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Electrochemical Roughening of Thin-Film Platinum Macro and Microelectrodes

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Cover Letter

Lawrence Livermore National Laboratory

April 2, 2019

Dear Dr. Wu,

Please find enclosed our fourth (R3) revision of manuscript JoVE59553, entitled “Electrochemical Roughening of Thin-Film Platinum Macro and Microelectrodes” for consideration as an article in *The Journal of Visual Experiments*.

We have revised the manuscript to address all changes requested by editors. The revisions are indicated by track changes in the version of the revised manuscript document entitled 59553_R3. We believe these revisions now make the filmed (highlighted) portion of the manuscript less than 2.75 pages.

In this work, we present a method to electrochemically roughen thin-film without comprising the fidelity of the film. Previously published electrochemical methods for roughening of thicker films damage thin-film electrodes. Our modified method can be used for the roughening of micro or macro think-film electrodes. Finally, we demonstrate how to characterize the active surface area of both the macro and microelectrodes.

All authors have seen and approved the submission of this manuscript. This work is based on techniques we first reported in Ivanovskaya AN, Belle AM, Yorita AM, Qian F, Chen S, Tooker A, Garcia Lozada R, Dahlquist D, Tolosa VM. “Electrochemical Roughening of Thin-Film Platinum for Neural Probe Arrays and Biosensing Applications,” *J. Electrochem. Soc.* 2018 vol 165, issue 12, G3125-G3132. Additionally, there has been a published patent application filed for this work under number US 2017 0350034.

Sincerely,

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TITLE:

Electrochemical Roughening of Thin-Film Platinum Macro and Microelectrodes

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KEYWORDS:

electrochemical roughening, high surface area electrode, neuromodulation, neural stimulation, microelectrode, platinum, electrical stimulation, electrophysiology, biosensor

SUMMARY:

This protocol demonstrates a method for electrochemical roughening of thin-film platinum electrodes without preferential dissolution at grain boundaries. The electrochemical techniques of cyclic voltammetry and impedance spectroscopy are demonstrated to characterize these electrode surfaces.

ABSTRACT:

This protocol demonstrates a method for electrochemical roughening of thin-film platinum electrodes without preferential dissolution at grain boundaries of the metal. Using this method, a crack free, thin-film macroelectrode surface with up to 40 times increase in active surface area was obtained. The roughening is easy to do in a standard electrochemical characterization laboratory and incudes the application of voltage pulses followed by extended application of a reductive voltage in a perchloric acid solution. The protocol includes the chemical and electrochemical preparation of both a macroscale (1.2 mm diameter) and microscale (20 µm diameter) platinum disc electrode surface, roughening the electrode surface and characterizing the effects of surface roughening on electrode active surface area. This electrochemical characterization includes cyclic voltammetry and impedance spectroscopy and is demonstrated for both the macroelectrodes and the microelectrodes. Roughening increases electrode active surface area, decreases electrode impedance, increases platinum charge injection limits to those of titanium nitride electrodes of same geometry and improves substrates for adhesion of electrochemically deposited films.

INTRODUCTION:

Nearly five decades ago, the first observation of surface enhanced Raman spectroscopy (SERS) occurred on electrochemically roughened silver[1]. Electrochemical roughening of metal foils is still attractive today because of its simplicity over other roughening methods[2,3] and its usefulness in many applications like improving aptamer sensors[4], improving neural probes[5], and improving adhesion to metal substrates[6]. Electrochemical roughening methods exist for many bulk metals[1,5,7-10]. Until recently, however, there was no report on the application of electrochemical roughening to thin (hundreds of nanometers thick) metal films[6], despite the prevalence of microfabricated thin-film metal electrodes in a number of fields.

Established methods to roughen thick platinum (Pt) electrodes[5,8] delaminate thin-film Pt electrodes[6]. By modulating the frequency of the roughening procedure and the electrolyte used for the for the roughening, Ivanovskaya et al. demonstrated Pt thin-film roughening without delamination. That publication focused on using this new approach to increase the surface area of platinum recording and stimulation electrodes on microfabricated neural probes. The roughened electrodes were demonstrated to improve recording and stimulation performance and improve adhesion of electrochemically deposited films and improve biosensor sensitivity[6]. But this approach also likely improves surface cleaning of microfabricated electrode arrays and enhances the capabilities of thin-film electrodes for other sensor applications (e.g., aptasensors) as well.

The approach to roughen thin-film macroelectrodes (1.2 mm diameter) and microelectrodes (20 µm diameter) is described in the following protocol. This includes preparation of the electrode surface for roughening and how to characterize the roughness of the electrode. These steps are presented along with tips on how to optimize the roughening procedure for other electrode geometries and the most important factors to ensure an electrode is roughened nondestructively.

PROTOCOL:

CAUTION: Please consult all relevant safety data sheets (SDS) before use. Several of the chemicals used in this protocol are acutely toxic, carcinogenic, oxidizing and explosive when used at high concentrations. Nanomaterials may have additional hazards compared to their bulk counterpart. Please use all appropriate safety practices when carrying out this protocol including the use of engineering controls (fume hood) and personal protective equipment (safety glasses, gloves, lab coat, full length pants, closed-toe shoes).

1. Cleaning the Pt electrode(s) before initial characterization and surface roughening

1.1. Chemically clean the electrodes under ozone with a laboratory UV-ozone cleaner at 80 °C for 10 min.

1.2. Soak the portion of the probe containing the electrode(s) in a solvent (e.g., a 30 min soak in acetone for the microelectrodes demonstrated in this protocol).

NOTE: Other methods may be more effective for removing organics from the electrodes depending on electrode housing and geometry, but this solvent soaking works well for the electrodes in the protocol.

1.3. Electrochemically clean the surface of all electrodes by repetitive potential cycling in an acidic solution of perchloric acid. The perchloric acid solution does not need purging to change the concentration of any gasses present.

1.3.1. Load settings onto the potentiostat to apply cyclic voltammograms (CVs) to the electrodes. Scan from -0.22 V to 1.24 V vs Ag|AgCl (or -0.665 V to 0.80 V vs mercury sulfate reference electrode (MSE), the reference used for roughening) at a scan rate of 200 mV/s.

NOTE: Regardless of reference material used, all potentials in this paper are given with respect to Ag|AgCl (saturated with KCl) reference electrode. The potential offset between the MSE (containing 1.0 M H_2SO_4) used in this study and Ag|AgCl (saturated with KCl) is 0.44 V[11].

1.3.1.1. In the EC-Lab Software, under the **Experiment** tab, press the **+** sign to add electrochemical technique. In the pop-up window, **Insert techniques** will appear.

1.3.1.2. Click on **Electrochemical techniques**. When it expands, click on **Voltamperometric techniques.** When that expands, double click on **Cyclic Voltammetry – CV**. **1-CV** line will appear in the **Experiment** window.

1.3.1.3. In the **Experiment** window, fill in the following parameters:

Ei = 0 V vs Eoc
dE/dt = 200 mV/s
E1 = -0.665 V vs Ref
E2 = 0.8 V vs Ref
n = 200
Measure <I> over last 50% of the step duration
Record <I> averaged over N = 10 voltage steps
E Range = -2.5; 2.5 V
Irange = Auto
Bandwidth = 7
End scan Ef = 0 V vs Eoc

1.3.2. Submerge the electrode tip of the device in a 500 mM perchloric acid ($HClO_4$) solution that also contains a Pt wire counter electrode and MSE reference.

NOTE: To avoid alterations in the electrochemical processes from chloride ion contamination, a chloride-free reference electrode (e.g., leakless Ag|AgCl or MSE, etc.) must be used for all tests performed inside acidic electrolytes in this protocol.

1.3.3. Connect one electrode or short several electrodes of a multielectrode device together as the working electrode.

1.3.4. Connect the working, counter, and reference electrodes to the potentiostat.

1.3.5. In the EC-Lab Software, in the **Experiment** window, press **Advanced settings** on the left.

1.3.6. Under **Advanced settings**, select **Electrode configuration** = **CE to ground**. Connect the working, counter and reference electrode to the instrument leads as shown on the Electrode connection diagram.

1.3.7. Press the **Run** button (green triangle under **Experiment** window) to begin the experiment.

1.3.8. Perform repetitive potential cycles until the voltammograms visually appear to overlap from one cycle to the next. This typically occurs after 50-200 CVs.

2. Electrochemical characterization of the electrode surface before roughening

2.1. Perform all electrochemical characterizations in the 3-electrode configuration described above in steps 1.3.2 - 1.3.4. All potentials in the following steps are given with respect to a Ag|AgCl reference electrode. Use a Pt wire as the counter electrode. Use a conventional Ag|AgCl electrode for characterization performed in phosphate buffered saline (PBS), but use a leakless Ag|AgCl or MSE as the reference for all tests performed in acidic solutions.

2.1.1. Load settings on the potentiostat for the application of CVs from -0.22 to 1.24 V vs Ag|AgCl (or -0.665 V to 0.80 V vs MSE) at a scan rate of 50 mV/s. Submerge the electrode tip of the device in a beaker of deoxygenated 500 mM $HClO_4$ (deoxygenated with N_2 gas for ≥10 min) that also contains a Pt wire counter electrode and MSE reference.

2.1.1.1. In the EC-Lab Software, under the **Experiment** tab, press the **+** sign to add electrochemical technique. In the pop-up window, **Insert techniques** will appear.

2.1.1.2. Click on **Electrochemical techniques**. When it expands, click on **Voltamperometric techniques**. When that expands, double click on **Cyclic Voltammetry – CV**. **1-CV** line will appear in the **Experiment** window.

2.1.1.3. In the **Experiment** window, fill in the following parameters:

Ei = 0 V vs Eoc
dE/dt = 50 mV/s
E1 = -0.665 V vs Ref
E2 = 0.8 V vs Ref
n = 10
Measure <I> over last 50% of the step duration
Record <I> averaged over N = 10 voltage steps
E Range = -2.5; 2.5 V
Irange = Auto
Bandwidth = 7
End scan Ef = 0 V vs Eoc

NOTE: The only differences between this setup and that described previously in step 1.3 are the use of deoxygenated 500 mM $HClO_4$ and ensuring that only one electrode is used as the working electrode. In the EC-Lab Software, in the **Experiment** window, press **Advanced settings** on the left.

2.1.1.4. Under **Advanced settings**, select **Electrode configuration** = **CE to ground**. Connect the working, counter and reference electrode to the instrument leads as shown on the Electrode connection diagram.

2.1.1.5. Press the **Run** button (green triangle under **Experiment** window) to begin the experiment.

2.1.1.6. Perform repetitive potential cycles until the voltammograms visually appear to overlap from one cycle to the next.

2.1.2. Calculate the electrode surface area from the hydrogen adsorption peaks of the highly reproducible (overlapping) CVs using the method of J. Rodríguez, et al.[11].

2.1.2.1. Determine the charge associated with adsorption of a hydrogen monolayer (Q) to the electrode surface by integrating the two cathodic peaks of a CV between the potentials where the cathodic current deviates from the double layer current (V_i) and the hydrogen evolution starts (V_f) after subtracting the charge associated with monolayer charging (Q_{dl}). Scan rate (v) also effects this adsorption. Use the equation below to determine Q.

$$\mathrm{Q} = \frac{1}{\nu}\int_{V_i}^{V_f} IdV - Q_{dl}$$

Graphical representation of integrated area can be found in J. Rodríguez, et al.[11].

2.1.2.2. Calculate the effective surface area (A) of an electrode by dividing Q by the charge density of the formation of hydrogen monolayer (k). For an atomically flat polycrystalline Pt surface, k = 208 μC/cm^2.

$$A = Q / k$$

2.1.3. If the two cathodic peaks of a Pt CV are poorly resolved, estimate the electrode surface area from the double layer capacitance at the electrode-solution interface. Use of the approach described in step 2.1.1 when hydrogen peaks are poorly resolved will lead to inaccurate results.

2.1.3.1. Measure the impedance spectra of a single electrode under open circuit conditions in PBS (pH 7.0, 30 mS/cm conductivity). Submerge the electrode tip of the device in PBS that also contains a Pt wire counter electrode and MSE reference. Connect one electrode at a time as the working electrode. Next, use a potentiostat to apply an impedance sign wave with an amplitude of 10 mV over the frequency range 1 Hz – 100 kHz.

2.1.3.1.1. In the EC-Lab Software, under the **Experiment** tab, press the **+** sign to add electrochemical technique. In the pop-up window, **Insert techniques** will appear.

2.1.3.1.2. Click on **Electrochemical techniques**. When it expands, click on **Impedance Spectroscopy**. When that expands, double click on **Potentio Electrochemical Impedance Spectroscopy**. **1-PEIS** line will appear in the **Experiment** window.

2.1.3.2. In the **Experiment** window, fill in the following parameters:

Ei = 0 V vs Eoc
fi = 1 Hz
ff = 100 kHz
Nd = 6 points per decade
In Logarithmic spacing
Va = 10 mV
Pw = 0.1
Na = 3
nc = 0
E Range = -2.5; 2.5 V
Irange = Auto
Bandwidth = 7

2.1.3.3. In the EC-Lab Software, in the **Experiment** window, press **Advanced settings** on the left.

2.1.3.4. Under **Advanced settings**, select **Electrode configuration** = **CE to ground**. Connect the working, counter and reference electrode to the instrument leads as shown on the Electrode connection diagram.

2.1.3.5. Press the **Run** button (green triangle under **Experiment** window) to begin the experiment.

2.1.4. Determine the double layer capacitance from the electrode's impedance spectra (collected in step 2.1.4.1) by fitting the spectra with an equivalent circuit model using impedance analysis software.

NOTE: Analysis in representative results and in Ivanovskaya, et al.[6] was carried out with the impedance analysis fitting tool Z Fit.

2.1.4.1. In the EC-Lab Software, click **Load data file** under **Experiment list** menu.

2.1.4.2. Select **Nyquist Impedance** plot type at the top menu bar.

2.1.4.3. Click **Analysis**, then select **Electrochemical Impedance Spectroscopy**, and click **Z Fit.**

2.1.4.4. When then **Z-Fit Bio-Logics** pop-up window appears, click the **Edit** button

2.1.4.5. Select **Display circuit with 2 elements** and choose **R1 + Q1** from the list of equivalent circuit models. Click **OK**.

2.1.4.6. Expand the **Fit** section of the pop-up window and make sure that the settings are **Randomize + Simplex**, stop randomize at 5000 iterations, and stop fit on 5000 iterations.

2.1.4.7. Press the **Calculate** button and observe initial fit spectra added to the plot. Press **Minimize** and observe finalized fit.

2.1.4.8. Adjust fit boundaries (green circles) to exclude noisy or distorted data from the fit. Estimated fit parameters will appear under **Results** section.

2.1.5. Ensure that the calculated equivalent circuit model fits a Nyquist plot of the data that includes ohmic resistance (R) in series with a constant phase angle (CPE).

2.1.5.1. Take note of the double layer capacitance value (Q) that is part of CPE in the equivalent circuit model.

2.1.5.2. Estimate the change in surface area as a ratio of Q measured before and after roughening since double layer capacitance (Q) increases linearly with active surface area[12].

3. Electrochemical roughening of a macroelectrode

NOTE: Electrochemical roughening is driven by series of oxidation/reduction pulses that result in oxide growth and dissolution. In the case of a weakly adsorbing anion (like $HClO_4$), this dissolution is accompanied by Pt crystallite redeposition while in the case of strongly adsorbing anions (like H_2SO_4) this process results in preferential intergrain Pt dissolution that creates microcracks in the electrode surface[6]. Therefore, usage of high purity $HClO_4$ electrolyte is essential to prevent microcracks in the electrode surface.

3.1. Use a potentiostat able to apply voltage pulses with the 2 ms pulse width to roughen macroelectrodes. This procedure can be done with either potentiostat on the accompanying materials list.

3.2. Program the following parameters into the potentiostat to roughen a 1.2 mm diameter Pt disk macroelectrode.

3.2.1. Begin the roughening protocol with a series of oxidation/reduction pulses between -0.15 V (V_{min}) and 1.9 – 2.1 V (V_{max}) at 250 Hz with a duty cycle of 1:1 for 10 – 300 s. The duration of pulse application determines the extent of roughening, the longer the pulsing the more roughening occurs. Use **Figure 1A** and the discussion as a guide to help determine the specific parameters required to achieve a particular surface roughness.

3.2.1.1. Open the VersaStudio program.

3.2.1.2. Expand the **Experiment** menu and select **New**.

3.2.1.3. In the **Select Action** pop-up window that appears, choose **Fast potential pulses** and enter the desired file name when prompted. **Fast potential pulses** line will then appear under **Actions to be performed** tab.

3.2.1.4. Fill out the following under the **Properties of Fast Potential Pulses/Pulse properties**. Enter **Number of pulses** = 2, **Potential (V) 1** = -0.39 vs Ref for 0.002 s, and **Potential (V) 2** = 1.56 vs Ref for 0.002 s.

3.2.1.5. Under **Scan properties**, fill out: **Time per point** = 1 s, **number of cycles**: 50000 (for 200 s duration).

3.2.1.6. Under **Instrument properties,** enter **Current range** = **Auto**.

3.2.2. Program the potentiostat to immediately follow the series of pulses with a prolonged application of a constant reduction potential (-0.15 V (or -0.59 V vs MSE) for 180 s) to fully reduce any oxides produced and stabilize the electrode surface.

3.2.2.1. In the VersaStudio Software, press the **+** button to insert a new step.

3.2.2.2. Double click on **Chronoamperometry**.

3.2.2.3. Enter **Potential (V)** = -0.59, **Time per point (s)** = 1, and **Duration (s)** = 180.

3.2.3. Use the visual representation of the paradigm described in steps 3.2.1. and 3.2.2 (**Figure 2**) to aid in programming the potentiostat.

NOTE: Specific parameters will vary for different electrode geometries but using the parameters above as a starting point and then varying V_{max} and pulse duration is the recommended method to optimize roughening parameters for other geometries. Using a high purity $HClO_4$ solution is essential for this step.

3.3. Submerge the electrode containing the tip of the device in 500 mM $HClO_4$ that also contains a Pt wire counter electrode and MSE reference electrode. Then connect an individual electrode as the working electrode and apply the pulsing paradigm to roughen the electrode.

3.4. In VersaStudio, press the **Run** button at the menu to start roughening.

4. Electrochemical roughening of a microelectrode

4.1. Use a potentiostat that can apply voltage pulses with the 62.5 µs pulse width to roughen microelectrodes. The VMP-300 potentiostat on the materials list is not capable of applying these short pulses, while the VersaSTAT 4 potentiostat can apply the rapid pulses required to roughen thin-film microelectrodes.

4.2. Program the following parameters into the potentiostat to roughen a 20 µm diameter Pt disk microelectrode fabricated flush with its insulating material. The roughening protocol can be applied to a single electrode or several electrodes shorted together (see additional explanation in step 4.3).

4.2.1. Begin the roughening protocol with a series of oxidation/reduction pulses between -0.25 V (V_{min}) and 1.2 – 1.4 V (V_{max}) at 4000 Hz with a duty cycle of 1:3 (oxidation:reduction pulse widths) for 100 s. Use guidance in the discussion to help determine the specific parameters required for other electrode geometries.

4.2.1.1. Open the VersaStudio program.

4.2.1.2. Expand the **Experiment** menu and select **New**.

4.2.1.3. In the **Select Action** pop-up window that appears, choose **Fast potential pulses** and enter the desired file name when prompted. **Fast potential pulses** line will then appear under **Actions to be performed** tab.

4.2.1.4. Fill out the following under the **Properties of Fast Potential Pulses / Pulse properties,** enter **Number of pulses** = 2, **Potential (V) 1** = -0.49 vs Ref for 0.0625 ms, and **Potential (V) 2** = 1.06 vs Ref for 0.1875 ms.

4.2.1.5. Under **Scan properties**, fill out: **Time per point** = 1 s, and **number of cycles**: 400,000 (for 100 s duration).

4.2.1.6. Under **Instrument properties**, enter **Current range = Auto**.

4.2.2. Program the potentiostat to immediately follow the series of pulses with a prolonged reduction potential (-0.20 V for 180 s) to fully reduce any oxides produced and stabilize the chemistry of the electrode surface.

4.2.2.1. In the VersaStudio Software, press the **+** button to insert a new step.

4.2.2.2. Double click on **Chronoamperometry.**

4.2.2.3. Enter Potential (V) = -0.64, Time per point (s) = 1, and Duration (s) = 180.

NOTE: Using a high purity $HClO_4$ solution is essential for this step.

4.3. Submerge the electrode containing tip of the device in 500 mM $HClO_4$ that also contains a Pt wire counter electrode and MSE reference. Then connect an individual electrode or several shorted electrodes as the working electrode and apply the pulsing paradigm. In potentiostatic mode, electrodes can be shorted when trace resistance within the device is small. In that situation, ohmic drop through a device is negligible so all shorted electrodes will experience the applied potential.

4.4. In VersaStudio, press the **Run** button at the menu on the top of the screen to start the roughening.

NOTE: Roughening of microelectrodes may require adjustment of the pulsing parameters depending on the electrode geometry, Pt composition, and topology (e.g.*,* well depth for an electrode recessed in insulating material). Start with the parameters listed here and modify the V_{max} value to begin optimization of roughening parameters for different electrode geometries. The different pulsing parameters for three different geometries are summarized in **Table 1**.

5. Characterization of electrode surface after roughening

5.1. Determine the increase in effective surface area of macroelectrodes using steps 2.1.1-2.1.5.

5.2. Determine the increase in effective surface area of microelectrodes using steps 2.1.1-2.1.5.

5.3. Observe the changes in electrode appearance after roughening in optical microscopy as a loss of metal shininess (see Representative Results) and in scanning electron microscopy (SEM)[6] as an obvious decrease in surface smoothness.

REPRESENTATIVE RESULTS:

A schematic showing the voltage application for roughening both macroelectrodes and microelectrodes is shown in **Figure 2**. Optical microscopy can be used to visualize the difference in the appearance of a roughened macroelectrode (**Figure 3**) or microelectrode (**Figure 4**). In addition, electrochemical characterization of the Pt surface using impedance spectroscopy and cyclic voltammetry can readily show the increased active surface area of a roughened macroelectrode (**Figure 1**) and microelectrode (**Figure 5**). The relationship between surface roughness and the number of roughening pulses applied (pulsing duration) is shown for macroelectrodes in **Figure 4**. For each new electrode geometry, within both the macroelectrode and microelectrode regimes, optimization of roughening parameters will likely be needed to obtain the ideal roughened surface for different applications. **Table 1** presents an example of different roughening parameters to maximally increase electrode active surface area for different electrode geometries.

FIGURE AND TABLE LEGENDS:

Figure 1. Roughened Pt macroelectrode electrochemical characterization. (**A**) Roughness factor as a function of pulse duration during roughening of macroelectrodes (1.2 mm diameter) in 0.5 M $HClO_4$ with V_{max}= 1.9 V and V_{min}= -0.15 V, 250 Hz pulses applied for differing durations. (**B**) Cyclic voltammetry (scan rate of 100 mV/s) of a Pt macroelectrode roughened in 0.5 M $HClO_4$ with V_{max}= 1.9 V pulse amplitude, 250 Hz 300 s pulsing resulting in a 44x area increase measured in 0.5 M $HClO_4$ before (blue) and after (red) roughening.

Figure 2. Schematic of voltage pulsing paradigm for electrode roughening. Roughening begins with a series of oxidation/reduction pulses between a reductive, typically negative potential (V_{min}) and an oxidative, typically positive potential (V_{max}) immediately followed by a prolonged, constant application of a reductive potential to fully reduce any oxides produced by pulsing and stabilize the chemistry of the electrode surface.

Figure 3. Optical microscopy images of Pt macroelectrodes. Electrode surface (**A**) as sputtered before roughening and (**B**) after roughening in perchloric acid solution. Parameters for roughening are found in **Table 1**. Each electrode is 1.2 mm in diameter. SEM of the electrode surfaces can been seen in Ivanovskaya, et al.[6].

Figure 4. Optical microscopy images of Pt microelectrodes roughened in perchloric acid solution. Parameters for roughening are found in **Table 1** with the amplitude of V_{max} as the only difference between the electrodes shown here. From left to right V_{max} = (**A**) 1.2, (**B**) 1.3, (**C**) 1.4 (V vs Ag|AgCl). Each electrode is 20 µm in diameter. SEM of the electrode surfaces can been seen in Ivanovskaya, et al.[6].

Figure 5. Roughened Pt microelectrode electrochemical characterization. (**A**) Impedance of roughened Pt microelectrode (20 µm disk) in PBS. The measured impedance (black circle) over the frequency range of 10 Hz – 100 kHz is shown overlaid by the modelled impedance (red x) from the equivalent circuit model. (**B**) Cyclic voltammetry (scan rate of 500 mV/s) of Pt microelectrode roughened in 0.5 M $HClO_4$ with V_{max}= 1.4 V pulse amplitude measured before (blue) and after (red) roughening. The roughened electrode has a 2.6x increased active surface area calculated from a ratio of roughness factors described in step 2.1.3 (surface roughness before = 1.48, surface roughness after = 3.8).

Table 1. Optimized parameters for roughening of different electrode geometries.

DISCUSSION:

The electrochemical roughening of thin-film macroelectrodes and microelectrodes is possible with oxidation-reduction pulsing. This simple approach does require several key elements to nondestructively roughen thin-film electrodes. Unlike foils, roughening of thin metal films may lead to sample destruction if parameters are not properly chosen. Critical parameters of the roughening procedure are pulse amplitude, duration and frequency. Additionally, ensuring electrode cleanliness and perchloric acid purity prior to the procedure are critical to prevent electrode damage. The presence of organics or contaminates from the microfabrication process can contribute to destruction of the electrode via corrosion or delamination. Therefore, it is critical to ozone clean and solvent soak the device as well as to electrochemically prepare the electrode surface before the roughening begins.

Electrochemical roughening is driven by series of oxidation/reduction pulses that result in repetitive oxide growth and dissolution. In the case of a weakly adsorbing anion (like $HClO_4$), this process is accompanied by Pt crystallite re-deposition. But, in the case of a strongly adsorbing anion (like H_2SO_4), this process results in microcrack formation due to preferential intergrain Pt dissolution[6]. The presence of chloride can also cause the destruction of the electrode during the roughening process. For this reason, it also critical to use high purity perchloric acid, a chloride free (or leakless) reference electrode and eliminate any other potential sources of chloride contamination.

If using impedance to estimate the surface area of microelectrodes (step 2.1.4), keep these things in mind. The impedance spectra of a clean Pt electrode in PBS under open circuit conditions should result in a linear Nyquist plot. This linearity indicates a purely capacitive response. Significant bending or deviations from linearity would indicate charge transfer due to the slow kinetics of dissolved oxygen reduction[6]. In the impedance analysis software, an equivalent circuit model is used to fit curves to this Nyquist plot. This equivalent circuit model consists of ohmic resistance (R) in series with a constant phase element (CPE), where R is composed of the device trace electrical resistance and ionic resistance of the solution and the CPE represents the double layer capacitance at the electrode-solution interface. The CPE parameters of double layer capacitance (Q) and exponent (α) are extracted from fitting the impedance spectra. Typically observed Q values for clean, sputtered Pt in PBS are close to 50 $\mu F/ s^{\alpha-1} cm^2$ (in good agreement with the range 10–60 $\mu F/cm^2$ observed on smooth metal electrodes in similar tests[6,12]).

The electrodes here were all discs of 250 nm thick sputtered Pt, fabricated flush with the flexible polyimide material that insulates the array[6,13,14]. The roughening parameters will be different for different electrode geometries within the macroelectrode and microelectrode scales (shown in **Table 1**) and will need optimization for new electrode geometries. While not investigated here, there may also be differences in the parameters needed to roughen electrodes of the same geometry based on their topography (e.g., how recessed into the insulating substrate the electrode sits or if the electrode is created through evaporation instead of sputtering). Optimal roughening parameters may depend on the thin-film fabrication techniques used to create the device because the way a film is created may influence grain size and the preferential orientation of Pt crystalline domains in the Pt which may alter the metal reactivity.

With this roughening approach, larger electrodes can withstand a greater V_{max}. This larger pulse amplitude enables 10x greater increases in the roughness factor of macroelectrodes compared to microelectrodes. This limits the applicability of the technique for roughening of microelectrodes if a more than 10x increased roughness is needed. Roughened 1.2 mm diameter macroelectrodes with a 44x increase in surface area showed charge injection limits of 0.5 – 1.39 mC/cm^2, which are comparable to titanium nitride and carbon nanotube materials and 2 – 4 times greater than untreated platinum samples[6].

In addition to the Nyquist plots shown in **Figure 5A** to characterize roughening's effect on microelectrodes, Bode plots for the impedance of roughened macroelectrodes and microelectrodes are shown in Ivanovskaya, et al[6]. From these Bode plots, the impedance at 1 kHz for an optimally roughened macroelectrode is 2.5x lower than the electrode before roughening (208.7 kΩ for untreated to 83.7 kΩ for the roughened electrode). And for microelectrodes, the impedance at 1 kHz was lowered ~2x (from 672 kΩ untreated to 336 kΩ for the roughened electrode).

Critical protocol parameters are pulse amplitude, duration and frequency and they need adjustment depending on the electrode size and morphology. When optimizing the roughening parameters for a new electrode type, start with the parameters in **Table 1** and begin varying V_{max}. Fine tuning of the roughness factor (or a desired surface area) can then be achieved by varying pulse duration. While the specific pulsing parameters may need slight modification depending on the electrode geometry, topology and Pt composition, this roughening technique can be used to improve adhesion of electrodeposited films and improve electrode characteristics such as impedance, charge injection limits and charge storage capacity as demonstrated in Ivanovskaya, et al.[6].

Recipes for electrochemical roughening of metal foils have existed for nearly five decades[1] and electrochemical roughening of metal is still attractive because of the approach's simplicity and utility. But, use of this simple approach to roughen thin-film electrodes was not as straight forward and there was little information available on the procedure to successfully roughen thin metal films. With the approach described here, thin-film electrodes can now be easily electrochemically roughened. These roughened electrodes can be used to improve recording and stimulation electrodes in neural probes, improve adhesion of electrochemically deposited films to substrates, improve biosensor sensitivity, improve thin-film based aptasensor sensitivity, or to clean electrode arrays after fabrication.

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DISCLOSURES:

The authors declare no competing financial interests.

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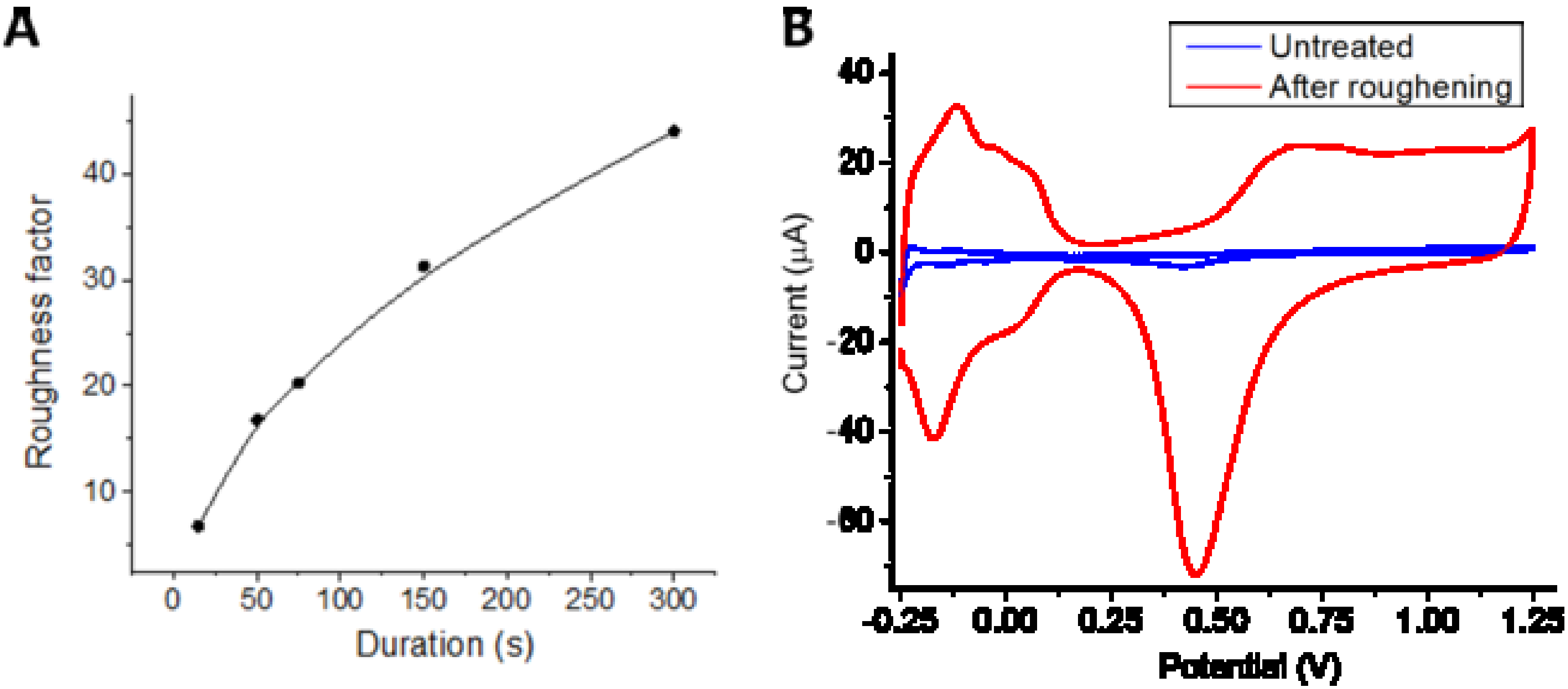
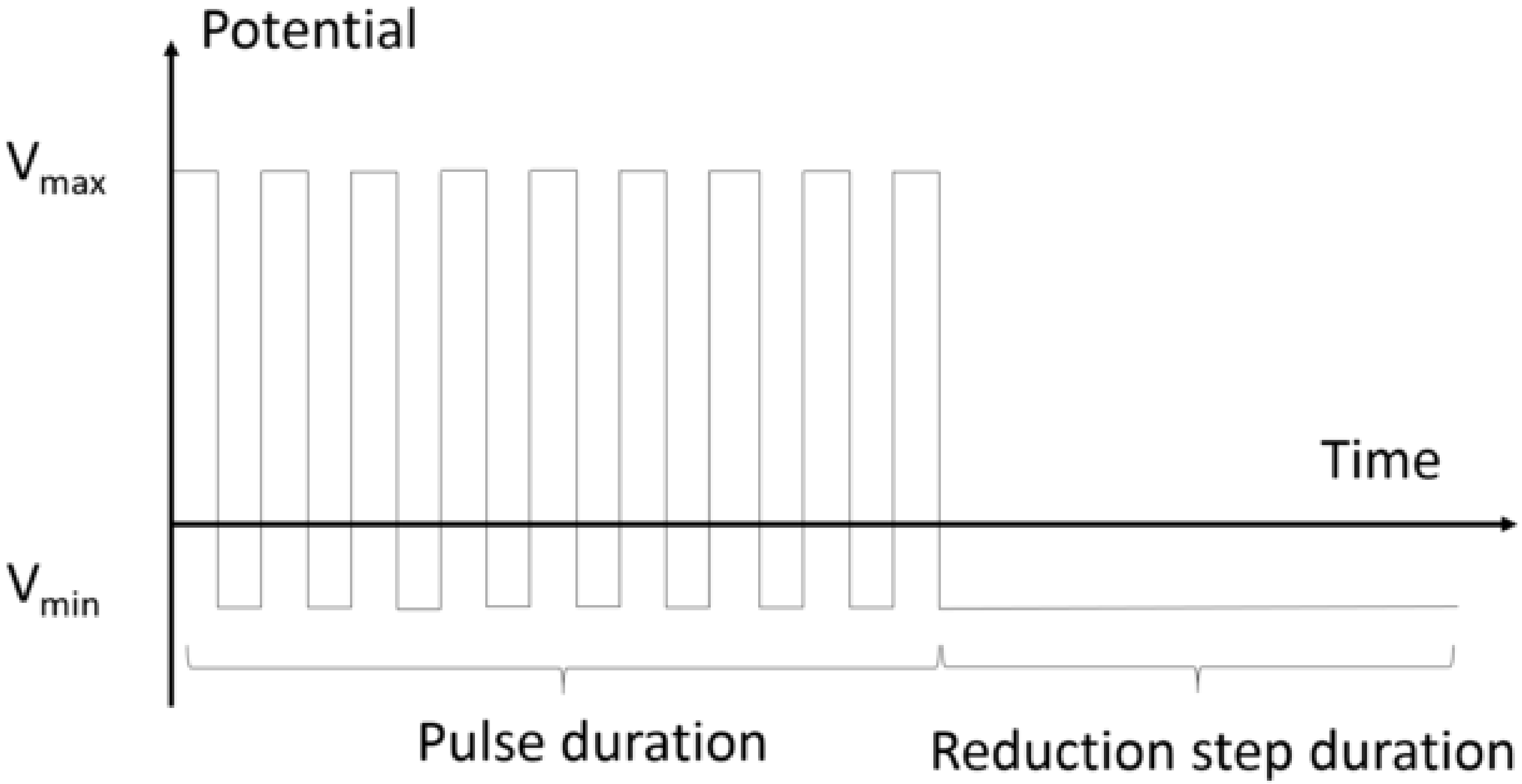
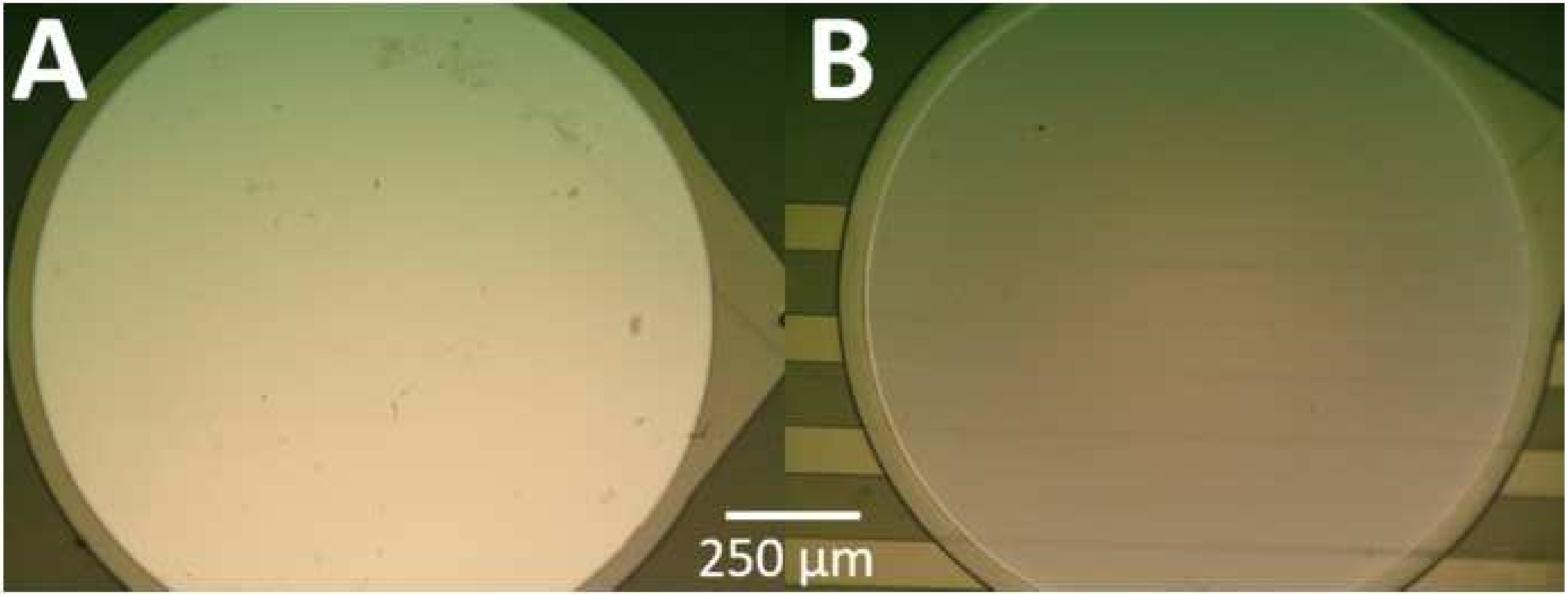
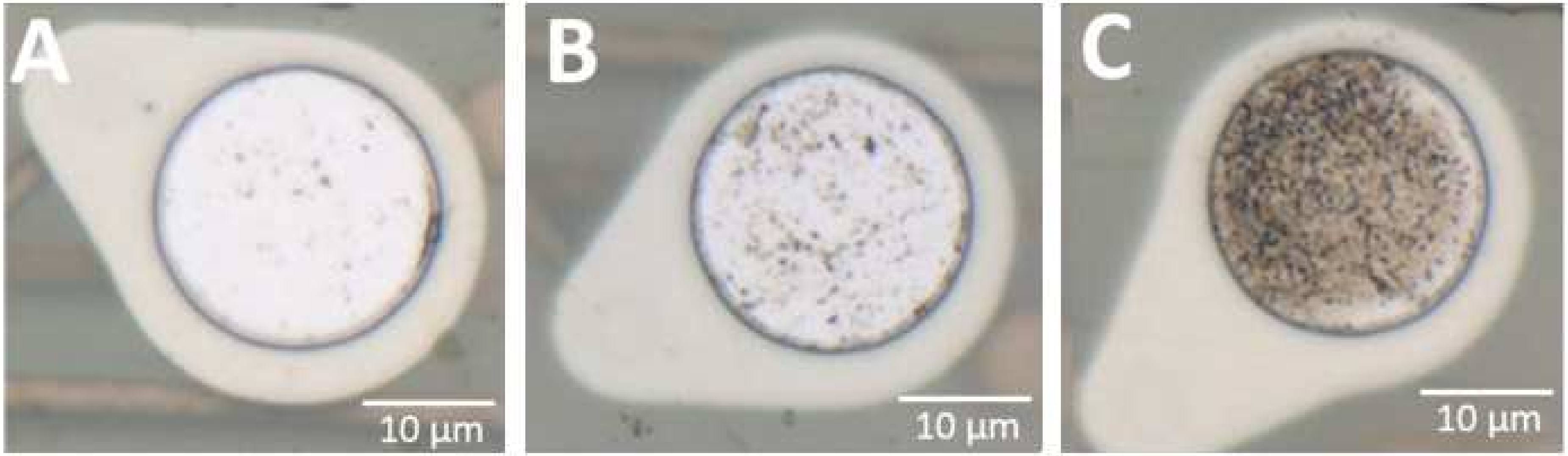
Figure1


A
Roughness factor
10
20
30
40
0
50
100
150
200
250
300
Duration (s)
B
Untreated
After roughening
Current (μA)
40
20
0
-20
-40
-60
-0.25
0.00
0.25
0.50
0.75
1.00
1.25
Potential (V)


Potential
V_{max}
Time
V_{min}
Pulse duration
Reduction step duration


A
B
250 µm


A
10 µm
B
10 µm
C
10 µm

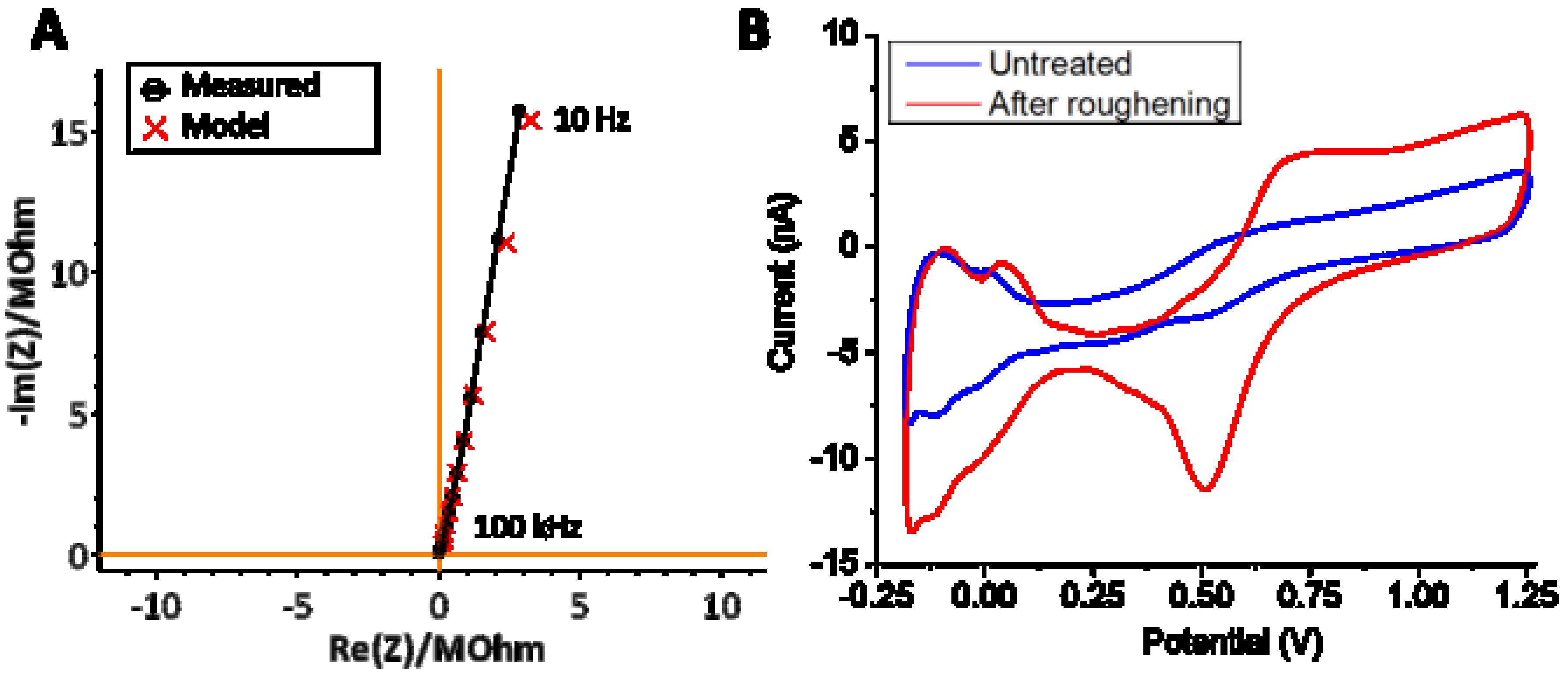

A
Measured
Model
10 Hz
100 kHz
-Im(Z)/MOhm
Re(Z)/MOhm
0
5
10
15
-10
-5
0
5
10
B
Untreated
After roughening
Current (nA)
Potential (V)
10
5
0
-5
-10
-15
-0.25
0.00
0.25
0.50
0.75
1.00
1.25

Table1

	Potential Pulses					Constant Potential		Roughness factor (a) estimated from CV (b) estimated from EIS
Electrode Geometry	V_{min} (V)	V_{max} (V)	Frequency (Hz)	Duty cycle	Duration (s)	Potential (V)	Duration (s)	
1.2 mm diameter Pt disk	-0.15	1.9 – 2.1	250	1:1	10-300	-0.15	180	44 (a)
20 µm diameter Pt disk	-0.25	1.2 - 1.4	4000	1:3	100	-0.25	180	2.6 (a) 2.7 (b)
10 µm diameter Pt disk	-0.25	1.1	4000	1:3	100	-0.25	180	2.2 (b)

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Acetone	Fisher Scientific, Sigma Aldrich or similar	n/a	Laboratory grade
EC-Lab Software	Bio-Logic Science Instruments	n/a	For instrument control and data analysis
Leakless Silver/Silver Chloride Reference	eDAQ Company, Australia	ET069-1	Free from chloride anion contamination (or other type of chloride free electrode e.g. Mercury sulfate electrode)
Mercury Sulfate & Acid Electrode Kit	Koslow, Scientific Testing Instruments	5100A	glass, 9mm version
Milipore DI water	MilliporeSigma	n/a	Certified resistivity of 18.2 MΩ.cm (at 25°C)
Perchloric acid, 99.9985%	Sigma Aldrich	311421	High Purity
Phosphate-buffered saline	Teknova	P4007	10mM PBS with 100mM NaCl, pH 7 or similar product from elsewhere
Platinum Wire Auxiliary Electrode (7.5 cm)	BASi	MW-1032	Counter electrode
Pt macroelectrodes	Lawrence Livermore National Laboratory	n/a	1.2 mm diameter, 250 nm thick Pt disc electrodes insulated in polyimide. More information in Reference 9.

Pt microelectrode arrays	Lawrence Livermore National Laboratory	n/a	20 µm diameter 250 nM thick Pt disc electrodes insulated in polyimide. More information in Reference 9.
Sulfuric acid, 99.999%	Sigma Aldrich	339741	High Purity
UV & Ozone Dry Stripper	Samco	UV-1	for cleaning electrodes
VersaSTAT 4 Potentiostat	AMETEK, Inc.	n/a	Good time resolution for pulsing tests
VersaStudio Software	AMETEK, Inc.	n/a	For instrument control
VMP-200 Potentiostat	Bio-Logic Science Instruments	n/a	Low current resolution option is preferable for measurements with microelectrodes

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We have revised manuscript #JoVE59553_R3 based on the comments of editorial reviewers. These revisions are indicated tracked changes in the revised manuscript (59553_R3.docx). Our responses to the reviewer’s comments are in **bold** below following the reviewer’s original comments below.

1. The highlighted protocol steps are over the 2.75 page limit (including headings and spacing). Please highlight fewer steps for filming.
   The highlighted steps have been reduced to 2.75 pages.