Supplemental Material for: "Interpreting Interfacial Semiconductor-Liquid Capacitive Characteristics Impacted by Surface States: A Theoretical and Experimental Study of $CuGaS_2$"

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A. Theoretical Model Parameter Values

TABLE S1. Theoretical Model Parameters

Parameter and Value	Description
$E_G = 2.41\ eV$	semiconductor band gap [1]
$\epsilon_{r,sc} = 5.8$	semiconductor dielectric constant [2]
$N_L = 0.5\ M$	supporting electrolyte concentration
$\epsilon_{r,L} = 80$	water dielectric constant [3]
pH = 13.7	solution pH

Note that the theoretically assumed pH of 13.7 yields only a very minor $\sim$0.01 V shift in theoretical fits compared to pH=13.5. A pH of 13.7 is taken considering the theoretical value corresponding to 0.5 M of OH^- groups – though experimental activity may be slightly lower. No data could be found for the pH at the which the drop in the Stern layer is zero at equilibrium for $CuGaS_2$, hence it was assumed that $pH_{PZC} = 7$.

B. Experimental Results

Variations in the estimated electron affinity and doping concentration in Table S2 can be attributed to ion adsorption and frequency dispersion [4].

TABLE S2. Experimentally Determined Parameters as a Function of Frequency

Frequency (Hz)	Doping Density (cm^{-3})	V_{FB} (V vs. Ag/AgCl)	Electron Affinity (eV)
10	1.25×10^{18}	-1.05	3.83
50.11872	1.25×10^{18}	-1.05	3.83
100	1×10^{18}	-1.05	3.83
501.1872	1×10^{18}	-1.05	3.83
1000	9.2×10^{17}	-1.05	3.83
2511.886	8.2×10^{17}	-1.05	3.82
5011.872	7.31×10^{17}	-1.05	3.82
10000	5.73×10^{17}	-1.05	3.81

C. Nyquist Plots

We fitted the Nyquist plots in the frequency range from 100 kHz to 1 Hz [5]. The complete set of Nyquist plot fits, based on the Randles circuit, are provided in Fig. S1. From this fitting, the Randles circuit can be seen to hold up well within the potential range from −1.15 V to +0.3 V (vs. Ag/AgCl) and the frequency range selected.

D. Conventional Flat Band Potential and Doping Concentration Calculations

The flat band potential (V_{FB}) can be calculated through the straight-line intercept of a Mott-Schottky plot for electrodes that do not contain significant surface state concentrations. But this is not feasible when surface states are present in abundance, due to the resulting non-linear Mott-Schottky plot as shown in Fig. S2. Indeed, several possible "linear sections" on the Mott-Schottky plot can be utilized to estimate the flat band potential. Here, we examine two scenarios frequently chosen when assessing the flat band potential [6–8]. The values are shown in Table S3. Obviously, these estimates suffer from a wide degree of uncertainty. Furthermore, the flat band potential estimate fluctuates with respect to frequency. This means that we cannot arrive at a convergent flat band potential estimate through this strategy. Similar difficulties are encountered when estimating the doping density (N_D) through a linearity-based approach when surface states are present in abundance.

TABLE S3. Experimental Estimates Using a Linearity-Based Approach

Frequency (Hz)	Flat band Potential (V vs. Ag/AgCl)		Doping Density (cm^{-3})	
	Case 1	Case 2	Case 1	Case 2
10	−2.45	−0.58	3.1×10^{16}	1.6×10^{17}
50.11872	−1.93	−0.73	4.7×10^{16}	1.6×10^{17}
100	−1.99	−0.75	9.9×10^{16}	1.7×10^{17}
501.1872	−2.05	−0.75	5.4×10^{16}	2.5×10^{17}
1000	−1.94	−0.75	6.1×10^{16}	2.6×10^{17}
2511.886	−1.98	−0.77	6.6×10^{16}	2.8×10^{17}
5011.872	−2.00	−0.78	7.4×10^{16}	3.3×10^{17}
10000	−2.13	−0.81	8.4×10^{16}	3.5×10^{17}

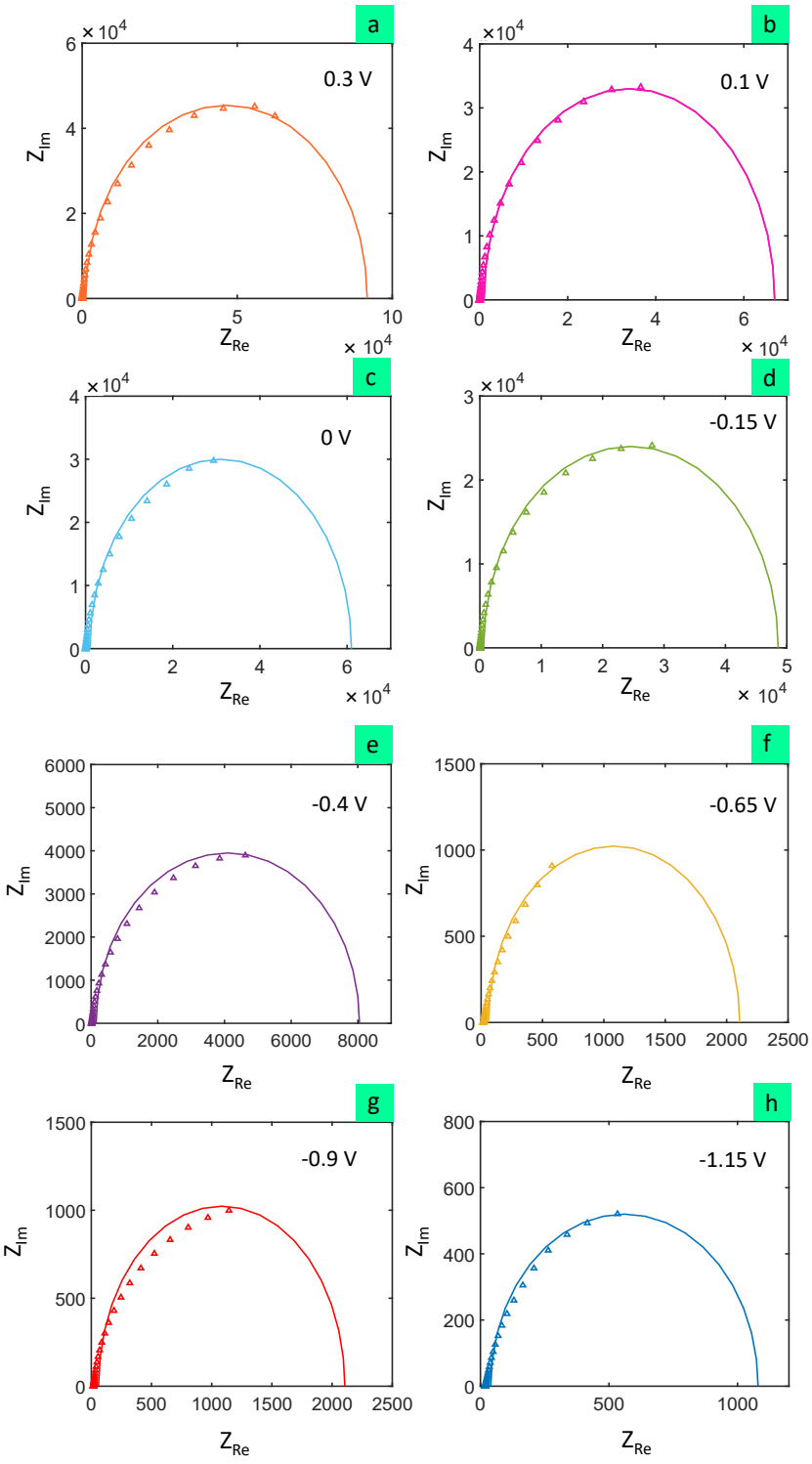

FIG. S1. The Nyquist plot fits based on a Randles circuit at biases of 0.3 V, 0.1 V, 0 V, −0.15 V, −0.4 V, −0.65 V, −0.9 V and −1.15 V (vs. Ag/AgCl) are shown in (a) through (h), respectively.

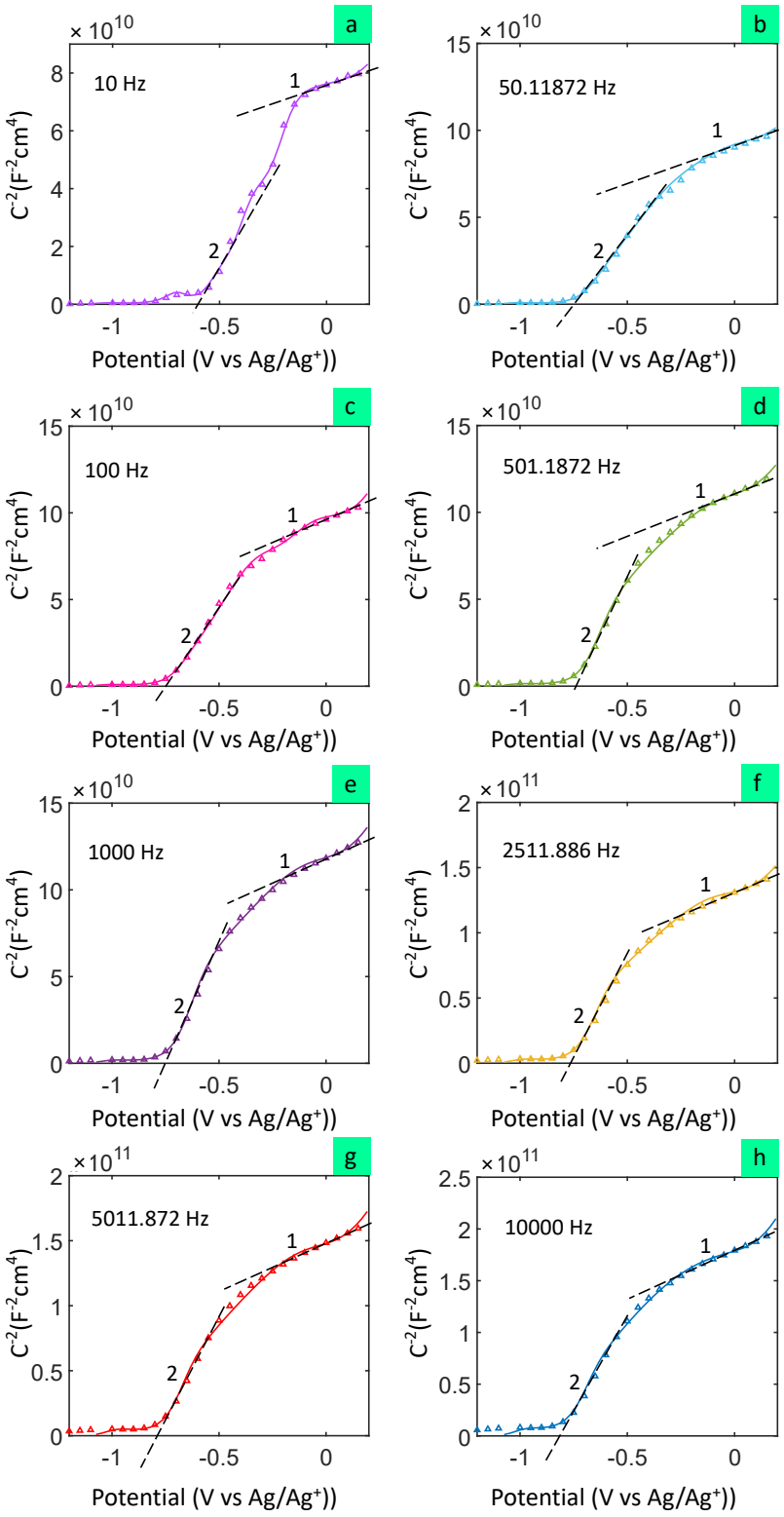

FIG. S2. The frequency dependent measured (triangles) and calculated (solid lines) Mott-Schottky capacitance of a $CuGaS_2$ anode at frequencies between 10 Hz to 10000 Hz are shown in (a) to (h) respectively. Case 1 and Case 2 fits (black dashed lines) are utilized to demonstrate a linearity-based assessment of the flat band potential and doping density.

E. Numerical Model

The numerical model utilized in this work can be found via the link below:
`http://www.physics.mcgill.ca/~bevankh/Codes/SurfaceStateCode.zip`

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