Supporting Information

Evaluating the Role of Acidic, Basic, and Polar Amino Acids and Dipeptides on a Molecular Electrocatalyst for H₂ Oxidation

Nilusha Priyadarshani Boralugodage, Rajith J. Arachchige, Garry W. Buchko, Arnab Dutta†‡,
Wendy J. Shaw*
Pacific Northwest National Laboratory, Richland 99352

1. ³¹P NMR of the all six complexes
2. ³¹P NMR to show the stability with time
3. Cyclic voltammetry of CyGly in methanol
4. Cyclic voltammetry of the Ni(II/I) only for CyLys and CySer
5. Cyclic voltammetry of Cy(GlyPhe) and Cy(PheGly) in THF
6. Cyclic voltammetry evaluating origin of H₂ production
7. Cyclic voltammetry in of CyAsp and CyLys in the presence of a base (triethyl amine)
8. Scan rate dependence for all six complexes
9. Proton-proton TOCSY of Cy(GlyPhe) and Cy(PheGly)
Figure S1. The $^{31}$P NMR spectra of all of the complexes in methanol at 25 °C, collected at 500 MHz proton frequency.

Figure S2. The stability of the complexes was demonstrated by comparing of the $^{31}$P NMR spectra of the hydrogen addition product of Cy(GlyPhe), (H)$_2$Cy(GlyPhe), complex in methanol at 25 °C, collected at 500 MHz proton frequency immediately after preparation (bottom) and four days after preparation (top).
Figure S3. Cyclic voltammetry of CyGly (0.05 mM) in methanol. Black: under 1 atm N₂; red: under 1 atm of H₂. All data were collected using a glassy carbon electrode with a 0.2 Vs⁻¹ scan rate at 25 °C.

Figure S4. Left, CyLys (0.02 mM) and right, CySer (0.05 mM) in methanol showing full (black) and partial (red) scans of cyclic voltammetry to result in a more reversible Ni(II/I) wave. All data collected were collected using a glassy carbon electrode at a scan rate of 0.2 Vs⁻¹.
**Figure S5.** Cyclic voltammetry of Cy(GlyPhe) (left) and Cy(PheGly) (right) in THF showing more reversible Ni(I/0) couples due to increased solubility of the Ni(0) species in THF.
Figure S6. The nature of the H$_2$ production catalysis (heterogeneous vs homogeneous) was determined using a series of cyclic voltammetry experiments. Black: A full scan of 0.05 mM CyAsp in (0.5mM) HTFSI solution in 0.1 M tetrabutyl ammonium tetrafluoroborate (TBABF$_4$) electrolyte in methanol at a 0.5 V s$^{-1}$ scan rate. Red: A partial scan of the same solution, stopping at the wave maximum. Blue: A partial scan of the glassy carbon electrode after the previous scan after rinsing (not polishing) the electrode in 0.5 mM HTFSI in methanol at a 0.5 V s$^{-1}$ scan rate. Based on this data it is not definitive whether the H$_2$ production wave is due to a heterogeneous wave, or a mechanism catalytic at the Ni(0), though the significant wave remaining upon running in the absence of any complex is most consistent with a heterogeneous process.
Figure S7. Cyclic voltammetry in of CyAsp (0.01 mM), CyLys (0.01 mM), and Cy(PheGly) (0.01 mM) under N$_2$ in methanol as a function of added base. For CyLys, the H$_2$ production wave reduces as acid is neutralized and a wave attributed to the Ni(I/0) is more prominent. Adding more base to fully remove the H$_2$ production resulted in dissolution of the CyLys complex and a concomitant loss of all of the electrochemical waves. Both CyAsp and Cy(PheGly) lose all signal due to reduced solubility upon the addition of base. All data were collected with a glassy carbon electrode at a scan rate of 0.2 Vs$^{-1}$ at 25 °C.

Figure S8. Scan rate dependence of H$_2$ oxidation catalytic current for CyAsp (0.02 mM), CyLys (0.02 mM), CySer (0.09mM), Cy(GlyPhe) (0.06 mM), Cy(PheGly) (0.05 mM) and Cy(AspPhe) (0.06mM) in methanol under 1 atm H$_2$. Scan rate independence was observed at 0.2 Vs$^{-1}$ for all complexes.
Figure S9. TOCSY spectra of (H)$_2$Cy(PheGly) and (H)$_2$Cy(GlyPhe) in $d_8$-THF at 25°C collected at 500 MHz at mixing period of 80 ms.