

Engineering an electrochemical sensor for the characterization of bond vibration frequencies of a chemical analyte.

Chaitanya Gupta¹, Shuai Chang¹
and
Roger T. Howe^{1*}

¹Department of Electrical Engineering, Stanford University,
Stanford, CA 94305, USA

E-mail: rhowe@stanford.edu

Traditional electrochemical interfaces are comprised of an electrically biased electrode-electrolyte interface, where charge exchange occurs between electronic energy levels of the electrode and a redox-active ion in the electrolyte. Coupling between electrical transport phenomena and the chemistry at such electrochemical interfaces yields a unique platform, capable of electrical transduction of molecular-scale chemical information.¹ Molecular species at the electrode-electrolyte interface can affect the charge transfer process either through direct electronic coupling with the electrode phase, or through indirect coupling via Coulombic interactions with the tunneling electrons that are exchanged between the electrode and electrolyte phases of the electrochemical interface.² The observables of current, voltage and charge, as measured in a typical charge transfer experiment, present an ensemble-averaged description of the individual interactions determining the overall charge transfer phenomenon. The ensemble averaged nature of the measurements in most electrochemical sensing systems limits the applicability of the sensing systems to the detection of redox-active molecules that directly couple electronically with the metal electrode and exhibit electronic resonances within the working voltage range for aqueous electrolytes. Consequently, much of the recent progress in electrochemical sensing technology has focused on enhancing the detection limit of such sensing platforms.³ However, much of the molecular-level chemical information describing the non-redox active species that may also be present in the electrolyte, which is encoded in the acquired current/voltage signal, is lost as background information. The loss of information makes the discrimination of these non-redox active analytes difficult, narrowing the scope of investigation for the electrochemical-charge-transfer-process-based sensing platforms. A platform capable of characterizing molecular species that couple weakly to the metal electrode itself, but which interact electrostatically with the charge being exchanged between electrode and redox-active species in the electrolyte would greatly enhance the utility of the electrochemical charge transfer process as an information transduction mechanism.

In this paper, a design methodology is proposed for electrochemical interfaces that are engineered specifically to transduce information about the intra-molecular bond vibrational frequencies of non-redox active molecular analytes. A quantum statistical model of a generalized charge transfer process, developed by the authors, will be presented as the underpinning for the design method. Minimization of electronic and nuclear entropy will be derived from the presented model, as the necessary condition required for resolving vibrational frequency information, and we will also describe select experimental strategies that may be implemented for total entropy minimization. The discussed experimental strategies will

describe the design principles guiding the fabrication of the physical sensing front-end as well as the engineering of the instrumentation required for applying signals to the interface and for acquisition of the data containing the vibrational mode information.

¹ Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed., John Wiley.

² Nitzan, A. *Chemical Dynamics in Condensed Phases*, 1st Ed., Oxford University Press.

³ Bakker, E. *Anal. Chem.*, **2004**, 76, 3285