

# Electrochemical Analysis of Silver-CNT Electrode

## Based Biosensors

Jonathan Hammond, Jong-Hoon Kim and Sun Ung Kim\*

Electrochemical Engineering Lab, School of Engineering and Computer Science (ENCS), Washington State University

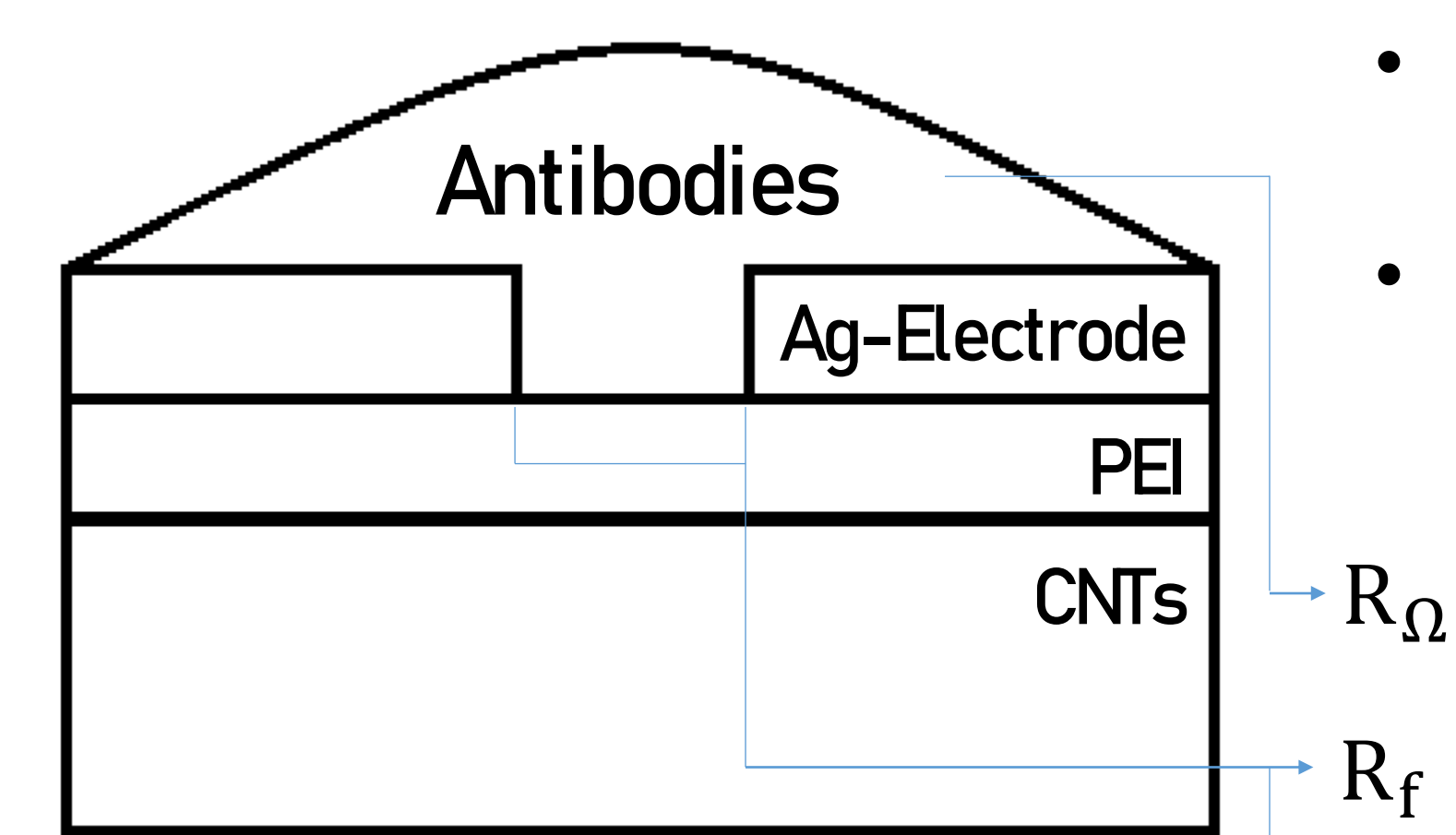
Washington State University  
Vancouver



### Abstract

There have been continuous demands to develop better biosensors, which identify the presence of a particular biological strain within a fluid sample, in an inexpensive, readily available and reliable manner. Our research aims to analyze the degradation mechanism in silver-CNT electrode-based biosensors, using electrochemical analysis methods. These sensors were developed with and without a conducting polymer layer, polyethyleneimine (PEI), across the CNT surface, as the PEI can improve the precision of such devices. However, the sensors are suffering from continuous change in resistance, therefore, we executed an electrochemical analysis using electrochemical impedance spectroscopy (EIS). The resistance and capacitance of a fluid bio-sample was measured and compared to resistance and capacitance of the fluid solvent. By repeated EIS experiments on the same sensors over time, we observed that the sensors experience their most dramatic decay within the first 8 hours of production and completely settled after 2 weeks. This might be explained by the fact that CNTs are known to experience oxidation, which can change their material properties. To identify if this is the cause of the decay, we took sensors immediately after manufacturing, both with and without a PEI layer and placed them inside a vacuum chamber for a 7-hour period. We observed an initial increase in resistance from both sensors immediately after removing them, after which they resumed their previously observed rate of decay; indicating that oxygen does contribute to the degradation.

### Sensors



- Current is applied to the Ag-electrode
- Resistance and capacitance is generated in the antibodies and antibody interface



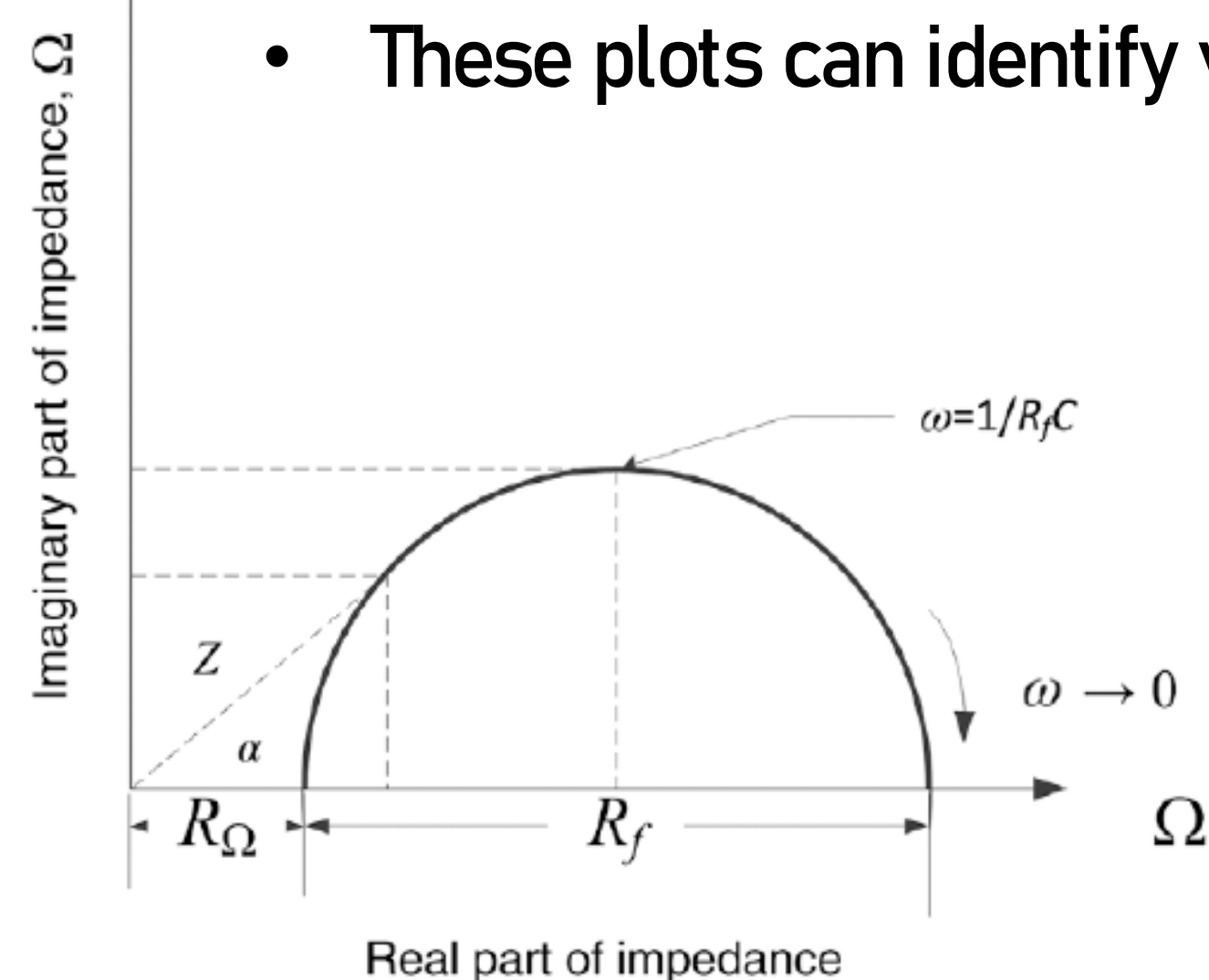
- Antibody parameters can be compared to reference sensor
- Antigen concentration can be identified

### Electrochemical Impedance Spectroscopy (EIS)

$$Z(\omega) = R_{\Omega} + \frac{1}{\frac{1}{R_f} + j\omega C}$$

### Nyquist Plots

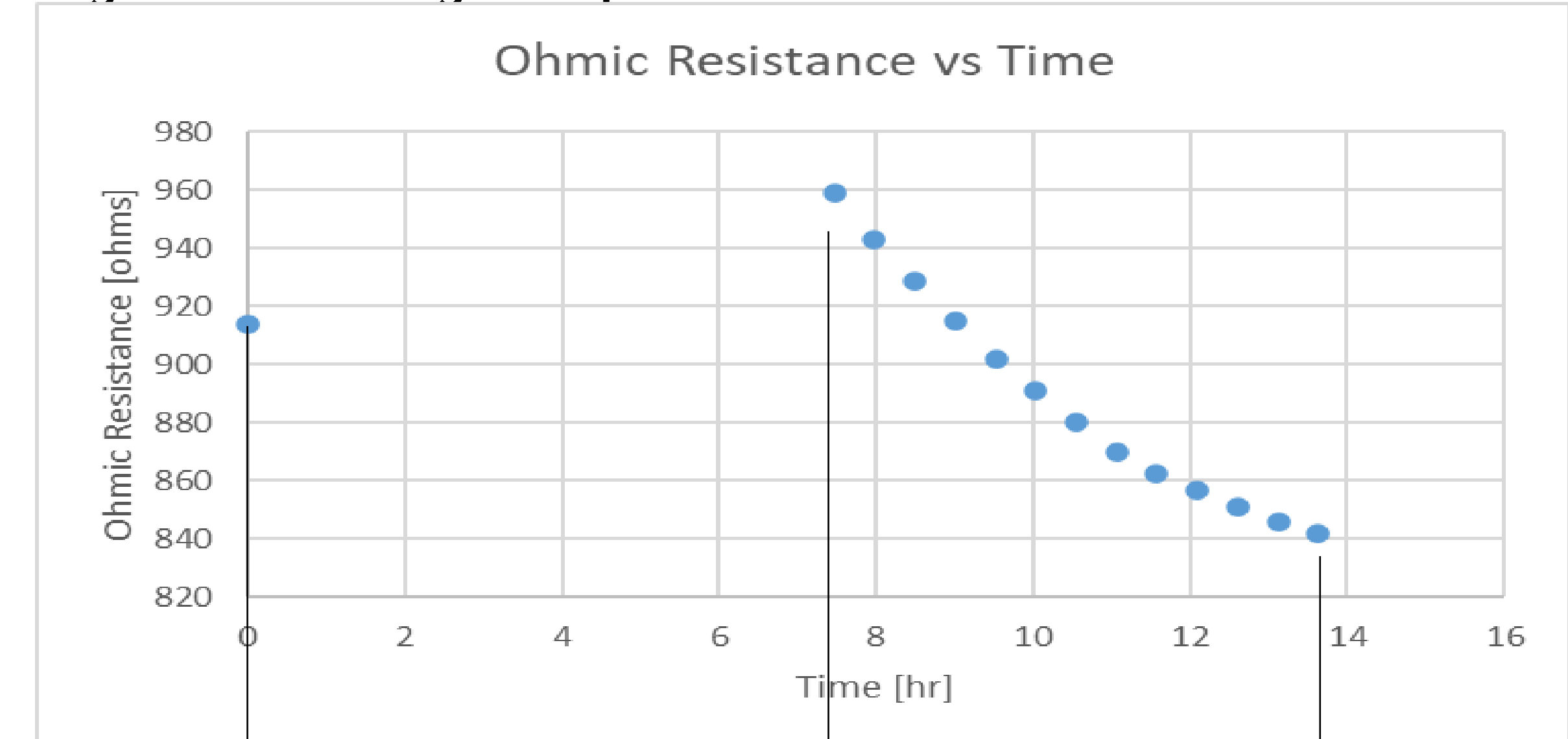
- The real values of impedance are plotted across the imaginary values of impedance
- These plots can identify values of resistance and capacitance



- $R_{\Omega}$ : Ohmic resistance in the electrolyte [ohms]
- $R_f$ : Faradic resistance in the electrode/electrolyte film [ohms]
- $C$ : Double layer capacitance between the electrode and electrolyte [Farads]

### Problem

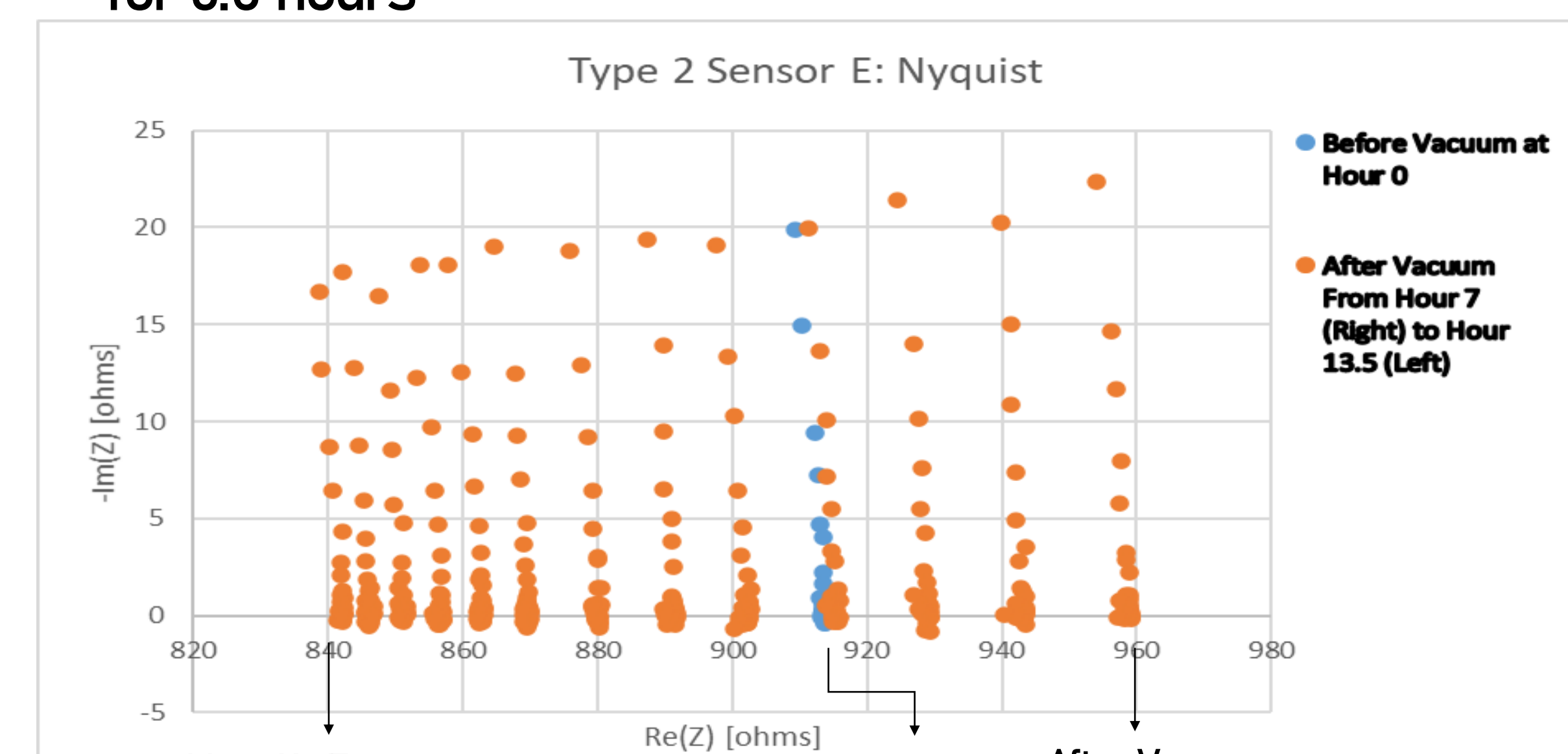
The electrical resistance and capacitance of the biosensors is known to decay with time. Our goal is to identify the cause of degradation using an equivalent circuit model.



Before Vacuum      After Vacuum      After Air Exposure

### Experiment

- To identify if oxidation was a cause of decay, an EIS experiment was performed on a freshly fabricated sensor.
- The sensor was then placed in a vacuum chamber for 7 hours.
- Once removed, the sensor was tested with EIS every half hour for 6.5 hours



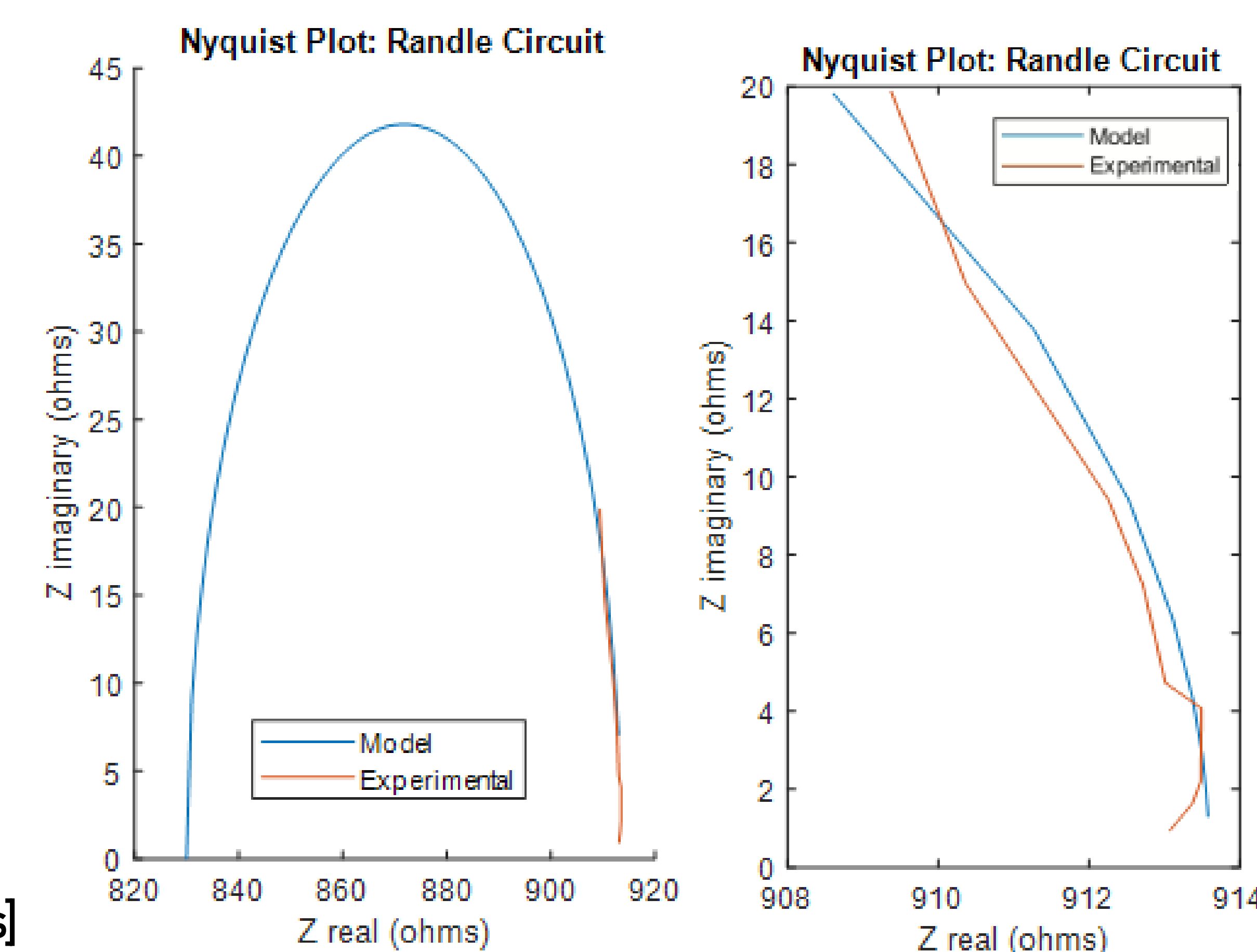
After Air Exposure      Before Vacuum      After Vacuum  
Figure shows EIS experiments taken before going into a vacuum chamber (blue) and after coming out of the chamber (orange) then experiencing decay from the right to left

- The EIS data follows a semicircular pattern, but only a section of the circle is visible, thus it appears as a line

### Model

- Nyquist plots of the sensor resistance, behave as incomplete semicircles
- The model can generate these both full and incomplete circles to identify  $R_{\Omega}$ ,  $R_f$  and  $C$

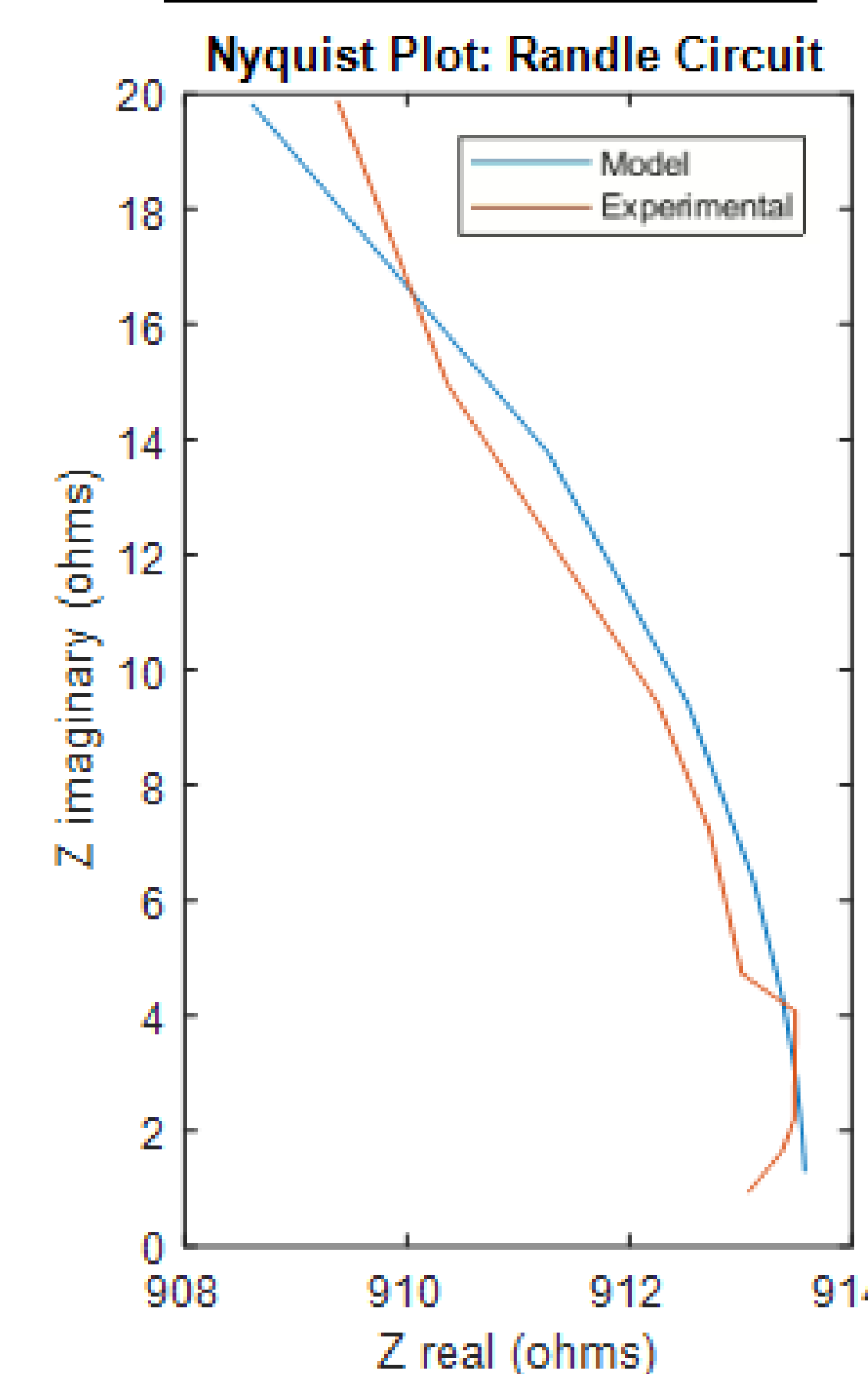
### Model of Sensor Data Before Vacuum



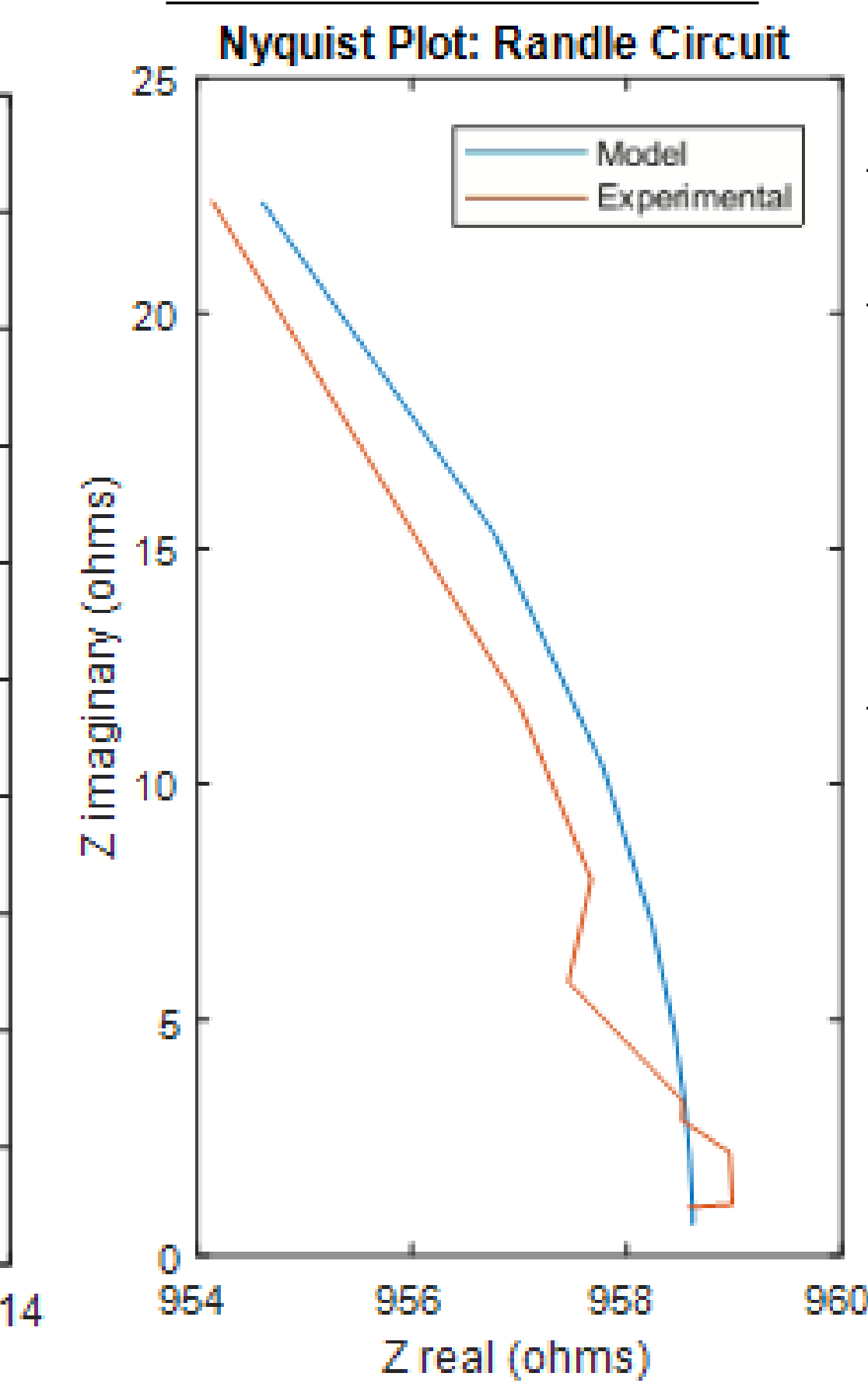
- Above left shows semicircle model over experimental data
- Above right shows semicircle model over experimental data

### Results

#### Before Vacuum



#### After Vacuum



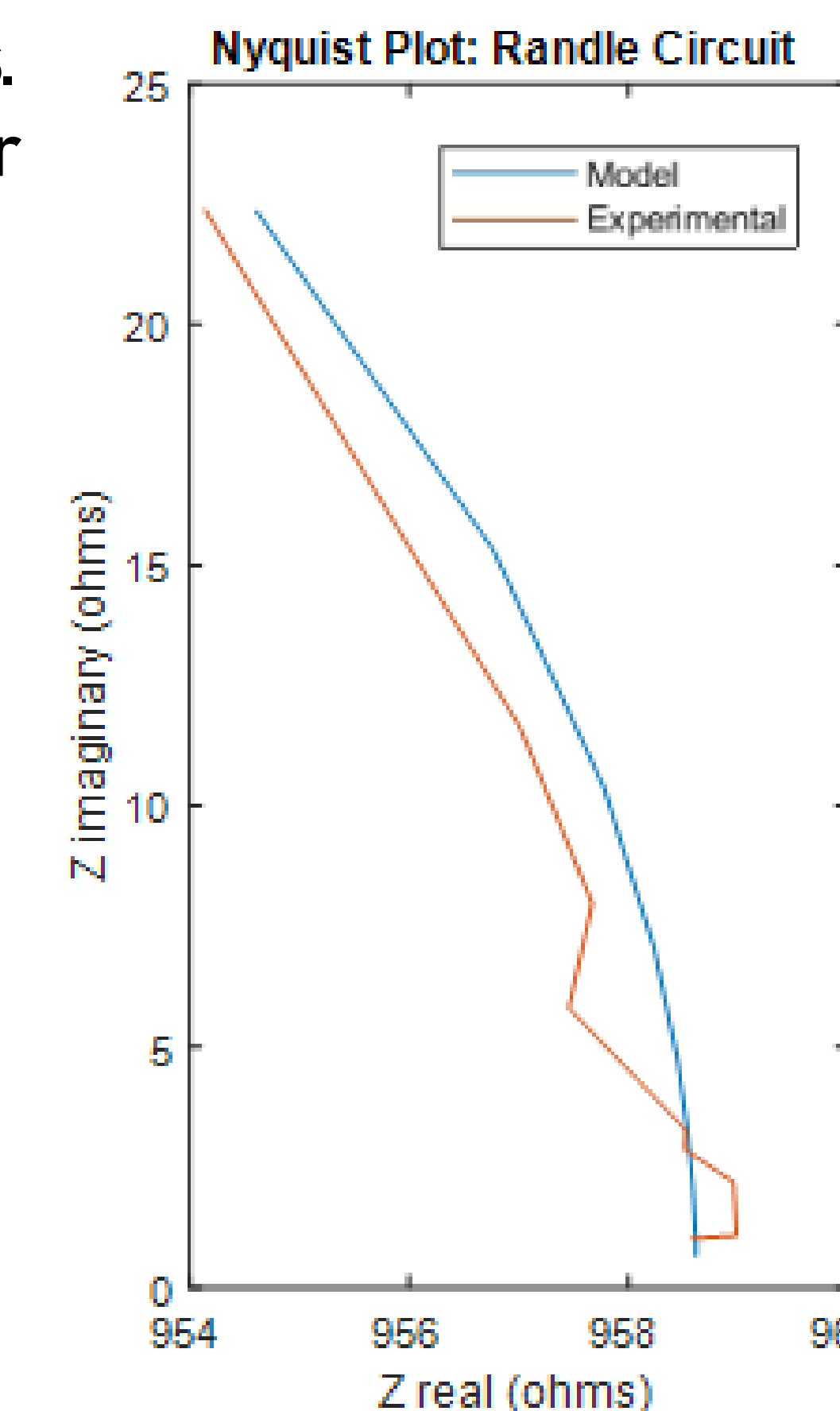
#### Before Vacuum

- $R_{\Omega} = 830 \Omega$
- $R_f = 83.6 \Omega$
- $C = 4.8 \times 10^{-8} F$

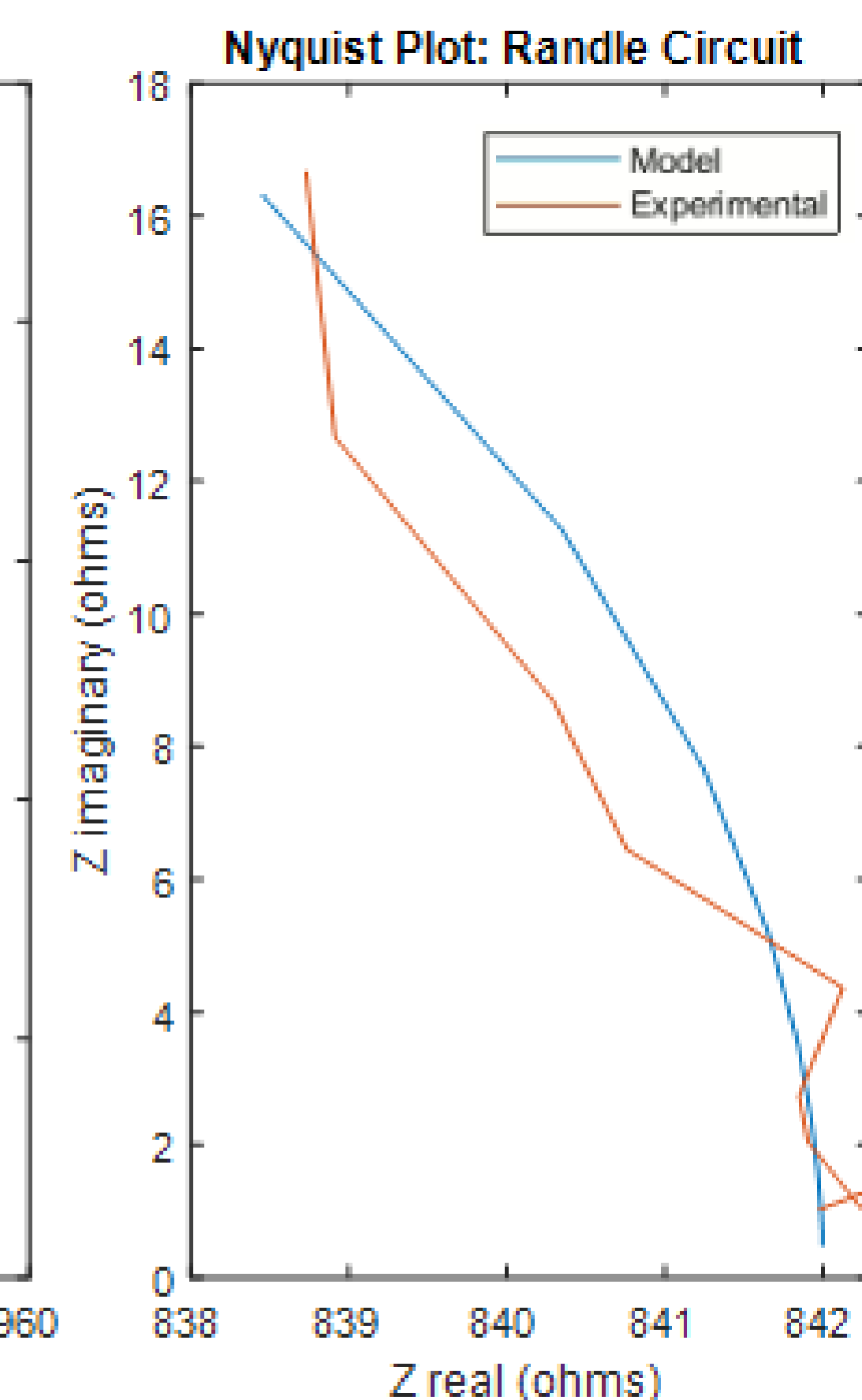
#### After Vacuum

- $R_{\Omega} = 830 \Omega$
- $R_f = 128.62 \Omega$
- $C = 2.22 \times 10^{-8} F$

#### After Vacuum



#### After 6.5 hours of Air Exposure



#### After Vacuum

- $R_{\Omega} = 830 \Omega$
- $R_f = 128.62 \Omega$
- $C = 2.22 \times 10^{-8} F$

#### After Air Exposure

- $R_{\Omega} = 763.4 \Omega$
- $R_f = 78.6 \Omega$
- $C = 4.4 \times 10^{-8} F$

- While in the vacuum chamber: no observable changes in the ohmic resistance while the Faradic resistance and the capacitance increase.
- While exposed to air: ohmic and Faradic resistance decay while the capacitance increases

### Conclusions

- An Electrode based biosensors is losing its electrical resistance with time.
- While in a vacuum chamber, sensors with and without PEI layers did underwent changes in Faradic resistance
- While in a vacuum chamber, sensors with and without PEI layers did underwent decay in both Ohmic and Faradic resistance
- **Future Work:** Use a higher capacitance electrolyte to extend the length of the semicircle arc

### References

- [1] Ronkainen NJ, Halsall HB, Heineman WR. Electrochemical biosensors. Chemical Society Reviews. 2010;39(5):1747-63.
- [2] Lopez GA, Estevez MC, Soler M, Lechuga LM. Recent advances in nanoplasmonic biosensors: applications and lab-on-a-chip integration. Nanophotonics. 2017;6(1):123.
- [3] Fernández-Sánchez C, McNeil CJ, Rawson K. Electrochemical impedance spectroscopy studies of polymer degradation: application to biosensor development. TrAC Trends in Analytical Chemistry. 2005 Jan 1;24(1):37-48.
- [4] Koh AL, Gidcumb E, Zhou Q, Sinclair R. Observations of carbon nanotube oxidation in an aberration-corrected environmental transmission electron microscope. ACS nano. 2013 Mar 26;7(3):2566-72.
- [5] Fuller TF, Harb JN. Electrochemical engineering. John Wiley & Sons; 2018 Mar 20.