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Collisions or Adsorption: An Electrochemical Random Walk Decides

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Collisions or Adsorption: An Electrochemical Random Walk Decides

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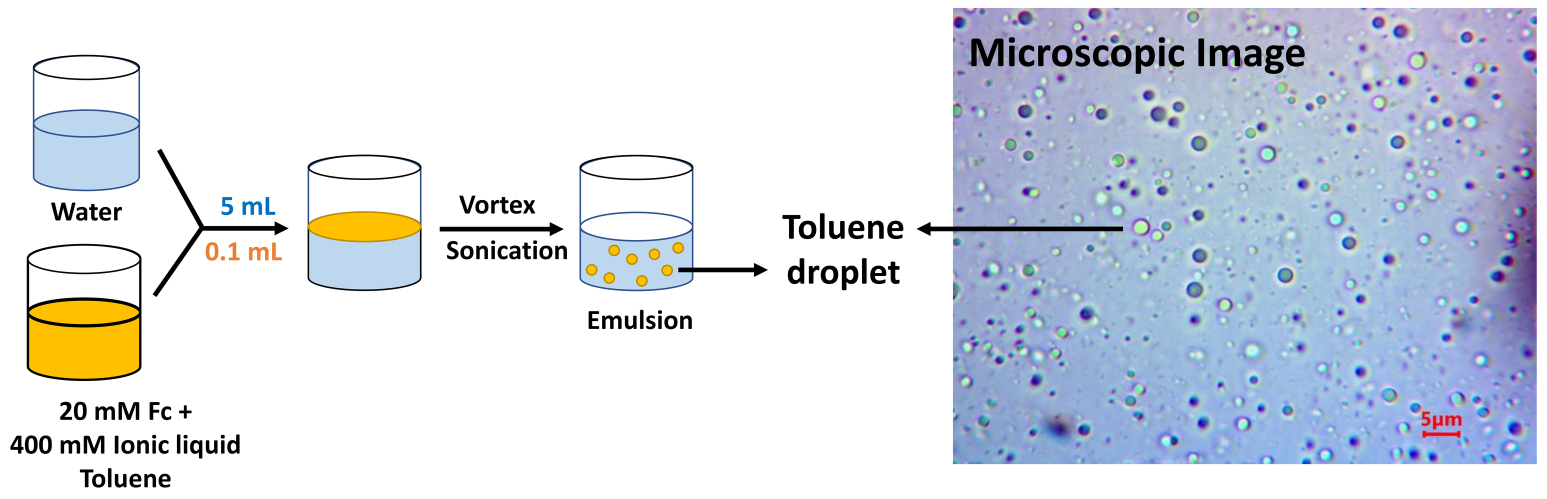
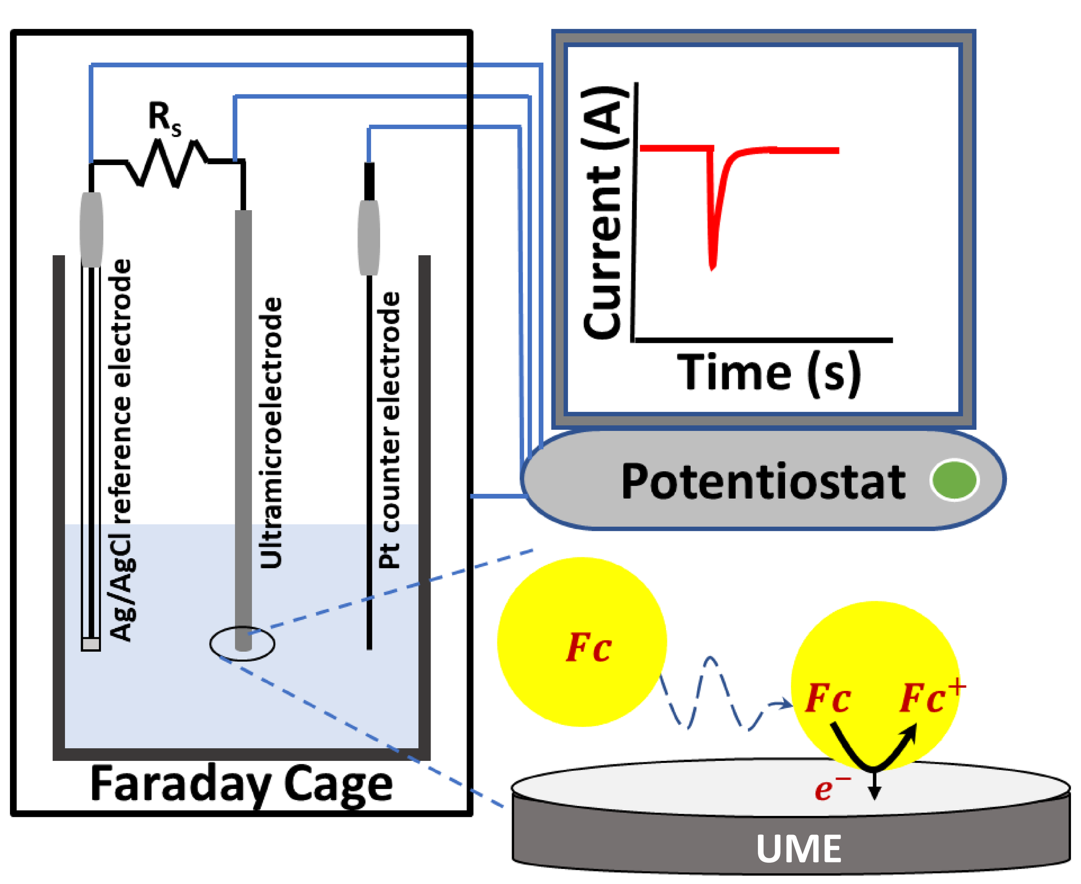
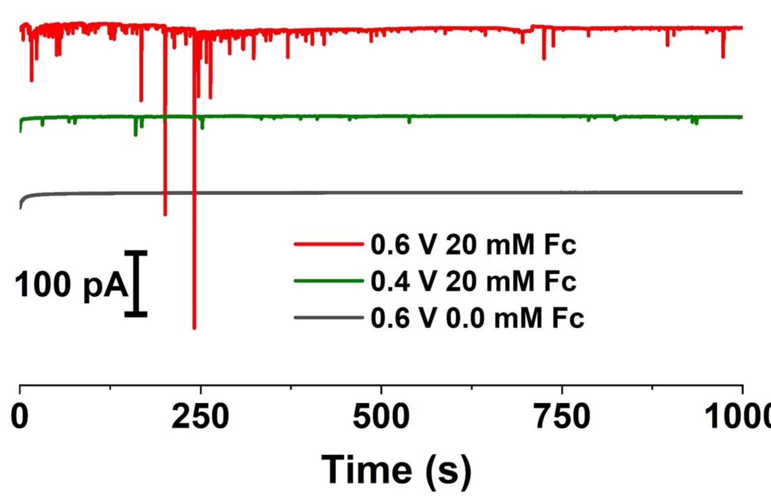
Single-Entity Electrochemistry (SEE) is an approach that interrogates one entity at a time, be that a cell, a nanoparticle, or a single molecule.[1-2] This is achieved by measuring the change in electrochemical current or potential (SEE-signal) from entity collisions or adsorption using an electrode of similar dimensions.[1] The magnitude and shape of SEE signals depend on the underlying mechanism of the particle with the electrode surface.[3-4] Herein we report a comprehensive investigation combining experiments with an electrochemical random walk simulation to elucidate the electrochemical response of single emulsion droplet on ultramicroelectrode (UME). For instance, we show that for a 1 µm-droplet containing 20 mM ferrocene (Fc) and 1.01 pC charge, one adsorption event transfers 99% of charge during ~0.6 s, while multiple elastic collisions only deliver 0.58% in ~0.7 s. This observation ratifies another aspect of reactivity for SEE including molecules, whereby the current signal of redox active entities that attach irreversibly to an electrode, is not limited by electrode collision frequency but rather the probability of adsorption per collision. These results point to a heightened sensitivity and speed when relying on adsorption instead of elastic collisions for sensing applications.

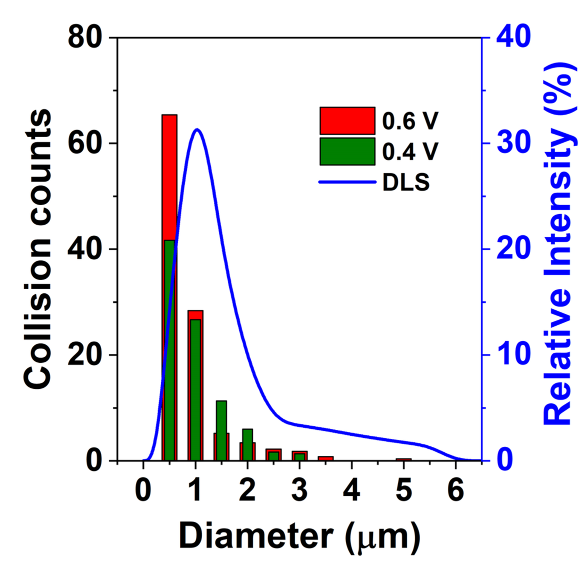
Emulsion model system

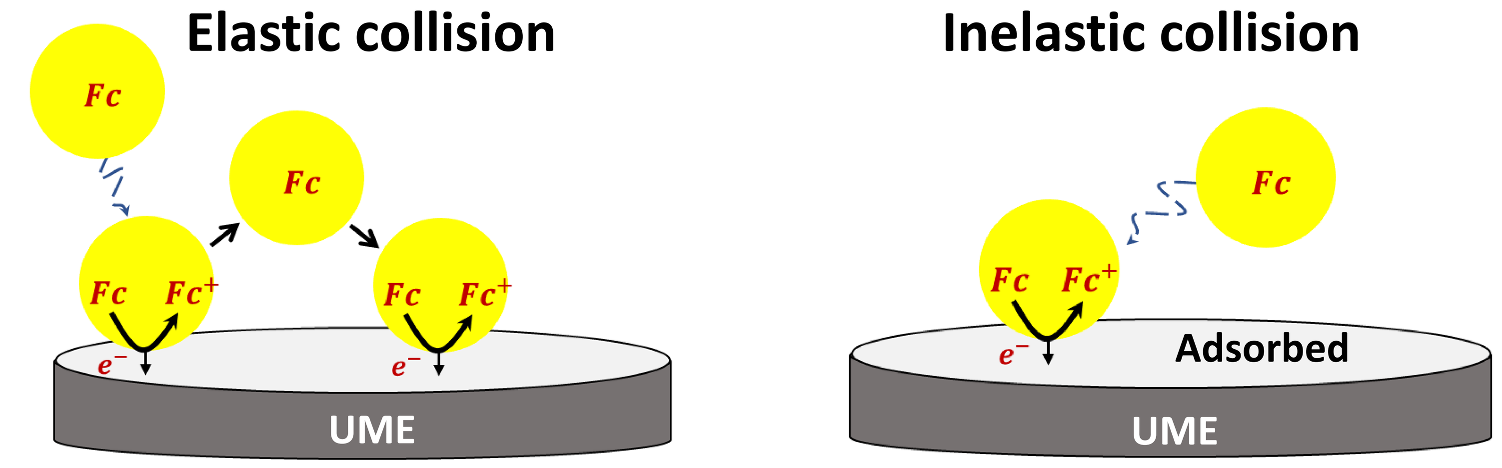


SEE of model emulsion system

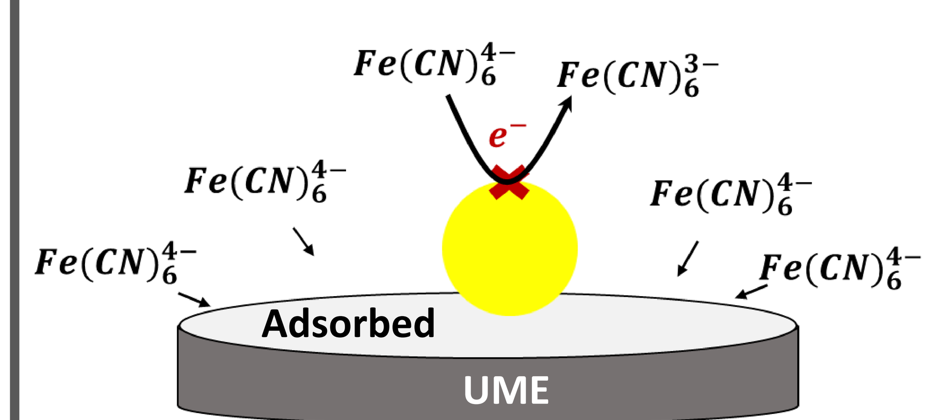


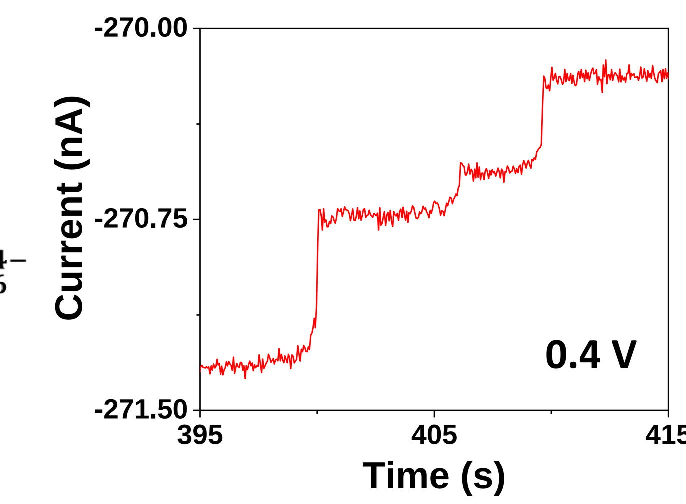




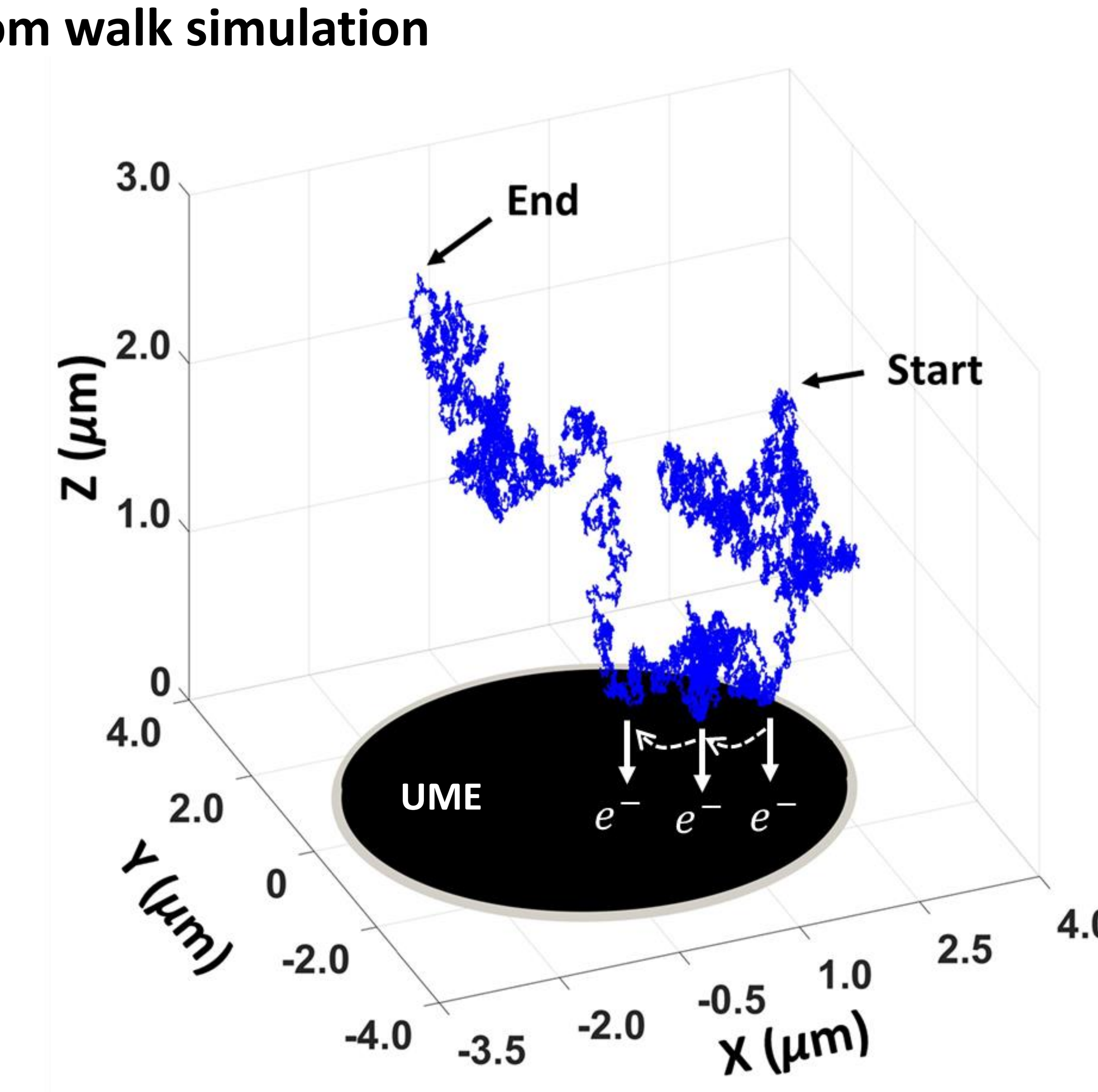


Electrode blocking experiment

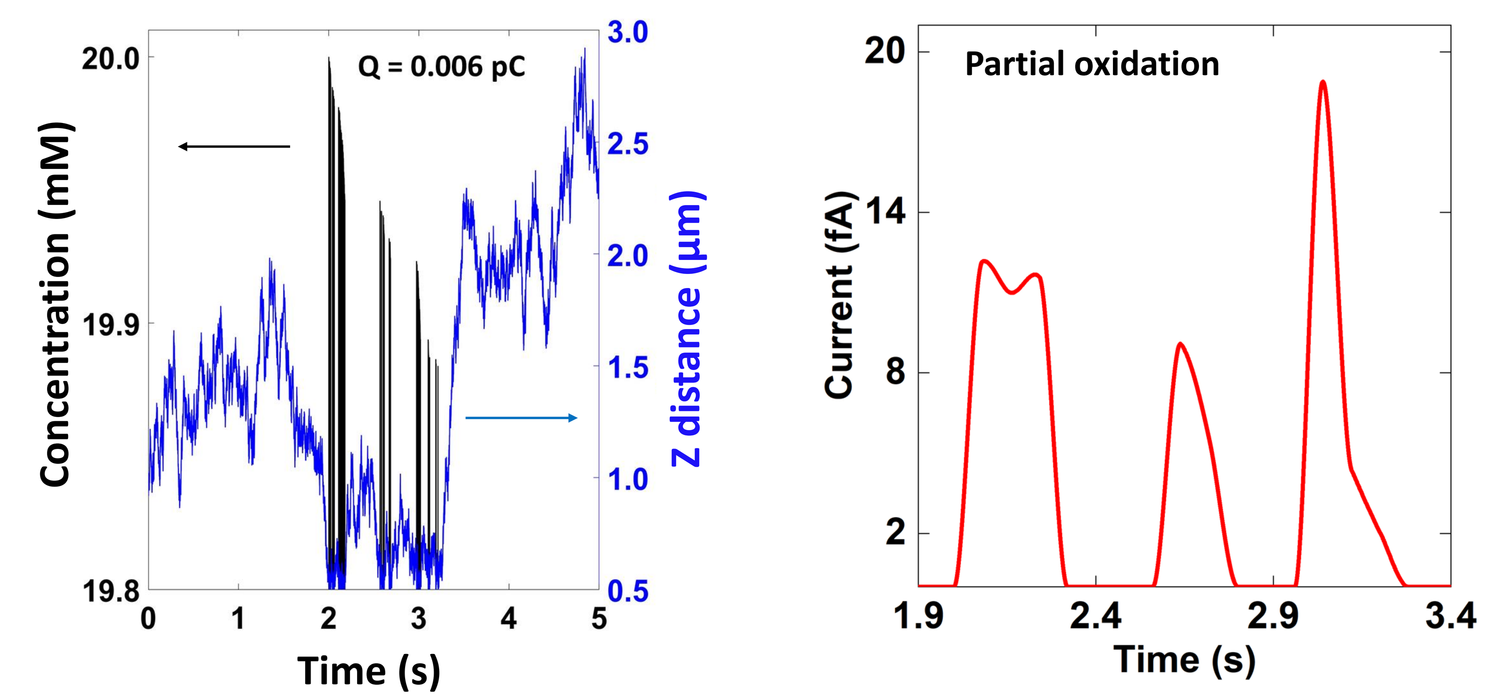




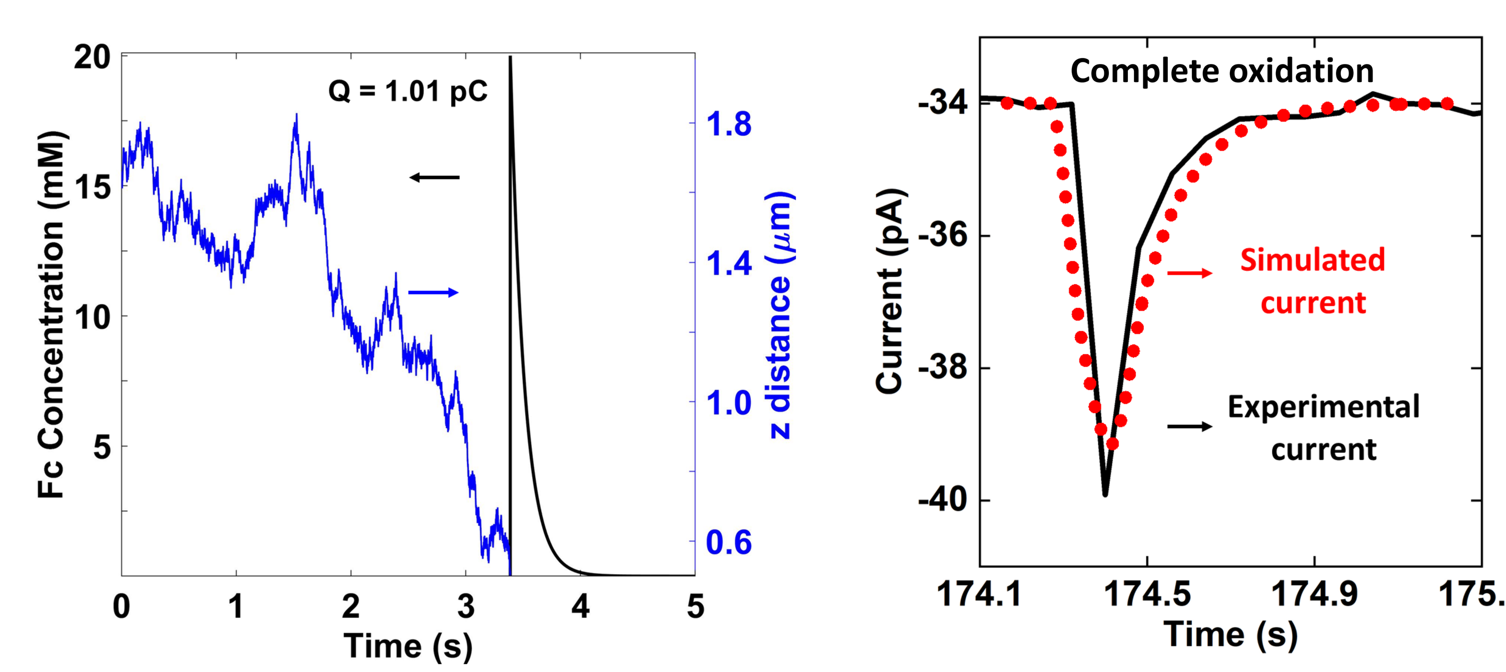
Random walk simulation



Inefficient electrolysis (Elastic collision)



Efficient electrolysis (Adsorption)



Conclusion and Future Work:

- Electrochemical current peaks observed in $i - t$ recordings, come from single adsorption events instead of diffusional collisions.
- Adsorption and collision are both driven by diffusion, but the former is an amplification of the latter.
- One adsorption event delivers the same amount of charge as ~5.5 million collisions.
- Adsorption is expected to be advantageous against elastic diffusional collisions.
- Develop an adsorption probabilistic model based on a finite number of adsorption sites
- Determine the effect of simultaneous occurrence of adsorption events on the SEE-signal.
- Determine the metabolic oxidase-reductase pathway of bacterial cells using SEE.

Reference:

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