Title
Micromachined Amperometric Nitrate Sensor

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Introduction: Need for A Micromachined Amperometric Nitrate Sensor

- **Why nitrate sensor is important?**
  - ***In-situ Nitrate-contamination monitoring* in surface and ground water**
  - **Environmental science research**
    ex) Contaminant source zone assessment
    Moisture and nutrient distribution in heterogeneous desert soil
- **Sensor requirements**
  - Small size, stand-alone and remote operation , low detection limit (<10 μM)
- **Current methods to detect nitrate ions (spectroscopy, chromatography, electrophoresis) require complex sample preparation and typically large equipment**
- **Electrochemical sensor is relatively simple and easy to miniaturize**
  - ***Potentiometric sensor*** (ex. pH electrode)
    $E_m = \text{const.} + 0.059 \ln[H^+]$ (V)
  - ***Amperometric sensor*** (ex. oxygen sensor)
    $O_2 + 2H_2O + 4e^- = 4OH^-$
    $i_m = 4FAk_m[O_2]$ (A)
- **Advantage of an amperometric sensor**
  Lower detection limit and sensitivity

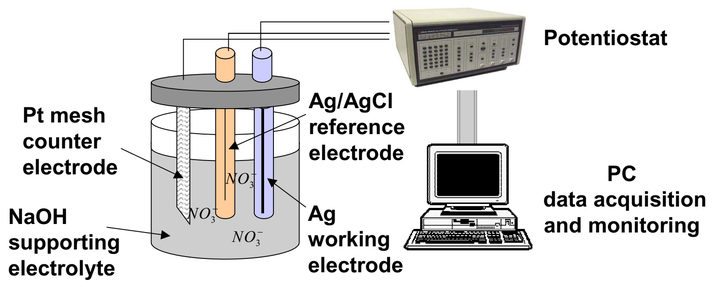
Problem Description: Design a miniaturizable electrochemical sensor

- **Selecting a electrochemical cell suitable for nitrate detection**
  - Select working electrode, counter electrode, reference electrode, and supporting electrolyte
  - Common electrodes (Pt, Au, C, etc.) are not sensitive to nitrate species
  - Hydrogen evolution in acidic electrolytes interferes with nitrate reduction
  - Cyclic voltammetry is used to compare electrodes and electrolytes
- **Removing oxygen interference**
  - Oxygen dissolved in aqueous electrolyte (≅ 0.26 mM) interferes with the nitrate detection and increases the minimum detection limit
  - Purging oxygen by nitrogen gas is not applicable for micromachined nitrate sensors deployed in the field
- **Applying chronocoulometry**
  - Measure charge equivalent to the amount of nitrate reduced
  - Can be used to remove oxygen before measure nitrate
  - Current integration reduces noise

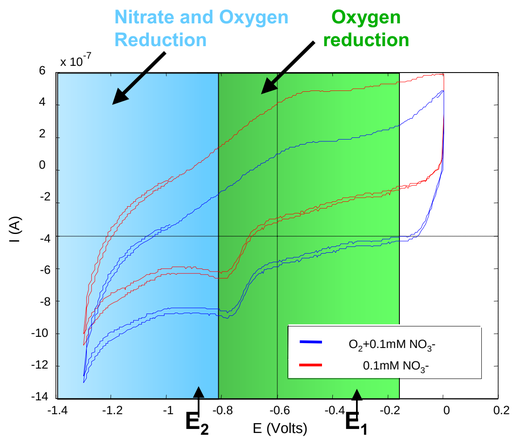
Proposed Solution:

Proposed Electrochemical Cell

- **Selected cell**
  - Ag working electrode (high sensitivity to nitrate ion)
  - Pt mesh counter electrode
  - Ag / AgCl reference electrode
  - NaOH supporting electrolyte (avoids hydrogen evolution)
- **Linear calibration curve (10 μM ~ 100 mM)**
  - The proposed cell is feasible for sensitive nitrate detection



Removal of Oxygen Interference



Cyclic voltamogram of nitrate with and without dissolved oxygen (0.01M NaOH, v=50mV/s, 0.1mM NO_3^-)

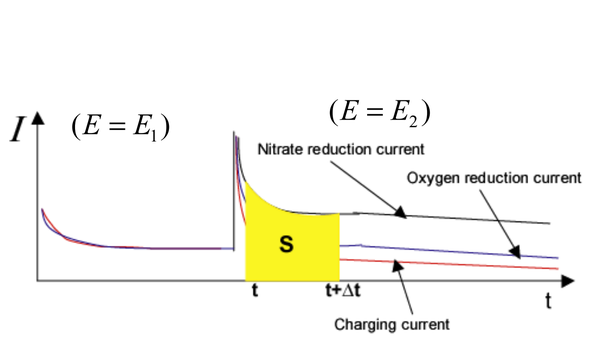
- **A simple and effective differential approach**
  - Oxygen is reduced at potentials ≤ E_1
  - Nitrate is reduced at potentials ≤ E_2
  - Since $E_2 < E_1$, both oxygen and nitrate are reduced at E_2
  - Nitrate reduction current = (nitrate + oxygen reduction current at E_2) – (oxygen reduction current at E_1)

Application of Chronocoulometry

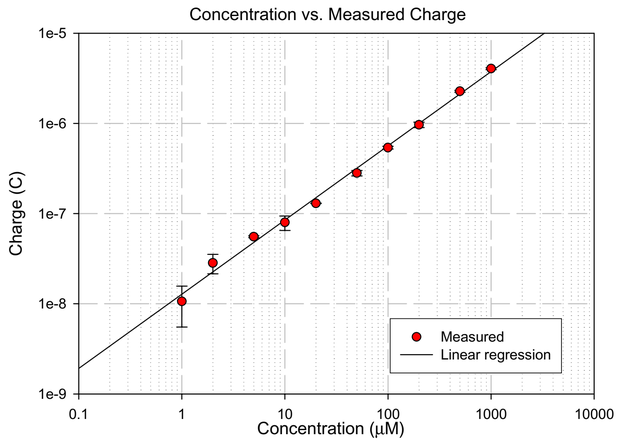
- **Measure charge *S*(Δt, t) (integration of the transient current response) instead of mere current when a potential step ($E_1 \rightarrow E_2$) is applied**

$$S(t,\Delta t) = \frac{2nFAC_o^* D_o^{1/2}(\sqrt{t+\Delta t} - \sqrt{t})}{\pi^{1/2}} + C_d(E_{s2} - E_{s1})e^{-t/\tau}(1 - e^{-\Delta t/\tau})$$

- ***S*(Δt, t) is not only proportional to nitrate concentration but also exponentially-decaying double-layer-charging current**
- **High sensitivity and low detection limit can be achieved by minimizing charging current and maximizing nitrate current with numerical optimization of *S*(Δt, t)**
- **Linear relationship between the nitrate concentration and *S*(Δt, t)**

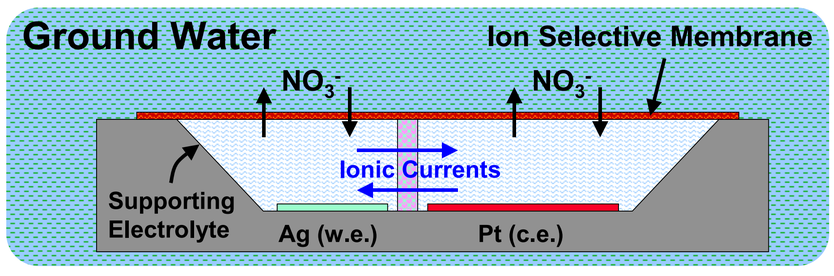


Double-layer-charging current and nitrate reduction current when a potential step is applied



Calibration curves. Experimental condition is 0.01M NaOH, Δt = 1 sec , t = 0.021 sec

Proposed Micromachined Nitrate Sensor



- **Microfabrication**
- **Semi-permeable ion-selective membrane**
  - Allows nitrate ions to diffuse into a micromachined electrochemical cell selectively