

Liquid Cell TEM Studies of Galvanic Displacement Reactions in Aqueous Solutions

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Galvanic displacement reactions are a versatile approach to achieving sophisticated nanostructure engineering. One key application is the formation of nanopatterned surfaces, such as Ni decorated with Pd nanoparticles, which act as highly catalytic substrates for subsequent electroless deposition [1]. Another application is the formation of magnetic nanoparticles with axial or radial compositional modulation [2] and a variety of applications [3]. Precise engineering of the final morphology relies on a deep understanding of the reaction pathways involved. Although *ex situ* microscopies provide critical information, the ability to record the process as it takes place is expected to contribute to a deeper understanding [4]. Liquid cell TEM, especially when coupled with electrochemical control and analytical capabilities, provides the needed tool for measuring structural and chemical changes in liquids [4-6]. Here, we use *in situ* liquid cell TEM to examine a model system, galvanic deposition of Pd nanoparticles on Ni in an acidic solution, and extend our materials system toward other metal films.

We examined galvanic displacement reactions in samples consisting of 20-50 nm thick Ni films deposited by electron beam evaporation onto a 50 nm thick silicon nitride membrane that makes up one viewing window of the liquid cell. These films were imaged in a FEI CM30 TEM, operated at 300 kV [7], in a continuous flow Hummingbird Scientific LC-TEM holder [8, 9]. Deionized water was introduced into the liquid cell to remove air bubbles, after which a solution was introduced containing 0.1M HCl or H₂SO₄ with ppm levels of PdSO₄. We used low dose imaging protocols and verified that the solutions can be examined for long periods (hours) without visible beam effects. We observe two different reactions. At long times, we see corrosion of the Ni film under the beam, presumably due to reactive species produced by radiolysis. **Figure 1** presents slow Ni corrosion in deionized water (pH = 7) under irradiation, in an example where PdSO₄ is not introduced. This process took place at a flow rate of 5 μ l/min and zero voltage applied to the electrode. The electron beam causes dissolution by creating reactive radiolytic species in water, i.e. hydrated electrons and radicals, which convert Ni to ions [5, 6, 9]. Dissolution appears to take place via the general corrosion mode (Fig. 1a). To obtain quantitative reaction kinetics, the average image brightness was analyzed as a function of irradiation time (Fig. 1b), showing an induction time (Fig. 1c). The second reaction observed is the galvanic displacement reaction itself (**Figure 2**). Here, nucleation and growth of Pd particles tens of nm in diameter is visible when 0.1M H₂SO₄ (pH = 1) with ppm levels of PdSO₄ is flowed (Fig. 2c). Simultaneously, Ni dissolution takes place. Compared to the reaction without the Pd additive, Ni dissolution is accelerated in the presence of Pd; this is as expected since Ni goes into solution as Pd precipitates (Fig. 2a). In the example shown, preferential dissolution is visible at grain boundaries. The dissolution rate increases with the flow rate (Fig. 2b). Solution pH and additives also change the overall reaction rate of the film.

We will describe the kinetics of these processes in solutions of different pH and Pd concentration, and also discuss corrosion reactions in other metals, Cu, Au, and Pt. Measurements of the local variations - morphology, composition, nucleation sites (grain boundaries vs. within grains) and the etching rate of the substrate as a function of solution composition, pH, and thickness - provide insights into galvanic reaction

processes with good spatial and temporal resolution that can help towards morphological control of the final nanostructured surface.

References:

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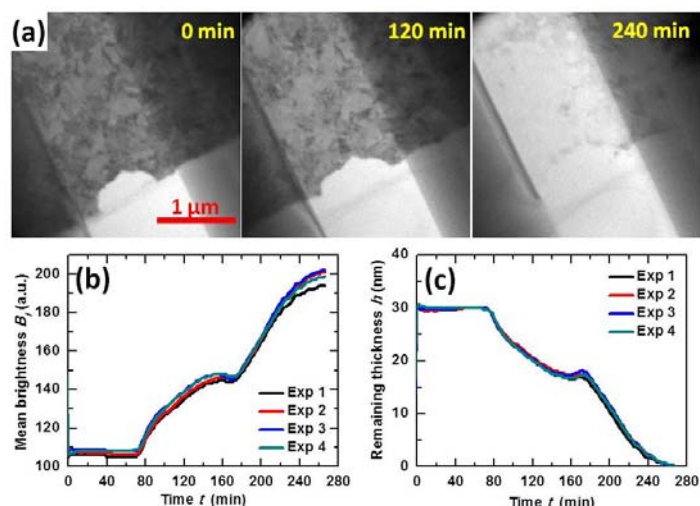


Figure 1. (a) Dissolution of a Ni film in deionized water (pH = 7) at a flow rate of 5 $\mu\text{l}/\text{min}$ and constant irradiation. (b) Measured brightness changes of ~ 30 nm-thick Ni film as a function of the irradiation time. Several experiments are shown. (c) Estimated remaining thickness of the Ni films.

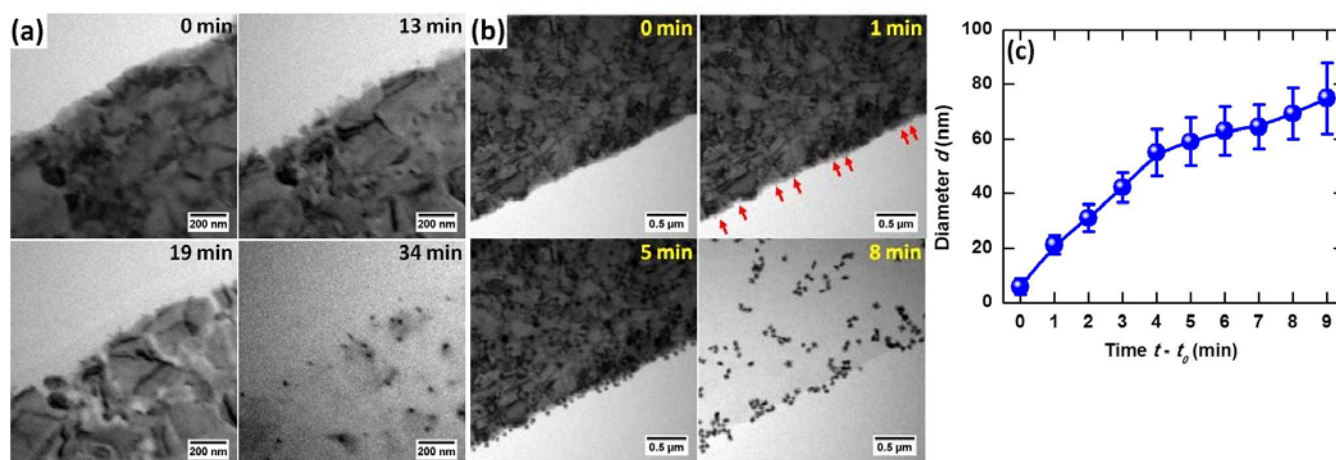


Figure 2. (a) Formation of Pd particles and simultaneous dissolution of Ni film in 0.1M H_2SO_4 (pH = 1) solution with ppm levels of PdSO_4 and without electrolyte flow. (b) The same solution at higher flow rate. (c) Size evolution of Pd particles versus time, with t_0 the time at which particles are first visible.