

Electroless Deposition of Palladium at Bare and Templated Liquid/Liquid Interfaces

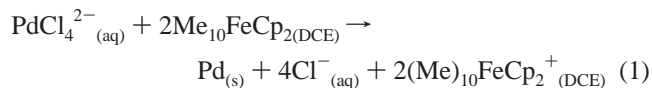
Robert A. W. Dryfe,* Andrew O. Simm, and Brett Kralj

Department of Chemistry, University of Manchester Institute of Science & Technology, P.O. Box 88, Manchester M60 1QD, United Kingdom

Received July 29, 2003; E-mail: robert.dryfe@umist.ac.uk

The growth, and subsequent characterization, of metallic nanoparticles has received much attention in recent years.^{1,2} Solution phase methods of deposition, generally involving the reduction of a precursor cation, have been developed from two-phase liquid/liquid³ (L/L) and colloidal systems.⁴ Electrochemical methods have also been employed to reduce metals on solid substrates,⁵ with templates such as porous films^{6,7} or lyotropic liquid crystalline phases⁸ controlling the deposit structure on the nanometer scale. Two-dimensional films have also been grown electrochemically by bringing a working electrode in close proximity to a L/L interface.^{9,10} Here, we report the combination of various aspects of the above approaches to induce the electroless deposition of Pd at the L/L interface, with and without the presence of a membrane template.

An aqueous solution of ammonium tetrachloropalladate is brought into contact with a solution of decamethylferrocene in 1,2-dichloroethane (DCE).¹¹ Within a few minutes, the straw-yellow aqueous phase loses its color, accompanied by a change in color of the organic phase from amber to green. The simultaneous appearance of a dark gray film at the L/L interface suggests that the following heterogeneous reduction is operative:



where $\text{Me}_{10}\text{FeCp}_2$ denotes the ferrocene derivative. The formation of metallic Pd was supported by filtration of the solid species, using a 100 nm pore diameter track-etched polyester membrane, and energy-dispersive X-ray analysis of the solid residue, following washing with water and acetone (Figure 1). The formation of metallic Pd is consistent with the reduction potentials of the relevant species, because the E^0 value of the Pd precursor in 1 M chloride solution is ca. 0.55 V more positive than that of the ferrocene derivative in DCE.^{12,13}

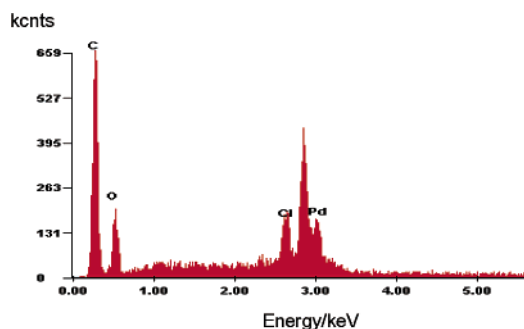


Figure 1. Energy dispersive X-ray analysis obtained for the metallic residue formed at the L/L interface, following filtration.

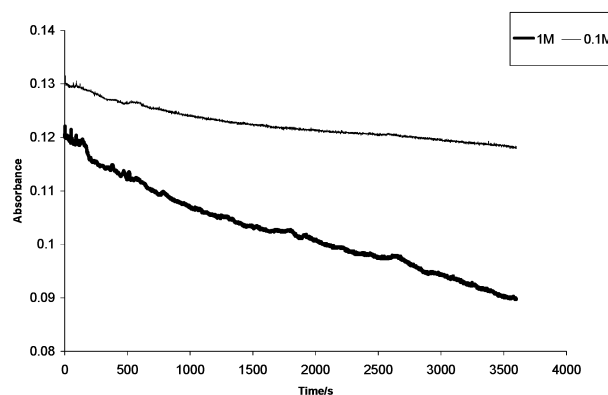


Figure 2. Time-dependence of the absorption maximum for 1 mM aqueous phase tetrachloropalladate solution, on contact with DCE containing 2 mM decamethylferrocene. The DCE phase in both cases contained 0.1 M tetrabutylammonium perchlorate. The aqueous phase in the upper trace contained 0.1 M lithium perchlorate and 1.0 M lithium chloride. In the lower trace, the aqueous phase contained 1.0 M lithium perchlorate and 0.1 M lithium chloride. The aqueous phases in both cases also contained 0.05 M lithium sulfate.

Both the kinetics, and ultimately the equilibrium position, of a heterogeneous electron-transfer process such as (1) ought to be a function of the interfacial potential, $\Delta\phi$, of water relative to DCE. A common ion, such as perchlorate, controls $\Delta\phi$ via:¹⁴

$$\Delta\phi = \Delta\phi^{\circ'} + \frac{RT}{zF} \ln \frac{a_{i,\text{org}}}{a_{i,\text{aq}}} \quad (2)$$

where $\Delta\phi^{\circ'}$ is the formal distribution potential of ion i between water (aq) and DCE (org) and other symbols have their usual meanings. Equation 2 implies that an increase in the interfacial potential results when the aqueous phase perchlorate concentration exceeds that of the organic phase (neglecting ion pairing and the nonideality of the solutions). Given the high overall driving force for Pd deposition, variation in $\Delta\phi$ will be manifested as changes in the rate, rather than the extent, of deposition. This suggestion was borne out experimentally, as the time-dependence of the visible absorption maximum of the aqueous solution reveals (Figure 2).¹⁵ The morphology of the deposit also changed to a denser, more compact form as $\Delta\phi$ was increased, as optical microscopy of the deposits following filtration suggests (see Supporting Information).

The L/L electroless deposition process is potentially very useful, because it may readily be combined with the template deposition approach.^{6,7} Metallic particles are thus dispersed and retained within a porous membrane, whereas the deposits formed at the bare interface agglomerate to form ill-defined structures.

We have recently reported the potentiostatically controlled growth of dispersed Pd by deposition at the alumina-modified L/L interface,

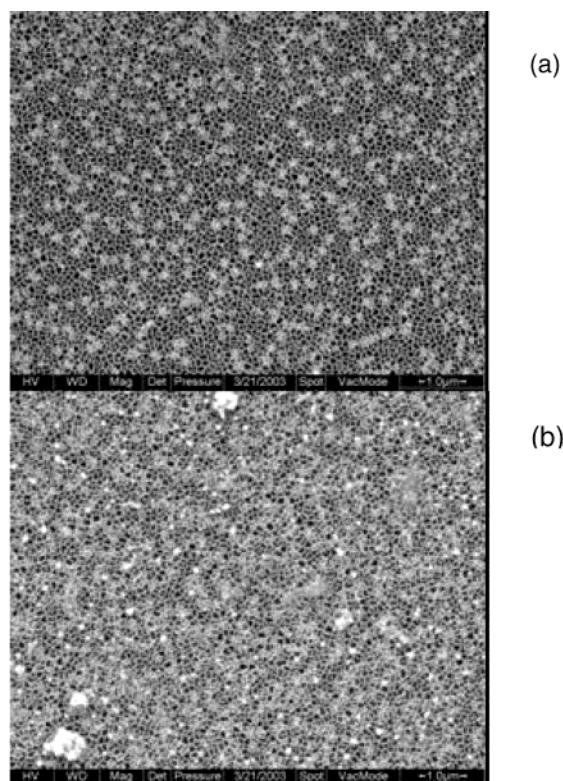


Figure 3. Scanning electron micrographs (SEM) of Pd deposited in alumina membranes using the electroless method, after (a) 5 min and (b) 10 min of contact between the DCE and aqueous solutions. The DCE phase contained 2 mM decamethylferrocene and 0.1 M tetrabutylammonium perchlorate. The aqueous phase contained 1 mM tetrachloropalladate and 0.1 M lithium perchlorate. The lighter color corresponds to Pd; the scale bar in the bottom right of the images corresponds to 1 μm . Note in (b) that some “spillover” of Pd to form larger aggregates is seen.

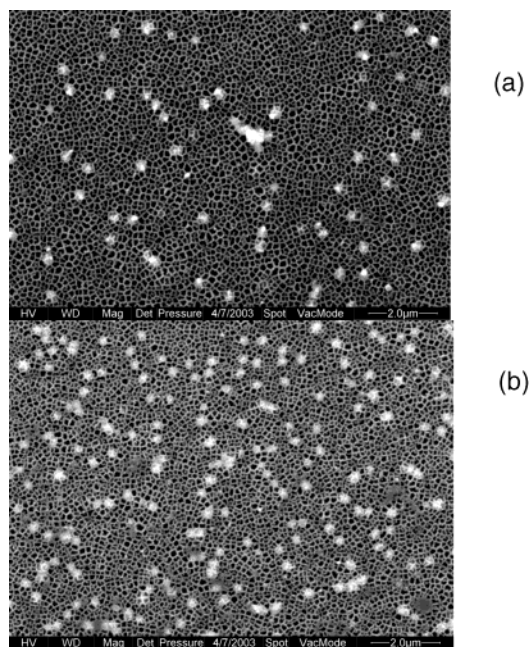


Figure 4. SEM of Pd-loaded alumina membranes after 30 min of electroless deposition. The organic phase was identical to Figure 3. The aqueous phase contained 1 mM ammonium tetrachloropalladate and (a) 0.01 M lithium perchlorate or (b) 0.05 M lithium perchlorate. The scale bar in the bottom right of the images corresponds to 2 μm .

formed by placing the denser DCE phase above the aqueous phase.^{16,17} Transmission electron microscopy suggests that the

particles develop a finite thickness and, hence, electronic conduction pathways may allow deposit growth.¹⁷ We have thus transposed the electroless deposition method to the alumina-modified L/L interface with spontaneous Pd deposition being induced as above, leading to the pale gray membranes taking on a progressively dark gray luster as deposition proceeded. Time- and potential-dependent deposition of Pd within the alumina pores is confirmed by scanning electron microscopy (Figures 3 and 4, also confirmed by energy-dispersive X-ray analyses).¹⁸ Liquid/liquid voltammetry, using the tetraethylammonium ion, was used as a probe of the Pd-loaded membranes (see Supporting Information),¹⁹ indicating that the final deposit retained some porosity. For the early part of the deposition at least, the template gives a simple way to localize the growth of metal particles to a predefined dimension (in this case, 100 nm). Finally, the electroless aspect of this procedure imparts exceeding simplicity to the process.

We believe the route presented here, leading to the facile deposition of nanometer scale metallic particles within an oxide support, will be of technological utility, for example, in catalyst preparation. We are currently investigating the relationship between deposit structure and deposition conditions and the deposition of other materials, in a variety of porous structures.

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Supporting Information Available: Optical microscopy of filtered Pd deposits and liquid/liquid voltammetry of ion transfer as a function of deposition time (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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