Probing the Three Phase Interface to Understand Electrochemical Screening of Gas Phase Pollutants

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This investigation aims to address critical barriers impeding the advancement of electrochemical detection of gas phase pollutants such as NO, CO_2, etc. Electrochemical sensing holds a great promise in the control of greenhouse gas accumulation in the atmosphere by providing portable, low cost, selective, sensitive, rapid and compact screening solutions. Current issues that plague electrochemical sensing are inadequate sensitivity, inferior selectivity or discrimination, low limits of detection and sluggish response time. These issues stem from cross-contamination, modified reaction rates due to co-existence of multiples analytes, and surface poisoning [1].

The hypothesis of this investigation is that the challenges faced by electrochemical sensing modality can be solved by a systematic and molecular level understanding of the kinetics and dynamics of the three phase interface (electrode/electrolyte/gas) subjected to varying analytes and their concentration. A non-Nernstian, mixed potential type electrochemical gas sensor is chosen as the model to test the research hypothesis [2-4]. The choice of mixed potential sensor is due to its simple transduction principle, uncomplicated sensor configuration, the availability of theoretical and experimental description of the sensor behavior. Mixed potential sensors rely on the fact that two dissimilar electrodes along with an oxygen-ion-conducting electrolyte (figure 1) exhibit different non-equilibrium potentials in the presence of a reducing/oxidizing gas and oxygen at high temperature. The operating temperature and the three phase interface significantly govern the sensor response.

Atmospheric pollutants such as NO, CO_2 , etc are non-equilibrium gas mixtures which show the tendency to reach thermodynamic equilibrium depending on temperature, time of residence and catalytic reactions. In addition, elementary steps in gas phase reactions as a function of temperature, their kinetics and electrode-gas interactions affect the stability, selectivity and response time of sensors. For example, if a sensor shows a fast response to concentration changes of the measured analyte, the cross sensitivity to other gases tends to be lower and the signal stability higher. Hence, in order to optimize the sensors to achieve the desired performance specifications, the sensor mechanism needs to be studied in detail, i.e. the nature of the intermediate species and the rate-determining steps in gas-solid interaction. An earlier investigation [5] revealed NO_2 inhibition of the catalytic reaction of NO and O_2 over Pt leading to diminished sensitivity to NO and cross-sensitivity to other analytes. The rate inhibition by NO_2 was attributed to the fact that NO_2 adsorbs preferentially on the surface because of its high sticking coefficient on Pt, keeping it oxidized and preventing adsorption of other species.

The **core tasks** specific to this proposal are to (a) theoretically understand the thermal decomposition of analytes, (b) heterogeneous catalysis studies at the three phase interface, and (c) derive a reaction mechanism and kinetic model explaining cross-sensitivity and surface poisoning, etc.
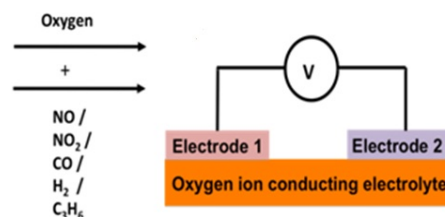
Figure 1. Mixed Potential based Electrochemical Sensor Model to Test Hypothesis

For screening different air pollutants using mixed potential based sensors, the knowledge about their thermal decomposition mechanisms, interaction with interfering analytes and resultant products are critical as they guide systematic predictions about unknown molecules and guide the design of next generation of detectors. Quantum chemistry computation can be used to elucidate decomposition pathways of analytes and their interaction with interfering substance such as water vapor. In this task, quantum chemical calculations using the B3LYP hybrid density functional [6] will be performed on each of the species (of diverse chemistry) in the reaction scheme. Calculated molecular parameters, such as vibrational spectra and moments of inertia, are then used to calculate free energies, which can then be converted into rate constants for each reaction channel using transition state theory (TST) and Rice-Ramsperger-Kassel-Marcus (RRKM) theory [7].

In this heterogeneous catalysis study, the analytes of different concentrations will be passed over catalytic electrode and electrolyte materials. The resulting product after catalysis will be analyzed either using mass spectroscopy or gas chromatography. The formation of intermediate species and the chemical state of the catalyst materials will be evaluated using X-ray Photoelectron Spectroscopy and UV Photoelectron Spectroscopy. The experiments will be repeated for different temperatures. The analytes of interest are NO, CO_2, CH_4, water vapor, CO, C_3H_6 , NH_3 and other common interferents. The electrode materials of interest are strontium doped lanthanum chromite, Pt, Au, lanthanum manganite, and nickel oxide. Yttria-Stabilized Zirconia will be used as the electrolyte. Alumina will be of interest as a packaging material. For the one year project, the analytes for investigation will be limited to NO, CO and NH_3. The electrode material for investigation will be limited to strontium doped lanthanum chromite and YSZ as electrolyte.

References

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