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Short communication

Metal deposition via electroless surface limited redox replacement

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ABSTRACT

The development of electroless SLRR (ESLRR) utilizing a galvanic cell configuration is demonstrated at a proof-of concept level by the deposition of epitaxial Ag layers on Au. ESLRR is realized via the connection and subsequent disconnection of an Au working electrode (WE) to a Pb "executive" electrode (EE). The connection leads to the underpotential deposition of a Pb monolayer at the WE driven by the stripping of an equivalent amount of Pb from the EE. The disconnection then enables the galvanic displacement of the Pb monolayer by Ag. 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. This approach can be extended to a variety of metal-substrate pairs widely applicable in electrocatalysis and energy applications.

1. Introduction

The deposition of smooth continuous thin metal films is an area of wide interest for academic and industrial applications. Thin films allow for unique properties of metals that differ from the bulk to be exploited as well as device cost minimization. One of the dominant objectives driving the thin film deposition field is the development of low cost high activity, typically Pt-based, fuel cell catalysts [1]. The deposition of such thin films has not been trivial. Conventional overpotential deposition (OPD) of Pt has illustrated a tendency to nucleate and grow in three dimensional clusters [2,3]. Overcoming this tendency Uosaki et al. have shown the growth of continuous 2D thin films via OPD, however at a very slow deposition rate, 4 ML per hour [4]. Surface limited redox replacement (SLRR) is a technique that has been developed to overcome many of the hindrances faced by OPD, and has seen many applications in the synthesis of high activity fuel cell catalysts with low Pt loading [5,6]. Introduced by Brankovic et al. [7], SLRR utilizes the monolayer limited nature of underpotential deposition (UPD) of a sacrificial metal coupled with a subsequent galvanic displacement of that layer by a more noble metal of interest. To date SLRR has been applied to the realization of monolayer Pt coatings on a variety of metals and alloy nanoparticles [1] and to the deposition of epitaxial films of Ag, Cu, Au, Pt, Ru, and Pd on noble metal substrates [7–13].

Conventionally SLRR has been carried out through a multiple immersion approach [7,8] flow cell set-up [10,13,14] and more recently in a one-cell approach developed by our group [9]. The one-cell approach has been effectively applied to the growth of Cu [9], Ag [8], Au [11], and Pt [12,15]. Traditionally SLRR utilizes the application of a potential by an external source (i.e. potentiostat) in order to realize the formation of the UPD sacrificial layer (SL) [7–13], and subsequent open circuit displacement of the SL [9]. However, recent scaling of SLRR up to the production of industrial quantities of state-of-the-art catalysts renders this protocol energy intensive and difficult to implement without the use of a high-power potentiostat/rectifier. To that end, alternative approaches relying on less energy intensive scenarios might be beneficial with ease of application and cost effectiveness. Recently, a couple fundamental [16] and applied reports [17] discuss aspects of electroless generation of UPD SL that in turn could lead to the realization of controlled metal deposition without the use of an external power source. Herein the utilization of an electroless SLRR (ESLRR) protocol employing a galvanic couple instead of an external source to power the SL formation has been explored. The growth of Ag on Au with underpotentialy deposited Pb (Pb_{UPD}) used as sacrificial metal [7,8] is chosen to reveal the fundamental concept and illustrate at a proof-of-concept level the feasibility of the proposed approach for ultrathin film growth.

More specifically, the Pb_{UPD} SL on the Au working electrode (WE) is realized by a short-term contact (in short) with a Pb "executive" electrode (EE) that in a conventional three-electrode cell would be the counter electrode (CE). The galvanic couple realized upon this contact enables the application of a kinetically controlled potential on the Au electrode that is slightly positive of the Pb/Pb^{2+} reversible potential. This potential allows for the formation of a full Pb_{UPD} layer on the Au surface powered by the oxidation of equivalent amount of elemental Pb from the EE. Disconnection of the short activates SLRR that, proceeds as usual in one-cell configuration, closing the loop for controlled

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growth, thus completing a cycle of Ag layer deposition without the external power.

2. Materials and methods

Polycrystalline Au (d = 0.6 cm) and Au(111) (d = 0.9) disks of 2 mm thickness were used as WE. Prior to use each was mechanically polished to 1 μm using alumina slurry (Buehler) and then electropolished following a procedure described elsewhere [11]. After annealing to "red-hot" in propane flame and cooling in N_2 atmosphere the electrode was immersed in a three electrode cell in a "hanging meniscus" configuration [11]. The solution used for ESLRR of Pb by Ag consisted of 0.1 M $NaClO_4$ (Sigma, 99.95%), 0.01 M $HClO_4$ (GFS Chemical, 70% redistilled), 0.001 M $Pb(ClO_4)_2$ (Aldrich, 99.995%), and 0.0005 M $AgClO_4$ (GFS Chemicals, 99.999%). All solutions were made using Barnstead Nanopure® water and high-purity grade chemicals as received from the vendors. Prior to use all solutions were thoroughly deoxygenated with ultrapure N_2 for at least 30 min.

In the growth studies a Pb wire was used as EE (instead of CE) and was isolated in a glass tube (with 6–8 μm separator membrane) containing identical solution to the one of the growth cell excluding Ag ions. All potentials in the paper (unless otherwise noted) are reported versus a mercury-mercurous sulfate electrode (MSE). The growth process was automated utilizing a setup and protocol described elsewhere [11,12]. However, instead of using potentiostat, the WE and EE were connected in short for 1 s. Characterization of deposited Ag films was carried out by cyclic voltammetry of Pb_{UPD} and Ag stripping experiments in a solution of 0.1 M $NaClO_4$, 0.01 M $HClO_4$ and 0.001 M $Pb(ClO_4)_2$. All electrochemical characterization experiments were performed by CH Instruments, model 400a potentiostat and its coupled software. Also, Pt wire was used as CE.

STM characterization was performed in situ with an Agilent 4500 SPM microscope, using 2100 Controller and Pico Scan software in solution where the potential control was provided by Agilent 300S Pico bipotentiostat. Tips for the STM experiments were electrochemically etched in 1.6 M $CaCl_2$ from $Pt_{0.9}Ir_{0.1}$ wire using an AC voltage of 25–30 V and subsequently insulated with Apiezon wax.

3. Results and discussion

In order to illustrate the potential realized between the WE and EE upon connection a mixed potential diagram is provided in Fig. 1A. Under the assumption of O_2-free environment, this diagram clearly shows that the anodic current of Pb oxidation (EE) and the cathodic current of Ag reduction (on WE) become equal in magnitude (absolute values used for clarity) at the galvanic couple potential generated by connecting in short both electrodes [18]. With the Pb oxidation exhibiting a Butler–Volmer behavior and the Ag reduction being governed by diffusion limitations, the resultant potential should be about 30 mV positive of the Pb/Pb^{2+} reversible potential of (~−0.870 V). This potential is negative enough (see Pb_{UPD} potential ranges on both Ag and Au in Fig. 1A, inset) to result in the formation of a complete Pb_{UPD} layer on the WE, powered by the dissolution of equivalent amount of Pb from the EE.

Potential transients of replacement events showing uninterrupted potential control are seen in Fig. 1B. It can be clearly seen that the executive electrode applies a relatively consistent potential. Also, no potential drift associated with possible transformation of the executive electrode could be seen. The potential applied is in satisfactory agreement with that predicted via the mixed potential diagram. More flexibility in the potential control could be achieved by manipulating the oxidative kinetics of EE. The analysis of the transients presented in Fig. 1B suggests almost identical exchange behavior in the growth of Ag via ESLRR with that exhibited during the course of conventional SLRR deposition [8].

In order to quantitatively determine the amount of Ag deposited with each cycle, stripping of accordingly grown layers was performed by anodic potential scans. The stripping curves are presented in Fig. 2 along with an inset showing the relationship of charge vs. the number of ESLRR events. It can be seen that the expected dependence features a coarse linear trend showing between 1.5 and 1.8 ML of deposited Ag per SLRR event; this is slightly higher than that expected of 1.6 ML based solely on the charge of a Pb UPD ML [7,8]. The morphology of ESLRR grown films and their stripping were characterized by in situ STM. A Ag film deposited by 5 ESLRR events on Au(111) is shown in Fig. 2 (left inset) at a potential of 0.250 V (Pb/Pb^{2+}). It can be observed that the deposit features a morphology typical for SLRR growth entailing homogeneous island nucleation followed by island coalescence upon multiple SLRR cycles [8,9,11]. The Ag was subsequently stripped and the image taken at 1.0 V (Pb/Pb^{2+}) following stripping is presented in Fig. 2 (right inset). This figure shows the disappearance of large islands and the morphology characteristic of Au bulk-terminated surface consisting of monatomic steps and large terraces. The remainder of small uniform islands can be attributed to a partial Ag UPD layer present at this potential as illustrated by Garcia et al. [19].

Following a single ESLRR event the electrochemical behavior of the deposit coincides with that of bulk Ag (Fig. 3A). This is in agreement with findings of Pauling et al. [20] on the screening effect of UPD metals. Additional insight on this is obtained by the in situ STM insets presented

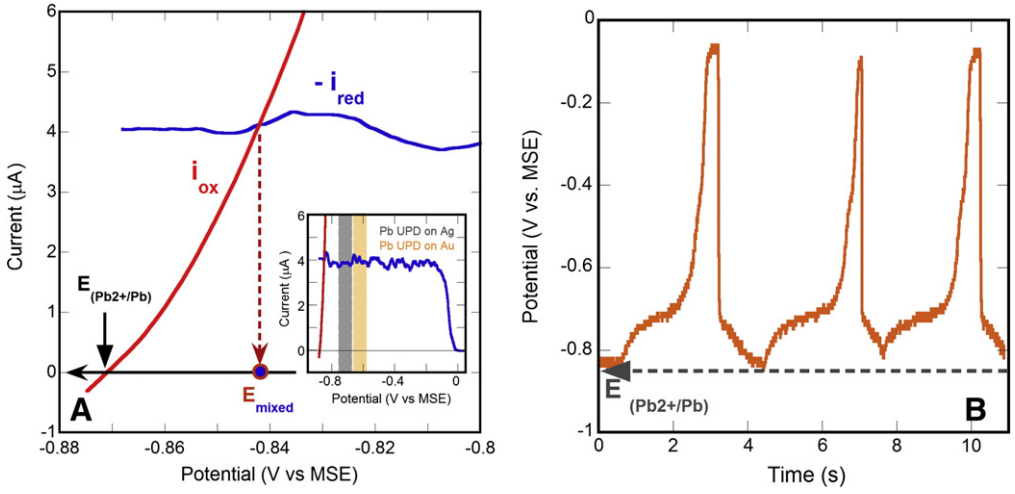

Fig. 1. A. Mixed potential diagram illustrating potential, E_{mix} upon realization of Ag–Pb galvanic couple. Ag reduction on Au (blue) and Pb oxidation (red) carried out separately at a sweep rate of 1 mV s^{-1}. Inset: Same plot in the entire potential range. B. Potential transient of ESLRR deposition of Ag on Au (poly).