

Supporting Information

Donor-Dependent Kinetics of Interfacial Proton-Coupled Electron Transfer

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Table of contents

Title	Pages
Experimental methods	S4-S5
Calculation of Tolman cone angle for diisopropylethylammonium	S5
Order determination	S5
Discussion of possible mechanisms of Au-catalyzed HER	S5-S7
Figure S1. Raw galvanostatic Tafel data in acetonitrile with TEAH ⁺ proton donor.	S8
Figure S2. Raw galvanostatic Tafel data in acetonitrile with DIPEAH ⁺ proton donor.	S8
Figure S3. Tafel data with TEAH ⁺ proton donor collected in forward and reverse directions in acetonitrile.	S9
Figure S4. Tafel data with DIPEAH ⁺ proton donor collected in forward and reverse directions in acetonitrile.	S9
Figure S5. Rotation rate dependence of TEAH ⁺ HER activity in acetonitrile.	S10
Figure S6. Rotation rate dependence of DIPEAH ⁺ HER activity in acetonitrile.	S10
Figure S7. Tafel data at five different TEAH ⁺ concentrations in acetonitrile.	S11
Figure S8. Tafel data at five different DIPEAH ⁺ concentrations in acetonitrile.	S11
Figure S9. Cyclic voltammograms at five different TEAH ⁺ concentrations in acetonitrile.	S12
Figure S10. Cyclic voltammograms at four different DIPEAH ⁺ concentrations in acetonitrile.	S12
Figure S11. Order plot for TEAH ⁺ based on CV data.	S13
Figure S12. Order plot for DIPEAH ⁺ based on CV data.	S13
Figure S13. Three independent sets of Tafel data in water with TEAH ⁺ donor.	S14
Figure S14. Three independent sets of Tafel data in water with DIPEAH ⁺ donor.	S14
Figure S15. Tafel data with TEAH ⁺ proton donor collected in forward and reverse directions in water.	S15
Figure S16. Tafel data with DIPEAH ⁺ proton donor collected in forward and reverse directions in water.	S15
Figure S17. Rotation rate dependence of TEAH ⁺ HER activity in water.	S16

Figure S18. Rotation rate dependence of DIPEAH ⁺ HER activity in water.	S16
Figure S19. Three independent sets of Tafel data in acetonitrile with TEAD ⁺ donor.	S17
Figure S20. Three independent sets of Tafel data in acetonitrile with DIPEAD ⁺ donor.	S17
Figure S21. Tafel data in acetonitrile with TEAH ⁺ proton donor at varying TBA PF ₆ concentrations.	S18
Figure S22. Tafel data in acetonitrile with TEAH ⁺ proton donor with varying TEA concentrations.	S18
Figure S23. Tafel data in acetonitrile with DIPEAH ⁺ proton donor with varying DIPEA concentrations.	S19
Figure S24. Tafel data in acetonitrile for TEAH ⁺ ad DIPEAH ⁺ on a different Au rotating disk electrode.	S19
Figure S25. Cyclic voltammograms recorded after Tafel data collection for TEAH ⁺ .	S20
Figure S26. Cyclic voltammograms recorded after Tafel data collection for DIPEAH ⁺ .	S20
Figure S27. Tafel data in acetonitrile with TEAH ⁺ proton donor with and without trace H ₂ O.	S21
Figure S28. Tafel data in acetonitrile with DIPEAH ⁺ proton donor with and without trace H ₂ O.	S21

Experimental Methods

Chemicals and Materials. Tetrabutylammonium hexafluorophosphate (99%), trifluoromethanesulfonic acid (Reagent Plus, > 99%), trifluoromethanesulfonic acid-d (99.5 atom % D), sodium perchlorate (99.99% trace metals basis), and perchloric acid (70%, 99.999% trace metals basis) were obtained from Sigma Aldrich and were used as received. Diisopropylethylamine (Reagent Plus, > 99%) was obtained from Sigma Aldrich and purified by distillation over CaH₂ prior to use. Triethylamine (Sigma Aldrich, >99%), and acetonitrile (EMD Chemicals) were purified and dried prior to use by passing through a Glass Contour Solvent Purification System (SG Water USA, LLC). All aqueous electrolyte solutions were prepared with reagent grade water (Millipore, 18.2 MΩ-cm resistivity). Gold rotating disk electrodes were obtained from Pine Research Instrumentation, Inc. Hg/HgO and Ag/AgCl reference electrodes were obtained from CHI instruments, Inc. and BASi Inc. respectively. Platinum wire (99.9%) was obtained from Alfa Aesar.

General Electrochemical Methods. All electrochemical experiments were conducted at ambient temperature (21 ± 1 °C) using a Gamry REF 600 potentiostat or Biologic VSP potentiostat, and a high surface area Pt-mesh counter electrode. Unless otherwise stated, a platinum mesh was used as the counter electrode. Hg/HgO was used as the reference electrode for experiments conducted in alkaline electrolytes, whereas a Ag/AgCl pseudo-reference electrode was used for experiments conducted in non-aqueous electrolyte. Hg/HgO reference electrodes were stored in 1 M KOH solution in between measurements and were periodically checked relative to pristine reference electrodes to ensure against potential drift. Electrode potentials for experiments conducted in aqueous media were converted to the reversible hydrogen electrode (RHE) scale using $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.094 \text{ V} + 0.059(\text{pH}) \text{ V}$, whereas electrode potentials for experiments conducted in acetonitrile were referenced vs the internal standard, ferrocene. Ag/AgCl electrodes were stored in 0.5 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile in between measurements.

Preparation of Trialkylammonium Triflate Salts. Tetraethylammonium triflate, TEAH⁺OTf⁻, and diisopropylethylammonium triflate, DIPEAH⁺OTf⁻, were prepared in an N₂ glovebox by combining equimolar amounts of the corresponding amine with trifluoromethanesulfonic acid in diethyl ether. The resulting white precipitate was isolated by filtration and washed with diethyl ether to yield the desired ammonium salt. The same procedure, with substitution of trifluoromethanesulfonic acid-d for trifluoromethanesulfonic acid, was used to prepare TEAD⁺OTf⁻ and DIPEAH⁺OTf⁻ salts.

Galvanostatic Tafel Data Collection. Steady-state current-potential (Tafel) data were collected by conducting controlled-current electrolysis using polycrystalline Au rotating disk working electrodes (RDE). In all cases, catalytic currents reached steady state within 1 minute, and the endpoint current was taken as the steady state value. Experiments in acetonitrile were conducted in the presence of 0.5 M TBAPF₆ supporting electrolyte at a working electrode rotation rate of 2000 rpm unless otherwise stated. Experiments in aqueous media were conducted at pH 10.7 in the presence of 1 M NaClO₄ at a working electrode rotation rate of 2000 rpm. Typical values of R_u for acetonitrile solutions ranged from 45-50 Ω and for aqueous solutions ranged from 5-10 Ω. Potential values were corrected for uncompensated ohmic loss ($E_{\text{real}} = E_{\text{measured}} - iR_u$). The data shown in the Tafel plots (Figures 1, 3, 4) are the average and standard deviation of 3 independent Tafel runs. Raw, unaveraged data for these three runs are shown in **Figures S1, S2, S9, S10, S15**,

and **S16**. In all cases, the applied current values were normalized by the geometric area of the Au RDE (0.196 cm²).

Calculation of Tolman Cone Angle for Diisopropylethylammonium. Since DIPEA is asymmetrically substituted, the Tolman cone angle was calculated using a weighted average of the cone angles reported for TEA and triisopropylamine (TIPA). TEA has a cone angle of 150°, and TIPA has a cone angle of 220°, so the cone angle of DIPEA is:

$$\frac{2(220^\circ) + 1(150^\circ)}{3}$$

Order determination. To determine the reaction order in proton donor, galvanostatic Tafel data were collected at several acid concentrations, as shown in Figures S7 and S8. For each concentration, a best fit line was determined relating the potential to the log of the current density. From these best fit lines, the current density at a given potential was interpolated. For example, the best fit line for the Tafel plot collected in the presence of 100 mM DIPEAH⁺OTf⁻ was:

$$E = -0.158 \text{ V dec}^{-1} \times \log(j) - 1.95 \text{ V}$$

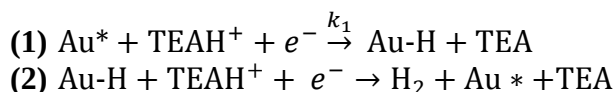
So, at -1.4 V vs Fc⁺/Fc, the interpolated value for the log of the current density was -3.48.

Five potentials that were within the range of linear Tafel data collection were selected for each donor, and for each of these potentials, log(*j*) was plotted vs the log of the acid concentration (Figure 2). The slopes of these lines represent the order in proton donor.

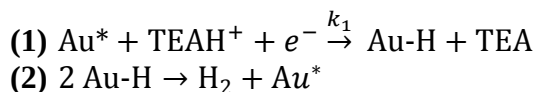
Discussion of possible mechanisms of Au-catalyzed HER.

Au-catalyzed HER must proceed through one of two pathways:

Pathway One:



Pathway Two:

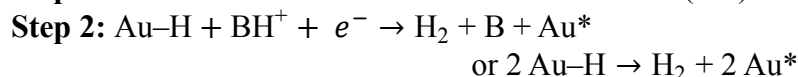
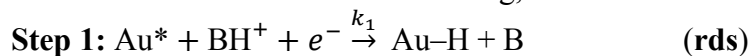


In Pathway One, the first step is a proton-coupled electron transfer (PCET) to form a surface Au-H bond, commonly referred to as the Volmer step. This step is followed by another PCET step to form H₂ (Heyrovsky step). Pathway Two consists of a Volmer step followed by the recombination of two surface Au-H species (Tafel step) to make H₂. We note that the calculated surface adsorption energy for H atoms on Au is weak. The ΔG_{Au-H} = 0.39 eV, which is about 0.7 eV lower than those calculated for metals that exhibit high H-coverage under HER conditions, such as Pt and Pd. Thus, we will exclude all mechanistic sequences involving high Au-H coverage during catalysis. We are now left with three possible mechanistic pathways: rate-limiting Volmer step, rate-limiting Heyrovsky step, or rate-limiting Tafel step.

Rate-determining step	Range of possible α values	Range of possible Tafel slopes (mV dec ⁻¹)	Reaction order in TEAH ⁺ or DIPEAH ⁺
Volmer	0-1	> 60	1
Heyrovsky	1-2	30-60	2
Tafel	2	30	2

Rate-limiting Volmer step:

If Au-H bond formation is rate-limiting, the mechanism can be written as follows:



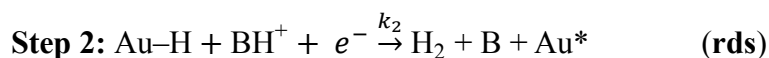
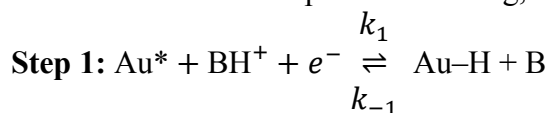
Since the first step is rate-limiting, we write it as irreversible, and we cannot distinguish between Pathways One and Two (Heyrovsky and Tafel steps). This leads to the following rate law:

$$v = 2Fk_1(a_{\text{BH}^+})\theta_{\text{Au}^*}e^{\frac{\beta EF}{RT}}$$

where F is Faraday's constant, k_1 denotes the potential-independent rate constant for the CPET step, a_{BH^+} is the activity of proton donor in the electrochemical double layer, and θ_{Au^*} is the surface concentration of Au active sites (Γ_{Au^*} , in mol/cm²) divided by the total surface concentration of Au atoms (Γ_{max}), β is the symmetry factor, E is the overpotential for the electron-transfer step, R is the gas constant, and T is the temperature. From this rate law, we predict a first order dependence in proton donor (TEAH⁺ or DIPEAH⁺) concentration. Since β values can range from 0 to 1, Tafel slopes greater than 60 mV dec⁻¹ can be consistent with a rate-limiting Volmer step, although if $\beta = 0.5$, we expect a Tafel slope of 120 mV dec⁻¹. In this sequence, $\beta = \alpha$, and can range from 0 to 1.

Rate-limiting Heyrovsky step:

If the second PCET step is rate-limiting, the mechanism is as follows:



Based on this mechanistic sequence, we write the rate law as:

$$v = 2Fk_2[\text{Au-H}](a_{\text{BH}^+})e^{\frac{\beta EF}{RT}}$$

We take Step 1 to be in quasi-equilibrium and substitute for [Au-H] in the rate law:

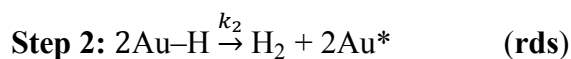
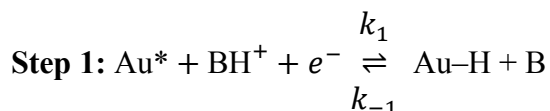
$$K = \frac{k_1}{k_{-1}} = \frac{[\text{Au-H}][\text{B}]}{[\text{Au}^*][\text{BH}^+]e^{\frac{EF}{RT}}}$$

$$\Rightarrow v = 2Fk_2 \frac{k_1}{k_{-1}} \theta_{\text{Au}^*} (a_{\text{BH}^+})^2 e^{\frac{(\beta+1)EF}{RT}}$$

This rate law suggests that HER is second order in proton donor, and predicts Tafel slopes in the range of 30-60 mV dec⁻¹, with a 40 mV dec⁻¹ slope if $\beta = 0.5$. For this sequence, $\alpha = \beta + 1$, and we expect α values between 1 and 2.

Rate-limiting Tafel step:

If the recombination of two Au-H species is rate-limiting, the mechanism is the following:



And the rate law is:

$$\nu = 2Fk_2[\text{Au-H}]^2$$

Again, take Step 1 to be in quasi-equilibrium and substitute in for [Au-H]:

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{Au-H}][\text{B}]}{[\text{Au}^*][\text{BH}^+]e^{\frac{EF}{RT}}}$$

$$\Rightarrow \nu = 2Fk_2\left(\frac{k_1}{k_{-1}}\right)^2 \theta_{\text{Au}^*}^2 (a_{\text{BH}^+})^2 e^{\frac{2EF}{RT}}$$

This rate law also suggests that HER is second order in proton donor. Importantly, since electron-transfer is not rate-limiting, there is no β in the rate-limiting step, and the expected Tafel slope is 30 mV dec⁻¹ at room temperature. This corresponds to an expected α of 2.

As all the other sequences would be expected to give rise to reaction orders of 2 and significantly larger transfer coefficients, our data are most consistent with a rate-limiting Volmer step (CPET).

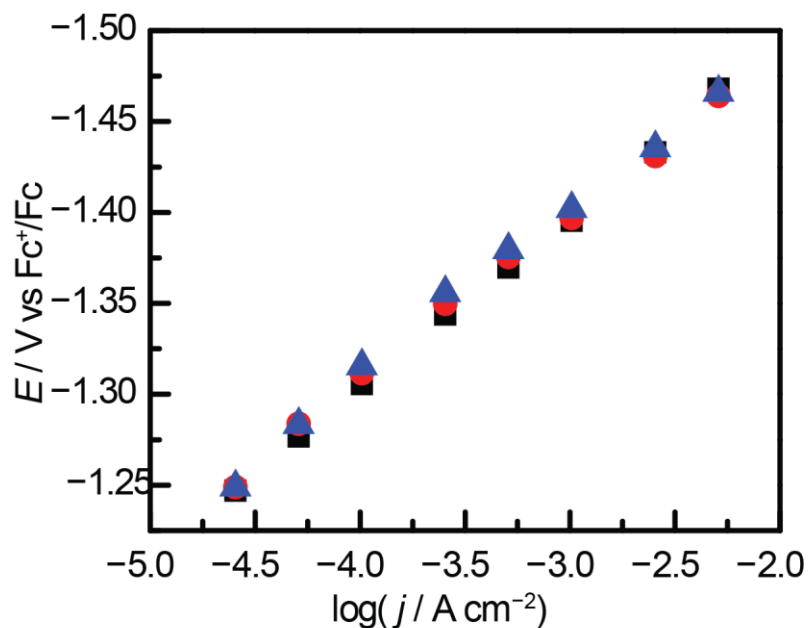


Figure S1. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA. The polycrystalline Au working electrodes were polished between runs.

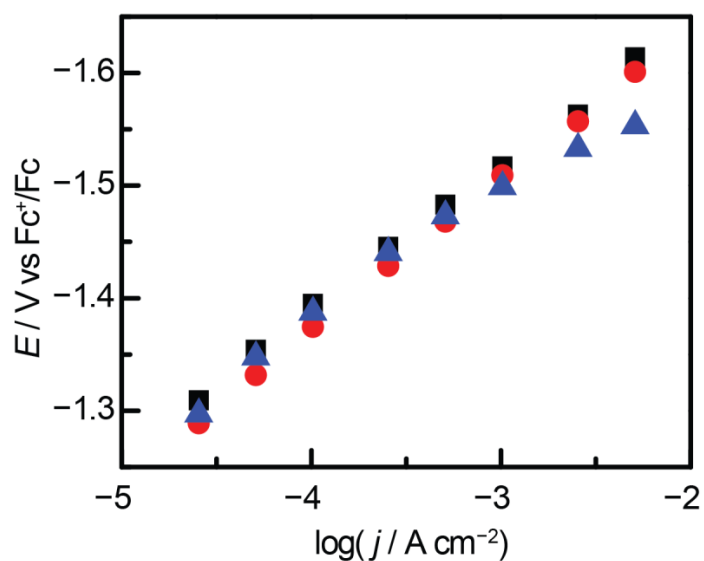


Figure S2. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA. The polycrystalline Au working electrodes were polished between runs.

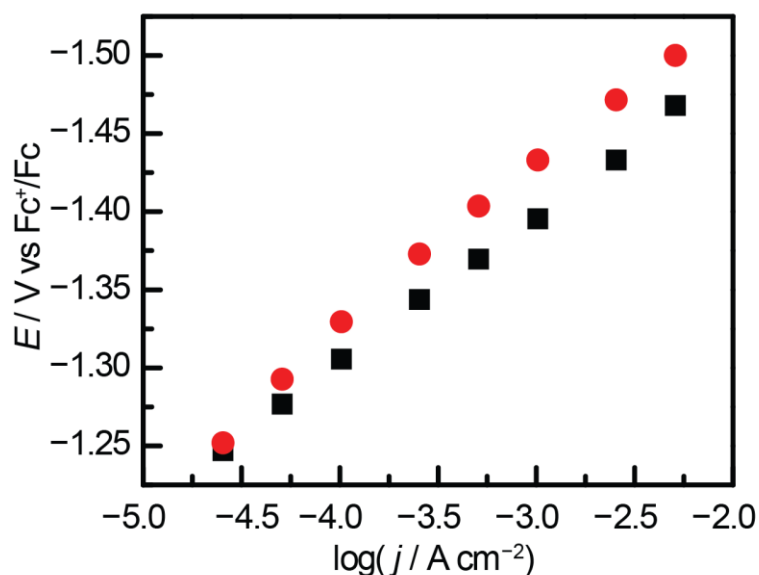


Figure S3. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA. Data were collected from high current densities to low current densities (black) and then from low current densities to high current densities (red) without polishing the electrode in between.

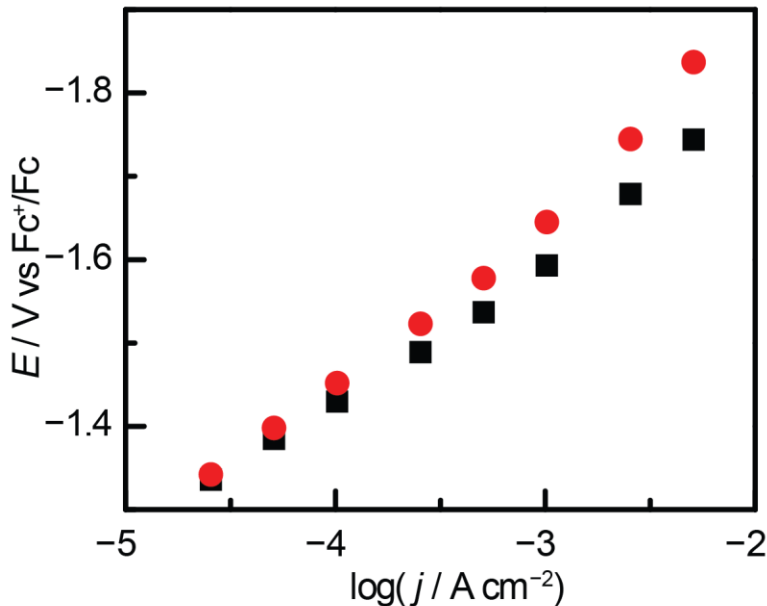


Figure S4. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA. Data were collected from high current densities to low current densities (black) and then from low current densities to high current densities (red) without polishing the electrode in between.

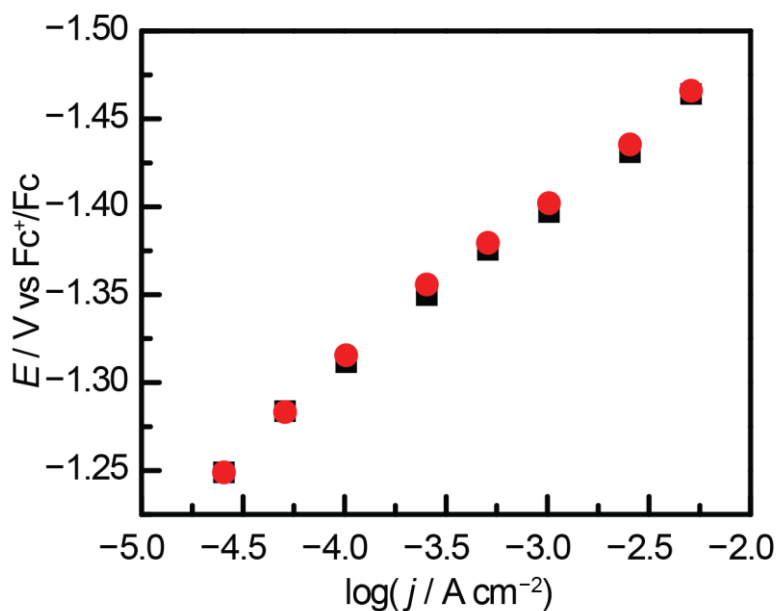


Figure S5. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA at an electrode rotation rate of 1000 (red) and 2000 rpm (black).

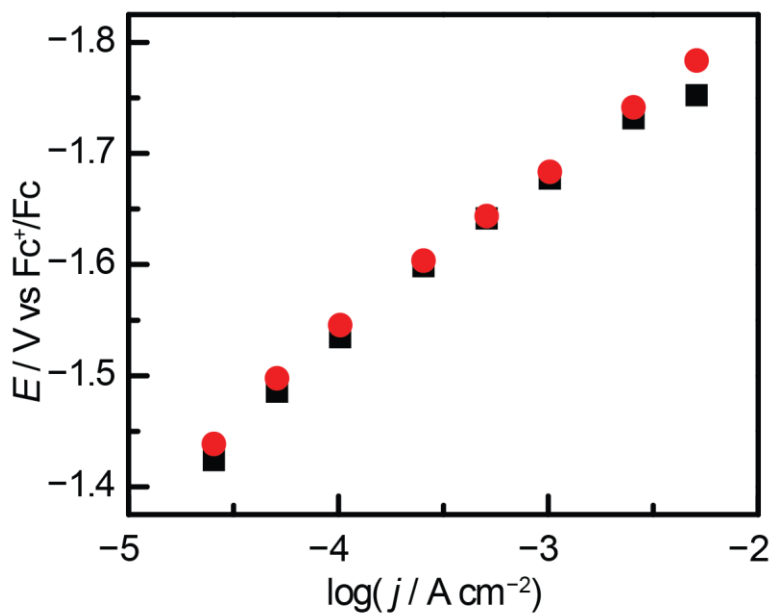


Figure S6. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA at an electrode rotation rate of 1000 (red) and 2000 rpm (black).

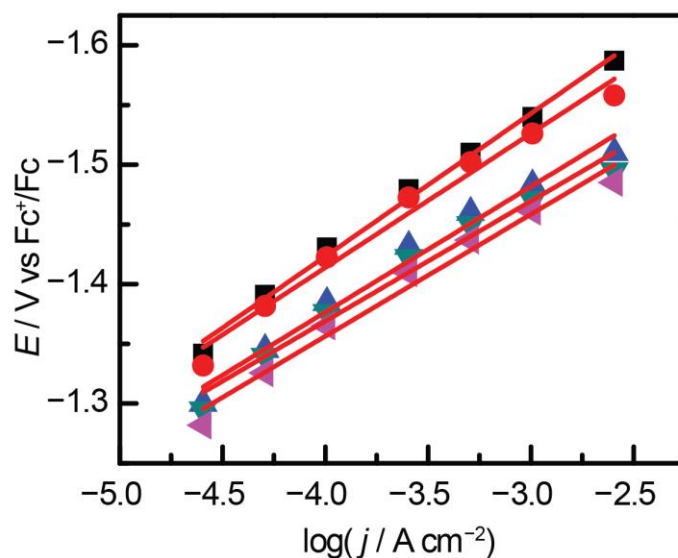


Figure S7. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF_6 acetonitrile electrolyte containing: 5 (black), 10 (red), 20 (blue), 50 (teal green), and 100 mM (purple) $\text{TEAH}^+\text{OTf}^-$.

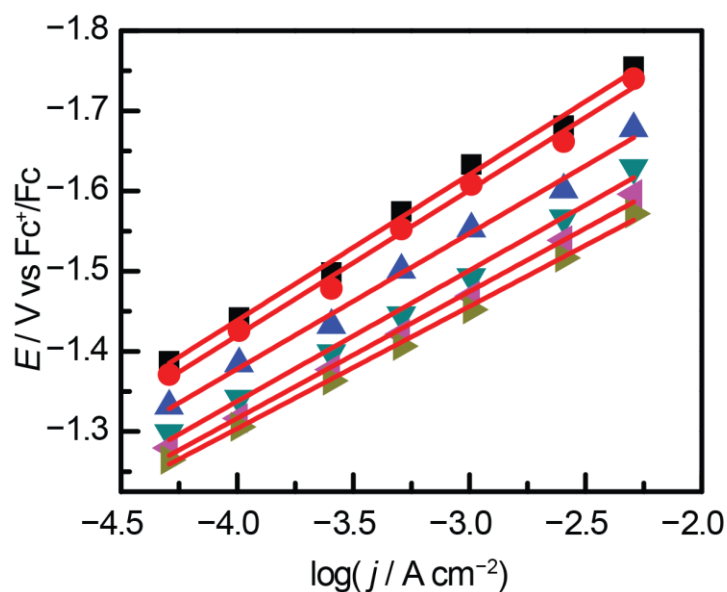


Figure S8. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF_6 acetonitrile electrolyte containing: 5 (black), 10 (red), 20 (blue), 50 (teal green), and 100 mM (purple) $\text{DIPEAH}^+\text{OTf}^-$.

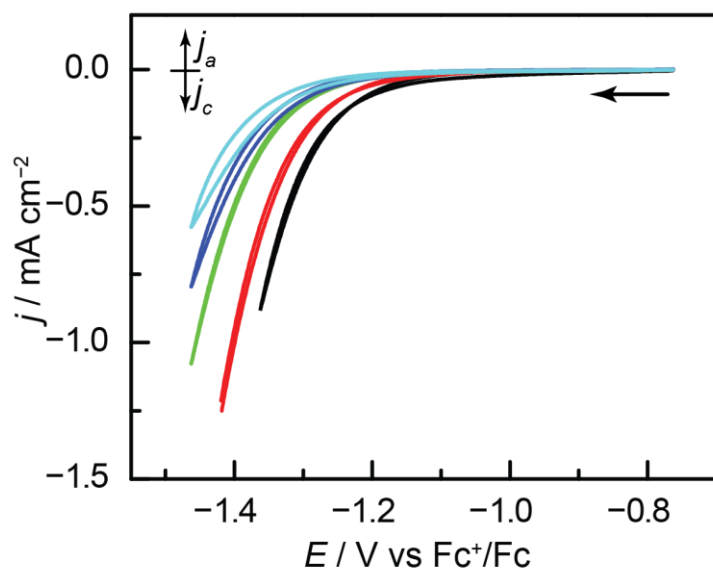


Figure S9. Cyclic voltammograms (10 mV s⁻¹) recorded in 0.5 M TBAPF₆ acetonitrile electrolyte containing: 5 (light blue), 10 (dark blue), 20 (green), 50 (red), and 100 mM (black) TEAH⁺OTf⁻.

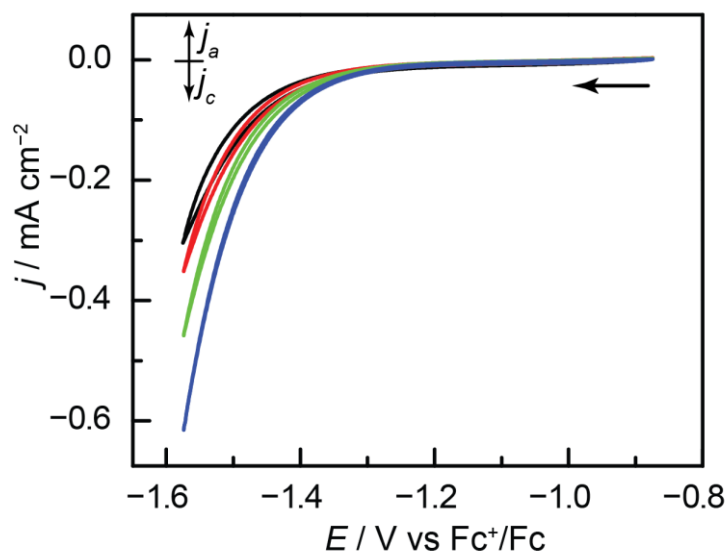


Figure S10. Cyclic voltammograms (10 mV s⁻¹) recorded in 0.5 M TBAPF₆ acetonitrile electrolyte containing: 5 (black), 10 (red), 20 (green), and 50 (dark blue) DIPEAH⁺OTf⁻.

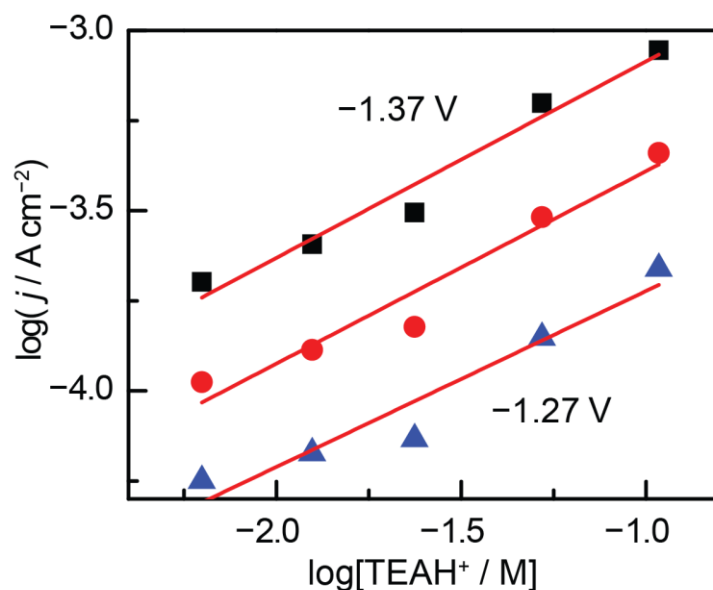


Figure S11. Hydrogen evolution catalytic current density vs concentration of TEAH⁺. Points correspond to current densities at -1.27 V, -1.32 V, and -1.37 V in cyclic voltammograms (10 mV s⁻¹) recorded on polycrystalline Au in acetonitrile containing 0.1 M TBA PF₆. The slope is 0.5 at all potentials.

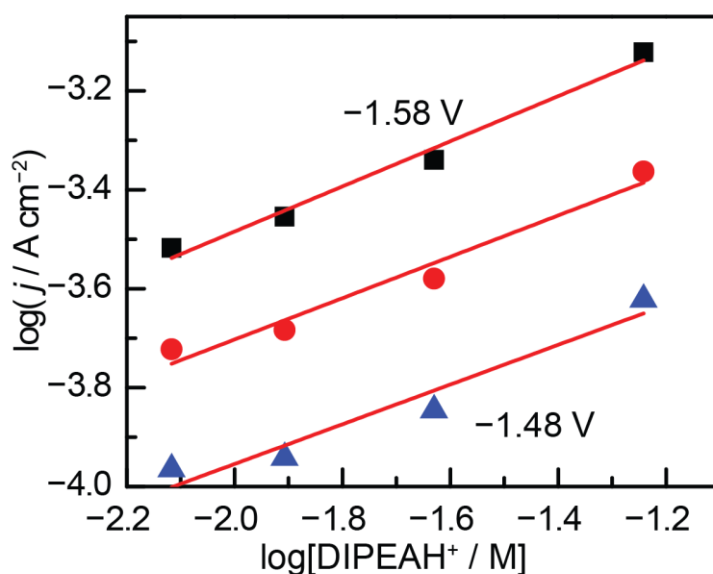


Figure S12. Hydrogen evolution catalytic current density vs concentration of DIPEAH⁺. Points correspond to current densities at -1.48 V, -1.53 V, and -1.58 V in cyclic voltammograms (10 mV s⁻¹) recorded on polycrystalline Au in acetonitrile containing 0.1 M TBA PF₆. The slopes range from 0.4 to 0.5.

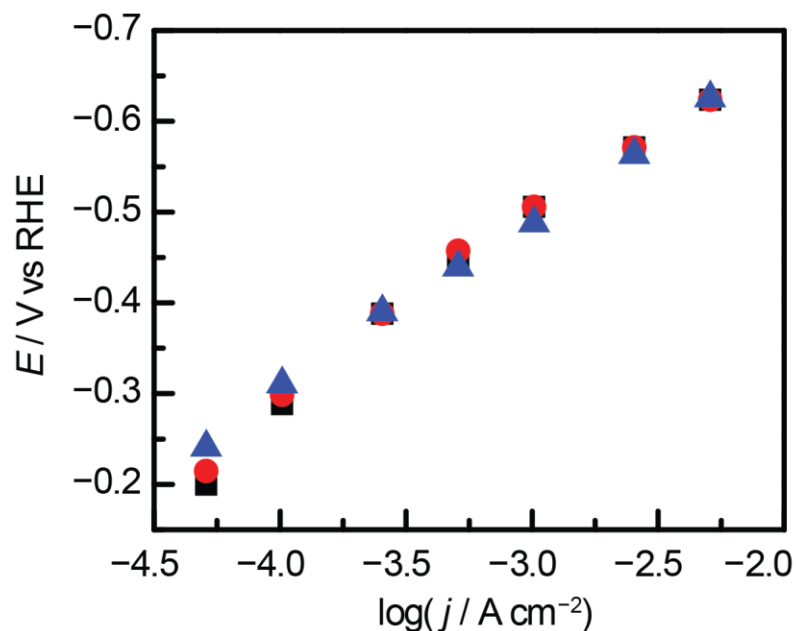


Figure S13. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM TEAH⁺ClO₄⁻ and 2.5 mM TEA (pH 10.7). The polycrystalline Au working electrodes were polished between runs.

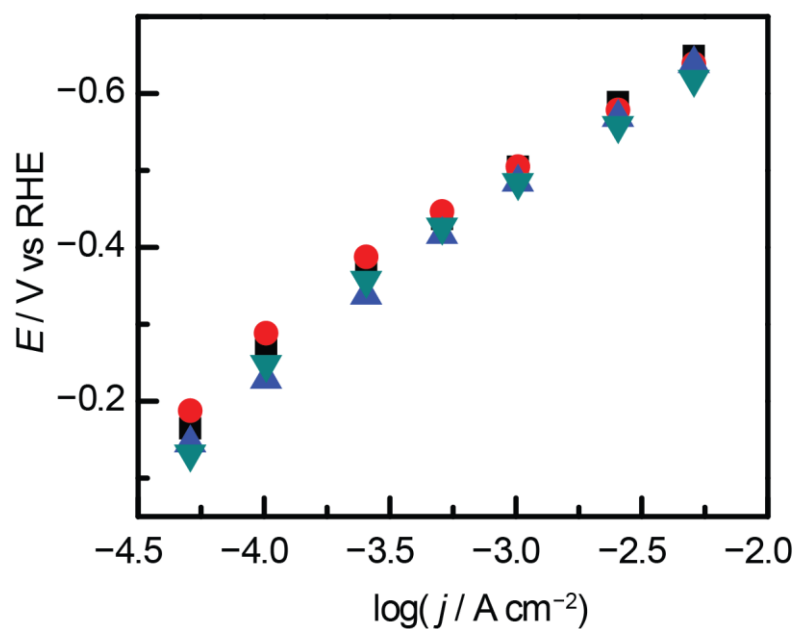


Figure S14. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM DIPEAH⁺ClO₄⁻ and 2.5 mM DIPEA (pH 10.7). The polycrystalline Au working electrodes were polished between runs.

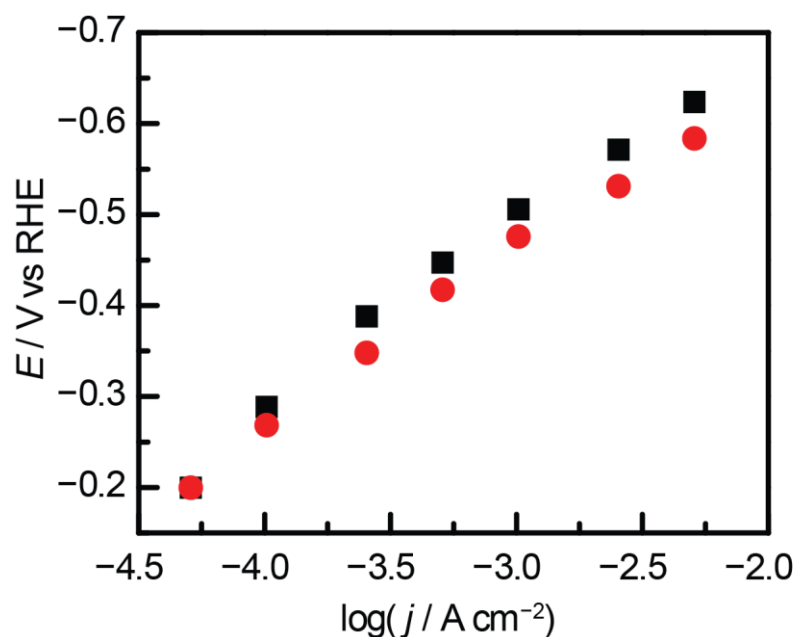


Figure S15. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM TEAH⁺ClO₄⁻ and 2.5 mM TEA (pH 10.7). Data were collected from high current densities to low current densities (black) and then from low current densities to high current densities (red) without polishing the electrode in between.

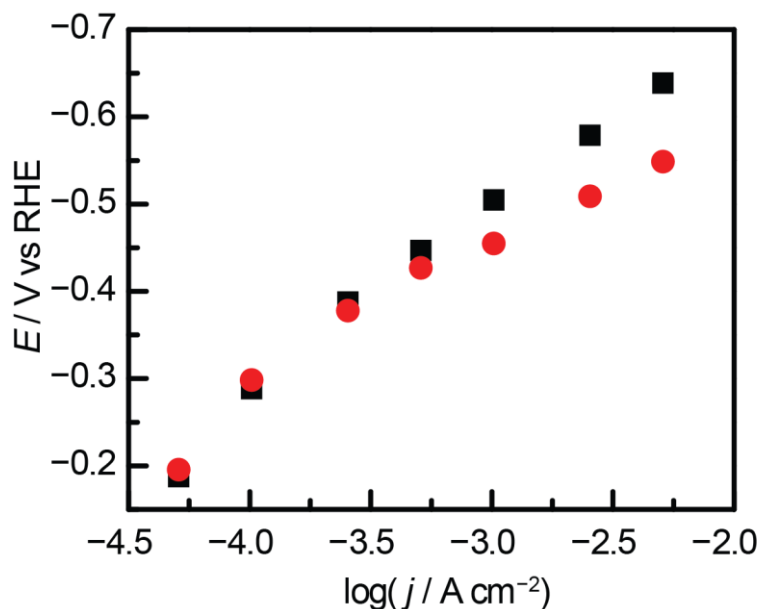


Figure S16. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM DIPEAH⁺ClO₄⁻ and 2.5 mM DIPEA (pH 10.7). Data were collected from high current densities to low current densities (black) and then from low current densities to high current densities (red) without polishing the electrode in between.

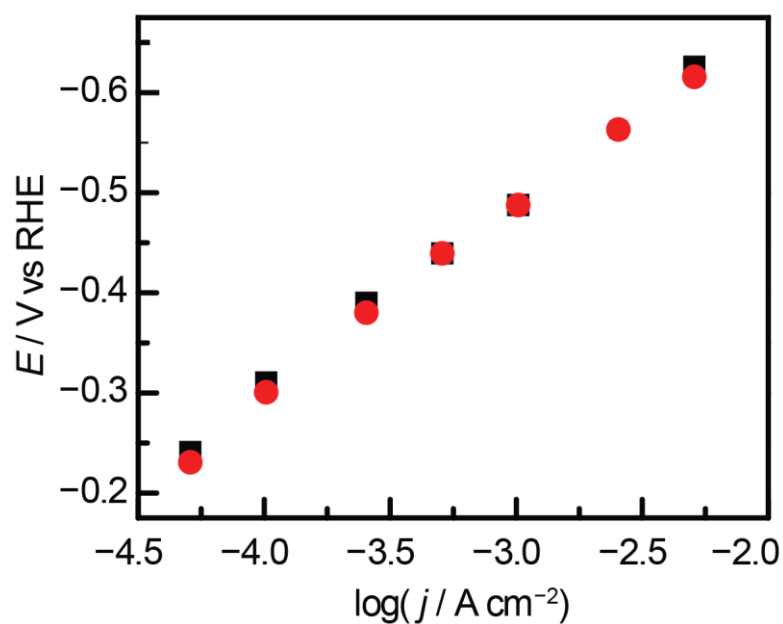


Figure S17. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA at an electrode rotation rate of 1000 (red) and 2000 rpm (black).

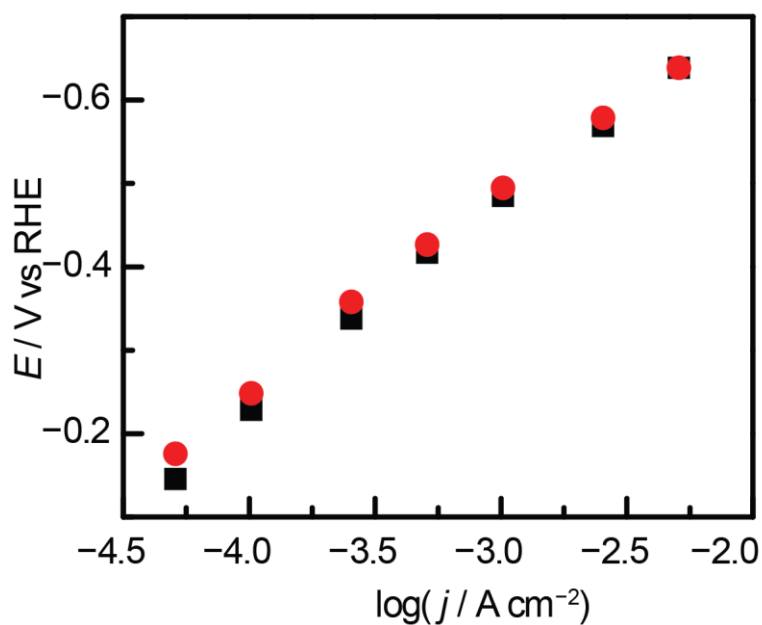


Figure S18. Galvanostatic Tafel data for hydrogen evolution collected in 1.0 M NaClO₄ aqueous electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA at an electrode rotation rate of 1000 (red) and 2000 rpm (black).

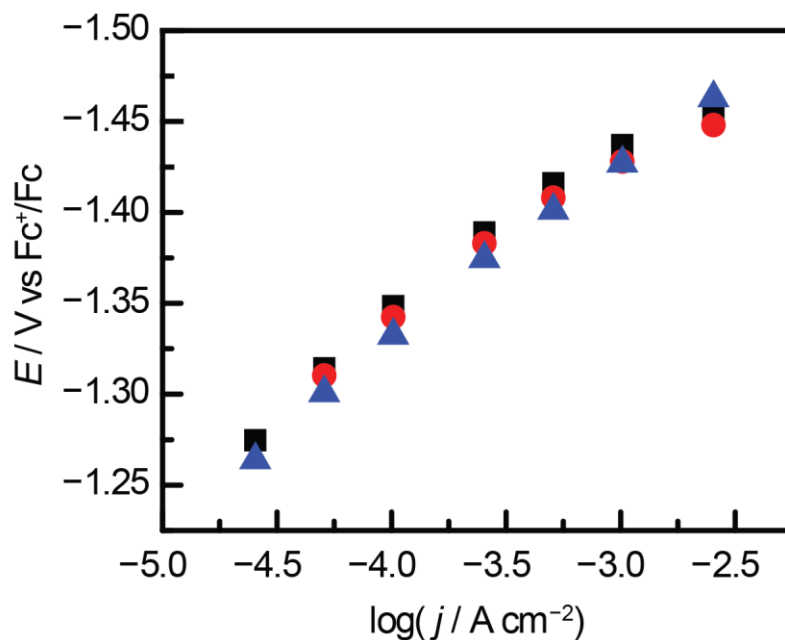


Figure S19. Galvanostatic Tafel data for deuterium evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAD⁺OTf⁻ and 2.5 mM TEA. The polycrystalline Au working electrodes were polished between runs.

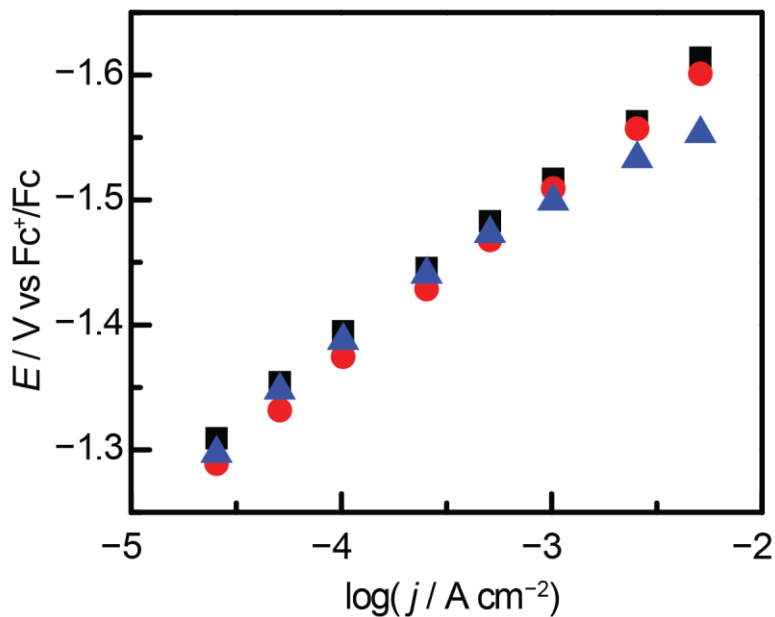


Figure S20. Galvanostatic Tafel data for deuterium evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA. The polycrystalline Au working electrodes were polished between runs.

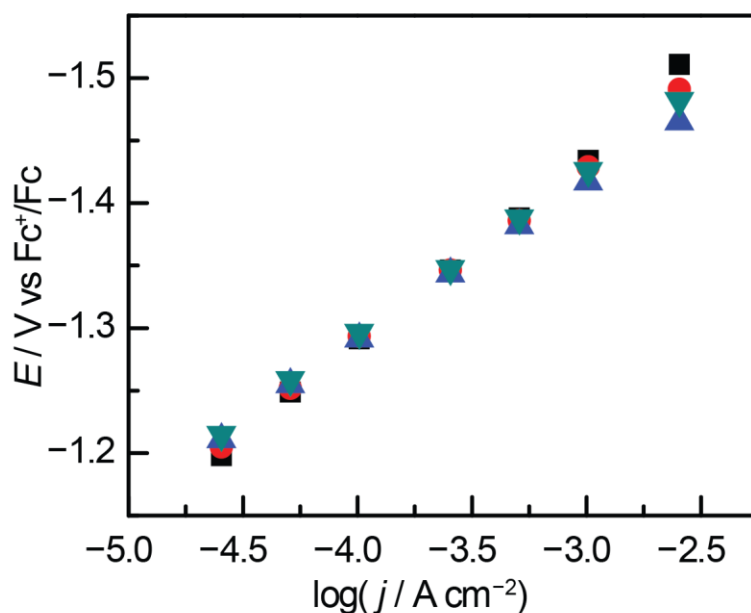


Figure S21. Galvanostatic Tafel data for hydrogen evolution collected in acetonitrile in the presence of 10 mM TEAH⁺OTf⁻ and 0.1 M (black), 0.2 M (red), 0.5 M (blue) and 1.0 M (green) TBAPF₆ supporting electrolyte.

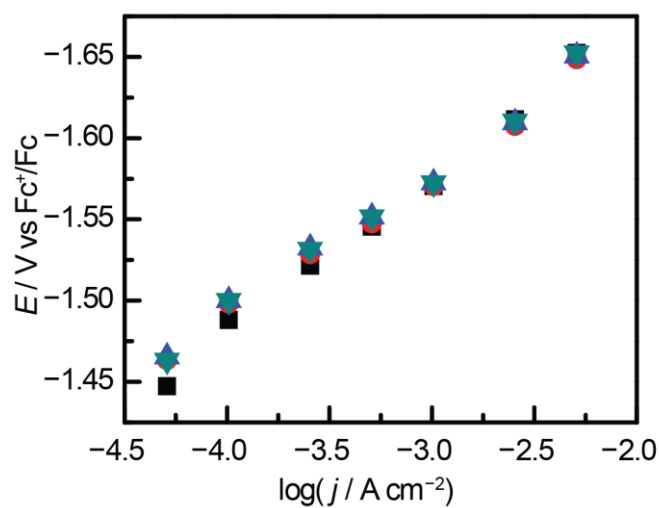


Figure S22. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.1 (black), 4.3 (red), 8.6 (blue), and 17.1 mM (green) TEA.

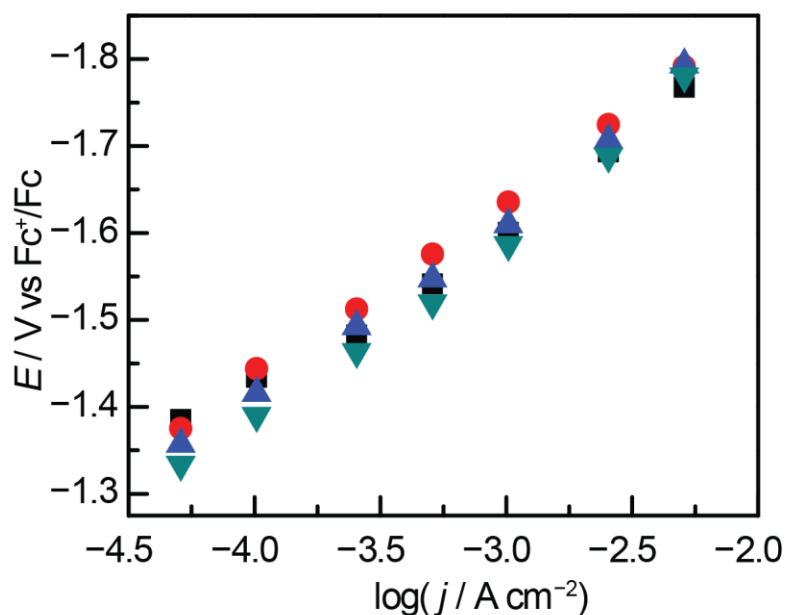


Figure S23. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.3 (black), 4.6 (red), 9.2 (blue), and 18.4 mM (green) DIPEA.

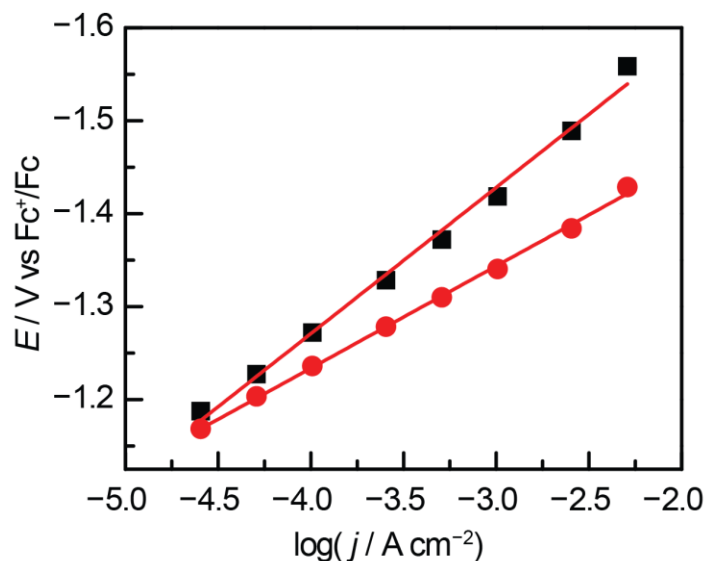


Figure S24. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA (red) and 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA (black) on a different Au RDE than the one used in **Figure 1**. The Tafel slopes are similar to those in **Figure 2**; however, this Au RDEs appears to be more active than the other Au RDE when normalized by geometric surface area. We attribute this higher activity to a greater roughness factor.

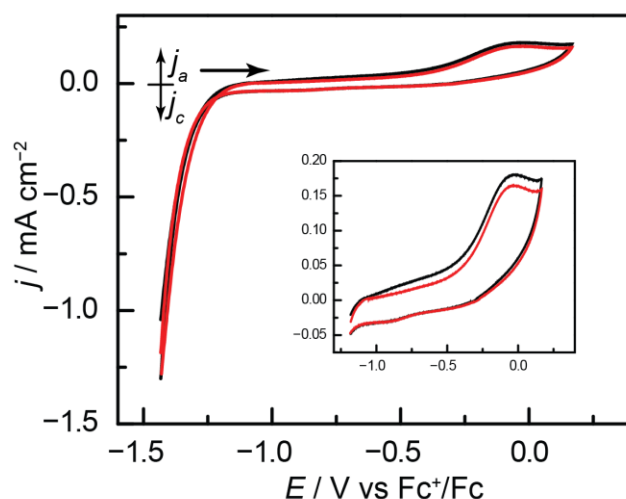


Figure S25. Cyclic voltammograms (50 mV s^{-1}) collected immediately after a full Tafel data collection on polycrystalline Au in 25 mM TEAH⁺OTf⁻, 2.5 mM TEA, and 0.5 M TBA PF₆. The scan began at the most negative potential and swept to the most positive potential. The black trace is the first sweep, and the red trace is the second sweep. The inset is a zoom-in on the most positive region and shows only one redox feature corresponding to TEA oxidation.

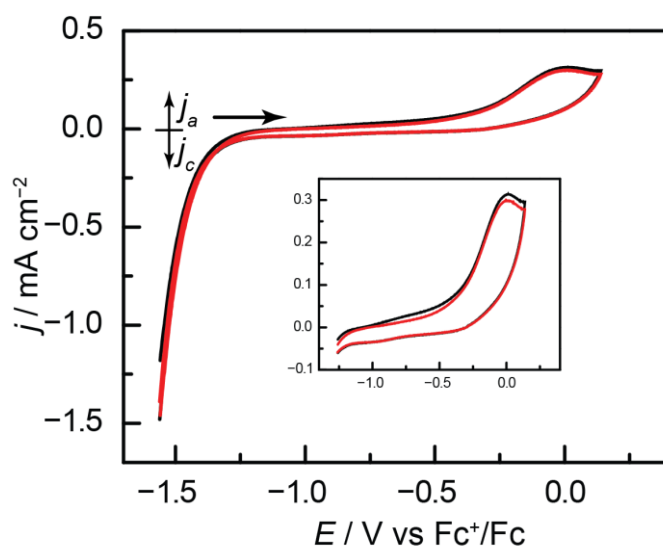


Figure S26. Cyclic voltammograms (50 mV s^{-1}) collected immediately after a full Tafel data collection on polycrystalline Au in 25 mM DIPEAH⁺OTf⁻, 2.5 mM DIPEA, and 0.5 M TBA PF₆. The scan began at the most negative potential and swept to the most positive potential. The black trace is the first sweep, and the red trace is the second sweep. The inset is a zoom-in on the most positive region and shows only one redox feature corresponding to DIPEA oxidation.

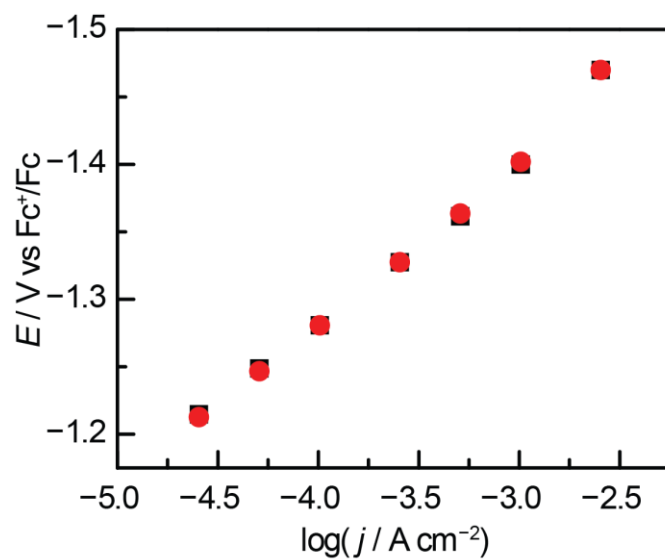


Figure S27. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM TEAH⁺OTf⁻ and 2.5 mM TEA without (black) and with 30 ppm H₂O.

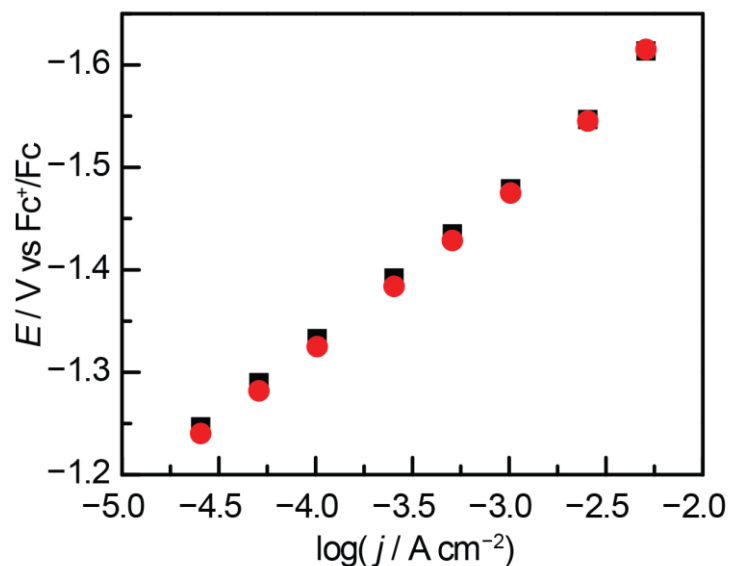


Figure S28. Galvanostatic Tafel data for hydrogen evolution collected in 0.5 M TBAPF₆ acetonitrile electrolyte containing 25 mM DIPEAH⁺OTf⁻ and 2.5 mM DIPEA without (black) and with 30 ppm H₂O.