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Ultrathin Film $\text{Pt}_x\text{Pd}_{(1-x)}$ Alloy Catalysts for Formic Acid Oxidation Synthesized by Surface Limited Redox Replacement of Underpotentially Deposited H Monolayer

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Received: 17 February 2020; Accepted: 5 March 2020; Published: 9 March 2020

Abstract: This work emphasizes the development of a green synthetic approach for growing ultrathin film $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy catalysts for formic acid oxidation (FAO) by surface limited redox replacement of underpotentially deposited H sacrificial layer. Up to three-monolayers-thick $\text{Pt}_x\text{Pd}_{(1-x)}$ films with different composition are generated on Au electrodes and characterized for composition and surface roughness using XPS and electrochemical methods, respectively. XPS results show close correlation between solution molar ratio and atomic composition, with slightly higher Pt fraction in the deposited films. The accordingly deposited $\text{Pt}_{42}\text{Pd}_{58}$ films demonstrated remarkable specific and mass activities of up to 35 mAcm^{-2} and 45 Amg^{-1} respectively, lasting for more than 1500 cycles in FAO tests. This performance, found to be better twice or more than that of pure Pt counterparts, renders the $\text{Pt}_{42}\text{Pd}_{58}$ films comparable with the frontrunner FAO catalysts. In addition, the best alloy catalyst establishes a nearly hysteresis-free FAO CV curve a lot earlier than its Pt counterpart and thus supports the direct FAO pathway for longer. Overall, the combination of high Pd activity and CO tolerance with the remarkable Pt stability results in highly active and durable FAO catalysts. Finally, this facile and cost-effective synthetic approach allows for scaling the catalyst production and is thus appropriate for foreseeable commercialization.

Keywords: formic acid oxidation; PtPd alloy catalyst; E-ALD by SLRR; ultrathin films; fuel cells

1. Introduction

As devices that make use of alternative energy sources in the transportation industry, stationary power stations, and portable electronics, fuel cells have been at the center of research and development advancements in the past half century. They offer better energy conversion efficiency, and feature high energy density along with minimal-to-zero environmental polluting emissions [1–4] compared to fossil fuel engines. Platinum (Pt) has the best catalytic properties and thus finds use in chemical and petrochemical industries, auto-exhaust purification, as well as in fuel cell industry [5]. Pt is one of the platinum group metals (PGM), which are all expensive and scarce, thus making them unfit for use in mass production. Therefore, commercial fuel cell production faces the need to minimize the platinum group metals' (PGMs') loading upon their most common application as cathodes and anodes in fuel cells.

Direct liquid fuel cells (DLFCs) provide some solutions to problems faced by hydrogen fuel cells and batteries for portable devices [6,7]. They are convenient in terms of ease of storage and transportation, instant recharging or refilled fuel cartridge replacement, as well as high energy density liquid fuels among other factors [8–12]. Among the DLFCs, direct formic acid fuel cells (DFAFC) are better positioned future portable device power sources. This is due to the advantageous features

they possess, which include low crossover rate through the Nafion membrane [13–15], rapid formic acid oxidation reaction (FAO) rate [15,16], non-toxicity [15], non-flammability, and low operating temperature [16]. The major disadvantage of FA is its low volumetric energy density [17]. So far, Pt has been the main catalyst for FAO reaction in DFAFCs [18–22]. The FAO reaction on Pt surface has been found to proceed via a dual pathway mechanism, dehydrogenation, which is the main and favorable pathway that involves a fast reaction via a reactive intermediate (direct pathway). The other pathway is dehydration (indirect pathway) which proceeds via a step in which CO, a catalyst poisoning species, is formed [18,22–24]. The reactive intermediate, formerly believed to be a hydroxycarbonyl (COOH_{ads}) has been confirmed via spectroscopic detection as a bridge-bonded formate species (HCOO_{ads}) on Pt electrode and its decomposition to CO_2 is a rate determining step (rds) [18,25–31]. Other researchers have argued that the intermediate species is an active site blocking species since the reaction occurs via weakly adsorbed FA molecules ($\text{HCOOH}_{\text{ads}}$) [32]. This argument was however debunked since it was proved that the direct pathway for sure utilized the HCOO_{ads} as a reactive intermediate [26]. The use of pure Pt as a catalyst for formic acid oxidation therefore encounters difficulties due to notorious CO poisoning [33,34]. The formate and CO adsorbed on the Pt influence the kinetics of each other [26]; while CO inhibits further adsorption of formate and suppresses its decomposition to CO_2 , adsorbed formate is believed to suppress the oxidation of CO to CO_2 by blocking sites for adsorption of the oxidizing species (water or OH) [26]. Pd exhibits higher initial catalytic activity than Pt and could be considered as a cost-effective alternative to Pt. However, Pd based catalysts suffer from instability in long term usage [35] and recently soaring cost more than double the price of Pt. The FAO reaction proceeds on Pd predominantly via direct pathway since the Pd surface exhibits very weak affinity for CO binding [35,36]. In order to develop high performance DFAFCs, many issues need to be resolved; these include minimal loading of the expensive PGMs, designing materials with high catalytic activity, and excellent durability features for feasible commercialization. In realizing that, Pt- and Pd- based catalysts have undergone tremendous studies in different designs and structures to find the optimal composition of an ideal catalyst. For instance, FAO has been studied using single crystal faces of Pt [37–39], polycrystalline Pt (Pt_{poly}) [18,21,33,40–42] and on other metals such as Au, Pd, and Rh. To enhance the Pt performance, effort has been made to either (1) modify the surface with adatoms of other metals such as Ru [43], Ag [44], Ge [45,46], Sn [45], Pb [46], As [46], Sb [46,47], and Bi [47–50]; or (2) form alloys of Pt with other metals like Pd [21,37,51] and Ru [15,51–55] that would specifically promote the direct FAO pathway [21,36,56]. Other alloys studied so far include but not limited to, Pt-Cu [57], Pt-Au [58–64], Pt-Pd [65–67], and Pt-Ag [68,69], each one of them works differently by bi-functional mechanism, ligand effect, and/or ensemble effect [58,59], suppressing the indirect pathway thus enhancing FAO reaction. Pt-Au is believed to catalyze via ensemble effect. The enhanced activity by adatom decorations of Pt is attributed to ‘third body effect’, where the third body prevents surface poisoning by CO chemisorption. While until recently the FAO community has considered bi-metallic catalysts, most recent research effort identified several multi-metallic catalysts that produce the best results with minimal Pt or PGM loading, e.g. Au-Cu-Pt [70,71], Pd-Cu-Co [72], Pt-Au-Ru [73], Pt-Pd-Cu [74–76], Pt-Sn-Bi [77], and Pd-Ni-Cu [78].

Our recent research has been focused on Pt-bimetallic nanostructures with strained overlayers, Pt-X alloys or intermetallic systems as well as 2D-3D nanoclusters, that exhibit a potential for making active and durable catalysts. The bonding between the overlayer and substrate results in electronic and geometric effects that ultimately impact the activity and selectivity of the overlayer catalyst [79–82]. The bimetallic nanostructures exhibit different features associated with size, shape, morphology, and surface composition, all of which influence substantially the FAO catalytic activity [83]. It is important to understand how surface defects and strains on the pseudomorphic overlayers affect their catalytic behavior; for instance, the latter is associated with d-band center shifting and thus influences adsorption in heterogeneous catalysis [80,84,85]. Generally, conformal Pd on Pt or $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy deposition can be achieved via ‘spontaneous’ deposition [86,87] or surface limited redox replacement (SLRR) of a less noble sacrificial element [88–93] as first demonstrated by Brankovic et al [94]. Our

research group has developed many SLRR based protocols for deposition of various noble metals on a number of substrates and one of which is used to deposit the catalytic thin films of Pt and Pd on Au via H_{upd} [95,96]. The ability to control the thickness and the morphology of the deposit via SLRR protocols helps one to prepare a catalyst with the desired loading and morphology.

Following this lead, herein we present results on the development of an approach for deposition of smooth and contamination-free ultra-thin films of Pt, Pd, and $Pt_xPd_{(1-x)}$ on flat, polycrystalline Au (Au_{poly}) substrate and on their subsequent assessment for activity and durability in FAO tests. The catalysts are synthesized utilizing the electrochemical atomic layer deposition (E-ALD) by SLRR of H underpotentially deposited (H_{upd}) sacrificial layer [95,96]. The synthetic process is followed by a morphology/surface roughness assessment done by H_{upd} and Cu_{upd} while surface elemental composition analysis is carried out via X-ray photoelectron spectroscopy (XPS) characterization work, respectively. Finally, all ultra-thin films of Pd, Pt, and $Pt_xPd_{(1-x)}$ with different atomic percent ratios are subjected to comparison based on results of potentiostatic and potentiodynamic FAO testing activities.

2. Materials and Methods

2.1. Electrochemical Cell Set-Up

A three-electrode electrochemical cell set-up was used throughout the study both for the E-ALD synthetic work and for the catalysis testing experiments. In that cell, the working electrodes were mounted on a conductive vacuum holder and immersed in an electrolyte via a hanging meniscus configuration [97]. The reference electrode (RE), a saturated mercury-mercurous sulfate electrode (MSE) with a potential of 0.650 V versus the normal hydrogen electrode (NHE), was used for all the experiments unless stated otherwise. A Pt wire was used as counter electrode (CE) in all experiments. All potentials in this work are reported versus MSE unless stated otherwise, and all the current densities are normalized with respect to the geometric area of the substrate (polycrystalline gold electrode used) as alike with the cases of plain Pt and Pd, no considerable roughness was developing during the alloy deposition process [95]. All electrolyte solutions used were prepared using Barnstead Nanopure® (BNP) water ($>18\text{ M}\Omega\text{cm}$) and high purity grade chemicals as received from the vendors. These electrolytes were purged with ultrapure N_2 for at least 30 min before any deposition, characterization, or catalytic testing routines were carried out.

2.2. Electrode Preparation

Polycrystalline gold, Au_{poly} , discs (99.99% purity) of 0.6 cm diameter and 0.2 cm thickness were used as substrates or working electrodes for all experimental work, both electrochemical and morphological characterization. They were mechanically polished down to 0.05 μm grit using water-based, de-agglomerated alumina slurry (Buehler). After thoroughly rinsing with water, the WEs were immersed in warm concentrated HNO_3 to remove any remnants of the polishing paste before another thorough rinse with BNP water. The WEs were then annealed to 'red-hot' with a propane torch for at least 5 min before being cooled rapidly in ultrapure N_2 atmosphere to avoid surface oxidation/contamination. They were then covered with a droplet of the BNP water to prevent surface contamination during their transfer to the electrochemical cell.

2.3. Characterization of Au Electrodes before Use

Lead under potential deposition (Pb_{upd}) cyclic voltammetry (CV) was performed on the Au substrates (Au_{poly} WEs) to ascertain good surface quality and determine the electrochemical surface area (ECSA), before any (Pt, Pd or alloy) deposition. The Pb_{upd} solution is comprised of 0.1 M $NaClO_4$ (Sigma, 99.95%), 0.01 M $HClO_4$ (GFS Chemical, 70% redistilled), and 0.003 M $Pb(ClO_4)_2$ (Aldrich, 99.995%). Pb wire was used as a pseudo-reference electrode (PRE) and the Pt wire as the CE in the ECSA experiments. Cu_{upd} was also conducted to characterize the WEs before deposition of the catalyst. Conditions are shown in the electrochemical testing and characterization section below.

The measurements were performed using Model AFCBP Bipotentiostat (Pine Instruments) interfaced through GPIB connection with a PC for control and data collection by PineChem 2.80 software.

2.4. $Pt_xPd_{(1-x)}$ Alloy Ultrathin Film Growth:

The growth of $Pt_xPd_{(1-x)}$ thin films on Au surface is conducted by SLRR of H_{upd} in a one cell configuration. The electrolyte used contained A mM $PdCl_2$ (Aldrich, 99.99%), B mM K_2PtCl_4 (GFS Chemical, 98%), 30 mM HCl (J.T. Baker®, 36.5–38 %), and 0.1 M H_2SO_4 (GFS Chemical, redistilled) and was purged with ultrapure N_2 for at least 30 min before growth experiment was conducted. Solutions with $[PdCl_4^{2-}]/[PtCl_4^{2-}]$ molar ratios ranging from 16.7% Pt = (5:1) to 100% (0:6) $[PtCl_4^{2-}]$ were used to synthesize $Pt_xPd_{(1-x)}$ ultrathin films. To realize for instance, 5:1 Pd:Pt molar ratio, A was 0.05 mM and B was 0.25 mM. For 100% Pd, A was 0.30 mM while for 100 % Pt, B was 0.30 mM. For the intermediate ratios, the solution volumes were selected accordingly to obtain the targeted atomic ratios of the alloy. The SLRR protocol consisted of five successive steps (unless stated otherwise) of H_{upd} formation by a potential pulse of 1 s to -0.600 V vs. MSE followed by a galvanic displacement step occurring at open circuit potential (OCP) [95]. The deposition work was performed by open circuit chronopotentiometry using a Princeton Applied Research (PAR) Model 273 Potentiostat/ Galvanostat coupled with Corrware Software. Data was collected by a PicoLog software.

2.5. Electrochemical Testing and Characterization

H_{upd} and Cu_{upd} cyclic voltammetry experiments were used to characterize the deposited Pt, Pd, and PdPt thin films for surface compositional changes and possible surface roughness development. The H_{upd} CV was carried out in 0.5 M H_2SO_4 (GFS Chemical, highest purity grade, redistilled) over a potential range of 0.100 to -0.670 V vs. MSE at a sweep rate of 50 mVs^{-1} . The Cu_{upd} CV was performed in 3 mM $CuSO_4$ (J.T. Baker, 99.8%), 0.1 M H_2SO_4 solution at a sweep rate of 20 mVs^{-1} . The potential range is 0.02 to 0.7 V vs. Cu/Cu^{2+} pseudo-reference electrode (PRE). The characterization of PdPt films was administered and monitored using same instruments and software as those in the Pb_{upd} characterization work as detailed above.

2.6. Compositional Analysis

XPS characterization of $Pt_xPd_{(1-x)}$ alloy and Pd thin films grown by 40–50 SLRR events was carried out via a PHI 500 Versaprobe, Scanning ESCA (electron spectroscopy for chemical analysis) microprobe from Physical Electronics which has Ar sputtering gun for surface cleaning and depth profiling. Spots on the sample surface were irradiated by a scanned and focused monochromatic Al $K\alpha$ X-ray (1468.6 eV) beam. The spot size was a 10 to 200 μm X-ray at 100 W with pass energy of 187.75 eV for survey scan (0–1400 eV) and 23.5 eV for region spectra. The take-off angle was 45° . The emitted electrons were analyzed by hemispherical analyzer with 16 channels. The atomic composition of the prepared $Pt_xPd_{(1-x)}$ thin film as well as presence of Cu contaminant on Cu_{upd} grown thin films was inferred from peak positions and intensity.

2.7. Formic Acid Oxidation Testing

Formic acid oxidation catalytic testing was performed on the thin films of the $Pt_xPd_{(1-x)}$ alloys and single metal (Pt and Pd) thin films in 2 M $HCOOH$ (JT Baker, 88%) and 0.10 M $HClO_4$ from -0.510 to $+0.550$ V vs. MSE at a scan rate of 50 mVs^{-1} repetitively until the current density decreased to about 10% of the initial value, when the catalyst is deemed ‘virtually dead’. After a given number of FAO cycles, the catalyst was transferred to a H_{upd} and then Cu_{upd} testing cells successively to ensure that the surface was still intact and to measure the particular electrochemically active surface area (ECSA) [93,96,98–100]. Potentiostatic (constant potential, CP) testing was performed in the same FA solution at 0.00 V vs. MSE [70] for up to 12 hours on as-grown catalysts. H_{upd} , Cu_{upd} and FAO CVs were performed before and after the CP test to check for ECSA and catalytic activity and then use the results to infer durability information.

3. Results and Discussion

3.1. Catalyst Deposition by SLRR of H_{upd}

The surface of the substrate, Au_{poly} , was confirmed to be ready for deposition experiments by producing typical Pb_{upd} [96] and Cu_{upd} [100] voltammetry curves with characteristic peaks. As seen in Figure 1A,B the Pb_{upd} CV curve and Cu_{upd} CV shows mainly the dominant low index faces, mainly Au(111) and to some extent Au(100) and Au(110) [101]. The epitaxial growth via SLRR requires a high-quality substrate surface for best morphological characteristics of the deposited catalyst film. As detailed in the Materials and Methods section, the growth of Pd, Pt, and PdPt alloys on the Au substrate is conducted in a one cell configuration via SLRRs involving formation of a H_{upd} layer and its displacement by either $[\text{PdCl}_4^{2-}]$ [96], or $[\text{PtCl}_4^{2-}]$, or both of these complex ions in particular ratios [102]. The alloy thin films grown for this study were deposited via five successive SLRR cycles and the pure Pt film deposition involved 10 SLRR cycles. Figure 1C shows a typical potential transient of a $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy deposited illustratively via 10 SLRR cycles. As expected, the growth starts with the application of a potential pulse to -0.600 V vs. MSE for 1s. The application of that potential enables the formation of a UPD monolayer of H (H_{upd}) serving as sacrificial element, and about 1 at % of the growing noble metal(s), i.e., Pd, Pt, or a mixture of both [91]. Then the potential control was being released so that the spontaneous redox replacement of the adsorbed H, leads to the deposition of the stoichiometric equivalent amount of Pd, Pt, or $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy on the Au_{poly} substrate. Thus, the successive application of five SLRR cycles resulted in the deposition of 2.0 to 2.5 equivalent monolayers (MLs) thick alloy films [96] that constitutes the minimum amount Pt and/or Pd needed for activity and durability catalytic testing. It needs to be noted that in the cases of plain Pd and/or $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy deposition, the SLRR process was being initiated by forming a H_{upd} layer on underpotentially deposited Pd layer on the Au substrate surface [96]. As per the deposition of plain Pt film, the H_{upd} was being initially formed on spontaneously deposited Pt sub-monolayer formed by PtCl_4^{2-} complex reduction in the course of the first few SLRR cycles [87]. Owing to that, the deposition of a sufficient amount of Pt and catalytically comparable to the amount of material in the alloy counterparts was carried out typically by 10 SLRR cycles instead of five.

Figure 1. (A) and (B) typical Pb_{upd} and Cu_{upd} CV curves registered at a sweep rate of 20 mVs^{-1} and (C) typical potential transient captured in the course of successive application of 10 SLRR events for the growth of a PtPd alloy film by displacing a H_{upd} layer.

3.2. Compositional Characterization by XPS

Characterization work done by XPS and EDS on a metal-thin film grown via SLRR techniques, was performed in the past to determine the film's composition and the potential presence of traces of residual sacrificial element [103,104]. When Pt thin films grown via Pb_{upd} and Cu_{upd} were analyzed, at least 4 at % Pb and 13 at % Cu, respectively were found to be alloyed during the SLRR cycles with the accordingly grown Pt thin film [91]. The very strong interaction between Pb and all low-index Pt

faces [105] is evidenced by Pb_{upd} layer formation/stripping at underpotential as high as 0.9 V, which is much higher than the SLRR cut-off potential. As mentioned earlier, it is assumed that in a typical SLRR cycle, the UPD layer formation is accompanied by the co-deposition of approximately 1% growing metal of interest; it is believed that a minimal alloying between growing and sacrificial metals is likely to occur at that point [91]. The surface may be stabilized via intermetallic formation that is known to exist in UPD systems whose constituents feature bulk immiscibility at equilibrium [106]. Also, depending on how high the cut-off potential is during the redox replacement reaction, different amounts of the sacrificial metal remains trapped in the growing film due to incomplete exchange with the growing metal. The more positive the potential, the less quantity of the UPD metal is trapped by the growing metal and is thus eventually incorporated in the deposited alloy. Thus, different ratio compositions of alloys of UPD metal and the growing metal can be eventually found in accordingly deposited thin films. This assumption is corroborated by Figure 2 showing an XPS characterization experiment performed on Pd film grown on Au_{poly} by SLRR of Cu_{upd} layer instead of H_{upd} one. The analysis of the included XPS spectrum clearly shows certain level of Cu incorporation in the Pd film. Unlike that, no H atoms are expected to be incorporated in the bulk of Pt and Pd films of a few MLs of thickness as thermodynamically, H would always float on the surface of these metals. Therefore, in pursuit of contamination-free deposition, our group developed an environmentally clean synthetic approach that uses H_{upd} in the growth of metal thin films that can adsorb H, such as Pd and Pt [96].

Figure 2. XPS results for the composition of a Pd thin film grown via E-ALD by SLRR of a Cu_{upd} layer.

In the present work, XPS was used to determine the at % ratio between Pt and Pd in alloy films grown by the SLRR deposition approach based on H_{upd} . The XPS peaks associated with Pt and Pd in three alloys with different Pt/Pd ratio are presented in the plots in Figure 3A–C and their relationship with the plating solutions composition is further summarized in the figure caption. As can be seen in the legends of Figure 3, there is a systematic trend of finding higher Pt content in the deposited film as compared to the one anticipated based on the solution ratio of $[\text{PtCl}_4^{2-}]$: $[\text{PdCl}_4^{2-}]$ chloride complexes, respectively. This discrepancy can be attributed to a number of factors for instance, that Pt is more noble ($\text{PtCl}_4^{2-} = +0.755$ V vs. SHE) than Pd ($\text{PdCl}_4^{2-} = +0.591$ V vs. SHE) and thus due to potential difference it is possible that some secondary displacement of already deposited Pd atoms by the growing Pt before the cut-off potential could take place [107,108]. Another supporting factor is that Pt has a higher work function compared to Pd [109]. Finally, the extra Pt in the deposit could also be due to the slightly faster displacement kinetics between Pt and H atoms as compared to that of the competing Pd counterpart [110,111]. The analysis of all XPS composition characterization results suggest that the solution composition ratio between Pt and Pd chloride complexes could still be used

for relatively accurate control of the Pt:Pd ratio in large compositional range of alloy films deposited by SLRR of H_{upd} .

Figure 3. XPS results (presented numerically in the legends) for compositional analysis of $Pt_xPd_{(1-x)}$ thin films grown by E-ALD of H_{upd} in solutions with $PtCl_4^{2-}:PdCl_4^{2-}$ ratios: (A) 2:1, (B) 1:1, and (C) 1:2.

3.3. Thin Film Characterization and Potentiodynamic FAO Testing

The purpose of this activity was to create a potent thin film catalyst for small organic molecules in general and specifically for FAO process in fuel cells. During FAO testing, as mentioned above, the as-prepared catalyst was characterized with H_{upd} and Cu_{upd} to ascertain that the growth had occurred in a conformal and quasi-epitaxial way and that the accordingly grown films exhibit limited to none roughness development for up to five MLs grown by SLRR of H_{upd} . More specifically, previous work on SLRR growth of Pd has shown that roughness starts to develop after deposition of 30 MLs [96]. Since the assumption is that the redox reaction rate for both Pd and Pt during growth is not substantially different, the number of Pt or $Pt_xPd_{(1-x)}$ alloy MLs is closely correlated to that of Pd growth via H_{upd} . The catalysts' surface morphology dynamics has been monitored by the same tests at different times during FAO testing in order to assess potential changes owing to loss of catalyst material. Thus, H_{upd} and Cu_{upd} CV runs were systematically performed to measure the exact ECSA after a number of cycles. For a reference, Figure 4 shows the behavior of about five MLs thick Pt film, in surface roughness characterization and FAO testing. There, Figure 4A presents Cu_{upd} CVs both on Au_{poly} substrate and on a Pt thin film grown by 10 SLRR cycles. The gradual restructuring of the CV with FAO cycling progress depicts the loss of Pt leading to transformation of the initially uniform layer into a network of Pt clusters. In addition, Figure 4B shows H_{upd} CVs for the as grown Pt thin film and demonstrates the progressive decrease in surface area thus corroborating the trend to depletion of Pt on the catalyst's surface. Figure 4C shows the FAO CVs which confirms the wearing out of the catalyst as evidenced by the decreasing peak and overall current densities with the increasing number of cycles. As with earlier reported results of our group on FAO catalysts testing [93,95], this behavior is seen in all catalysts developed and tested in this particular study.

Figure 5 presents the results of surface roughness characterization and FAO testing of a typical $Pt_xPd_{(1-x)}$ alloy thin film deposited by five successive SLRR events from a solution with 1:2 molar ratio of Pt and Pd complexes, respectively. As it can be seen, from Figure 5A,B, the Cu_{upd} and H_{upd} CVs registered initially on the as-deposited alloy film (0 cycles) suggest slightly rougher initial surface as compared to the Pt counterpart in Figure 4. This can be attributed to the differences in the Pt and Pd growth kinetics that happen to bring a little off-balance previously well-optimized deposition protocol for both metals depositing separately [95,96]. Also, the CV dynamics with FAO cycling suggests an intermediate decay trends between those of pure Pt and Pd, i.e., the dissolution of Pd being faster while that of Pt appearing slower so that the dissolution rate of Pt_xPd_{1-x} catalyst is found somewhere in-between. Overall, the surface area decrease transpires also in Figure 5C that presents directly the result of FAO testing. A closer look at the CV curve in the initial 50 FAO cycles shows some general trends in current density and peak potentials for both FAO and CO oxidative stripping manifested by the presence of two peaks clearly seen in the anodic potential sweep. The FAO peak is

mostly associated with the impact of Pd that when being alone features no CO [36] stripping peak throughout the potential range of testing. This is because Pd does not favor the indirect pathway of FAO oxidation reaction, and thus, it does not adsorb the COH intermediate which is responsible for the CO chemisorption [18]. At the same time, the appearance of CO stripping peak is clearly associated with the presence of Pt in the alloy. In addition, that peak is higher and more positive for the as-grown film; then it becomes smaller with time and shifts negatively (from 0.24 V to 0.21 V) with the number of cycles. It is noteworthy that the positive shift not only continues but drives a transformation of the FAO CV curve to a nearly hysteresis-free appearance normally typical for pure Pd catalysts. However, knowing that Pd dissolves at faster rate than Pt, we could conclude that the CV curve transformation after 500 FAO cycles is due to a transition of the alloy catalyst from a continuous film to a dense network of $Pt_xPd_{(1-x)}$ clusters with unknown composition. These clusters likely combine the effect of higher activity for Pt clusters on Au in comparison with Pt continuous films [79] with the upward shift of the d-band in Pd thin layers on Au [112] thus becoming more active than their constituents' counterparts.

Figure 4. Surface area characterization before and during FAO tests of Pt thin film deposited by 10 SLRR events: (A) Cu_{upd} and (B) H_{upd} at sweep rates 20 mVs^{-1} and 50 mVs^{-1} , respectively. (C) Potential cycling FAO testing at a sweep rate of 50 mVs^{-1} for different number of cycles as detailed in the legends.

Figure 5. Surface area characterization before and during FAO tests of $Pt_{42}Pd_{58}$ thin film (1:2 molar solution ratio): (A) Cu_{upd} and (B) H_{upd} at sweep rates 20 mVs^{-1} and 50 mVs^{-1} , respectively. (C) Potential cycling FAO testing at a sweep rate of 50 mVs^{-1} for different number of cycles as detailed in the legends.

A closer look at the specific and mass activities of the $Pt_{42}Pd_{58}$ catalyst in Figure 5C suggests that FAO reaction undergoes an unusual rate increase between the negative scans the 1st and the 50th FAO cycle. It is also noteworthy that the specific and mass activities of the $Pt_{42}Pd_{58}$ catalyst (35 mAcmm^{-2} and 45 Amg^{-1}) practically increase at least twice that of the Pt catalyst (17 mAcmm^{-2} and 17 Amg^{-1}), respectively and the two-fold difference persists for at least 1500 cycles or more. The overall superior performance of the $Pt_{42}Pd_{58}$ catalyst in comparison with its pure Pt counterpart can be attributed to

the synergistic effect of both metals working together and thus combining their strengths in a unique fashion, not only in continuous film configuration but also in the intermediate appearance of dense alloy cluster network as discussed earlier in this section. Finally, the comparison between Figures 4C and 5C suggests that the Pt₄₂Pd₅₈ alloy catalyst features a durability that is comparable to that of its pure Pt counterpart.

Figure 6 shows the electrochemical characterization of Pt₂₈Pd₇₂ alloy grown by SLRR of H_{upd} in a solution with 1:4 ratio of [PtCl₄²⁻]:[PdCl₄²⁻] complexes. From the UPD curves in Figure 6A,B, the surface roughness appears to be controlled fairly well during the alloy deposition process and its dynamics during the FAO testing process coincides with the change of the specific and mass activities seen in the cathodic peak of all FAO CV curves. The analysis of the catalyst's performance in the beginning of FAO testing suggests that its initial mass activity is almost equal to the pure Pt catalyst. Also, as with its Pt₄₂Pd₅₈ counterpart, the alloy catalyst in Figure 6 starts behaving quite close to pure Pd just after 250 cycles. This behavior compared to the one presented earlier in Figure 5, suggests that the Pd enrichment makes the Pt_xPd_(1-x) alloy catalyst less stable and thus make it difficult to even survive 1500 cycles, while the 42 at % (1:2 solution ratio) Pt alloy appears to still perform measurably by that mark and longer. Interestingly enough, in both cases of Pt_xPd_(1-x) alloy catalysts testing, the nearly hysteresis-free FAO CV curve is achieved a lot earlier in comparison with the pure Pt counterpart and at substantially higher current density/mass activity. This implies that while a large fraction of Pd is undoubtedly lost in the testing, some of it still stays in the dense cluster network remaining from the ones intact ultrathin film catalyst. The presence of Pd in the clusters apparently promotes the catalytic activity towards FAO thereby making both Pt_xPd_(1-x) alloy catalysts to perform better than their pure Pt counterpart. On the other hand, it turns out that the presence of a limited amount of Pt in a Pd film and/or in a cluster network considerably improves the durability of the catalyst as well.

Figure 6. Surface area characterization of Pt₂₈Pd₇₂ thin film (1:4 molar solution ratio) before and during FAO tests by (A) Cu_{upd} and (B) H_{upd} at sweep rates 20 mVs⁻¹ and 50 mVs⁻¹, respectively. (C) Potentiodynamic FAO testing at a sweep rate of 50 mVs⁻¹ for different number of cycles as detailed in the legends.

3.4. Constant Potential (Potentiostatic) FAO Testing

Additional information on the accordingly synthesized catalysts which provides another perspective to their durability was obtained by FAO testing at a constant potential. Before and after such test was performed, a few CV cycles were performed to ensure that the catalyst establishes its best working performance and to measure the surface area charges due to any dissolution of the catalyst. The catalyst was then continuously held at a potential of 0.00 V vs. MSE for up to 12 hours. Chosen based on previous FAO testing work [70], this potential is considerably positive to the FAO process on-set potential and to the H_{upd} potential range of the catalysts. Therefore, the reaction occurs without a potential influence of a H_{upd} layer as well [113]. At the same time, shortly after the application of that potential, the FAO current first reaches a maximum value and then becomes lower and lower gradually tending to level off after a few hours of the testing process. The results presented

in Figure 7A show an overall good stability for all the $\text{Pt}_x\text{Pd}_{(1-x)}$ compositions, but rather different initial activities. The compositions emphasizing presence of Pt in the range between 25 and 65 at % show better initial catalytic activity compared to pure Pt. Interestingly enough, the presence of less than 20% Pt in the catalytic alloys (not shown here) results in lower current density than pure Pt and all other alloys but it appears still durable if operated at constant potential. At the chosen testing potential, it is expected that most compositions would support the direct FAO reaction pathway. However, it appears that with this potential (0.00 V vs. MSE), being not high enough to oxidize CO_{ads} to CO_2 in the course of long-term testing, even small amounts of CO generated by the FAO stay adsorbed on the surface and gradually block more and more of the active FAO centers. A closer look at Figure 7A suggests that, except in the later testing stages, the $\text{Pt}_{42}\text{Pd}_{58}$ (1:2 solution ratio) could still be identified as the best catalytic performer in this study. In agreement with the cycling tests, that catalyst reaches highest current density in the initial testing stages and maintains equal or better activity for at least 8 hours of its performance evaluation. Also, while not showing any significant activity boost throughout the testing, the $\text{Pt}_{28}\text{Pd}_{72}$ catalyst (1:4 solution ratio) performs remarkably steady and features activity higher than the pure Pt catalyst throughout the entire experiment. Finally, Figure 7B presents Cu_{upd} CV curves registered before and after the CP testing on the surface of $\text{Pt}_{28}\text{Pd}_{72}$ alloy catalyst. It is clearly seen that not much change occurs during the testing, which suggests a remarkable robustness and sturdiness for the tested catalyst of interest.

Figure 7. (A) Long term FAO testing of $\text{Pt}_x\text{Pd}_{(1-x)}$ alloy catalysts with different composition at constant potential of 0.00 V vs. MSE. (B) Surface area characterization by Cu_{upd} of $\text{Pt}_{28}\text{Pd}_{72}$ alloy catalyst (1:4 molar solution ratio) before and after the FAO test; the Cu_{upd} CV curve on pure Au_{poly} is presented for reference.

4. Conclusions

Ultrathin film $\text{Pt}_x\text{Pd}_{(1-x)}$ catalysts were synthesized on Au_{poly} substrate by successive SLRR cycles of H_{upd} . The atomic composition determined by XPS showed a trend towards slightly more Pt into the deposit than anticipated based on the solution molar concentration ratio of PtCl_4^{2-} and PdCl_4^{2-} complexes. The as-deposited films featured no considerable surface roughness according to thorough ESCA measurements performed by Cu_{upd} and H_{upd} assays. Potential cycling tests for FAO reaction demonstrated that the $\text{Pt}_{42}\text{Pd}_{58}$ catalyst synthesized from molar solution PtCl_4^{2-} : PdCl_4^{2-} ratio of 1:2 showed the best specific and mass activity of up to 35 mA cm⁻² and 45 A mg⁻¹, respectively along with durability comparable to identically synthesized pure Pt counterpart catalyst. The alloy catalyst seconded its excellent performance in constant potential tests by maintaining higher activity for about eight hours in comparison with all other alloy counterparts, including pure Pt. Also, $\text{Pt}_x\text{Pd}_{(1-x)}$ ($x = 28\%$ and 42%) catalysts were found to undergo earlier transition to nearly hysteresis-free FAO CV curve along with sustaining at that performance mode substantially longer than a pure Pt catalyst.

This result indicates that as with the continuous films, $Pt_xPd_{(1-x)}$ clusters, forming inevitably because of a catalyst material loss during testing, exhibit superior FAO performance in comparison with pure Pt cluster networks. In conclusion, the facile and cost-effective synthetic approach demonstrated in detail in this work allows for scaling the catalyst production and thus for foreseeable commercialization.

Author Contributions: The authors contributed equally to this manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded in part by the National Science Foundation, Division of Chemistry, CHE-1310297.

Acknowledgments: The authors want to thank Anju Sharma for the help with XPS data collection.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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