/10.1017/S143192761400926X Published online by Cambridge University Press