

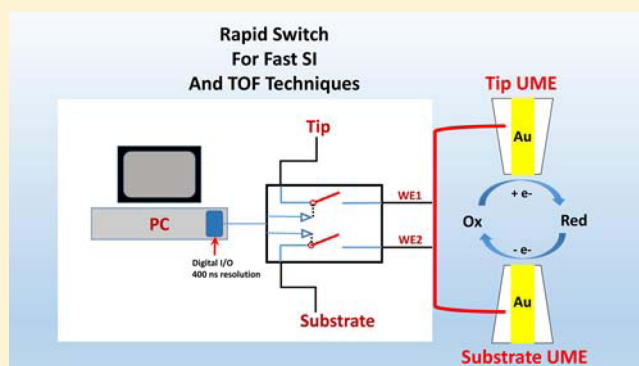
# Switching Transient Generation in Surface Interrogation Scanning Electrochemical Microscopy and Time-of-Flight Techniques

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## Supporting Information

**ABSTRACT:** In surface interrogation scanning electrochemical microscopy (SI-SECM), fine and accurate control of the delay time between substrate generation and tip interrogation ( $t_{\text{delay}}$ ) is crucial because  $t_{\text{delay}}$  defines the decay time of the reactive intermediate. In previous applications of the SI-SECM, the resolution in the control of  $t_{\text{delay}}$  has been limited to several hundreds of milliseconds due to the slow switching of the bipotentiostat. In this work, we have improved the time resolution of  $t_{\text{delay}}$  control up to ca. 1  $\mu\text{s}$ , enhancing the SI-SECM to be competitive in the time domain with the decay of many reactive intermediates. The rapid switching SI-SECM has been implemented in a substrate generation–tip collection time-of-flight (SG–TC TOF) experiment of a solution redox mediator, and the results obtained from the experiment exhibited good agreement with that obtained from digital simulation. The reaction rate constant of surface  $\text{Co}^{\text{IV}}$  on oxygen-evolving catalyst film, which was inaccessible thus far due to the lack of  $t_{\text{delay}}$  control, has been measured by the rapid switching SI-SECM.



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Scanning electrochemical microscopy (SECM) has been implemented widely in the last several decades for imaging, screening of local chemical activities, and microfabrication.<sup>1</sup> Its power is that electrochemical kinetic measurements can be carried out at steady state, thus avoiding problems with double layer capacitance charging and surface processes. However, it is also possible to use transient techniques with SECM to extend the information available in certain measurements. For example, a mode of SECM was developed for quantitative study of surface adsorbates.<sup>2,3</sup> This technique, termed surface interrogation SECM (SI-SECM), utilizes two size-matched ultramicroelectrodes (UMEs) tip and substrate, at a close proximity such that the analyte generated by one electrode (tip or substrate) is detected quantitatively at the other without leaving the tip–substrate gap. Redox titration of surface adsorbates was enabled by the use of SI-SECM.<sup>2</sup> Furthermore, kinetic information about surface electron transfer and chemical reactions was extracted by use of time-dependent studies.<sup>4</sup> Early applications of the SI-SECM were on surfaces that are relatively well-known and less reactive, such as gold and platinum oxides.<sup>2,3</sup> The technique proved to be robust and useful in studying such surfaces; however, with its more recent applications to reactive surface adsorbates, such as hydroxyl radicals<sup>5,6</sup> and high oxidation state transition metals,<sup>4,7</sup> the SI-SECM has been revealing shortcomings in its time resolution arising from the intrinsic switching time delays associated with commercial potentiostats.<sup>4</sup> Therefore, a method for finer control of the delay time between generation and interrogation

is desired for the detection of fast-reacting surface intermediates. In this contribution, we describe a newly developed external switching device. We also show that the same transient technique can be used with solution species generated at the substrate. This uses the same switching functions as those of the SI-SECM thereby achieving the time resolution necessary for the analysis of fast-reacting surface intermediates. A set of substrate generation–tip collection (SG–TC) experiments using a well-behaved redox couple (1,1'-ferrocenedimethanol; FcDM) in solution were performed with varying delay times between SG and TC. The recorded SG–TC behavior was fit to the results from a digital simulation to verify that the switching device is working correctly in tandem with the SI-SECM. Finally, a surface titration of the CoP, oxygen evolution reaction (OER) catalyst was performed with the enhanced setup and was compared to the results from a recently published study.<sup>4</sup> The improved time resolution of the SI-SECM reported here allowed for the direct measurement of the kinetic rate constant of the reactive  $\text{Co}^{\text{IV}}$  centers in their reaction with water.

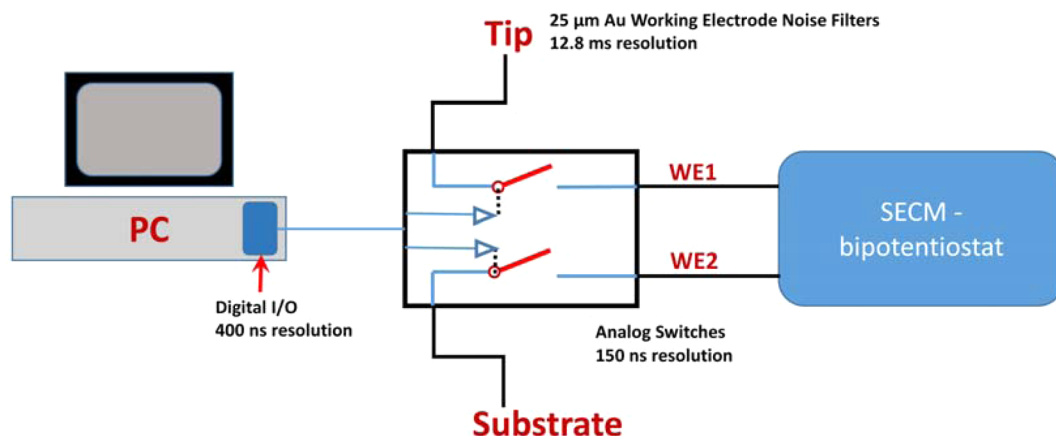
## EXPERIMENTAL SECTION

**General.** All solutions were prepared using a Milli-Q deionized water (18.2 M $\Omega$ , 4 ppb total oxidizable carbon).

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Scheme 1. Process Diagram of the Rapid Switching Device for the SI-SECM<sup>a</sup>

<sup>a</sup>The time resolutions for each component are described.

Potassium nitrate (99%, Aldrich), anhydrous potassium phosphate monobasic (99% Fisher), anhydrous potassium phosphate dibasic (99% Fisher), dimethyl methylphosphonate (97%, Acros), cobalt nitrate hexahydrate (98%, Acros), 1,1'-ferrocenedimethanol (98%, Acros), and potassium hexachloroiridate (99.95%, Alfa-Aesar) were used as received. Gold wires (99.99+%) of 25 μm diameter was purchased from Goodfellow (Devon, PA). The gold wire was used to fabricate the SECM tips as described elsewhere.<sup>1</sup> All electrodes used in this study had an RG (radius of metal electrode/radius of the glass sheath) of ca. 1.3 and were polished with alumina paste on microcloth pads prior to use. The surface of the electrodes was cleaned with an acidic piranha solution (1:1 v/v 40% H<sub>2</sub>O<sub>2</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>) before the experiments. The CoP<sub>i</sub> water oxidation catalyst films (of nanometers to several micrometers) were anodically deposited (0.95 V vs Ag/AgCl) on a conducting substrate (25 μm Au UME) from a Co<sup>2+</sup> containing water solution (0.5 mM Co(NO<sub>3</sub>)<sub>2</sub> in 0.1 M pH 7 phosphate-buffered deionized water).<sup>8,9</sup> For all electrochemical measurements a Ag/AgCl reference electrode and a platinum wire counter electrode were used.

**Instrumentation and SECM Conditions.** SECM experiments were conducted on a CHI920C SECM station bipotentiostat and its built-in software (CH Instruments; Austin, TX). Chronoamperometry was chosen as a detection technique in the SI-SECM experiments. The tip and the substrate electrodes (both 25 μm Au UME) were positioned at distances at which generation–collection efficiency was unity (1.8 μm for CoP<sub>i</sub> titration experiments and 2.0 μm for 1,1'-ferrocenedimethanol experiments, respectively). Tip–substrate alignment and approach were performed as described in our previous work.<sup>4</sup> In each experiment, the substrate was stepped to  $E_{\text{Subs}}$  for a time  $t_{\text{step}} = 20$  s (5 s for 1,1'-ferrocenedimethanol experiments) followed by a potential step back to open circuit. Respective amperometric detection was performed by stepping the potential of the tip after a delay time  $t_{\text{delay}}$ . A total collection time was 15 s. The redox mediator solutions employed in this work consisted of 1.5 mM 1,1'-ferrocenedimethanol and 0.8 mM potassium hexachloroiridate in 0.1 M potassium phosphate-buffered water at pH 7 ± 0.1. Switching of the two working electrodes of the SECM was performed by an external switch that is depicted in Scheme 1. The analog switch used in the device is a model DG412 switch (Maxim Integrated,

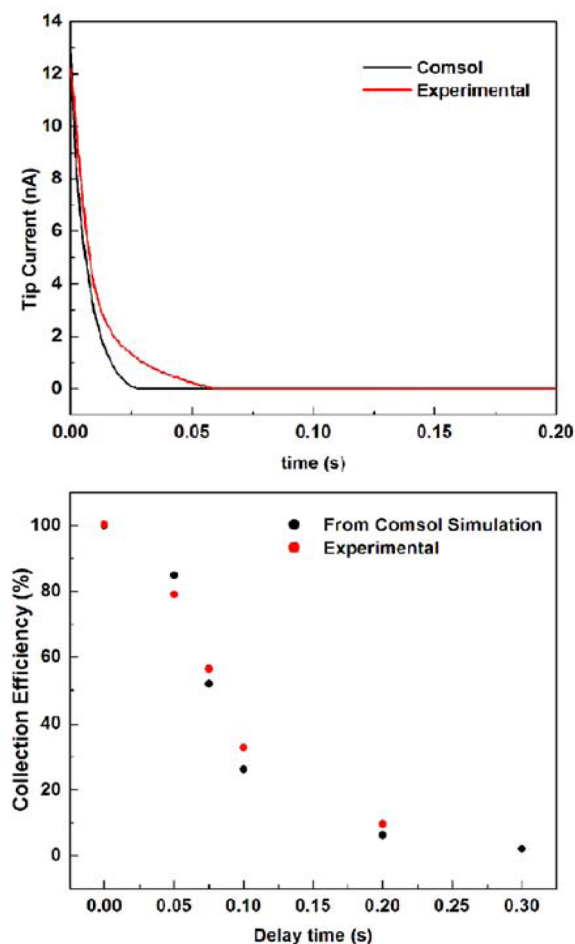
San Jose, CA), with switching times of less than 150 ns. The DG412 switch is expected to exhibit leakage currents of 5–7 pA in the operation voltage range and therefore should not affect the outcome of the experiments described here. A National Instruments NI6023E digital I/O board, with a sampling rate of 12 kS/s, handled the switch-computer communication in our device. When coupled with the operating computer, the NI6023E board routinely clocked a data communication time of <400 ns. The resolution for the delay time control should be at most the sum of maximum time resolution of the computer communication (<400 ns) and that of the DG412 switch operations (<300 ns) and therefore should allow us a sub 1 μs control of the delay time. Computer simulation of the substrate generation–tip collection (SG–TC) experiments was performed using COMSOL Multiphysics software (version 4.2). A simulation model employed in this work is similar to those utilized in previous work,<sup>2,3,7</sup> and the details on the present simulation can be found in the Supporting Information.

## RESULTS AND DISCUSSION

**Time-Dependent SG–TC Study of FcDM with the Rapid Switching SI-SECM and Digital Simulation of the Resulting Data.** The external switching device working in tandem with the SI-SECM is depicted in Scheme 1. The sole function of the device is to switch both working electrodes—WE1 (tip) and WE2 (substrate)—on (step to applied potential) and off (open circuit) rapidly and with accurate control of the delay time. The delay time,  $t_{\text{delay}}$ , is the time between substrate generation and tip interrogation (see Figure S2 for details). As mentioned in our previous work,<sup>4</sup> the SI-SECM was marred by its sluggish time resolution (estimated to be hundreds of milliseconds) that is related to the time required for the bipotentiostat to turn off one of its working electrodes and turn on the other. This limited its time range for the quantitative detection of very reactive intermediates.<sup>4</sup> The device introduced in this work improves the time resolution of the SI-SECM to 12.8 ms (12.8 ms for the overall system,  $t_{\text{delay}}$  controlled with 1 μs resolution), which is much faster than that of our previous system and competitive with the lifetimes of many important reaction intermediates.

To test the time resolution of the switching device, a set of SG–TC experiments was conducted using 1.5 mM FcDM in a

2  $\mu\text{m}$  tip–substrate gap. In an experiment, the substrate electrode was poised to an oxidizing potential (0.4 V, 5 s), fully oxidizing the FcDM to FcDM<sup>+</sup> in the tip–substrate gap. Followed by this substrate generation, the substrate returned to open circuit. After a time delay (0–200 ms), the transient tip collection began by applying a reducing bias (0 V) at the tip, reducing the substrate generated FcDM<sup>+</sup> back to FcDM. Typical amperograms of the transient SG–TC experiments are displayed in Figure S7. Delay time ( $t_{\text{delay}}$ ) between SG and TC was varied (from 0 s up to 200 ms) in this set of experiments, and the decrease in the collection efficiency was monitored as a function of  $t_{\text{delay}}$  as the substrate-generated FcDM<sup>+</sup> diffused out of the tip–substrate gap. The same set of experiments was also digitally simulated using COMSOL Multiphysics (version 4.2; see Supporting Information for details). Experimental chronoamperograms of the SG–TC experiments and those obtained from COMSOL simulation are presented in Figures S3 and S4. An example fit of the experimental chronoamperogram (at  $t_{\text{delay}} = 50$  ms) to that obtained from the simulation is displayed in Figure 1. The simulated amperogram exhibited a good fit considering the existence of capacitive charging current



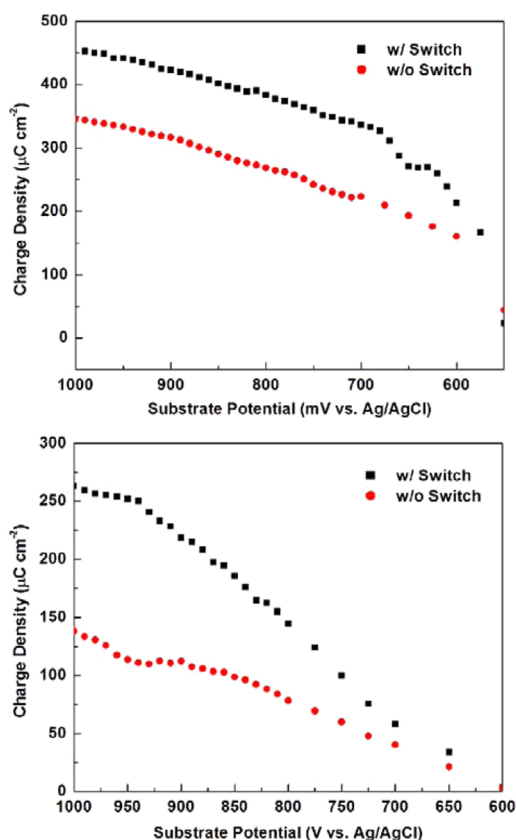
**Figure 1.** Chronoamperogram from a SG–TC experiment (experimental and COMSOL simulation) of 1.5 mM FcDM in 0.1 M phosphate-buffered water at pH 7 (tip collection current shown,  $t_{\text{delay}} = 50$  ms; top panel). The collection efficiency of the SG–TC experiments as a function of  $t_{\text{delay}}$  is displayed in the bottom panel. The experimental results revealed a good fit to that from COMSOL simulations. The diffusion profile of substrate generated FcDM<sup>+</sup> as a function of  $t_{\text{delay}}$  can be found in Figure S2.

for the real UME. The collection efficiencies of the SG–TC experiments are plotted as a function of  $t_{\text{delay}}$  in the bottom panel of Figure 1, and the experimental data exhibited good agreement to that obtained from the digital simulation. It is assuring to observe good agreement between the experiment and the simulation at small  $t_{\text{delay}}$ , which confirmed that the switching device is able to finely and accurately control  $t_{\text{delay}}$  (also confirmed by a computer-controlled feedback loop, see Figure S7). Moreover, it is encouraging to observe a collection efficiency of 100% when  $t_{\text{delay}} = 0$  ms, indicating that the switching device is capable of performing SG–TC with minimal time delay as intended in its design. Currently, the time resolution of our setup is limited by the noise filtration associated with rapid data collection (see Scheme 1), which may be improved upon by isolation of electrical and vibrational noises, suggesting that this setup should be capable of approaching ca. 1  $\mu\text{s}$  time resolution imposed by the digital I/O circuitry.

#### SI-SECM Investigation of the CoP<sub>i</sub> OER Catalyst with Improved Time Resolution.

In our recent report on the SI-SECM investigation of the CoP<sub>i</sub> OER catalyst,<sup>4</sup> we have expressed our frustrations about the less than ideal switching time of the SI-SECM. With the enhanced setup at hand, the CoP<sub>i</sub> OER catalyst has been studied by the SI-SECM once again (for experimental details, see ref 4). Identical redox mediators (FcDM<sup>+</sup> for Co<sup>III/II</sup> and Co<sup>IV/III</sup>, and IrCl<sub>6</sub><sup>2-</sup> for Co<sup>IV/III</sup>) were employed to those used in the previous work.<sup>4</sup> The surface titration experiments were performed in similar fashion to the transient SG–TC experiments explained in the previous section. Briefly, the substrate was poised to an oxidizing bias ( $E_{\text{Subs}}$  ranging from 0.5 to 1.0 V in 10 mV intervals, for 20 s) generating surface-active species of interest Co<sup>III</sup> and Co<sup>IV</sup>. The substrate returned to open circuit, and followed by a  $t_{\text{delay}}$  (0 s to 200 ms, see Figure 3), tip titration began by applying a reducing bias (0 V for FcDM and 0.4 V for IrCl<sub>6</sub><sup>3-</sup>) at the tip generating the titrant (FcDM or IrCl<sub>6</sub><sup>3-</sup>). The chronoamperograms from the titration experiments at various substrate potentials ( $E_{\text{Subs}}$ ) are presented in Figures S5 and S6. The collected amperograms were integrated and converted to charge densities at the corresponding  $E_{\text{Subs}}$  values to yield surface titration curves for the CoP<sub>i</sub> OER catalyst displayed in Figure 2. As shown in the overlay of the titration curves obtained from this work and that from our previous work<sup>4</sup> (Figure 2), it is clear that less than quantitative titration of the surface sites was accomplished in our previous report. Titration charge densities of ca. 70 and 120  $\mu\text{C}\cdot\text{cm}^{-2}$  were additionally collected through the implementation of the rapid switching device for Co<sup>III/II</sup> and Co<sup>IV/III</sup>, respectively. Moreover, a more defined plateau of charge density at the end of Co<sup>III/II</sup> titration was observed with the rapid switching device (Figure 2, top panel) at  $E_{\text{Subs}} = 640$  mV. Our previous assignments of Co<sup>III/II</sup> and Co<sup>IV/III</sup> potentials<sup>4</sup> have been anodically shifted due to the less than quantitative titrations. From our improved titration curves, the Co<sup>III/II</sup> transition occurs at  $E_{\text{Subs}}$  of ca. 650 mV, followed by the Co<sup>IV/III</sup> at  $E_{\text{Subs}}$  at ca. 700 mV. The Co<sup>IV/III</sup> potential obtained from FcDM<sup>+</sup> titration is in good agreement with that obtained from IrCl<sub>6</sub><sup>2-</sup> titration (Figure 2, bottom panel).

It was possible to measure the pseudo-first-order rate constant of Co<sup>III</sup> in its reaction with water with our previous setup.<sup>4</sup> However, the rate constant for fast-decaying Co<sup>IV</sup> was only estimated ( $>2$  s<sup>-1</sup>) and not directly measured because the previous setup did not have the necessary fine control of the

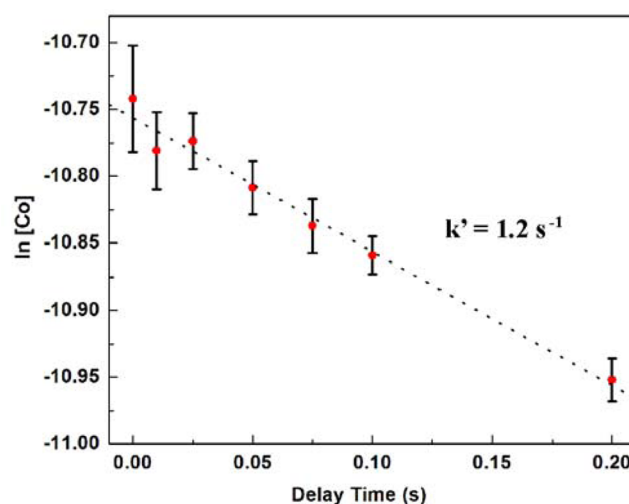


**Figure 2.** Coulometric titrations of surface redox activity of the CoPc OER catalyst are shown. The top panel displays the titration of  $\text{Co}^{\text{III/II}}$  ( $E_{\text{Subs}}$  of ca. 650 mV) and  $\text{Co}^{\text{IV/III}}$  ( $E_{\text{Subs}}$  of ca. 700 mV) by  $\text{FcDM}^+$ . The bottom panel shows  $\text{Co}^{\text{IV/III}}$  titration by  $\text{IrCl}_6^{2-}$ , with the onset of ca. 650 mV in good agreement with that observed in the titration by  $\text{FcDM}^+$ .

$t_{\text{delay}}$  in the time range of  $\text{Co}^{\text{IV}}$  reaction ( $<100$  ms). A time-dependent study of  $\text{Co}^{\text{IV}}$  reaction with water was carried out with the SI-SECM equipped with the rapid switching device. A delay time window was probed ( $0 \text{ ms} < t_{\text{delay}} < 200 \text{ ms}$ ) that was not accessible previously. For a pseudo-first-order reaction with water, the rate constant ( $k'$ ) of the reactive specie  $\text{Co}^{\text{IV}}$  is determined by the slope of the  $\ln[\text{Co}]$  versus  $t_{\text{delay}}$  plot.<sup>4</sup> From the  $\ln[\text{Co}]$  versus  $t_{\text{delay}}$  plot (Figure 3), the slope of the best-fit line was  $1.2 \pm 0.2$ , indicating that  $k'$  for  $\text{Co}^{\text{IV}}$  in its reaction with water is  $1.2 \text{ s}^{-1}$ . This  $k'$  value is similar to that estimated from our previous work ( $2 \text{ s}^{-1}$ ).<sup>4</sup> The fine and accurate control of  $t_{\text{delay}}$  enabled by the rapid switching device allowed for the direct measure of the formerly inaccessible  $k'$  of the  $\text{Co}^{\text{IV}}$ –water reaction. The rapid switch SI-SECM setup introduced here should find wide applications to other reactive catalyst surfaces or even to SG–TC of homogeneous reactive species.

## CONCLUSIONS

A considerable improvement in the time resolution of the SI-SECM was made through the introduction of the rapid switching device (Scheme 1). The ability to finely control the  $t_{\text{delay}}$  between active species generation (at substrate) and tip interrogation is powerful, because this control of the reaction window allows for the extraction of the kinetic parameters of the reaction of interest. It is imperative that the control of  $t_{\text{delay}}$  is fine and accurate compared to the lifetime of the reactive intermediate, and with our new rapid switching device ( $t_{\text{delay}}$



**Figure 3.**  $\ln[\text{Co}]$  vs  $t_{\text{delay}}$  plot. The slope of the best-fit line represents the  $k'$  of the pseudo-first-order reaction of  $\text{Co}^{\text{IV}}$  and water. A  $k'$  of  $1.19 \text{ s}^{-1}$  was obtained.

resolution of ca.  $1 \mu\text{s}$ ) we have achieved time resolution comparable or better than many reactive intermediates. The rapid switching SI-SECM was implemented in a SG–TC experiment of FcDM with small  $t_{\text{delay}}$  ( $<200$  ms) and revealed a good agreement to the results produced from digital simulations. Also, the reaction rate constant of  $\text{Co}^{\text{IV}}$  in OER, which could only be estimated previously,<sup>4</sup> was directly measured using the rapid switching SI-SECM. We expect the SI-SECM introduced in this work to find wide applications in investigating many important reaction intermediates.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b03542.

Description of the digital simulation model (COMSOL) and surface interrogation chronoamperograms (PDF)

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### Notes

The authors declare no competing financial interest.

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