REVIEW PAPER

Recent Advances in the Growth of Metals, Alloys, and Multilayers by Surface Limited Redox Replacement (SLRR) Based Approaches

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Abstract

In the realm of ever increasing importance of nanotechnology, the deposition of ultrathin metal / alloy layers with perfect structure and unique functionality becomes an objective of paramount importance. In the last decade many research groups have been working on the development and application of a new method for epitaxial thin film growth that employs a surface limited redox replacement (SLRR) as a building block reaction. The multiple repetition of this reaction enables the controlled deposition of a monolayer of metal or alloy per cycle. Work in the field has been done on the development of SLRR deposition protocols along with understanding and modelling of the SLRR reaction kinetics, on comparative studies of SLRR based routines, and on other deposition approaches. Most recently, the development of SLRR was extended to the application of all-electroless approaches for carrying out the SLRR (ESLRR). In this paper an overview of all SLRR, ESLRR and related approaches is presented. The description of the background and reaction formalism introduces the method with emphasis on its general applicability and limitations. The discussion then continues with the description of experimental approaches for carrying out a deposition process by SLRR. In this section specific consideration is given to the deposition by shuttling of the working electrode, the flow-cell configuration, the one-cell configuration, and the all-electroless approaches for realizing the repetitive application of a single-cycle SLRR reaction. Next, the ability of these approaches to produce epitaxial, flat and uniform deposits will be discussed through results of electrochemical, in-situ scanning tunneling microscopy, X-ray Photoelectron Spectroscopy and other characterization experiments showing

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advantages and limitations of SLRR growth in a variety of systems classified into three categories. In the first of these categories Cu, Ag, and Au are used as model systems to introduce the deposition by SLRR. In the second category Pd and Ru deposition by SLRR has been discussed. In the third category all studies concerning a variety of scenarios for Pt deposition by SLRR are presented and in the last part of that section deposition of alloys and multilayers is critically discussed. The paper then continues with a section presenting and discussing modelling approaches of studying the kinetics of a single-cycle SLRR reaction and concludes with the presentation of the extension of modelling to a system where multi-cycle SLRR deposition processes have been investigated. The analysis in this part focuses on the kinetic parameters of the replacement reaction like rate constant, order of the reaction, type of adsorption behavior of the sacrificial metal etc. Finally, this section concludes with a discussion of the mechanistic aspects of the SLRR reaction and more specifically on the factors impacting the deposition process and in turn the resulting structure, morphology, uniformity and continuity of the accordingly grown thin films. The paper also touches upon applied aspects of the SLRR deposition and mainly presents some basic level test results of catalysts synthesized by related deposition protocols. Finally, a glimpse into the future of this rapidly developing field is also provided.

Keywords: SLRR, E-ALD, galvanic displacement, catalysts, deposition, growth, alloys, multilayers

1. Introduction

The thin-film growth modes operating in metal epitaxy are Frank–van der Merve (FVM) or Layer-by-Layer (2D) growth and Volmer-Weber or 3D-cluster growth. An intermediate scenario is presented by the Stranski-Krastanov (SK) transition mechanism associated with initial nucleation and growth of 2D film proceeding to 3D growth for the rest of the deposition process [1]. Step-flow growth is a multilayer FVM growth and occurs in some systems at certain step density and deposition flux. As long as any of the FVM growth modes is operating during the deposition the resulting film is in registry with the underlying substrate. However, the vast majority of studied heteroepitaxial systems display either 3D or SK growth mode at ambient temperature even in submonolayer regime [2]. In addition, owing to kinetic issues, even overlayer/substrate systems that are thermodynamically expected to grow in 2D mode growth, exhibit a deposition behavior dominated by the development of largely separated 3D clusters. This naturally supported trend is highly unfavorable for a wide variety of practical purposes that require flat, uniform and continuous 2D metal and alloy layers. Such layers, that follow the structure and morphology of the underlying substrate, exhibit low resistivity and electromigration [3]. Their ultrathin configuration enables the formation of surface alloys or layered structures without bulk analogs [4, 5] and their continuity allows for complete substrate screening thus rendering them optimal candidates for corrosion protection applications. Also, ultrathin epitaxial functional layers have been actively developed for the functionalization of low-cost, catalytically inactive substrates in the synthesis of potent catalysts for fuel-cell applications [6].

The strong interest in the growth of smooth, uniform and continuous homo- and heteroepitaxial metal layers has served as the inspiration and goal of many researchers in the field of electrodeposition. Layers of this kind are difficult to achieve even by deposition at room temperature in ultrahigh vacuum (UHV) where no side effects and /or contamination obstructs the growth process. Improvement can only be seen at sufficiently elevated temperature where the mobility of the depositing atoms increases and

allows for the growth of uniform and continuous deposits that reproduce to a large extent the crystallography and (in general) morphology of the underlying substrate. However, all UHV based deposition approaches are expensive and require sophisticated setups and specifically developed logistics for carrying out the growth routines. This motivates efforts in the development of alternative approaches that would be cost-effective and simpler.

A major advance toward the electrodeposition (that is cost-effective and easier to control than UHV) of smooth, epitaxial metal deposits was made by Sieradzki et al. with the development of defect mediated growth (DMG) [7] and surfactant mediated growth (SMG) [8]. The protocols employed in these techniques assume either co-deposition of the growing metal (Ag or Cu) with a reversibly deposited mediator metal (typically Pb^{2+}) (DMG) [7, 9] or use of pre-deposited submonolayer of a “surfactant” metal (Pb^{2+}) (SMG)[8] that floats on the top of the depositing metal and facilitates the 2D growth. The applicability of these methods employing underpotentially deposited (UPD) [10-12] mediators was successfully demonstrated by growth of both “perfect 2D” monolayer to bilayer Ag films [13] and commercially thick Ag and Cu epitaxial deposits on Au (111) substrates [7-9]. The surfactant mediation of Pd deposition by H UPD layers was used recently for the growth of one dimensional nanostructures [14] Although results of structural characterization and elemental analysis suggest smooth and inclusion free epitaxial films grown by DMG and SMG [7-9, 13], these methods are still subject to some limitations and practical inconvenience that need to be addressed. For instance, both methods are tunable over a variety of parameters, including metal concentrations, scan rate, potential limits and submonolayer coverage that are mutually dependent and thus difficult to balance. Also, the thickness control (via charge measurements) during growth is hindered by the interference of factors such as side reactions and double layer charging that, especially in DMG, are manifested by currents comparable to (or even exceeding) the deposition current level. Finally, while very low, the possibility for the incorporation of mediator into the deposit cannot be completely ruled out. Indeed, for many

systems of growing metal and surfactant mediator with significant negative free energy of mixing, ΔG_{mix} , an alloy deposition instead of surfactant mediated growth is observed [15]. In that case, instead of floating on the surface of the depositing metal the surfactant mixes with the depositing atoms thus enabling the deposition of new portion of surfactant atoms along with the atoms of the growing metal. This scenario effectively works as if the redox potential of the less noble metal is shifted positively and thus a co-deposition with the more noble metal is enabled [15]. This approach allows for deposition of alloys with different composition controlled by (i) the choice of deposition potential and (ii) the concentration of the more noble metal. This is referred to as underpotential alloy co-deposition (UPCD) [16] and has been studied in detail and implemented for the growth of alloys with controlled thickness, structure, and composition. One direction of UPCD studies followed the deposition of Pt alloys aimed at applications in the electronic industry (Pt-Co, Pt-Fe) [17-20] and catalysis (Pt-Cu, Pt-Pb) [21-23]. From a fundamental standpoint UPCD has been of interest with its ability to produce metastable configurations in electrodeposited Au-Ni alloys [24] and to ensure a great deal of compositional control by even inverting the thermodynamics of the co-depositing metals (Au-Cu alloys) [25, 26].

An alternative to the earlier developed mediation methods that addresses successfully some of the above described limitations is the electrochemical deposition by surface limited redox replacement (SLRR) reaction introduced first by Brankovic et al [27, 28] for sub-monolayer to monolayer coatings with applications in fuel cell catalysis. Realized as a “building block” reaction that can be repeated multiple times the SLRR can be regarded as a solid foundation of a new approach for the growth of epitaxial thin metal, alloy and multilayer films. The SLRR emphasizes for the first time in metal deposition, the unique decoupling of controlled-potential formation of underpotentially deposited (UPD) sacrificial layer and electroless redox replacement of this layer by a more-noble growing metal. This unique feature provides the best conditions for carrying out of a purely “adlayer controlled” [27] deposition process that ensures maximum reproducibility of the underlying substrate morphology. The latter statement can be

understood in analogy with the well-established approach for growth of compound semiconductors by electrochemical atomic layer epitaxy (EC ALE) developed in early nineties of last century by Stickney et al [29]. First application of several successive SLRR steps for the growth of a Pt film thicker than 1 ML were made by Weaver et al [30] in an attempt to generate a continuous Pt coating for the development of SERS active substrates. The pursuit of implementation of the SLRR approach as a method for the growth of metals, alloys and multilayers began in the middle of last decade with the work of Dimitrov et al [31-34] and Stickney et al [35, 36]. This early work of both groups demonstrated in general categories the SLRR as superior to any other deposition technique in the growth of ultimately flat and uniform metal thin films of Cu, Ag, and Pt.

The elementary SLRR step is based on the irreversible galvanic displacement of an underpotentially deposited (UPD) monolayer (ML) of sacrificial metal U on substrate $S(h,k,l)$ by more noble metal G^{g+} ions. The amount of deposited as a result of the SLRR, metal G is controlled by reaction stoichiometry, structure (introducing the packing density factor ρ_U presenting number of M atoms per one substrate atom) and coverage θ_U of the UPD ML before the SLRR process beginning, (Equation 1) [37].

Here, u and g are the oxidation states of UPD metal U and more noble metal G . The subscripts s and aq indicate the physical state of the metal (aq states for *aqueous* solution phase and s for *deposited*). Thus, in the case of growth of Ag ($g=1$) by SLRR of a full Pb UPD sacrificial layer ($u=2$) where $\rho_{Pb} \approx 0.65$ one would expect 1.3 ML of Ag to be deposited in one step [34]. Also, the stoichiometry of SLRR in cases of more than one state of oxidation for G could be complicated as in such case the specific contribution of each of the applicable redox pathways to the deposition process should be known to calculate the outcome of one deposition event. For example, in the case of Cu UPD ML, the Cu(I) ions are thermodynamically more favorable than Cu(II) if the presence of Cl^- is the only complexing anion in the

near region of the electrode/solution interface [37]. Employed for the development of a deposition method following the above introduced SLRR reaction the general growth strategy along with specific deposition configuration / scenarios is schematically presented in Figure 1. In the scheme a substrate

Figure 1

with deposited ***under potential control*** in step **A** upd monolayer of less-noble metal, ***U***, is subjected in to an ***electroless*** redox replacement by a more-noble metal of interest, ***G***, in step **B** where the potential control is discontinued [7, 8]. As a result, in step C a monolayer of ***G*** is deposited on the substrate ***S***. The protocol employed in SLRR is enabled for heteroepitaxial systems (***S-G***) in which the displaced (sacrificial) metal, ***U***, deposits underpotentially not only on the substrate, ***S***, but also on the growing metal, ***G***, (step **D**) so that the “building block” reaction can be repeated as many times as desired. This would allow for the growth of thicker layers as illustrated in step **E** that presents the simplest configuration of SLRR growth routine. The SLRR method can be employed for the growth of deposits with more complex shape, structure and composition depending upon the targeted application of fundamental or practical importance. An example of SLRR application with fundamental emphasis is associated with epitaxial growth on plain or templated single crystalline surfaces where ordered structures of cylindrical holes with different diameters are generated by conventional [38] or “soft” lithography [39, 40] (step **F**). This study is aimed at exploring the spatial limits (down to a couple of nm) in the growth of confined metal nano-ensembles with surface stress properties showing noticeable departure from those of the corresponding bulk metal phase [41, 42]. More practically oriented applications of SLRR can be directed at the controlled deposition of (i) single-phase epitaxial alloy clusters and/or layers (step **G**) or (ii) of metal multilayers (step **H**) with specific functionality aimed at final applications in the fuel cell industry and hydrogen economy (catalysts for oxygen reduction reaction (ORR), hydrogen evolution (HER) and oxidation reaction (HOR) [43]) and electronic industry (giant magnetoresistance [44, 45]).

Motivated by a variety of the above described scenarios or their modifications in the last ten years, many research groups have been implementing SLRR for the growth of thin metal and alloy films with different applications. The aim of the present paper is to present a concise review of the advances in the fundamental background, development, optimization, modeling and application of SLRR based approaches. Aiming at this general objective, the narrative will first introduce the main experimental approaches for carrying out the SLRR based deposition process. Next, key advances in systems of sacrificial / growing metal for which SLRR growth routines have been developed will be presented. Here, along with the growth of single metal structures / layers the controlled deposition of alloys and multilayers will also be briefly described. Following this, theoretical, modelling, and mechanistic aspects associated with the single-cycle SLRR reaction will be critically discussed and conclusively summarized vis-à-vis the perspectives of the SLRR approach in the near future. Finally, specific applications of fuel cell catalysts developed by SLRR deposition of functional coatings of metals and alloys (with thicknesses from sub-monolayer to thin films) will be illustratively presented and critically compared for functionality and durability with prominent catalysts synthesized by alternative approaches.

2. Experimental Approaches

The growth by SLRR has been handled differently by the research groups involved in its development and application. Depending upon the specific objectives, to date there have been four different ways in carrying out the SLRR deposition process. Historically, the first approach was proposed by Brankovic et al [27, 28] in the original paper introducing an SLRR reaction and mastered further by Adzic's group for synthesis of state of the art catalysts [46]. It revolved around **shuttling of a working electrode (WE)** through electrolytes with different functionality that reflects completely the SLRR concept of multiple immersions. An alternative way to very closely translate the SLRR concept to a practical language is the **flow-cell approach** allowing for successive flux of different electrolytes through the deposition cell. This approach was introduced first in early nineties of last century by Stickney et al

for the growth of compound semiconductors be electrochemical atomic layer deposition [29] and adopted more recently by Cukrowski et al for studies relevant to SLRR deposition [47]. In another recently introduced approach, a simplification of the shuttling approach proposed by Dimitrov et al resulted in the establishment of the so called **one-cell approach** that brought both metal (sacrificial and growing) ions in a single electrochemical cell [31]. While the one-cell approach does not reflect as directly the SLRR concept compared to the previous two SLRR methods, it enables simpler handling of the deposition process by precise kinetic control of UPD and galvanic displacement in a single SLRR reaction[31]. Most recently work has been done to eliminate the use of external power source in the SLRR deposition process with the development of purely **electroless SLRR growth scenarios** [48, 49] that in the next paragraphs will be referred to as **ESLRR**. Next in this section specific details on all SLRR deposition approaches are provided.

2.1. The Shuttling Approach

The shuttling approach has been used for SLRR deposition since the beginning of this century with the objective to completely separate the formation of a sacrificial (UPD) layer and its galvanic displacement by a more noble growing metal. Proposed early on by Brankovic et al [27] without detailed experimental description the shuttling approach inspired the development of setups with different level of sophistication (Vukmirovic et al [46, 50, 51] and Dimitrov et al [32, 34]) that would enable multiple WE immersion in different electrolytes in oxygen-free environment. In these setups the WE is typically mounted on a holder for work in a “hanging meniscus” configuration [52]. The SLRR growth takes place in a multiple (three [34] or four [51]) compartment electrochemical setup, which allows for multiple immersion of the WE in different solutions and /or ultra high purity rinsing water. In this configuration one of the compartments is a three-electrode cell where the sacrificial layer deposition takes place using normally a wire of the UPD metal as a pseudo-reference electrode (PRE) and a Pt wire serving as a counter electrode. Two other compartments contain the solution with the growing metal ions for the

galvanic displacement, and Barnstead Nanopure water for rinsing, respectively. In some cases the presence of fourth compartment enables the separate rinsing of the WE between both steps of a single SLRR event. A vertical and in-plane (rotational or translational) mobility of the WE enables the spatial separation of all steps comprising the SLRR reaction. All compartments are incorporated in a controlled environment compartment [34] or glove box [37], equipped with purging gas outlets and/or vacuum pump connectors that ensure efficient oxygen evacuation. Ultra high purity (UHP) N₂ or Ar are typically used as purging gas for de-oxygenation. An indispensable part of the setup for running SLRR growth in shuttling configuration is also a potentiostat that executes the formation of a sacrificial layer on the WE. A simplified shuttling setup for a single-cycle SLRR only has been proposed by Adzic's group specifically for a high-yield single-cycle SLRR deposition of Pt or Pt-based alloys [46]. A more sophisticated setup hosted in a glove box and allowing for controlled WE rotation has been more recently used by Brankovic et al for kinetic studies and catalyst design through a single step SLRR growth (Figure 2) [37]. Overall, the

Figure 2

shuttling approach is most straightforward and practical for a single replacement deposition. It also represents best the SLRR concept and as such is most suitable for kinetic and mechanistic studies of a single-cycle SLRR reaction. The key advantage of such applications is the minimization of the impact / interference of side reactions/effects [33]. Also, it is believed to serve very well the single-cycle coating of catalysts for variety of applications. However, the WE handling in multi-cycle SLRR deposition process carried out in shuttling configuration is difficult and would require sophisticated technical arrangements for potential automation. Also, the WE transfer from cell to cell without potential control carries high risk for reduced efficiency of the SLRR deposition especially in multi-cycle applications [31]. That is why, impurity control and thorough oxygen evacuation are both critical for the successful shuttling approach's application.

2.2. The Flow-Cell Approach

The flow-cell approach relies on its suitability for automation of the SLRR deposition process as well as on convenience of designing a flow cell that could be used in conjunction with a surface sensitive method for characterization of the growing deposit [35, 36]. The best known in the literature flow-cell setup was first proposed by Stickney et al for the handling of E-ALD deposition processes[29]. Adopted lately for automated SLRR deposition of metals the flow-cell setup of Stickney's group has even been recently commercialized [53]. Basically, a flow-cell setup consists of pumps, valves, cell, and a potentiostat, all computer controlled using a custom software developed to control the deposition process [53]. The pump heads, valves, and tubing are confined in a compartment isolated from the ambient atmosphere to limit interference with oxygen. The electrochemical flow cell is normally designed in a thin-layer configuration, to enable laminar flow over the WE. Designed with controllable thickness and transparent opening the flow-cell allows the deposition process to be visually monitored. Typically, thin Au films deposited on glass slides are used as WE. The SLRR cycles are controlled by the custom software that serves to open and close valves based on prescribed duration and/or potential thresholds with a main objective to run successively electrolytes with specific functionality and rinsing water as needed for multi-cycle SLRR deposition[47]. Some sophistications of the flow-cell approach proposed recently by Cukrowski et al led to the development of a setup with exchangeable cells with controlled hydrodynamic flux profile that enable controlled electrolyte hydrodynamics capability [54]. The versatility of that setup allows for studies not only of a single metal deposition but also for investigation of alloy and multilayer growth by SLRR based protocols [47, 54]. The key advantage of the flow-cell approach is its natural suitability for in-situ monitoring of the morphology, structure and even composition of the growing layer by coupling the deposition cell with scanning probe microscopy (STM, AFM), low energy electron diffraction (LEED), Auger Spectroscopy, etc setups [47, 54, 55]. The complete automation of all SLRR related steps allows primarily for hand-free operation and thus provides natural

convenience for thorough oxygen-evacuation. These advantages render the flow-cell approach as best suited for in-situ monitoring and characterization of multi-cycle SLRR deposition scenarios. The flow-cell approach is also subject to some natural limitations inherent in the structure of the growth cell. More specifically, it has been reported that films tend to grow unevenly and in turn feature varied roughness depending upon the proximity to the electrolyte inlet and outlet [56, 57]. This issue that apparently is strongly related to a concentration gradient across the flow cell in the onset of the replacement step of the SLRR cycle has been addressed by introducing complexing agents to the growth solution for slowing down the deposition process and thus minimizing the trends to uneven growth [57, 58]. While positive effect has been obtained in general, the latter intervention carries risks for lowering the efficiency and contaminating the deposit. Another issue can be associated with potential cross contamination of electrolytes when the flow-cell approach is applied to the growth of very thick alloy and/or multilayer films that involves a high number of switching between different electrolytes and rinsing water.

2.3. The One-Cell Approach

Aiming at the significant simplification of the shuttling approach and considerable cost-effective alternative to the flow-cell approach Dimitrov et al proposed the one-cell approach for SLRR deposition [31]. Compromising on the complete separation of the steps of the SLRR cycle, the proposers of this approach substantially improve the operational simplicity and cost reduction. In the one-cell approach the WE is immersed normally in hanging meniscus configuration over the course of the entire SLRR process in a single three-electrode cell with electrolyte containing ions of both the sacrificial and growing metal purged thoroughly with ultra high purity inert gas (N_2 or Ar) for oxygen evacuation [33]. Key for the successful application of the one-cell approach is the careful control of the kinetics of UPD layer formation and subsequent galvanic displacement reaction. This control is administered by choosing high enough concentration of the sacrificial (UPD) metal ions so that the sacrificial layer would form under kinetic control upon a very short potential pulse [31, 59]. The solution should also contain

low enough concentration of the growing metal ions so that mass transport control is stipulated and thus only a negligible amount will plate during the potential pulse for UPD layer formation [59]. Yet, the growing metal concentration should be at least an order of magnitude higher than the steady-state oxygen concentration in the thoroughly purged electrolyte. Under these circumstances, once the UPD layer is formed, the potential control is discontinued and the more noble growing metal ions oxidize the atoms of the sacrificial metal without interference with side oxidative processes such as ORR [33]. Overall, the best choice of both ion concentrations would keep the fraction of electrodeposited growing metal lower than 1% during UPD layer formation [59]. The one-cell approach is very attractive with its operational simplicity and when applicable has been used by many groups for the purposes of fundamental or applied research involving SLRR deposition [60-62]. It ensures best efficiency in comparison with the shuttling and flow-cell methods as neither changes of electrolytes / water nor exposure to the environment ever take place in the one-cell deposition configuration. Also, the SLRR deposition in one-cell configuration requires no more sophistication than a routine electrochemical experiment and can be controlled even by commercially available software that comes with the potentiostat used for the establishment of potential control [59]. However, there have been some issues that are associated with insufficient separation of both steps comprising a single SLRR event leading to the electrodeposition of excess amount of growing metal (more than 1%) during the UPD formation step. Also, in solutions with relatively low concentration of growing metal ions, the successive application of SLRR cycles in the realm of stagnant electrolyte could lead to a difference in the deposition kinetics over the course of multi-cycle SLRR growth process. Finally, the odds of sacrificial metal incorporation in the deposit in SLRR deposition carried out in one-cell configuration are higher in comparison with the counterpart approaches [59].

2.4. The Electroless SLRR Approach

Most recently different developments have produced evidences for the applicability of ESLRR as approach that involves use of alternative (electroless) ways to generate the sacrificial layer, instead of utilizing an external power source [63-65]. Such ideas are mainly motivated by the need of coating very large surface areas for catalyst development that would require high-power potentiostat / rectifiers. So far, some of these ways include adsorptive surface termination with a hydrogen monolayer [49] or the reduction power of an executive electrode (EE) made out either of the sacrificial (or similar in terms of reduction potential) metal [48] or of Pd saturated with absorbed hydrogen [66]. Commonly of similar or identical nature to the UPD metal the EE allows upon connection on short for application of a UPD forming potential on the WE, the magnitude of which is understood through the basics of mixed potential theory [67]. This eventually results in UPD layer formation on the working electrode coupled with the oxidative stripping of an equivalent amount of material from the executive electrode (see

Figure 3

Figure 3). The connection between working and executive electrodes can subsequently be released in order to allow for the galvanic displacement of the UPD layer and an ESLRR cycle to be realized. This connection and disconnection can then be repeated as many times as necessary in order to grow films of desired thicknesses. Alternatively, hydrogen terminated surface of Pt-group metals realized by simple adsorption can be exposed to a solution containing the growing metal of interest (more noble than hydrogen) to initiate a galvanic displacement reaction that will eventually generate a monolayer coating of the growing metal [49]. Overall, the electroless SLRR approach can be carried out successfully either in shuttling or in one-cell configuration. Owing to the identical nature of the galvanic displacement reaction with and without potential control involved in the growth, films deposited by ESLRR feature no morphological, structural and/or compositional differences with their SLRR counterparts. In case of when adsorbed hydrogen is used as sacrificial layer [48, 66] the use of shuttling approach is virtually the

only option as purging the next portion of hydrogen for the following SLRR step would reduce ions of the growing metal. Ultimately, the key advantage of the ESLRR approach is associated with its suitability for systems with excessive surface area of the WE (seen mainly in coating of large quantities of nanoparticulate catalysts) where very powerful potentiostats / power supplies are needed for depositing a sacrificial layer. Recent reports attest to an ongoing effort in finding engineering solutions for implementing ESLRR in the commercial production of fuel cell catalysts [49, 65]. Among the drawbacks of using SLRR one would consider complications associated with tunability of application of desired mixed potential for sacrificial (UPD) layer formation [66]. More specifically, the flexibility along these lines is strictly limited by the nature of the EE used and by the concentration its ions, that in a pre-selected combination would ensure only one potential. In order to apply another potential one would need to go for at least a different EE ion concentration. Another limitation of ESLRR is the need to isolate in an efficient way the EE from the solution containing ions of the growing metal so that a spontaneous galvanic displacement between EE and G is avoided. Should a membrane be used for this isolation, one would have to likely deal with management of certain membrane potential that would pull positively the applied mixed potential.

3. Deposition by SLRR in Different Systems

In the last decade a variety of systems consisting of the SLRR growing of metals, alloys and even multilayers on different substrates were studied by implementing a choice of the previously introduced approaches. This section will present mostly results on the growth process, morphology and structure of the deposits, roughness evolution during the growth, potential impurity incorporation in different systems. This overview material will be structured in several sections focused first on the SLRR deposition of a variety of metals, followed by SLRR deposition specifically of Pt (that carries special interest), and completed by the SLRR deposition of alloys and multilayers (with specific applications).

3.1. SLRR Growth of Metals Other Than Pt

3.1.1. Ag and Au Deposition: A single step SLRR deposition of Ag on a Au (111) substrate using Cu as sacrificial metal was first shown by Brankovic et al to result in the formation of a bilayer of Ag [27]. According to the authors, stripping of that bilayer produces a polarization curve that is identical to the curve typically obtained from the stripping of Ag UPD bilayer [68]. Later on work of Dimitrov et al extended this introductory experiment to multiple application of SLRR for the growth of Ag thin films using Pb and Tl as sacrificial metals [32, 34]. Cyclic voltammetry and scanning tunneling microscopy

Figure 4

(Figure 4) used to monitor the growth clearly show a “quasi-perfect,” two-dimensional growth of up to 35 monolayers of Ag on Au (111). A complementary kinetic study of Pb and Tl UPD layer stability at open-circuit potential identifies the oxygen reduction reaction as key oxidative competitors of Ag in the proposed displacement protocol [33]. Analysis of the morphology evolution during the growth of Ag by the displacement of Pb and Tl UPD layers identifies the one-to-one exchange scenario Ag–Tl as more efficient for longer maintenance of a layer-by-layer silver deposition model [32]. The excellent quality of layers deposited by monolayer-restricted galvanic displacement is manifested by a steady UPD voltammetry and ascertained by an overall flat and uniform surface morphology maintained during the entire growth process. No evidences for sacrificial metal incorporation were found in the Ag deposit [32]. It is noteworthy that the yield per SLRR cycle over the course of Ag growth was in the range 95-100% accounting for 0.76 ML and 1.58 ML Ag (vs a ML of Ag (111)) when Tl and Pb were used as sacrificial metals, respectively. This very high yield obtained regardless of the shuttling or one-cell approach served as the first validation of equation (1) as applicable throughout the SLRR deposition process [34]. A more recent paper demonstrated at a proof of concept level the application of the newly proposed ESLRR approach for the deposition of Ag on Au (111) [48]. In that work Pb EE was connected to the Au WE in order to drive the formation of a Pb UPD layer on the working electrode by the stripping

of an equivalent amount of Pb from its surface. The Pb electrode is subsequently disconnected to enable a typical SLRR event to occur. This purely electroless deposition method allows for perfectly controlled growth which may be repeated to form multiple layers. Electrochemical and in-situ STM characterizations of deposited Ag films show high-quality 2D-growth with no roughness development for up to 50 ESLRR cycles [48]. The proposed approach successfully reproduces results obtained earlier by conventional SLRR and constitutes a feasible option for straight forward and cost-effective thin film deposition in a variety of metal-substrate pairs at an industrial scale of operations.

The development of a Au deposition protocol employing the SLRR of Pb UPD layers by $[\text{AuCl}_4]^-$ ions has been carried out only in one-cell configuration[69]. Open circuit chronopotentiometry and electrochemical quartz-crystal micro balance (EQCM) were used for studying the kinetics and assessing the yield from a single SLRR event. An over-stoichiometric amount of deposited Au first detected by the EQCM experiments and validated by separate pulse experiments has been attributed to the reduction in each SLRR event of a pre-adsorbed layer of $[\text{AuCl}_4]^-$ ions. This phenomenology, known as “spontaneous deposition” and studied thoroughly by Strbac et al for the deposition of Pt, Ru, and Os [70, 71], along with strict control over the Pb UPD coverage enables the finely tunable Au deposition in the sub-monolayer to monolayer range. After one replacement event on Pt (111) the deposit displays cyclic voltammetry that has the features and charge of a nearly complete Pb UPD layer as would be observed on a Au (111) substrate [72]. The results of the SLRR study in this coverage range are very similar with those of Attard et al [73]. High quality epitaxial Au has been grown for up to 40 SLRR events as also evidenced by ex-situ STM. However, growth of thicker films yields a significant surface roughness evolution of 2.5 times. The thicker deposit features a dendritic structure when viewed via scanning electron microscopy. For comparison, experiments on growth of Au mediated by the use of Pb UPD used as a surfactant demonstrated a similar transition to dendritic growth while the conventional bulk deposition of Au produced a uniform 3D layer without dendritic appearance at identical amounts of

deposited metal [69]. STM results suggest that the surface roughness is likely due to Au islands that nucleate over the course of mediated growth and at some point evolve rapidly in the vertical direction to thus seed the dendritic growth transition. X-ray photoelectron spectroscopy shows less than 1 at% Pb incorporated in the Au deposit and rules out defect induced roughening. Despite its complexity, the SLRR of Pb by Au proves to be a viable method for quick and cost effective growth of continuous homo- or heteroepitaxial Au ultra-thin films [69].

3.1.2. Cu Deposition: Studies on the SLRR deposition of Cu on Au (111) were reported in flow-cell [36, 74-77] and in one-cell configuration [31]. In a flow-cell Stickney et al used Cu UPD to deposit the first Cu atomic layer on a Au (111) substrate, modified with an atomic layer of I atoms [36]. The utilization of SLRR to deposit subsequent Cu layers involved initial formation of Pb UPD on the already Cu-coated surface. It was demonstrated that the yield of the deposition process was strictly dependent on the potential applied for Pb UPD layer formation with efficiency more than 90% seen at potentials where full Pb ML was formed[36]. High efficiency and reasonably flat morphology was also seen for the application of up to five SLRR cycles for the growth of Cu in the presence of Cl^- ions [74]. However, in the absence of halide ions the surface morphology of the deposit was rougher than anticipated. This effect can be attributed to some extent to the limitations of the flow-cell use that were discussed earlier in this paper. Electrochemical annealing and halide introduction were found to improve the deposit morphology making it substantially better than that of conventionally bulk-deposited Cu (Figure 5). The

Figure 5

surface structures observed were consistent with the literature [78], except that $\sqrt{3} \times \sqrt{3}$ R30 structure observed for Cu deposition on I-coated Au (111) appeared at higher Cu coverages (more than 2 ML) from that expected based on the literature [79]. The use of flow a cell was also extended to the growth of thicker Cu deposits by up to 500 SLRR cycles on Au films on glass. Interestingly enough, while the thicker films were displaying expected homogeneity and overall appearance at the end of the growth

process, a flattening of the surface was reported in these experiments during the first 30 cycles [76]. The flow-cell deposition approach was also extended by Stickney et al to the growth of thinner [77] and thicker [75] Cu films on Ru substrates. Reasonable efficiency over the first 8 SLRR cycles was reported [77] and levelling of the deposit across the flow cell for the thicker (up to 200 SLRR cycles) Cu films was attributed to the presence of citrate ions in the deposition solution [75].

Alternatively, the growth of ultrathin Cu films on Ag (111) and Au (111) substrates by SLRR was attempted with the implementation of the shuttling approach [31]. However it was discovered that switching cells even in a thoroughly de-oxygenated environment led to the substantial loss of efficiency owing to enhanced activity of the ORR on a Cu substrate [80]. Thus, unlike in the case of Ag grown by SLRR, the shuttling approach was deemed inapplicable for Cu SLRR deposition [31]. A remedy for this shortcoming was found by the application of the one-cell approach for SLRR deposition [31]. Cyclic voltammetry (CV), in situ STM, and X-ray diffraction were employed to monitor the two-dimensional growth and characterize the structure of up to 100 ML of Cu. Similar to the flow-cell study, the growth was carried out with Pb UPD used as the sacrificial metal. Open-circuit potential monitoring during the replacement reaction was used to control the completion of each deposition event. Anodic film stripping of accordingly deposited Cu layers indicated that the efficiency was close to 100% resulting in an average yield of about 0.6 ML Cu (vs a ML of Cu (111)) per SLRR cycle. The excellent surface quality of an epitaxially grown Cu film was determined by distinct Pb UPD voltammetry and ascertained by in situ STM showing uniform surface morphology maintained during the entire growth process. High-resolution STM imaging of a Pb UPD layer deposited on accordingly grown Cu films with thickness of 100 equivalent MLs reveals a structure identical to that of Pb on Cu(111) (Figure 6) [31]. Also Auger

Figure 6

Spectroscopy and X-ray photoelectron spectroscopy (XPS) elemental analysis showed no traces of Pb incorporation into accordingly deposited Cu films. Overall, the use of flow-cell during UHV-EC studies

appears to produce consistent results in terms of the deposition efficiency and lack of incorporated impurities during the SLRR growth of Cu.

In recent development, R. Akolkar et al employed a one-cell SLRR approach for the growth of Cu with Zn UPD as a sacrificial layer in alkaline media thus realizing a Pb-free Cu deposition routine [81]. Following this protocol each SLRR step provides a monolayer of Cu on the substrate surface. Repetition of the SLRR cycles results in the growth of multi-layers of Cu with controlled thickness while minimizing surface roughness. The proposed Cu deposition process is attractive as it eliminates the use of Pb-containing chemistries used in previous formulations of Cu e-ALD; and utilizes an alkaline (pH = 11.2) water-based electrolyte thus minimizing concurrent processes like hydrogen co-evolution. In this work, the authors report cyclic voltammetry, electrochemical quartz crystal microbalance, and anodic stripping coulometry experiments to study the deposition and characterize accordingly grown Cu films with up to 10 fold repetition of the SLRR cycle. Results of the characterization process suggest a relatively flat growth (roughening of about 1.4 times @ 10 layer thickness) and reasonably high efficiency of 86 %. It has been also suggested that the use of Zn-UPD as the sacrificial layer could open pathways for enabling SLRR based routines for the growth of other metals, like Ni and Co, whereby the most frequently used sacrificial metals Pb and Cu cannot work [81].

3.1.3. Pd and Ru Deposition: The deposition of Pd on Pt (111) and on Au (111) by the SLRR of a pre-deposited UPD layer of Cu was studied in detail by Soriaga et al [82] and Stickney et al [57], respectively. The results obtained are of significant interest given the applicability of thin Pd coatings in a variety of scenarios associated with fuel-cell catalysis [83, 84]. Ultrathin Pd films, at coverages that ranging from 0.5 to 8 ML, were found completely free of any residual Cu after the displacement-by-Pd step. Analysis of the current-potential profiles in the hydrogen-adsorption region seconded by results of a LEED study indicated that at one monolayer coverage, the film was essentially pure terrace, devoid of steps, which did not exhibit hydrogen absorption [82]. At higher coverages, gradual roughness development

manifested by the emergence of a voltammetric peak characteristic of hydrogen adsorption–desorption at step sites and weakening of the LEED signal, respectively, was associated with a Stranski–Krastanov transition leading eventually to a 3D growth mode. Investigating the film thickening the authors of [82] found terrace and step voltammetric peaks still noticeable even at a Pd-film thickness of 8 ML. However, the diminishing intensity of the latter peaks was clearly exhibited, indicating the growing role of the appreciable absorption into the Pd deposit due to its evolution into a bulk layer. The hydrogen dynamics indicating transition to absorption domination between 4 and 8 ML of thickness for the Pd film suggests that bulk properties of thin Pd films could be expected at about 5 ML and thicker films.

Pd thin films were formed by the SLRR of Cu UPD layers on polycrystalline Au substrates in an electrochemical flow deposition system [57]. The initial step was Cu UPD, followed by its exchange for Pd ions at open circuit, and finishing with a blank rinse to complete the cycle. Deposits were formed with up to 75 cycles and displayed proportional deposit thicknesses. It was demonstrated by electron probe microanalysis (EPMA) that excess Pd deposition at the flow cell ingress occurs when the SLRR deposition of Pd takes place in a solution containing PdCl_2 salt only [57]. Such results suggested according to the authors that the SLRR mechanism did not involve direct transfer between a Cu UPD atom and a Pd^{2+} ion directly occupying the Cu UPD atom position. Instead, it was proposed that the so-called local-cell mechanism took place in which electrons are transferred through the metallic surface to reduce Pd^{2+} ions near the surface where their activity is highest. It was also hypothesized that if the cell was filled completely before a significant fraction of the Cu UPD atoms had been oxidized then the deposit would be homogeneous. To assess this hypothesis, EDTA and excess chloride [58] were used to complex Pd^{2+} ions, with the general being aim to slow down the Cu – Pd exchange rate. Both complexing agents led to a decrease in the rate of replacement, producing more homogeneous films [57, 58]. Although the use of EDTA improved the homogeneity, it also decreased the deposit thickness by a factor of 3 compared to the thickness obtained via the use of chloride. Thus, chloride was found to be an

effective Pd^{2+} complexing agent, which must be present in a significant excess (like $[\text{Cl}^-]/[\text{Pd}^{2+}] = 500$) in order to decrease the Pd-for-Cu exchange rate considerably and make the direct exchange between Cu and Pd the preferred SLRR growth mechanism [58]. Also, a comparison of the Cu UPD coulometry with the anodic stripping of SLRR grown Pd deposits in the presence of the chloride complex indicated that the exchange efficiency for the replacement was $95 \pm 6\%$. A clear distinction between hydrogen adsorption and absorption was seen in CV results for a 25 SLRR cycle film, suggesting complete screening of the underlying Au. XRD characterization of a 75 SLRR cycle Pd film grown in the presence of chloride complex showed it to be polycrystalline with a predominant (220) orientation matching the (220) grain domination of the Au substrate thus hinting generally at epitaxial deposition [57].

In an application of the optimization effort discussed in the previous paragraphs Pd nanofilms were also formed on Au (111) single crystal bead electrodes [85] with SLRR where Cu UPD was used as a sacrificial metal in the presence of the chloride complex [58]. EC-STM images after one, two, and three cycles revealed monatomic steps and steady morphology development with multiple cycles, indicating a layer-by-layer growth mode. The linear relationship between Pd coverage and cycle number ascertained the layer-by-layer growth operating for nanofilms deposited with up to 30 cycles [85]. These results appeared superior to those of Pd deposited by conventional electrodeposition, in which Kolb et al. observed 3D growth after the bulk electrodeposition of 3 MLs of Pd on Au (111). This comparison illustrated the capability of SLRR to sponsor the growth of flat and uniform epitaxial films in a variety of systems. This finding seconds several other cases where ultra thin SLRR films have exhibited superior quality to that of a comparably thick layers of the same metal electrodeposited directly using bulk deposition [7, 8]. In all of these cases, when more than a couple of MLs (usually two) of metal were deposited, the bulk electrodeposition resulted in roughening, while the SLRR generated deposits remained epitaxial. The unique control over deposit thickness afforded by the SLRR method proved useful for studying the effect of Pd film thickness on the hydrogen adsorption and absorption features,

in part because for thicker Pd films hydrogen absorption masks voltammetry for adsorption. CVs of nanofilms deposited using 1 to 30 SLRR cycles were performed in 0.1 M H_2SO_4 . The underlying Au displayed a significant influence on the positions for hydrogen adsorption/desorption features in deposits formed with fewer than five cycles. Hydrogen absorption occurred for films formed with more than two cycles and produced an average H/Pd ratio of 0.6, in agreement with the literature. All Pd nanofilms deposited displayed features corresponding to the adsorption of hydrogen, even those formed with only one or two cycles. An EC annealing procedure in halide-free H_2SO_4 was also developed. CVs indicated improved surface ordering evidenced by sharper peaks and increased reversibility for adsorption/desorption, producing a surface closely resembling an ideal Pd (111). Characterization of a 60-cycle Pd deposit using X-ray diffraction pole figures showed the Pd (111) crystal planes to be epitaxial in orientation with the Au (111) substrate. Overall, the use of SLRR has been shown to facilitate a range of experiments where the amounts and morphology of Pd deposits must be known and controlled on the atomic scale. In the formation of nanofilms, the ability of SLRR to control the amounts deposited at the atomic level is invaluable. It is one thing to electrodeposit homogeneous layers under well-controlled conditions on a perfectly flat single crystal using an overpotential and another to deposit a conformal monolayer on complex surface structures, such as catalysts and powders, with the atomic layer control provided by an SLRR based method.

Developmental work was done by Stickney et al also for the SLRR growth of Ru on a Au substrate by using a Pb UPD sacrificial layer [86]. Accordingly grown Ru films demonstrated known from the literature XRD pattern and CV curves. A slow negative trend of the OCP during the first 20 SLRR cycles suggested no continuous coverage for such thicknesses of the deposit. Initial ex situ STM studies revealed very flat films for up to 200 SLRR cycles, with overall roughness of a couple of nanometers. However, the development of grains in the deposit suggests an overall roughening nucleated in the very beginning of the growth process. The charges for Pb UPD suggested a negligible increase in deposit surface area,

while CV results on Ru oxidation and reduction after 200 SLRR cycles contradicted the Pb UPD result with a difference of an order of magnitude higher area. This result is yet to be understood. Growing Ru by implementing the SLRR concept was found also efficient for the removal of even traces of Pb (less than 1 at% as measured by EPMA), especially in the case of when the process was completed with the stripping step of the cycle [86].

3.2. SLRR Growth of Pt thin films

3.2.1. Pt Deposition by SLRR of Cu UPD: The first use of a Cu UPD layer for the SLRR deposition of Pt was reported by Brankovic et al in 2001[27] where the Pt deposit on Au (111) surface made a 2D submonolayer consisting of partially interconnected clusters. Since that time single-cycle SLRR deposition by Cu UPD of Pt and other catalytically active metals and alloys often containing Pt have been heavily exploited by Adzic et al for coating of a nanoparticulate support in the design of catalysts for fuel cell applications[6, 87, 88]. That is why there has been a steady interest in the investigation of details associated with the mechanistic and kinetic aspects of the galvanic displacement of Cu by Pt. In 2010 Brankovic et al explored the stoichiometry of the said redox exchange reaction [37]. A linear dependence between amount of deposited Pt and coverage of the replaced Cu UPD monolayers was observed. The analysis in that work also showed that the oxidation state of Cu during a galvanic displacement reaction is predominantly 1^+ , suggesting that four Cu UPD adatoms were displaced by a depositing Pt adatom bringing the exchange Cu/Pt ratio to 4:1 instead of 2:1 (Figure 7). The domination

Figure 7

of Cu^+ vs Cu^{2+} was rationalized through the Cu(I) ion stabilization by the excess of Cl^- ions in the near electrode vicinity resulting from the destruction of the Pt(II) or Pt(IV) complexes participating in the SLRR reaction carried out on perchlorate based solution[37]. Interestingly enough, no such stabilization was observed in sulfate electrolytes [37]. Historically, shortly after the first SLRR publication Weaver et al[30]

followed this up with multiple SLRR cycles (4, 8) using not only PtCl_6^{2-} but also PtCl_4^{2-} to displace the Cu UPD layer. In this study it was concluded that the Pt deposition yield increased when PtCl_4^{2-} was used and that some roughening was occurring with the increase of the number of cycles. The first systematic study of the growth of Pt thin films on Au by the SLRR of Cu UPD at the atomic level carried out by Stickney et al [35] demonstrated the densification of a Pt cluster network leading to an ordered layer in the presence of I^- ions acting as a surfactant. It was also shown that after the application of three or more SLRR cycles, a (3 x 3)-iodine structure characteristic for I atoms adsorbed on Pt(111)[89], could be observed. Thus, SLRR was found applicable not only for surface modification but also for the growth of ultrathin and continuous Pt films[35]. In another study of Stickney's group [56] Pt deposits formed by the SLRR of Cu UPD sacrificial layers appeared to depend in thickness / morphology upon how positive the OCP drifted during the exchange step, and how much rinsing was performed before dropping the potential negative for the UPD of the sacrificial layer. This dependence indicated that adsorbed at positive potentials Pt complex reduces upon application of negative potential for Cu UPD layer formation and contributes to the overall deposition yield [56]. A strict potential and time control helped to minimize the earlier mentioned spontaneous Pt deposition in the standard SLRR layout [37, 70]. The contribution of the "spontaneously" deposited Pt accounting for as high as 20-25% depending upon the specifically chosen growth protocol was also acknowledged by Brankovic et al [37]. Another study of Pt thin film growth by SLRR of Cu UPD carried out in an one-cell configuration reported the retardation of the SLRR rate during the transition from substrate Au to coated with Pt surface attributed to the difference in reversibility of Cu UPD on Au and Pt [59]. It was also found that Cu was incorporating in Pt films grown by SLRR at rates up to 13 at% [59] depending upon the experimental conditions employed in the growth. Incorporation of Cu into the depositing Pt in the flow-cell configuration was also confirmed in the work of Stickney et al where the Pt:Cu ratio of order of 10:1 was determined[56]. All multi-cycle studies of Pt growth by the SLRR of Cu UPD reported considerable roughening of the deposit with the

number of cycles as well [56, 59]. Attempts have been made to understand the roughening mechanism looking into the exchange ratio, potential ranges, anion type etc. The work along these lines is ongoing.

3.2.2. Pt Deposition by SLRR of Pb UPD: The first systematic study of multi-cycle Pt deposition by SLRR of Pb UPD layers using $[\text{PtCl}_4]^{2-}$ was presented by Dimitrov et al [59]. Performed in an one-cell configuration this work demonstrates in detail the complexity of Pt deposition by SLRR and presents a comparison at different points of the use of Pb and Cu UPD as sacrificial layers [59]. It is shown that it is possible with only one SLRR event of Pb UPD to form a Pt film on Au that behaves like pure Pt in the H UPD reaction (see Figure 8). To corroborate this result open circuit chronopotentiometry and quartz-

Figure 8

crystal microbalance experiments demonstrated steady displacement kinetics and a yield that is higher than the stoichiometric (1:1) Pt(II) - Pb exchange ratio. The higher yield was attributed to the presence of extra reduction power that could be attributed to the oxidative adsorption of OH_{ad} and/or to H adsorption/desorption phenomena, both reported to take place along with the UPD of Pb layers on Pt surfaces [90, 91]. The overall high yield was also demonstrated by STM observation of a dense Pt cluster network that forms on the Au surface even after one-step SLRR of the Pb UPD layer. Analysis of the STM results shows that the accordingly grown Pt layer significantly exceeds in cluster density and area coverage the Pt deposit identically generated but with the use of Cu UPD (Figure 9) [59]. This comparison is also supported by already discussed results of Brankovic et al [37] emphasizing the 2:1 Cu

Figure 9

– Pt(II) exchange ratio owing to the stabilization of Cu^{1+} state of oxidation. It was also seen that unlike the decreasing rate of exchange in the Pt(II) – Cu system the redox replacement of Pb by Pt(II) exhibited overall faster and relatively constant rate throughout of the deposition process [59]. CV curves of H UPD on Pt layers grown by SLRR of Pb UPD and ex-situ STM results both showed that no substantial

roughness evolution takes place on the growing Pt layer up to 10 replacement events. Even more, the Pt films consist of small clusters that show very similar size (diameter) and distribution for different thicknesses. For these films, the H-UPD area measurements agree well with this finding, whereas in the case of Cu UPD the same approach of roughness assessment suggests a surface area increase. This result is also supported by the findings of Stickney et al who reported the substantial roughening of Pt deposits grown by the SLRR of Cu UPD in a flow cell configuration [56]. Also, no evidence of the presence of low-index faces other than (111) were found by XRD characterization of a thicker Pt layer, grown by SLRR of Pb UPD on Au (111) textured films which implies an epitaxial growth in that system[59]. An EDS compositional analysis of the Pt layers grown by SLRR suggests incorporation of a about 4 at% Pb when Pb UPD was used as sacrificial metal in the deposition process. It was also shown that the amount of Pb incorporated into the Pt deposit depended strictly upon the so-called “stop potential [56]” chosen as positive limit in the course of SLRR protocol[59]. More recently, Vasiljevic et al exploited this finding to expand on a study of controlled design of Pt – Pb surface alloy [61] with application in organic fuel oxidation that will be discussed in more detail later in this paper. A detailed study of Pt deposition by the SLRR of Pb UPD in a flow-cell was also reported by Stickney et al [56]. Alike with the one-cell study, substantially shorter exchange time (by about 9 times) was reported when Pb UPD was used as sacrificial metal in comparison with Cu UPD. Also, about twice more Pt was reported to deposit when Pt(II) complex was used instead of Pt(IV) to displace the Pb UPD layer as well as the deposit’s surface similarly to the one-cell study was overall found flatter in comparison with the use of Cu UPD layer [56]. Unlike in the one-cell work, no incorporated Pb was found in the Pt deposit within the limits of detection in the flow-cell study. In this study issues with the deposition of excess Pt during SLRR deposition related to how positive the OCP drifted during the exchange step, and how much rinsing was performed before initializing next SLRR cycle were demonstrated [56]. To limit the OCP, a “stop potential” step was incorporated. It was shown that the higher the stop potential used, the more Pt that was deposited.

This was associated with the stronger adsorption of Pt complexes at higher potentials. This warranted longer blank rinses before the initialization of the next SLRR cycle in order to prevent the spontaneous deposition from happening during the UPD step. Using Pb UPD as a sacrificial layer, with a stop potential near 100 mV (vs Ag/AgCl), and increased blank rinsing, the expected rate of Pt nanofilm growth was observed, which was consistent with the layer by layer mode anticipated in a desired SLRR deposition configuration [56]. Further optimization of the above described SLRR deposition in a flow-cell is ongoing in order to obtain the best morphology and efficiency results.

3.2.3. Pt Deposition by SLRR of H UPD and ESLRR: A surface limited redox replacement (SLRR) protocol for the growth of Pt thin films using adsorbed H or also called underpotentially deposited H (H-UPD) was first demonstrated in an one-cell configuration [92]. In contrast to the previously discussed studies on SLRR deposition the use of H UPD constitutes the first application of the SLRR protocol in a single-cell configuration using a nonmetal UPD system. Utilizing H-UPD to mediate Pt growth is of significance for “green” Pt deposition in that it minimizes the use of environmentally hazardous chemicals by precluding possible mediator metal incorporation that has been reported in standard Pt SLRR protocols. It is noteworthy that the pre-seeding with Pt or Pd was performed if a substrate that did not feature H UPD was used in the deposition process [59, 93]. Open circuit chronopotentiometry and EQCM experiments demonstrated steady displacement kinetics manifested by relatively constant displacement rate throughout the deposition process and a yield that is equal to the expected stoichiometric Pt(II)–H exchange ratio (1:2). CV characterization of Pt films shows that the growth via SLRR of H-UPD results in an increase of the surface roughness with the number of replacement steps. A comparison of this result with results of previous studies suggest that the roughening with H UPD used as sacrificial layer is more than that with Pb but considerably less than that observed when Cu is used as the sacrificial layer [56, 59]. The uneven exchange ratio of the SLRR reaction and the direct exchange mechanism are seen as factors sponsoring the roughness evolution [92]. The morphology of as-

deposited films has been analyzed by Scanning Tunneling Microscopy. Moreover, the roughness of SLRR deposited Pt films has been compared with films grown in the same solution at two different overpotentials: without adsorbed H (bulk deposition) and with H-UPD floating on the surface i.e. H-

Figure 10

surfactant mediated growth [8, 14]. The results show clear advantages of using the SLRR approach which generates films with nearly two times lower roughness than the ones grown by bulk deposition and SMG (Figure 10). Finally, the generality of the SLRR protocol based on H-adsorption was demonstrated by extending its applicability to Pd nanosystems, i.e. 2 ML Pd films on Au and Pd nanocubes. The properties of platinized surfaces with 30 SLRR steps were subjected to formic acid oxidation tests and were shown to agree with generally expected behavior of Pt-like surfaces, although Pt films deposited on NPs suggested the possibility of Pd–Pt alloying [94]. In a study of a different nature, adsorbed from gas phase H on a Pd surface was used to develop a strategy for preparing such materials that combines important properties from an applied stand point like (i) scalability (especially on high-surface-area substrates, e.g. powders); (ii) uniform deposition, even on substrates with complex, three dimensional features; and (iii) low-temperature processing conditions that preserve nanopores and other nanostructures. Not long ago, Stickney et al presented a method that exhibits these properties and makes simplified use of reagents that could be H terminated by simple adsorption [49]. By exposing Pd powder to dilute hydrogen in nitrogen gas, sacrificial surface PdH is formed along with a controlled amount of dilute interstitial hydride. Once the flow of reagent gas is terminated, the addition of metal salts facilitates controlled, electroless deposition of an overlayer of subnanometer thickness. This process can potentially be cycled to create thicker layers. The approach is carried out under ambient processing conditions [49]. The hydride-mediated reaction is electroless in that it has no need for connection to an external source of electrical current. This according to earlier discussion in this paper enables deposition on high-surface-area substrates having rich, nanoscale topography as well as on

insulator-supported catalyst particles. STEM-EDS measurements showed that conformal Rh and Pt surface layers can be formed on Pd powder with this approach. A growth model based on energy-resolved XPS depth profiling of Rh-modified Pd powder is in general agreement. After two cycles, deposits are consistent with 70–80% coverage and a surface layer with a thickness from 4 to 8 Å. STEM-

Figure 11

EDS spectral maps demonstrated that uniform coverage occurred even on narrow cavities and protrusions with subnanometer dimensions, suggesting that this method is amenable to substrates having irregular surfaces or complex 3D features (Figure 11). Furthermore, this method can be used to modify the surface of commercially available Pd/C, a material routinely used for chemical catalysis. This method is a general, scalable, and mild strategy for deposition of atomic scale layers of metals on a variety of substrates. Finally, a recent work of Dimitrov et al demonstrates the extension of ESLRR [48] to the deposition of Pt on polycrystalline Au through the displacement of Pb and Cu [66]. This study was first carried out with the use of Pb and Cu executive electrodes explored by the utilization of their respective cations as sacrificial mediators. Next, a “green” Pd-H electrode was also explored with Pb²⁺ used as sacrificial metal. Mixed potential diagrams were presented in order to predict the potential of each executive electrode, and potential-time curves were also shown to demonstrate both the transient

Figure 12

(right after the contact between WE and EE was established) and steady-state potential behavior for each respective electrode [66]. Pb and Cu exhibited expected mixed potential behavior with immediate potential establishment (Figure 12) whereas the Pd-H electrode featured a slow steady-state potential realization associated with the poor reversibility of H absorption / desorption on Pd surfaces [95]. It was shown that the deposition of a thin Pt layer on the Pd-H (Pt, Pd-H) electrode enhanced the reversibility of H absorption and desorption resulting in viability of the electrode [66]. Pt films grown by ESLRR up to 200 replacement events were characterized electrochemically via H UPD. Also in agreement with

morphology results obtained by conventional SLRR, films deposited via Pb mediation exhibited slow surface area evolution whereas the surface area development was much faster when Cu mediation was used. Morphology characterized by scanning tunneling microscopy carried out for up to 10 displacement events, exhibits uniform nucleation followed by cluster growth, overlapping and eventual merging during subsequent ESLRR cycles.

3.2.4. Self-Terminating Growth of Pt Governed by ion adsorption and H UPD: In another study a very smart use of interplay between strong Cl^- ion adsorption and H UPD was used to enable a self-terminating rapid electrodeposition of Pt ML films from a $\text{K}_2\text{PtCl}_4\text{-NaCl}$ electrolyte demonstrated on Au (111) starting substrate by Moffat et al [96]. While this approach does not involve SLRR layout, it emphasizes an atomic layer deposition like scenario whereby under specific experimental conditions the Pt growth was terminated at monolayer level at potentials just negative of H-reduction. It is believed that a complete H UPD layer alternates the double-layer structure and thus enables the self-termination mechanism [96]. The surface could be reactivated for further Pt deposition by stepping the potential to more positive values, where the H UPD layer is stripped and fresh sites for the adsorption of $[\text{PtCl}_4]^{2-}$ and Cl^- anions become available. Periodic pulsing of the potential was carried out from a range positive to the Pt potential of zero charge, where the surface is blocked for deposition by adsorbed $[\text{PtCl}_4]^{2-}$ and Cl^- anions, to negative values where the H UPD covers the entire surface. This pulsing enables the sequential deposition of two-dimensional Pt layers demonstrated clearly by EQCM measurements

Figure 13

(Figure 13) and STM characterization [96]. The thickness of the Pt films can be controlled at will depending upon specific applied purposes. The most valuable aspect of the accordingly deposited layers of Pt is their applicability for initial deposition over a variety of substrates that could be initially terminated by a layer of deposited anions and that could then be coated with exactly one layer of Pt by extinguishing the growth by H UPD. Realized in this way, The Pt deposition process could continue until

the desired thickness is achieved. The proposed method has been recently applied for functionalization of catalysts with application in fuel-cells magnetics and microelectronics [97-99].

3.3. Deposition of Alloys and Multilayers

The deposition of alloys and multilayers using SLRR based protocols has still been under developed in comparison with their single metal counterparts. Most of the interest that would motivate the developmental effort associated with alloy deposition at the present time is related to the synthesis of efficient and durable catalysts [100]. This is additionally supported by ongoing studies on a variety of nanoparticulate binary and even tertiary alloy catalysts for oxygen reduction, hydrogen and organic fuel oxidation [87]. That is why all studies implementing SLRR protocols in the growth of alloy thin films are heavily focused on the deposition of binary alloys of Pt with other metals [50, 61, 101, 102]. This is why the first section of this section will present an overview of recent developments in this field.

3.3.1. Deposition of Binary Alloys by SLRR: The first alloy deposition by SLRR was carried out by Adzic et al [50] in systems encompassing binary alloys of Pt with other metals that can potentially boost the catalytic performance toward the ORR in comparison to pure Pt. This work was preceded by another where electrocatalysts were made with a Pt monolayer supported on pre-selected foreign metal nanoparticles [103, 104]. The reported new class of ORR electrocatalysts in Adzic group's work consisted of Pt alloyed with another late transition metal ($M = \text{Ir, Ru, Rh, Pd, Au, Re, or Os}$) deposited as a monolayer on the surfaces of Pd (111) single crystals or carbon-supported Pd nanoparticles [50]. The deposition was handled in a very similar fashion as it would be carried out for pure Pt deposition and was carried out in a single step shuttling configuration. This configuration was realized by immersing a pre-coated with Cu UPD layer substrate in a solution containing concentrations of Pt and M complexes that would eventually ensure a Pt_3M composition. Accordingly deposited electrocatalysts were found to have a very high activity compared to that of pure Pt ORR catalysts and a considerably lower Pt content.

A gain in current density up to a factor of 400%, compared to all-Pt, has been realized by replacing part of the Pd-supported Pt monolayer with another transition metal, M, where M = Ir, Ru, Re, or Os [50].

In another work, Dimitrov et al compared the catalytic activity toward for formic acid oxidation of Pt₄Cu nanocubes and nano-octahedra with Pt₄Cu (100) and (111) alloy thin films. This work introduced for the first time use of multi-cycle SLRR based deposition protocol of for epitaxial growth of thin alloy films using Pb UPD sacrificial layer [102]. In this effort the thin alloy films were prepared by up to 30 SLRR cycles for deposition on Au (111) and (100) substrates. Unlike the previously considered work, an XPS characterization suggested that the pre-selected Pt(II) to Cu(II) concentration ratio in the deposition solution provided less than expected atomic fraction of Cu in the accordingly deposited film. Also, similarly to the pure Pt deposition by SLRR [59], a noticeable amount of incorporated Pb (up to 8 at%) was found in the deposited film. Characterization of the alloy thin films with H UPD CV curves ascertained the preferential orientations of the deposited films [102]. Overall, when compared to pure Pt the Pt₄Cu catalysts deposited by SLRR in this work exhibited superior performance toward formic acid oxidation in terms of activity and durability [102].

In a study with more emphasis on the growth aspects of alloy catalyst design Vasiljevic et al used the fine tuning of Pt(II) – Pb exchange during Pt SLRR deposition to design two-dimensional Pt–Pb nanoalloys with controlled thickness, composition, and structure [61]. The electrochemical behavior of these alloys has been systematically studied as a function of alloy composition. In that study, a two-step SLRR protocol based on the galvanic replacement of underpotentially deposited monolayers of Pb with Pt was used to grow epitaxial Pt_{1-x}Pb_x (x < 0.1) alloys of up to 10 ML thickness on Au substrates. It was shown that by pre-selecting different “end potentials” of the galvanic displacement step, the Pb atomic content can be controlled in the films (Figure 14) [61]. CV tests of accordingly deposited alloys showed

Figure 14

that the adsorption of both H and CO exhibits similar and systematic trend to lower values with increase in the Pb content. These measurements, commonly used in electrocatalysis for the determination of active surface areas of Pt, suggested low nominal area values. Indeed, measured in that way, the surface area turns to be much lower than one would anticipate based on the net Pt composition in the alloy as measured by XPS [59, 61]. Such discrepancy in both values suggests a strong screening effect of Pb on the adsorption of both H and CO. In addition, changes in alloy composition resulted in a negative shift in the potential of the peaks of CO oxidation that scales with the increase of Pb content. The results suggest impact of electronic and bifunctional effects of incorporated Pb on the redox behavior of Pt. The study of Vasiljevic et al illustrated the potential of the SLRR methodology, for controlled design of two-dimensional bimetallic Pt nanoalloys. Careful tailoring of the alloy structure and composition can be essential in the fundamental studies of electrocatalytic behavior as a function of the nature of alloying metal and its content in the alloy catalyst [105, 106].

A study for use of SLRR in the growth of bimetallic PtRu nanofilms in a flow-cell on Au electrodes was published recently by Stickney et al [107]. In this study, PtRu nanofilms were formed using SLRR for Pt and Ru, with Pb UPD used as sacrificial layer. The choice of Pb UPD instead of Cu UPD was warranted by its more suitable potential range and faster exchange rate with the growing metals [56]. The composite PtRu SLRR cycle consisted of successive iteration of single-cycle Pt(IV) and Ru(III) replacement reactions with pre-deposited Pb UPD along with rinsing with blank solution between the SLRR cycles. PtRu nanofilm thickness was generally controlled by the number of iterative cycle repetition. The Pb UPD charge and OCP changes during replacement were also monitored throughout the deposition process. PtRu nanofilms with atomic ratios of 70%/30%, 82%/18%, and 50%/50% Pt/Ru were reportedly deposited by 25 composite SLRR cycles on Au coated glass slides [107]. Mild to moderate surface roughening was observed during the deposition process. The PtRu films were then characterized by CO adsorption and electro-oxidation to determine their overpotentials. The 50%/50% PtRu nanofilms were

found to exhibit best CO tolerance and highest electro-oxidation activity even in comparison with pure Pt, and pure Ru [108] (Figure 15).

Figure 15

3.3.2. Catalyst Design and Deposition of Multilayers by SLRR: In an effort to develop method for the synthesis of multilayered bimetallic Ru|Pt nanoclusters, supported on glassy carbon, Cukrovski et al reported for the first time the use of a flow-cell setup for running SLRR deposition of two metals [47]. In this work the nanoclusters were synthesized via SLRR reactions involving sacrificial Cu, deposited prior to the formation of each individual noble metal layer, in a sequential fashion. It was demonstrated that the Cu adlayers control the morphology and electrochemical properties of the resultant nanostructures [47]. A specifically designed electrochemical flow-cell was used not only for automated sequential electrodeposition of the multilayered nanoclusters with controlled composition but also for subsequent electrochemical and electrocatalytic tests carried out on as-deposited alloys. Sequentially deposited Ru|Pt nanoclusters on glassy carbon electrodes were found to exhibit superior electrocatalytic activity to methanol electro-oxidation in comparison with the single metal Pt nanoclusters and Pt-Ru alloy nanostructures, also co-deposited by SLRR [47] (Figure 12). Moreover, it has been established that the electrochemical process taking place at the Ru|Pt nanoclusters followed the bifunctional mechanism. Electrokinetic studies of the oxygen reduction reaction (ORR) were also performed. Analysis of hydrodynamic linear sweep voltammetric experiments, performed at various flow rates in oxygen-saturated acidic medium, revealed that the Pt and Ru|Pt nanoclusters exhibited direct four- and two-electron ORR pathways, respectively [47]. In a follow up to this work, Cukrowski et al presented a study of the electrochemical, surface and bulk compositional properties of multilayered nanoclusters of Pt and Au, deposited by sequential SLRR on glassy carbon using again Cu as the sacrificial metal [54]. Variations of open-circuit potentials during redox-replacement steps indicated the thermodynamically-favored formation of Pt(s) and Au(s). Unique bimetallic interfacial active sites, Pt|Au or Au|Pt, were effectively

generated as evidenced by their distinct surface electrochemistry and multicomponent X-ray photoelectron spectral features. The bulk and surface-to-near surface distribution of Pt and Au appeared to be influenced by the stoichiometry of the SLRR reactions of the deposited metals with the Cu sacrificial layer through which the nanoclusters were synthesized. Interactions between metal centers, carbon and oxygen containing surface functional groups on the glassy carbon appeared to have played a significant role in the overall stabilization and catalytic activity of the nanoclusters. Profound effects were also found on interfacial charge-transfer and adsorptive properties involving CO and its subsequent electro-oxidation to CO₂, as well as on the electrocatalytic activity involving the formic acid oxidation reaction, where the Pt-rich (Pt|Au) exhibited the highest activity.

The deposition of multilayers by SLRR with modulation thickness greater than one monolayer was also studied by Dimitrov's group[109]. The interest was focused on the successive growth of Ag and Cu on Au (111) substrate using Pb UPD as sacrificial layer [31, 32]. The SLRR was performed in one-cell configuration for each of the metals of interest so that the deposition was carried out in two different cells containing Cu²⁺ and Ag⁺ ions, respectively. The aim of that study was to assess the SLRR approach's capacity to produce flat and uniform epitaxial layers that could screen the underlying substrate at minimum thickness. The outcome of such study was expected to shed light on the applicability of SLRR protocols for the growth of multilayers with sharp interlayer interface and low modulation thickness comparable to those routinely deposited in UHV [110]. In this work the surface morphology and crystallographic orientation as shown in Figure 16. Results of this study are presented in this figure with

Figure 16

aim to ascertain the quality of the successively deposited layers and bare Au (111) substrate (illustrated with inserted schematic) assessed by Pb UPD CV curves (Figure 16A) and in-situ STM micrographs (Figure 16B). CV curves of Pb UPD on Ag (111) and Cu (111) are also presented as insets to the main CV

plots for comparison. It is clearly seen that 30 MLs (~ 8 nm) of Ag and 20 MLs of Cu (~ 4 nm) deposited epitaxially in quasi-2D growth mode are sufficient enough to screen electrochemically the underlying metal and to develop remarkably flat and uniform morphology guaranteeing a general interface

Figure 17

thickness that would be considerably smaller of the modulation thickness [109]. An additional layer of characterization of as-deposited multilayered structures is provided by their subsequent anodic stripping shown in Figure 17. Stripping of 30Ag19Cu10Ag and 30Ag19Cu20Ag (the coefficients reflect # of monolayers) sequenced metal layers are associated with two anodic peaks at around 0.62 and 0.89V vs Pb^{2+}/Pb PRE, which corresponds to the electro-dissolution of copper and silver, respectively. While the dissolution of the copper layer that is sandwiched between two silver layers starts at a potential of 0.55 V Pb^{2+}/Pb , pure copper dissolution in same experimental condition is initiated at 0.4 V. This 0.15 V difference of Cu dissolution potential implies a de-alloying-like behavior and suggests that a silver layer can confine the underlying copper and prevent the dissolution to a large extent. Apparently, complete passivation of Cu dissolution can be achieved after the passivating Ag layer reaches a thickness of 30ML of Ag (30Ag19Cu30Ag). Similar in nature experimental results, albeit in different (cross-section) configuration, have been shown by Sieradzki and co-workers by silver selective dissolution of Ag-Au multi-layer structures system grown in UHV to achieve a controlled modulation thickness [110].

The field of catalyst design at sub-monolayer level has been pioneered by recent work of Brankovic et al that presents a study of the nucleation of Pt deposited via SLRR of Cu UPD ML [111]. Results showed that Pt nucleation depends directly on the coverage of Cu UPD on the Au(111) substrate. Maximum nucleation density was measured at coverage of 0.63 of the Cu UPD layer. Expectedly, minimum in the average cluster size of the nucleated Pt was determined at the same coverage. The analysis of the experimental results and the developed analytical model identified the redox replacement stoichiometry, rate constant and reaction order as the key parameters affecting the Pt

nucleation density and the average cluster size. Overall, it was demonstrated that for faster SLRR reactions one should expect higher nucleation density and lower average cluster size at fixed initial coverage of the UPD layer to be replaced [111]. Also, conditions associated with larger stoichiometric ratio and lower reaction order at fixed UPD layer coverage would lead to higher Pt nucleation density and smaller nanoclusters as well. On the contrary, if larger clusters with lower overall density are needed for the specific catalytic application the authors recommend a reaction solution with no complexing ability toward Cu and low Pt^{4+} ion concentration. Overall, the optimization of above considered parameters vis-à-vis specific requirements of the Pt catalyst enabled a design of the optimum experimental conditions leading to the desired morphology associated with the nanocluster ensemble. In a step to further depth of design and control Brankovic et al demonstrated the synthesis of a cluster-structured, single layer, bi-metallic RuPt catalyst on Au(111). This catalyst is synthesized using SLRR of underpotentially deposited Cu and Pb monolayers through a two-step process [112]. According to the authors the resulting 2D RuPt monolayer nanoclusters have a unique core-edge (CE) structure with a Ru core and Pt at the edge along the perimeter. The RuPtML-CE/Au(111) catalyst was deposited using a complex procedure in which the RuML/Au(111) is deposited first by the SLRR of Cu UPD layer. Then, in a second step, a small amount of Pb is deposited via UPD on RuML/Au(111) at underpotential of 275 mV. The Pb atoms are then replaced by Pt(IV) [37]. In this synthetic route the most sophisticated element is associated with very careful tailoring of the Pb UPD potential (best choice of 275 mV [112]) prior to the Pt SLRR in the last step. Ideally, this tailoring is aimed at generating of a row of Pb atoms around the Ru clusters that upon redox replacement with Pt(II) would result in C(Ru)E(Pt) cluster structure (Figure 18). Once the catalyst was synthesized, its activity was evaluated using CO monolayer

Figure 18

oxidation as the probe reaction. Cyclic voltammetry demonstrates that the 2D RuPt core-edge catalyst morphology is significantly more active than either Pt or Ru monolayer catalysts. Density functional

theory calculations in combination with infra-red spectroscopy data point toward oscillating variations (ripples) in the adsorption energy landscape along the radial direction of the Ru core as the origin of the observed behavior. Both, CO and OH experience a thermodynamic driving force for surface migration towards the Ru-Pt interface, where they adsorb most strongly and react rapidly. The authors believe that the complex interplay between epitaxial strain, ligand and finite size effects is responsible for the formation of the rippled RuPt monolayer cluster, which provides optimal conditions for a quasi-ideal bifunctional mechanism for CO oxidation, in which CO is adsorbed mainly on Pt, and Ru provides OH to the active Pt-Ru interface [112].

4. Modelling and Mechanistic Aspects of the SLRR Deposition Process

Work has been done since the very beginning of the development of SLRR based protocols in order to understand best the kinetics of a single-cycle replacement reaction [113, 114] and lately also the deposition process as sequence of multiple replacement reactions [115]. Activities along these lines focus mostly on modelling of the potential time dependence at open circuit potential when the redox replacement takes place. Also, related results have been used to derive some indirect conclusions on mechanistic aspects of the replacement reaction and more specifically on assessing the impact of both, direct exchange growth and local cell mechanism [27, 28].

4.1. Modelling of a Single-cycle SLRR Reaction:

The first effort on modelling a single-cycle SLRR reaction with aim to understand the kinetics of the galvanic displacement process was made by Dimitrov et al [113]. In this work the redox exchange between a Pb UPD layer and oxidizing agents such as dissolved oxygen and/or more noble metal ions at OCP has been modeled analytically and the developed kinetic equations have been experimentally validated. The proposed model is focused on the dependence of UPD-layer stripping kinetics upon a

galvanically coupled reduction process [113]. Mathematically, this is manifested by a balance between (i) the overall UPD stripping charge determined by anodic polarization curve that consists of double-layer and faradaic components and (i) the cathodic charge steadily accumulating with the ongoing reduction. The modelling work results in the derivation of Equation (2) for the time of stripping $t_{str}(E)$ of a UPD layer featuring either Langmuir [116] or Frumkin [117] type adsorption behavior as function of

$$t_{str}(E) = \frac{C_{DL}(E-E_i) + zFI \left[0.5 - \frac{1}{\pi} \arctan\left(\frac{E_p-E}{\Delta E}\right) \right]}{\left[0.5 + \frac{1}{\pi} \arctan\left(\frac{E_p-E}{\Delta E}\right) \right] (I_1 - I_2) + I_2} \quad (2)$$

the potential E over the course of stripping process (see Equation 2). In this equation C_{DL} is the capacitance of the double layer per unit area, E_i is the potential of stripping process initiation, E_p and ΔE are the peak potential and the full-width at half maximum of the stripping curve, respectively, Γ_s is the number of UPD metal atoms at maximum coverage of the electrode, and I_1 and I_2 are the steady-state current densities measured under the assumption of mass transport limitations on the electrode with and without the UPD layer, respectively. The model has been validated for ORR driven oxidative stripping of a Pb UPD layer on Cu (111) and Ag (111) surface at OCP [33] by fitting experimentally obtained OCP transients to the analytically derived equations. The proposed model has been also ascertained by the comparison of experimentally measured parameters with best-fit values derived by fitting experimentally obtained OCP transients by the model equation. An excellent match between theory and experiment in that work validated the proposed analytical model for systems where the reduction counterpart in the galvanic displacement reaction takes place under mass transport limitations that naturally exist in most of the applied SLRR protocols. In a spin-off of this work an analytical approach for determining trace amounts of Pb and Tl in drinking water was developed based on slowing down the kinetics of nitrate electroreduction by the competitive formation of Pb or Tl UPD layers on a Cu electrode [118].

A step in the further development of modelling views of a single-cycle SLRR reaction was made by Brankovic et al by generalizing the involved phenomenology to include a reduction counterpart of the galvanic displacement that proceeds under kinetic limitations [114]. This work was done in consideration of systems in which a Pt(IV) complex displaces Pb or Cu UPD layers on Au (111) electrode. The analytical and experimental components of this activity consider separately cases in which the reduction reaction in the galvanic displacement takes place under either mass transport control (referred to as TLRR) or kinetic control (referred to as SLRR in ref. [114]). While the derivation of analytical solution for the kinetically zero order ($N = 0$) TLRR case phenomenologically coincides with the results of Dimitrov et al [113] the case where kinetic limitations operate yields a complex Equation (3)

$$E = E_{\theta \rightarrow 0} - \frac{RT}{mF} \left[\ln \left(\frac{(1+Kt)^{\frac{1}{1-N}}}{1-(1+Kt)^{\frac{1}{1-N}}} \right) + f(1+Kt)^{\frac{1}{1-N}} + g(1+Kt)^{\frac{3}{2-2N}} \right] \quad (3)$$

describing a first-order ($N = 1$) displacement reaction of a UPD layer following the adsorption model of Bruckenstein et al [119] that includes the Langmuir adsorption behavior [116] and the impact of Temkin [120] and Frumkin [117] adsorption related factors f and g , respectively. In this equation K is the rate constant of the displacement reaction, m is the state of oxidation of the UPD metal ions, and $E_{\theta \rightarrow 0}$ is the potential where no UPD atoms are present on the substrate surface. The quantification of the kinetic parameters for metal deposition in regimes associated with the SLRR and TLRR of UPD layers using the developed theoretical framework enables the estimate of important kinetic parameters, as rate constants, reaction half time etc, and also allows for fitting of experimental data of sophisticated experimental design with strict control of deposition flux, or manipulation of nucleation kinetics (Figure

Figure 19

19). Generally the results and analysis in that work suggest that the kinetics of Pt deposition via SLRR reaction depend strongly on the nature of the UPD layer [114]. The comparison between the deposition

experiments with Pb/Au (111) and Cu/Au (111) in H₂SO₄ acidified electrolyte suggested that faster deposition kinetics should be expected with Pb as the UPD metal featuring lower work function. In addition, the nature of the anions in the supporting electrolyte has been identified for the first time as factor playing an important role on the SLRR kinetics. It has been concluded that in systems where chloride is the only complexing anion in the supporting electrolyte, the observed trend between the kinetics of Pt SLRR deposition of Cu and Pb UPD layers can be reversed. In the case of Pb/Au (111) the choice of supporting electrolyte has a significant effect on the kinetics of the Pt deposition while in the case of Cu/Au (111) no significant effect has been observed. The results of this work also expectedly showed that the concentration of depositing ions/complex (Pt(IV)) has a direct effect on the SLRR kinetics. Overall, a higher concentration of depositing ions/complex yields faster kinetics of deposition process via both SLRR and TLRR reactions. This finding along with the necessary kinetic analysis provides an effective and easy approach to achieve the optimum metal (Pt) deposition rate depending on the desired deposit morphology and its application. The work of Brankovic et al with its complexity and conclusions covers only a single-cycle replacement reaction of a SLRR deposition process [114]. In the case of multi-cycle SLRR deposition employed for thin film growth applications a change of the parameters associated with the deposition kinetics should be taken into account owing to change of the UPD/substrate interface after each single SLRR deposition event [69, 92].

4.2. Modelling of a Multi-cycle SLRR Reaction:

An attempt to address the above mentioned challenge was recently made by Cukrowski et al in a work where SLRR deposition of Pt thin film on a polycrystalline Au by UPD of Cu used as sacrificial metal was carried out in multi-cycle sequentially implemented redox replacement reactions. Modelling of Cu UPD anodic stripping curves, using a combined adsorption isotherm (of Temkin and Frumkin type), allowed the authors to described the potential dependence of the monolayer surface coverage of Cu

UPD on Au film and to determine the final oxidation state of the stripped Cu as +2. Using the general modelling outcome of the earlier considered study of Brankovic et al [114] for kinetically controlled displacement reaction, stoichiometric aspects and phenomenological reaction kinetics of the SLRR reaction involving Cu UPD and Pt(IV) were carried out [37]. The observed curve-fitting solutions compellingly suggested that the SLRR reaction mechanism at various deposition cycles involved re-oxidation of Cu UPD adlayers to Cu^{2+} ions. According to the authors of this work the SLRR reaction investigated here was determined as second-order with respect to Cu UPD on bare Au substrate and somewhere in the range around 1.3 on subsequent cycles whereby the surface was increasingly covered

Figure 20

by Pt. The magnitude of the overall SLRR rate constant was found to decrease gradually with increase of the Pt layer thickness, confirming earlier experimental results obtained in this system where faster reaction kinetics on bare Au film substrate were seen in comparison to that on thickening Pt deposits [115] (Figure 20). The trend in the apparent Gibbs free energy of the SLRR reaction also exhibited increasing spontaneity with reaction time towards steady-state. The gradual change of substrate effects from predominantly Au to Au|Pt and subsequently Pt|Pt interfacial characteristics also appeared to influence the interplay of adatom interactions, overall reaction kinetics and thermodynamics of phase formation via SLRR reaction. Overall, the physico-chemical models systematically investigated in this work can be useful in design of multilayered systems where successive UPD and SLRR processes form integral parts in their fabrication.

4.3. Mechanistic Aspects of the SLRR Deposition:

To date no sufficient experimental data is present in the literature so that a quantitative view of the SLRR mechanism be considered and finalized as step-by-step reaction pathway. However, basic knowledge known facts and the experimental results of work carried out in the field of SLRR deposition

allow for building a general working hypothesis on the operating mechanism and specific pathways for a variety of systems where SLRR growth is applicable. Following sequentially the phenomenology associated with a single-cycle SLRR we will make an attempt to sketch out the potential reaction pathways that would mainly affect the deposit morphology and continuity. According to our view, at a relatively high concentration of the displacing metal so that we could assume the presence of sufficient amount of growing metal ions in solution, the galvanic displacement reaction is driven by the potential established by the sacrificial (UPD) metal that could be (from what we have known so far) Cu, Pb, and Tl. Under these circumstances sensing a potential more negative than their equilibrium potential the growing metal ions are attracted to the electrode as they are more electropositive than the sacrificial metal by definition. From this point on there are two limiting ways for the redox exchange to take place. One possibility is each UPD atom to be replaced by a growing metal atom that would eventually occupy its place in the deposit. This mechanism we will refer to as direct exchange growth [27, 28]. The second way that the exchange could preferentially take the course of calls for the oxidation of the sacrificial metal and the reduction of the growing metal to take place at different places on the electrode surface and the electrons to be transferred through the highly conductive substrate. The second limiting case we will call local cell growth [27, 28]. Both pathways are presented schematically in Figure 21. Looking

Figure 21

at the schematic one sees that the direct exchange growth resulting in a flat and uniform layer warrants the strong specific attraction between sacrificial and growing metal. Should such strong attraction exist than spatial arrangement favoring the direct pathway would satisfy the general requirement for lowering of the surface free energy as interpreted for a general UPD process in electrochemical context [11] and also following arguments explaining the surfactant mediation role of various UPD layers [8]. Subsequently, a stoichiometric redox exchange, initialized as a first approximation regardless of the substrate morphology, should facilitate the formation of large clusters that grow laterally and eventually

merge to yield a continuous epitaxial deposit. Nucleation and growth on flat terraces will be favored in this case as nucleation centers as displacement initialization centers because of the well-known fact that in a typical UPD system the stripping process always starts on terrace sites where the bonding to the substrate is weaker in comparison with steps and kink sites [121]. Following this line of thoughts one would recommend a consideration of the underpotential for the UPD system Sacrificial / Growing metal. Thus, one would recommend Pb as sacrificial metal for the SLRR growth of Pt taking into account the 0.3-0.4 V higher underpotential of Pb on Pt vs Cu on Pt [59] even if the exchange between Pt(IV) complex and Cu proceeds predominantly by direct exchange mechanism as indirectly determined in impedance study by Podlovchenko et al [122] . Another factor that undoubtedly impacts the morphology and continuity of the SLRR grown deposit is the stoichiometric ratio (see Equation 1) as it directly influences the yield of a single displacement reaction. Let us assume, for the sake of this argument, that every displacing atom will take the deposition site of the displaced one. Then, in the case of Ag growth using Tl as sacrificial metal, where displacing and displaced metals manifest equal state of oxidation 1:1, the odds for obtaining a layer that perfectly reproduces the substrate morphology are substantially higher in comparison with Pb where the stoichiometric ratio is 2:1 [32]. In the latter case, there will be an extra atom of Ag per one atom of Pb which position in the growing layer will be uncertain even upon perfect direct exchange mechanism operating in the growing system [32]. This extra atom will either occupy a spot next to its neighbor into the growing layer or will contribute to the nucleation of a second layer that takes place before the completion of the first one. A third factor that cannot be disregarded is the packing density factor ρ_M^{UPD} presenting number of M atoms per one substrate atom (Equation 1). To consider this factor in a favorable way to a flat morphology of the growing layer one should choose a sacrificial metal that would a packing factor with the growing metal that is closest to 1. Thus, if the other two factors (underpotential and stoichiometric ratio) are similar or identical like in the case of the SLRR growth of Au with Pb or Cu as sacrificial metal choices, one should

give preference to the Cu which would likely ensure closer to one packing density [37, 59]. Along with these three factors, the overall structure and morphology of an SLRR deposited layer will also depend on the concentration of the depositing metal[111] and nature of the deposition solution (anion content [114], type of complex if any [111], etc). Finally, the specific placement of the growing atoms will also depend upon other factors such as surface diffusivity of the growing metal atoms, stress accumulation into the growing layer, and specific energy to overcome the so-called Schwoebel's barrier [123]. Carrying out mathematical modeling and numerical simulations can significantly help to quantitatively address this matter.

5. Summary and Future Directions

This review presents an attempt to summarize the progress in the development of a variety of SLRR based protocols and approaches for the growth of metal, alloys and multilayers with application in different fields of fundamental and applied research. It has been shown that at present time there are four different approaches to handle SLRR based deposition protocols with the shuttling approach being mostly used for single-cycle reactions and the flow-cell and one-cell approaches being employed preferentially for the growth of thicker deposits. Owing to their best applicability in fuel cell catalysis Pt, Pd, and alloys containing these two metals have been in the focus of most SLRR deposition studies. It has been demonstrated that Cu UPD, Pb UPD, and H UPD layers can equally be successfully be used for the growth of Pt, and Cu UPD and H UPD can be employed best as sacrificial layer in the growth of Pd. The flow-cell approach has been demonstrated as most suitable for the growth of multilayers with specific applications in catalysis and sensing. Also, increasing activity has been seen in the field of SLRR for the deposition of alloys with specific focus on the design of very precisely tailored, highly active and / or CO tolerant catalysts for fuel cell application. The kinetics of a single-cycle SLRR reaction has been studied by analytical modelling for systems dominated by both mass transport and kinetic control

governing the reaction kinetics. The excellent match between models and experiment suggests good understanding of the dynamics of SLRR at this level. Efforts have been made to extend quantitatively the modelling of the dynamics in the kinetics of a multi-cycle SLRR deposition process. Still insufficient at present time is the understanding of the detailed mechanism and controlling factors operating in and governing different systems where SLRR deposition is implemented.

Overall, developed for the time span of about ten years, the SLRR deposition approach has become the best choice for surface functionalization with monolayer to ultra thin film coatings with specific functionality. When future developments are envisioned one would wish that more work is done on being able to design smart experiments that will allow for determining directly the mechanism(s) operating during SLRR growth in different systems. Undoubtedly, upcoming also is a massive effort in the field of alloy / multilayer SLRR deposition with fine tuning of the outcome to craft eventually potent and durable catalysts of the future. Finally, efforts can be expected on extending the scope of the SLRR deposition routines to a wider variety of systems including highly reactive metals and alloys and to the deposition of more noble metals on less noble substrates. Success in addressing the latter challenge would broaden enormously the suitability of the SLRR deposition approach to a wide variety of new and unforeseen applications.

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Figure Captions

Figure 1. Schematic, illustrating the growth strategy intended for different final structures resulting from growth based on SLRR reaction.

Figure 2. Experimental routine followed during deposition via surface-limited redox replacement of CuUPD/Au(111). Reproduced from ref. [37] by permission of The Electrochemical Society.

Figure 3. Composite picture illustrating Pb-Ag mixed potential diagram to show the applied potential and the Pb UPD potential range (left) and the potential transient registered at OCP during the SLRR reaction along with STM images before and after deposition (right). Reproduced from ref. [48] by permission of Elsevier.

Figure 4. Cyclic voltammetry of bare and coated with Ag layers Au (111) in 3×10^{-3} M $\text{Pb}(\text{ClO}_4)_2 + 1 \times 10^{-1}$ M NaClO_4 and pH= 2 at a sweep rate of 10 mV/s. STM images 570×570 nm illustrating a (A) thermally reconstructed Au (111) surface inset size 60×60 nm and (B) the same surface after lifting of the reconstruction. Images (C) and (D) show the morphology evolution with the growth of 2 and 40 Ag layers, respectively. The Z-range is 1.5 nm for A, B, and C and 2.5 nm for (D). Reproduced from ref. [34] by permission of The Electrochemical Society.

Figure 5. In situ STM images of (a) after Cu UPD on I-modified Au (111) 20×20 nm, (b) after Cu UPD on I-modified Au(111) 300×300 nm, (c) after Cu UPD and one Cu replacement 300×300 nm, (d) 3 min after Fig. 7c 300×300 nm, (e) after Cu UPD and two Cu replacements 300×300 nm, (f) after Cu UPD and three Cu replacements 200×200 nm. Reproduced from ref. [36] by permission of The Electrochemical Society.

Figure 6. (A) STM image 240×240 nm with cross-sectional analysis (inset) illustrating the morphology evolution after 25 displacement events with fifteen grown Cu layers. (B) High-resolution STM image 6×6

nm illustrating the (4×4) Moire atomic structure of a Pb UPD layer on Cu (111) grown by SLRR. Reprinted with permission from ref. [31], Copyright (2007) American Chemical Society.

Figure 7. Representative 100×100 nm STM images after segmentation for three different Pt deposition experiments: A Pt = 25.5% ML, Cu = 0; B Pt = 35.6% ML, Cu = 63% ML; and C Pt = 41% ML Cu = 73% ML. Reproduced from ref. [37] by permission of The Electrochemical Society.

Figure 8. CV of H UPD on Au (poly), Pt (poly), and after 1 replacement of Pt on Au (poly) as labeled. Scan rate: 0.050 V/s. Solution: 0.5 M H₂SO₄. Reprinted with permission from ref. [59]. Copyright (2011) American Chemical Society.

Figure 9. Ex situ STM micrographs showing the surface of Pt films grown on Au (111) by SLRR of Pb UPD with (A) 1 replacement event and (B) 10 replacement events. (C) Pt films grown on Au (111) by SLRR of Cu UPD with 1 replacement event. Frame size: (90×90) nm². Reprinted with permission from ref. [59]. Copyright (2011) American Chemical Society.

Figure 10. Comparison of roughness of Pt films deposited from 10⁻¹M NaClO₄+ 10⁻³M HClO₄+ 5×10⁻⁴M K₂(PtCl₄) solution using different methods: surface limited redox replacement using H-UPD marked SLRR, potentiostatic bulk deposition at -0.280 V marked OPD and potentiostatic bulk deposition at -0.745 V in H-UPD region marked SMG. (a) Cyclic voltammetries of Pt films of equivalent thicknesses of 2.5 ML in 0.1 M H₂SO₄ obtained with 50 mVs⁻¹. (b) Roughness factor change with increasing Pt amount obtained by integration of H-UPD charge from cyclic voltammetries as illustrated in (a). Reprinted from ref. [92], with permission from Elsevier.

Figure 11. Pd and Rh maps for PdRh with two cycles of deposition (top) and a line scan showing the change in Rh atomic fraction across 25 nm, originating within the particle and extending across the surface. Reprinted with permission from ref. [49]. Copyright (2014) American Chemical Society.

Figure 12. Initial potential time transients showing the establishment of mixed potentials for (A) Pb EE and Pb mediation, (B) Cu EE and Cu mediation (C) Pd-H and Pt,Pd-H EEs with Pb mediation. *Insets:* Potential transients demonstrating the potential changes in the course of ESLRR subsequent steps for the systems in (A) and (B) plots. Reprinted from ref. [48], with permission from Elsevier.

Figure 13. Sequential deposition of Pt monoatomic layers by pulsed deposition in a pH=4 solution. (A) Mass change accompanying each potential pulse. (B) EQCM mass increase is converted to thickness and compared with XPS measurements. XPS analysis of the EQCM specimen (blue diamond) and a series of Pt films deposited on Au-coated Si wafers (black squares) are shown. From ref. [96]. Reprinted with permission from AAAS.

Figure 14. Schematic presentation of the SLRR protocol used to electrodeposit $\text{Pt}_{1-x}\text{Pb}_x$ alloys. Different alloy compositions are formed by changing the potential limit E_2 of OCP step termination. Ref. [61], open access. (M.P. Mercer, D. Plana, D.J. Fermín, D. Morgan, N. Vasiljevic, *Langmuir*, 31 (2015) 10904-10912.)

Figure 15. Composite picture depicting (left) a cartoon scheme of SLRR prepared PtRu 50/50 Pt/Ru (base alloy) nanofilm electrode and (right) CO stripping voltammetry on 50/50 Pt/Ru (base alloy) electrode with various surface-ending layers in 0.5 M H_2SO_4 . Scan rate: 10 mVs^{-1} . Reprinted with permission from ref. [107]. Copyright (2014) American Chemical Society.

Figure 16. Composite picture depicting (A) CV of Pb UPD on bare Au (111) electrode and STM image $300 \times 300 \text{ nm}$, Z-range 2 nm, (B) CV of Pb UPD on 20 Ag MLs deposited by SLRR on Au (111) electrode and STM image $300 \times 300 \text{ nm}$, Z-range 3 nm, (C) CV of Pb UPD on SLRR deposited 20 Cu MLs on the layer in (B) and STM image $300 \times 300 \text{ nm}$, Z-range 4 nm, and (D) CV of Pb UPD on SLRR deposited 30 Ag MLs on the layer in (C) and STM image $300 \times 300 \text{ nm}$, Z-range 7 nm. The *Insets* in (B) and (C) illustrate for comparison CV of Pb UPD on bare Ag (111) and Cu (111) electrodes, respectively.

Figure 17. Anodic stripping of different Ag-Cu structures presented by liner scan voltammetry curves in positive direction at sweep rate of 1 mVs^{-1} . (Brown-red) 10 MLs of SLRR deposited pure Cu, (Black) 30 MLs of bulk deposited Ag on the Cu in brown-red curve, (Red) 10 MLs of Ag deposited by SLRR on the Cu in brown-red curve, (Green) 20 MLs of Ag deposited by SLRR on the Cu in brown-red curve, and (Blue) 30 MLs of Ag deposited by SLRR on the Cu in brown-red curve.

Figure 18. Representative STM image of the surface morphology for (left) PbUPD/RuML/Au(111)@ $\Delta E=275 \text{ mV}$, and (right) RuPtML-CE/Au(111) obtained from SLRR solution containing Pt^{2+} . The cartoons above the STM images illustrate the proposed nanocluster structures (Ru – red, Pb – blue, Pt – light gray, n – oxidation state of Pt^{n+} ion). The SLRR reaction stoichiometry within the arrow indicates the process causing the morphology change from left to right. Reprinted from ref. [112], with permission from Elsevier.

Figure 19. Open circuit potential transients for Pt deposition (A) via SLRR of PbUPD/Au (111) and (B) via SLRR of CuUPD/Au (111), in $10^{-3} \text{ M Pt}(\text{ClO}_4)_6^{2-} + 0.1 \text{ M H}_2\text{SO}_4$ electrolyte with 1000 rpm rotation rate. The bright gray solid lines (green and red) represent the model fit (Eq. (18)) to experimental data. Insets show the representative morphology of deposited Pt. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) Reprinted from ref. [114], with permission from Elsevier.

Figure 20. Trends of the parameters (A) k_r , (B) N_{or} , (C) Eu_{0-0} , and (D) variations in interaction parameters f and g obtained from modelling with Eq. (10) for various deposition cycles during electrochemical generation of the multilayered electrode system $n(\text{Pt})\text{Cu}/\text{Au}$ film. Reprinted from ref. [115] with permission from Elsevier.

Figure 21. Schematic illustrating the progress of direct exchange (left) and local cell mechanism (right) SLRR deposition process taking place over the course of two cycles.

Charge transfer via direct $U^0 - G^{2+}$ interaction.

First Displacement Event

Second Displacement Event

Charge transfer via local cell mechanism.

● Au atom
● Me atom
● Ag atom