Enhanced Adhesion of Ultrathin Nanoporous Au Deposits by Electrochemical Oxidation of Glassy Carbon

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Electrochemical (EO) and Thermochemical (TO) oxidation have been considered as means for improved adhesion of metals to glassy carbon (GC) substrates. In this paper, we report on the development and optimization of the electrochemical oxidation (EO) method for achieving improved adhesion of ultrathin Au deposits to GC. Our new approach combines the advantages of both TO and EO oxidation treatments to achieve enhanced adhesion without significant loss of the catalyst. The TO and EO oxidation treatments were performed at glassy carbon (EOGC) substrates using a two-step process: first, a TO treatment is used to drive the formation of an oxidized surface layer, and second, an EO treatment is used to promote the adhesion of the Au deposit to the GC substrate. The TO treatment increases the oxidation of the GC surface, while the EO treatment promotes the adhesion of the Au deposit to the GC surface. This two-step process results in a highly adherent Au deposit that exhibits enhanced activity in electrochemical reactions, such as oxygen reduction and oxidation, compared to Au deposited by other methods. The improved adhesion of the Au deposit to the GC substrate is attributed to the formation of a heterogeneous Au-GC interface, which enhances the interfacial electron transfer and improves the performance of the electrocatalytic reactions. This work demonstrates the potential of combining TO and EO oxidation treatments to achieve improved adhesion of metal deposits to GC substrates, which is of great importance for electrocatalytic applications in areas such as energy conversion, environmental sensing, and biosensing.

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a graphitic oxide with commonly shown quinone termination.\textsuperscript{21,28–33} These functionalities then tend to activate an easier oxidation reduction pathway that allows for, following initial reduction of a portion of the oxide layer, a more negative oxidation potential upon subsequent cycles. In addition the oxidation at this potential is limited to charges that are slightly more than previously reduced oxide layer indicating a reversible redox couple, shown to be a quinone-hydroquinone transition.\textsuperscript{29,29,31} With the formation of oxide species on the surface of the GC, there is the potential for the improvement of the interactions between substrate and deposit, leading eventually to increased background reaction rate.\textsuperscript{29,34} Due primarily to the improved interactions between substrate and growing metal, EO has been investigated for improvement of different layers adhesion to GC for more than two decades. Kepley and Bard first studied the optical properties of electrochemically active layers of GC up to 1 mm thick.\textsuperscript{30} Sullivan et al. showed that the capacitance EO treated GC is directly related to the thickness of the affected active layer\textsuperscript{35} and Maruyama et al. have showed that the capacitance EO treated GC is directly related to the thickness of the affected active layer\textsuperscript{36} and Maruyama et al. have studied by cyclic voltammetry the Nafion/GC interface treated by EO to impart hydrophilicity.\textsuperscript{29} All cited articles refer to the EO treatment as instrumental in increasing the activity of GC.

\textbf{Paper’s objective.—} Although prior works have shown the generation of oxidized layers during electrochemical oxidation and its application has been studied in various areas, this is the first report of the effect of electrochemical oxidation on the continuity and adhesion of NPG deposits on GC. This paper is aimed at utilizing electrochemical oxidation to fabricate high quality NPG layers featuring enhanced adhesion on the GC substrate. By employing some of our previously developed routines and comparing results of this activity to our previous work on thermochemical oxidation,\textsuperscript{23,25,36} the research in this paper will primarily focus on (i) the morphology of the GC substrate and NPG layer as a result of electrochemical oxidation studied by Scanning Electron Microscopy (SEM) and the unique characteristics of electrochemically oxidized GC during deposition, dealloying\textsuperscript{25} and Pb UPD surface area (SA) determination;\textsuperscript{37} (ii) the wettability of differently pre-treated GC surfaces assessed by contact angle measurements and its surface morphology after oxidation; (iii) the adhesion of Au\textsubscript{0.3}Ag\textsubscript{0.7} thin films on electrochemically oxidized and control (untreated) GC substrates by measuring the surface area by Pt UPD and the total amount of dissolved Ag of identical alloy-deposit batches before and after a rotating disk electrode (RDE) adhesion assessments which simulate an unsteady testing environment.

\textbf{Experimental}

\textit{Electrode preparation.—} Cylindrical glassy carbon working electrodes (Goodfellow, Huntingdon, England; diameter 5 mm) were mechanically polished down to 1 μm with alumina slurry (Buehler, Lake Bluff, IL, USA), then rinsed by Barnstead Nanopure water (R ≥ 18.2 MΩ cm) and sonicated for 2 minutes in ethanol. After sonication, they were dried under ultra high purity N\textsubscript{2} (less than 1 ppb of O\textsubscript{2}, CO, CO\textsubscript{2} and moisture). All GC electrodes prepared through these sequential steps will be called “untreated” in this work. In all deposition and dealloying experiments the GC electrodes (regardless of pre-treatment) were brought in contact with the electrolyte in hanging meniscus configuration as described elsewhere.\textsuperscript{38}

\textit{Electrochemical oxidation.—} After mechanical polishing, GC samples were electrochemically oxidized using a solution containing 0.1 M HClO\textsubscript{4} (GFS Chemical, 70% redistilled). The oxidation process was administered on freshly polished GC samples in a three-electrode cell at a constant potential of 1.47 V using Hg/HgSO\textsubscript{4} as reference electrode and a Pt wire as counter electrode (CE). The current was monitored to achieve the desired thickness of the oxidation. The time corresponding to the desired thickness was calculated by the following formula:

\[
\text{Time (s)} = \left( \frac{T_d}{0.947} \right) \times 3600
\]

\(T_d\) is the targeted thickness in μm, \(I\) is the nominal current monitored in mA and \(A\) is the electrode area in cm\textsuperscript{2}. The average growth rate of 0.94 μm/h normalized per current density of 1 mA cm\textsuperscript{-2} is calculated based on results of others\textsuperscript{29,35,39} as it was demonstrated in these sources that the thickness of the oxidized GC film depended mostly on the current density and increased linearly with oxidation time. Following oxidation, the samples were rinsed thoroughly with Barnstead Nanopure water and dried under ultra high purity N\textsubscript{2}.

\textit{Thin film alloy deposition.—} Au\textsubscript{0.3}Ag\textsubscript{0.7} thin films were electrochemically deposited in solutions containing 0.6 mM Au(1Cl) (GFS Chemicals, 99.995%) and 1 mM AgClO\textsubscript{4} (GFS Chemicals, 99.995%) (3.2 ratio) in 0.1 M Na\textsubscript{2}SO\textsubscript{4} (Alfa AESAR, Ward Hill, MA, USA; ≥ 99%). The alloys were deposited on treated and untreated GC samples in a three-electrode cell at a constant potential of ~0.40 V using Ag/Ag\textsuperscript{+} pseudo reference electrode (PRE) (~0.600 V, SHE). A Pt wire was used as counter electrode (CE). The cell was purged with ultra high purity N\textsubscript{2} for 20 min prior to deposition. The thickness of the films was controlled by the duration of the deposition run. An identical fixed charge of 50 mC cm\textsuperscript{-2} in all experiments was aimed at depositing identical amounts of alloy with a given composition for all samples. However, with the thickening of the oxidized layer part of this charge was being consumed for GC reduction and less Ag-Au alloy was being deposited. The exact amount of deposited alloy was assessed by monitoring of the ratio of charge of de-alloyed Ag (see next step) to the total deposition charge density. Following alloy deposition, the samples were rinsed thoroughly with Barnstead Nanopure water and dried gently under ultra high purity N\textsubscript{2}. Next, Pb UPD was performed immediately to determine the SA of the deposited thin film alloys.\textsuperscript{37}

\textit{The dealloying process.—} Selective removal of Ag from the Au\textsubscript{0.3}Ag\textsubscript{0.7} thin film alloy (de-alloying) carried out by linear sweep voltammetry scanning the potential from ~0.010 V to 1.20 V versus Ag/Ag\textsuperscript{+} PRE at a sweep rate of 0.2 mV s\textsuperscript{-1} to obtain NPG. The dealloying experiments were also performed in a three-electrode cell, and the solution used was 1 mM AgClO\textsubscript{4} and 0.1 M HClO\textsubscript{4} (GFS Chemical, 70% redistilled). A Pt wire was used as CE. A Princeton Applied Research (PAR) Model 273 Potentiostat/Glavonostat with Corrware Software was used in the de-alloying runs as well as in the GC oxidation and all deposition experiments.

\textit{Surface area measurements.—} Pb UPD was performed after alloy deposition (as described in the previous section) and after de-alloying each times to determine the SA\textsuperscript{37} of as-deposited precursor and the synthesized NPG. The measurements were performed by cyclic voltammetry in a three-electrode cell with Pt wire served as the CE. The solution used containing 0.1 M NaClO\textsubscript{4} (Sigma, 99.995%), 3 mM PbClO\textsubscript{4} (Aldrich, 99.995%) and 0.01 M HClO\textsubscript{4}. The solution was also purged with ultra high purity N\textsubscript{2} for 20 min prior to Pb UPD experiments and N\textsubscript{2} gently passed over the surface of the solution during the anodic scans. The BASi Epsilon Electrochemical Workstation was used for cycling the potential at a sweep rate of 20 mVs\textsuperscript{-1} from 0.600 to 0.010 V versus Pb/Pb\textsuperscript{2+} PRE (~0.200 V vs. SHE). Charge was integrated from the curve and was recorded as the average of the forward and reverse scans. The surface area of NPG was obtained simply by dividing the average charge by 300 μC/cm\textsuperscript{2}, which is the charge density of a Pt UPD layer on a flat polycrystalline Au electrode, prepared by a procedure described elsewhere.\textsuperscript{40}

\textit{Adhesion assessment.—} NPG fabricated on modified GC was subjected to rotation using a Pine MRS Rotator System which was operated by a Pine MRS Motor Controller. The rotation was administered at open circuit potential for two hours at 1600 rpm in a solution of 0.1 M HClO\textsubscript{4}. Surface area measurements were performed by using Pb UPD before and after rotation, the differences were quantified to determine any loss of material on GC. Adhesion tests were also performed alternatively by comparing the average amount of stripped Ag in de-alloying process of two identical three-sample sets of deposited
Au$_{0.3}$Ag$_{0.7}$ alloy samples with a target deposition charge density of 50 mC/cm$^2$ before and after rotation. The assessment relies on statistical arguments assuming identical amount and composition of the alloy deposited in six different runs. Therefore, the first three electrodes represent the maximum amount of material that could be dealloyed, assuming all deposits to be similar. The following three represent the material lost during testing. The adhesion is then determined by comparing the dealloyed charge of the tested samples to the theoretical maximum dealloyed charge of the untested samples. For better clarity, Figure 1 shows a detailed schematic for the overall experiment.

**Results and Discussion**

**Electrochemical oxidation of GC and Au$_{0.3}$Ag$_{0.7}$ alloy deposition.**— The steady-state current of the electrochemical oxidation process (Figure 2A, inset) was monitored in order to determine the appropriate amount of time to achieve the desired thickness of the oxidized layer. Different oxidation times were employed in order to assess potential correlation between the oxidized layer thickness and the strength of adhesion of both current decay steps, respectively. Apparently, the peak current behavior associated with about an order of magnitude shorter time for the oxidized sample, 0.1 μm, 0.25 μm, and 0.50 μm thickness of EO are shown for comparison, it is clearly seen that the most heavily oxidized sample, 0.5 μm EO, features the highest initial current and requires the longest time (>100 seconds) to reach the first step preceding the second decay lasting more than 100 seconds extra until the current reaches normal levels. The least oxidized sample, 0.1 μm, exhibits a qualitatively similar (two-step) behavior associated with about an order of magnitude shorter time for both current decay steps, respectively. Apparently, the peak current height and the time for the first decay step are both proportional to the thickness of oxidized layer. At the same time, the second decay step is considerably less affected by the thickness of the originally oxidized layer. This observation implies the contribution of a separate reduction process taking place along with the alloy deposition that is performed in that potential range. Most likely this concomitant process could be associated with a partial or complete reduction of the oxidized layer as detailed in the experimental section.29,35 Different the appropriate amount of time to achieve the desired thickness of the deposition process (Figure 2A, inset) was monitored in order to determine adhesion test results.

**Figure 1.** Schematic representing the dealloying based assessment of the adhesion test results.

**Figure 2.** Chronoamperograms for alloy deposition on (A) EOGC with differ-ent oxidized layer thickness (0.10, 0.25, and 0.50 μm) and (B) untreated, TO and EO. Inset: Chronoamperogram depicting typical EO experiment.
Figure 3. (A) Pb UPD curves before and after dealloying for EOGC with different 0.1 μm thickness of the oxidized layer. Sweep rate: 20 mV.s⁻¹ (B) SEM image of NPG deposit on the same sample. Inset: Higher magnification image depicting part of the same sample.

Figure 4. SEM images of NPG deposited (A) untreated GC, (B) 0.25 μm EO GC, (C) 0.50 μm EO GC, (D) 1.00 μm EO GC, (E) 1.50 μm EO GC, and (F) bulk Au substrate.

As mentioned earlier the comparison with untreated GC suggests a distinct increase in the area of the UPD curves for EOGC samples (Figure 3), as well as diminishing peaks for samples both before and after dealloying. This would normally suggest that there is an increased overall background activity that could be associated either with higher substrate surface area or with enhanced reversible redox activity beyond the Pb UPD phenomenon. Should an increase of the surface area be the reason one would expect a higher steady state deposition current after the second step in Figure 2 that would be proportional to the thickness of the originally oxidized layer. As no such effect or trend is seen in Figure 2 the enhanced capacitance current in the Pb UPD CV curves must be a result of an enhanced redox activity associated with the EO pretreatment of the GC surface. There is good precedent demonstrating an increase in background charging currents on glassy carbon following EO treatments affirming this result.21,29,30,35 This effect on NPG can be primarily attributed to the lack of continuity of the alloy and NPG following deposition as illustrated by Figure 3B. This implies that the EO makes the Pb UPD based surface area measurements somewhat ambiguous, rendering the technique less effective for measuring SA and monitoring its dynamics upon de-alloying or adhesion testing.

SEM images were taken to examine the GC surface in most representative way after administering the dealloying process. Figure 4 shows NPG deposited onto untreated and EO GC. NPG on Au is also shown for comparison in Figure 4F. Figure 4A shows NPG on untreated GC with considerable coverage, as expected. Figure 4B–4E represent NPG on EOGC samples with increasing amounts of EO and oxidation layer thicknesses. It is clearly evident that the coverage and quality of the deposit drastically decreases with increased oxidation. As a result, the higher the oxidized layer thickness is the less dense and more sporadic nucleation is observed. The 0.25 μm and 0.5 μm samples demonstrate the most comparable coverage to the untreated samples. Apparently, more charge is associated with the reduction of thicker GC oxide and the relative contribution of the alloy deposition decreases respectively.

Overall, the analysis of results presented in Figures 2 –4 suggests a considerable impact of the EO on the substrate behavior of accordingly treated GC electrodes. Clearly the oxidized layer reduction...
taking place during the alloy deposition not only reduces the efficiency but also affects the GC redox behavior in the typical potential range of Pb UPD on Au and Ag surfaces. The depth of the above analysis is limited only to deduction made on indirect observations, yet it suits generally the purpose of the present work. It is thusly essential that one acknowledges that the exact nature of the final and/or by-products of the consequentially observed GC oxidation-reduction transition are not identified in this work. But, based on previous work, it can be deduced that surface termination and resulting reversible oxidation and reduction are attributed to a quinone-hydroquinone transition.28,29,31,32

Contact angle measurements and focused ion beam with scanning electron microscope (FIB/SEM) characterization.— In light of work of others suggesting univocally termination of the GC surface with oxygen-containing species during EO treatment21,28–33 one would expect impact of the said treatment on the wetting properties/hydrophilicity of the GC surface. Contact angle measurements are carried out in this study to assess trends in the wetting properties of untreated, EO and TO treated GCs vis-à-vis an anticipated adhesion enhancement with the surface becoming more hydrophilic. The hydrophilicity of EOGC electrodes was determined by measuring the average equilibrium static contact angle (CA) of a drop of DI water on the surface of the GC. Contact angles were measured for comparison on GCs that were untreated and thermally oxidized along with those oxidized electrochemically to different thickness. The wetting properties of the GC surface are illustrated in Figure 5 and the average equilibrium static contact angles are shown in Table I. As seen from Figure 5, untreated GC (Fig. 5A) has an average CA of 84° ± 3, which is considered a hydrophobic surface. The thermally oxidized GC sample (TOGC) that was reported before, is included here as a reference in Figure 5F and listed with an average CA of 51° ± 10.25 Apparently, the contact angle significantly decreased for TOGC when compared to untreated GC showing an increase in hydrophilicity. In our previous work analysis of different results led to the conclusion that this decrease could be associated with surface roughening.25 Continuing with the analysis it is clear that the CA decreases even more for the electrochemically oxidized GC (EOGC), reaching lows of about 30°.

The large difference in CAs between untreated GC and EO GC indicates that the electrochemical oxidation promotes a significant increase of the surface hydrophilicity. This increase is likely caused by termination of the surface with oxygen-containing groups identified by others as a combination of quinone-like functional groups as a result of the EO process.28,29 Taking into account the lack of a significant difference or trend in CA of all EO samples, one would conclude that the contact angle just relates to the surface of the sample as all EOGC have identical surface termination regardless of the different oxidized layer’s thickness.

To further study the oxidized surface, FIB/SEM has been applied and the cross-sectional SEM images are presented in Figure 6. For a comparison, a cross section of a TOGC electrode shown on the left, and an untreated GC sample featuring flat surface with no open pores is also provided (lower inset). For both images, the top portion presents a Pt coating layer, the bottom portion shows the GC bulk unaffected by thermal or electrochemical oxidation, and the interface between

| Oxidation Treatment     | Average Equilibrium Static Contact Angle |
|-------------------------|------------------------------------------|
| Untreated               | 84 ± 3                                   |
| Electrochemical (0.25 μm) | 48 ± 3                                   |
| Electrochemical (0.50 μm) | 30 ± 2                                   |
| Electrochemical (1.00 μm) | 37 ± 6                                   |
| Electrochemical (1.50 μm) | 40 ± 1                                   |
| Thermochemical          | 51 ± 10                                  |

Figure 5. Images of equilibrium static contact angle measurements for (A) untreated GC, (B) EOGC 0.25 μm, (C) EOGC 0.5 μm, (D) EOGC 1.0 μm, (E) EOGC 1.5 μm, and (F) TOGC.

Figure 6. FIB/SEM cross section images of oxidatively treated GC (A) TO, (B) 0.50 μm EO. Upper insets: Higher magnification of the GC-Pt interface. Lower insets: Cross section image of untreated GC surface for comparison.
Adhesion tests.— As mentioned earlier the adhesion testing was performed by using two independent methods; the first method was the Pb UPD approach for measuring surface area before and after rotation. Figure 7 shows the Pb UPD CV curves obtained on NPG deposited on untreated GC and EOGC with different oxidized layer thickness, while Table II lists the accordingly calculated surface area data. Based on these calculations, the TO and EO treatments both improved the adhesion significantly, as the surface area retention rate remains quite large, at nearly 90%. However, certain ambiguity is cast on the results associated with EO treatment because of the poor quality of the Pb UPD CVs (poorly defined peaks and high background and/or charging current). This becomes even more obvious when comparing said results with the considerably better defined Pb UPD CVs obtained on untreated GC and TOGC. Overall, these results again suggest that the Pb UPD approach has limited capacity in the adhesion assessment and in this case is an ineffective tool for measuring surface area and confidently determining adhesion.

Due to the limitation of Pb UPD, an alternative de-alloying based assessment of the retained alloy material (not NPG because the assessment involves the de-alloying itself, see Figure 1) after rotation was also employed. For EOGC samples, the various thicknesses of the oxidation layer were examined ranging from 0.10 μm to 0.50 μm. Figure 8 shows the detailed dealloying curves of EO samples with three different oxidation thicknesses. It is clearly seen that the dealloying curves for EOGC samples are different from those registered on untreated or TOGC samples. The difference is manifested by the presence of two peaks observed in the linear sweep voltammetry.
gram best seen in Figure 8A. While the nature of these two peaks is not immediately clear from the beginning of our analysis one can clearly see that the dealloying contributes only partially to the total anodic charge density (see Table III). More specifically, Table III shows overall anodic charges which are about 2 to 7 times higher than the total alloy deposition charge density. Also, Table III shows clearly a substantial increase of the total anodic charge with the increase of the initially oxidized layer thickness. This finding is supported in a more obvious way by the curves in Figure 8A–8C where the second peak (in the range 0.75 V to 1.10 V) clearly increases with the increase of the oxidized layer thickness while the first one (0.45 V – 0.65 V) stays relatively unchanged. The observed phenomenology suggests that the second peak is clearly not result of the dealloying whereas the first peak/shoulder is most likely associated with the selective Ag dissolution. While further work is needed to determine the exact nature of the second peak, one can speculate that this peak is also due to the quinone-hydroquinone transition that manifests itself following initial GC oxidation.28,29,31 This is further verified by the clearly observed in Figure 8, peak current / charge dependence upon the initial oxidation time and consequently, thickness of the oxidized layer.29 The assessment of the RDE test-results then focuses strictly on comparison of de-alloying charges associated with the potential range to negative 0.70 V (Figure 9). The limitation is based on consideration of the 0.10 μm dealloying curve (Figure 8A) for determining best the potential range limited by the onset and end of the dealloying. Additional support for the dealloying potential limits is provided by the analysis of the dealloying curve of NPG on TOGC presented in Figure 8D. Therefore, the dealloying charge before and after rotation tests of samples on EOGC with 0.10 μm, 0.25 μm, and 0.50 μm oxidized layer thickness in Figure 9 was measured by integration of the polarization curve ending at a potential of 0.7 V.

| Sample         | Before Rotation (mC cm⁻²) | After rotation (mC cm⁻²) |
|----------------|---------------------------|-------------------------|
| Untreated      | 37.35                     | 22.90                   |
| 0.10 μm EO     | 114.36                    | 105.39                  |
| 0.25 μm EO     | 178.86                    | 178.03                  |
| 0.50 μm EO     | 350.64                    | 351.12                  |

Table IV summarizes the dealloying charges before and after rotation for samples with different oxidized layer thickness after the discussed above correction. Alike with the results presented in Table II, it is obvious that the EO treatment substantially boosts the adhesion of NPG layers to the GC surface. The retention rate for EO treated samples is steadily at an average of about 90% whereas the untreated samples retain slightly more than 50% NPG material. It is noteworthy that owing to the deposition inhibiting role of the EO discussed earlier alloy growth for longer times than usual was administered on GC substrates with 0.50 and 1.00 μm oxidized layer thickness to ensure enough deposited material for the tests. This is the reason for the higher deposition charge densities for said samples seen in the Table IV. However, from Table IV, the comparison between ED samples (which represents the dealloyed samples) and ER samples (represents the adhesion tested samples) shows no significant differences in the retention rate, regardless of the oxidized layer thickness. Similar extent of retention rate improvement was also observed on thermally oxidized GC samples in our previous work.25 There, the enhanced adhesion was attributed mainly to the pore opening and consequent surface area increase resulting from the thermal treatment.25,41
Electrochemical polarization curves in the narrower potential range limited only to the selective dissolution of Ag from GC with different thickness of the oxidized layer (from results in Figure 9).

Table IV. Ag dissolution charge before and after RDE testing with different thickness of the oxidized layer (from results in Figure 9).

| Sample       | Before Rotation, ED (mC.cm⁻²) | After rotation, ER (mC.cm⁻²) | % charge difference | % SA left |
|--------------|-------------------------------|-------------------------------|---------------------|-----------|
| Untreated    | 37.35                         | 22.90                         | 62%                 | 55%       |
| 0.10 μm EO   | 33.18                         | 30.05                         | 90%                 | 90%       |
| 0.25 μm EO   | 35.52                         | 32.85                         | 93%                 | 88%       |
| 0.50 μm EO   | 48.78                         | 46.05                         | 95%                 | 89%       |
| 1.00 μmEO    | 55.73                         | 52.13                         | 93%                 | 88%       |

Figure 9. Anodic polarization curves in the narrower potential range limited only to the selective dissolution of Ag from GC with different thickness of the oxidized layer (A) 0.10 μm EO, (B) 0.25 μm EO, (C) 0.50 μm EO, (D) TO GC. Sweep rate: 0.2 mV.s⁻¹.

Conclusions

Electrochemical oxidation of GC is found to alter substantially the substrate behavior. As a result, the GC surface becomes increasingly passive with the oxide layer thickening but the adhesion of the NPG layer to EOGC substrates improves substantially even with the shortest EO treatments. The enhanced adhesion was studied and proven by Pb UPD measurements and dealloying–based adhesion assessment of NPG layers supported on GC electrodes subjected to rotation at 1600 rpm for two hours. The Pb UPD voltammetry produced ambiguous CV curves on EO samples and owing to that shortcoming the accordingly obtained results are deemed semi-quantitative in this work. The alternative dealloying method results also displayed significant adhesion improvement, as dealloying charges were found very close for as-dealloyed samples and adhesion tested ones. Overall, it can be stated that alike the thermal treatment studied earlier by our group, EO led to substantially improved adhesion of NPG to GC substrate.

The EO treatment led also to hindered nucleation and lack of continuity in the deposited alloy precursor. SEM results confirmed the low cluster density and ascertained the discontinuity of accordingly grown deposits. Pb UPD measurements before and after dealloying in agreement with the SEM results demonstrated less surface area development on thicker oxidized layer, indicating deterioration of the NPG synthesis on such EOGC substrates. Given the obvious quality decrease of NPG with thickening of the oxidized layer there is an inherent trade-off between increased oxidation, continuity of the deposit and enhanced adhesion. The critical analysis of all results suggested that oxidation thickness in the range 0.10 to 0.25 μm displayed an adequate level of deposition coverage as well as sufficient oxygen species termination to ensure early best NPG adhesion.

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