This work presents a study focused on optimization of the growth of Pd thin films by surface limited redox replacement (SLRR) of an underpotentially deposited (UPD) Cu layer in a one-cell configuration, and their thorough characterization. The growth was monitored by open-circuit chronopotentiometry and deposited films were consequently characterized for roughness evolution by HUPD and CuUPD cyclic voltammetry (CV) while the film thickness was evaluated using anodic stripping voltammetry and integration of the accumulated stripping charge. The growth of smooth Pd films was observed for ∼15 successively grown equivalent monolayers (MLs) of Pd followed by a rapid transition to 3D growth. A comparison with counterpart results of Pd SLRR deposition in a flow-cell where no such growth-mode change occurs suggests that the transition seen in one-cell is likely associated with establishment of mass-transport limitations. Close examination of SLRR transients, in-situ STM results on the flat grown layers, and SEM images of the surface after the transition occurs confirm the likelihood of growth kinetics evolution. Finally, this one-cell specific shortcoming was addressed by the introduction of SLRR-cycle disruption along with forced convection, which resulted in the smooth growth of Pd films on Au up to 26 Pd MLs.

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Sticky et al. managed to complete 75 SLRR cycles at an exchange efficiency of about 95%. The high maintenance and relatively high operation cost, makes the automated flow cell system less cost effective than the one-cell approach that features simplicity of operation and the comfort of having all solution components for E-ALD via SLRR in a single solution vessel. Although the one-cell approach addresses some drawbacks experienced in the automated flow-cell set-ups, it also has some limitations including, among others, the inevitable transitioning to diffusion-limited growth in the course of thicker film deposition. Such a transitioning has been recently believed to facilitate systems growing in a quasi-2D mode to proceed inevitably transitioning to diffusion-limited growth in the course of set-ups, it also has some limitations including, among others, the inevitable transitioning to diffusion-limited growth in the course of thicker film deposition. Such a transitioning has been recently believed to facilitate systems growing in a quasi-2D mode to proceed eventually to a 3D deposition leading to growth of dendrites. In this work, we present a study on the SLRR growth of Pd thin films in a one-cell configuration using Cu as a sacrificial metal. Along with detailed optimization effort assessing the impact of absolute and relative concentrations of Pd2+ and Cl− ions on the deposition outcome (kinetics and morphology), of interest to this work has been the transitioning to dendritic growth and development of protocols to minimize its adverse effects on the Pd growth in general. More specifically, the growth of Pd is conducted and studied by potential pulse routines and open circuit chronopotentiometry (OCCP). The film roughness is assessed by H_{UPD} and Cu_{UPD} cyclic voltammetry (CV) experiments and the film thickness (deposition efficiency) was determined by anodic stripping voltammetry (ASV) of Pd films following all test and characterization routines. In situ STM experiments were also performed to monitor the growth process and to observe the transition from 2D to 3D dendritic growth. SEM results show the dendritic growth through the images of the surface morphology. XPS results also show that negligible Cu residues remain in the Pd thin films as grown on the Au substrate.

**Experimental**

**Electrode preparation.**—The working electrodes for all electrochemical and morphological characterization experiments in this work are polycrystalline Au_{pol} discs (0.9999 purity) of 6 mm diameter and thickness of 2 mm. Their preparation involves mechanical polishing down to 1 μm using water-based, de-agglomerated alumina slurry (Buehler). After which, they are rinsed with water before being immersed in warm concentrated HNO3 to remove any polishing residual particles, followed by thorough rinsing with Barnsted NanoPure water (18.2 MΩ cm). Next, the Au disks are electropolished via protocol described elsewhere. The final step of preparation involves carefully annealing the electrodes to red-hot in a propane torch for minimum 5 min before cooling rapidly in ultrapure nitrogen atmosphere to avoid surface oxidation. The process is terminated with a droplet of the Barnstead NanoPure water to prevent surface contamination. These electrodes are then mounted onto a conductive vacuum holder and immersed in the electrolyte via a hanging meniscus configuration in a three-electrode cell for surface characterization and subsequently, for thin film growth. All electrochemical experiments were performed in three electrode cells using solutions made from ultra-high purity grade chemicals as received from the vendors and Barnsted NanoPure water. A saturated Mercury-Mercurous Sulfate Electrode (MSE) is used as reference electrode in most experiments unless stated otherwise. Also, a Pt wire serves as the counter electrode (CE) in all experiments. All potentials in the manuscript are presented versus MSE (except the Cu_{UPD} and Pd_{UPD} characterization experiments) and all current densities are normalized with respect to the geometric area of the electrode. The Single crystalline Au (111) (1.0 cm in diameter and 2 mm thickness, Monocrystal Company) used for morphology characterization in in-situ STM experiments were prepared following a procedure described in detail elsewhere.

**Initial characterization of Cu_{pol} electrodes.**—The Au electrodes are characterized using Pd_{UPD} CV to determine the quality of their surfaces before Pd deposition as well as to determine the electrochemical surface area (ECSA). The solution composition for Pd_{UPD} experiments is given elsewhere. The CV measurements were performed using Model AFCBP Bipotentistat (Pine Instruments) interfaced with a PC through the PineChem software (Version 2.80). Pb wire was used as a pseudo-reference electrode (PRE).

**Pd Ultra-thin film growth.**—The formation of the ultra-thin layers of Pd on Au was performed via different number of SLRR events in a one cell configuration. The optimized deposition solution made of 0.3 mM PdCl2 (Aldrich, 99.99%), 30 mM HCl (J.T. Baker, 36.5–38%), 3 mM CuSO4 (Aldrich, 99.99%) and 0.1 M H2SO4 (GFS Chemical, redistilled 95–98%) was purged with ultrapure N2 for at least 30 min. In all experiments, purging of ultrapure N2 continued throughout the experiments to minimize oxygen interference. Similarly to a procedure used for the SLRR deposition of Pt, one SLRR cycle involves the formation of a conformal submonolayer or monolayer of Cu_{UPD} by application of a potential pulse to a potential of −0.35 V (MSE) for 1s followed by a redox replacement step by the more noble metal – Pd, occurring at OCP until the potential reaches a cutoff value in the range 0.00 to −0.05 V. The cycles could either be run continuously or be broken into successive groups of four runs, until the total number of intended cycles is reached. During the breaks, the working electrode is pulled out of the growing solution (without opening the cell) and the solution is shaken to homogenize the components before it is placed back in the hanging meniscus for further SLRR runs. The Pd thin-film growth protocols were administered and monitored using a potentiostat/galvanostat Princeton Applied Research (PAR) Model 273 coupled with Corware Software. Data on the continuous SLRR transients was collected on a PC by analog-to-digital DrDAQ Data Logger controlled by PicoLog software.

**Electrochemical testing and characterization.**—The H_{UPD} and Cu_{UPD} CV curves were used for electrochemical characterization of the as-grown Pd thin films. The H_{UPD} CV was conducted in 0.5 M H2SO4 (GFS Chemical, highest purity grade, redistilled) within a potential range that minimizes H absorption i.e. 0.1 V to −0.67 V (vs MSE) at a sweep rate of 50 mV s−1. We conducted the Cu_{UPD} characterization via CV in 3 mM CuSO4 (J.T. Baker, 99.8%), 0.1M H2SO4 solution using Cu wire as PRE at a sweep rate of 20 mV s−1. The characterization of these Pd thin films was done using the instruments and software used for Pd_{UPD} characterization mentioned early.

**Anodic stripping of Pd films.**—When characterization of the thin-films of palladium on gold is done, anodic stripping of the same films is done by ASV in a 0.1 M HCl (J.T. Baker, 36.5–38%) solution over a potential range −0.3 to 0.4 V against MSE as a reference electrode. The ASV sweep rate 3 mV s−1 and was controlled by Model AFCBP Bipotentistat (Pine Instruments) interfaced with a PC through the Aftermath Data Organizer software.

**In-situ STM monitoring and characterization.**—In-situ STM was carried out utilizing an Agilent 4500 SPM microscope, a 2100 controller and PicoScan software (version 1.14) in an analogous solution to the optimized one as described in the deposition protocol section above but with ratio [Cl−]/[Pd(II)] = 8. The potential was controlled by an Agilent 300S Pico Bipotentistat, and a Pt ring and Pd wire were used as counter and reference electrodes respectively. The growing solution was also purged with ultra-high purity N2 to minimize oxygen interference during the experiment. STM tips were fabricated by etching Pt0.5Ir0.5 wire in 1.6 M CaCl2 utilizing an AC voltage of 25–30 V, followed by insulation with Apiezon wax to minimize the tip exposure to solution thus minimizing leakage currents during the experiments.

**X-Ray photoelectron spectroscopy (XPS) surface characterization.**—XPS was carried out with a PHI 5000 VersaProbe, Micromanaging ESCA Microscope from Physical Electronics with a scanned and focused monochromatic Al (Ka) X-ray beam for resolved chemical analysis. The spot size was 200 mm, take-off angle was 45° and pass energy of 117.40 eV were used for...
even at the optimal ratio \([\text{Pd(II)}/\text{EDTA}]\) but as mentioned earlier the growth outcome was unsatisfactory the Pd ions were complexed EDTA to slow down the exchange reaction these complexes can exist in many forms based on Cl− and exchange efficiency concerns. The work of both Uosaki\(^1\) and complexing agent was needed to address both growth homogeneity of conductive substrates.\(^{16,18,23,27,31}\) As mentioned earlier, in the work elements in the growth of epitaxial thin films of metals on a variety step.

The predominant crystallographic surface orientation of the Au substrate influences the structure of the growing Pd thin metal layer. To assess their quality, the Au electrodes used in this work are characterized by PbUPD (Figure 1A) and CuUPD CV curves (Figure 1B) in which both shapes and features are typical to polycrystalline Au with strongly dominating (111) surface orientation. Work on electrodes of the same or comparable quality was also reported in our previous publications.\(^{26}\) Samples must exhibit the typical peaks that represent low-index Au facets of (111), (110) and (100) to indicate the readiness of the substrate for the deposition step.

Both Cu and Pb have been demonstrated to be effective sacrificial elements in the growth of epitaxial thin films of metals on a variety of conductive substrates.\(^{15,16,18,23,27,31}\) As mentioned earlier, in the work of Stickney’s group,\(^2\) Cu was found to be a better sacrificial element relative to Pb for Pd thin film growth via SLRR. Therefore, growth via SLRR using Cu UPD was preferred to that of Pb UPD. In their work, using the flow cell system led to a known issue manifested by a differential Pd deposition along the cell width with more Pd depositing at the ingress region where Pd activity is highest in the beginning of each SLRR step. This resulted in higher rate of exchange at the ingress relative to the solution introduction time.\(^6\) To solve this issue, the Pd ions were complexed EDTA to slow down the exchange reaction but as mentioned earlier the growth outcome was unsatisfactory even at the optimal ratio \([\text{Pd(II)}/\text{EDTA}] = 1\). A more labile (weaker) complexing agent was needed to address both growth homogeneity and exchange efficiency concerns. The work of both Uosaki\(^1\) and Kolb\(^2,20\) demonstrated that Pd(II) ions form more labile complexes with Cl− ions relative to EDTA. Dependent upon Cl− concentration these complexes can exist in many forms based on Cl− - H2O ligand exchange, and are thereby presented as \([\text{PdCl}_x\text{(H}_2\text{O})_{1-x}]^{2-x}\).\(^{28,34}\) Stickney’s work showed that use of Pd(II) complexes with Cl−, resulting in a known negative shift of Pd reduction potential by \(\sim 0.3\) V due to the presence of less free Pd(II) ions,\(^{35}\) leads to formation of high-quality deposits.\(^6\) The reported optimized concentration ratio that resulted in best quality of Pd films deposited by SLRR in flow cell system, was \([\text{Cl}^-]/[\text{Pd(II)}] = 500.\(^6\)

**Results and Discussion**

**Initial Au electrode characterization.**—The predominant crystallographic surface orientation of the Au substrate influences the structure of the growing Pd thin metal layer. To assess their quality, the Au electrodes used in this work are characterized by PbUPD (Figure 1A) and CuUPD CV curves (Figure 1B) in which both shapes and features are typical to polycrystalline Au with strongly dominating (111) surface orientation. Work on electrodes of the same or comparable quality was also reported in our previous publications.\(^{26}\) Samples must exhibit the typical peaks that represent low-index Au facets of (111), (110) and (100) to indicate the readiness of the substrate for the deposition step.

The potential transition from quasi-2D growth to dendritic growth inevitably impacts the potential transient associated with SLRR deposition in one cell configuration. Figures 3A and 3B, present typical potential transients reflecting the potential changes in the course of each SLRR cycle at different Cl−/Pd(II) concentration ratios. Apparently, the duration of one cycle is directly dependent on the strength of complexation between Pd(II) and Cl− which is affected indirectly by the ratio between these ions as they form a variety of complexed species, \([\text{PdCl}_x\text{(H}_2\text{O})_{1-x}]^{2-x}\) thus making the Pd less available to the growth process (compare Figs. 3A and 3B). Also, if no mass transport limitations are impacting the deposition all cycles should have identical duration (Figure 3A). Some difference could be expected only in the very beginning when the Au surface is still not completely covered by Pd (Fig. 3B). Overall, as also seen in Figure 3B, the potential transients during SLRR deposition in one-cell configuration could be used as an early indicator of likely growth mode transitioning manifested by prolonging of single-cycle duration. These observations could be cross-compared later with those from the CV and ASV experiments.

**SEM characterization.**—Scanning Electron Microscopy (SEM, Zeiss Supra 55 VP) coupled with an in-lens detector at an accelerating voltage of 10 kV and a working distance of 2 mm was performed for morphological characterization of as-grown Pd films on Au electrode discs.

**Figure 1.** CV curves of PbUPD (A) in 0.1 M NaClO4, 0.01 M HClO4, and 3 mM Pb(ClO4)2 solution, and CuUPD (B) in 3 mM CuSO4, and 0.1 M H2SO4 solution on Aupoly electrode. Sweep rate: 20 mVs−1.
Figure 2. CV curves of HUPD at sweep rate of 50 mV s\(^{-1}\) (A), and CuUPD at sweep rate of 20 mV s\(^{-1}\) (B) on Pd films deposited on Au\(_{\text{poly}}\) electrode with different number of SLRR cycles. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mV s\(^{-1}\) (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

Figure 3. Potential transients following the SLRR deposition of Pd films in one-cell setup in a solution with Pd\(^{2+}\) ion concentration of 0.3 mM and [Cl\(^{-}\)]/[Pd\(^{2+}\)] ratio of 100 (A), and 500 (B).
Figure 4. CV curves of \( \text{HUPD} \) at sweep rate of 50 mVs\(^{-1} \) (A), and \( \text{CuUPD} \) at sweep rate of 20 mVs\(^{-1} \) (B) on Pd films deposited on Au(poly) electrode with different number of SLRR cycles. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mVs\(^{-1} \) (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

and (as needed) ultimately validated by direct imaging, such as SEM and/or STM.

The optimization of the SLRR deposition routines in one cell continued with preserving the \([\text{Cl}^-]/[\text{Pd(II)}]\) ratio of 8 but increasing by a factor of 2 the absolute concentrations of said ions. Unfortunately, no significant difference was registered during the characterization tests (not presented). In a marginal improvement the transition to roughening occurred between the 6th and 10th cycle instead of 4th and 7th in the experiment presented in Figure 2. Overall, the CV curves and the departure from linearity in the stripping tests confirm the transitioning from layer-by-layer to 3D growth at higher [Pd(II)] as well. A higher [Pd(II)] concentration could provide favorable conditions for longer quasi-2D growth. However, such concentration is inapplicable for SLRR in one-cell as it will promote a substantial contribution of electrodeposited Pd during the sacrificial layer formation step taking place under potential control.\(^{25} \)

Growth dependence on the \([\text{Cl}^-]/[\text{Pd(II)}]\) ratio.—Next we optimized the overall \([\text{Cl}^-]/[\text{Pd(II)}]\) ratio for the one-cell system. A starting point was the optimal ratio from Stickney’s work in the flow cell system, whereby deposition experiments used a concentration ratio of \([\text{Cl}^-]/[\text{Pd(II)}]=500 \). The CuUPD CV characterization curves presented elsewhere\(^{38} \) suggested that there was virtually no roughness development even with 20 SLRR events however, a further quantification of the Pd from the anodic stripping curves revealed that such concentration ratio had a drawback of very low exchange efficiency, whereby the 20 SLRR cycles were found to result in the deposition of less than 3 MLs of Pd. As explained elsewhere in this work, the higher the concentration of the \( \text{Cl}^- \) ions the stronger Pd-Cl\(^{-} \) complexation, this ultimately reduces the exchange efficiency during the SLRR deposition process. This is explained by the high value of formation constant for the \([\text{PdCl}_x[\text{H}_2\text{O}]_{4-x}]^{2-x} \) complex, formed as a result of \( \text{H}_2\text{O}–\text{Cl}^- \) ligand exchange, \( \beta_4 = 10^{11.53} \), which depicts a very stable complex. As a result of this stability the concentration of free Pd(II) ions is very low.\(^{34} \) This condition in turn indirectly favors the side reactions such as ORR, which are suppressed due to \( \text{N}_2 \) purging, but cannot be completely excluded via this approach, over Pd reduction, thus further contributing to lowered deposition efficiency.

Further experimental designs for optimization of the conditions maintained the absolute concentration of Pd(II) ions fixed but changed the concentration ratios from \([\text{Cl}^-]/[\text{Pd(II)}]=500 \) to 100 and 170. Figure 4 shows the best results of accordingly optimized Pd growth by SLRR of Cu UPD layer (at \([\text{Cl}^-]/[\text{Pd(II)}]=100 \)) as demonstrated by CV characterization and subsequent anodic stripping of all accordingly grown Pd thin films. It is clearly seen from the results in Figure 4 that there was smooth growth up to the 12th cycle and a substantial roughness evolution after 20 cycles of SLRR growth. The inference from the Figures 4C and 4D confirm the smooth growth of Pd thin films up to the 12th SLRR cycle which is equivalent to 16 MLs of Pd deposited. The perfect linear trend of charge (equivalent number of monolayers) against the number of SLRR cycles up to the 12th cycle (in Fig. 4D) acts as evidence of the same. Just like other reported results, the transition toward 3D, the dendritic growth is evident in...
this experiment and it occurs from 12th cycle onward i.e. after 15 MLs of deposited Pd.

Overall, the optimization study of Pd deposition by SLRR of Cu UPD along with results from earlier work, whereby Pd was grown by replacement of H UPD layers, both conducted in one cell system, suggested the persistent presence of a 2D to 3D transition at different growth thickness. This transition has been attributed to dendritic growth occurring upon establishment of mass-transport limitations at the growing interface. Then, as a result of the hindered transport of the [PdCl\textsubscript{x} [H\textsubscript{2}O]\textsubscript{4–x}]\textsubscript{2–x} complex, the growing surface, a progressively formed concentration gradient (from zero on the electrode surface to the bulk concentration) serves to enhance the vertical growth of any 3D clusters nucleated in the initial deposition stages leading eventually to dendrite formation. Therefore, we present, in the following part of our work some surface characterization and elemental analysis results that are aimed at assessing aspects of the Pd layer quality before and after the transition.

**In-situ STM characterization (setting the limits of flat growth).** — The evolution of Pd film deposit morphology was explored as a function of the number of SLRR cycles completed via in-situ STM. This was done to gain insight into the deposition growth mode and morphological evolution that drives the transition to dendritic growth. These films were deposited with a [Cl\textsuperscript{−}]/[Pd(II)] = 8 ratio, to ensure that roughness evolution could be observed over the time of deposition. Figure 5A illustrates the un-reconstructed Au (111) single crystal substrate. The morphology of the substrate exhibits large terraces separated by mono-atomic steps or step bunches. The terraces are also decorated with a small coverage of Au clusters that are a result of the lifting of the Au (111) surface reconstruction. In Figure 5B it can be seen that following the completion of first SLRR cycle the surface is uniformly covered by a minimum of one Pd ML, based on the deposition efficiency determined by the ASV, and evidenced by the loss of sharp step edge boundaries initially present on the substrate. Following the first SLRR cycle additional Pd clusters atop the pre-nucleated Pd underlayer are also present. These clusters are preferentially located at defect sites that are originally present on the Au (111) substrate, i.e. step edges and clusters that result from lifting of the Au (111) reconstruction. Similar preferential cluster nucleation and growth has been demonstrated in deposition systems in which the growing metal exhibits a high melting point, and consequently slow surface diffusion. After two SLRR cycles, the clusters grow in size and merge where the size prohibits further lateral growth, at this time the step edges are completely decorated with Pd clusters. After two SLRR cycles there is also evidence of additional layer-by-layer deposit propagation on terraces external to the nucleated clusters. This additional growth is especially evident in branching extending from the largest island present in the upper right corner of Figure 1A, branching indicated by the arrow in Figure 5C. This additional layer-by-layer growth indicates a continued epitaxial relationship between the film and the substrate. Following five SLRR cycles (Figure 5D), additional clusters nucleate on the substrate terraces and there is little exposed flat terrace remaining. Finally, following 10 SLRR cycles there are few recognizable features present from the initial substrate, and instead the surface is uniformly covered with large Pd clusters some of which are clearly thicker than the majority in the dense cluster network as seen in Figure 5E.

The cluster deposition and growth following five Pd SLRR cycles on Au is likely responsible for the roughness evolution that is seen in the UPD voltammetry. Similar cluster deposition and growth is seen in the deposition of Pt on Au via SLRR and conventional methods. However, in the deposition of Pt on Au a pseudomorphic overlayer never develops. The pseudomorphic overlayer present in this system is likely to be as a result of the strong interaction between Pd and Au, an interaction that ultimately promotes Pd UPD layer formation on Au and in alternative systems. Interestingly, D. Kolb et al. showed that following the conventional electrodoposition of 10 layers of Pd on Au a fractal deposit morphology is developed, a morphology quite different from that seen in Figure 5. However, that work does not utilize a pre-nucleated Cu UPD wetting layer, which likely promotes more uniform growth in cluster form across the entire substrate. In addition, the Pd deposition overpotential applied by a nucleated Cu UPD layer in this work is significantly greater than that

![Figure 5.](image)

(A) Au (111) single crystal substrate, (B-D) in situ STM images of successive SLRR cycles of Pd displacement of Cu on Au (111). 150 × 150 nm, I\textsubscript{c} = 1 nA, (Images taken under potential control at film-established OCP).
used in Ref. 32, ultimately increasing deposition rate and reducing time for adatom reorganization.

**XPS characterization (elemental analysis).**—The results from the XPS analysis presented in Figure 6 suggest the presence of practically only trace amounts of Cu not exceeding 2–3 at% in the deposited by SLRR Pd film. The sample analysis shows also the minor presence of other elements which can be attributed to oxidation of Pd and adsorption of adventitious C based oxides (O1s and C1s, respectively), with trace amounts of Al from the mechanical polishing and Cl\(^-\) from the growth solution. This level of incorporated Cu agrees very well with the results obtained by Stickney’s group\(^{23}\) for Pd grown by SLRR of Cu UPD in flow cell, demonstrating 0.9 and 1.7 at% for 15 and 25 cycle grown layers, respectively. The slightly higher limiting level of incorporated Cu in our work could be attributed to the thicker Pd layer (grown by 50 SLRR cycles) used in the XPS analysis. Given the trend of amount of incorporated Cu increase with the number of cycles in Stickney’s work, one would not be surprised to see leveling of the Cu content at 2.5 to 3.0 at%. While many studied SLRR based growth approaches for other systems result in no sacrificial metal incorporation, the low level of Cu inclusion in the present case could somewhat be expected given the high bulk miscibility of Pd and Cu manifested by the formation of a single-phase alloy over the entire compositional range.\(^{32}\) This generally suggests no statistically significant difference in the Cu incorporation in Pd layers deposited by one-cell and flow cell approaches. Also, the practically negligible presence of incorporated Cu atoms in the Pd film is largely insufficient to serve as source of lattice strain that could promote structural defects at low film thickness. Therefore, it is highly unlikely to believe that the observed transitioning to dendritic growth demonstrated clearly by the results presented in Figure 2 is a result of Cu incorporation. That is why in the next paragraph we present a closer look on the surface morphology of Pd layer grown by 50 SLRR cycles (after the roughening occurred, Fig. 2) and more detailed analysis of the entire SLRR deposition kinetics.

**SEM characterization and Chrono-potentiometry results.**—Figure 7A presents top view of a Pd film deposited by 50 SLRR cycles under the optimized experimental conditions that were used for deposition of Pd films in a solution with [Cl\(^-\)]/[Pd(II)] ratio of 170 that falls within the previously optimized range. The brighter spots on the SEM image clearly demonstrate presence of clusters that have grown predominantly in vertical direction. While the image quality is insufficient to reveal a typical dendritic structure, one can certainly associate the substantially higher surface roughness measured by the analysis of the H and Cu UPD characterization results in Figures 4A and 4B with the presence of distinct 3D structure on top of the Pd film as well as some fine nanoporosity evidenced by the darkest contrast regions. In order to better understand the transition from a well-established quasi 2D deposition seen in the STM images in Figures 5 to 3D growth leading to the surface morphology seen in Figure 7A we present 25 cycles of the potential transient registered during the growth of the SEM characterized Pd film (Fig. 7B). A closer look at the transient suggests relatively steady cycle duration to about 11 to 13 of the successive SLRR steps. Then, the duration of the subsequent cycles persistently increases. Such continuous retardation of the redox exchange reaction could be due either to change in the interaction of the growing film with the sacrificial metal or the reduction of the growing-metal-ion concentration. However, no reason for interaction changes between sacrificial layer and growing metal film could be seen given the (virtually) contamination free Pd deposition.
Figure 8. CV curves of H$_{\text{UPD}}$ at sweep rate of 50 mV s$^{-1}$ (A), and Cu$_{\text{UPD}}$ at sweep rate of 20 mV s$^{-1}$ (B) on Pd films deposited on Au$_{\text{poly}}$ electrode with different number of disrupted SLRR cycles and forced convection. Anodic stripping curves for as deposited Pd films at sweep rate of 3 mV s$^{-1}$ (C), and thickness of the films in equivalent MLs as a function of SLRR cycles (D).

(see XPS results). Therefore, the most likely reason for transition to 3D growth remains to be a gradual alteration of the exchange reaction kinetics, transitioning from activation to mass-transport controlled. The likelihood of such kinetic transition was first brought up and demonstrated analytically by B. Rawlings et al. through a recently drafted model describing the kinetics of successive SLRR cycle in one cell configuration. Under these circumstances, 3D clusters formed in the course of the cluster network densification seen already in Figure 5E could serve as nucleation centers of the yet-to-be-grown dendritic structure. As mentioned in the Introduction, transitioning from quasi 2D to dendritic growth has also been shown to occur in the SLRR and surfactant mediated growth of Au on Pt surfaces as well as in the deposition of Pd on Au by SLRR of H$_{\text{UPD}}$. It is noteworthy that the deposition process in both SLRR systems exhibiting said transition was handled in one-cell configuration.

**SLRR deposition with disruption of the growth process.**—All results presented earlier in this work indisputably demonstrate that the SLRR growth of Pd on Au in a one-cell system is associated with transitioning from layer-by-layer to 3D, dendritic growth at a certain point of the deposition process, dictated by deposition conditions. Even more, the transition appears to be an inevitable phenomenon and its commencement time depends on the concentration of the growing metal. At the same time no evidence for such transition could be found in the experiments of Stickney et al. in the same system, but carried out in an automated flow-cell setup. Most likely this is due to the absence of mass-transport limitations in the flow cell system whereby (unlike in the one-cell case), each SLRR cycle is initiated at maximum concentration of [PdCl$_x$(H$_2$O)$_{4-x}$]$^{2-x}$ complex in the near electrode vicinity. This inference is seconded by the significantly shorter time needed for a single SLRR cycle in flow cell compared to one-cell configuration under identical other growth conditions. Indeed, this is not surprising given the naturally existing identical starting conditions before each SLRR cycle in the flow-cell setup as opposed to the steadily decreasing growing metal concentration in the near electrode vicinity in one-cell configuration. Having recognized the inherent phenomenon of transitioning to 3D growth in a one-cell environment, we decided to optimize the deposition process by disrupting the growth after several successive SLRR cycles accompanied by introducing electrolyte convection during the break. The convection of the electrolyte homogenized the solution and refreshed the concentration of the Pd ions in the interface on placing the Au electrode back in the hanging meniscus position. Then, the growth was resumed for another set of successive cycles until the next interruption. Figure 8 presents summary of the characterization of one such optimized deposition experiment performed by SLRR in a one-cell configuration. The growth in that case was administered in multiples of four successive SLRR cycles with a 30-second growth interruption accompanied with forced electrolyte convection (swirling). The CV characterization by both H$_{\text{UPD}}$ and Cu$_{\text{UPD}}$ reveals virtually no roughness development even after 24 SLRR cycles of growth. It is worth noting that this resulted in the deposition of continuous...
Pd film with a smooth morphology and thickness of 26 equivalent MLs. This is almost twice the thickness of the thickest smooth film (before the 2D-3D transition) presented earlier in Figure 3. While this result is comparable with results obtained in flow cell, not even a single experiment carried out in conventional one-cell configuration mode (without interruption and convection) came even close to this quality of growth in our previous optimization attempts. This result is seconded by the stripping experiments (Figures 8C and 8D) suggesting almost perfectly linear increase of the grown layer thickness of up to 26 equivalent MLs deposited by 24 SLRR cycles in one-cell configuration.

Conclusions

In conclusion, this work has demonstrated the use of one-cell setup for the growth of Pd thin films on polycrystalline Au electrodes using E-ALD by SLRR of CuPd99 sacrificial layer. Results reported elsewhere, utilizing an automated flow-cell to deposit Pd films on Au have been critically compared with ones obtained in this work. The Cu contamination in Pd films deposited in one-cell found to be up to 3 at% is at a comparable level to the reported in flow-cell counterparts. It is seconded by the stripping experiments (Figures 8C and 8D) suggesting almost perfectly linear increase of the grown layer thickness of up to 26 equivalent MLs at Pd(II) ion concentration of 0.3 mM and cell was optimized to yield smooth and continuous films of thickness up to 15 equivalent MLs at Pd(II) ion concentration of 0.3 mM and configuration.

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