A Less-Explored Surface Property: The Electrical Double Layer and Its Molecular Interrogation Capability

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layer (EDL) forms Introduction. Electrical double spontaneously through thermodynamic interaction between electrons and ions at a solid-liquid interface (SLI). A close examination of the literature reveals that in the classical EDL theories^[1] the ionic species were assumed to follow Boltzmann distributions with no electron transfer across the SLI. In our previous works^[2-3], we reexamined the problem by considering the ionic and molecular interactions within the compact and diffuse layers along with an electrochemical process under the governing principles of the Poisson, Nernst-Plank and Butler-Volmer equations. We, on the one hand, confirmed that the ionic concentration did follow a Boltzmann distribution only when the net current across the SLI is zero, and on the other hand, expanded the dealing of ions and molecules inside the EDL without assuming zero electron transfer. One importance implication of this is that it allows us to use either a charging or Faraday current to perturb the thermodynamic equilibrium state of the EDL. In this study we push further to perturb the EDL for molecular interrogation at a surface inside a nanopore.

Materials and Methods. As previously reported^[4] a nanopore with a diameter of 2 nm was formed in a supporting layer of silicon nitride (50 nm thick) and a conducting layer of gold (5 nm thick). An aqueous supporting electrolyte (typically NaF) was driven through the nanopore under an applied electric field. The metal layer was charged with a small, constant, electrical current (37.4 \pm 3.2 pA) and the charging potential was measured as the baseline EDL potential. When the solution also contained analyte molecules, the translocation of individual analyte molecules will cause transient changes in both the ionic current and EDL potential. The magnitude of the steady-state current and potential were measured with respect to the baselines.

Results and Discussion. Fig.1 shows how ionic/molecular interrogation at an EDL works. When a circular flat-gold-disc electrode (d =1.6 mm) is exposed to 0.5 M H₂SO₄ solution, we measured the capacitance (CP) curve rather than the traditional cyclic voltammograms (CV curve). In the CP curve the captured characteristic features include: 1) reorientation of water molecules at the Au surface in an acidic solution at -0.14 V; 2) the potential of zero charge (PZC) of the Au surface at ~0.24 V; 3) the onset of *adsorption* of sulfate and bisulfate ions to the Au surface at ~ 0.54 V; 4) the hydronium (H₃O⁺) assisted lattice formation of sulfate ions at ~0.85 V.



C Au oxidation region

These features show the remarkable sensitivity of the EDL effect in revealing ionic and molecular events occurring at a surface.

To demonstrate the analytical capabilities of this EDL interrogation method, the changing properties of Cerium Oxide nanoparticles (2-3 nm radius) under a redox environment (by exposing the nanoparticles either to NH4OH or H2O2) were characterized utilizing the nanopore setup. The measured EDL potential signals for Cerium Oxide nanoparticles were shown in Fig.2, where the EDL potential increases with the addition of H2O2 and quickly reach a maximum level, while the addition of NH4OH results in a decrease in signal magnitude to a minimum level. The change in the EDL signal reflects a change in the radius of the nanoparticles owing to possible formation of ceriaperoxo complexes on the particle surface. Alternatively, an increase in particle size can be the result of partial reduction of Ce^{4+} to Ce^{3+} . The latter ions possess substantially higher ionic radius, which affects lattice parameter of the compound, leading to the particle size increase.



Fig.2 – EDL potential signal from Cerium Oxide nanoparticle in various concentrations of either ammonium hydroxide (NH₄OH) or hydrogen peroxide (H₂O₂).

Conclusions. Exploiting the interfacial EDL structure as an analytical means to interrogate ionic and molecular properties is a groundbreaking shift in paradigm for molecular interrogation. In demonstrating the functionality of this new method, subtle changes in Cerium Oxide nanoparticles due to exposure to different redox environment was captured. This direct molecular interrogation using a simple EDL nanopore device will be a clear departure from the conventional bioanalytic techniques. Because intermediate molecules will be unnecessary, interaction between analyte targets and electrode surfaces can be dynamic and reversible as well as static and irreversible, and the sensing surface will be rugged with long functionality and shelf life.

References.

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