

Article

Mechanistic Analysis of Hydrogen Evolution Reaction on Stationary Polycrystalline Gold Electrodes in H₂SO₄ Solutions

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Abstract: An impedance model based on the Volmer–Heyrovsky–Tafel mechanism was developed to study the kinetics of the hydrogen evolution reaction on polycrystalline gold electrodes at moderate overpotentials in aqueous H₂SO₄ (0.5 and 1.0 M) solutions. The model was optimized on data from potentiodynamic polarization and electrochemical impedance spectroscopy, and model parameters were extracted. Consistent with expectations, the magnitude of the impedance data indicated a higher rate of hydrogen evolution at lower pH. Also, the fractional surface coverage of adsorbed hydrogen (θ_{Hads}) increases with increasing overpotential but the small value of θ_{Hads} indicates only weak adsorption of H on gold. Tafel slopes and exchange current densities were estimated to be in the range of 81–124 mV/dec, and 10^{-6} and 10^{-5} A/cm² in H₂SO₄ (0.5 and 1.0 M), respectively. The results show that the model accounts well for the experimental data, such as the steady-state current density. Sensitivity analysis reveals that the electrochemical parameters (α_1 , α_2 , k_1^0 , k_{-1}^0 , and k_2^0) associated with the kinetics of the hydrogen evolution reaction have a major impact on the calculated impedance but the standard rate constant for hydrogen oxidation reaction (k_{-2}^0) does not strongly affect the calculated impedance.

Keywords: HER; impedance; modeling; gold; polarization; H₂SO₄



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1. Introduction

An important renewable energy source that can be used in place of fossil fuels to combat the alleged anthropogenic global warming is hydrogen [1,2]. Although hydrogen can be produced from the steam reforming of natural gas [3–5], there is intense interest in producing it sustainably via the electrolysis of water [6–8]. The current technology, however, is expensive and inadequate, thus necessitating the development of new high-performance electrocatalysts [9,10]. In addition, the mechanisms and the associated kinetics of the hydrogen evolution reaction (HER) on gold have not been investigated extensively [11–13]. In the present work, our emphasis is on polycrystalline gold because the cost of preparing single-crystal substrates for large-scale use as electrocatalysts in practical applications would be prohibitive.

Noble metals like platinum, gold, and silver as either bulk electrodes or in the form of nanoparticles were extensively studied as model systems [14–20]. Gold offers unique features as a useful model electrode for the HER over a wide range of potentials in various solutions, despite its moderate activity for the HER in an acidic solution [21–26]. Numerous studies were conducted on gold stationary and rotating disk electrodes in acidic and alkaline solutions, mostly using the common dc-polarization techniques to measure exchange current density and Tafel slopes but considerably less attention has focused on the kinetics of the HER [26–34].

For example, Kibler et al. [21] studied the relationship between reconstruction of the Au(111) single-crystal surface and HER activity. They reported that the kinetics of

this reconstruction depend greatly on the applied potential. Furthermore, they raised the possibility of the hydrogen oxidation reaction (HOR) on gold in the presence of molecular hydrogen, either added externally or formed as a consequence of potential cycling towards negative potentials. The authors detected a HOR peak in the positive sweep if the electrode potential was held at a sufficiently large negative potential and attributed it to thermal reconstruction of the surface of the electrode. This result serves as evidence for the possibility of the HOR on gold, despite a common belief that clean bulk gold electrodes lack the ability to oxidize molecular hydrogen. Perez et al. [22] studied the activity of low-index gold single crystals for the HER in acidic solutions and reported the following order of catalytic activity: Au(111) > Au(100) > Au(110). Kahyarian et al. [25] developed a mechanistic model to evaluate possible HER mechanisms to address the polarization behavior of the HER on gold in mildly acidic solutions. They concluded that the overall reaction can be accurately described by the Volmer–Heyrovsky mechanism, which incorporates an intermediate surface diffusion step. Sasaki et al. [26] concluded that due to a wide variation in the reported b -value of the Tafel slope of the HER on gold in an acidic solution, the Tafel slope cannot be viewed as a definitive indicator of the mechanism behind HER. Therefore, to better understand the HER mechanism, they divided the overall reaction into its individual elementary steps and directly compared their rates using the exchange current density of each individual step. They reported that exchange current density in acidic solution varies linearly with pH which implies that the electron-transfer step in sulfuric acid involves the reduction of hydronium ions.

The catalytic activity of gold nanoparticles in sulfuric acid solution was examined by Wang et al. [27] through electrochemical cycling. Their results demonstrated a notable improvement in the HER activity, characterized by a reduction in overpotential and Tafel slope. This enhancement was assigned to the formation of “stepped-like” structures, which were generated by consecutive electrochemical cycling within the double-layer region. In another study, Meethal et al. [35] utilized an inverted rotating disc electrode to mechanistically model the kinetics of HER on a gold electrode in perchloric acid and in sodium hydroxide solutions. Their findings indicated that the Volmer–Heyrovsky–Tafel (VHT) mechanism best described the kinetics of the HER in highly acidic solutions. Additionally, they observed that diffusion played a significant role in the HER process at higher overpotentials.

A powerful method for extracting mechanistic information is the evaluation of electrochemical models based on data from electrochemical impedance spectroscopy (EIS) [36–49]. This method uses a small ac potential at different frequencies to perturb electrochemical reactions occurring at the electrode/solution interface, which produces an ac current response associated with the electrochemical processes and the passive resistive and capacitive elements present in the system (e.g., the double-layer capacitance). As a result of the small perturbation, physical models can be developed by linearizing the electrochemical equations to study capacitance behavior, diffusion, and Faradaic reactions at the electrode/solution interface [36–39].

Several EIS studies reported on the kinetics of the HER, with either simple electrical equivalent circuits (EECs) or the kinetics parameters correlated to EECs elements used to interpret the results [39–44]. For instance, Laisa et al. [40] investigated the HER mechanism on a Raney nickel electrode in a 1.04 M NaOH solution using the EIS technique. According to their findings, chemically activated electrode materials exhibit a preference for the Volmer–Tafel mechanism as the primary pathway for the HER, in which the Volmer reaction serves as the controlling step, accompanied by minor involvement of the Heyrovsky reaction. However, they also observed that electrochemical activation leads to an improvement in the electrocatalytic behavior of the electrode material towards the HER. As a result, the Volmer–Heyrovsky mechanism becomes the favored route, with both steps playing significant roles in determining the reaction rate.

Nicolic et al. [41] examined how in situ ionic activation, achieved through the combined use of three d-metals (Ni, Co, and Mo), influences both the mechanism and kinetics

of the HER. Their investigation involved conducting polarization and EIS measurements and found that the simultaneous deposition of Ni, Co, and Mo species on the Ni cathode led to the creation of numerous active sites for hydrogen adsorption. Additionally, they observed a synergistic effect that resulted in an electronic structure conducive to the HER, ultimately contributing to significant improvements in the kinetics of the reaction. Alobaid et al. [42] studied the mechanism and kinetics of the HER and oxygen evolution reaction on nickel iron layered double hydroxide (NiFe LDH) in a basic electrolyte, using experimental linear sweep voltammetry and EIS techniques. According to their findings, the HER is primarily controlled by the Heyrovsky step, with the reaction mechanism depending on the applied potential. At low potentials, the mechanism initiates with the Volmer step, followed by parallel Tafel and Heyrovsky steps. However, at higher potentials, the mechanism transitions into a consecutive combination of the Volmer and Heyrovsky steps. Franceschini et al. [43] characterized a Ni catalyst for the HER in alkaline solutions using rotating disk electrodes and EIS techniques. They reported the rate-determining step on fresh nickel is the one-electron Volmer reaction, while catalytic activity for activated nickel through chronoamperometry decreases and exhibits a strong temperature dependence. Furthermore, they reported that hydrogen adsorption on fresh nickel follows the Langmuir isotherm while it shifts to Temkin for activated nickel. Ohmori et al. [44] studied the mechanism of the HER kinetics on a Au electrode in hydroxide solutions and reported the kinetics of the HER exhibit a slow discharge mechanism that remains consistent across the entire range of solution concentrations.

Existing studies on HER kinetics using EIS have not delved into mechanistic investigation, particularly on gold electrodes in an acidic solution. Given the recent resurgence of interest in gold catalysis, including water-splitting [6–8] and HER [11–13], the primary aim of the work in this paper was to assess whether the current mechanism of the HER can be used to accurately model the process on gold and to allow extraction of valuable kinetic parameters. We believe this approach is essential to corroborate and build upon established knowledge. As such, our work both validates the VHT mechanism for gold and reports the first (to our knowledge) comprehensive set of kinetic parameters for the HER on this metal using EIS. Specifically, we optimized a kinetic model based on the EIS data by implementing a genetic-based optimization algorithm [45], which was proven to be effective in extracting accurate and reliable model parameters [45–47]. This study, therefore, fills a research gap by employing an impedance-based physical model to probe the HER mechanism on stationary polycrystalline gold electrodes in H_2SO_4 (0.5 and 1.0 M) solutions at moderate overpotentials.

2. Experimental

2.1. Materials

Gold (99.999%, VEM Vacuum Engineering, Santa Clara, CA, USA), sulfuric acid (95–98%, EMD, La Grange, IL, USA), hydrochloric acid (EMD, 37%), nitric acid (EMD, 70%), and silver nitrate (99.8%, Fisher Scientific, Hampton, NH, USA) were used as received. Water, purified to $18.2 \text{ M}\Omega\cdot\text{cm}$ using a Millipore Simplicity UV system, was used in all experiments described in this article.

2.2. Electrochemical Measurements

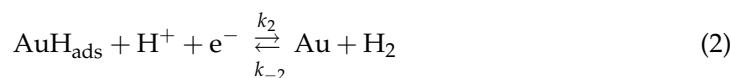
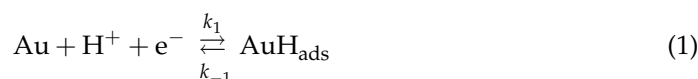
Polycrystalline gold electrodes were prepared by evaporating 100 nm of gold onto a 5 nm titanium adhesion layer on glass substrates. The gold working electrodes were cleaned chemically in dilute aqua regia (0.5 M HNO_3 , 1.5 M HCl) for 7 min, and then electrochemically by cycling the potential between 0.5 and 2.0 V (versus SHE) in deaerated H_2SO_4 (0.5 or 1.0 M) solutions (having measured pH values of 0.6 and 0.25) seven times at a scan rate of 100 mV/s. A commonly employed method to activate the gold surface is by cleaning via cyclic voltammetry, which involves repeatedly scanning the potential from the double-layer region to the oxide-formation region [35]. Such a method is also useful

for detecting the presence of reducible cations (e.g., Ag^+ from the Ag/AgNO_3 reference electrode, in our case) but no such peaks were found.

These studies used a traditional three-electrode system, with gold as the working electrode, platinum wire as the counter electrode, and aqueous Ag/AgNO_3 (10 mM) as the reference electrode (+0.8 V versus SHE). All solutions were purged with H_2 (5.16% in N_2) gas for about 20 min to ensure saturation, and potentials are reported vs. SHE, unless stated otherwise. Potentiodynamic polarization (PDP) data were recorded in H_2SO_4 (0.5 and 1.0 M) solutions from 0.0 to -0.3 V vs. SHE with scan rates of 1 mV/s using a VersaSTAT3 potentiostat. All potentials reported here were corrected for the ohmic drop using the solution resistance calculated from the EIS data. The EIS measurements were performed potentiostatically over a frequency range of 10 kHz–0.1 Hz by superimposing a sinusoidal excitation of 10 mV (peak-to-peak) on the chosen polarization potentials (-0.12 to -0.25 V vs. SHE) imposed by a VersaSTAT3 potentiostat. All electrochemical measurements were conducted at temperatures of 20 and 24 °C in H_2SO_4 (0.5) and H_2SO_4 (1.0 M), respectively.

3. Model Development

The HER is generally regarded as proceeding through three steps (Equations (1)–(3)), known as the VHT mechanism [13]. The initial adsorption of protons from the solution is referred to as the Volmer reaction (Equation (1)). In the second reaction (Equation (2)), the “Heyrovsky step”, a proton from the solution combines with the adsorbed hydrogen (H_{ads}) and an electron to produce H_2 , which diffuses into the solution. The “Tafel step” (Equation (3)) provides an additional route to H_2 by the reactive elimination of two adjacent adsorbed surface hydrogen atoms.



The Faradaic current density (i_F) corresponding to the VHT mechanism is given by:

$$i_F = F[-k_1(1 - \theta)C_1 + k_{-1}\theta - k_2\theta C_1 + k_{-2}C_2(1 - \theta)] \quad (4)$$

where C_1 and C_2 represent the H^+ and H_2 concentrations in solutions, k_1 , k_{-1} , k_2 , and k_{-2} represent the forward and reverse rate constants for Reactions (1) and (2), respectively, θ represents the fractional coverage of H_{ads} , and F is the Faraday constant. The concentration gradients for H^+ and H_2 are ignored in the model derivation since the measurements are performed in the moderate overpotential in which diffusion does not contribute significantly. However, this may not be correct at higher overpotentials. The rate constants are expressed as:

$$k_1 = k_1^0 e^{-a_1(E - E_{\text{eq}})} \quad (5)$$

$$k_{-1} = k_{-1}^0 e^{b_1(E - E_{\text{eq}})} \quad (6)$$

$$k_2 = k_2^0 e^{-a_2(E - E_{\text{eq}})} \quad (7)$$

$$k_{-2} = k_{-2}^0 e^{b_2(E - E_{\text{eq}})} \quad (8)$$

$$k_3 = k_3^0 \quad (9)$$

$$k_{-3} = k_{-3}^0 \quad (10)$$

Here, E is the applied potential, E_{eq} is the standard equilibrium potential [E_{eq} : 0.0025 V vs. SHE in H_2SO_4 (0.5 M), E_{eq} : 0.023 V vs. SHE in H_2SO_4 (1.0 M)], k_i^0 is the standard rate

constant of Reactions (1)–(3), $b_i = \frac{n\alpha_i F}{RT}$, and $a_i = \frac{n(1-\alpha_i)F}{RT}$. The current is a function of surface coverage (θ) and V , the total differential of Equation (4) is then:

$$di = \left(\frac{\partial i}{\partial \theta} \right)_E d\theta + \left(\frac{\partial i}{\partial E} \right)_\theta dE \quad (11)$$

Therefore,

$$\frac{1}{Z_f} = \left(\frac{\partial i}{\partial \theta} \right)_E \frac{d\theta}{dE} + \left(\frac{\partial i}{\partial E} \right)_\theta \quad (12)$$

where $Z_f = \frac{dE}{di}$. The partial differentials are then easily obtained as:

$$A = \left(\frac{\partial i}{\partial \theta} \right)_E = F[k_1 C_1 + k_{-1} - k_2 C_1 - k_{-2} C_2] \quad (13)$$

$$B = \left(\frac{\partial i}{\partial E} \right)_\theta = F[a_1 k_1 C_1 - a_1 k_1 \theta_{ss} C_1 + b_1 k_{-1} \theta_{ss} + a_2 k_2 \theta C_1 + b_2 k_{-2} C_2 - b_2 k_{-2} C_2 \theta_{ss}] \quad (14)$$

The variation of θ with time resulting from the imposition of the sinusoidal excitation can be calculated from the mass balance equation, assuming Langmuir adsorption conditions:

$$\Gamma \frac{d\theta}{dt} = k_1 C_1 (1 - \theta) - k_{-1} \theta - k_2 C_1 \theta + k_{-2} C_2 (1 - \theta) - k_3 \theta^2 + k_{-3} (1 - \theta)^2 C_2 \quad (15)$$

Taking the total differential of Equation (15) and noting that for a sinusoidal variation (16)

$$\frac{d\Delta\theta_{ss}}{dt} = j\omega\Delta\theta_{ss} \quad (16)$$

we obtain

$$H = \frac{d\theta_{ss}}{dE} = \frac{-a_1 k_1 C_1 (1 - \theta_{ss}) - b_1 k_{-1} \theta_{ss} + a_2 k_2 C_1 \theta_{ss} + b_2 k_{-2} C_2 (1 - \theta_{ss})}{k_1 C_1 + k_{-1} + k_2 C_1 + k_{-2} C_2 + 2k_3 \theta_{ss} + 2k_{-3} C_2 (1 - \theta_{ss}) + j\omega\Gamma} \quad (17)$$

The steady-state fractional surface coverage can be obtained by solving the following second-order quadratic equations:

$$(k_{-3} C_2 - k_3) \theta_{ss}^2 + (-k_1 C_1 - k_{-1} - k_2 C_1 - k_{-2} C_2 - 2k_{-3} C_2) \theta_{ss} + (k_1 C_1 + k_{-2} C_2 + k_{-3} C_2) = 0 \quad (18)$$

We define the parameters as follows to solve the steady-state fractional surface coverage θ_{ss} :

$$a = k_{-3} C_2 - k_3 \quad (19a)$$

$$b = (-k_1 C_1 - k_{-1} - k_2 C_1 - k_{-2} C_2 - 2k_{-3} C_2) \quad (19b)$$

$$c = (k_1 C_1 + k_{-2} C_2 + k_{-3} C_2) \quad (19c)$$

$$\theta_{1ss} = \frac{\left(-b + (b^2 - 4ac)^{\frac{1}{2}} \right)}{2a} \quad (19d)$$

$$\theta_{2ss} = \frac{\left(-b - (b^2 - 4ac)^{\frac{1}{2}} \right)}{2a} \quad (19e)$$

Only θ_{2ss} gives positive values; therefore, θ_{1ss} can be eliminated from the admittance equation.

Substitution of Equations (13), (14) and (17) in Equation (12) gives the admittance as follows:

$$\frac{1}{Z_f} = Y_f = F[(A \times H) + B] \quad (20)$$

The total impedance of the system can then be expressed as:

$$Z_T = R_s + \left[\frac{1}{Z_f} + \frac{1}{Z_{cdl}} \right]^{-1} \quad (21)$$

where Z_f is the Faradaic impedance for the HER, which is the inverse of the interfacial admittance (Equation (20)), Z_{cdl} represents the double-layer capacitor's impedance, and R_s is the solution resistance. The double-layer capacitance in the circuit was changed to a constant phase element (CPE) because, as found in this work, depressed semicircles are typically seen on solid electrodes in the Nyquist plane. The need for this modification reflects the inhomogeneity of the polycrystalline electrode surface, which creates a variety of capacitive states, and consequently, a distribution in the relaxation time. The impedance of the CPE is described in Equation (22):

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (22)$$

where Y_0 is a constant relating to the electrode capacitance and n is a constant that reflects the depression angle.

4. Model Optimization Procedure

In the first step, the pre-exponential rate constants and charge-transfer coefficients were estimated by optimizing the DC part of the model on the experimental PDP data. The best-fit parameters obtained from the first step were then used as initial guesses to optimize the model on the experimental EIS data. The optimization of the model on the PDP data was run in MATLAB, Version R2021a, and the optimization of the model on the EIS data was performed using a genetic curve-fitting approach, implemented in Igor Pro (Version 8.04, WaveMetrics, Inc., Portland, OR, USA) with a custom software interface powered by Andrew Nelson's "gencurvefit" package [46].

5. Results and Discussions

5.1. Optimization of the Model on Potentiodynamic Polarization (PDP) Data

Figure 1 shows the DC part of the model optimized on the experimental PDP data in H_2SO_4 (0.5 and 1.0 M) solutions, and the best-fit parameters are summarized in Table 1. In Figure 1, the red lines demonstrate the experimental PDP data and the black dashed lines show the simulated PDP data; as can be seen, a near-perfect match exists between the experimental and simulated PDP data (very small values of χ^2). This demonstrates that the model accounts for the experimental data well. The model parameters, including charge-transfer coefficients and pre-exponential rate constants, are summarized in Table 1 and are used as initial guesses in the model optimization on EIS data in the final step of this analysis. The reduced goodness-of-fit at lower potentials may be attributed to the surface diffusion of hydrogen reported to occur at a lower potential [24], a factor that our model disregards.

Table 1. Best-fit parameters obtained from the model optimization on the experimental PDP data.

	$k_1^0(\text{cm}\cdot\text{s}^{-1})$	α_1	$k_{-1}^0(\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1})$	$k_2^0(\text{cm}\cdot\text{s}^{-1})$	α_2	$k_{-2}^0(\text{cm}\cdot\text{s}^{-1})$	$k_3^0(\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1})$	$k_{-3}^0(\text{cm}\cdot\text{s}^{-1})$
0.5 M	1.78×10^{-7}	0.49	5.92×10^{-5}	4.45×10^{-4}	0.73	1.34×10^{-3}	1.94×10^{-3}	9.78×10^{-4}
1.0 M	4.03×10^{-7}	0.63	3.20×10^{-7}	1.67×10^{-6}	0.74	4.58×10^{-6}	4.75×10^{-4}	1.23×10^{-4}

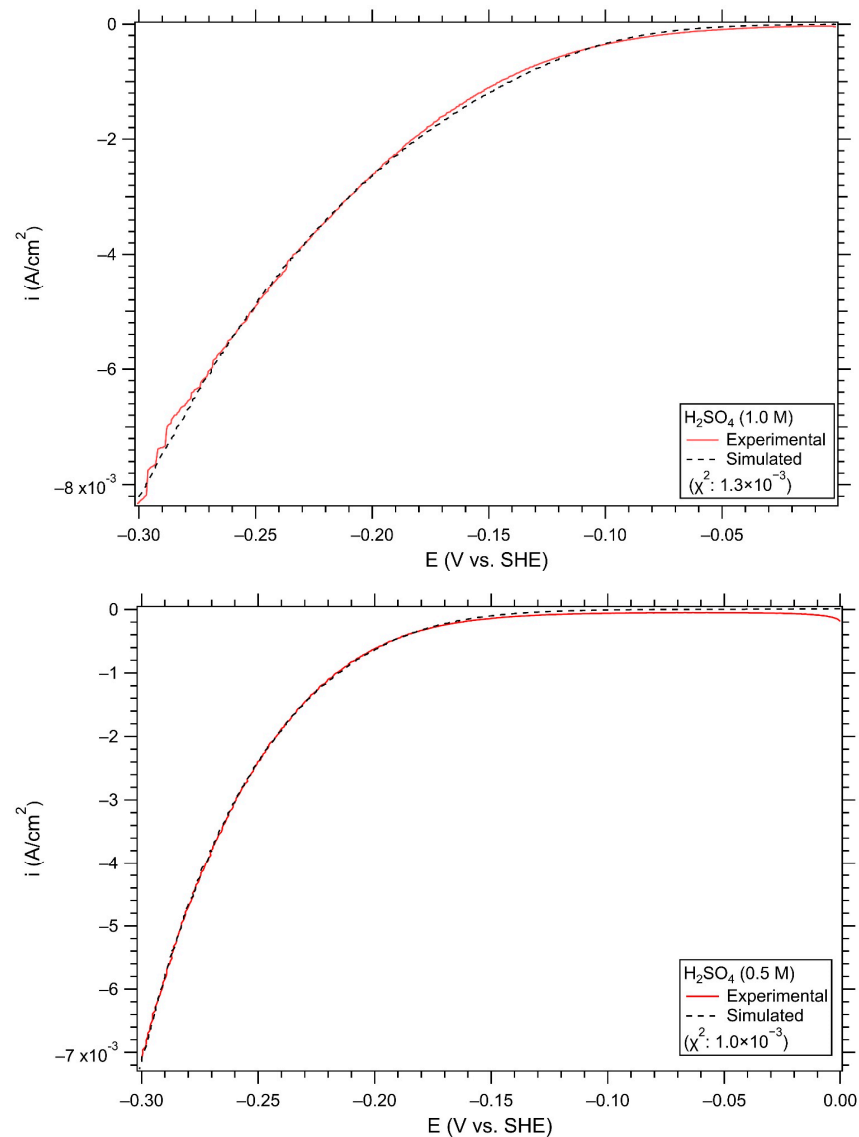


Figure 1. Optimization of the model on potentiodynamic polarization (PDP) data in H_2SO_4 (0.5 and 1.0 M).

5.2. Validity of the Impedance Data

Linear system theory (LST) requires that causality, stability, linearity, and finiteness must all be met by the system under consideration [49–51]. Therefore, a linear Kramer–Kronig transformation (KKT) was used to verify that all EIS data satisfy these important criteria. Figure 2 illustrates the KKT of the EIS data collected in H_2SO_4 (0.5 and 1.0 M) at various potentials. The results indicate that the LST constraints are fulfilled by the excellent agreement between the predicted imaginary and real components from KKT and the experimental data. Any data points that did not satisfy the KKT were eliminated before further analysis.

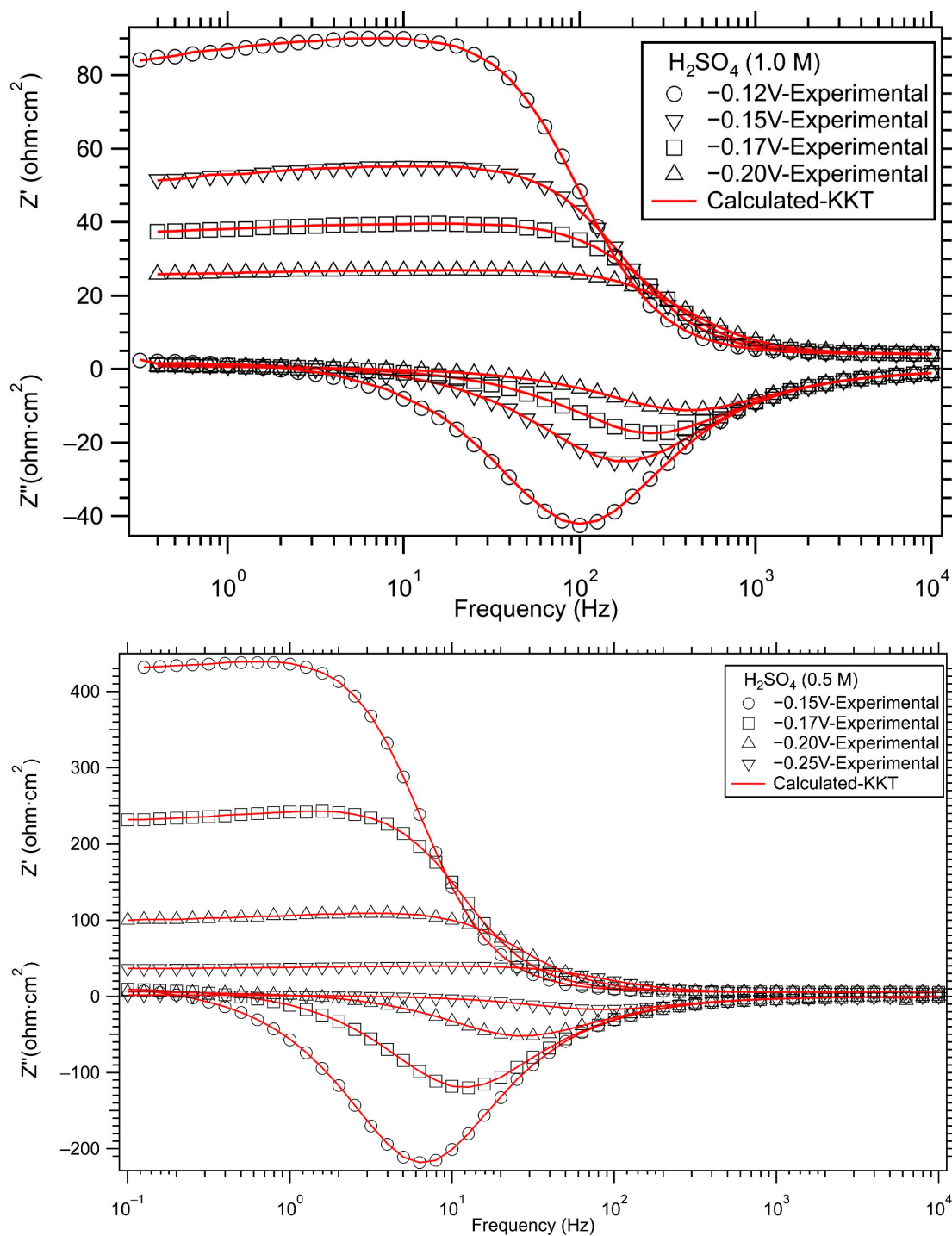


Figure 2. Kramers–Kronig transforms of the real and imaginary components of the EIS data.

5.3. Model Optimization on the EIS Data

Figure 3 shows Nyquist and Bode phase plots of the EIS spectra for the HER on polycrystalline Au in H_2SO_4 (0.5 and 1.0 M) solutions as a function of potential, based on the optimized impedance model. The kinetic parameters obtained from the optimization are summarized in Tables 2 and 3. The Nyquist plots are depressed semi-circles with an inductive response at lower frequencies, representing adsorption–desorption of the H_{ads} intermediate. Also, upon increasing the concentration of the sulfuric acid solution (lowering the pH) and increasing the applied cathodic potential, the magnitude of the impedance decreases, indicating more facile electron transfer. These graphs also show the best-fit

results derived from the suggested mechanism as solid lines. The excellent agreement between the experimental findings and those predicted by the model provides evidence that the proposed mechanism is viable and provides confidence that the parameter values are adequate to explain the experimental findings.

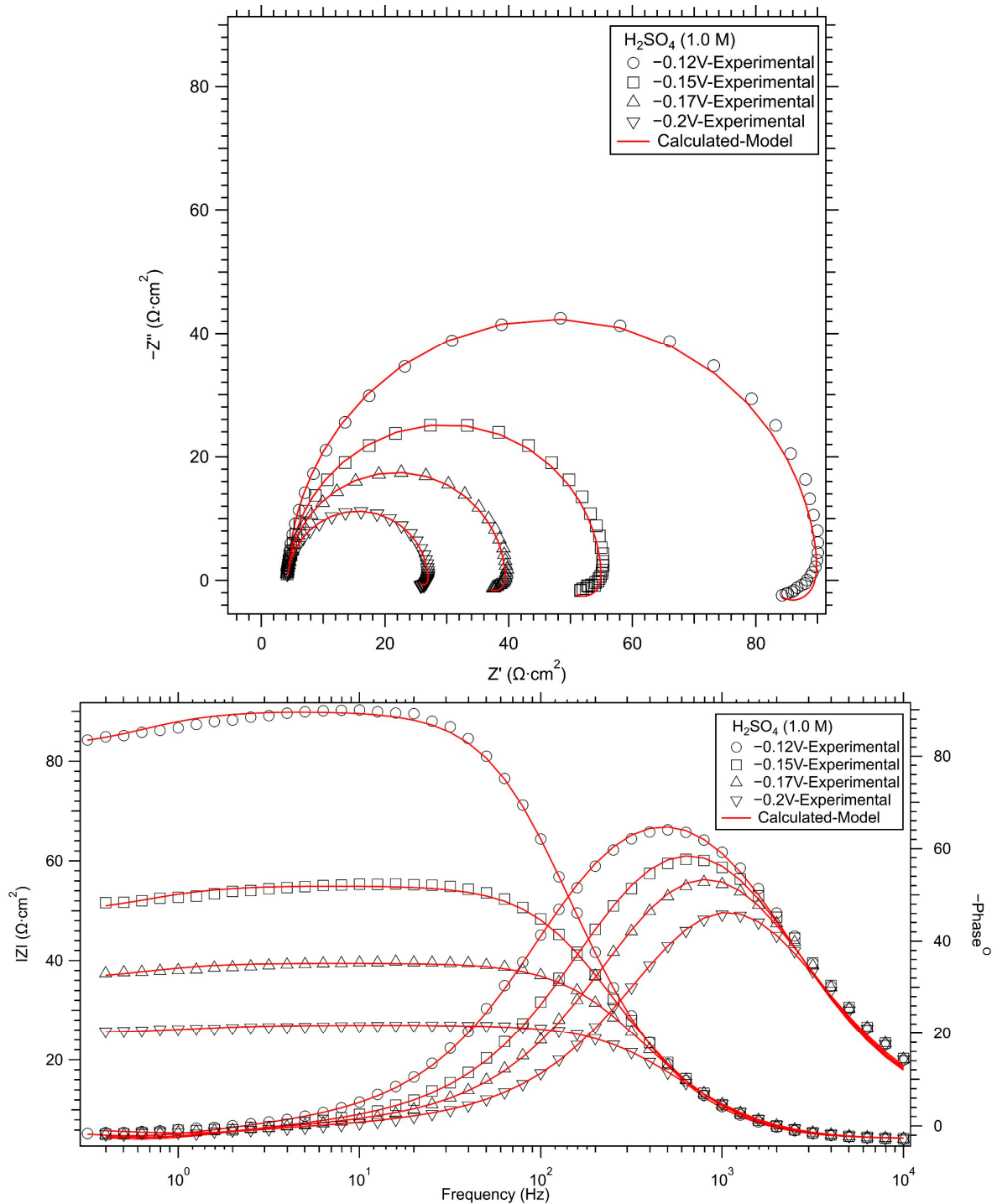


Figure 3. Cont.

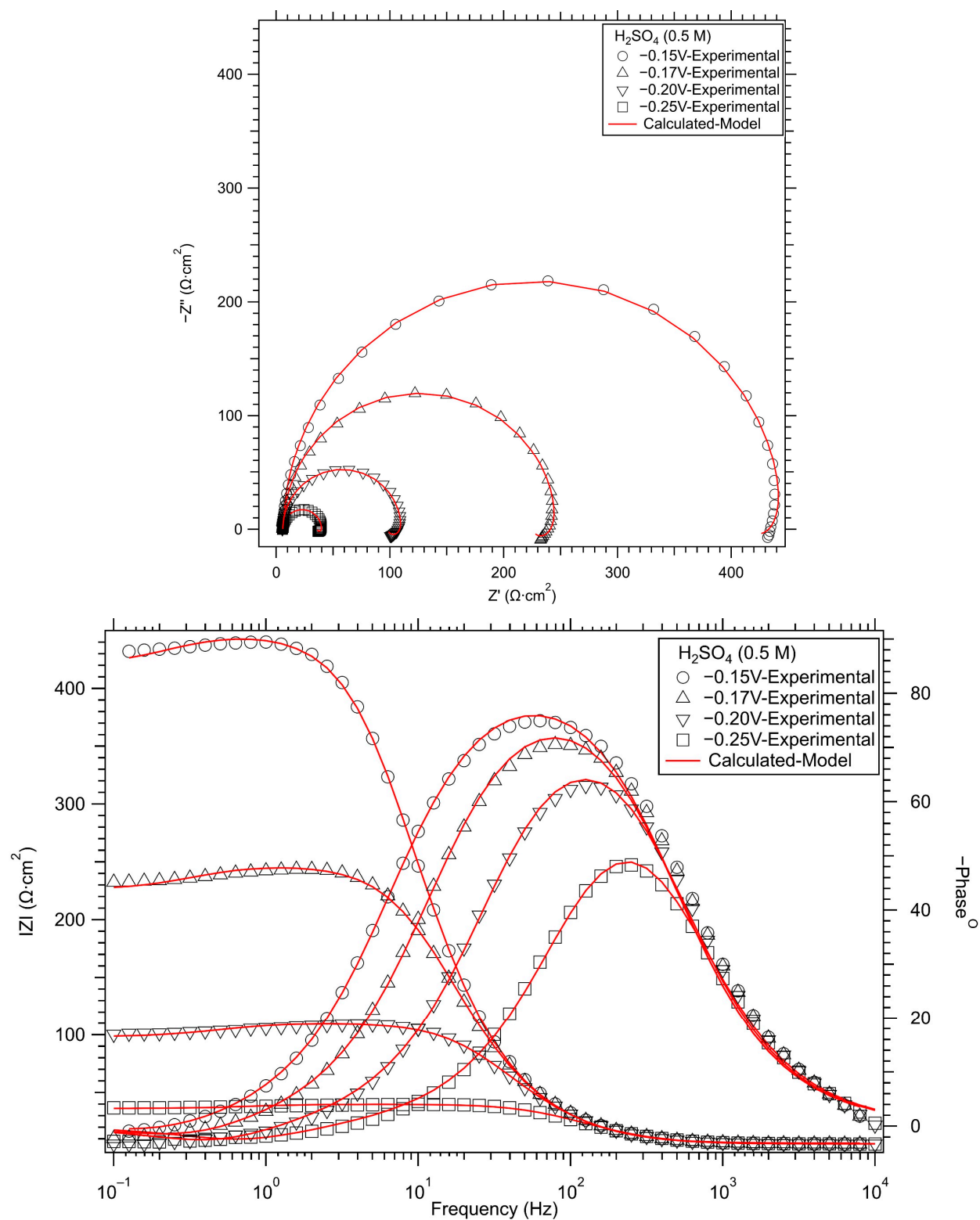


Figure 3. Nyquist and Bode plots of the EIS spectra for the HER on Au in aqueous H_2O_4 (0.5 and 1.0 M) solutions, at several cathodic overpotentials. The model predictions are shown as lines, and the experimental data are shown as points.

Table 2. Best-fit parameters and calculated rate constants obtained from the model optimization on experimental EIS data in H₂SO₄ (0.5 M).

H ₂ SO ₄ (0.5 M)	−0.15 V	−0.17 V	−0.20 V	−0.25 V
k_1^0 (cm·s ^{−1})	1.07×10^{-7}	1.28×10^{-7}	1.97×10^{-7}	7.09×10^{-7}
k_1 (cm·s ^{−1})	1.38×10^{-6}	2.49×10^{-6}	5.95×10^{-6}	2.31×10^{-5}
k_{-1}^0 (mol·cm ^{−2} ·s ^{−1})	5.54×10^{-12}	5.86×10^{-12}	5.96×10^{-12}	2.34×10^{-11}
k_{-1} (mol·cm ^{−2} ·s ^{−1})	1.82×3	1.24×10^{-13}	5.96×10^{-14}	3.48×10^{-14}
k_2^0 (cm·s ^{−1})	2.18×10^{-6}	2.34×10^{-6}	3.55×10^{-6}	8.19×10^{-6}
k_2 (cm·s ^{−1})	4.07×10^{-6}	7.12×10^{-6}	1.37×10^{-5}	3.82×10^{-5}
k_{-2}^0 (cm·s ^{−1})	5.35×10^{-6}	7.08×10^{-6}	5.61×10^{-6}	5.08×10^{-6}
k_{-2} (cm·s ^{−1})	2.39×10^{-8}	2.33×10^{-8}	7.17×10^{-9}	7.58×10^{-9}
k_3^0 (cm·s ^{−1})	8.26×10^{-7}	9.71×10^{-7}	4.78×10^{-7}	3.56×10^{-7}
k_3 (cm·s ^{−1})	8.26×10^{-7}	9.71×10^{-7}	4.78×10^{-7}	3.56×10^{-7}
k_{-3}^0 (cm·s ^{−1})	1.35×10^{-4}	3.11×10^{-4}	2.86×10^{-4}	7.78×10^{-5}
k_{-3} (cm·s ^{−1})	1.35×10^{-4}	3.11×10^{-4}	2.86×10^{-4}	7.78×10^{-5}
α_1	0.57	0.57	0.57	0.65
α_2	0.90	0.84	0.83	0.85
R_s (Ω)	6.22	6.12	5.82	5.59
Y_0 (S·s ⁿ ·cm ^{−2})	5.53×10^{-5}	5.50×10^{-5}	5.32×10^{-5}	5.25×10^{-5}
n	0.993	0.995	1.00	1.00
θ_{ss}	0.038	0.046	0.093	0.18
Γ (mol·cm ^{−2})	4.86×10^{-8}	4.99×10^{-8}	3.91×10^{-8}	4.49×10^{-8}

Table 3. Best-fit parameters and calculated rate constants obtained from the model optimization on experimental EIS data in H₂SO₄ (1.0 M).

H ₂ SO ₄ (1.0 M)	−0.12 V	−0.15 V	−0.17 V	−0.20 V
k_1^0 (cm·s ^{−1})	9.37×10^{-8}	1.42×10^{-7}	1.26×10^{-7}	1.34×10^{-7}
k_1 (cm·s ^{−1})	2.69×10^{-6}	5.16×10^{-6}	7.49×10^{-6}	1.22×10^{-5}
k_{-1}^0 (mol·cm ^{−2} ·s ^{−1})	3.71×10^{-12}	1.57×10^{-12}	3.69×10^{-13}	7.38×10^{-13}
k_{-1} (mol·cm ^{−2} ·s ^{−1})	3.85×10^{-13}	6.64×10^{-14}	1.17×10^{-14}	1.11×10^{-14}
k_2^0 (cm·s ^{−1})	6.02×10^{-6}	4.14×10^{-6}	4.89×10^{-6}	4.62×10^{-6}
k_2 (cm·s ^{−1})	8.94×10^{-6}	1.11×10^{-5}	1.40×10^{-5}	1.91×10^{-5}
k_{-2}^0 (cm·s ^{−1})	7.83×10^{-6}	2.63×10^{-6}	2.80×10^{-7}	1.31×10^{-7}
k_{-2} (cm·s ^{−1})	4.37×10^{-8}	8.22×9	4.29×10^{-10}	8.93×10^{-11}
k_3^0 (cm·s ^{−1})	1.56×10^{-6}	5.07×10^{-7}	4.47×10^{-7}	7.03×10^{-7}
k_3 (cm·s ^{−1})	1.56×10^{-6}	8.91×10^{-7}	4.47×10^{-7}	7.03×10^{-7}
k_{-3}^0 (cm·s ^{−1})	2.36×10^{-4}	7.34×10^{-5}	2.06×10^{-4}	7.81×10^{-4}
k_{-3} (cm·s ^{−1})	2.36×10^{-4}	7.34×10^{-5}	2.06×10^{-4}	7.81×10^{-4}
α_1	0.41	0.47	0.46	0.48
α_2	0.93	0.85	0.86	0.84
R_s (Ω)	4.30	4.31	4.25	4.22
Y_0 (S·s ⁿ ·cm ^{−2})	1.89×10^{-5}	1.77×10^{-5}	1.76×10^{-5}	1.79×10^{-5}

Table 3. Cont.

H ₂ SO ₄ (1.0 M)	−0.12 V	−0.15 V	−0.17 V	−0.20 V
<i>n</i>	0.992	0.997	0.995	0.991
θ_{ss}	0.052	0.11	0.14	0.15
Γ (mol·cm ^{−2})	4.87×10^{-8}	4.80×10^{-8}	4.52×10^{-8}	3.98×10^{-8}

Figure 4 shows the predicted steady-state current density calculated using the extracted parameters (Equation (4)) from model optimization on the EIS data. The experimental steady-state current density results and those predicted by the model correspond quite well, demonstrating that the proposed mechanism accounts for the HER on gold in H₂SO₄ (0.5 and 1.0 M) solutions well.

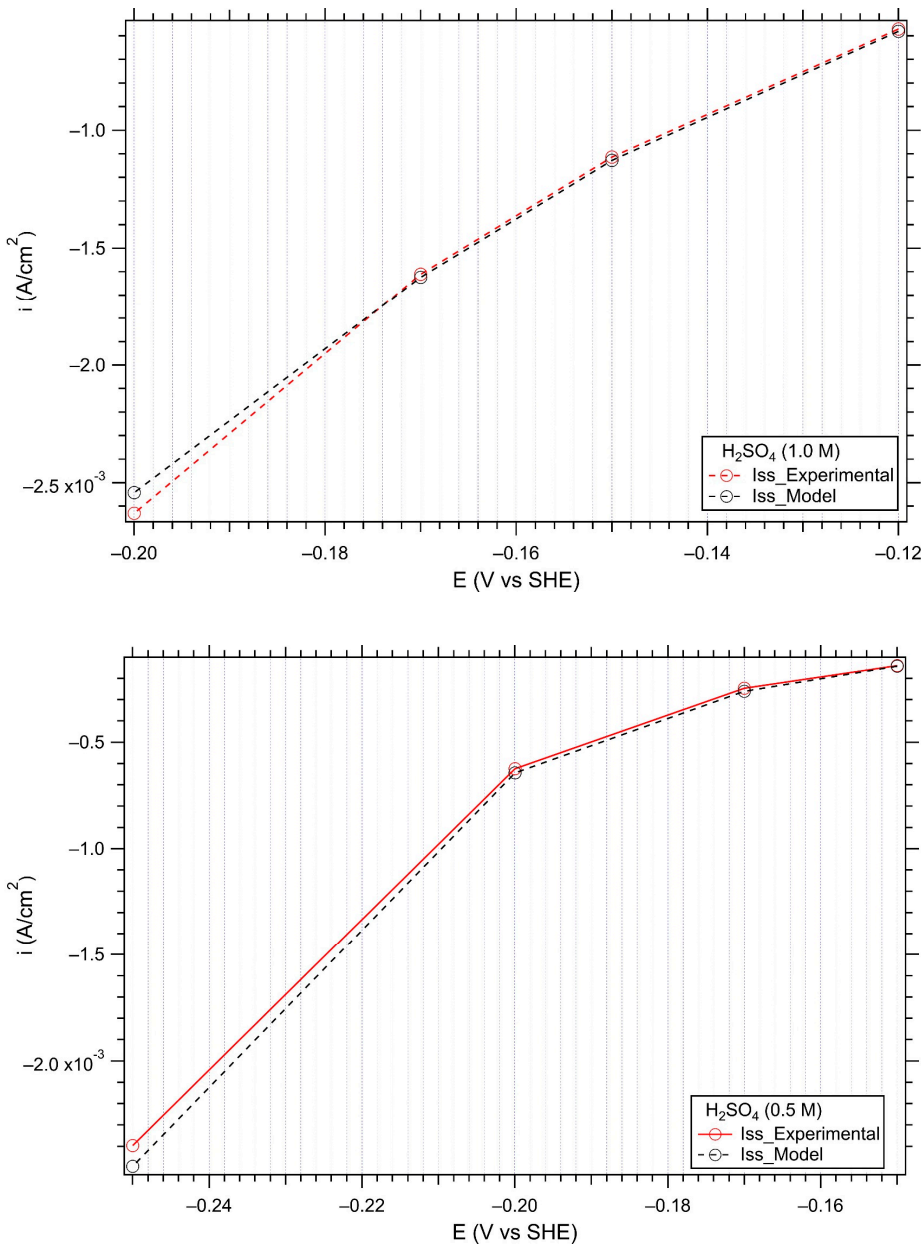
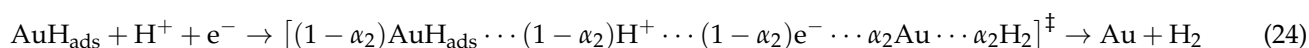
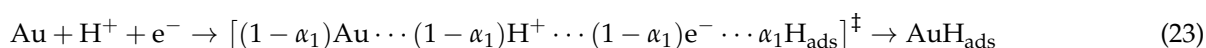


Figure 4. Steady-state current density predicted by the impedance model and comparison with the experimental values at each applied potential in H₂SO₄ (0.5 and 1.0 M) solutions.

Figures 5 and 6 show the calculated rate constants and estimated charge-transfer coefficients from optimization of the model on the EIS data for Reactions (1) and (2) as a function of potential. The rate constants for the forward reactions increase when increasing the overpotential, and the opposite occurs for the reverse reactions. The logarithm of the rate constants changes linearly with potential, in agreement with the theory of electrochemical kinetics [52]. In addition, no systematic dependency of the charge-transfer coefficients on potential is evident in Figure 6. The average values of the forward and backward standard rate constants for Reactions (1) and (2) (k_1^0 , k_{-1}^0 and k_2^0 , k_{-2}^0) in the 0.5 M H₂SO₄ solution are of the order of 10^{-7} (cm·s⁻¹) and 10^{-11} (mol·cm⁻²·s⁻¹), and 10^{-6} (cm·s⁻¹) and 10^{-6} (cm·s⁻¹), and (k_1^0 , k_{-1}^0 and k_2^0 , k_{-2}^0) in the 1.0 M H₂SO₄ solution are of the order of 10^{-7} (cm·s⁻¹) and 10^{-12} (mol·cm⁻²·s⁻¹), and 10^{-6} (cm·s⁻¹) and 10^{-6} (cm·s⁻¹), respectively. The estimated rate constants for the VHT steps exhibit a similar range of magnitude to the values reported in Meethal's study for the HER on gold in the HClO₄ solution [35]. Furthermore, as expected, the forward and backward standard rate constants values for Reaction 3 in both solutions remain relatively unaffected by changes in potential. The average values of the charge-transfer coefficients (α_1 and α_2) are 0.59 and 0.85 in 0.5 M H₂SO₄, and 0.45 and 0.87 in 1.0 M H₂SO₄, respectively. The average magnitudes of the charge-transfer coefficients obtained from our model optimization on both PDP and EIS data, however, do not align with the values reported in Meethal's study of HER kinetics on gold in a HClO₄ solution, (α_1 , 0.72; α_2 , 0.55) [35]. Those results have the opposite order of our model's prediction for those values in the 0.5 and 1.0 M H₂SO₄ solutions. The observed discrepancies in our experimental results could potentially be attributed to the choice of electrolytes used. In our study, we employed a sulfuric acid solution containing adsorbing anions such as bisulfate and sulfate [53]. In Meethal's experiment, however, the utilized perchloric acid and the perchlorate ions exhibit a lower affinity for adsorption onto gold surfaces. Furthermore, Meethal's model incorporates diffusion effects, which may have an impact on the determination of charge-transfer coefficients in the system.

In the context of the theory of partial charges for the kinetics of electrochemical processes, the transfer coefficient is a measure of the location of the activated complex (transition state) between the initial and final states. For Reactions (1) and (2), the partial-charge representation of the reactions may be written as:



where superscript “ $\ddagger$ ” designates the transition state. The schemes can be tested by setting α_1 and α_2 equal zero (initial state) and 1 (final state). As a result, the character of the transition state can be judged from the transfer coefficient, which is a measure of where it occurs along the reaction coordinate. Thus, if $0 < \alpha < 0.2$ the transition state is said to be “reactant-like”, if $0.8 < \alpha < 1$ the transition state is “product like”, and if $0.2 < \alpha < 0.8$ the transition state is intermediate between the reactants and products. Based on these considerations, the transition state for Reaction (1) is intermediate between reactants and products at both concentrations, whereas the transition state for Reaction (2) is product-like at both concentrations.

Furthermore, fractional surface coverages of adsorbed hydrogen (θ_{Hads}) on gold in aqueous H₂SO₄ (0.5 and 1.0 M) solutions, calculated from Equation (19e) and summarized in Tables 2 and 3. The fractional surface coverage of H_{ads} increases with an increasing overpotential; however, the small values of θ_{Hads} demonstrate a weak adsorption of hydrogen on the gold surface overall. The θ_{Hads} estimated in this study is in a good agreement with those values reported in the literature for the HER on gold in acidic solutions [24,35].

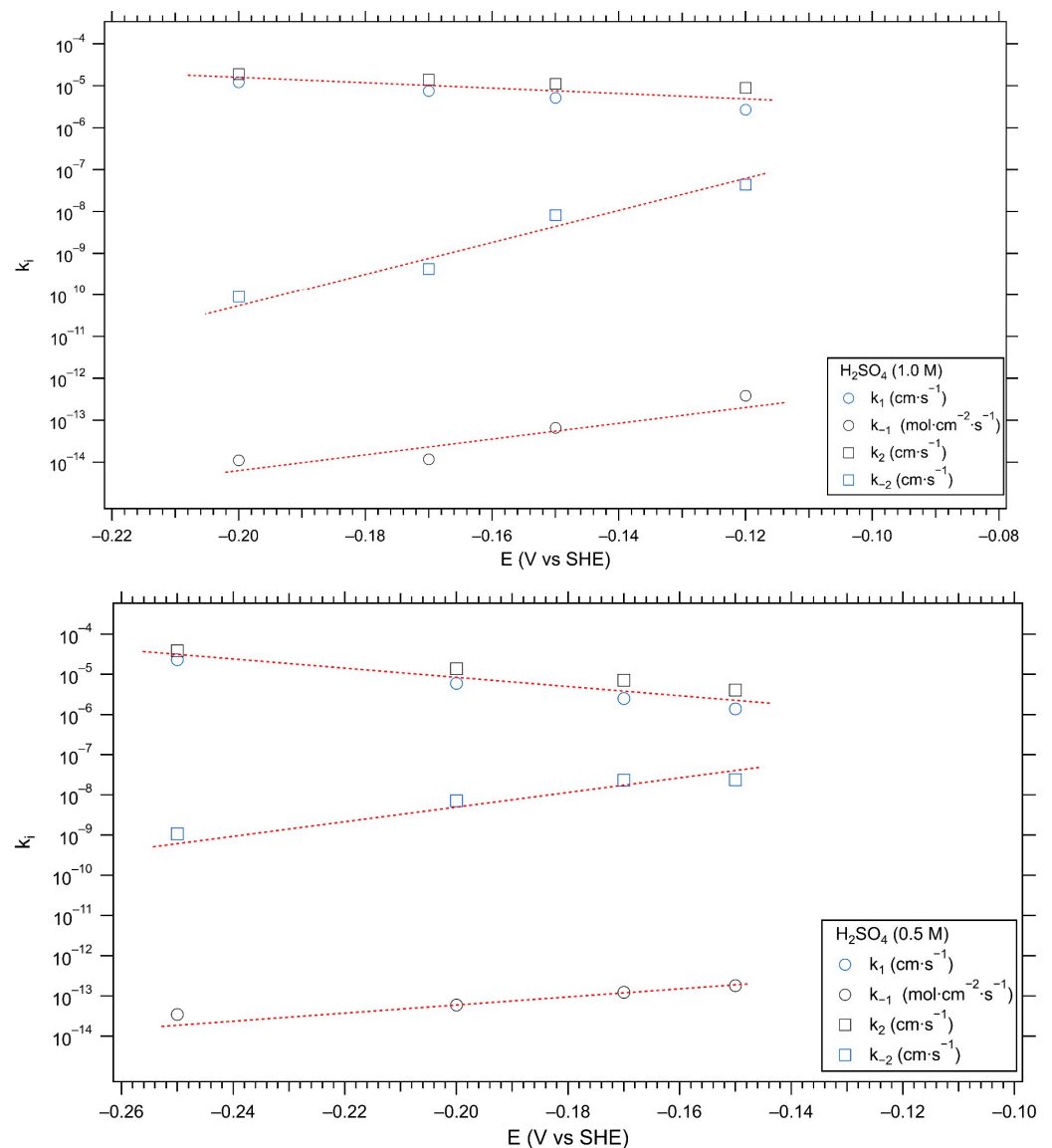


Figure 5. Calculated rate constants as a function of potential for HER reactions on gold in H_2SO_4 (0.5 and 1.0 M) solutions.

Figures 7 and 8 depict the comparison between the Tafel slope estimated from the experimental data and the Tafel slope predicted by the model in H_2SO_4 solutions (0.5 M and 1.0 M). The Tafel slope in H_2SO_4 (0.5 M) is estimated to be 81 mV/dec, while in H_2SO_4 (1.0 M) it is approximately 120–124 mV/dec. Literature reports of the Tafel slopes for the HER on gold in acidic solutions reveal two distinct slopes depending on the applied overpotentials [22,24,30,54–58]. At lower overpotentials, the Tafel slope ranges from 30 to 97 mV/dec, while at larger overpotentials, it falls within the range of 97 to 141 mV/dec [22,24,30,54–58]. The Tafel slopes predicted by the model optimizations align well with both the experimental data and the reported values in the literature. This agreement further validates the accuracy and reliability of the model's predictions.

Figure 9 illustrates the estimated exchange current density from the polarization data in H_2SO_4 solutions (0.5 M and 1.0 M). The exchange current densities are estimated from fitting experimental polarization data on Equation (25).

$$i = -i_0 \exp\left(\frac{-n \times F \times \alpha \times (E - E_{eq})}{R \times T}\right) \quad (25)$$

where i_0 is the exchange current density, F is the Faraday constant (96,485 Coulomb/mol), α is the charge-transfer coefficient, T is the temperature, R is the universal gas constant (8.314 J/mol.K) and E_{eq} is the equilibrium potential. Exchange current densities were estimated to be in the order of 5.64×10^{-6} and 1.62×10^{-5} in H_2SO_4 solutions (0.5 M and 1.0 M), respectively.

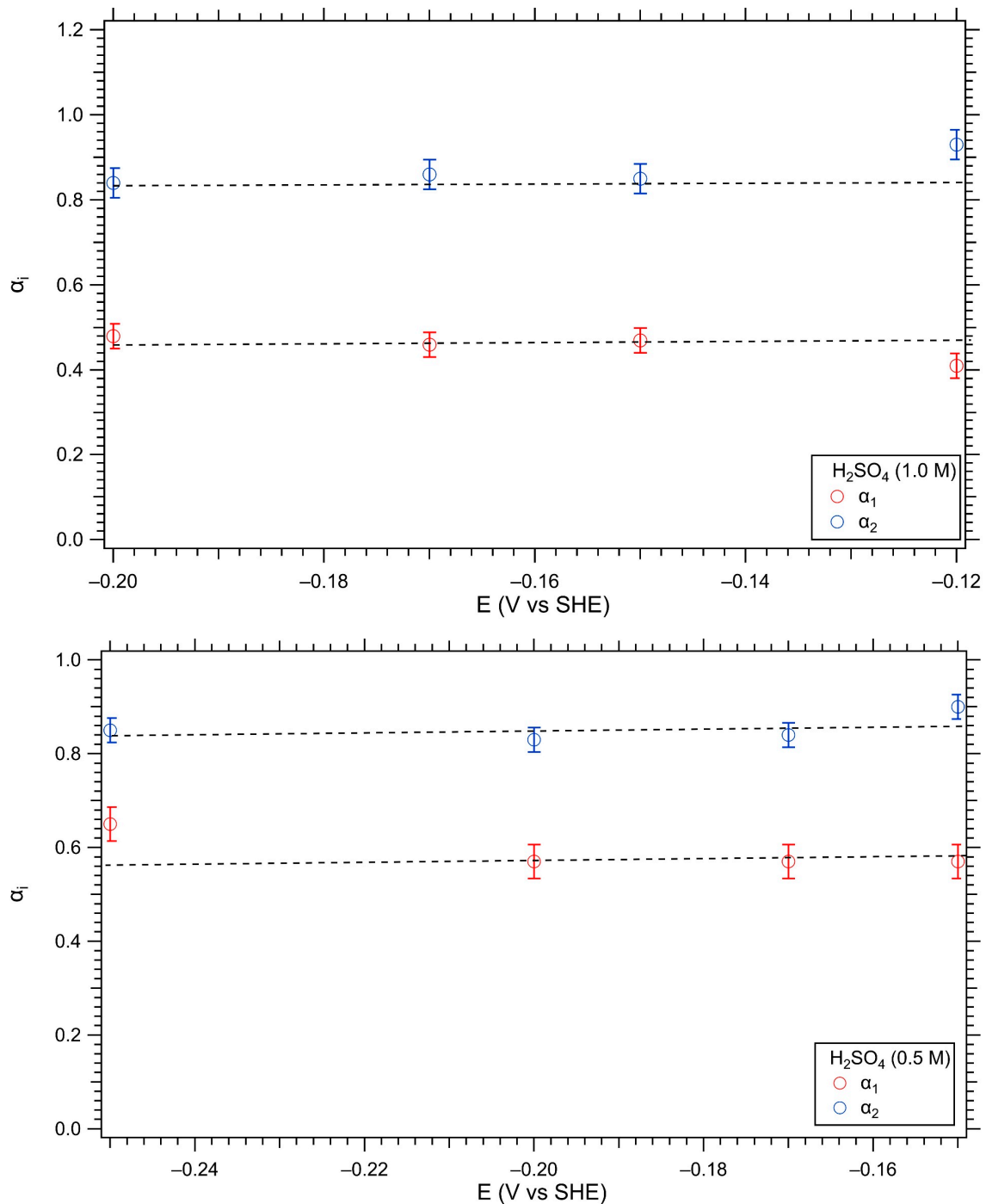


Figure 6. Estimated charge-transfer coefficients for Reactions (1) and (2) from the optimization of the model on EIS data in H_2SO_4 (0.5 and 1.0 M) solutions. The dashed lines are guides to the eye, not fits to the data.

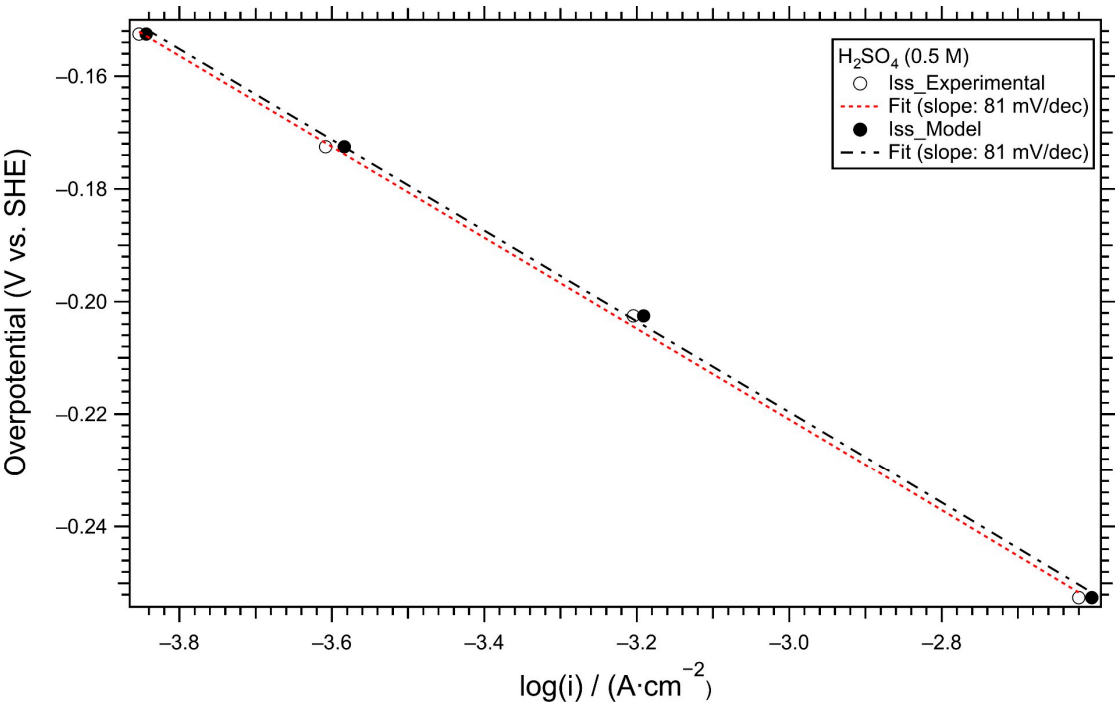


Figure 7. Estimated Tafel slope from steady-state current density of HER on gold in H_2SO_4 (0.5 M), open circles (Experimental), filled circles (Model), and dashed lines are the regression.

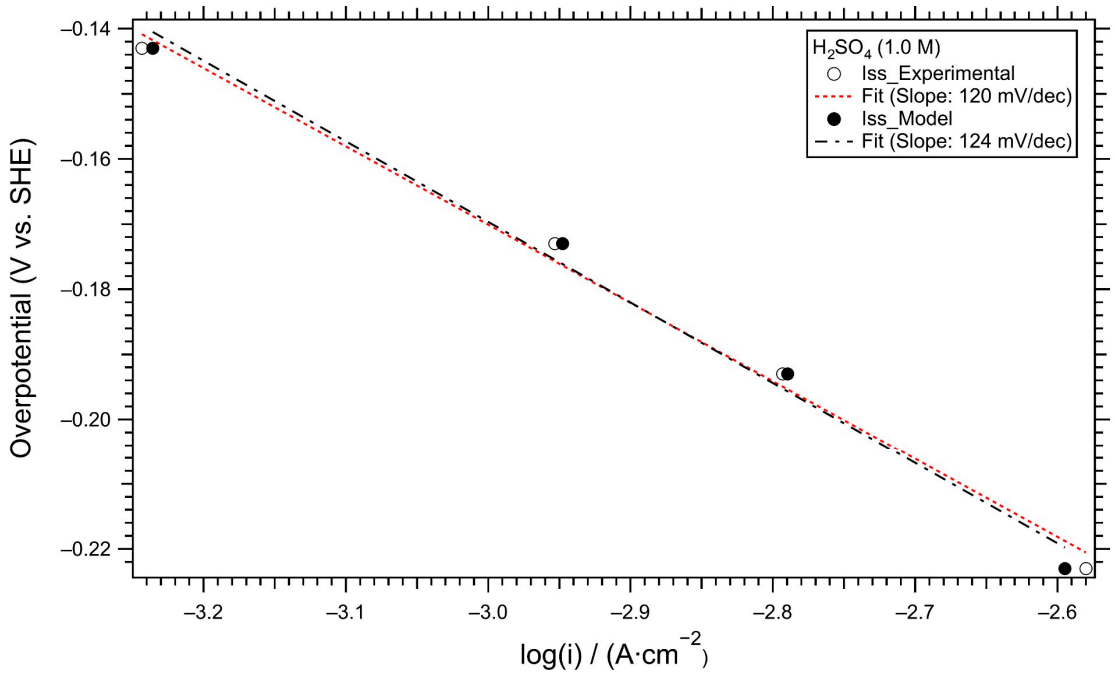


Figure 8. Tafel slope estimated from steady-state current density of HER on gold in H_2SO_4 (1.0 M), open circles (Experimental), filled circles (Model), and dashed lines are the regression.

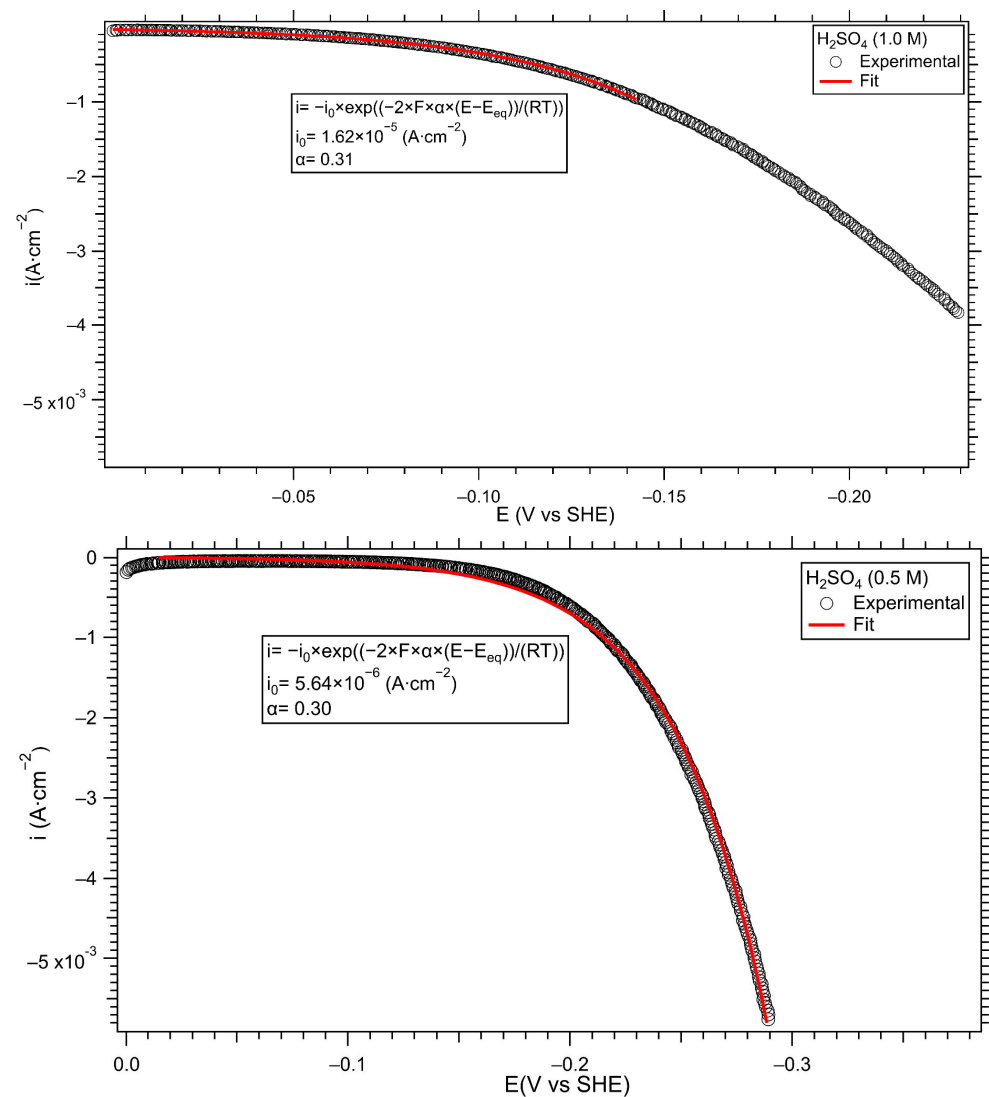


Figure 9. Estimation of exchange current densities of HER on gold in H_2SO_4 solutions (0.5 M and 1.0 M).

5.4. Sensitivity Analysis

To investigate the impact of the model parameters on the calculated impedance, a sensitivity analysis was conducted. In this analysis, each individual parameter was systematically varied to assess its corresponding effect on the total impedance [47]. Figure 11 present the outcomes of the sensitivity analysis carried out on the impedance for H_2SO_4 (0.5 and 1.0 M). It is evident that the charge-transfer coefficients and standard rate constants for the forward and reverse Reaction (1) and for the forward Reaction (2) have a major effect on the calculated impedance from moderate to lower frequencies where the impedance is more sensitive to Faradic (charge transfer) phenomena. The variation of the standard rate constant for the reverse Reaction (2), which is associated with the hydrogen oxidation reaction, does not impact the calculated impedance, which indicates that hydrogen oxidation may not occur at the potential range applied in this study.

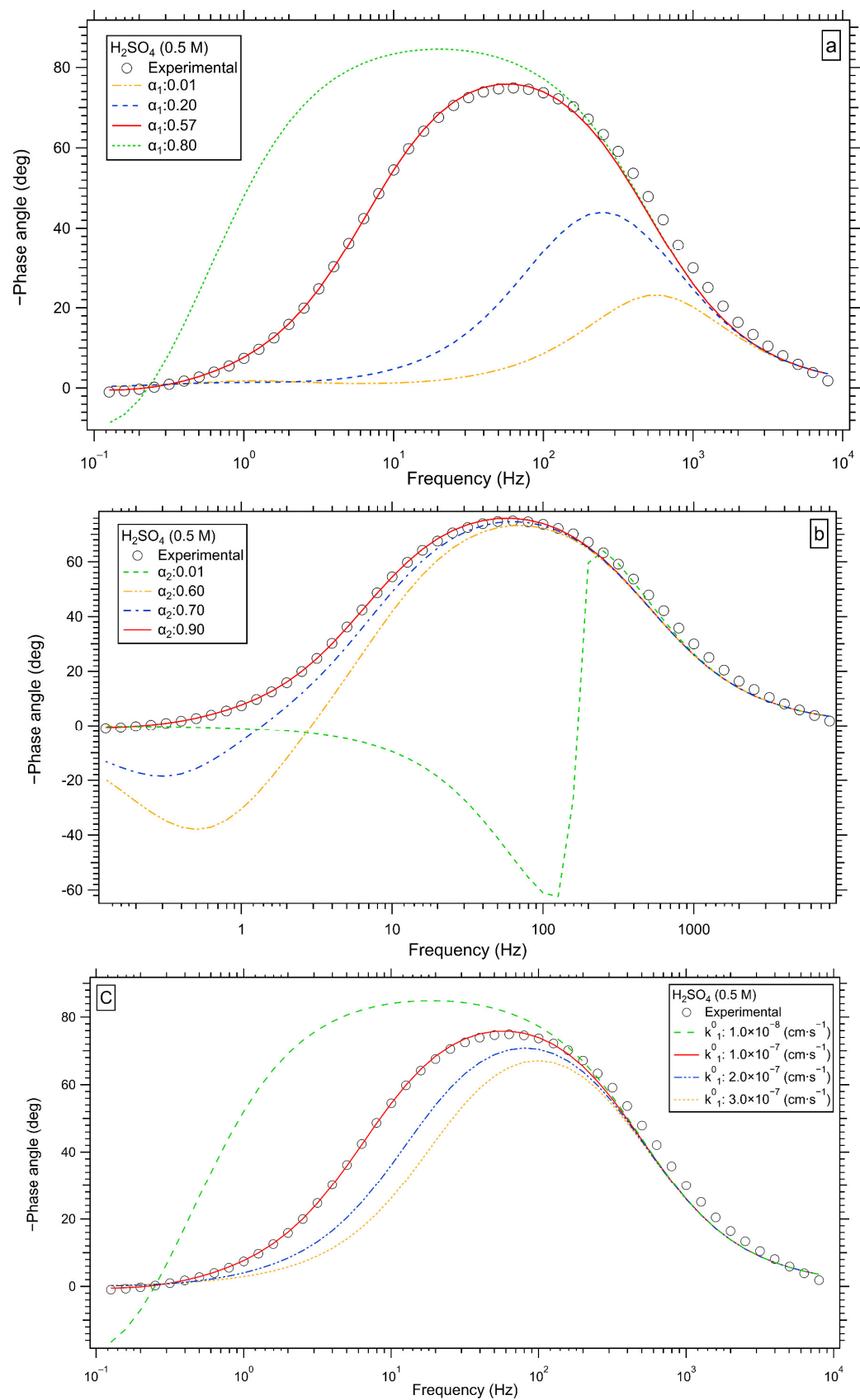


Figure 10. Cont.

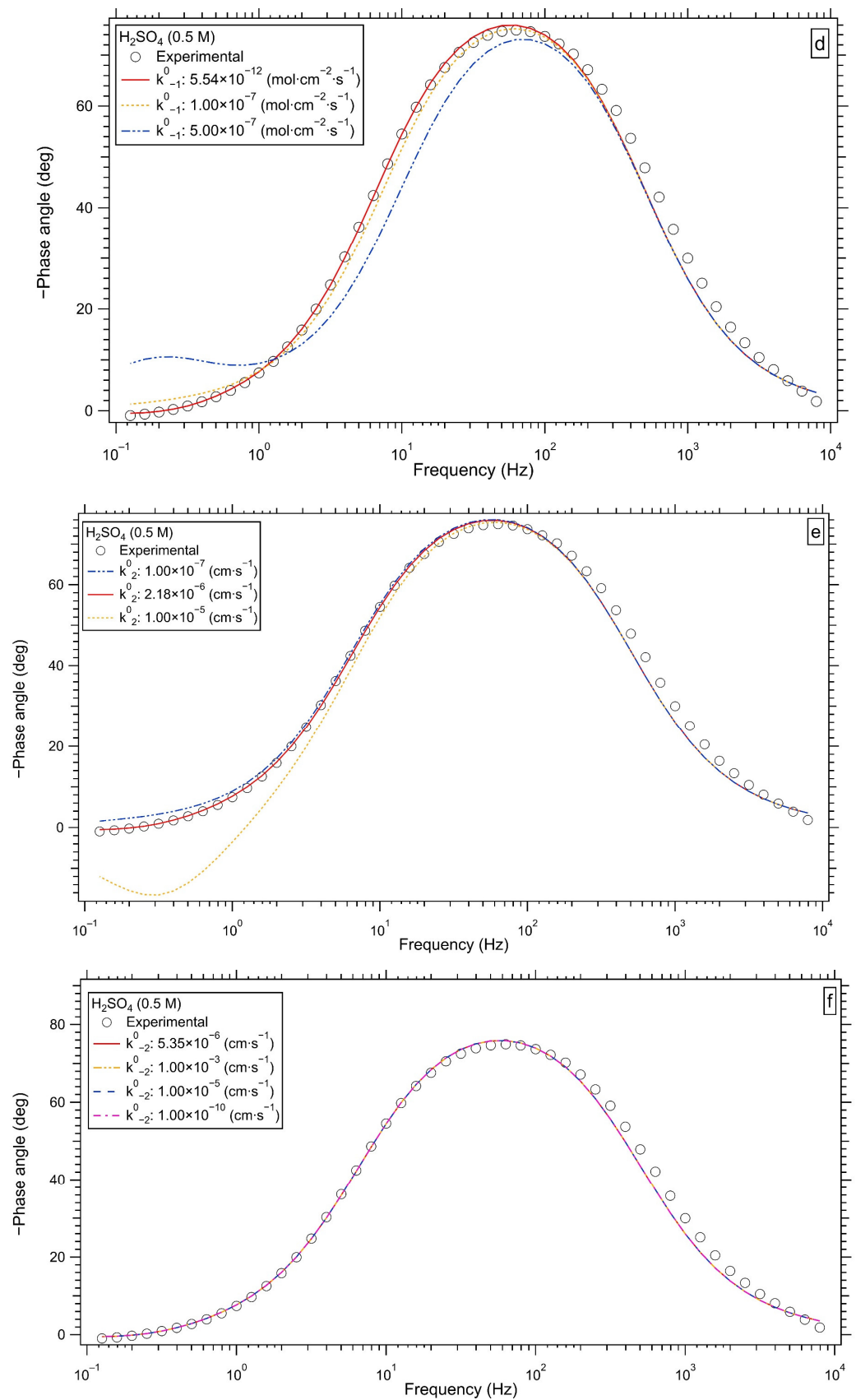


Figure 10. Sensitivity analysis of important electrochemical parameters of charge-transfer coefficients α_1 and α_2 (a,b), and standard rate constants of forward and backward Reactions (1) (c,d) and (2) (e,f) in H_2SO_4 (0.5 M).

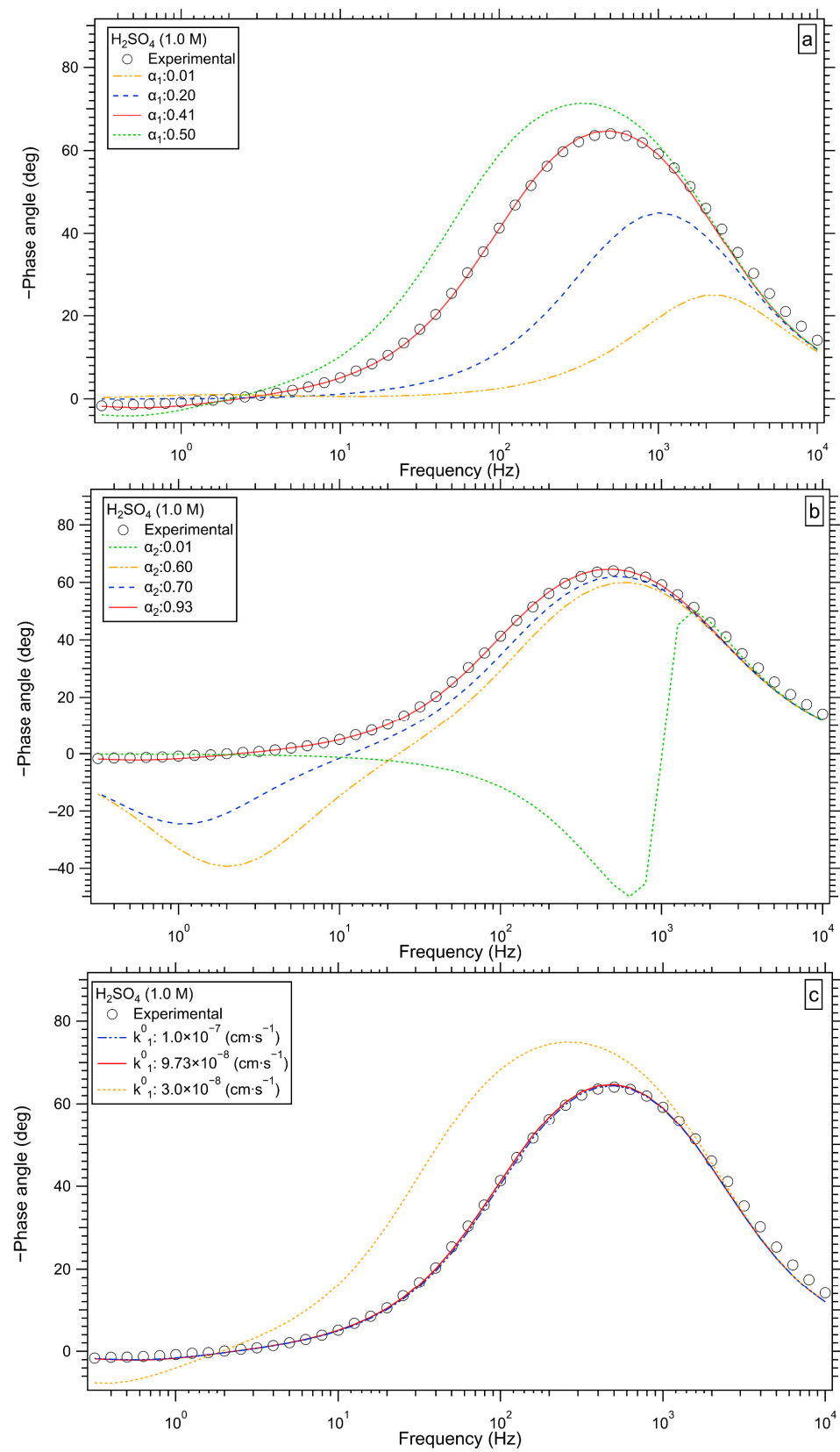


Figure 11. Cont.

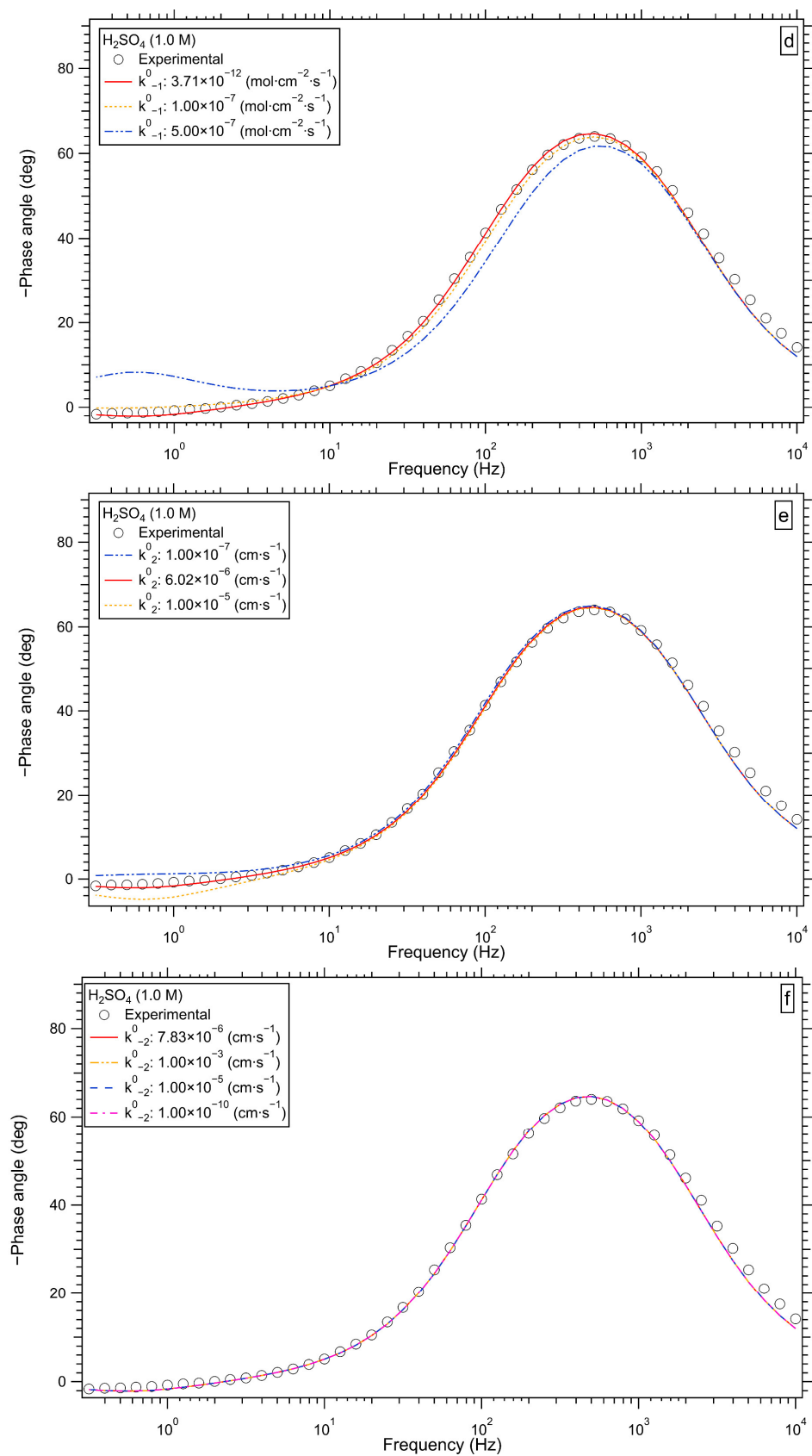


Figure 11. Sensitivity analysis of important electrochemical parameters of charge-transfer coefficients α_1 and α_2 (a,b), and standard rate constants of forward and backward Reactions (1) (c,d) and (2) (e,f) in H_2SO_4 (1.0 M).

6. Conclusions

The aim of this study was to investigate the kinetics of the HER on polycrystalline gold in aqueous H₂SO₄ solutions (0.5 and 1.0 M), to reveal mechanistically relevant information. To achieve this goal, we developed an impedance model based on the VHT mechanism. The model was optimized using experimental polarization (PDP) data and subsequently refined using electrochemical impedance spectroscopy data. By optimizing the model on the PDP data, parameter values for the HER were extracted. These parameters, including rate constants and charge-transfer coefficients, were then used as initial guesses for the optimization process on the EIS data.

The findings of the study revealed several significant insights. First, the fractional surface coverage of hydrogen ($\theta_{H_{ads}}$) increased as the overpotential increased, and a small value of $\theta_{H_{ads}}$ indicates a weak adsorption of H on gold. Additionally, through partial-charge analysis, the study identified the transition-state characteristics for two reactions. For Reaction (1), the transition state was found to be intermediate between reactants and products in both 0.5 M and 1.0 M H₂SO₄ solutions, whereas the transition state for Reaction (2) is “product-like” at both concentrations. These findings contribute to a deeper understanding of the kinetics of the HER on polycrystalline gold in H₂SO₄ solutions.

The Tafel slopes and exchange current densities in H₂SO₄ (0.5 and 1.0 M) were estimated to be in the range of 81–124 mV/dec and 10^{−6} to 10^{−5} A/cm², respectively. A sensitivity analysis was conducted on the impact of the kinetics parameters on the calculated impedance. This analysis indicated that the charge-transfer coefficients and standard rate constants for Reactions (1) and (2)—but not the standard rate constant for the reverse Reaction (2)—have a significant impact on the calculated impedance. Thus, the use of an optimized impedance model, combined with the insights gained from the experimental data, provides valuable improvements in accurately describing and predicting the behavior of the HER in this system.

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