



Ph.D Qualifying Exam

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The Paper to be Discussed

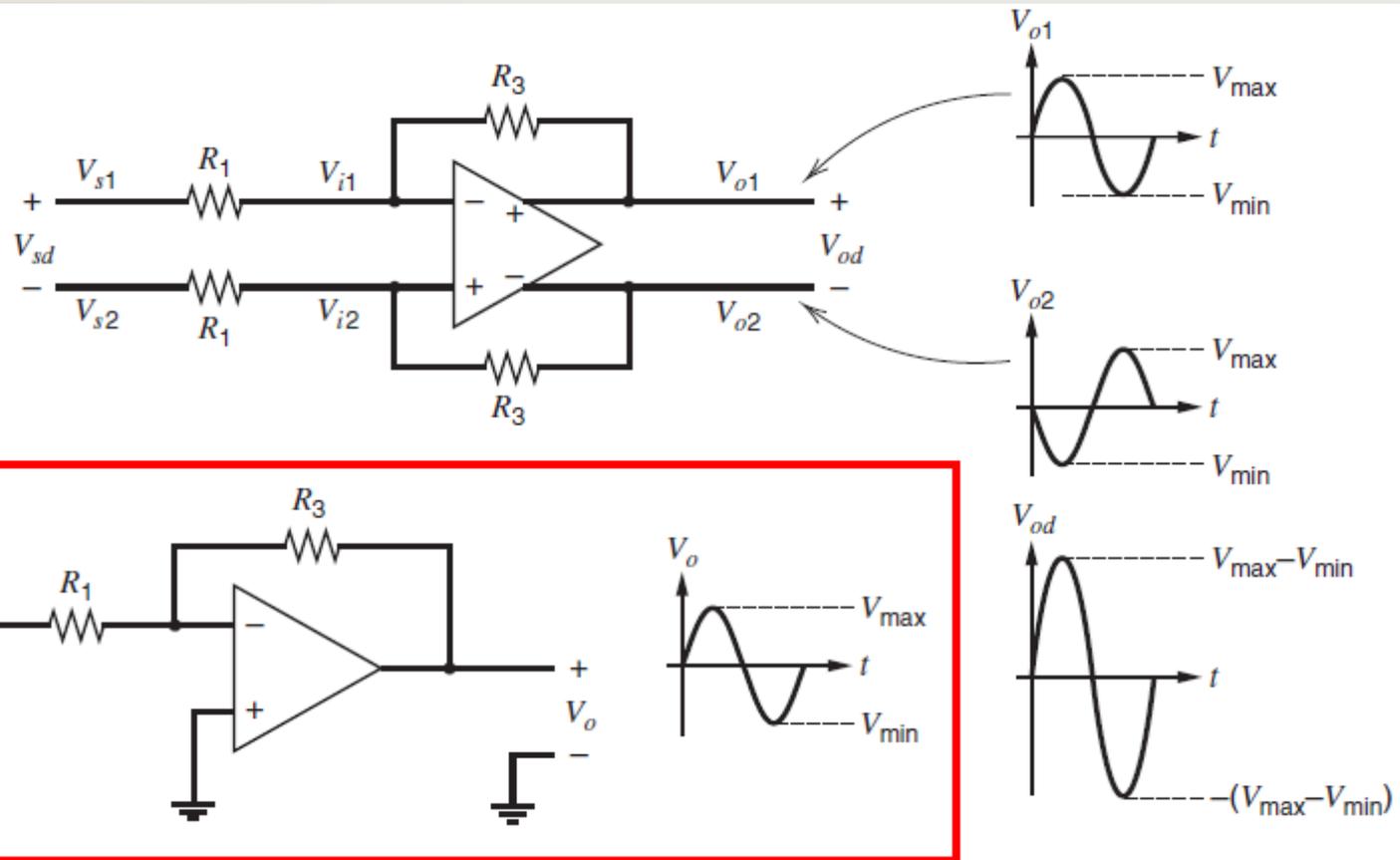
*Steven M. Martin, et al.,
“A Fully Differential Potentiostat,” IEEE Sensors
Journal, VOL. 9, NO. 2, February 2009.*



Motivation

- System level integration and minimization to accommodate an array of electrodes with CMOS technology.
- Maximizing the number of detectable analytes with the supply voltage scaled in CMOS technology.
- Introducing a new Fully Differential Potentiostat which outperforms its Single Ended counterpart.
- Additional properties of Fully Differential circuit are larger output swing, less susceptible to common mode noise , improved linearity (reduced even-order harmonics) and increased dynamic range.





The Diagram showing FD and SE structure.



Outline

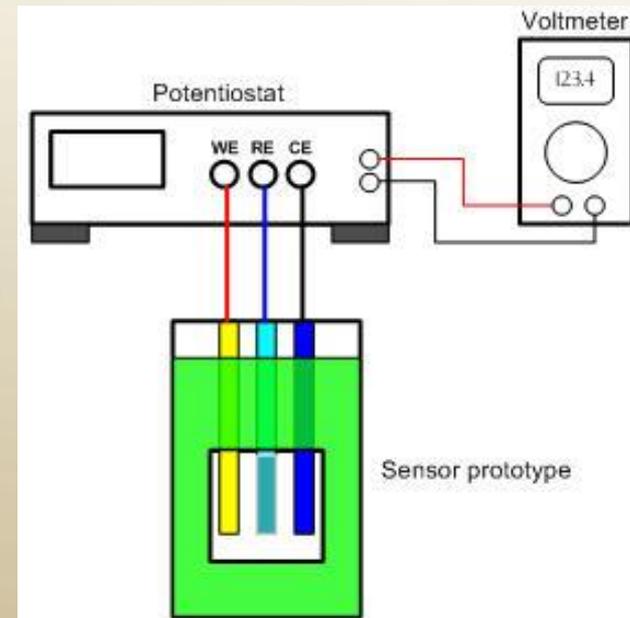
- Potentiostat and Amperometric Sensors.
- Single-Ended and Fully-Differential Potentiostat.
- Comparison of Non-idealities of SE and FD Potentiostat.
- The Design of FD Potentiostat.
- Experimental Results and Electrochemistry Analysis.
- Conclusion.



1. Potentiostat and Amperometric Sensors

What is a Potentiostat? Why do we use it?

- An Electronic interface for Biosensor.
- Induce a specified potential drop between a sensing electrode and a liquid solution.
- Supplies whatever voltage needed between working and counter electrodes to maintain specific voltage between working and reference electrode
- Serves to amplify the resulting current from the chemical reaction at the sensing electrode.



Standard Potential and Overpotential

- An analyte can be detected only when the applied potential is in excess of the chemical species' standard potential.
- Overpotential means the must apply potential before redox chemistry occurs.
- In aqueous solutions, the overpotential required to induce a redox reaction for a given chemical species is approximately equivalent to that species' standard potential.

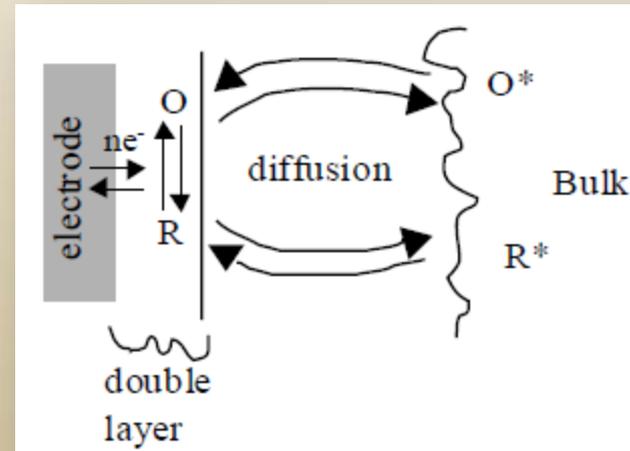
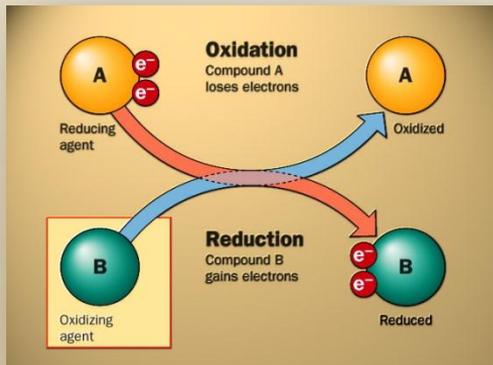
Nitric oxide is naturally found in the body; its function is conveying information between cells. It is electrochemically active. The reduction potentials for the NO/NO_3^- and NO/NO_1^- (one-electron reduced species) couples are +0.39 V and -0.35 V.



Faradaic Current

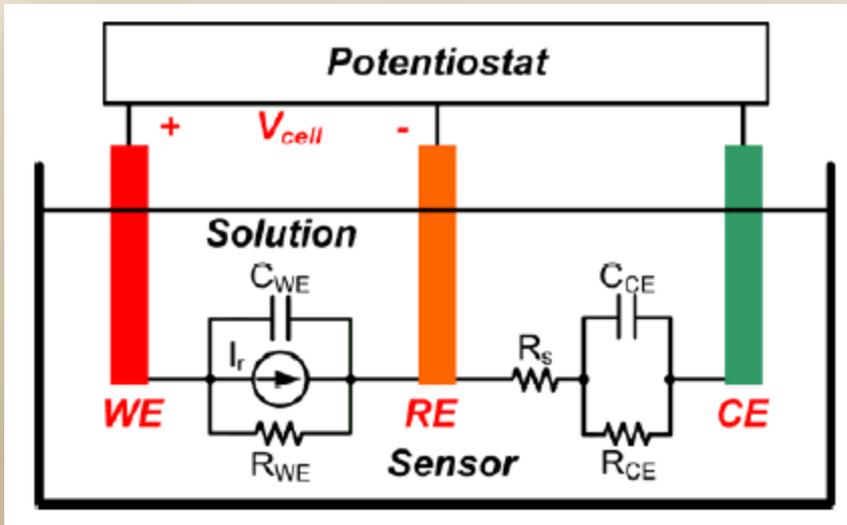
Under balance, without externally applied voltage, a single polarizable electrode in solution will develop a potential based on the ratio of the solution's chemical species

When a voltage sufficiently larger than this equilibrium potential is applied to the electrode, this forces the system out of equilibrium and results in a reduction/oxidation (redox) reaction of the form

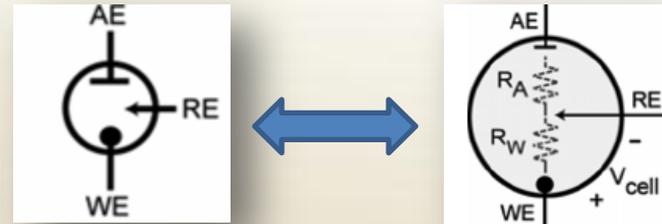


A Faradaic current I_f corresponding to the reduction or oxidation of some chemical substance.

Three-electrode Amperometric Sensor



A typical sensor configuration is the three-electrode amperometric cell.

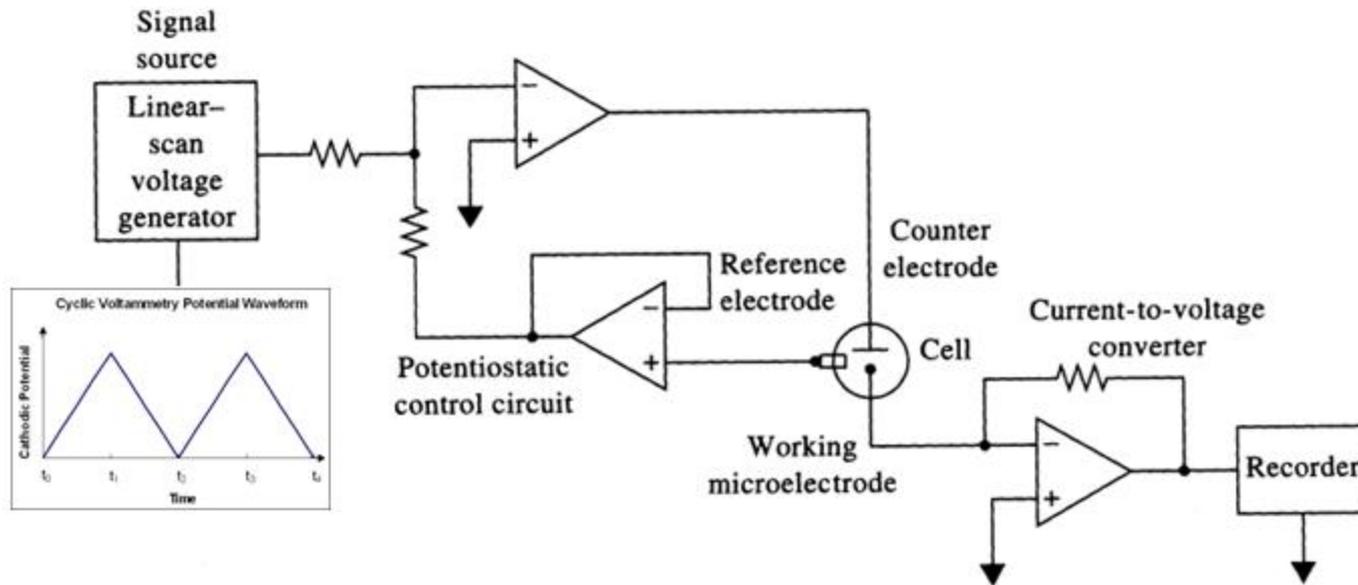


The potential between the electrode and solution which induces the faradaic reaction.

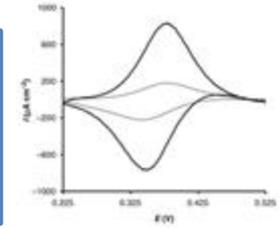
$$V_{WE} - V_{RE} \equiv V_{cell}$$

The AE enables the potential of the solution to be set via secondary redox reactions and sources the current necessary for the faradaic reaction.





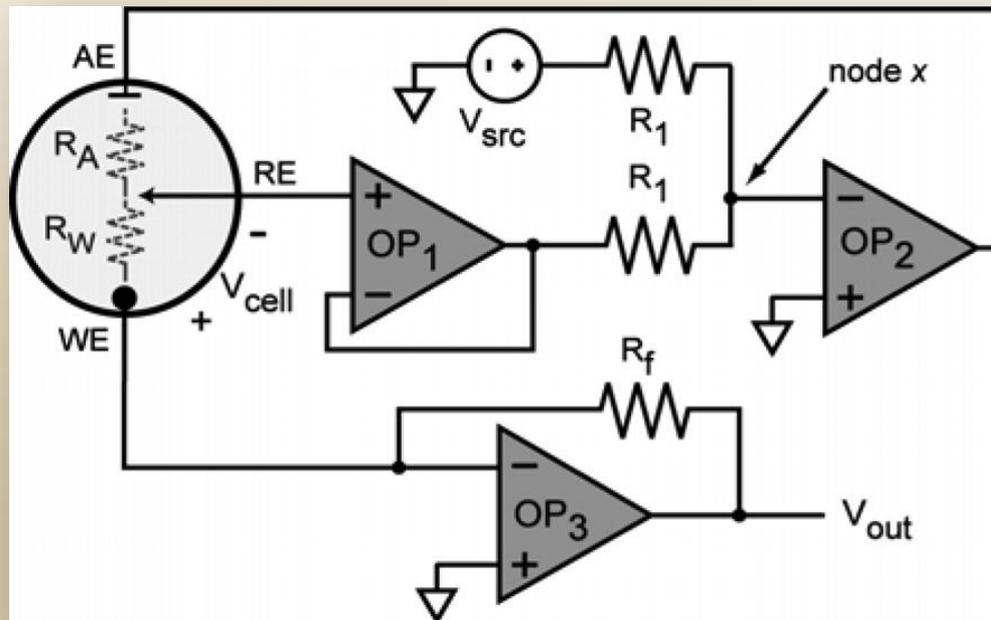
Changes in concentration are directly proportional to changes in current



Top Level Scheme showing Amperometric Sensor using Cyclic Voltammetry



2. Single-Ended and Fully-Differential Potentiostat



Single Ended Potentiostat

The voltage swing of V_{cell}

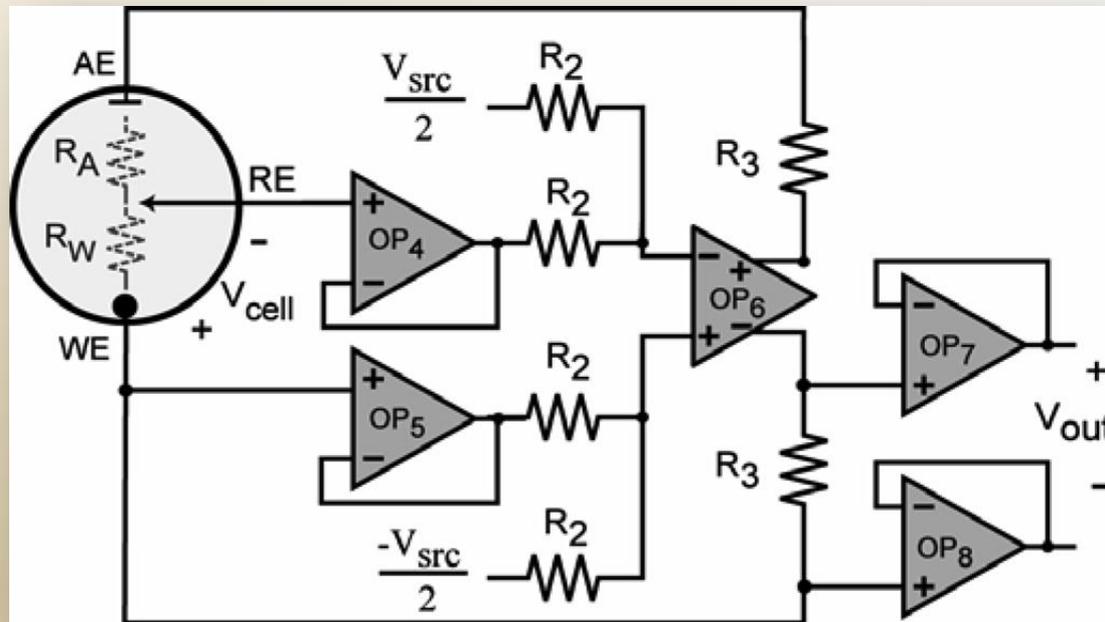
$$S_{SE} = |V_{dd} - V_{ss}| \frac{R_W}{R_W + R_A}$$

Amplification of sensor's faradaic current.

$$V_{outSE} = -I_f R_f.$$



Fully Differential Potentiostat



The differential voltage at its input terminals is ideally equal to zero

$$\frac{V_{src}}{2} + V_{RE} - \frac{-V_{src}}{2} + V_{WE} = 0.$$

$$V_{src} = V_{WE} - V_{RE}.$$

The voltage swing of Vcell

$$S_{FD} = 2 |V_{dd} - V_{ss}| \frac{R_w}{R_w + 2R_3 + R_A}.$$

Comparing this to the swing of the SE potentiostat
Assuming R3 is negligible, the voltage swing is doubled

$$\frac{S_{FD}}{S_{SE}} = \frac{2(R_w + R_A)}{R_w + 2R_3 + R_A}.$$

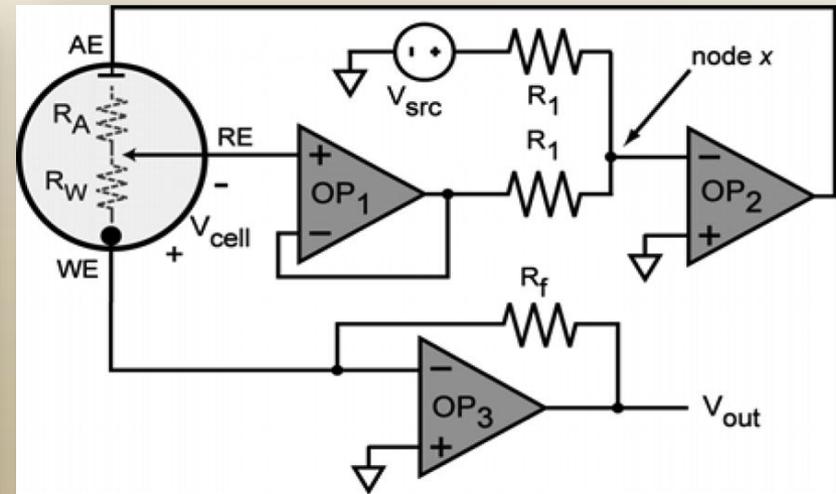
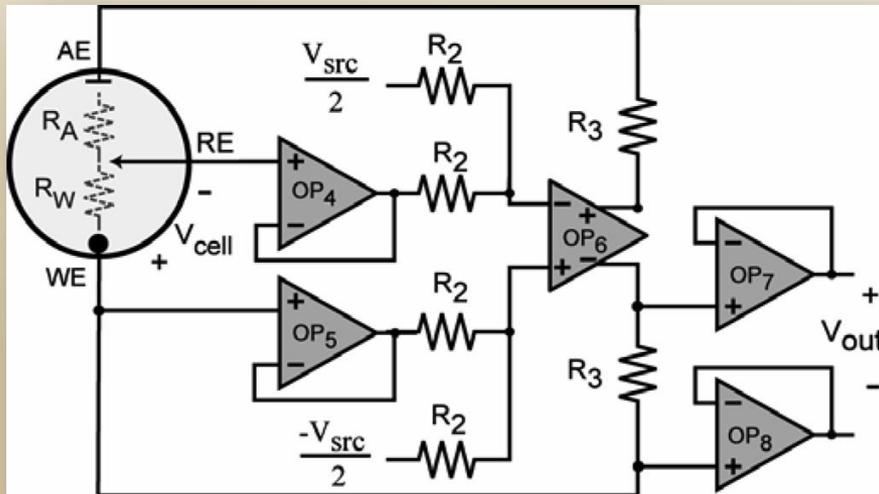
Amplification of sensor's faradaic current

$$V_{outFD} = -I_f R_3.$$



3. Comparison of Non-idealities of SE and FD Potentiostat

A. Transfer Function of $V_{\text{cell}} / V_{\text{src}}$



$$\left. \frac{V_{\text{cell}}}{V_{\text{src}}} \right|_{\text{FD}} = \frac{A_6 R_W (1 + A_4)}{2(1 + A_4)(R_W + 2R_3 + R_A) + A_4 A_6 R_W}$$

$$\left. \frac{V_{\text{cell}}}{V_{\text{src}}} \right|_{\text{SE}} = \frac{A_2 R_W (1 + A_1)}{2(1 + A_1)(R_W + R_A) + A_1 A_2 R_W}$$



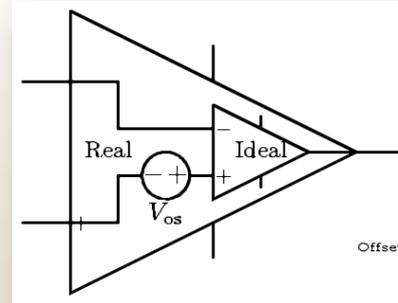
B. Op Amp Offset

$$V_{\text{cell,off}}|_{\text{FD}} = \frac{A_6 R_W (V_{o6} + V_{o4} + 2V_{o5})}{2(R_W + 2R_3 + R_A) + A_6 R_W}$$

$$V_{\text{cell,off}}|_{\text{SE}} = \frac{A_2 R_W (V_{o1} + V_{o3} + 2V_{o2})}{2(R_W + R_A) + A_2 R_W}$$

$$V_{\text{offset, SE}} = 0.7 \text{ mV}$$

$$V_{\text{offset, FD}} = 3.8 \text{ mV}$$



$$V_{\text{offset, SE}} = 0.9 \text{ mV}$$

$$V_{\text{offset, FD}} = 3.5 \text{ mV}$$

Differential Pair

$$\Delta V_{gs} = -\frac{\Delta\beta}{\beta} \frac{I_D}{g_m} + \Delta V_T$$

$$\sigma(\Delta V_{gs}) = \sqrt{\left(\frac{\sigma(\Delta\beta)}{\beta} \frac{I_D}{g_m}\right)^2 + (\sigma(\Delta V_T))^2}$$

$$\frac{\sigma(\Delta\beta)}{\beta} = \frac{A_\beta}{\sqrt{WL}}$$

$$A_\beta \sim 2\% \mu\text{m}$$

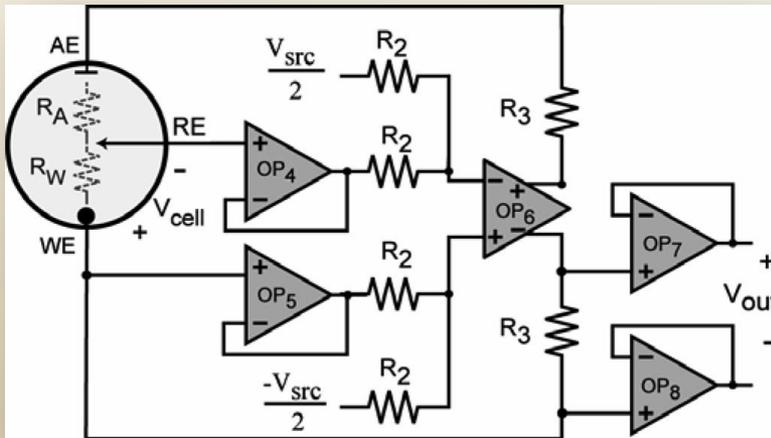
$$A_{Vt} = 16 \text{ mV} \mu\text{m}$$

$$\sigma_{\Delta V_t} = \frac{A_{Vt}}{\sqrt{WL}}$$

The offset voltage is considered to be a dc error and is present from the moment that power is applied until it is turned off, with or without an input signal.

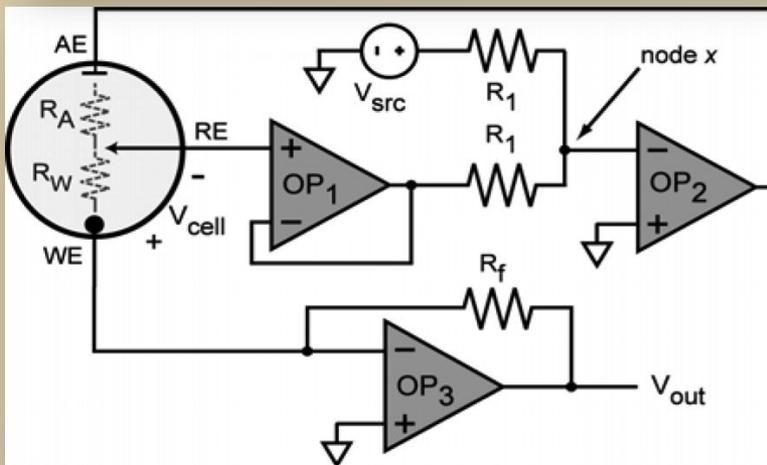


C. Noise



$$SNR = \frac{P_{\text{signal}}}{P_{\text{noise}}} = \left(\frac{A_{\text{signal}}}{A_{\text{noise}}} \right)^2,$$

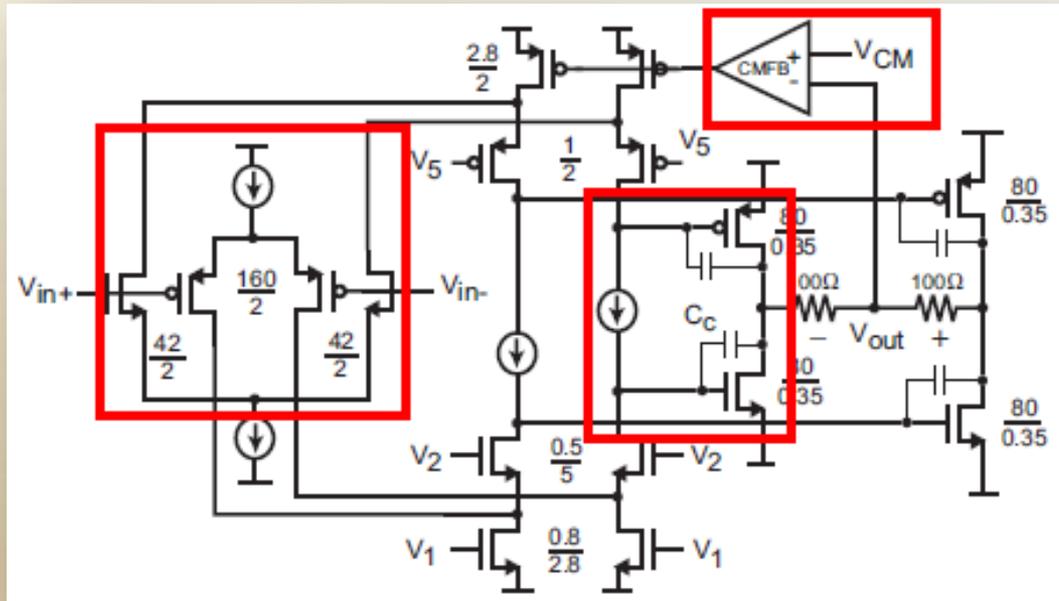
$$SNR_{\text{FD}} = \frac{(-I_f R_3)^2}{i_{n8}^2 R_3^2 + v_{n8}^2 + v_{n7}^2 + v_{R3}^2}$$



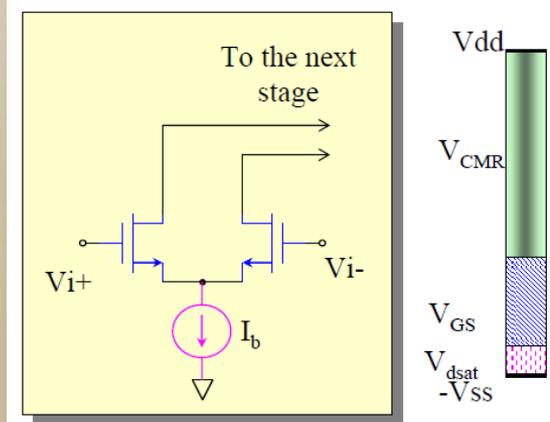
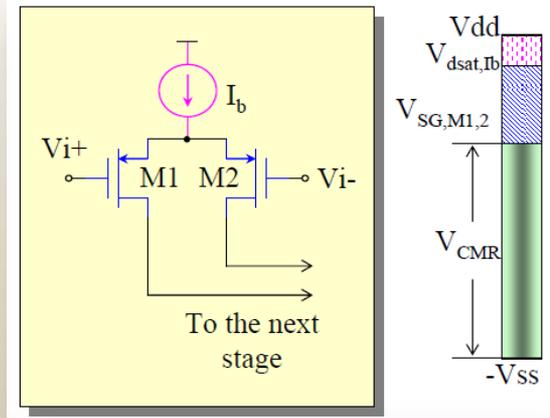
$$SNR_{\text{SE}} = \frac{(-I_f R_f)^2}{i_{n3}^2 R_f^2 + v_{n3}^2 + v_{Rf}^2}$$

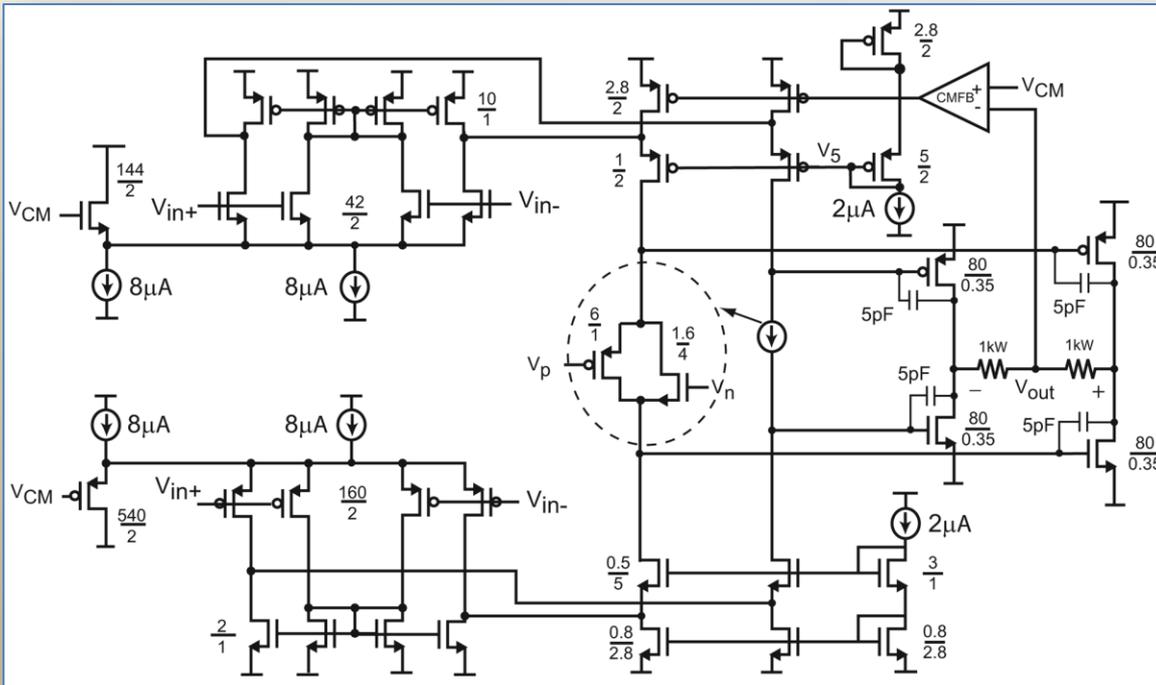
Total integrated Noise for SE and FD potentiostats are 2.9 mV and 2.5 mV

The Design of FD Potentiostat

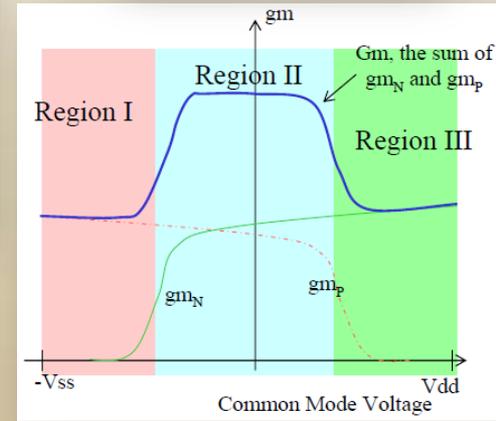
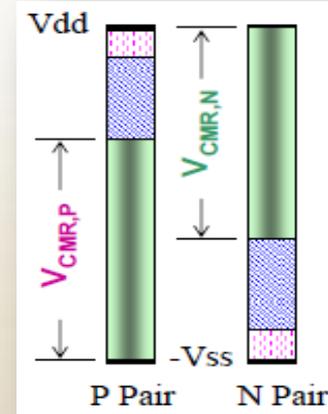


Traditional FD Structure with rail to rail input and class AB output stage.

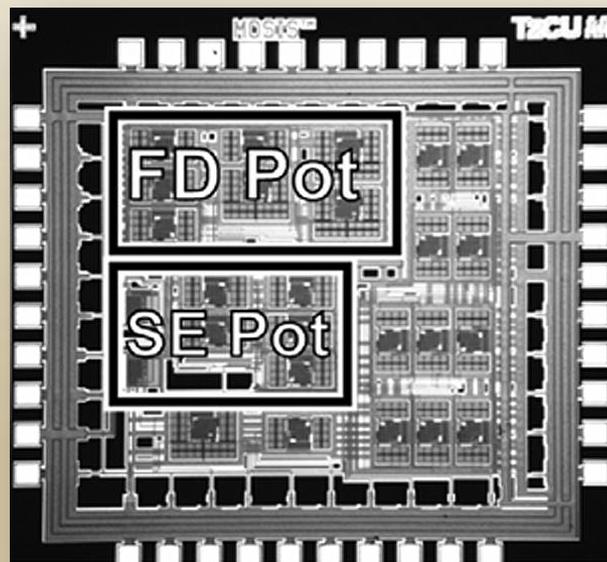




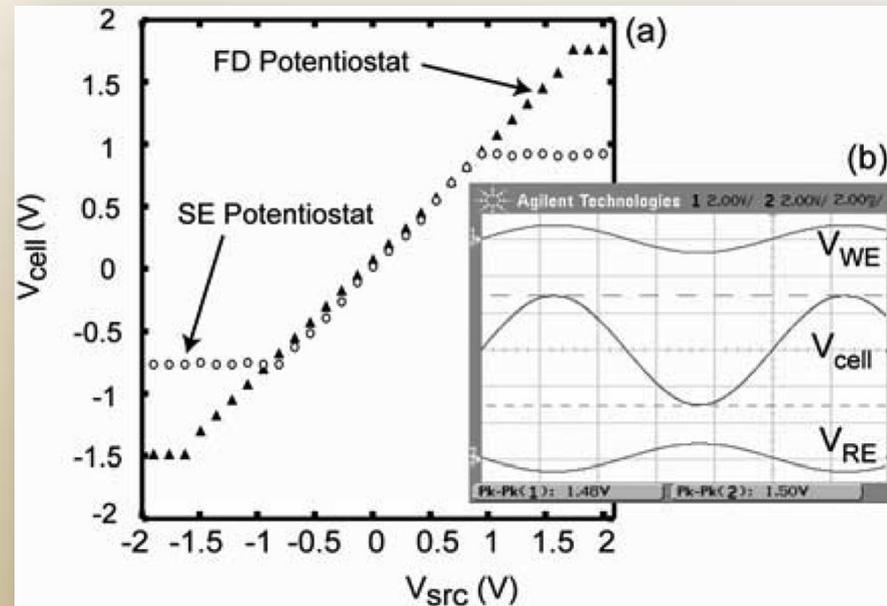
Presented Fully Differential structure



5. Experimental Results and Electrochemistry Analysis



Micrograph of the Potentiostat test chip on Silicon



Transfer function for both the FD and SE potentiostats



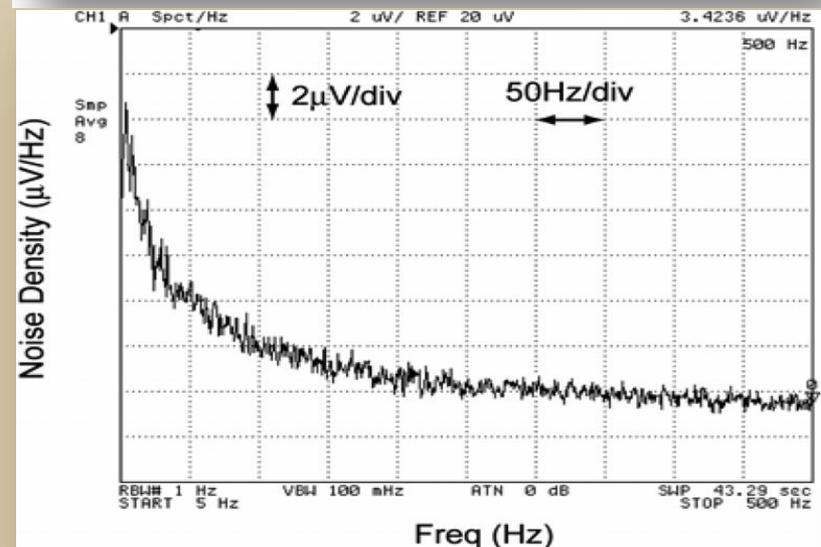
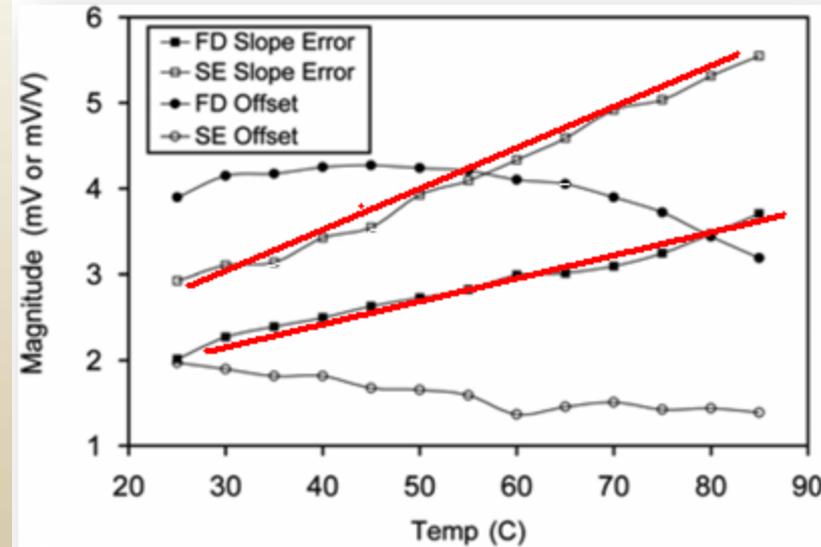
Experimental Results

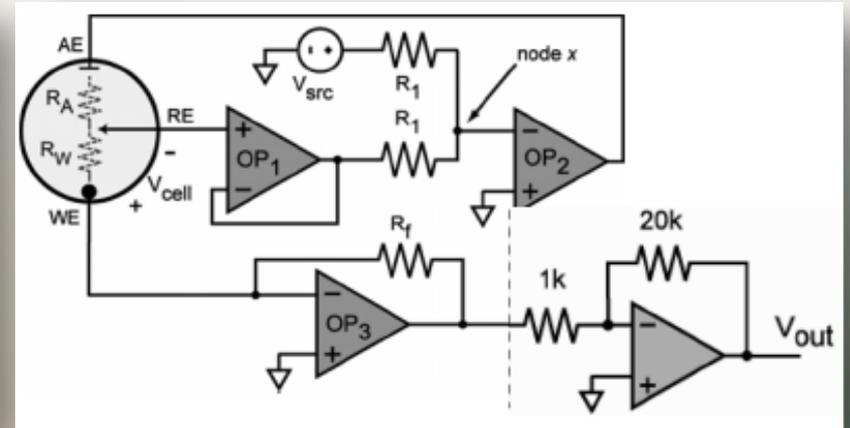
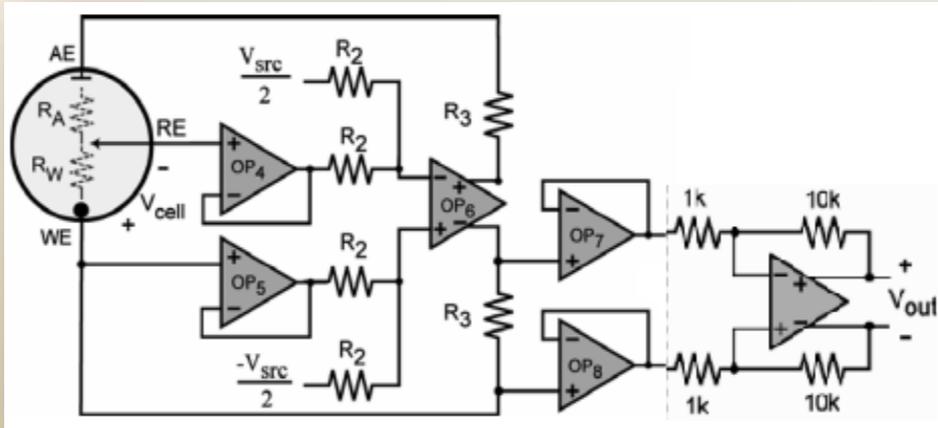
The plot of transfer function (V_{src} to V_{cell}) magnitude (with red line) and offset versus operating temperature

Fit to straight lines,
 The temperature coefficients for slope error are $20 \mu\text{V}/^\circ\text{C}$ (FD) and $50 \mu\text{V}/^\circ\text{C}$ (SE).
 The offset scales similarly for both potentiostats at $-10 \mu\text{V}/^\circ\text{C}$.

NSD of FD potentiostat's output

The total integrated noise in a 500 Hz bandwidth for the FD and SE potentiostats is 2.5 mV and 2.9 mV, respectively.





To further amplify the output voltage before sending the signal off chip, the of both the FD and SE potentiostats was routed through on-chip gain stages



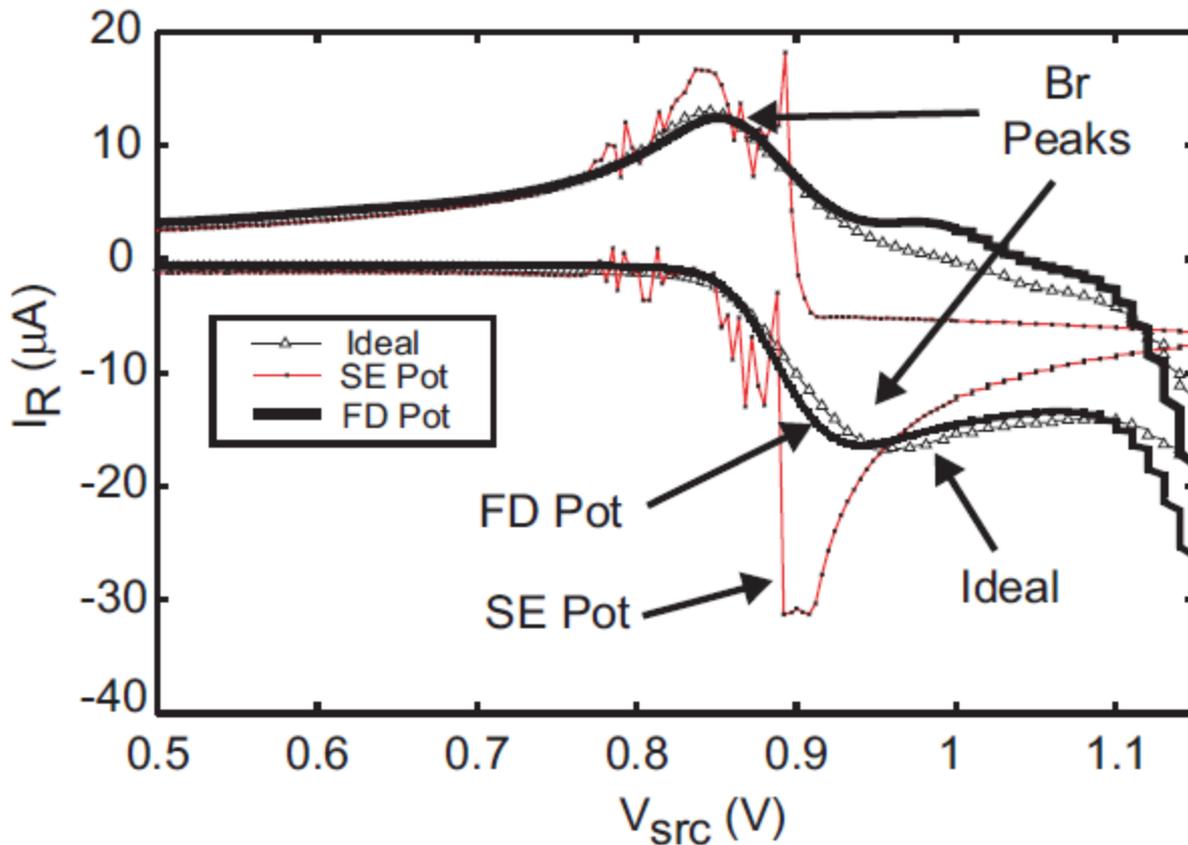
Summary of the Performance for FD and SE Potentiostats

Parameter	SE Pot	FD Pot	Units
Power Supply	1.8	1.8	V
I_{supply}	4.8	8.8	mA
Voltage Swing V_{cell}	1.6	3.2	V
Magnitude $V_{\text{cell}}/V_{\text{src}}$	0.966	0.944	V/V
Linearity $V_{\text{cell}}/V_{\text{src}}$	$R^2=0.999$	$R^2=0.998$	
Bandwidth	370	370	kHz
CMRR	65	86	dB
Dynamic Range V_{out}	56	63	dB

Dynamic Range (dB) is defined as the power ratio of the specified maximum output level over its noise floor.

$$DR = 10 \log \left(\frac{P_{\text{peak-signal}}}{P_{\text{noise}}} \right)$$

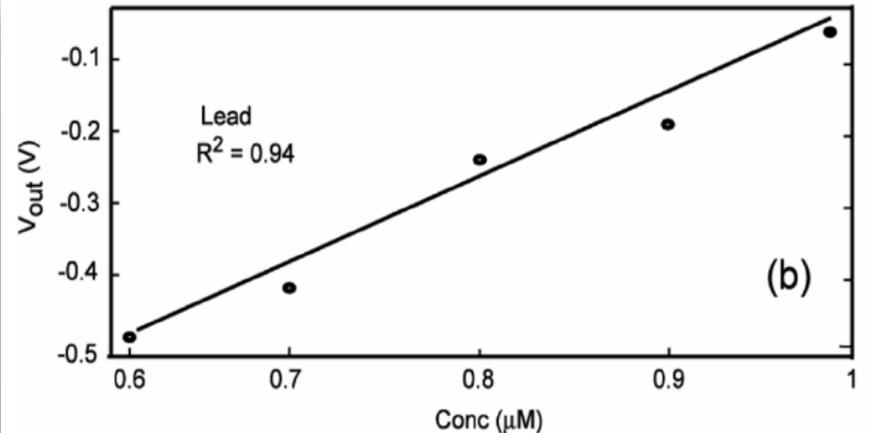
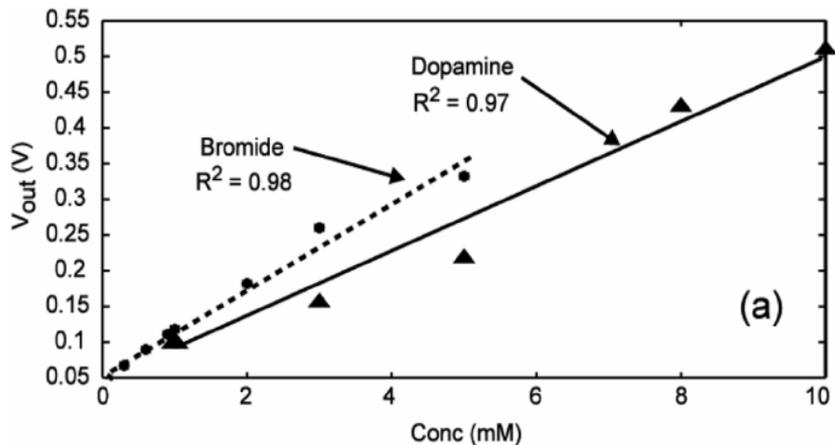




Detection of Br^- using a Pt electrode in a solution of 5mM NaBr, 100mM NaCl electrolyte.

CV of NaBr using a commercial potentiostat (ideal), the FD and SE integrated potentiostats.





Chemical calibration curves for (a) Br^- and (b) dopamine Pb^{2+}

Dopamine was dissolved into 10 mM Phosphate buffer solution, pH 7.4 in concentration of 0.2 to 10 mM.

Lead solutions were created with Concentration from 0.6 to 1 μM in 100 mM KCl, pH 4.3 buffer solution.

Calibration curve is a plot of how the instrumental response the so called analytical signal changes with the concentration of analyte in the unknown sample.



Conclusion

- This paper gives a comparison of the SE and FD structures when used as the potentiostat in Amperometric sensors.
- The presented FD potentiostat has its exclusive advantage on detecting large variety of analytes over its SE counterpart especially with the scaled CMOS technology. However, it consumes more power and circuitry is more complicated.
- In addition, the offset for both of the potentiostat is low because of the large size on the input transistors. This may not fit the requirements on the Microsystems which has stringent on chip area.



Thanks!
Questions?

