Supporting Information For:

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

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Description of the digital simulation model

Digital simulations in this work were performed on COMSOL Multiphysics version 4.2. The model employed is similar to those by previous works from our laboratory.[1-3] The 2D axial symmetry geometry used for the simulations is depicted in Figure S1.

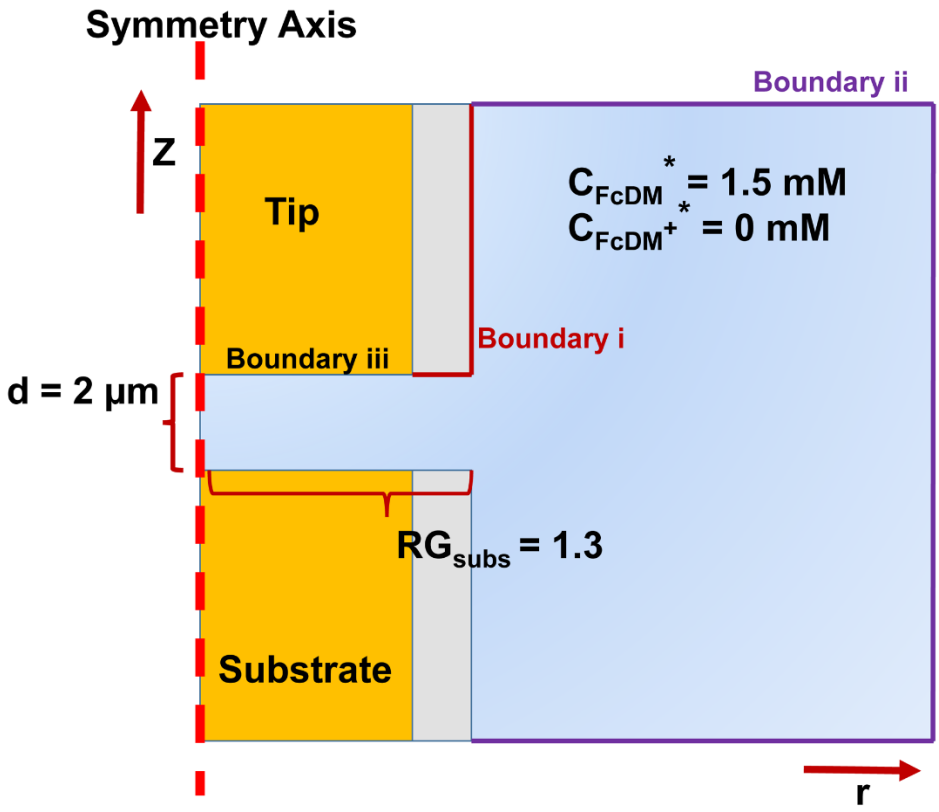

Figure S1. The 2D axial symmetry geometry used for the simulations (COMSOL version 4.2) in this work. Boundary i denotes no flux boundaries for the glass sheathes, Boundary ii denotes bulk concentration boundaries, and Boundary iii are electrode boundaries where flux occurs. Note that the figure is not to scale.

Mass transport was modeled for diffusion only according to equation S1:

$$\frac{\partial C_{FcDM^+}}{\partial t} = D_{FcDM^+}\left(\frac{\partial^2 C_{FcDM^+}}{\partial z^2} + \frac{\partial^2 C_{FcDM^+}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{FcDM^+}}{\partial r}\right)$$

No flux condition for Boundary i, bulk concentration condition for Boundary ii, and Butler-Volmer treatment for Boundary iii were employed similar to that used in our previous publications.[1-3]

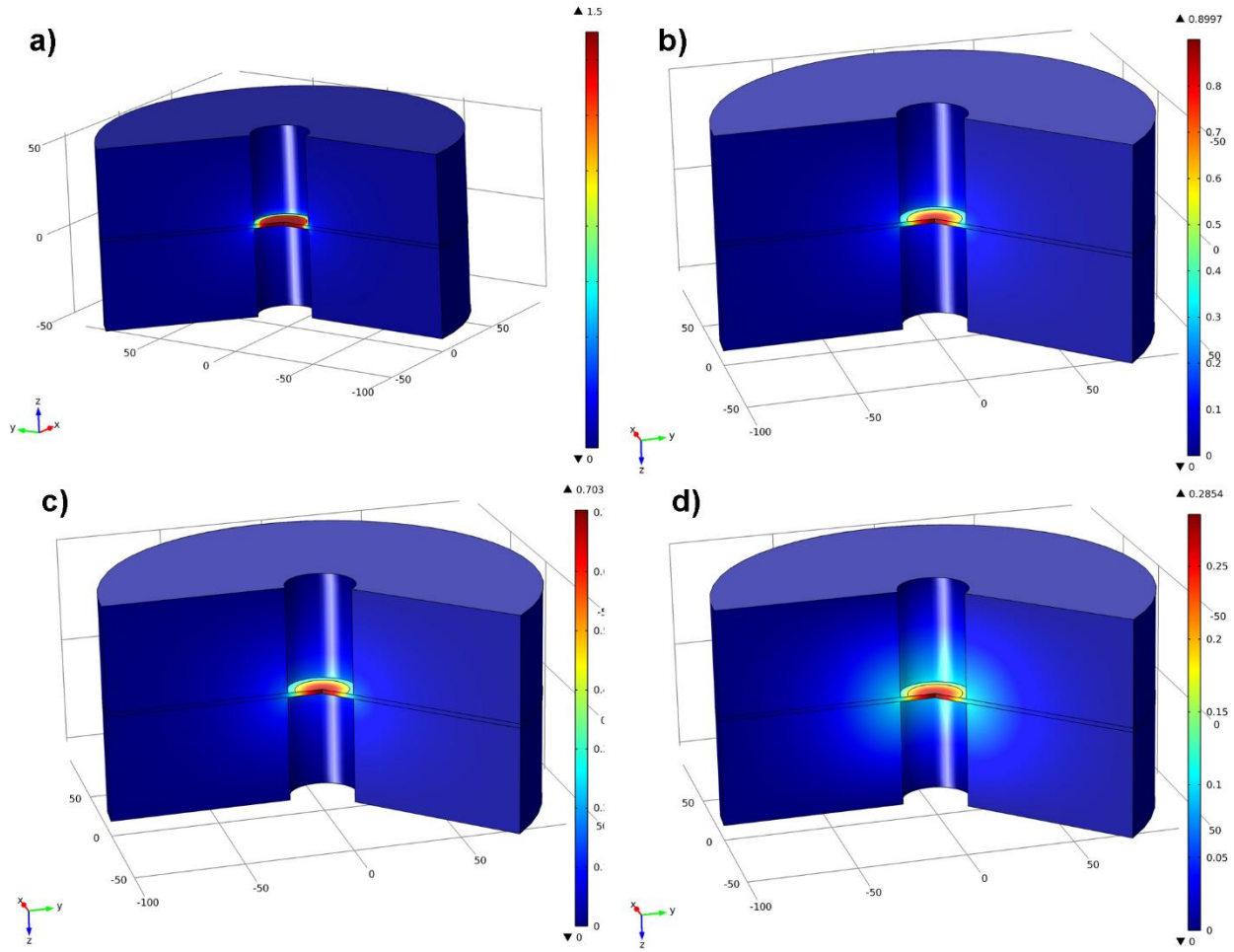

Figure S2. Diffusion of the substrate generated $FcDM^+$ out of the tip-substrate gap as a function of t_{delay} in 3D (0 ms – a, 75 ms – b, 100 ms – c, and 200 ms – d). Figure generated in COMSOL Multiphysics version 4.2.

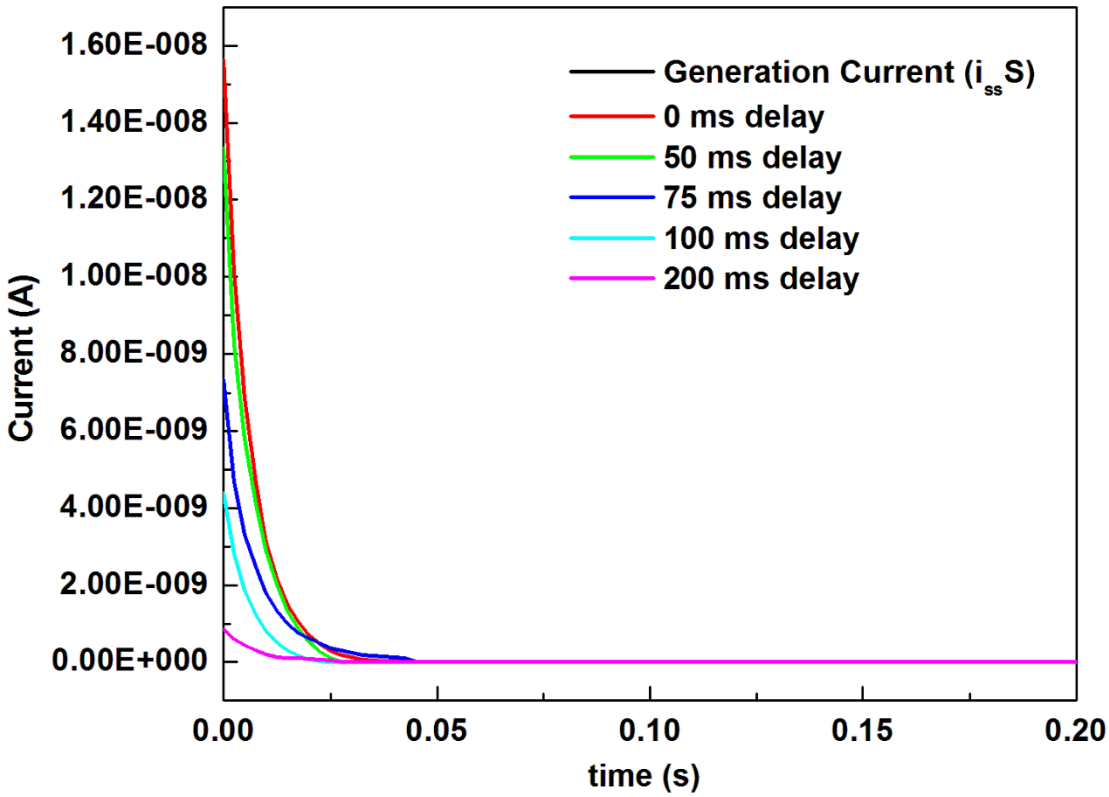

Figure S3. COMSOL simulated chronoamperograms of FcDM SG-TC experiments. Chronoamperogram of the generation experiment is displayed after subtraction of the steady-state current. A complete electrolysis of the tip-substrate gap occurs, and a superposition of the generation chronoamperogram and that of the 0 ms t_{delay} collection is noticeable.

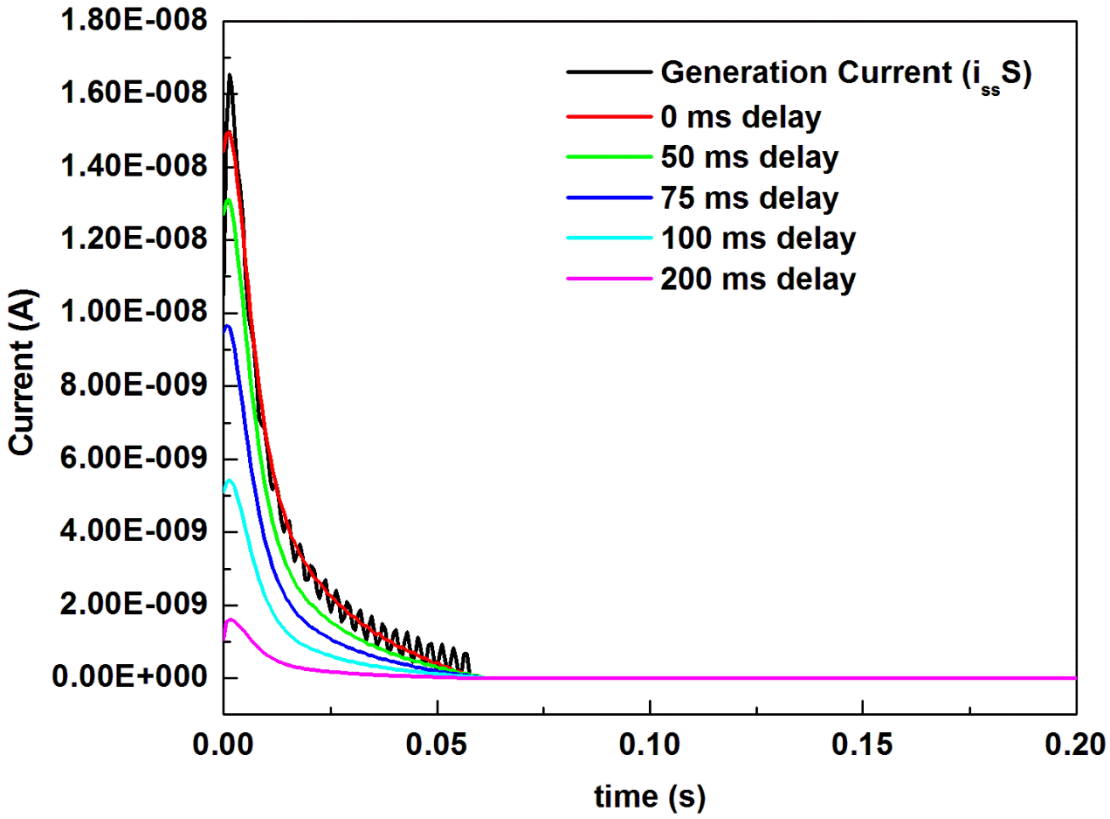

Figure S4. Experimental chronoamperograms of FcDM SG-TC experiments at various t_{delay} are plotted. Chronoamperogram of the generation experiment is displayed after subtraction of the steady-state current. Periodic noise in the generation chronoamperogram is due to the use of frequency filter smoothing out the noise in the collection currents. A good overlay of the generation chronoamperogram and that of the t_{delay} 0 ms collection is reassuring that our switching device handles the switching action with minimal delay. Small currents (< 50 pA) were treated as zero currents for ease of integration purposes.

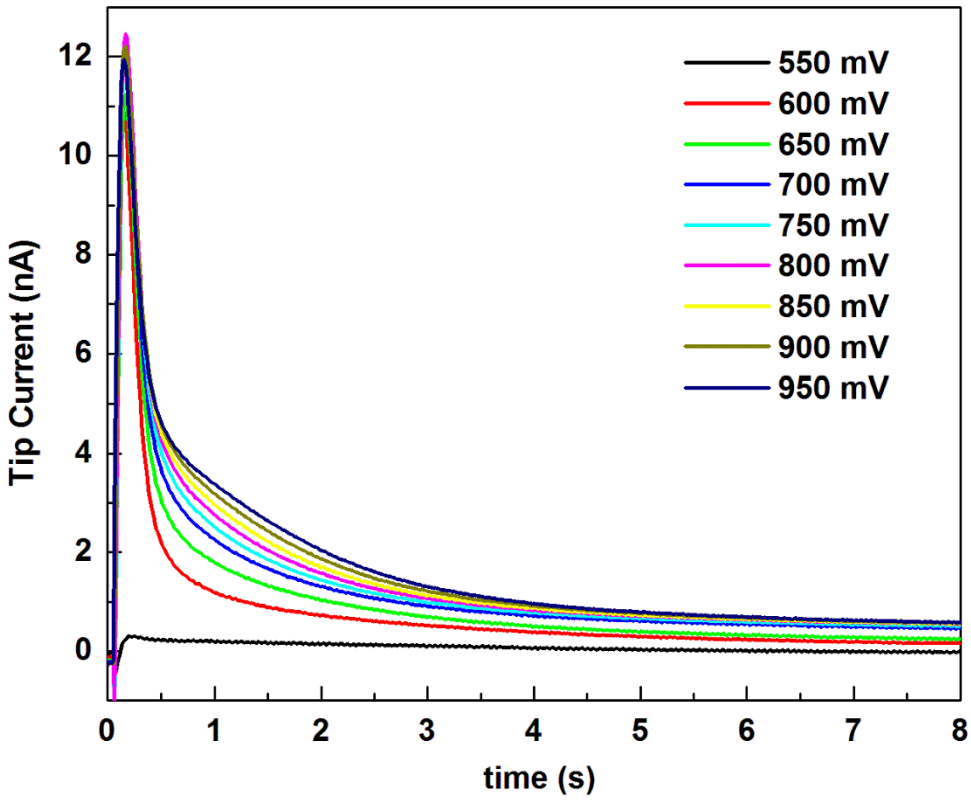

Figure S5. Surface interrogation chronoamperograms of CoP_i OER catalyst at various substrate potentials (inset legend) using $FcDM^+$ as the redox mediator.

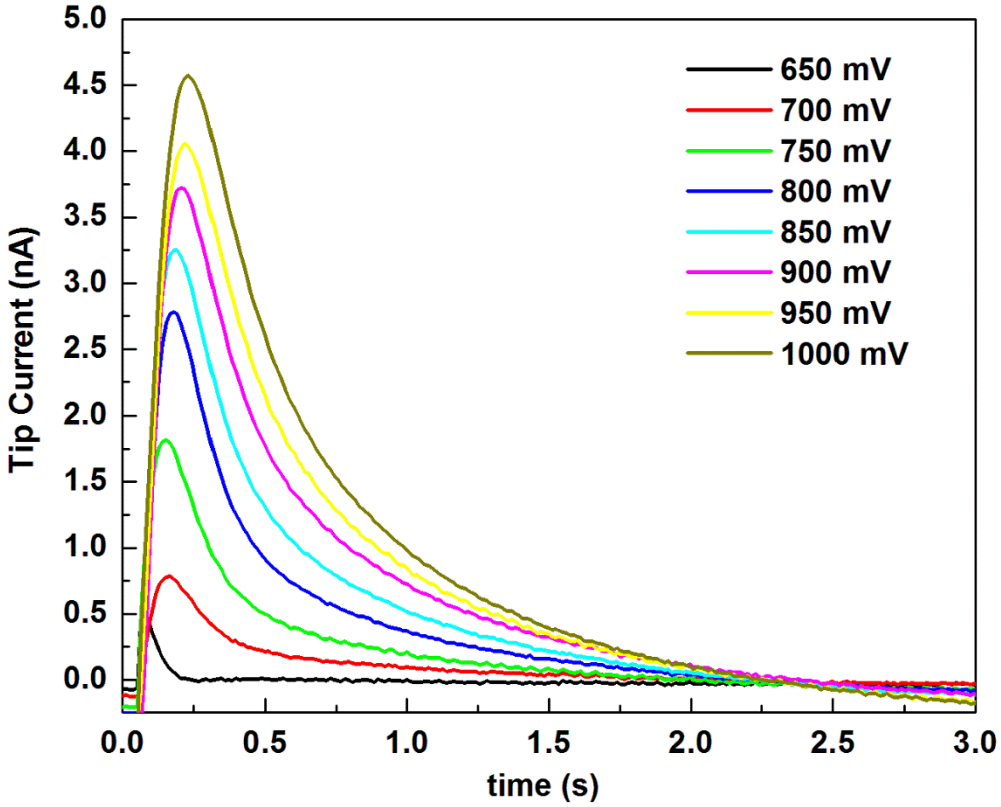

Figure S6. Surface interrogation chronoamperograms of CoP_i OER catalyst at various substrate potentials (inset legend) using $IrCl_6^{2-}$ as the redox mediator.

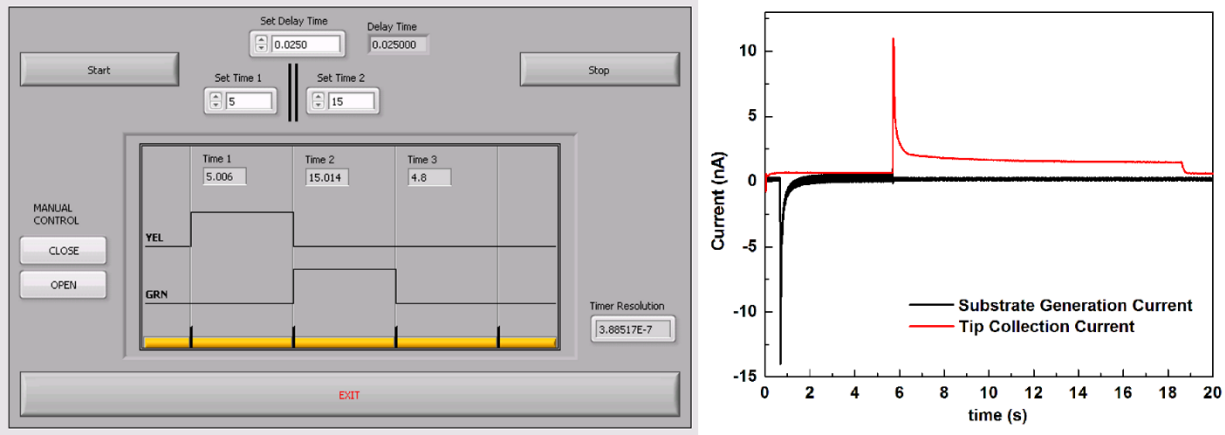

Figure S7. The LabView control panel used for the rapid switching device (left panel). Delay time resolution is measured by checking the computer clock before and after the signal operation (displayed in the bottom right corner). Sub 400 ns resolution is routinely recorded. A typical experimental amperogram is shown in the right panel.

References

1. Rodríguez-López, J.; Alpuche-Avilés, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 16985-16995.
2. Rodríguez-López, J.; Minguzzi, A.; Bard, A. J. *J. Phys. Chem. C* **2010**, *114*, 18645-18655.
3. Arroyo-Curras, N.; Bard, A. J. *J. Phys. Chem. C* **2015**, *119*, 8147-8154.