

Supporting Information

Synthesis of an Imine-type Nickel complex and investigation of its electrocatalytic activity for H₂ evolution

Lan H. Le;^a Ngoc H. Pham;^a Phong D. Tran;^a Tung H. To^{*a}

^a *University of Science and Technology of Hanoi, Vietnam Academy of Science and Technology*

18 Hoang Quoc Viet, Hanoi, Vietnam

*Corresponding author: to-hai.tung@usth.edu.vn

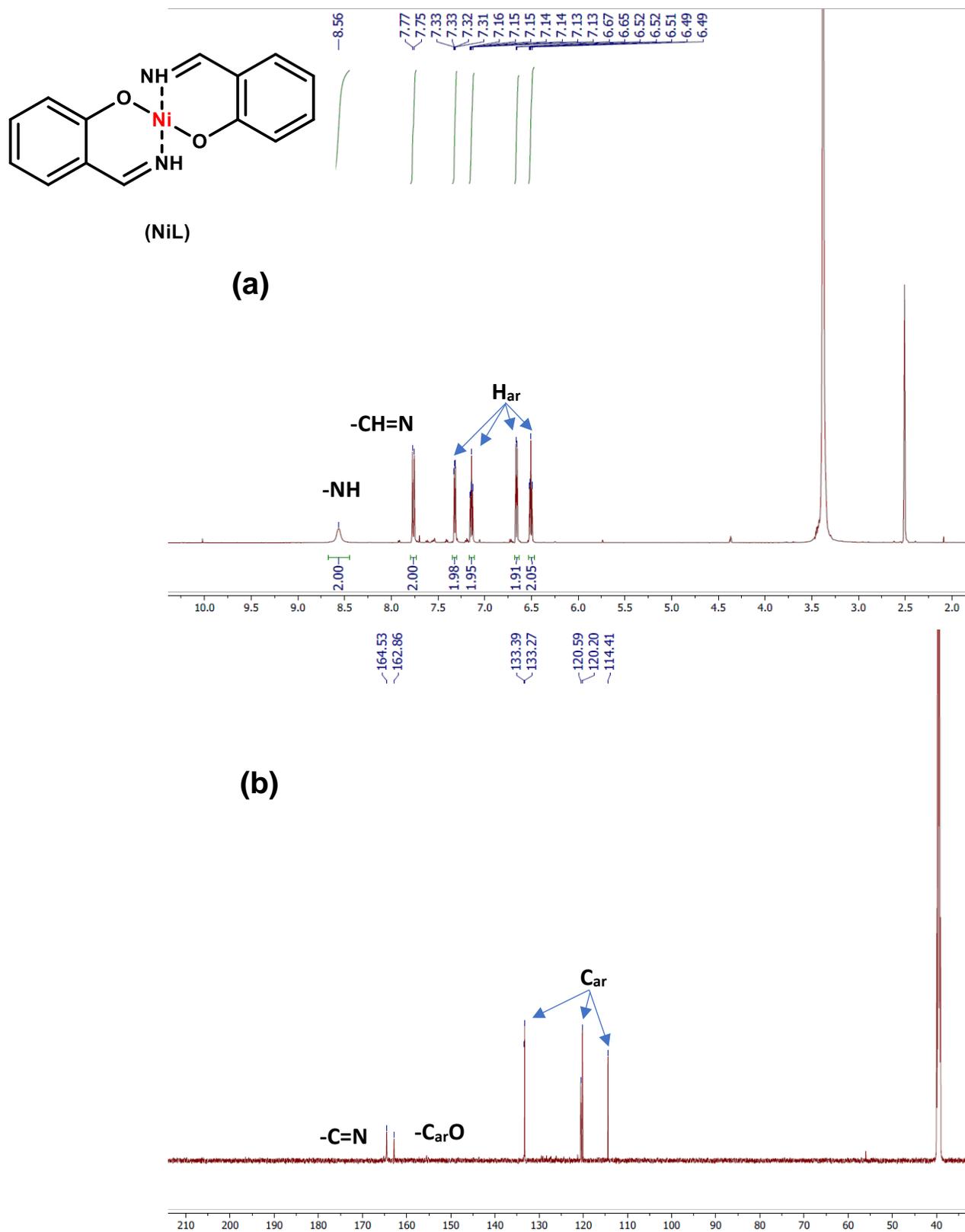


Fig. S1 $^1\text{H-NMR}$ (a) and $^{13}\text{C-NMR}$ (b) spectra of complex NiL

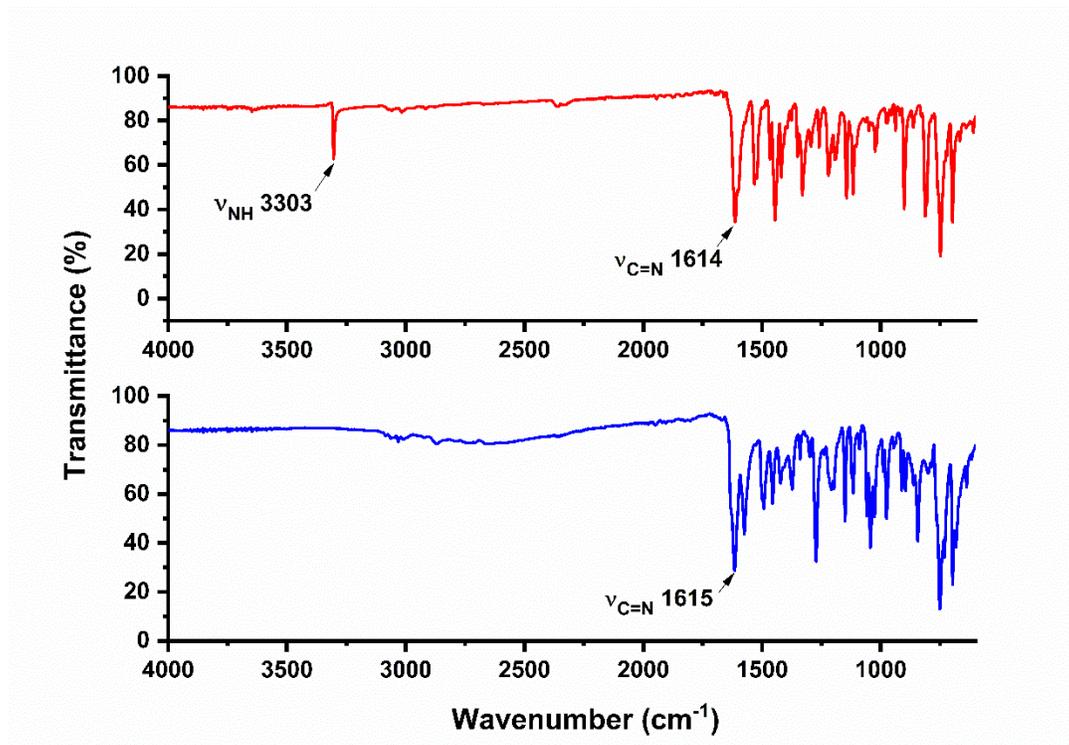


Fig. S2 FT-IR spectrum of complex **NiL** (red line) and pre ligand **M** (blue line)

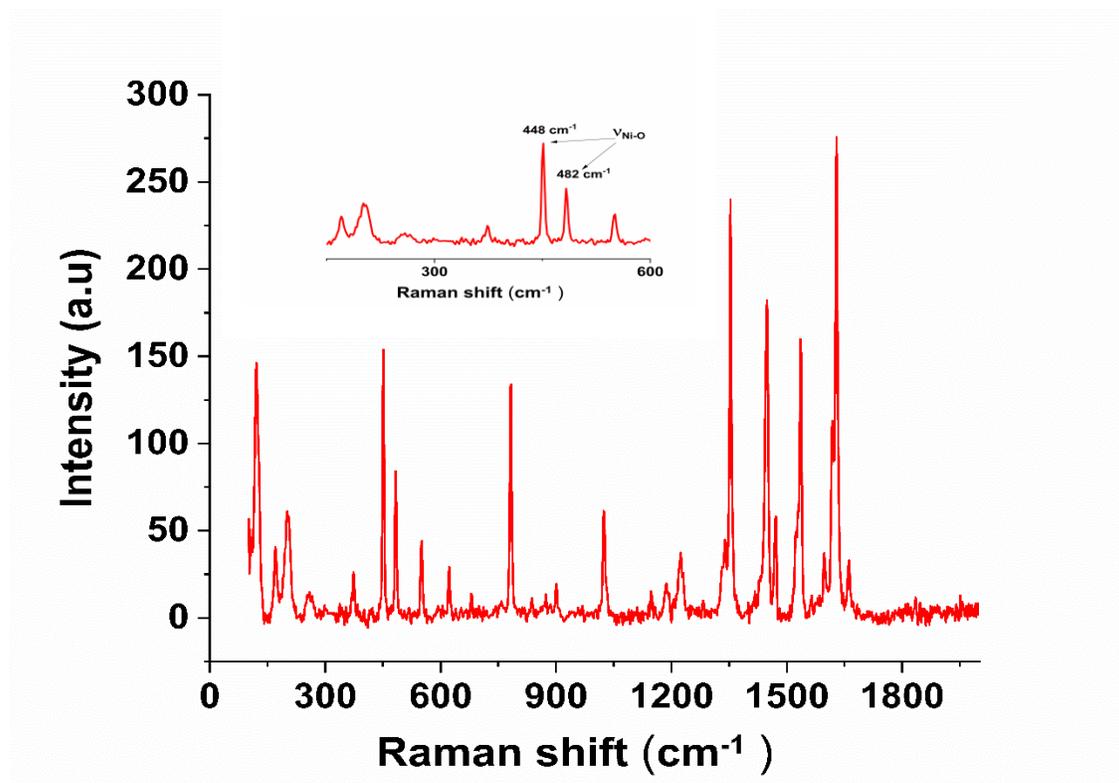
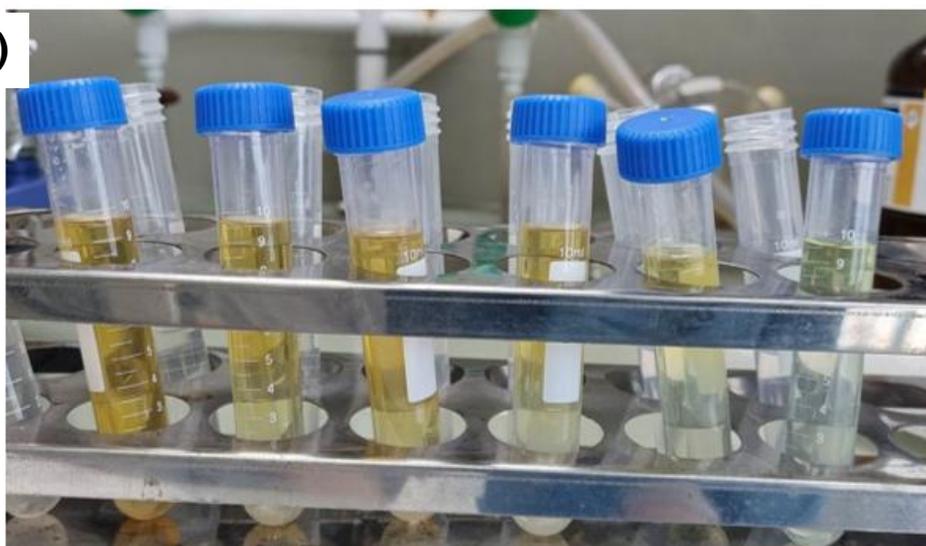


Fig. S3 Raman spectrum of complex **NiL**

(a)



Increase eq. mol of TFA



(b)

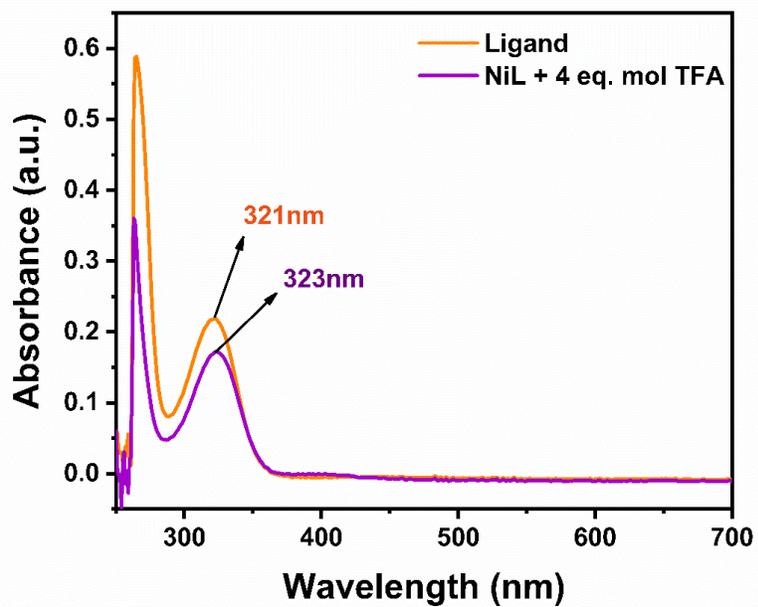


Fig. S4 The discoloration of the **NiL** following the increase of equivalent moles of TFA **(a)** and the UV-Vis spectrum of **NiL** with 4.0 eq. moles of TFA in comparison with pre-ligand

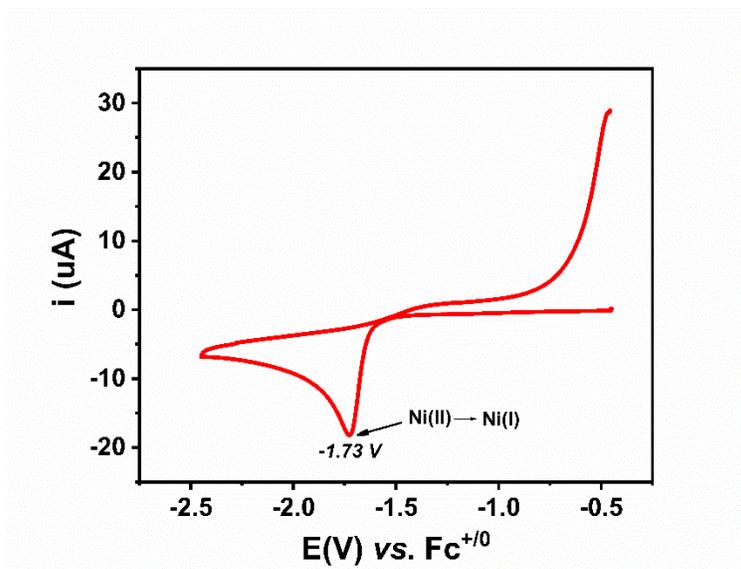


Fig. S5 Cyclic voltammograms of **NiCl₂ precursor** at a stationary glassy carbon electrode in DMF solutions with scan rate of 50 mV.s⁻¹

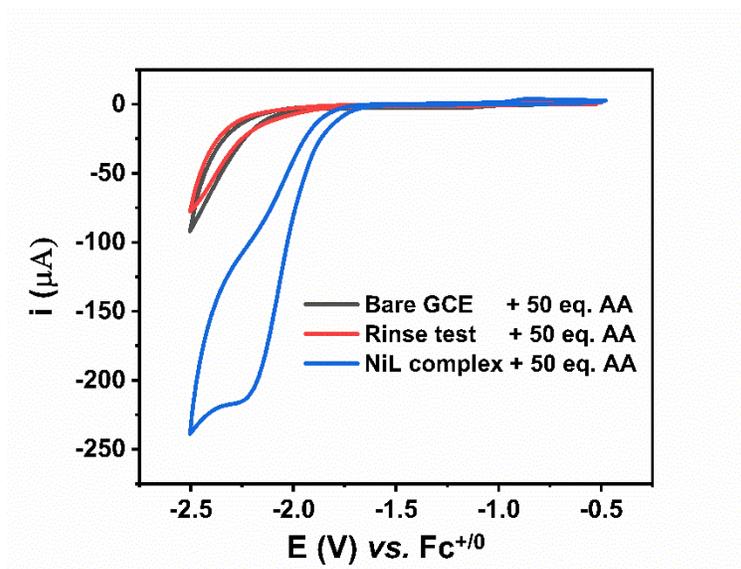


Fig. S6 “Rinse test” control experiments of **NiL** complex: The glassy carbon electrode, after participating the proton reduction in the presence of catalysts with 50 eq. moles of AA (blue line), was cleaned by DMF solvent washing and used as the working electrode in the proton reduction without catalysts (red line). The bare glassy carbon electrode was used as the reference in the same condition: 50 eq. moles of AA and no catalyst (scan rate at 50 mV.s⁻¹)

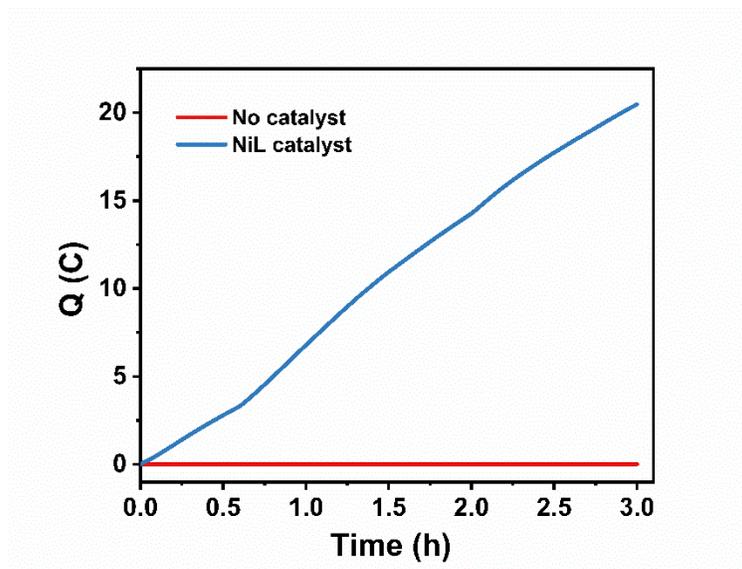


Fig. S7 Coulometry for bulk electrolysis at -2.05 V vs. $\text{Fc}^{+/0}$. The electrolytic solution contains 0.1 M TBATBF in DMF, 50 eq. Moles of Acetic acid: without catalysts (red line) or 1 mM of **NiL** (blue line).

- **Overpotential determination**

Determine the standard potential of Acetic acid in DMF: based on the equation (1) [1]

$$E^\circ(\text{HA}/\text{A}^-; \text{H}_2) = E^\circ(\text{H}^+/\text{H}_2) - 2.303(\text{RT}/\text{F})\text{p}K_{\text{a}(\text{HA})} + \varepsilon_{\text{D}} - (\text{RT}/2\text{F})\ln(\text{C}_0/\text{C}^{\circ}_{\text{H}_2}) \quad (1)$$

$$E^\circ(\text{H}^+/\text{H}_2) = -0.662 \text{ V (vs } \text{Fc}^{+/0}) \quad [2]$$

$\text{p}K_{\text{a}}$ of Acetic acid in DMF: 13.5

$$\varepsilon_{\text{D}} = 0.04 \text{ V}$$

C_0 : concentration of acetic acid (50 mM)

$\text{C}^{\circ}_{\text{H}_2}$: concentration of dissolved hydrogen at standard condition = 1.9 mM.

$$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}; T = 299\text{K}; F=96485$$

$$E^\circ(\text{HA}/\text{A}^-; \text{H}_2) = E^{\text{T}}_{1/2} = (-0.662) - [(2.303 \times 8.314 \times 299)/96485] \times 13.5 + 0.04 - [(8.314 \times 299)/(2 \times 96485)] \ln(50/1.9) = -1.46 \text{ V (vs. } \text{Fc}^{+/0})$$

$$\text{Overpotential} = E^{\text{T}}_{1/2} - E_{\text{cat}/2} = -1.46 - (-2.05) = 0.59 \text{ V (vs. } \text{Fc}^{+/0})$$

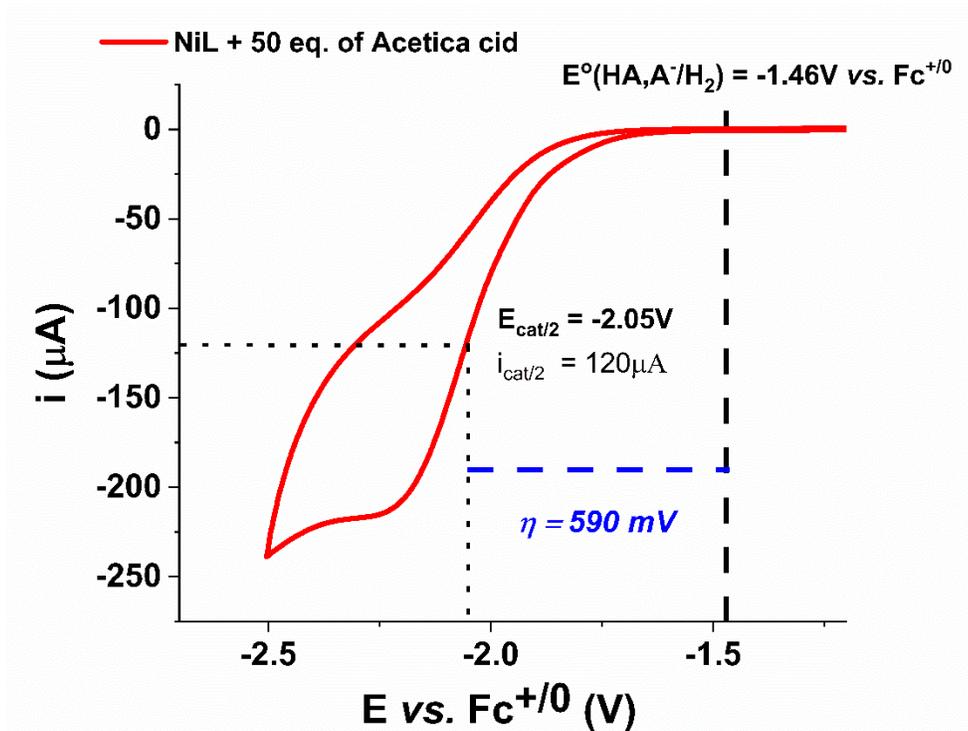


Fig. S8 Determination of $i_{cat/2}$; $E_{cat/2}$ and overpotential of complexes **NiL**

- **Diffusion coefficient**

Randle-Sevcik equation (**Equation 2**)

$$i_p = 0.4463nFAC \sqrt{nFvRTD} \quad (2)$$

i_p : cathodic peak current (A)

v : scan rate (V/s)

n : number of transferred electrons in redox event

R : Gas constant 8.314 J/mol.K

F : Faraday constant 96485 (C/mol)

T : Temperature 299K

A : electrode surface area 0.071 (cm²)

D : diffusion coefficient (cm²/s)

C : concentration of catalyst 1mM

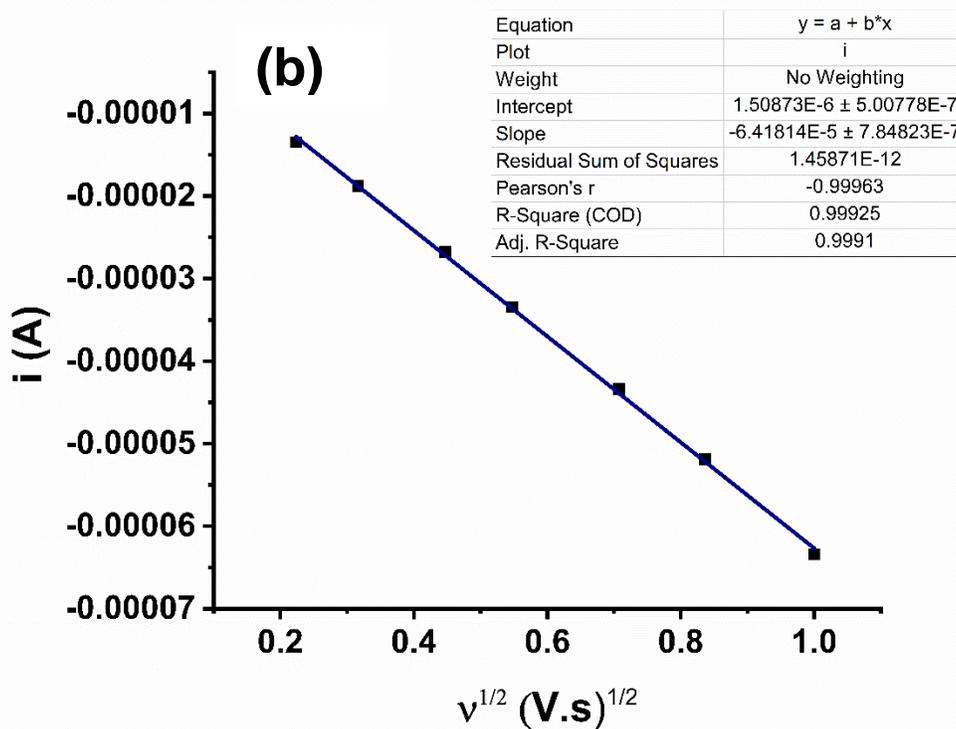
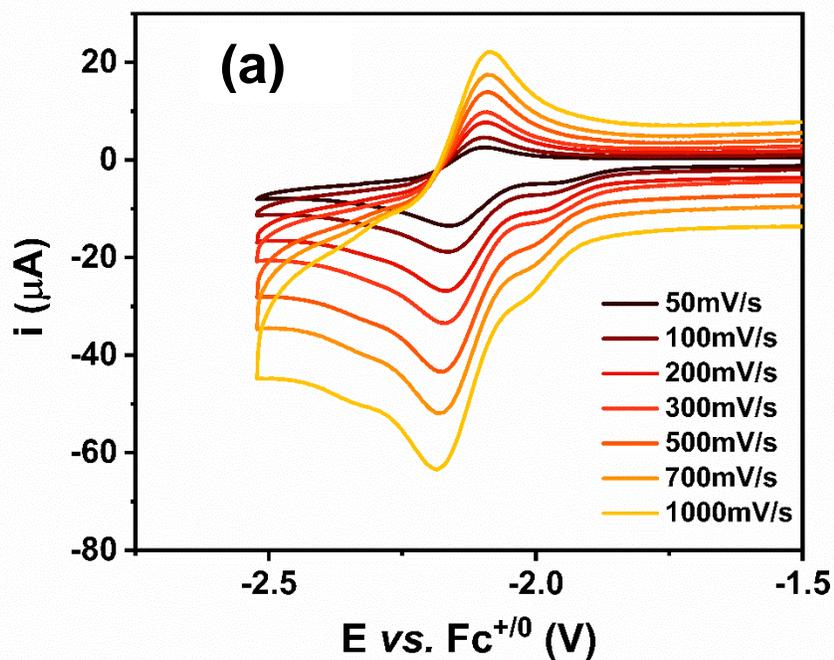


Fig. S9 Cyclic voltammograms of complex **NiL** (a) and the plots of i_p versus the square root of scan rate of complex **NiL** (b).

- Rate constant calculation

$$\frac{i_{cat}}{i_p} = \frac{n}{0.4463} \times \sqrt{\frac{RTk_{obs}}{Fv}}$$

i_p : cathodic peak current (mA)

v : scan rate 0.05 V/s

i_c : catalytic current (mA)

n : number of transferred electrons (2)

R : Gas constant 8.314 J/mol.K

F : Faraday constant 96485 (C/mol)

T : Temperature 299K

Table S1 The values of rate constants extracted from PCA with various concentration of acetic acid

| [AcOH] (M) | i_c (mA) | i_c/i_p (with $i_p = 11$ mA) | $k_{obs} = 1.93 \cdot 0.05 \cdot (i_c/i_p)^2$ (s^{-1}) | $k_{cat} = k_{obs} / [AcOH]^2$ ($M^{-2} \cdot s^{-1}$) |
|------------|------------|--------------------------------------|---|---|
| 0.01 | 79 | 7.09 | 4.85 | 48521.16 |
| 0.02 | 112 | 10.18 | 10.004 | 25010.25 |
| 0.03 | 156 | 14.18 | 19.41 | 21564.96 |
| 0.04 | 198 | 18.00 | 31.27 | 19541.25 |
| 0.05 | 238 | 21.64 | 45.17 | 18069.90 |
| 0.06 | 281 | 25.55 | 62.97 | 17492.51 |
| 0.07 | 321 | 29.18 | 82.18 | 16770.88 |
| 0.1 | 401 | 36.46 | 128.24 | 12824.23 |
| 0.12 | 486 | 44.18 | 188.37 | 13081.33 |
| 0.15 | 598 | 54.36 | 285.20 | 12675.40 |

References

- [1] V. Fourmond, P.-A. Jacques, M. Fontecave, V. Artero, *Inorganic Chemistry* **2010**, *49*, 10338-10347.
- [2] M. L. Pegis, J. A. S. Roberts, D. J. Wasylenko, E. A. Mader, A. M. Appel, J. M. Mayer, *Inorganic Chemistry* **2015**, *54*, 11883-11888.