

Supplementary Information

Metal surfaces catalyze polarization-dependent hydride transfer from H₂

Hai-Xu Wang, Wei Lun Toh, Bryan Y. Tang, Yogesh Surendranath*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts
02139, United States

*yogi@mit.edu

Table of Contents

General	S4
General procedure for the preparation of hydride acceptors $[A^+](PF_6^-)$ by salt metathesis	S5
Preparation of BIMD	S5
Supplementary Figure 1. ^1H NMR spectrum of BIMD in $CDCl_3$	S6
General electrochemical methods	S7
Experimental procedure for CV experiments of BIM $^+$ using a Pt planar electrode.....	S8
Supplementary Figure 2. Linear sweep voltammograms of BIM $^+$ under N_2 and H_2 using a planar Pt electrode.....	S8
Experimental procedure for the CV experiment of BIM $^+$ using Pt RDE	S9
Supplementary Figure 3. Linear sweep voltammogram of BIM $^+$ under H_2 using a Pt RDE.....	S9
Preparation of the Pt/PTFE GDE.....	S10
Supplementary Figure 4. A picture of Pt/PTFE GDE.....	S10
Assembly of H-cells using Pt/PTFE GDE.....	S11
Supplementary Figure 5. Undivided and divided H-cell setup with Pt/PTFE GDE as WE.....	S11
General procedure for CV experiments using Pt/PTFE GDE	S12
Supplementary Figure 6. Cyclic voltammograms of IrCp $^+$ under N_2 and H_2	S12
General procedure for HRR electrocatalysis using Pt/PTFE GDE.....	S13
Supplementary Figure 7. Chronoamperometric traces for HRR of BIM $^+$ and IrCp $^+$ under CPE conditions.....	S14
Supplementary Figure 8. Crude ^1H NMR spectrum after CPE of IrCp $^+$	S14
Experimental procedure for E_{OCP} measurements for thermodynamic studies	S15
Supplementary Figure 9. Nernstian dependence of E_{OCP} on the concentration ratio of HE $^+$ and HEH in MeCN.....	S16
Supplementary Figure 10. Nernstian dependence of E_{OCP} on the concentration ratio of BET_3 and $HBET_3^-$ in THF.	S16
General experimental parameters for EIS measurements	S17
Preparation of the platinized Pt electrode and measurement of ECSA	S17
Supplementary Figure 11. Variable scan rate CV plots in the double layer region for platinized and planar Pt electrodes.	S18
Supplementary Figure 12. Plot of capacitive current in the double layer region versus scan rate for platinized and planar Pt electrodes.....	S18
Supplementary Figure 13. EIS data for HRR of BIM $^+$ / BIMH with varying concentrations of BIM $^+$ / BIMH on a platinized Pt electrode.....	S19

Supplementary Figure 14. Plot of j_0 values calculated from the EIS data versus concentration of BIM⁺/BIMH	S19
Supplementary Table 1. Summary of fitting parameters for the EIS data measured using a platinized Pt electrode.....	S20
<i>Pretreatment of planar Pt, Pd, Ni, and Au electrodes and measurement of ECSA</i>	S21
Supplementary Figure 15. EIS data for HRR of BIM⁺/BIMH on Pd planar electrode.....	S22
Supplementary Figure 16. Fitting EIS data for HRR of BIM⁺/BIMH on Pd planar electrode by varying R_{CT} and CPE components.	S22
Supplementary Figure 17. EIS data for HRR of BIM⁺/BIMH using Ni planar electrode.....	S23
Supplementary Figure 18. Fitting EIS data for HRR of BIM⁺/BIMH on Ni planar electrode by varying R_{CT} and CPE components.	S23
Supplementary Figure 19. EIS data for HRR of BIM⁺/BIMH using Au planar electrode.....	S24
Supplementary Figure 20. Fitting EIS data for HRR of BIM⁺/BIMH on Ni planar electrode by varying R_{CT} and CPE components.	S24
Supplementary Table 2. Summary of fitting parameters for the EIS data measured using planar Pt, Pd, Ni, and Au electrodes.....	S25
Derivation of the Nernst equation for HRR	S26
References.....	S28

General

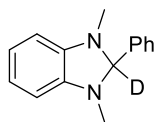
All syntheses were performed in solvents of ACS grade or better. 2-Phenylbenzimidazole, 2,2'-bipyridine, diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (**HEH**), diethyl 2,6-dimethylpyridine-3,5-dicarboxylate, tris(pentafluorophenyl)borane (**BCF**), sodium borodeuteride, and triethylamine (**TEA**) were obtained from Sigma Aldrich. Methyl iodide, sodium borohydride, acridine, dimethyl sulfate, Super-Hydride[®], triethylborane, borane tetrahydrofuran complex, and potassium hexafluorophosphate were obtained from Fisher Scientific. Pentamethylcyclopentadienyliridium(III) dichloride dimer was obtained from Strem, and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (**BIMH**) was obtained from Ambeed. **[BIM⁺](I⁻)**,¹ **[HE⁺](MeSO₄⁻)**,² (TBA)**[HBCF⁻]**,³ **[Acr⁺](I⁻)**,⁴ **AcrH₂**,⁵ and **[IrCp⁺](OTf⁻)**⁶ were prepared by literature methods and product purity was assessed by NMR. H₂ (Ultra High Purity) and Ar (Ultra High Purity) were purchased from Airgas. N₂ was house nitrogen from liquid nitrogen boil off. D₂ (99.96%) was purchased from Sigma Aldrich. Deionized water further purified by a MilliQ system (Millipore Type 1, resistivity of 18.2 MΩ cm) was used as the source of ultrapure water for all applications described below. Platinum planar electrodes (2 mm o.d.), gold planar electrodes (2 mm o.d.), and non-aqueous Ag/Ag⁺ reference electrodes were obtained from CH Instruments. Palladium planar electrode (3 mm o.d.) and nickel planar electrode (3 mm o.d.) were obtained from BASi. Pt/C (60 wt%) gas diffusion electrodes (GDE) were obtained from Fuel Cell Store. Pt foil (99.9% metal basis) was obtained from Thermo Scientific. Pt rotating disk electrodes (RDE, 5 mm o.d.) were obtained from Pine Research Instrumentation, Inc. Leakless Ag/AgCl reference electrodes were obtained from eDAQ and stored in MilliQ water between measurements. Polytetrafluoroethylene (PTFE) membranes (QL217: polypropylene backer, thickness 6–10 mil, pore size 0.1–0.2 micron) were obtained from Sterlitech Corp. NMR spectra were taken using either a Bruker Avance Neo spectrometer operating at 500.34 MHz or a Bruker Avance-III HD Nanobay spectrometer operating at 400.13 MHz.

General procedure for the preparation of hydride acceptors $[A^+](PF_6^-)$ by salt metathesis

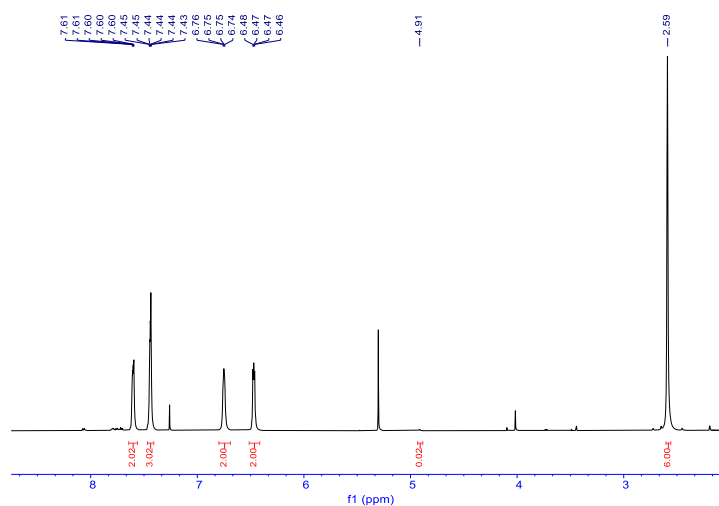
This general procedure is for the preparation of $[BIM^+](PF_6^-)$, $[HE^+](PF_6^-)$, and $[Acr^+](PF_6^-)$ from $[BIM^+](I^-)$, $[HE^+](MeSO_4^-)$, and $[Acr^+](I^-)$, respectively. $[A^+](X^-)$ (1 equiv, X = I or MeSO₄) was dissolved in MeOH at room temperature under air, and an aqueous solution of KPF₆ (100 equiv) was added in one portion. This caused immediate formation of precipitates which were collected by filtration. Recrystallization of the solid from Et₂O and MeCN afforded the desired PF₆⁻ salts in 60–80% yield. All the **BIM**⁺, **HE**⁺, and **Acr**⁺ species used in electrochemical experiments are their PF₆⁻ salts.

*Preparation of **BIMD***

The synthesis was adapted from a literature method.¹ $[BIM^+](I^-)$ (320 mg, 0.9 mmol) was dissolved in EtOH (15 mL) and DCM (5 mL), and the mixture was cooled to 0 °C under air. NaBD₄ (153 mg, 3.6 mmol) was added in small portions, and the mixture was stirred at room temperature for 1 h. The solvent was removed, and the residue was re-dissolved in DCM and filtered through a pad of Celite. After removing the solvent, the product was obtained as a white solid with 98% deuterium incorporation according to ¹H NMR.



1,3-Dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole-2-*d* (**BIMD**). ^1H NMR (500 MHz, CDCl_3) δ 7.65 – 7.56 (m, 2H), 7.49 – 7.39 (m, 3H), 6.75 (dd, $J = 5.4, 2.9$ Hz, 2H), 6.47 (dd, $J = 5.5, 3.2$ Hz, 2H), 2.59 (s, 6H).



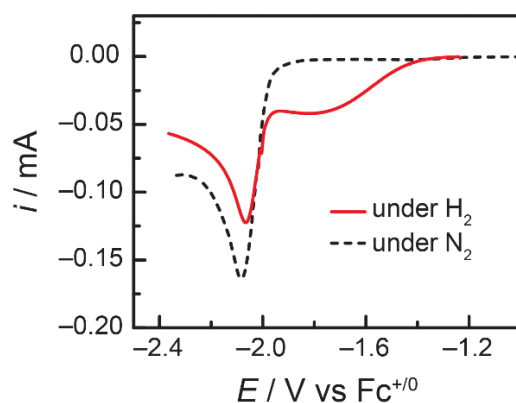
Supplementary Figure 1. ^1H NMR spectrum of **BIMD** in CDCl_3 . The peak at 4.91 ppm corresponds to **BIMH**, and thus the **BIMD** has a 98% isotopic purity by NMR peak integration.

General electrochemical methods

All electrochemical experiments were performed at ambient temperature (25 ± 1 °C) using a Biologic VSP 16-channel potentiostat or a Gamry Reference 600 potentiostat, and were conducted using a three-electrode setup under inert atmosphere (either in a N₂-filled glovebox or by sparging with Ar) unless otherwise noted. Rotation experiments were performed using a Metrohm Autolab RDE-2. All aqueous measurements used a leakless Ag/AgCl reference electrode (RE). All non-aqueous measurements used a non-aqueous Ag/Ag⁺ RE or a leakless Ag/AgCl RE as a pseudo-reference. At the end of each non-aqueous measurement, a small portion of ferrocene was added to the solution and a voltammogram was recorded to quantify the $E_{1/2}$ of the Fc⁺⁰ redox couple. All non-aqueous potentials were referenced to the Fc⁺⁰ redox couple. A Pt mesh counter electrode (CE) was used for all experiments using a three-electrode setup. All glassware used for electrochemical measurements was soaked in aqua regia for at least 30 minutes and thoroughly washed with MilliQ water prior to use. For non-aqueous measurements, the glassware was subsequently dried in an oven and then cooled while a stream of nitrogen was passed through the cell. Potentials were corrected for uncompensated Ohmic loss (iR_u) *in situ* via positive feedback at 85% of the measured value. R_u was measured using the R_u test function in the Gamry Framework software.

*Experimental procedure for cyclic voltammetry (CV) experiments of **BIM**⁺ using a Pt planar electrode*

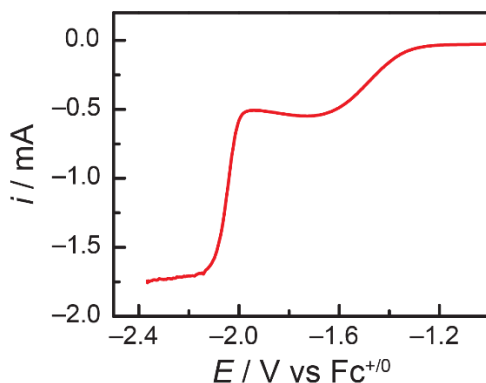
CV experiments were performed in an undivided cell using a Pt planar electrode as the WE, and the electrolyte solution contained a mixture of **BIM**⁺ (20 mM), TBAPF₆ (0.5 M), and MeCN (5 mL). Under 1 atm N₂, a voltammogram was recorded at a scan rate of 100 mV/s in order to investigate the outer-sphere reduction of **BIM**⁺. The cell was subsequently sparged with 1 atm H₂, and after the system reached equilibrium (as judged by a stable *E*_{OCF} value), a second voltammogram was recorded using the same experimental parameters.



Supplementary Figure 2. Linear sweep voltammograms of **BIM**⁺ under N₂ (black dashed trace) and H₂ (red solid trace) using a planar Pt electrode.

*Experimental procedure for the CV experiment of **BIM**⁺ using Pt RDE*

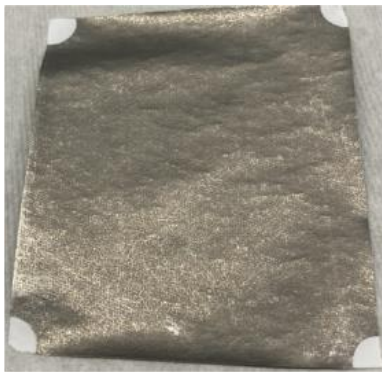
The CV experiment was performed in an undivided cell using a Pt RDE as the WE, and the electrolyte solution contained a mixture of **BIM**⁺ (10 mM), TBAPF₆ (0.5 M), and MeCN (15 mL). The cell was sparged with 1 atm H₂, and after the system reached equilibrium (as judged by a stable E_{OCP} value), a voltammogram was recorded at a scan rate of 100 mV/s. The HRR process (1st reduction wave) showed a peak shape rather than a plateau, suggesting that the Pt electrode may undergo passivation during HRR.



Supplementary Figure 3. Linear sweep voltammogram of **BIM**⁺ under H₂ using a Pt RDE.

Preparation of the Pt/PTFE GDE

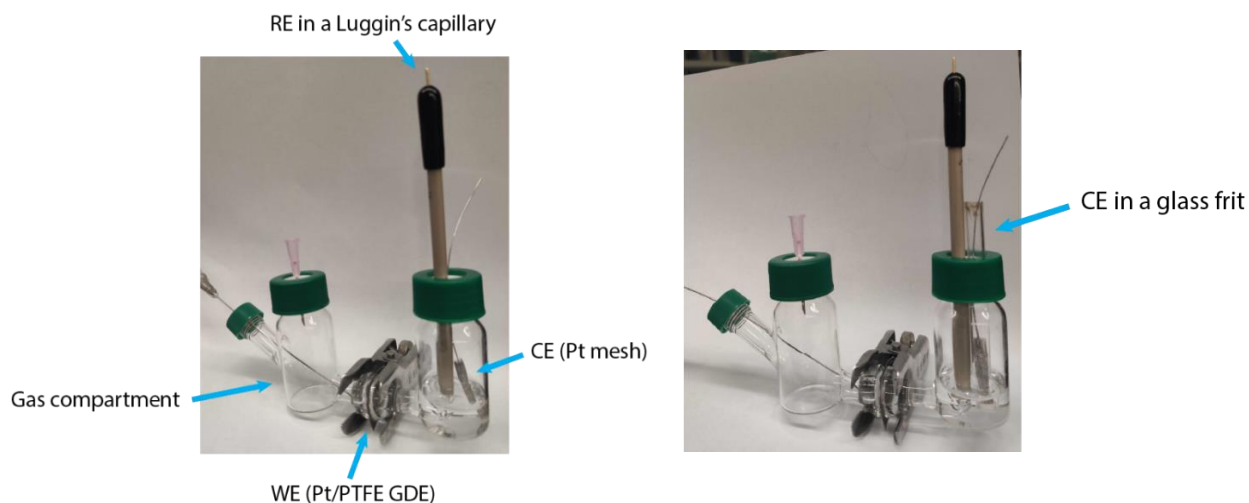
The preparation of Pt/PTFE GDE was performed similarly to previously reported methods.^{7,8} A Pt layer was sputter-deposited onto a PTFE membrane from a Pt target (99.99%) using an AJA sputtering system. The sputtering rate was $1 \text{ \AA s}^{-1}$ and the deposition was carried out for 50 min to reach a nominal thickness of 300 nm.



Supplementary Figure 4. A picture of Pt/PTFE GDE.

Assembly of H-cells using Pt/PTFE GDE

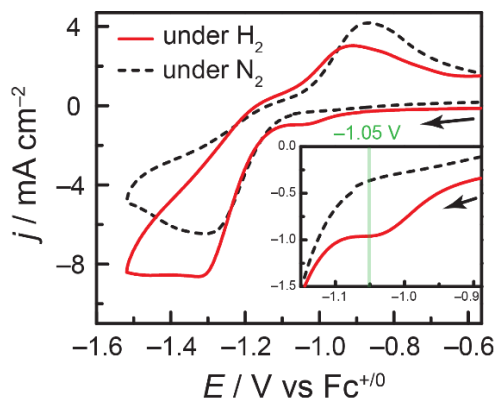
All experiments using the Pt/PTFE GDE were conducted in a custom-made glass body H-cell (Fig. S5). One compartment of the H-cell was the solution compartment containing electrolyte solution, RE, and CE, and the other compartment was for gas flow. Pt/PTFE GDE was sandwiched between the two compartments and sealed by two PTFE O-rings, with the Pt side facing the solution compartment and the PTFE side facing the gas compartment. The geometric surface area of Pt facing the electrolyte solution was 1 cm². N₂ or H₂ gas was aeriated in the gas compartment through a needle and the tip of the needle was placed close to the GDE to maximize gas transport. In the solution compartment, the RE was placed in a Luggin's capillary to minimize R_u , and the tip of the Luggin's capillary (diameter ~1 mm) was 1–2 cm away from the Pt/PTFE GDE. For measurements other than constant potential electrolysis (CPE), an undivided cell setup was used, wherein the CE was directly immersed into the electrolyte solution (Fig. S5, left). For CPE experiments, the solution compartment was constantly stirred by a magnetic PTFE stir bar at 700 rpm, and a divided cell setup was used and the CE was separated from the working compartment by a porous glass frit (Fig. S5, right). After assembly and prior to electrolysis, the cell was left to equilibrate for at least 15 min as judged by a stable E_{OCP} value.



Supplementary Figure 5. Undivided (left) and divided (right) H-cell setup with Pt/PTFE GDE as WE.

General procedure for CV experiments using Pt/PTFE GDE

To the solution compartment of the H-cell was added a mixture of A^+ (5 mM), TBAPF₆ (0.2 M), and MeCN (5 mL). The gas compartment was under N₂ atmosphere, and CV was performed at a scan rate of 100 mV/s to investigate the outer-sphere reduction of A^+ (1e-reduction for **BIM**⁺ and 2e-reduction for **IrCp**⁺). Then the gas compartment was sparged with H₂. After the whole system reached equilibrium (as judged by a stable E_{OCP} value), a voltammogram was recorded using the same experimental parameters.



Supplementary Figure 6. Cyclic voltammograms of **IrCp**⁺ under N₂ (black dashed trace) and H₂ (red solid trace). The reduction peaks at -1.3 V correspond to the outer-sphere 2e-reduction of **IrCp**⁺. Inset zooms into the region of the hydride transfer peak under H₂, and the HRR peak current density is similar to that of **BIM**⁺ as shown in Fig. 2a in the main text.

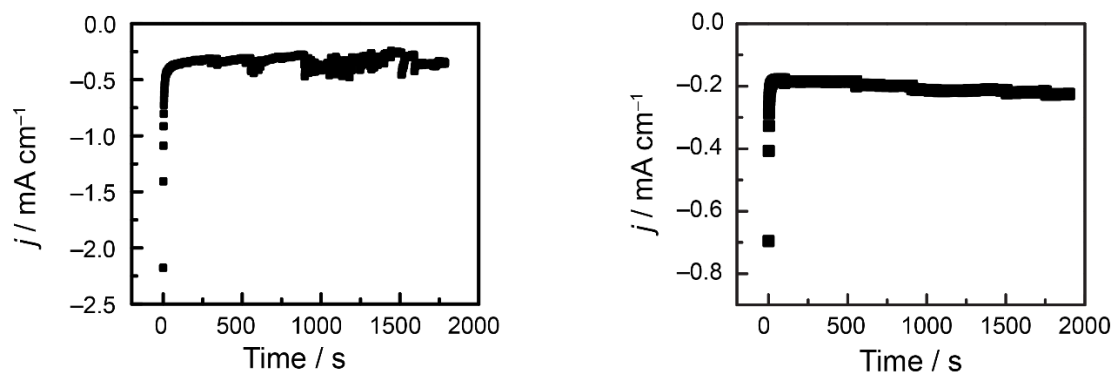
General procedure for HRR electrocatalysis using Pt/PTFE GDE

To the solution compartment of the H-cell was added a mixture of A^+ (10 mM), TBAPF₆ (0.5 M), and MeCN (5 mL), and the gas compartment was then sparged with H₂. After the whole system reached equilibrium (as judged by a stable E_{OCP} value), a chronoamperometry experiment was performed at the CPE potential. The observed current decayed rapidly in the initial stage (~2 min), which is likely due to a combination of double layer charging and possibly also electrode passivation, and then remained relatively stable. After 2 h (~1 C of charge has passed), electrolysis was stopped and the electrolyte solution was quickly removed from the H-cell. Chemical yield of HA was determined by ¹H NMR with PhTMS as the internal standard. For **BIM**⁺, a chemical yield of 16% was observed; for **IrCp**⁺, the yield was 9%. FE was calculated from the number of moles of product (n) and charge that has passed (Q) according to the following equation

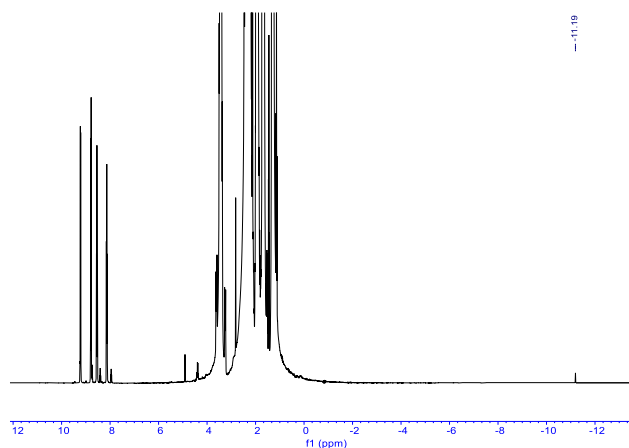
$$\text{FE} = \frac{nF}{Q} \times 100\%$$

For **IrCp**⁺, two additional control experiments were performed to assess whether the observed **IrCpH** product was formed via HRR. In the first experiment, the same reaction setup was used but the electrode was not polarized. After 2 h, <1% chemical yield of **IrCpH** was formed, showing negligible thermal (non-electrochemical) reaction of **IrCp**⁺ with H₂ and/or surface Pt–H. In the other control experiment, the same setup was used but carbon was used instead of Pt as the WE. After 2 h of CPE at the same potential, ~1% chemical yield of **IrCpH** was detected by NMR, demonstrating that outer-sphere 2e-reduction of **IrCp**⁺ followed by H₂ dissociation at the Ir(I) center minimally contributed to the formation of **IrCpH**.

When CPE was performed in an undivided cell, no conversion was observed for **BIM**⁺, indicating facile oxidation of **BIMH** at the Pt anode. Since the undivided cell setup can maintain solution stability, all the electrochemical measurements for thermodynamic and kinetic studies of HRR were performed in undivided cells. HRR of other hydride acceptors such as **HE**⁺, **BCF** and **Acr**⁺ could not be performed because when polarizing more negatively of the E_{OCP} values, outer-sphere ET processes interfered with hydride transfer to these substrates.



Supplementary Figure 7. Chronoamperometric traces for HRR of **BIM**⁺ (left) and **IrCp**⁺ (right) under CPE conditions.



Supplementary Figure 8. Crude ¹H NMR spectrum after CPE of **IrCp**⁺ (CD₃CN, 25 °C). The peak at approximately -11 ppm is attributed to the formation of **IrCpH** in accordance with reported spectroscopic data.⁶

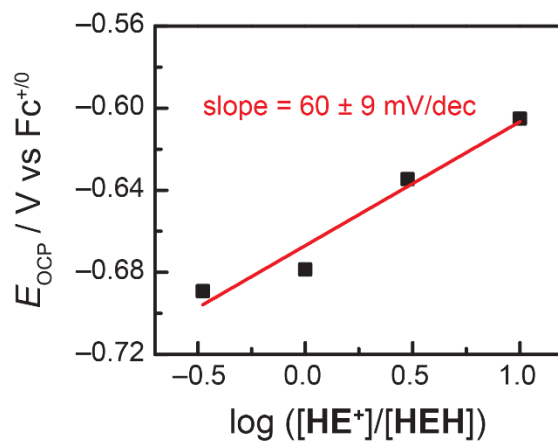
Experimental procedure for E_{OCP} measurements for thermodynamic studies

All E_{OCP} measurements were performed using a two-electrode setup consisting of a Pt/C GDE as WE and a leakless Ag/AgCl RE. 0.1 M TBAPF₆ in MeCN (5 mL) was used as the electrolyte solution. Steady state E_{OCP} values are reported and they were found to be stable for at least 15 min under the experimental conditions.

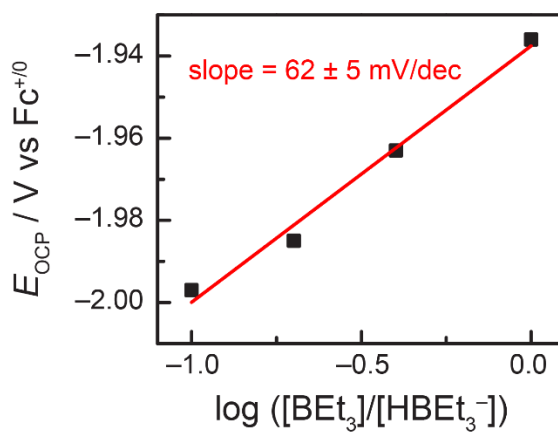
Fig. 3a in the main text was plotted based on two separate experiments. In the first experiment, 2.5 mM of **BIM**⁺ and 25 mM of **BIMH** were added to the electrolyte solution, affording a steady-state E_{OCP} value of -1.21 V at this 1:10 ratio of **A**⁺/HA. E_{OCP} values were then recorded by adding another 5.8 mM and 16.7 mM of **BIM**⁺ to reach 1:3 and 1:1 ratios of **BIM**⁺ and **BIMH**, respectively. In the other experiment, E_{OCP} values were measured by starting from 25 mM **BIM**⁺/2.5 mM **BIMH**, followed by 25 mM **BIM**⁺/8.3 mM **BIMH** and 25 mM **BIM**⁺/25 mM **BIMH** by adding **BIMH**.

Fig. 3b was obtained by measuring E_{OCP} values at different H₂ partial pressures, and the first measurement was made at 1 atm H₂, followed by a random order of H₂ partial pressures in the range of 0.1–0.6 atm H₂ by Ar dilution, and finally at 0.06 atm H₂. The reversibility of the system was then checked by returning back to 1 atm H₂ and the E_{OCP} value agreed well with the first measurement ($\Delta E_{\text{OCP}} < 5$ mV).

In Fig. 3c, the equilibrium HRR potential for **HEH/HE**⁺ was further verified by changing the concentration ratio as shown in Fig. S9, where a Nernstian scaling was obtained. In Fig. 3d, the equilibrium HRR potential for **HBEt**₃[−]/**BEt**₃ was also verified by changing the concentration ratio as shown in Fig. S10 where a Nernstian scaling was also observed.



Supplementary Figure 9. Nernstian dependence of E_{OCP} on the concentration ratio of HE^+ and HEH in MeCN.



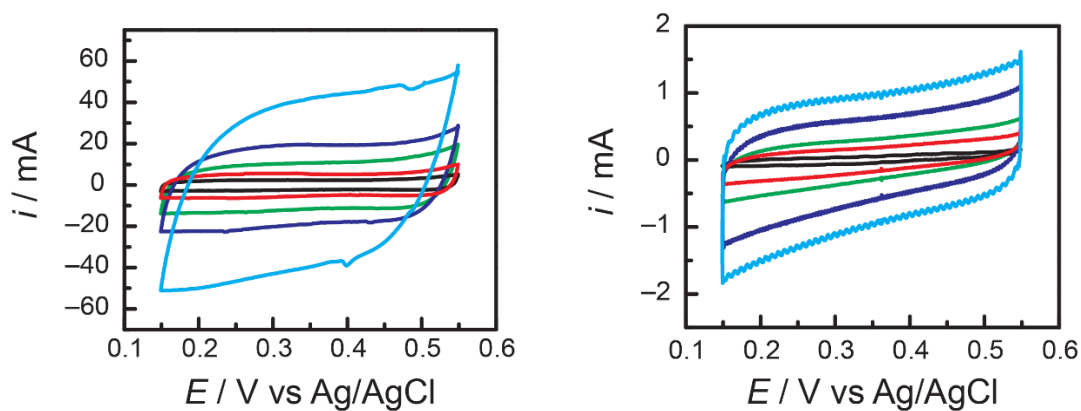
Supplementary Figure 10. Nernstian dependence of E_{OCP} on the concentration ratio of BEt_3 and HBEt_3^- in THF.

General experimental parameters for EIS measurements

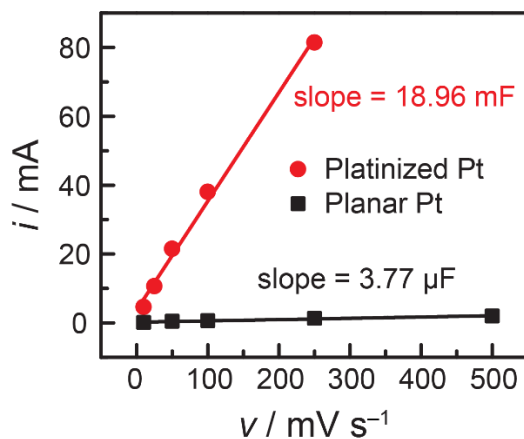
Except for Fig. S13, all EIS experiments were measured in undivided cells under 1 atm H₂ or D₂ in a glovebox and using a 0.1 M TBAPF₆ in MeCN (5 mL) solution containing a hydride or proton donor/acceptor pair (25 mM each). Potentiostatic EIS (PEIS) data were recorded with a peak-to-peak amplitude of 5 mV and frequencies ranging from 1 MHz to 1 Hz. High-frequency noise was omitted, and the quality of all shown PEIS data was verified by satisfying Kramers-Kronig relations.⁹ Unless otherwise stated, the data were fitted to the equivalent circuit shown in Fig. 6a in the main text using Gamry Echem Analyst and Pine AfterMath softwares. PEIS measurements for HRR of **BIMH/BIM**⁺ were performed using a platinized Pt electrode with high ECSA or a planar metal electrode with low ECSA. PEIS for HER/HOR of **TEAH/TEA**⁺ measured on the platinized Pt electrode only showed the Warburg impedance without any observable charge transfer components (semicircles), which is likely due to the faster kinetics of HER/HOR, and therefore the measurements for HER/HOR were only performed on a planar Pt electrode with low ECSA.

Preparation of the platinized Pt electrode and measurement of ECSA

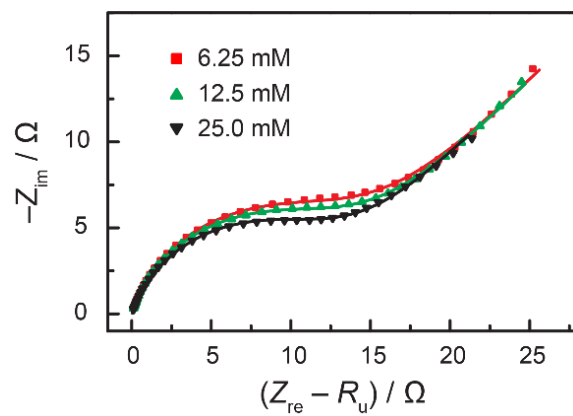
A polycrystalline Pt metal foil was cut into ca. 1.0 cm × 2.1 cm and vertically affixed to a Ti wire at the top to establish contact to the potentiostat clip. The Ti contact wire was then threaded through a septum to form a working electrode assembly. The geometric surface area of Pt foil in contact with electrolyte solution was ca. 4 cm². The Pt foil was first cleaned by CV cycling in 1 M H₂SO₄, and then platinized by electrodeposition using a H₂PtCl₆ (2 wt%) in 1 M HCl solution. The electrodeposition was performed at -0.15 V vs Ag/AgCl until 13 C of charge has passed. The platinized Pt electrode was then rinsed with copious amounts of MilliQ water and dried under a stream of air. ECSA was measured by CV studies under variable scan rates (v , 10–250 mV/s) using literature methods,¹⁰ and was calculated to be 365 cm², corresponding to a roughness factor of ~90.



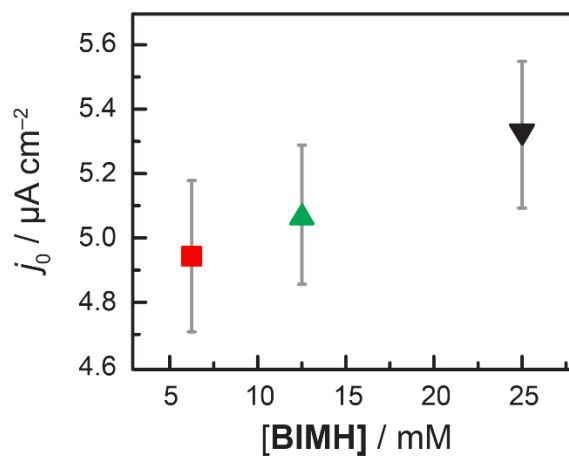
Supplementary Figure 11. Variable scan rate CV plots in the double layer region for platinized (left) and planar Pt (right) electrodes.



Supplementary Figure 12. Plot of capacitive current in the double layer region (0.35 V vs Ag/AgCl) versus scan rate for platinized and planar Pt electrodes. The ECSA can be calculated based on the slope and a constant of 52 μ F/cm² for Pt.¹⁰



Supplementary Figure 13. EIS data for HRR of **BIM⁺/BIMH** with varying concentrations of **BIM⁺/BIMH** on a platinized Pt electrode.



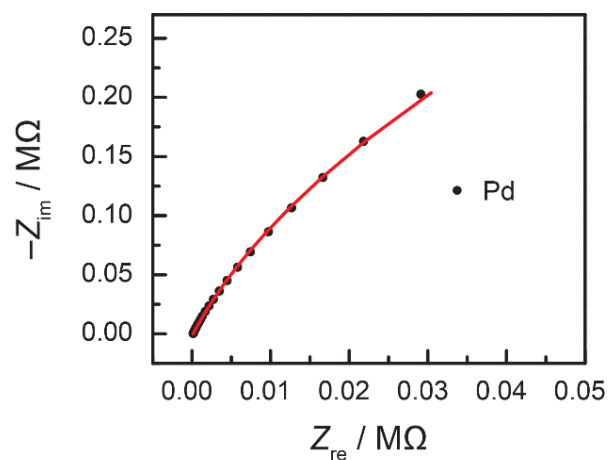
Supplementary Figure 14. Plot of j_0 values calculated from the EIS data versus concentration of **BIM⁺/BIMH**.

Supplementary Table 1. Summary of fitting parameters for the EIS data measured using a platinized Pt electrode

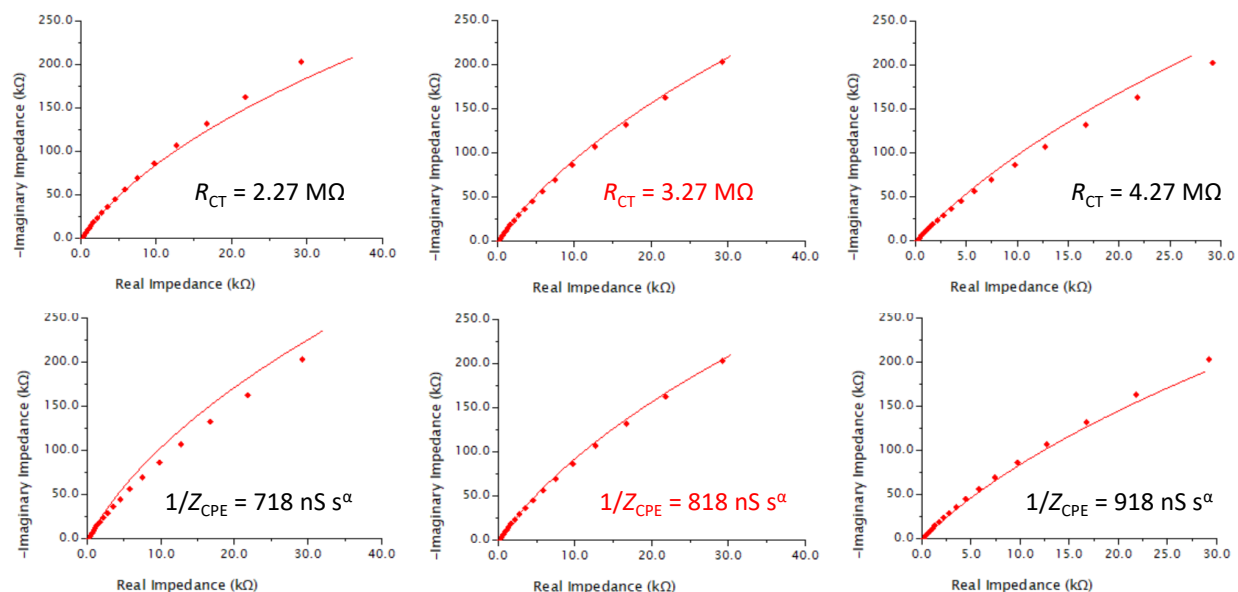
Conditions	6.25 mM BIM⁺/BIMH	12.5 mM BIM⁺/BIMH	25 mM BIM⁺/BIMH	25 mM BIM⁺/BIMD (1 atm D ₂)
R_{CT} (Ω)	14.2(8)	13.8(6)	13.2(6)	48.8(2)
R_u (Ω)	10.7(1)	8.7(1)	8.2(1)	11.4(1)
$1/Z_{CPE}$ ($\mu S \times s^a$)	323(69)	384(72)	528(97)	371(34)
α	0.80(3)	0.79(2)	0.78(3)	0.78(1)
$1/Z_w$ ($S \times s^{0.5}$)	0.0148(5)	0.0175(6)	0.0230(9)	0.0137(9)

Pretreatment of planar Pt, Pd, Ni, and Au electrodes and measurement of ECSA

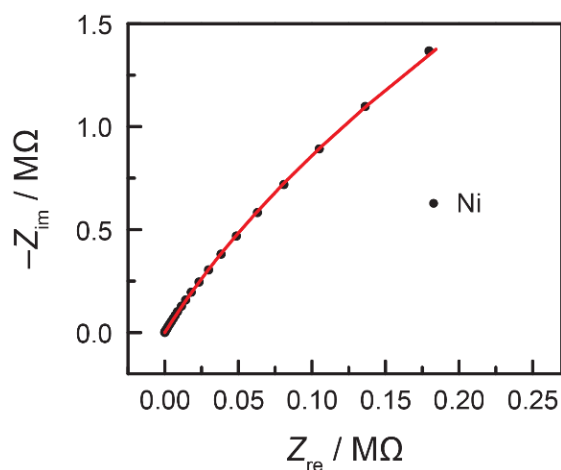
Each planar electrode was polished on a separate 0.3 μm alumina slurry prior to experiments. ECSA for the Pt electrode was measured by CV studies under variable scan rates (v , 10–500 mV/s, Fig. S11) using literature methods,¹⁰ and a roughness factor of ~ 2 was calculated (Fig. S12). Since all these electrodes have similar α values for the CPE component (Table S2) which indicates similar surface heterogeneity, this roughness factor is also assumed for polished Pd, Ni, and Au planar electrodes. The PEIS data were fitted using a Randles circuit without Warburg impedance since all the data measured are well within the activation-controlled region (Figs. S15, S17, and S19). To validate that the fitted curves represent the global minima for data simulation, fittings were also performed by changing R_{CT} and CPE components to values deviating from the optimized ones (Figs. S16, S18, and S20) to look for other possible local minima, and the optimized fitting data in Figs. S15, S17, and S19 generally showed the least fitting error and best fitting quality.



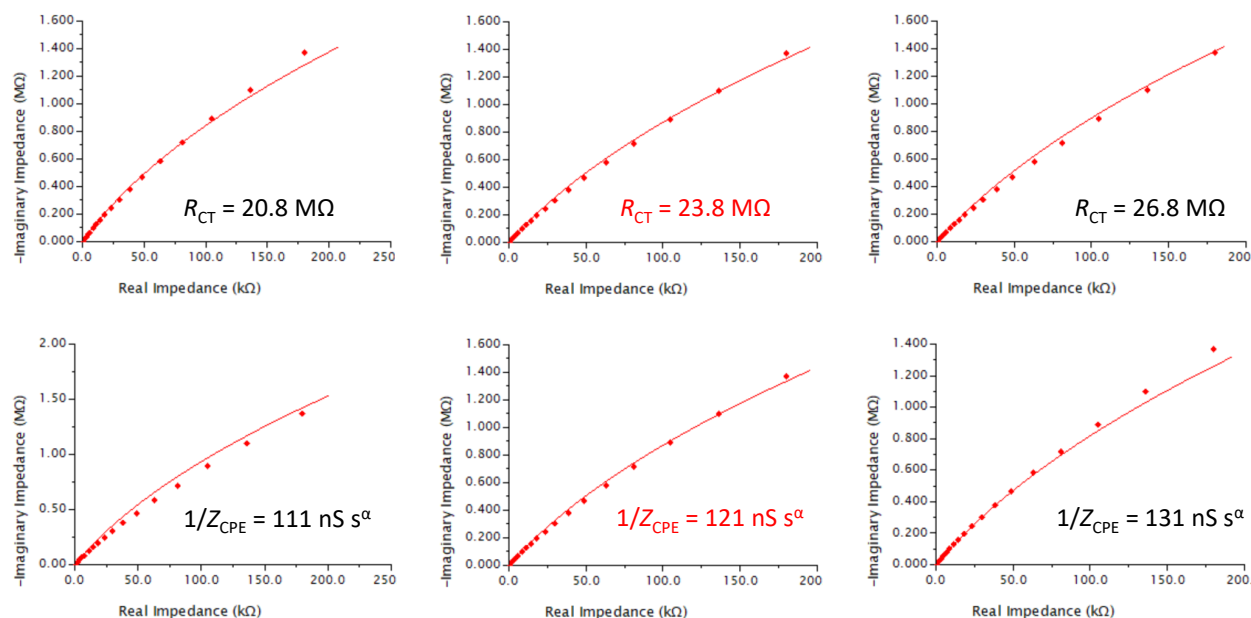
Supplementary Figure 15. EIS data for HRR of **BIM⁺/BIMH** on Pd planar electrode. Black dots are experimental data and red line is the optimized fitting curve.



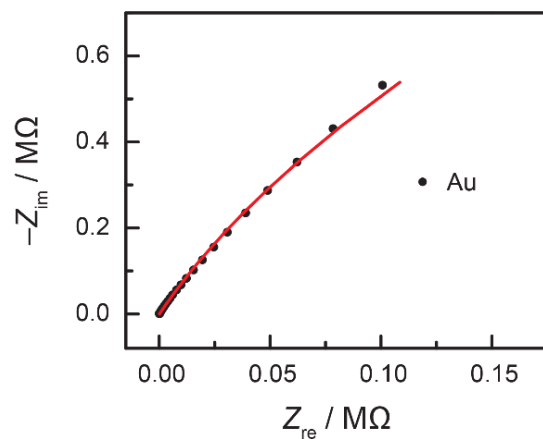
Supplementary Figure 16. Fitting EIS data for HRR of **BIM⁺/BIMH** on Pd planar electrode by varying R_{CT} (top row) and CPE (bottom row) components. Fitting was performed by fixing R_{CT} or $1/Z_{CPE}$ to the corresponding values, with the numbers in red being the optimized values obtained in Fig. S15.



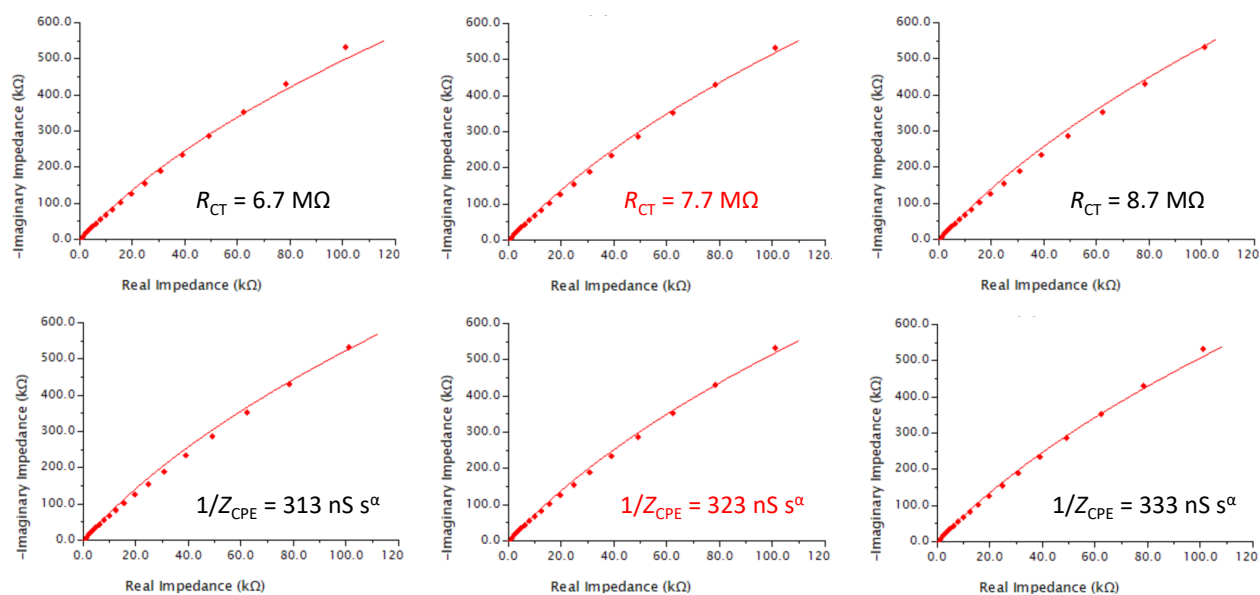
Supplementary Figure 17. EIS data for HRR of **BIM⁺/BIMH** using Ni planar electrode. Black dots are experimental data and red line is the optimized fitting curve.



Supplementary Figure 18. Fitting EIS data for HRR of **BIM⁺/BIMH** on Ni planar electrode by varying R_{CT} (top row) and CPE (bottom row) components. Fitting was performed by fixing R_{CT} or $1/Z_{CPE}$ to the corresponding values, with the numbers in red being the optimized values obtained in Fig. S17.



Supplementary Figure 19. EIS data for HRR of **BIM⁺/BIMH** using Au planar electrode. Black dots are experimental data and red line is the optimized fitting curve.



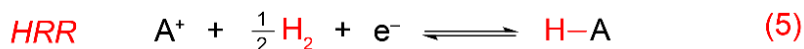
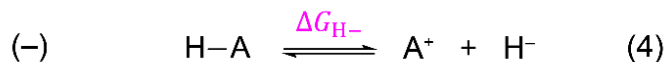
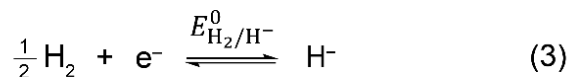
Supplementary Figure 20. Fitting EIS data for HRR of **BIM⁺/BIMH** on Ni planar electrode by varying R_{CT} (top row) and CPE (bottom row) components. Fitting was performed by fixing R_{CT} or $1/Z_{CPE}$ to the corresponding values, with the numbers in red being the optimized values obtained in Fig. S19.

Supplementary Table 2. Summary of fitting parameters for the EIS data measured using planar Pt, Pd, Ni, and Au electrodes

Electrode material	Pt	Pd	Ni	Au	Pt (HER/HOR)
R_{CT} (M Ω)	0.35(3)	3.27(1)	23.8(1)	7.7(1)	0.0565(6)
ECSA (cm ²)	0.0725	0.163	0.163	0.0725	0.0725
R_u (Ω)	124(3)	146(8)	127(9)	176(10)	929(12)
$1/Z_{CPE}$ (nS $\times$ s ^{α})	412(8)	818(46)	121(6)	323(20)	622(15)
α	0.941(3)	0.950(4)	0.951(4)	0.921(6)	0.882(4)

Derivation of the Nernst equation for HRR

Since eqs. 3–5 in Fig. 3 in the main text are in equilibrium:



the equilibrium potentials for eqs. 3 and 5 are equal:

$$E_{\text{eq}}(\text{eq. 3}) = E_{\text{eq}}(\text{eq. 5}) = E_{\text{OCP}} \quad (\text{S1})$$

The Nernst equation for eq. 3 is

$$E_{\text{OCP}} = E_{\text{H}_2/\text{H}^-}^0 + \frac{2.3RT}{2F} \log p_{\text{H}_2} - \frac{2.3RT}{F} \log [\text{H}^-] \quad (\text{S2})$$

$E_{\text{H}_2/\text{H}^-}^0$ is a constant and can be calculated based on the following thermochemical cycle with known literature values¹¹:



where the ΔG° values are in MeCN and referenced to $\text{Fc}^{+/0}$ for electrochemical half reactions. Thus, $E_{\text{H}_2/\text{H}^-}^0$ in MeCN at room temperature can be obtained as

$$E_{\text{H}_2/\text{H}^-}^0 = -\frac{\Delta G_{\text{H}_2/\text{H}^-}^\circ}{F} = -3.37 \text{ V (vs Fc}^{+/0}\text{)}$$

Since eq. 4 in Fig. 3 is at equilibrium, then

$$\Delta G_{\text{H}^-} = -RT \ln K(\text{eq. 4}) = -2.3RT \log \frac{[\text{H}^-][\text{A}^+]}{[\text{HA}]} \quad (\text{S3})$$

By rearranging eq. S3, we can get

$$-\frac{2.3RT}{F} \log [\text{H}^-] = \Delta G_{\text{H}^-} + 2.3RT \log \frac{[\text{A}^+]}{[\text{HA}]} \quad (\text{S4})$$

By combining eqs. S2 and S4, we get

$$E_{\text{OCP}} = E^0_{\text{H}_2/\text{H}^-} + \frac{2.3RT}{F} \log \frac{[\text{A}^+]}{[\text{HA}]} + \frac{2.3RT}{2F} \log p_{\text{H}_2} + \frac{1}{F} \Delta G_{\text{H}^-} \quad (6)$$

which is the Nernst equation (eq. 6) in Fig. 3 in the main text. In MeCN at room temperature, we can further get

$$E_{\text{OCP}} = -3.37 + 0.059 \log \frac{[\text{A}^+]}{[\text{HA}]} + 0.030 \log p_{\text{H}_2} + 0.043 \Delta G_{\text{H}^-} \quad (6)$$

If we directly derive the Nernst equation for eq. 5, it has the form of

$$E_{\text{OCP}} = E^0(\text{eq. 5}) + \frac{2.3RT}{2F} \log p_{\text{H}_2} + \frac{2.3RT}{F} \log \frac{[\text{A}^+]}{[\text{HA}]} \quad (\text{S5})$$

However, $E^0(\text{eq. 5})$ is not a constant because it depends on the choice of HA/A^+ . According to eq. 6, it can be easily derived that, for a given pair of HA/A^+ with thermodynamic hydricity value of ΔG_{H^-} :

$$\begin{aligned} E^0(\text{eq. 5}) &= E^0_{\text{H}_2/\text{H}^-} + \frac{1}{F} \Delta G_{\text{H}^-} \quad (\text{S6}) \\ &= -3.37 + 0.043 \Delta G_{\text{H}^-} \quad (\text{in MeCN at room temperature}) \end{aligned}$$

References

1. Lee, C. K. & Lee, I.-S. H. NMR studies of 2-aryl derivatives of benzimidazole, benzimidazolium ion, and benzimidazoline. *Heterocycles* **78**, 425 (2009).
2. Brook, P. R. & Karrer, P. Über Die Aufspaltung Des 1.2.6-Trimethyl-3.5-Dicarbäthoxy-1.2-Dihydropyridins Durch Säure Sowie Über Methylierungsprodukte Des p-Dihydro-2.6-Lutidin-3.5-Dicarbonsäure-Diäthylesters. *Justus Liebigs Ann. Chem.* **605**, 1-8 (1957).
3. Lawrence, E. J., Oganessian, V. S., Hughes, D. L., Ashley, A. E. & Wildgoose, G. G. An Electrochemical Study of Frustrated Lewis Pairs: A Metal-Free Route to Hydrogen Oxidation. *J. Am. Chem. Soc.* **136**, 6031-6036 (2014).
4. Eberhard, J., Peuntinger, K., Fröhlich, R., Guldi, D. M. & Mattay, J. Synthesis and Properties of Acridine and Acridinium Dye Functionalized Bis(terpyridine) Ruthenium(II) Complexes. *Eur. J. Org. Chem.* **2018**, 2682-2700 (2018).
5. van Leest, N. P., Grooten, L., van der Vlugt, J. I. & de Bruin, B. Uncatalyzed Oxidative C-H Amination of 9,10-Dihydro-9-Heteroanthracenes: A Mechanistic Study. *Chem. Eur. J.* **25**, 5987-5993 (2019).
6. Barrett, S. M., Pitman, C. L., Walden, A. G. & Miller, A. J. M. Photoswitchable Hydride Transfer from Iridium to 1-Methylnicotinamide Rationalized by Thermochemical Cycles. *J. Am. Chem. Soc.* **136**, 14718-14721 (2014).
7. Dinh, C.-T. *et al.* CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **360**, 783-787 (2018).
8. Dinh, C.-T., García de Arquer, F. P., Sinton, D. & Sargent, E. H. High Rate, Selective, and Stable Electroreduction of CO₂ to CO in Basic and Neutral Media. *ACS Energy Lett.* **3**, 2835-2840 (2018).
9. Orazem, M. E. & Tribollet, B. *Electrochemical Impedance Spectroscopy*. (2017).
10. Chen, D. *et al.* Determining the Active Surface Area for Various Platinum Electrodes. *Electrocatalysis* **2**, 207 (2011).
11. Wiedner, E. S. *et al.* Thermodynamic Hydricity of Transition Metal Hydrides. *Chem. Rev.* **116**, 8655-8692 (2016).