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## Energy dispersive-EXAFS of Pd nucleation at a liquid/liquid interface

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**Abstract.** Energy dispersive extended X-ray absorption fine structure (EDE) has been applied to Pd nanoparticle nucleation at a liquid/liquid interface under control over the interfacial potential and thereby the driving force for nucleation. Preliminary analysis focusing on Pd K edge-step height determination shows that under supersaturated conditions the concentration of Pd near the interface fluctuate over a period of several hours, likely due to the continuous formation and dissolution of sub-critical nuclei. Open circuit potential measurements conducted *ex-situ* in a liquid/liquid electrochemical cell support this view, showing that the fluctuations in Pd concentration are also visible as variations in potential across the liquid/liquid interface. By decreasing the interfacial potential through inclusion of a common ion (tetraethylammonium, TEA<sup>+</sup>) the Pd nanoparticle growth rate could be slowed down, resulting in a smooth nucleation process. Eventually, when the TEA<sup>+</sup> ions reached an equilibrium potential, Pd nucleation and particle growth were inhibited.

### 1. Introduction

Nucleation is currently the focus of considerable research activity in crystallisation science and crystal engineering and has been the subject of a number of reviews including [1, 2]. Particle formation from homogeneous solution involves nucleus (or nuclei) formation by self-association of solute molecules and subsequent phase-separation from the bulk solution. By following the solute and solution structure from the under-saturated through the supersaturated state to the regime of spontaneous particle formation, relationships to the structure of the crystallised final products may be established. However, there are considerable experimental challenges arising from the size of the nuclei (sub-nm range), their unknown composition, diffusive or convective movement, as well as the stochastic nature of



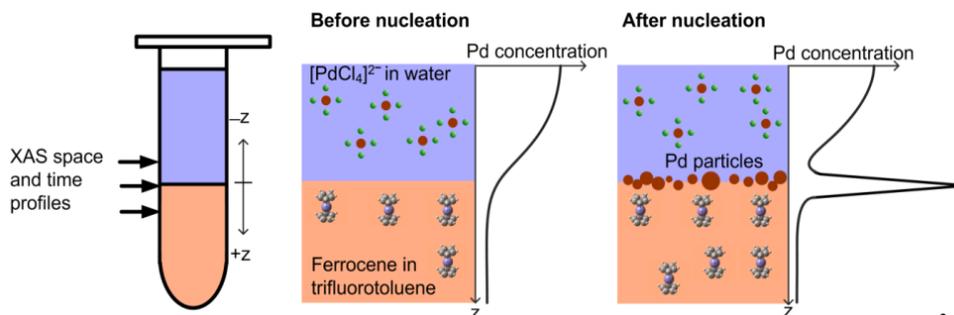
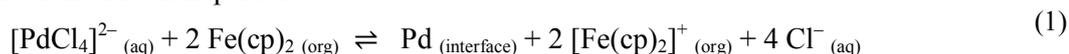


Figure 1. The liquid-liquid system used for studying nucleation. The aqueous layer contains  $[\text{PdCl}_4]^{2-}$  and the organic layer (trifluorotoluene) contains the reducing agent ferrocene. The build-up of metallic Pd nanoparticles is evident from the absorption coefficient profile along the vertical axis, through the aqueous, interfacial and organic phases. Reproduced from Ref. [14] with permission from the Royal Society of Chemistry.

nucleation events and the possibility that nuclei may be short-lived transient species present in very low concentrations [3, 4]. Techniques previously used include coupled solid and liquid state NMR, liquid-cell TEM, analytical ultracentrifugation with UV-Visible spectroscopy, small angle X-ray scattering (SAXS) and X-ray absorption fine-structure (XAFS) [5-8]. We monitor nucleation at a liquid-liquid interface by XAFS (figure 1). The liquid-liquid interface was between an aqueous phase containing  $[\text{PdCl}_4]^{2-}$  and an organic ( $\alpha\alpha\alpha$ -trifluorotoluene, TFT) solution containing ferrocene ( $\text{Fe}(\text{cp})_2$ ).  $[\text{PdCl}_4]^{2-}$  is reduced by  $\text{Fe}(\text{cp})_2$  at the liquid/liquid interface as per equation (1) [9], leading to the nucleation of Pd nanoparticles.



Such an interface between two immiscible liquids provides an elegant avenue to confining homogeneous nanoparticle nucleation and growth to a defined spatial region [9, 10]. This enables targeted analysis by specialist techniques such as XAFS [11-13] while permitting control of the thermodynamic driving force for nucleation by varying the concentration ratio of the redox couple [14]. Nucleation at the liquid/liquid interface results in a high local concentration of particles, providing spectroscopic contrast to enable observation of transient species in the early stages of nucleation [15, 16].

The energy dispersive EXAFS (EDE) work described here used the same experimental system that we employed in [14] where we reported evidence for a randomly fluctuating equilibrium at the liquid/liquid interface by quick EXAFS (QEXAFS) spectroscopy. The use of EDE at SOLEIL's ODE beamline allowed us to characterize the system with higher time resolution than in the previous QEXAFS study at B18/Diamond [14]. In this contribution we will focus on how inclusion of a common ion (tetraethylammonium,  $\text{TEA}^+$ ) in both phases fixes the interfacial potential and thereby achieves additional control over the growth process [17].

## 2. Experimental

Solutions were added to 2 mL Eppendorf safe-lock tubes (diameter 1 cm). The concentrations were 10 mM  $[\text{PdCl}_4]^{-}$  and 100 mM LiCl in the aqueous phase, in conjunction with 20 mM ferrocene and 10 mM [BTTPA][TFPB] in the TFT (organic) phase. In the system where we included  $\text{TEA}^+$ , the concentrations are 100 mM TEACl in the aqueous phase and 1 mM [TEA][TFPB] in the organic phase in addition to the reactants and background electrolytes mentioned above. XAFS data were obtained in transmission mode at the energy dispersive XAFS beamline, ODE at Synchrotron SOLEIL, Gif-sur-Yvette, France [18]. To follow the variation in palladium density the Pd K edge heights were estimated by taking the differences in absorption at 24,331.2 and 24,375.3 eV. We note that the use of a Pd-coated mirror in the ODE beamline optics resulted in a complicated, non-linear transmission function of the spectrometer around the Pd K-edge, which led to a noticeable distortion of the absorption spectrum in the XANES region. However, as the samples were all collected at the ODE beamline the data remains internally consistent. Spectra were collected at different vertical  $z$ -distances

to the interface. Lowest  $z$ -values (in mm) indicate measurements in the aqueous phase (*above* the interface), while highest values stem from the organic phase *below*. Further details on chemicals and EDE experiments are given in the Supporting Information.

### 3. Results and Discussion

An example of a time series of EDE spectra measured at a fixed position at the interface ( $z = 0.05$  mm) under conditions of supersaturation, but below the onset of spontaneous nucleation is shown in figure 2a and S1. The edge heights varied significantly with time, indicating Pd concentration fluctuations across the width of the beam ( $300 \mu\text{m}$ ), as expected for a stochastic nucleation equilibrium. A further example of the metastable state formation is shown in figure S2.

The time series profiles were monitored at several other distances relative to the interface ( $z$  values of 0.00, 0.05, 0.10, 0.15 and 0.20 mm). Edge height profiles as a function of time are plotted in figure 2b. Near the bulk of the aqueous phase ( $z = 0.00$  mm), there is a brief induction period of  $\sim 40$  minutes followed by density fluctuations over a period of 5-7 h. Nearer the interface ( $z = 0.05$  to 0.15 mm) these fluctuations were also visible and became more pronounced closer to the interface. The organic phase is at  $z = 0.20$  mm, just 0.05 mm below the region with the highest Pd concentration and strongest fluctuations. At  $z = 0.20$  mm the edge height is near zero due to the absence of Pd. No transfer of Pd from the aqueous phase took place. Our previous observations by QEXAFS [14] indicated stochastic Pd reduction and oxidation taking place near the interface, and not simply adsorption and desorption of Pd nanoparticles.

The density fluctuations observed in the XAFS data should be associated with potential variations at the liquid/liquid interface because  $[\text{PdCl}_4]^{2-}$  or ferrocene may become locally depleted through the formation of  $\text{Pd}^0$  and a ferricinium oxidation product. To examine this we applied the use of a common ion ( $\text{TEA}^+$ ) in both liquid phases. As the  $\text{TEA}^+$  is able to transfer between the two phases, an equilibrium potential is formed across the liquid/liquid interface and fixes the interfacial potential. Starting with a large excess of  $\text{TEA}^+$  in the aqueous phase,  $\text{TEA}^+$  is then able to partition into the organic phase, resulting in a negative biasing of the aqueous phase relative to the organic phase, slowing the electron transfer from ferrocene to Pd.

The EDE experiment under conditions of supersaturation was therefore repeated with inclusion of  $\text{TEA}^+$ . By comparing the experiments with (figure 2c) and without  $\text{TEA}^+$  (figure 2b) it can be seen that the addition of  $\text{TEA}^+$  resulted in a slight increase in the induction time before the onset of nucleation,

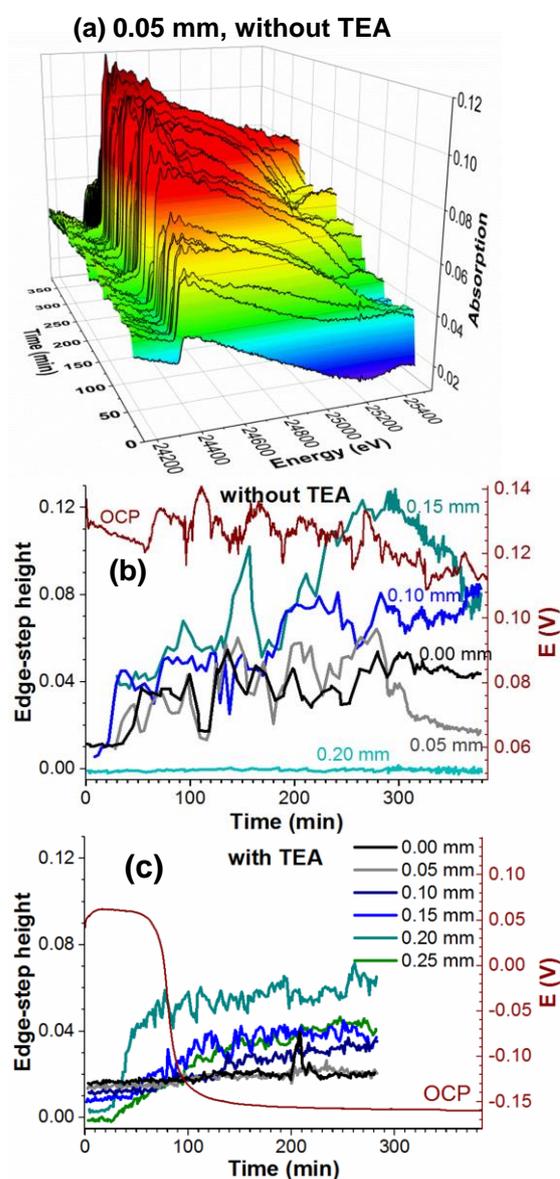


Figure 2. (a) EDE spectra collected at  $z = 0.05$  mm in the sample without  $\text{TEA}^+$ . (b) and (c) show the edge-step heights at different scan depths at the liquid/liquid interface for the sample (b) without added  $\text{TEA}^+$  and (c) with added  $\text{TEA}^+$ . Overlaid in (b) and (c) are the open circuit potentials.

followed by smoother Pd nucleation as can be seen from the suppressed fluctuations in edge-step heights. In order to confirm the potential dependence of the growth process, we also measured the open circuit potentials (OCP). Without added TEA<sup>+</sup>, the interfacial potential fluctuated with a similar frequency to the EDE-detected fluctuations (figure 2b). With TEA<sup>+</sup> added a relatively large decrease in potential ~100 minutes after the phases were connected took place before the potential stabilised (figure 2c). OCP stabilisation fitted well with the point at which Pd growth slowed down significantly. Although the potential scales were different for the two samples it is evident that electron transfer was slowed down by negatively biasing the aqueous phase, in accordance with previous electrochemical studies [9, 10].

## Conclusions

EDE monitoring of Pd nanoparticle nucleation in a galvanic liquid/liquid cell revealed a regime of spatial instability compatible with the density fluctuations expected when growth and dissolution of sub-critical Pd nuclei take place in a supersaturated state. Control of the interfacial potential by inclusion of a common ion (TEA<sup>+</sup>) in both phases slowed down the nucleation process when the aqueous phase had a negative potential bias relative to the organic phase. Open circuit potential measurements in a liquid/liquid electrochemical cell are in line with the EDE data, indicating that density fluctuations are accompanied by chemical potential variations near the liquid/liquid interface.

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