UNIVERSITY OF RHODE ISLAND
Department of Chemistry Ph.D. Seminar

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"Advanced Nanoelectrochemistry at Liquid-Liquid Interfaces: From Fundamental Understanding to Practical Applications"

HOST

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Advanced Nanoelectrochemistry at Liquid-Liquid Interfaces: From Fundamental Understanding to Practical Applications

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Herein, we study advanced nanoelectrochemistry focused on interfacial transport of redox-inactive drug ions and CO_3^{2-} at a nanopipet-supported liquid-liquid interface between two immiscible electrolytes (ITIES) to understand bacterial drug resistance and electron-transport efficiency in metal-reducing bacteria, respectively. Cyclic voltammetry and theoretical analysis revealed that drug (quinolones and sulfonamides) ion transfers (ITs) are three orders of magnitude slower than lipophilic tetrabutylammonium IT. Under mechanistic consideration of water-finger formation near the interface, the stronger interaction of water-finger with localized negative charges on carboxylate or amide groups leads to more retarded interfacial ITs, thereby causing the higher effective hydrophilicity of drug-ions during interfacial ITs. This physicochemical insight of drug permeability and its relationship with drug structures as well as a nanopipet-probe combined with nanoscale scanning electrochemical microscopy (nanoSECM) is further served to quantitatively assess bacterial drug resistance in real time at the single-cell level, where drug permeability and accumulation in live *Escherichia coli* cells are monitored *in situ*.

Additionally, we investigate governing factors in facilitated ITs at the nanoscale interface and develop nanoscale ion-selective amperometric probes using broadly available “Simon” type ionophores. Specifically, in CO_3^{2-} ITs as a model system, three key factors were experimentally and theoretically studied: (i) nanoscale cleanness at the interface, (ii) peculiar solubility of lipophilic ionophores and their ion complexes in the organic phase, and (iii) the kinetic analysis of IT with the mechanistic consideration including water-finger formation. This fundamental understanding was verified by quantifying CO_3^{2-} produced by metal-reducing bacteria, *Shewanella oneidensis*, via organic fuel oxidation. Further, this ion selective nanoscale probe combined with nanoSECM is employed to quantify how fast organic fuels are consumed and CO_3^{2-} are produced by bacteria, thus enabling to monitor the efficiency of bacteria in microbial fuel cells.