Electronic Supplementary Information for

A tridentate Nickel pincer for aqueous electrocatalytic hydrogen production

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General experimental

1. Cyclic voltammograms (CVs) in aqueous solution were collected using a 0.09 cm^2 basal plane graphite working electrode prepared by the method of Blakemore *et al.*,[1SI] a platinum wire counter electrode and an aqueous Ag/AgCl, KCl (sat) reference. In acetonitrile, a glassy carbon electrode was used as the working electrode and a Ag wire reference (referenced vs. NHE with ferrocene as external standard). For the aqueous electrochemistry 3 mL 0.1 M KCl aqueous solutions were used, with incremental amounts of acid added (1 M HCl, 40, 90, 140 µL). Basal plane graphite electrodes were preferred over glassy carbon electrodes in aqueous conditions due to low background currents in the absence of catalyst. Background CVs are provided in sections 1 and 2. CVs were recorded after addition of 4*10 µL 1 M HCl via volumetric syringe. All other CVs were recorded after rigorous exclusion of air via Argon purge. Data workup was performed on OriginPro v8.0988 and AfterMath Data Organizer Version 1.2.3383.
2. Kinetic isotope studies studies were carried out with a Pine AFCBP1 Bipotentiostat and a Pine MSR variable-speed rotator. The reference was a Ag/AgCl electrode (Bioanalytical Systems, Inc.) and the counter electrode was a platinum wire. The disc (surface area: 0.07 cm^2) material was basal plane graphite (with stabilizing resin around the graphite; from Pine). The disc was assembled in a Pine E6-series ChangeDisk Setup. The disk voltage was held at 0.5 V vs NHE for 30 min. Data were collected in 12 mL of a 0.1 M KCl solution containing 1 mM catalyst **1** and 20% HCl or 20% DCl (procured from Cambridge Isotopes) at 500 rpm.
3. Tafel Plots were constructured from short chronoamperometry experiments (dwell time: 60 seconds) at potentials lower than 0 V (vs NHE) at a glassy carbon electrode in a single-chamber, three-electrode configuration. The experiments were performed in 5.2 mL of a 0.1 M NBu_4BF_4 acetonitrile solution containing 0.2 mM catalyst and 200 µL of a 1 M aqueous HCl solution. Magnetic stirring was used to avoid diffusion limitations from concentration gradients at the working electrode.
4. The order of reaction with respect to acid was determined by analysis of cyclic voltammograms of 2 mM catalyst solutions with different acid concentrations. To a 0.1 M NBu_4BF_4 acetonitrile solution containing 2 mM catalyst (from the CVs of which i_p was determined at different scan rates), 5 µL increments of an aqueous 1 M HCl solution (also containing 0.1 M NBu_4BF_4) were added. The voltammograms thus collected at each acid concentration (for several scan rates) were used to obtain catalytic currents (denoted i_c). The ratio of i_c/i_p was plotted against acid concentration for the different scan rates. From the linear behavior at each scan rate, we conclude that our system obeys a rate law that is second order in acid. The slopes of the scan rate-dependent data were then used to calculate the third order rate constants.

5. The order in catalyst was determined from voltammograms collected at 100 mV/s with 3.5 mL of an acetonitrile 0.1 M NBu_4BF_4 solution with a concentration of 2.82 mM catalyst and 4 mM acid. Increments of 0.5 mL of a 0.1 M NBu_4BF_4 acetonitrile solution were added and the dilutions were adjusted to maintain a constant acid concentration. We assumed no large variations in the acid concentration throughout the experiment. From each voltammogram, i_c was plotted against catalyst concentration. From the linearity of the resulting graph we conclude that at reasonably low catalyst concentration first order behavior is observed.
6. Controlled potential headspace H_2 detection experiments were performed in a custom built two cylinder 50 mL bulk electrolysis H cell anode/cathode chamber separated by a coarse frit. The working electrode was a BASi RVC electrode referenced vs. Ag/AgCl (KCl_{sat}). Headspace H_2 detection was performed at the Yale Department of Geology on a calibrated mass spectrometer: dual inlet Thermo Finnegan MDT 253 and an air-tight bulk electrolysis H Cell equipped with a sampling port. 1 mL volumes of gas were compressed in the bellow to 10% then opened to the mass spectrometer.

1: Cyclic Voltammetry in nonaqueous conditions

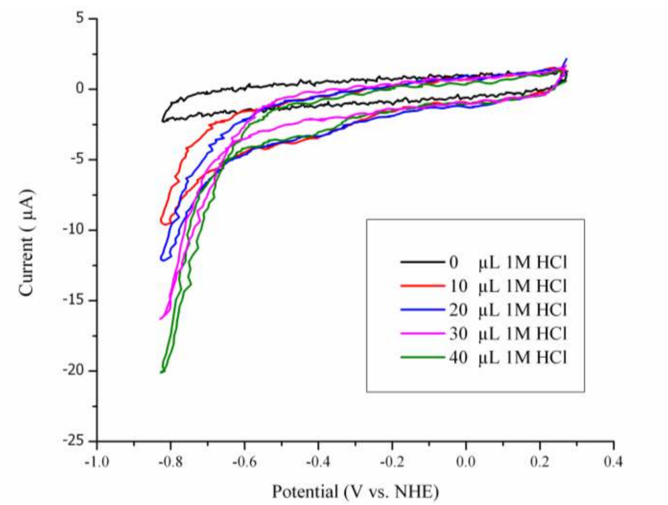
Table S1. Tabulated cyclic voltammetry data of a 2 mM nickel pincer complex (**1**) in 0.1 M NBu_4BF_4 acetonitrile solution at a glassy carbon working electrode.

Catalyst	1st reduction $E_{1/2}$	ΔE_1 Peak 1 separation[a]	2nd reduction $E_{1/2}$	ΔE_2 Peak 2 separation[a]	Oxidation $E_{1/2}$	ΔE_{ox} Oxidation peak separation[a]
Glassy carbon (Background)	n/a	n/a	n/a	n/a	n/a	n/a
1	0.162 V	0.162 V	-0.430 V	0.093 V	1.711 V	0.166 V

[a] Expected peak separation for a perfectly $1e^-$ reversible wave: 0.059 V

Cyclic voltammograms were recorded using a Teflon coated BASi glassy carbon working electrode, a platinum wire counter electrode and an 0.1 M nBu_4BF_4 acetonitrile solution versus a pseudoreference electrode: silver wire (BASi MF0) referenced externally vs. the Fc/Fc^+ couple at 690 mV vs. NHE. All CVs were recorded after rigorous Argon purge.

Figure S1-1. Cyclic voltammograms of a GC background 0.1 M NBu_4BF_4 acetonitrile solution (*black*) in the presence of 10 µL (*red*), 20 µL (*blue*), 30 µL (*purple*) and 40 µL (*green*) 1 M HCl (100 mV/s). Smoothed 5 point adjusted averaging was used to remove electrical noise.



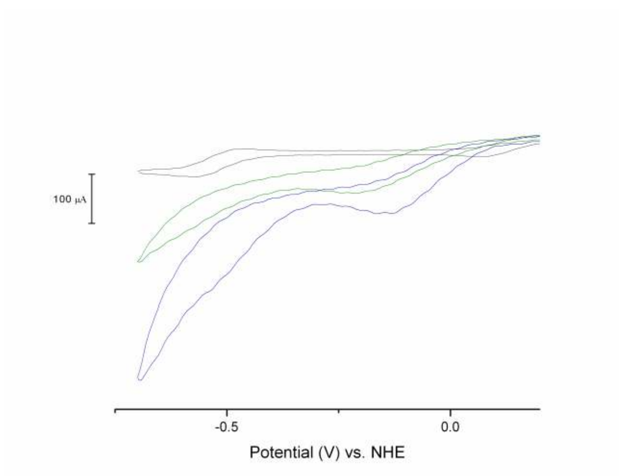


Figure S1-2. Cyclic voltammograms of 2 mM **1** in 0.1 M NBu_4BF_4 acetonitrile solution (*grey*) in the presence of 10 µL (*green*), 20 µL (*blue*) 1 M HCl (100 mV/s).

2. Cyclic voltammograms in aqueous conditions

Cyclic voltammograms were collected using a basal plane graphite electrode (0.09 cm^2) working electrode, a platinum wire counter electrode and an aqueous Ag/AgCl, KCl (sat) reference in 3 mL 0.1 M KCl aqueous solution with 1 mL acetonitrile added in the case of **5** with incremental amounts of acid added (HCl, 1 M, 4*10 µL followed by 2*50 µL). All CVs were recorded after rigorous Argon purge. We found that the background currents on a glassy carbon electrode were very high under these conditions.

Catalyst 1

Catalyst **1** is readily soluble in aqueous 0.1 M KCl. 2.5 mg catalyst were dissolved in 3 mL 0.1M KCl aqueous solution.

Figure S2-1. Cyclic voltammograms of background at basal plane graphite in 0.1 M KCl water solution (*black*) in the presence of 40 µL (*red*), 90 µL (*blue*), 140 µL (*purple*) HCl 1 M at 100 mV/s.

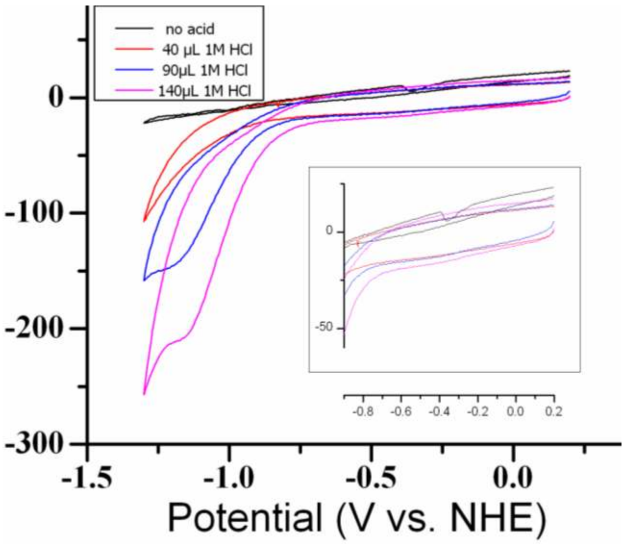


Figure S2-2. Cyclic voltammograms of background at basal plane graphite 3 mL 0.1 M aqueous KCl with 1 mL acetonitrile (*black*) in the presence of 40 µL (*red*), 90 µL (*blue*), 140 µL (*purple*) at 100 mV/s. (preferred conditions for catalyst **1** CVs)

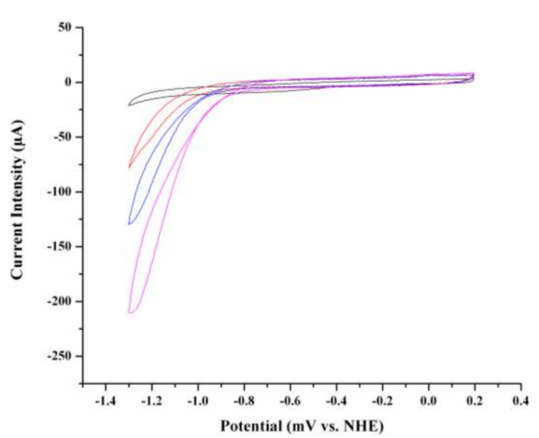
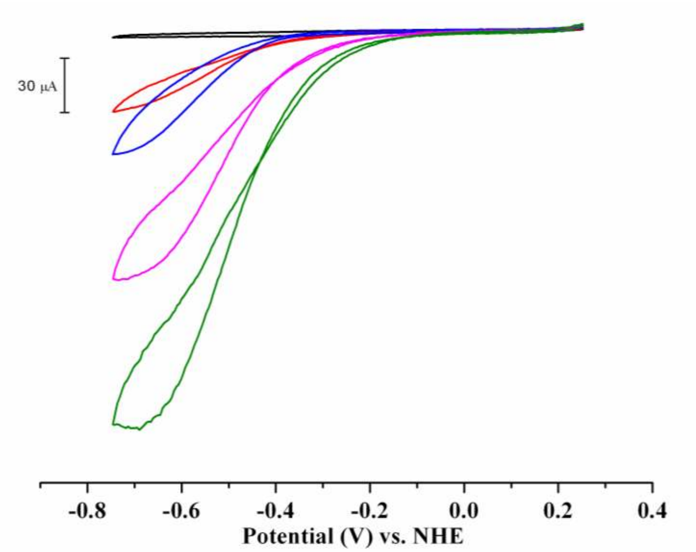
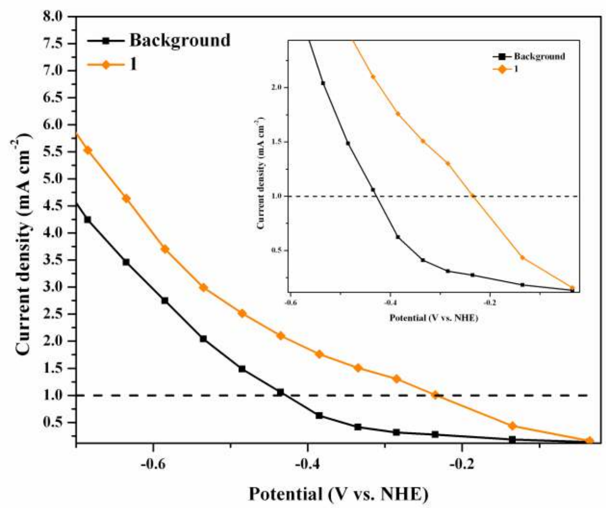


Figure S2-3. Cyclic voltammograms of background at a glassy carbon electrode of 0.1 M KCl water solution (*black*) in the presence of of 10 µL (*red*), 20 µL (*blue*), 30 µL (*purple*) and 40 µL (*green*) at 100 mV/s. Very high background currents- Basal plane graphite was preferred.



3. Pseudo-Tafel data

Figure S3-1. Steady state current density at the end of chronoamperometry experiments at progressively more negative potentials - chronoamperograms (dwell time: 60 sec) at a glassy carbon electrode: 5.2 mL acetonitrile NBu_4BF_4 solution containing 200 µL 1 M aqueous HCl at 0.2 mM catalyst with magnetic stirring. Since our [H+] = 0.04 M, the pH = - log [H+] = 1.43. Thus $E^{o\prime}$ = -84 mV vs. NHE corresponding to an approximate overpotential of -140mV.


Background
1
Current density (mA cm-2)
Potential (V vs. NHE)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.6
-0.4
-0.2

4. Computational details

Table S4-1. Relative energies of intermediates involved in the proton reduction cycle with catalyst **1** in H_2O**.**

	ΔG(soln) [kcal/mol]
$[1'(OH_2)]^{2+}$	0
$[1'(OH_2)]^{+}$	-95.7
***trans*-$[1'(OH_2)_2H]^{2+}$**	-69.7
***cis*-$[1'(OH_2)_2H]^{2+}$**	-56.1
$[1'(H)]^{+}$	-184.5
$[1'(H_2)]^{2+}$	-175.6
$[1'(OH_2)]^{2+}$ + H_2 - $2H^+$ - $2e^-$	-195.4

$[1'(OH_2)]^{2+}$

Ni	0.00178	0.035863	-0.12309
N	1.926952	0.280409	-0.079217
N	-0.008169	1.849595	-0.328952
N	-1.924365	0.241765	-0.244295
C	-2.330519	1.485803	-0.380517
C	-3.756115	1.935509	-0.487559
H	-4.444444	1.090614	-0.542916
H	-4.032065	2.548901	0.381551
H	-3.895085	2.561105	-1.378921
C	-1.207382	2.467701	-0.426036
C	1.181158	2.493108	-0.313805
C	1.204912	3.893682	-0.424221
H	2.140994	4.441234	-0.422753
C	-0.02645	4.575747	-0.540339
H	-0.033525	5.657648	-0.630901
C	-1.248955	3.868058	-0.539823
H	-2.192221	4.396349	-0.625302
C	2.3162	1.533854	-0.175119
C	3.735589	2.014127	-0.156935
H	3.882499	2.73917	0.654888
H	4.440389	1.192476	-0.020969
H	3.979957	2.530713	-1.095278
C	2.840243	-0.844517	0.023681
C	3.380401	-1.400351	-1.168524
C	3.071159	-0.82138	-2.536997
C	4.233495	-2.515885	-1.037941
H	4.664238	-2.959435	-1.931382
C	4.536499	-3.054747	0.225421

H	5.20008	-3.910859	0.303382
C	3.981687	-2.490066	1.38825
H	4.223645	-2.908396	2.361409
C	3.122258	-1.374166	1.313134
C	2.556978	-0.746412	2.574576
H	1.99864	-0.630662	-2.676398
H	1.472381	-0.586983	2.500438
C	-2.815394	-0.89761	-0.130791
C	-3.006038	-1.716386	-1.280785
C	-3.420541	-1.183406	1.123933
C	-3.834707	-2.849236	-1.145738
C	-2.391905	-1.362223	-2.623371
C	-3.226563	-0.297424	2.341548
C	-4.237721	-2.331057	1.20361
C	-4.447779	-3.154478	0.083782
H	-4.009926	-3.483704	-2.010185
H	-1.316454	-1.148507	-2.55135
H	-2.230886	0.158795	2.385293
H	-4.713879	-2.574433	2.149649
H	-5.085776	-4.029357	0.167276
H	2.747415	-1.385655	3.441412
H	3.020292	0.228869	2.779688
H	3.597748	0.128652	-2.705271
H	3.392292	-1.506244	-3.326755
H	-2.521415	-2.180976	-3.336808
H	-2.868877	-0.474012	-3.060926
H	-3.380646	-0.872015	3.260323
H	-3.963764	0.518727	2.355455
O	0.012103	-1.854901	0.091656
H	0.838163	-2.372412	0.180935
H	-0.811301	-2.385222	0.079604
O	-0.149469	1.884599	2.802135
H	0.238969	1.313342	3.495077
H	-0.512341	2.688685	3.226555

$[1'(OH_2)]^+$

Ni	-0.000025	0.047376	-0.05411
N	1.941761	0.301086	-0.180112
N	0.000201	1.888289	-0.051764
N	-1.941765	0.301416	-0.178734
C	-2.329609	1.577025	-0.210019
C	-3.763794	2.039182	-0.20461
H	-4.452653	1.200366	-0.328644
H	-4.008996	2.547904	0.737354
H	-3.943313	2.755183	-1.015943
C	-1.213897	2.521117	-0.27419
C	1.2143	2.520909	-0.274657
C	1.228207	3.891813	-0.571744
H	2.16765	4.413806	-0.722725
C	0.00029	4.584002	-0.696569

H	0.000348	5.643537	-0.930932
C	-1.227679	3.892037	-0.571314
H	-2.167087	4.414173	-0.722023
C	2.329889	1.57657	-0.211213
C	3.764144	2.038442	-0.206653
H	4.009965	2.547178	0.73512
H	4.452778	1.199503	-0.331098
H	3.943285	2.754342	-1.01817
C	2.855069	-0.815797	-0.087867
C	3.119043	-1.55921	-1.271732
C	2.55323	-1.126128	-2.610882
C	3.945168	-2.698108	-1.174245
H	4.164903	-3.271678	-2.071183
C	4.48885	-3.091225	0.06186
H	5.123688	-3.971046	0.121167
C	4.21073	-2.345893	1.220827
H	4.63212	-2.652089	2.175021
C	3.393935	-1.195081	1.172559
C	3.117036	-0.398361	2.433982
H	1.470064	-0.955181	-2.557965
H	2.055373	-0.15235	2.557512
C	-2.855599	-0.815023	-0.085951
C	-3.123738	-1.556321	-1.270105
C	-3.391282	-1.195615	1.175443
C	-3.950914	-2.694398	-1.171946
C	-2.560788	-1.122153	-2.610085
C	-3.109974	-0.400741	2.437089
C	-4.209242	-2.345539	1.224417
C	-4.491527	-3.088778	0.065086
H	-4.173746	-3.266455	-2.06909
H	-1.477424	-0.951861	-2.559327
H	-2.047358	-0.158032	2.558953
H	-4.628351	-2.652625	2.179332
H	-5.127209	-3.967958	0.124862
H	3.442857	-0.957022	3.317561
H	3.671096	0.551748	2.432265
H	3.005605	-0.184731	-2.952376
H	2.745014	-1.882371	-3.378605
H	-2.754684	-1.877508	-3.378151
H	-3.013435	-0.180179	-2.949645
H	-3.435887	-0.959149	3.320788
H	-3.661113	0.551057	2.437065
O	0.00049	-1.897003	0.115956
H	0.823534	-2.411309	0.223351
H	-0.821141	-2.411917	0.230608
O	0.005643	1.044255	2.956216
H	0.001878	1.584101	3.770583
H	0.001416	1.604115	2.151424

***trans*-[1'$(OH_2)_2$H]$^{2+}$**

Ni	-0.000124	-0.014747	0.093359
N	2.043508	0.335978	-0.054808
N	-0.000072	1.934439	-0.085212
N	-2.043606	0.335969	-0.055142
C	-2.35934	1.605807	-0.123974
C	-3.759092	2.151017	-0.202603
H	-4.501687	1.351685	-0.218041
H	-3.970562	2.804467	0.654594
H	-3.8837	2.759244	-1.108275
C	-1.19302	2.555241	-0.144171
C	1.192879	2.555248	-0.144051
C	1.228385	3.960663	-0.242407
H	2.167092	4.501593	-0.288979
C	-0.000066	4.65609	-0.285502
H	-0.000066	5.739161	-0.361761
C	-1.228516	3.960656	-0.242534
H	-2.167222	4.501582	-0.289198
C	2.35921	1.605827	-0.123751
C	3.75895	2.151059	-0.202454
H	3.97031	2.804867	0.654494
H	4.501584	1.351758	-0.217521
H	3.883611	2.758935	-1.10836
C	3.00623	-0.750852	-0.062232
C	3.273621	-1.391317	-1.306437
C	2.684582	-0.884284	-2.609328
C	4.148043	-2.497298	-1.303861
H	4.376203	-2.993073	-2.243496
C	4.743602	-2.948949	-0.112249
H	5.422117	-3.796484	-0.131551
C	4.472388	-2.2936	1.099555
H	4.946352	-2.636635	2.015876
C	3.598084	-1.186622	1.152776
C	3.325775	-0.531521	2.498394
H	1.587053	-0.813637	-2.573202
H	2.642088	-1.149462	3.104623
C	-3.006243	-0.750914	-0.062422
C	-3.273358	-1.391763	-1.306487
C	-3.598198	-1.186428	1.152625
C	-4.14765	-2.49784	-1.303739
C	-2.684201	-0.884976	-2.609423
C	-3.326133	-0.530949	2.498113
C	-4.472344	-2.293541	1.099581
C	-4.743315	-2.949246	-0.112082
H	-4.375606	-2.993909	-2.24327
H	-2.946252	-1.549911	-3.437186
H	-2.64302	-1.149009	3.104872
H	-4.946374	-2.636403	2.015934
H	-5.421703	-3.796886	-0.131244
H	4.24768	-0.454234	3.084747

H	2.919622	0.483278	2.414723
H	3.06015	0.116089	-2.864419
H	2.947202	-1.548749	-3.437286
H	-3.060238	0.115095	-2.865017
H	-1.586725	-0.813711	-2.573016
H	-4.248268	-0.453023	3.084027
H	-2.919394	0.483583	2.414269
O	0.000093	-2.053489	-0.035974
H	-0.814819	-2.57422	-0.17425
H	0.815454	-2.573715	-0.173527
H	0.000229	0.041956	-1.355166
O	0.000039	-0.036281	2.123878
H	0.812074	-0.190421	2.64343
H	-0.811219	-0.192487	2.644018

***cis*-[1’(OH$_2$)$_2$H]$^{2+}$**

Ni	-0.000022	-0.064172	-0.344123
N	-2.031572	0.249026	-0.184348
N	0.000002	1.846522	-0.049066
N	2.031509	0.248894	-0.18442
C	2.349536	1.527105	-0.087847
C	3.748754	2.068366	0.008761
H	4.496762	1.285117	-0.122228
H	3.908739	2.835284	-0.760383
H	3.917859	2.549768	0.981203
C	1.192726	2.47585	-0.075604
C	-1.192671	2.475908	-0.075454
C	-1.227565	3.884552	-0.075242
H	-2.166163	4.427535	-0.08237
C	0.000074	4.581512	-0.068133
H	0.000108	5.667257	-0.065577
C	1.227684	3.884487	-0.075412
H	2.166296	4.427444	-0.082686
C	-2.349543	1.527201	-0.087627
C	-3.748721	2.068536	0.009205
H	-3.908883	2.83524	-0.760118
H	-4.496789	1.285278	-0.121383
H	-3.917525	2.550221	0.981556
C	-2.994804	-0.813683	0.041822
C	-3.524393	-0.999664	1.354057
C	-3.230934	-0.076524	2.529387
C	-4.386494	-2.098111	1.564073
H	-4.797266	-2.261653	2.557066
C	-4.731158	-2.96643	0.517323
H	-5.405717	-3.797546	0.699811
C	-4.205554	-2.755894	-0.770292
H	-4.485821	-3.421914	-1.581713
C	-3.32317	-1.691231	-1.028202
C	-2.76667	-1.502583	-2.426022
H	-2.26322	0.434781	2.465814

H	-1.706531	-1.797241	-2.468946
C	2.99479	-0.813733	0.041722
C	3.524696	-0.999529	1.353843
C	3.322916	-1.691459	-1.028253
C	4.386943	-2.09787	1.563811
C	3.23148	-0.076318	2.529214
C	2.76608	-1.502988	-2.425957
C	4.205391	-2.756045	-0.770399
C	4.731371	-2.966335	0.517114
H	4.797986	-2.261227	2.556725
H	3.252413	-0.637959	3.469325
H	1.705946	-1.79771	-2.468624
H	4.485483	-3.422186	-1.581782
H	5.406037	-3.797376	0.699547
H	-3.301428	-2.132026	-3.142744
H	-2.869652	-0.463221	-2.773004
H	-4.003114	0.699517	2.620518
H	-3.252993	-0.637975	3.469573
H	4.004431	0.69889	2.620934
H	2.264385	0.436136	2.465209
H	3.300742	-2.13244	-3.142749
H	2.868855	-0.463642	-2.773037
O	-0.000159	-0.870706	1.590296
H	0.810667	-1.324182	1.898638
H	-0.809503	-1.327881	1.897071
H	-0.000145	-1.496899	-0.721499
O	-0.000429	0.362297	-2.407166
H	-0.810333	0.191114	-2.927046
H	0.809515	0.191765	-2.927187

[1’(H)]$^+$

Ni	0.000471	-0.115234	0.006187
N	1.921153	0.142816	-0.174599
N	0.000131	1.764982	0.006853
N	-1.920801	0.142166	0.175739
C	-2.302131	1.404394	0.215503
C	-3.717862	1.889417	0.352809
H	-4.404772	1.071549	0.577376
H	-3.785756	2.639519	1.150751
H	-4.049254	2.372017	-0.577012
C	-1.184061	2.387728	0.118546
C	1.183231	2.388129	-0.111691
C	1.222082	3.794623	-0.1202
H	2.157524	4.335739	-0.210687
C	-0.001722	4.489216	-0.003939
H	-0.002148	5.575194	-0.008282
C	-1.224814	3.794195	0.116382
H	-2.160956	4.334865	0.201903
C	2.301453	1.405142	-0.213466
C	3.716057	1.891724	-0.357895

H	4.04784	2.384855	0.56622
H	4.404487	1.073385	-0.575891
H	3.780668	2.633904	-1.163633
C	2.870893	-0.954781	-0.193653
C	2.927905	-1.766642	-1.356053
C	2.057578	-1.473317	-2.561014
C	3.811557	-2.861653	-1.360313
H	3.874005	-3.489227	-2.245703
C	4.603	-3.154426	-0.235159
H	5.274157	-4.00876	-0.249692
C	4.516095	-2.347986	0.910147
H	5.117553	-2.583838	1.784965
C	3.65503	-1.230489	0.955393
C	3.589054	-0.385243	2.216103
H	0.995458	-1.559303	-2.282533
H	2.603002	0.063991	2.375285
C	-2.870376	-0.955553	0.189484
C	-3.654085	-1.227949	-0.960524
C	-2.927589	-1.771137	1.349475
C	-4.515114	-2.345799	-0.918721
C	-3.58906	-0.38042	-2.219686
C	-2.056555	-1.482902	2.555303
C	-3.81135	-2.865951	1.350355
C	-4.602435	-3.155527	0.224021
H	-5.116127	-2.579061	-1.794551
H	-2.611661	0.09086	-2.366484
H	-0.994791	-1.577658	2.278247
H	-3.874293	-3.496037	2.233919
H	-5.27366	-4.009849	0.235962
H	3.833516	-0.995187	3.092684
H	4.323256	0.433568	2.186314
H	2.23012	-0.461028	-2.952416
H	2.256215	-2.185712	-3.367756
H	-3.808404	-0.994919	-3.099802
H	-4.342008	0.42148	-2.199639
H	-2.262553	-2.192764	3.362447
H	-2.220891	-0.468568	2.944905
H	-0.000585	-1.598871	-0.002197
O	-0.400357	1.222228	-3.072552
H	-0.483694	1.563299	-3.985254
H	-0.093734	0.293729	-3.088659
O	0.399307	1.205037	3.092546
H	0.081024	0.282847	3.15426
H	0.517617	1.579922	3.988557

$[1'(H_2)]^{2+}$

Ni	-0.000131	-0.051973	-0.003771
N	1.92104	0.170429	-0.174203
N	-0.000286	1.773993	-0.002636
N	-1.920983	0.169921	0.170515

C	-2.312986	1.425875	0.219926
C	-3.72902	1.894493	0.363037
H	-4.412936	1.064543	0.547347
H	-3.810805	2.610189	1.191302
H	-4.058641	2.415974	-0.546499
C	-1.18939	2.399811	0.120559
C	1.18868	2.400141	-0.125457
C	1.221389	3.805382	-0.128704
H	2.157492	4.344714	-0.222662
C	-0.000681	4.502291	-0.002718
H	-0.000859	5.588063	-0.002943
C	-1.222512	3.805041	0.123595
H	-2.158782	4.34409	0.217497
C	2.312721	1.426515	-0.222841
C	3.728983	1.895635	-0.362083
H	4.055471	2.418465	0.547799
H	4.413909	1.065833	-0.543265
H	3.813033	2.610333	-1.191005
C	2.828159	-0.959966	-0.15259
C	2.926357	-1.762258	-1.322759
C	2.180841	-1.406424	-2.595316
C	3.767025	-2.889053	-1.278167
H	3.872856	-3.510255	-2.163215
C	4.475599	-3.21445	-0.10593
H	5.117653	-4.090181	-0.087488
C	4.351374	-2.412547	1.040932
H	4.896452	-2.674655	1.943759
C	3.528689	-1.266841	1.046494
C	3.419755	-0.417365	2.30053
H	1.092948	-1.349458	-2.432735
H	2.411927	-0.015145	2.457636
C	-2.827381	-0.961084	0.153578
C	-3.533709	-1.269458	-1.041658
C	-2.918646	-1.762808	1.32476
C	-4.35512	-2.416083	-1.03111
C	-3.432168	-0.420801	-2.296856
C	-2.167662	-1.404686	2.593498
C	-3.758157	-2.890606	1.285199
C	-4.472463	-3.21745	0.116817
H	-4.904551	-2.679366	-1.930957
H	-2.426691	-0.013905	-2.45671
H	-1.081461	-1.336815	2.424082
H	-3.858684	-3.511444	2.171124
H	-5.113559	-4.093956	0.102193
H	3.690132	-1.007395	3.181671
H	4.117881	0.431827	2.267595
H	2.503835	-0.434557	-2.993584
H	2.359184	-2.158802	-3.36856
H	-3.701743	-1.013078	-3.176755
H	-4.134669	0.424741	-2.262951

H	-2.33415	-2.161125	3.365438
H	-2.497212	-0.437127	2.997051
H	-0.131529	-1.823314	-0.368627
O	-0.191237	1.186809	-3.058734
H	-0.587971	1.92159	-3.569774
H	0.194732	0.541049	-3.684337
O	0.185304	1.212666	3.057994
H	-0.202192	0.566777	3.682507
H	0.58202	1.946585	3.570281
H	0.13159	-1.824976	0.354154

$[1'(OH_2)]^{2+}$ + H_2

Ni	0.000606	0.020186	-0.100609
N	1.925634	0.261248	-0.052361
N	-0.008287	1.838316	-0.255733
N	-1.925508	0.230514	-0.206687
C	-2.330998	1.478206	-0.306372
C	-3.756793	1.931606	-0.392136
H	-4.446011	1.088976	-0.467833
H	-4.027076	2.519505	0.496189
H	-3.900691	2.582834	-1.264101
C	-1.207057	2.459841	-0.331603
C	1.181766	2.479768	-0.231212
C	1.206813	3.882459	-0.307083
H	2.143629	4.428688	-0.296936
C	-0.024238	4.568565	-0.399413
H	-0.030426	5.652416	-0.462873
C	-1.247565	3.862511	-0.409948
H	-2.190641	4.393794	-0.477362
C	2.316114	1.516192	-0.119302
C	3.736123	1.994061	-0.092047
H	3.88563	2.69976	0.736155
H	4.440111	1.168535	0.023131
H	3.979213	2.532112	-1.018604
C	2.837413	-0.866478	0.032936
C	3.372505	-1.409145	-1.167442
C	3.060086	-0.812525	-2.527459
C	4.224635	-2.527265	-1.052866
H	4.65186	-2.960787	-1.952901
C	4.531314	-3.081091	0.203105
H	5.193983	-3.938938	0.268844
C	3.981278	-2.529206	1.37435
H	4.225622	-2.959438	2.341709
C	3.123236	-1.411372	1.315194
C	2.562168	-0.798229	2.58561
H	1.987808	-0.616424	-2.660195
H	1.478282	-0.632639	2.514903
C	-2.816801	-0.911005	-0.119224
C	-3.014973	-1.697678	-1.290063

C	-3.413397	-1.231738	1.131116
C	-3.842295	-2.834339	-1.180845
C	-2.4111	-1.305683	-2.626697
C	-3.211203	-0.379814	2.371468
C	-4.229793	-2.381462	1.184514
C	-4.446986	-3.173804	0.043785
H	-4.022996	-3.444744	-2.061354
H	-1.338141	-1.080416	-2.554476
H	-2.213572	0.071278	2.423465
H	-4.699561	-2.651143	2.126604
H	-5.084023	-4.051058	0.107389
H	2.750807	-1.449859	3.443574
H	3.030095	0.172147	2.803235
H	3.588867	0.138026	-2.685552
H	3.376072	-1.488522	-3.326887
H	-2.534475	-2.109207	-3.35836
H	-2.900896	-0.413367	-3.041131
H	-3.36392	-0.97845	3.274954
H	-3.944668	0.438896	2.410442
H	0.107065	1.839913	-3.62739
H	0.127261	2.490208	-3.989964
O	0.010208	-1.875963	0.062026
H	0.836036	-2.395694	0.139629
H	-0.813424	-2.405513	0.038326
O	-0.144048	1.834708	2.876961
H	0.240176	1.247054	3.558431
H	-0.502615	2.632076	3.317379

5. Bulk electrolyses and H_2 measurement

Figure S5-1. Controlled potential experiments for headspace H_2 detection were performed at -1.1 V vs. NHE (1 h) in a custom built two cylinder 50 mL bulk electrolysis H cell anode/ 20 mL cathode chamber separated by a coarse frit: Catalytic run (*red*) cathode: 50 mL pH 1 HCl/0.1 M KCl 2 mM **1** anode: 20 mL pH 1 HCl/0.1 M. Background run (performed after the catalytic run) *black*: cathode: 50 mL pH 1 HCl/0.1 M KCl, anode: 20 mL pH 1 HCl/0.1 M. The working electrode was a BASi RVC electrode referenced vs. Ag/AgCl (KCl_{sat}).

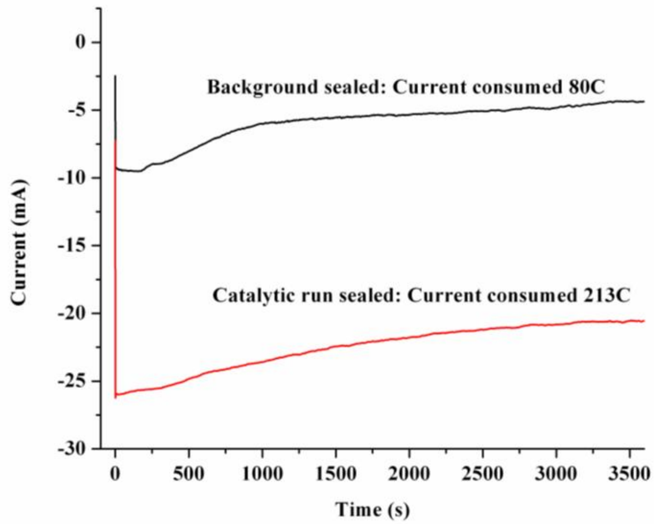


Figure S5-2. Quantitative Mass Spectrometry calibration of voltage response against H_2 detection with 15% He/H_2 mixed gas sample and 100% H_2. Duplicate Catalytic runs and run in the absence of catalyst are shown.

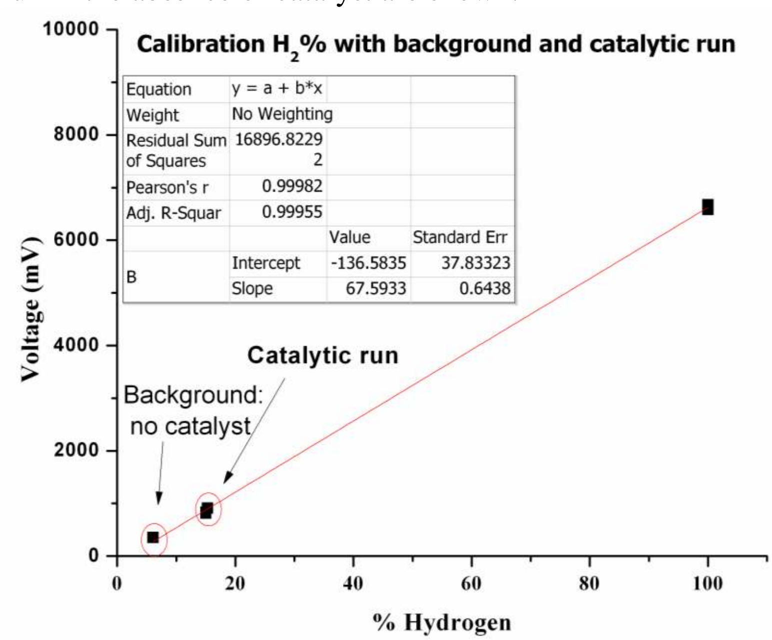
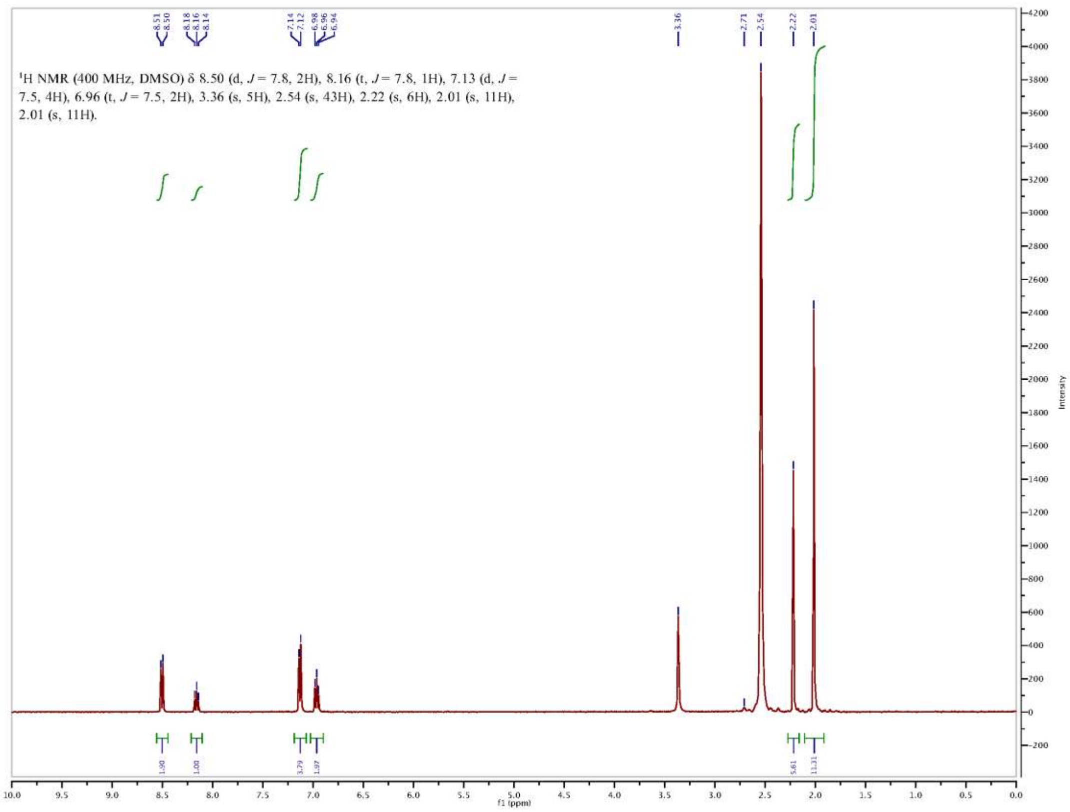


Figure 6: ^{1}H NMR spectrum of 1 in DMSO-d_6



7: Kinetics for proton reduction

Method for EC_{cat} rate determination obtained from DuBois *et al.* [2SI]

For a diffusion limited catalytic process that occurs at high enough $[H^+]$ that the concentration remains unchanged, the observed current obeys the following equation:

$$i_c = nFA[cat]\sqrt{Dk[H^+]^2} \qquad (\mathbf{1})$$

For a reversible one e^- wave, the current observed can be expressed as:

$$i_p = 0.443FA[cat]\sqrt{\frac{F\nu D}{RT}} \qquad (\mathbf{2})$$

Dividing (**1**) by (**2**) the following expression is obtained:

$$\frac{i_c}{i_p} = \frac{n}{0.4463}\sqrt{\frac{RT}{F}}\sqrt{\frac{k[H^+]^2}{\nu}} = 0.72\sqrt{\frac{k*[H^+]^2}{\nu}} \qquad (\mathbf{3})$$

A=area of the electrode, D is the diffusion coefficient of the catalyst, n=2 for H_2 production , R=8.314 J/(mol K), F= 96485 C/mol, υ scan rate in V/s, k is the third order rate constant

Linearity of :

1. *plots of i_c/i_p vs acid concentration confirms the electrocatalytic process is second order in acid*

2. *plots of i_c vs [catalyst] confirms the process is first order in catalyst*

The rate law for the third order process is derived as:

$$rate = k[H^+]^2[cat]$$

Where I_p did not correspond with the onset of catalysis , the metal centered reduction peak current at the respective scan rate was taken as I_p

Figure S7-1. Plot of i_c currents vs. concentration of catalyst **1** at 100 mV/s.

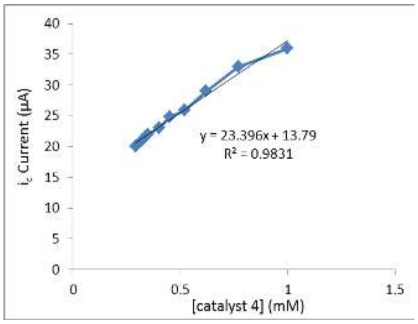


Figure S7-2. Plots of i_c / i_p ratios vs. acid concentration at 4 mM catalyst **1** at 25 mV/s, 50 mV/s, 100 mV/s and 200 mV/s.

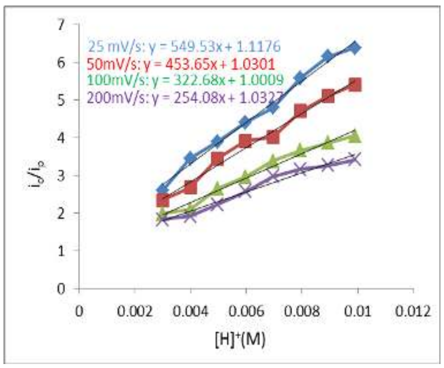


Figure S7-3. Plots of the slopes of i_c / i_p ratios vs. acid concentration in **Figure S8-2** vs. 1/(sqrt (υ)).

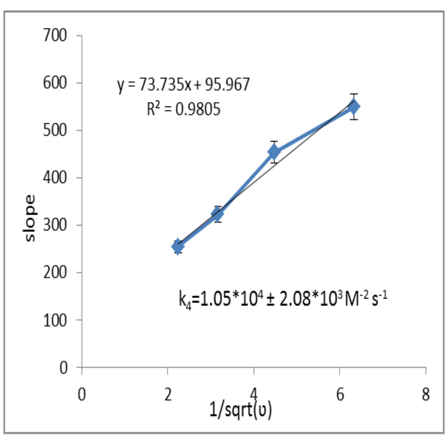


Table S7-1
Tabulated kinetic data for catalyst **1.**

Catalyst	k ($M^{-2}s^{-1}$)	Error value	%error on k	TOF (s^{-1})	Rate ($M\ s^{-1}$)[a]	Potential at 1mA cm^{-2} [b]	Slope	Numeric error on slope	%error on slope
1	$1.05*10^4$	$\pm 2.08*10^3$	19.82618142	105	0.525	-0.233V	73.64	7.3	9.913091

a. calculated for 0.1 M H^+, 5 mM catalyst
b. as determined by Tafel plots constructed from 60 s chronoamperometry experiments at progressively more negative potentials.

8. References

1SI. Blakemore, J. D.; Schley, N. D.; Balcells, D.; Hull, J. F.; Olack, G. W.; Incarvito, C. D.; Eisenstein, O.; Brudvig, G. W.; Crabtree, R. H. *J. Am. Chem. Soc.* 2010, *132*, 16017-16029.

2SI. a. Pool, D. H.; DuBois, D. L. *J. Organomet. Chem.*, 2009, *694*, 2858-2865.

b. Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J.T.; Rakowski DuBois, M.; DuBois, D. L. *J. Am. Chem. Soc.*, 2006, 128, 358–366.

The full reference 17 is given below:
Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.