Electronic Supplementary Information (ESI†)

Structural Modification of Nickel Tetra(thiocyano)corroles during Electrochemical Water Oxidation

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Appendix 1: Experimental Details of Electrochemical Measurement

Activation of carbon cloth

1 cm x 2 cm of carbon cloth was first washed with acetone twice under ultrasonication, then five times with water. Clean carbon cloth was dried at 50 °C for 12 h and treated with nitric acid for 4 h at 100°C. The activated carbon cloth was dried in an air oven at 50° C and used for catalyst deposition.[1]

Deposition of molecular catalyst on the carbon cloth

4 mg of molecular catalysts were dissolved in 100 mL of ethanol by using ultrasonication for 3 minutes, then 10 microliters of an ethanolic 0.05 wt% Nafion solution was added, then again sonicated for 2 minutes. The liquid was then dropped and cast onto activated carbon cloth (CC).

Electrochemical measurement

OER and HER experiments were conducted in a 1.0 M aqueous KOH solution in a single compartment having a three-electrode electrochemical cell. We used molecular complex@CC as the working electrode, a Pt wire counter electrode, and an Ag/AgCl as a reference electrode. The equation $E_{(RHE)} = E_{(Ag/AgCl)} + 0.097\ V + (0.059\ pH)\ V$ was used to convert the potentials provided above to the RHE.[2] A constant potential was used in a 1.0 M KOH solution to conduct a chronoamperometric experiment at 1.60 V vs. RHE. All CV and LSV have been 75% *iR* corrected. To understand this, the electrochemical activation of the molecular catalyst was performed to reach a constant current density. After that, 2 mg of $FeCl_3$ was added to the electrolyte solution, and the CV cycle was continued.[3]

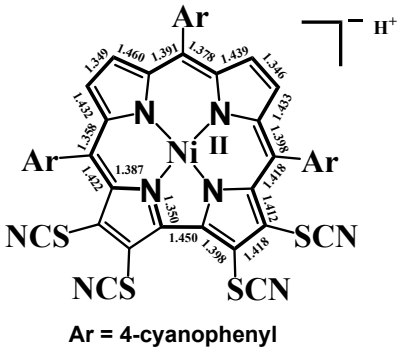
1. A. Indra, U. Paik and T. Song, *Angew. Chem. Int. Ed.,* 2018, **57**, 1241-1245.
2. B. B. Yu, Y. W. Hua, Q. Huang, S. Y. Ye, H. D. Zhang, Z. Yan, R. W. Li, J. Wu, Y. Meng and X. Cao, *CrystEngComm,* 2021, **23**, 4700-4707.
3. S. K. Pal, B. Singh, J. K. Yadav, C. L. Yadav, M. G. B. Drew, N. Singh, A. Indra and K. Kumar, *Dalton Trans.***,** 2022, **51**, 13003–13014.

Appendix 2: HOMA calculations

The HOMA values[1] of 2,3,17,18-tetra(thiocyano)-[5,10,15-tris(4-cyanophenyl)corrolato]nickel(II) (1) and [5,10,15-tris(pentafluorophenyl)corrolato]nickel(II) [2] were calculated using the C–C and C–N bond lengths obtained from their X-ray crystallographic structures, according to the following equations:[3]

$$\text{HOMA} = 1 - \frac{1}{n}\left\{\alpha_{CC}\sum\left(R_{opt} - R_i\right)_{CC}^{2} + \alpha_{CN}\sum\left(R_{opt} - R_i\right)_{CN}^{2}\right\}$$

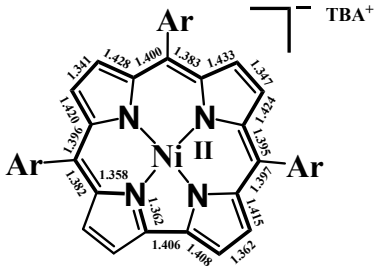
where n = number of bonds taken into summation, α = empirical constant, R_{opt} = optimal bond length and R_i = bond length of i^{th} bond.



Ar = 4-cyanophenyl

2,3,17,18-tetra(thiocyano)-[5,10,15-tris(4-cyanophenyl)corrolato] nickel(II), 1

HOMA=0.64



Ar = 2,3,4,5,6-pentafluorophenyl

Tris(pentafluorophenyl)corrolato] nickel(II)[2]

HOMA=0.81

Selected bond distances and calculated HOMA values[1] for single-crystal structures of 2,3,17,18−tetra(thiocyano)-[5,10,15-tris(4-cyanophenyl)corrolato] nickel(II), **1**, and [5,10,15-tris(pentafluorophenyl)corrolato]nickel(II).[2] The bonds used for HOMA calculations are indicated in bold lines.

References:

1. (a) J. Kruszewski and T. M. Krygowski, *Tetrahedron Lett.* 1972, 13, 3839– 3842; (b) T. M. Krygowski, H. Szatylowicz, O. A. Stasyuk, J. Dominikowska, M. Palusiak, *Chem. Rev.* 2014, 114, 6383– 6422; (c) C. P. Frizzo and M. A. P. Martins, *Struct. Chem.* 2012, 23, 375– 380.
2. Q. C. Chen, S. Fite, N. Fridman, B. Tumanskii, A. Mahammed and Z. Gross, *ACS Catal.*, 2022, **12**, 4310-4317.
3. (a) C. A. Hunter, J. K. M. Sanders, *J. Am Chem. Soc.,* 1990, **112**, 5525–5534; (b) R. Nozawa, H. Tanaka, W.-Y. Cha, Y. Hong, I. Hisaki, S. Shimizu, J.-Y. Shin, T. Kowalczyk, S. Irle, D. Kim, *Nat. Commun.* **2016**, *7*, 13620.

Table S1 Crystallographic data for **1**.

compound code	**1**
chemical formula	$C_{88}\ H_{30.40}\ N_{22}\ Ni_2\ S_8$
formula mass	1769.64
crystal system	Triclinic
crystal size (mm)	0.13×0.12×0.10
space group	*P-1*
Radiation	Mo *K*α
a(Å)	13.5052 (3)
b(Å)	16.0286 (4)
c(Å)	25.3258 (7)
α (deg)	97.682 (2)
β (deg)	102.718 (2)
γ (deg)	90.036 (2)
V(Å^3)	5297.2 (2)
Z	2
T(K)	100.01(11)
D_{calcd} (g cm^{-3})	1.109
measured reflections	46982
e data (R_{int})	11888 (0.0614)
parameters	1081
restraints	1004
μ (mm^{-1})	0.561
2θ range (deg)	6.43 – 50.00
R1 ($I>2\sigma(I)$)	0.0784
WR2 (all data)	0.2106
S (GooF) all data	1.025
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.884, -0.559

Table S2 UV-Vis. and electrochemical data for **1** and **2**.

Compound	UV–vis. Data [a] λ_{max} / nm (ε / $M^{-1}cm^{-1}$)	Electrochemical data[a,b]	
		Oxidation E^0, V (ΔE_p, mV)	Reduction E^0, V (ΔE_p, mV)
1	401 (70700), 418 (82700), 563 (35300), 592 (69000), 608 (92700)	+0.71 (80), +1.12 (80)	1.29
2	401 (71700), 418 (85500), 564 (31700), 592 (60600), 611 (87400).	+0.72 (80), +1.14 (80)	1.35

[a] In acetonitrile.

[b] The potentials are *versus* Ag/AgCl.

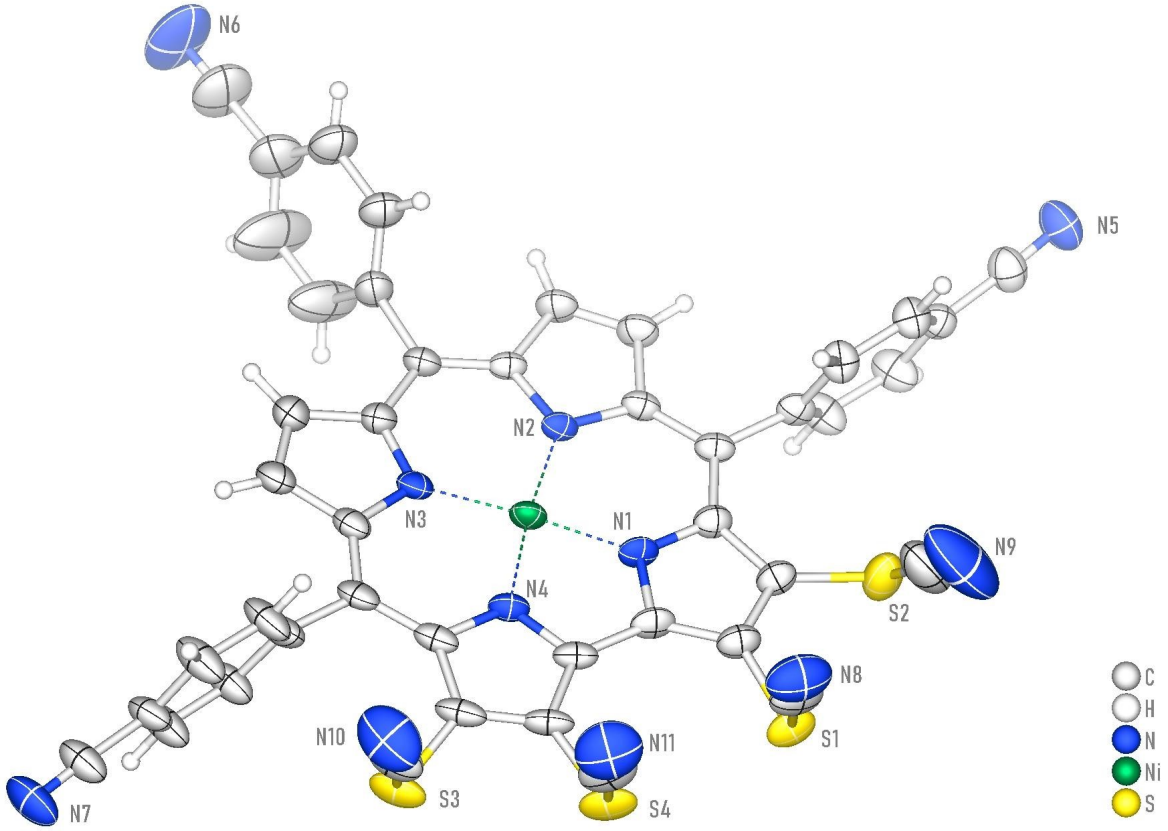


Fig. S1 Visualization of atomic displacement parameters (ADPs) in the X-ray crystallographic depiction of **1**.

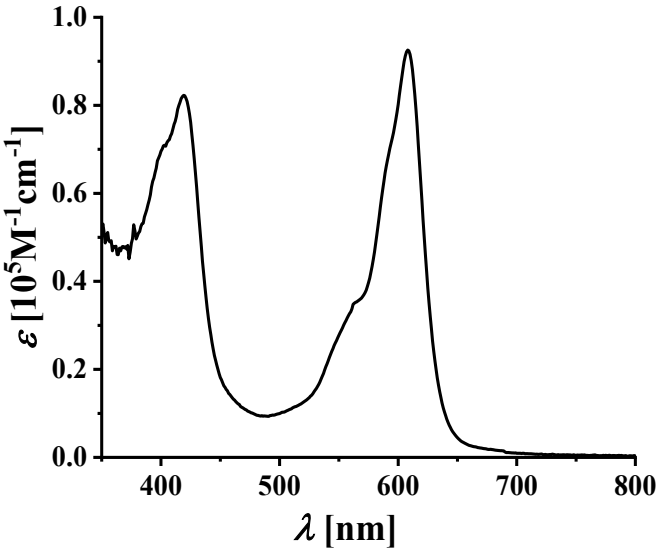


Fig. S2 Electronic absorption spectrum of **1** in acetonitrile at 298 K.

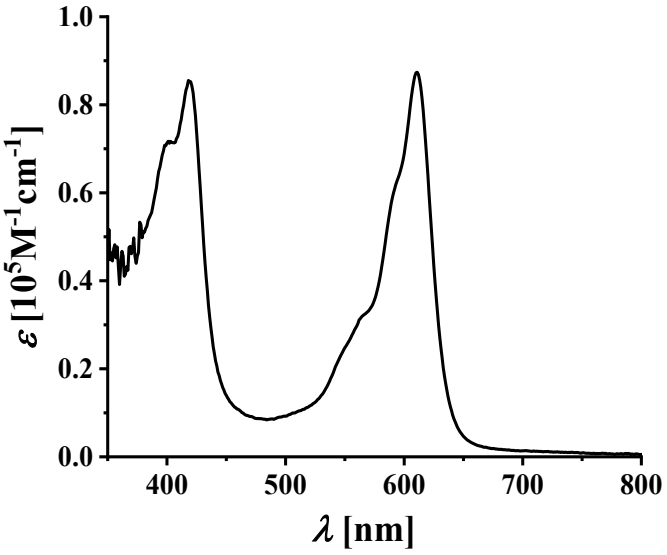


Fig. S3 Electronic absorption spectrum of **2** in acetonitrile at 298 K.

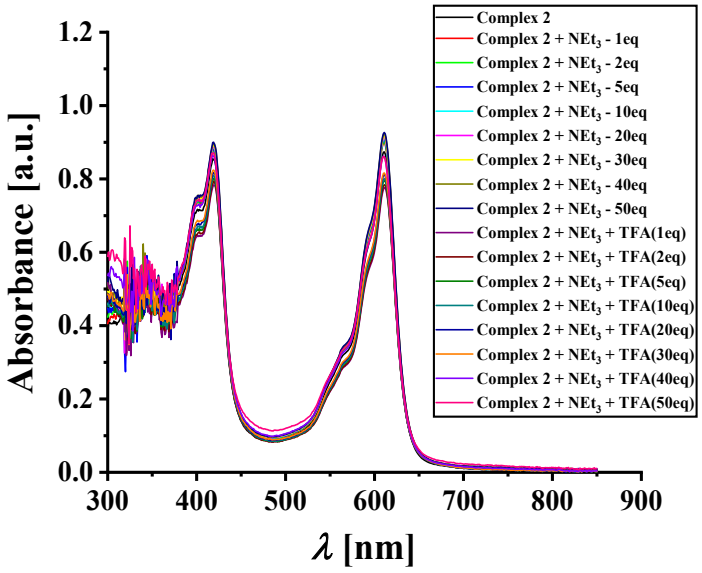
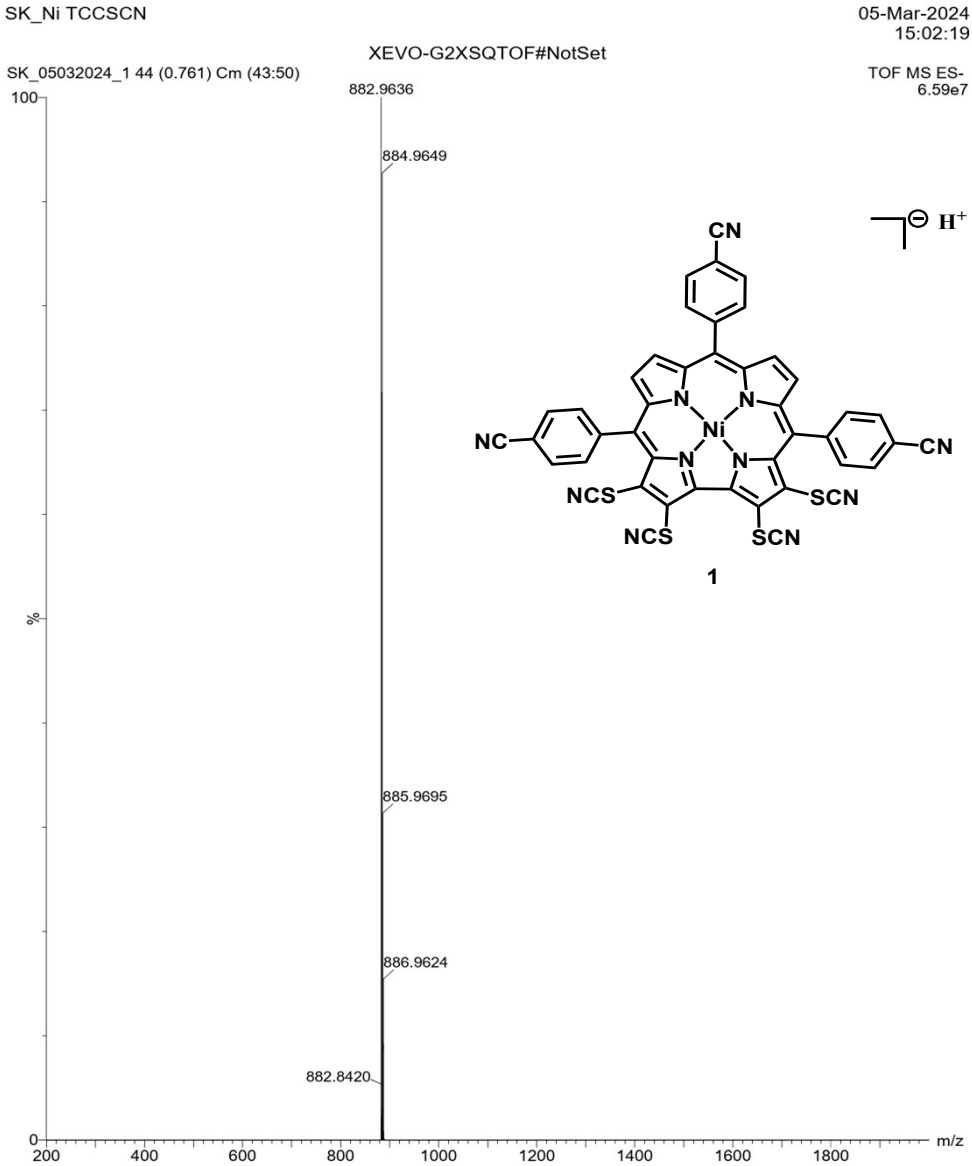


Fig. S4 Evolution of the electronic absorption spectra of **2** in the presence of excess triethylamine and trifluoroacetic acid in CH_3CN.


SK_Ni TCCSCN
05-Mar-2024
15:02:19
XEVO-G2XSQTOF#NotSet
SK_05032024_1 44 (0.761) Cm (43:50)
TOF MS ES-
6.59e7
882.9636
884.9649
885.9695
886.9624
882.8420
100
%
0
200
400
600
800
1000
1200
1400
1600
1800
m/z
CN
NC
CN
NCS
SCN
NCS
SCN
N
N
Ni
N
N
H+

1

Fig. S5 **(a)** ESI-MS spectrum of 2,3,17,18-Tetrathiocyanato-[5,10,15-tris(4-cyanophenyl)corrolato] nickel(II), **1** in CH_3CN shows the measured spectrum (experimental).

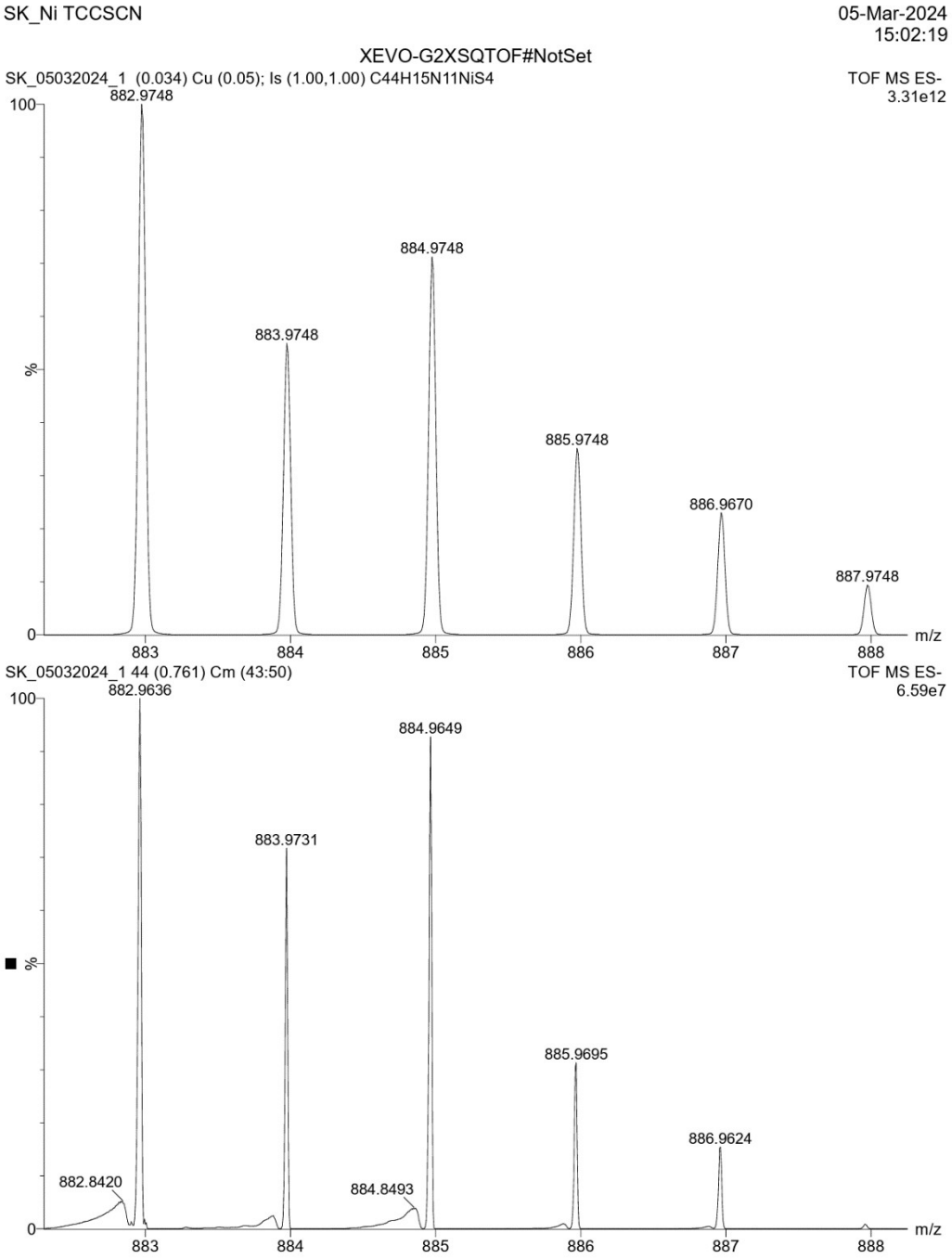


Fig. S5 **(b)** ESI-MS spectrum of 2,3,17,18-Tetrathiocyanato-[5,10,15-tris(4-cyanophenyl)corrolato] nickel(II), **1** in CH_3CN shows the isotopic distribution pattern (simulated).

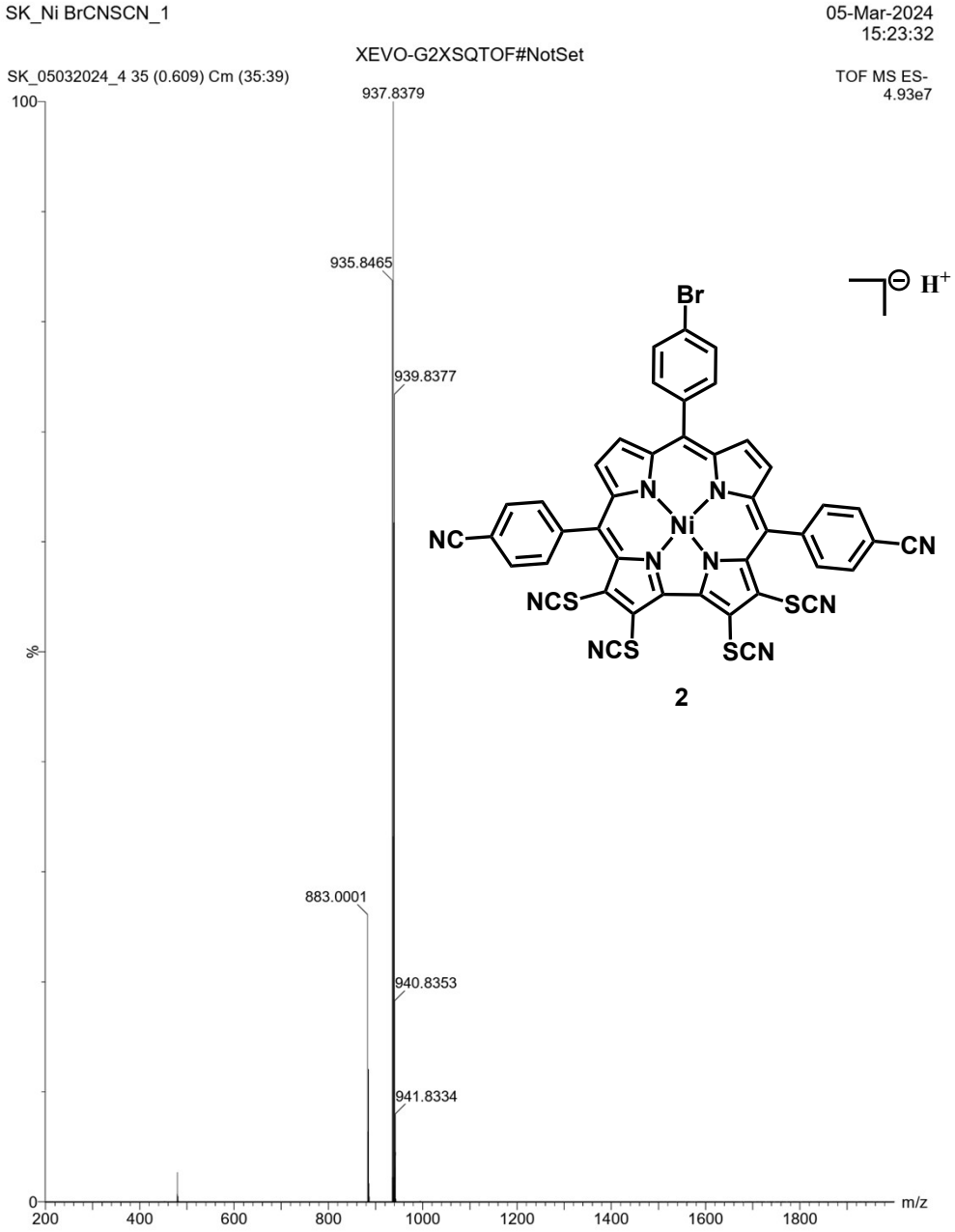


Fig. S6 **(a)** ESI-MS spectrum of 2,3,17,18-Tetrathiocyanato-[5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)-corrolato] nickel(II), **2** in CH_3CN shows the measured spectrum (experimental).

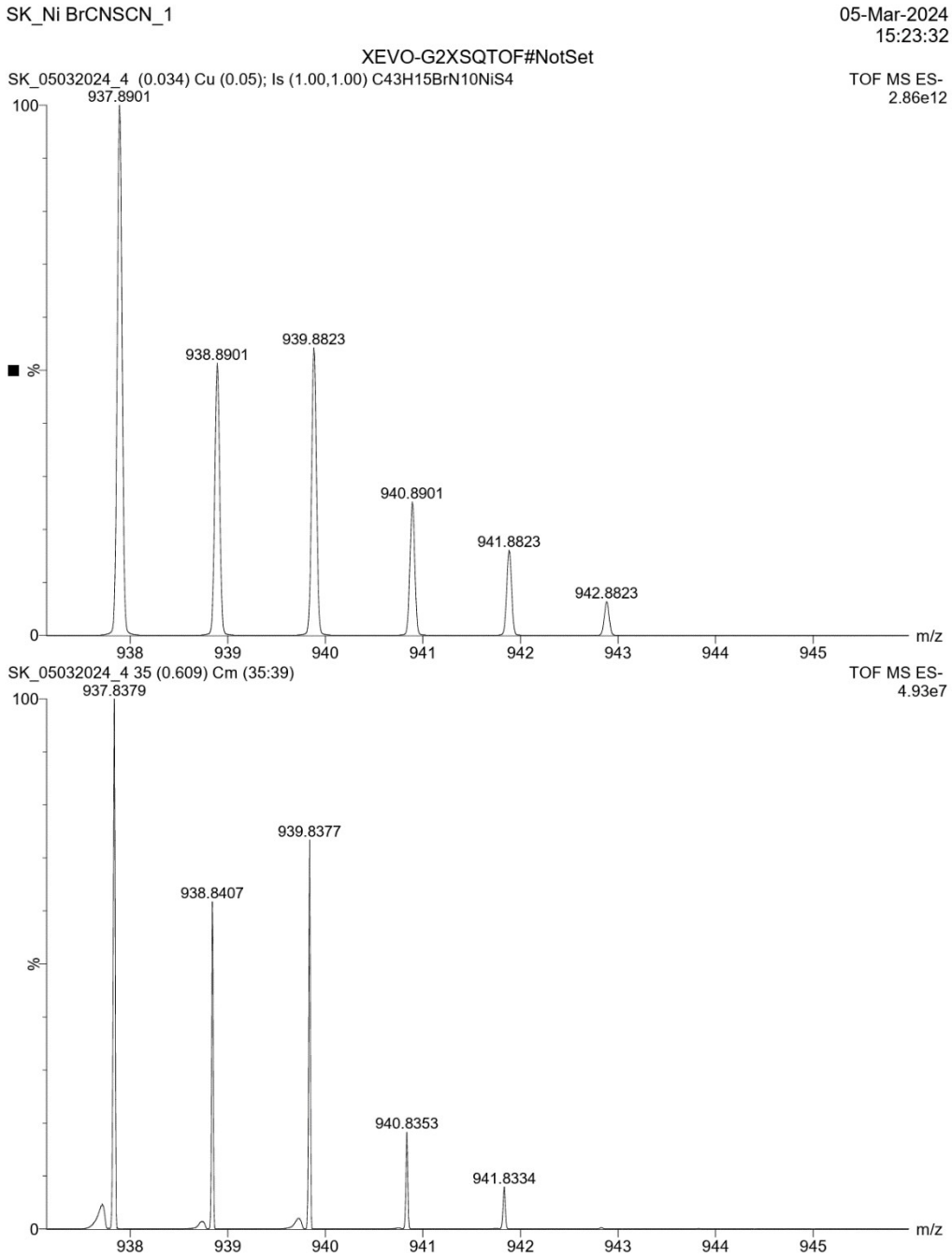


Fig. S6 **(b)** ESI-MS spectrum of 2,3,17,18-Tetrathiocyanato-[5,15-bis(4-cyanophenyl)-10-(4-bromophenyl)-corrolato] nickel(II), **2** in CH_3CN shows the isotopic distribution pattern (simulated).

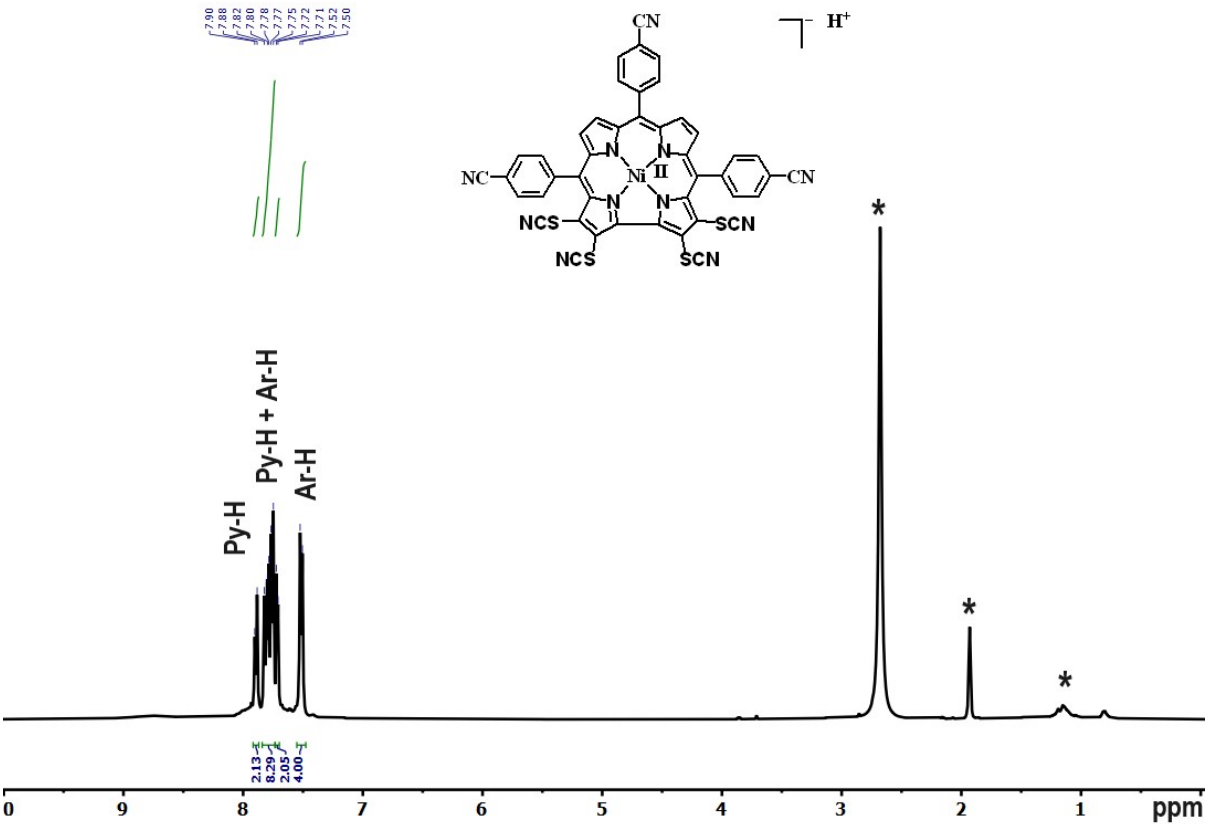


Fig. S7 ^{1}H-NMR spectrum of **1** in CD_3CN solution.

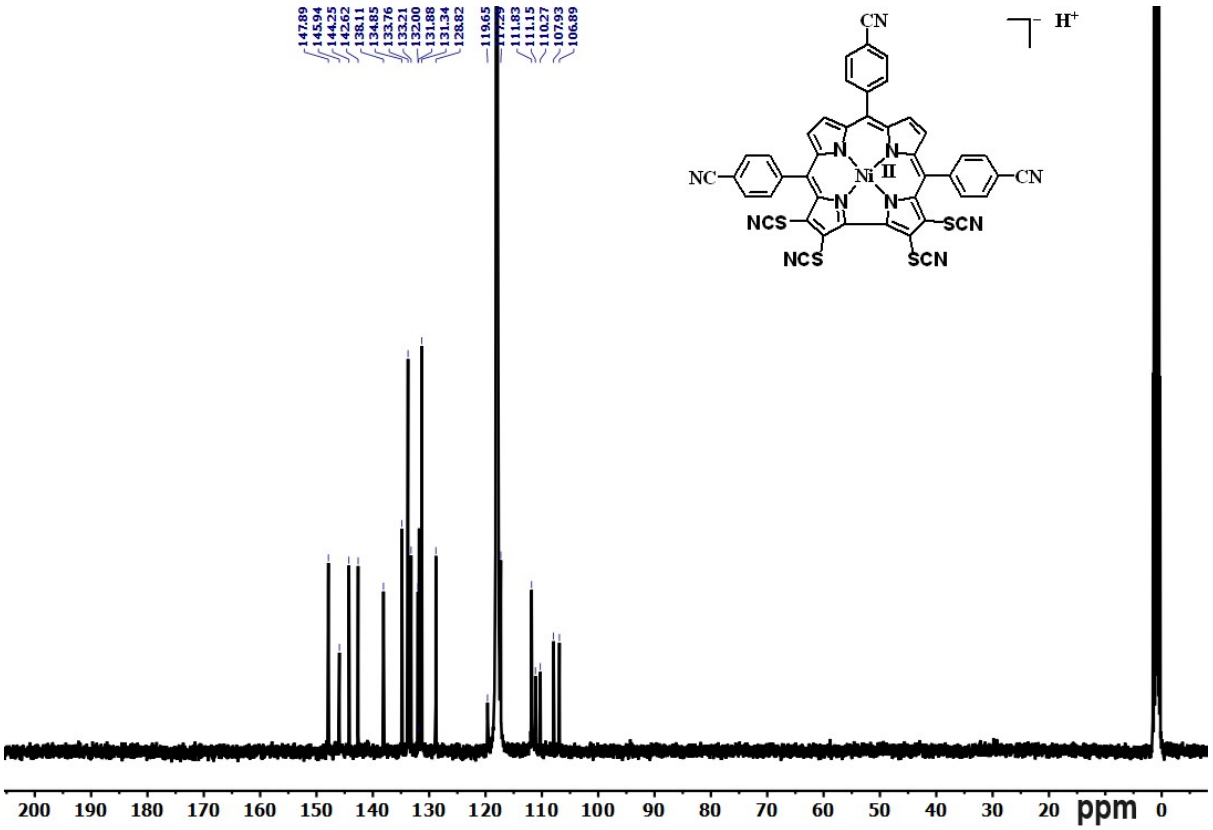


Fig. S8 ^{13}C $\{^{1}H\}$-NMR spectrum of **1** in CD_3CN solution.

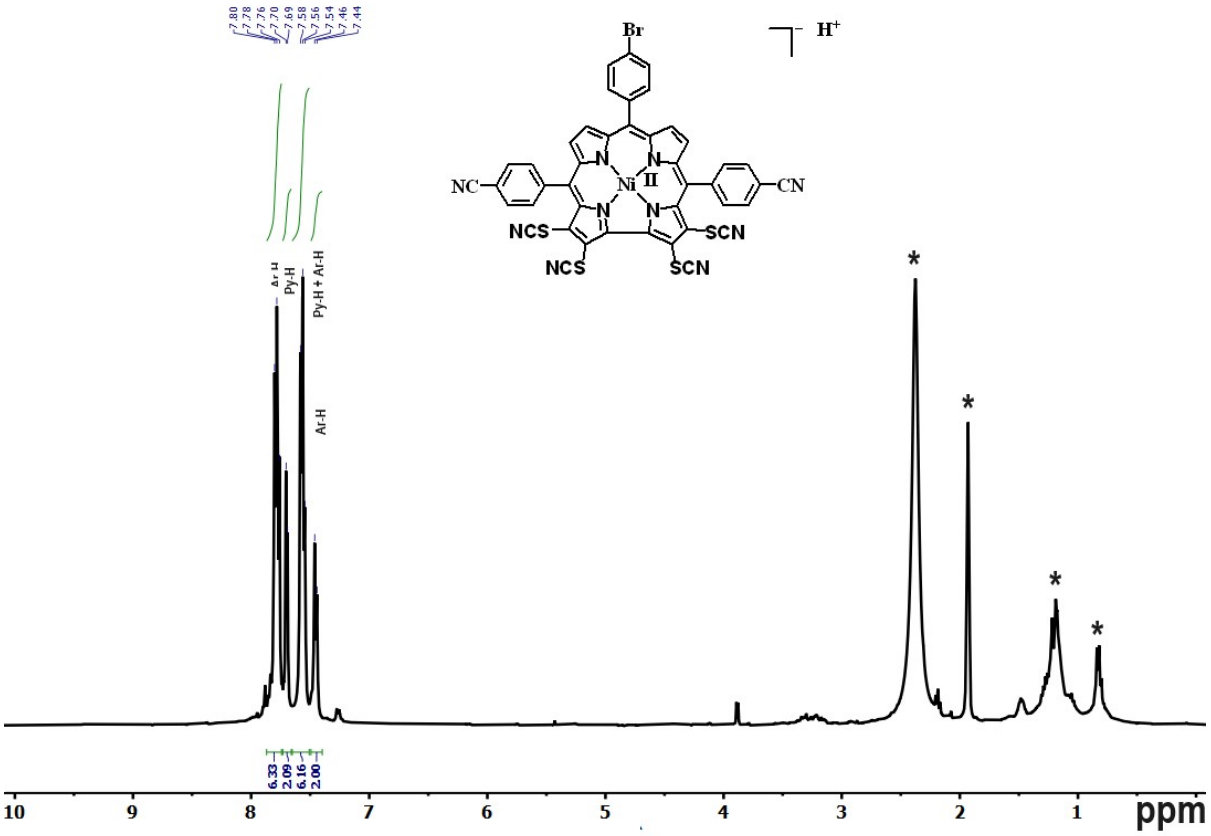


Fig. S9 ^{1}H-NMR spectrum of **2** in CD_3CN solution.

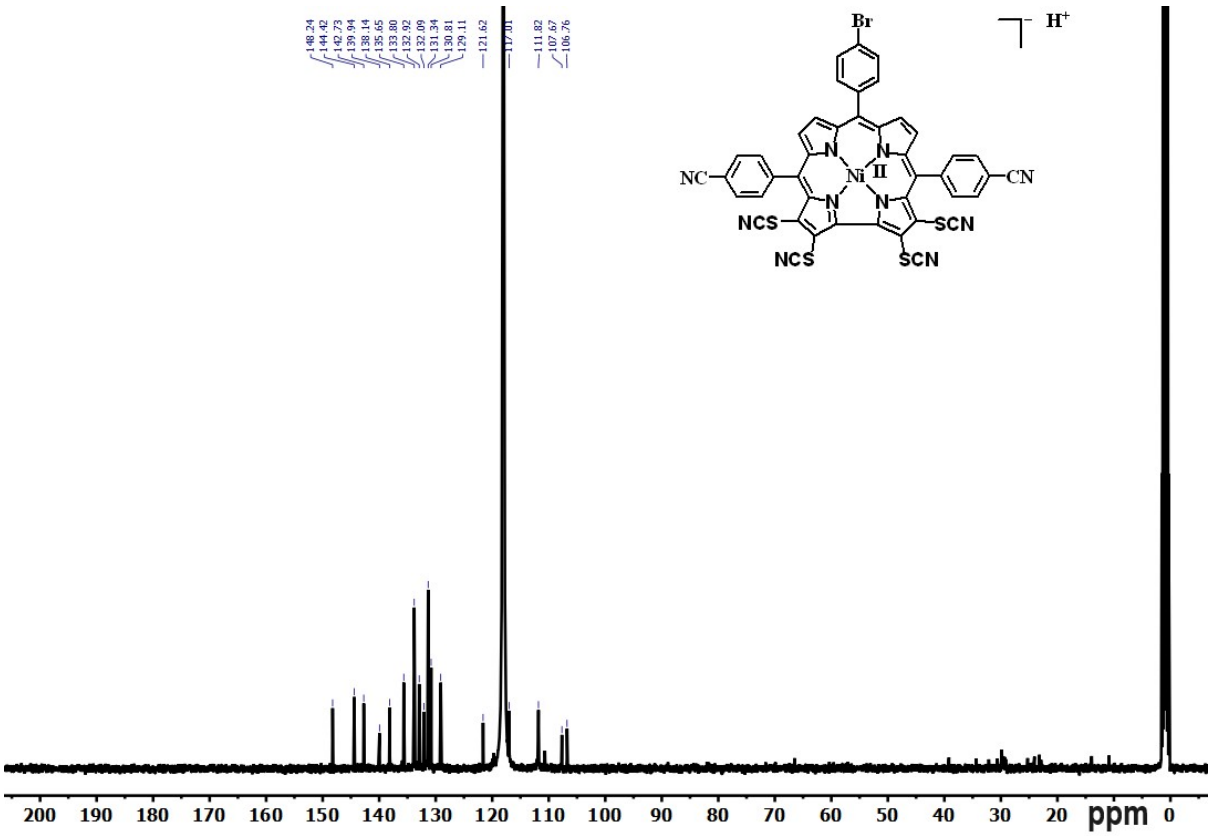


Fig. S10 ^{13}C $\{^{1}H\}$-NMR spectrum of **2** in CD_3CN solution.

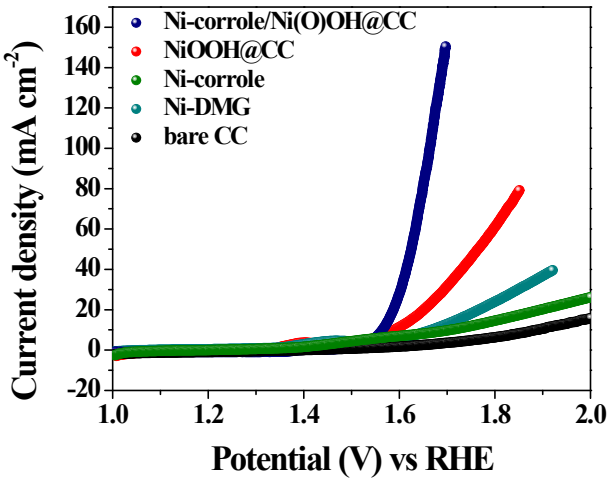


Fig. S11 LSV profiles of Ni(O)(OH)/Ni-corrole (active catalyst after 100 CV cycles), Ni(O)OH, Ni-corrole, and another molecular complex $Ni(dmgH)_2$ and bare CC in a 1.0 M aqueous KOH solution (scan rate 2 mV s^{-1}).

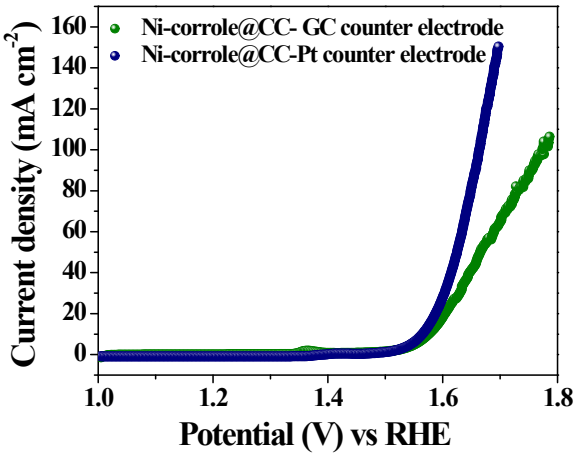


Fig. S12 LSV profiles of the Ni(O)(OH)/Ni-corrole@CC with Pt as counter electrode (blue) and Ni(O)(OH)/Ni-corrole@CC with respect to glassy carbon (green) as counter electrode in 1.0 M aqueous KOH solution.

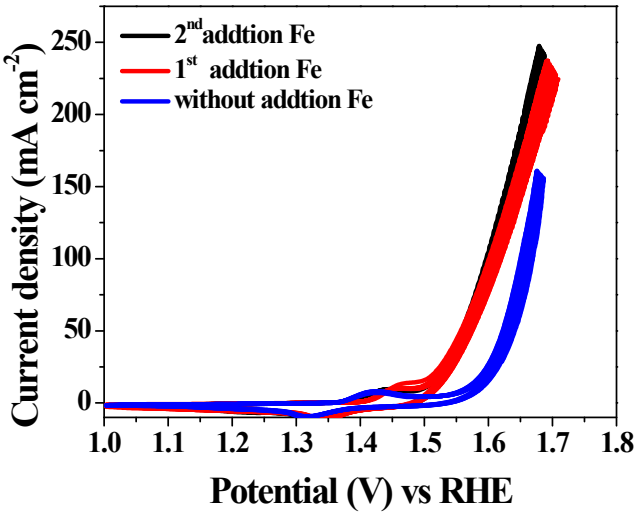


Fig. S13 Electrochemical activation of Ni(O)(OH)/Ni-corrole via the addition of Fe^{3+} to the electrolyte solution, as depicted by a CV cycle.

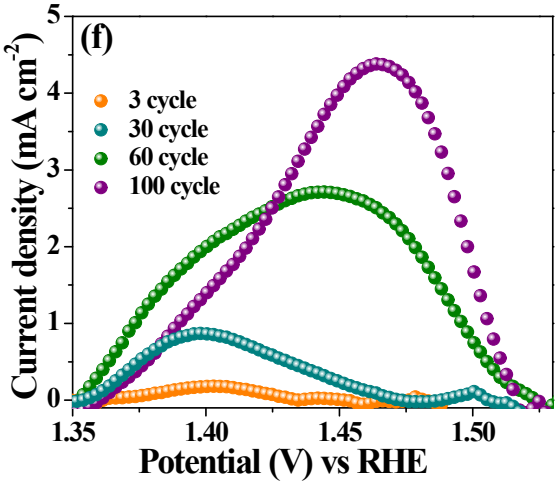


Fig. S14 Potential vs. current density plots showing the oxidation peak used for the area integration curve.

Appendix 3: Determination of the number of active sites of the Ni(O)(OH)/Ni-corrole with respect to the different activation cycles.

Determination of the Number of Active Sites after 3 cycle activation [3]

The area calculated (associated with the oxidation peak) = 0.0011 x 10^{-3} V A

The associated charge calculated is = 0.0011 x 10^{-3} V A / 0.005 V s^{-1} =2.2 x10^{-3} A s = 2.2 x10^{-4} C

Thus the number of electron transferred is = 2.2 x10^{-4} C / 1.602 ×10^{-19} C = 1.37 ×10^{15}

Since the oxidation of Ni^{2+} to Ni^{3+} is a single electron transfer reaction, the number of electrons calculated above is the same as the number of active surface sites.

Hence, the surface-active site that participated in OER is = 1.37 ×10^{15}.

Determination of the Number of Active Sites after 30 cycle activation [3]

The area calculated (associated with the oxidation peak) = 0.063 x 10^{-3} V A

The associated charge calculated is = 0.063 x 10^{-3} V A / 0.005 V s^{-1} = 12.6 x 10^{-3} A s = 12.6 x 10^{-3} C

Thus the number of electron transferred is = 12.6 x 10^{-3} C / 1.602 ×10^{-19} C = 7.86 ×10^{16}

Since the oxidation of Ni^{2+} to Ni^{3+} is a single electron transfer reaction, the number of electrons calculated above is the same as the number of active surface sites.

Hence, the surface-active site that participated in OER is = 7.86 ×10^{16}.

Determination of the Number of Active Sites after 60 cycle activation [3]

The area calculated (associated with the oxidation peak) = 0.309 x 10^{-3} V A

The associated charge calculated is = 0.309 x 10^{-3} V A / 0.005 V s^{-1} = 61.8 x 10^{-3} A s = 61.8 x 10^{-3} C

Thus the number of electron transferred is = 61.8 x 10^{-3} C / 1.602 ×10^{-19} C = 38.57 ×10^{16}

Since the oxidation of Ni^{2+} to Ni^{3+} is a single electron transfer reaction, the number of electrons calculated above is the same as the number of active surface sites.

Hence, the surface-active site that participated in OER is = 38.57 ×10^{16}

Determination of the Number of Active Sites after 100 cycle activation [3]

The area calculated (associated with the oxidation peak) = 0.381 x 10^{-3} V A

The associated charge calculated is = 0.381 x 10^{-3} V A / 0.005 V s^{-1} = 76.2 x 10^{-3} C

Thus, the number of electron transferred is = 76.2 x 10^{-3} C / 1.602 ×10^{-19} C = 47.56 ×10^{16}

Since the oxidation of Ni^{2+} to Ni^{3+} is a single electron transfer reaction, the number of electrons calculated above is the same as the number of active surface sites.
Hence, the surface-active site that participated in OER is = 47.56×10^{16}

Calculation of TOF [4]

$TOF = (j \times N_A) / (4 \times F \times n)$

Where,

j = Current density at 330 mV

N_A = Avogadro number

F = Faraday constant

n = Number of active Ni-sites

$TOF = [(10.12 \times 10^{-3}) (6.023 \times 10^{23})] / [(96485) (4) (47.565 \times 10^{16})]$

$= 3.32 \times 10^{-2}\ s^{-1}$

Table S3. Comparison of the number of active sites of the Ni(O)(OH)/Ni-corrole with respect to the different activation cycles**.**

S.No.	**Active catalyst**	**Number active sites**
1	Ni(O)(OH)/Ni-corrole (3^{rd} cycle)	1.37×10^{15}
2	Ni(O)(OH)/Ni-corrole (30^{th} cycle)	7.86×10^{16}
3	Ni(O)(OH)/Ni-corrole (60^{th} cycle)	38.57×10^{16}
4	Ni(O)(OH)/Ni-corrole (100^{th} cycle)	47.56×10^{16}

Reference:

1. A. K. Singh, S. Ji, B. Singh, C. Das, H. Choi, P. W. Menezes and A. Indra, *Mater. Today Chem*. 2022, **23**, 100668.
2. S. Anantharaj, M. Jayachandran and S. Kundu, *Chem. Sci.*, 2016, **7**, 3188-3205.

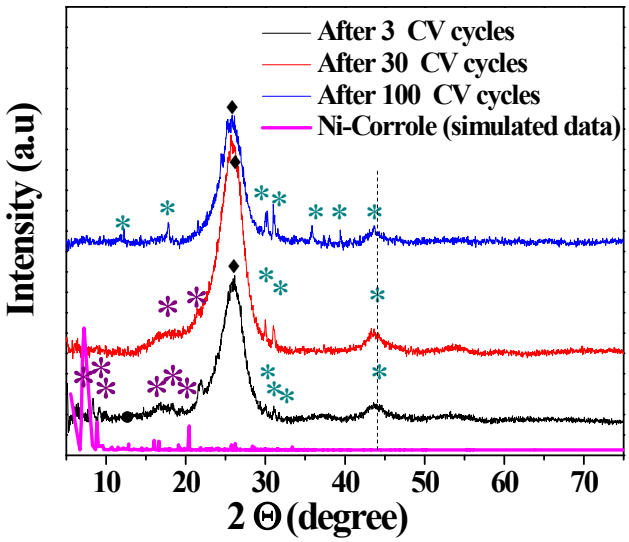


Fig. S15 PXRD of the Ni(O)(OH)/Ni-corrode after 3 CV cycles, 30 CV cycles, and 100 CV cycles.[5] (Purple*: Ni-corrole complex, Cyan*: Ni(O)OH, ♦: Carbon cloth)

Reference:

3. Z. Lin, P. Bu, Y. Xiao, Q. Gao and P. Diao, *J. Mater. Chem. A,* 2022, **10**, 20847–20855.

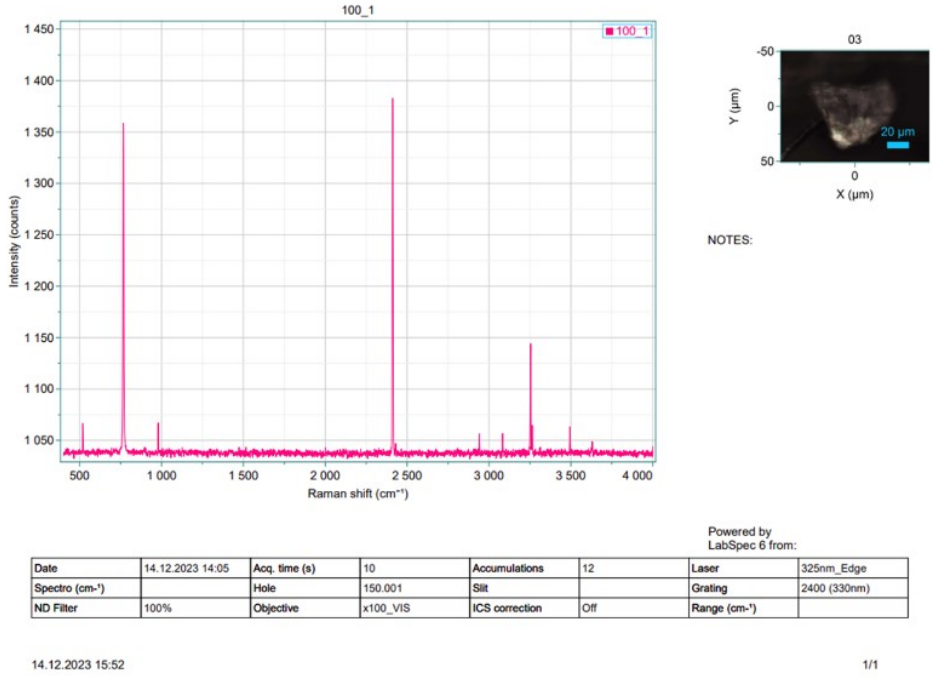


Fig. S16 Raman spectra of the Ni(O)(OH)/Ni-corrole after 100 cycles.[6]

Reference:

4. K. M. Cole, D. W. Kirk and S. J. Thorpe, *J. Electrochem. Soc*. 2018, **165**, 3122.

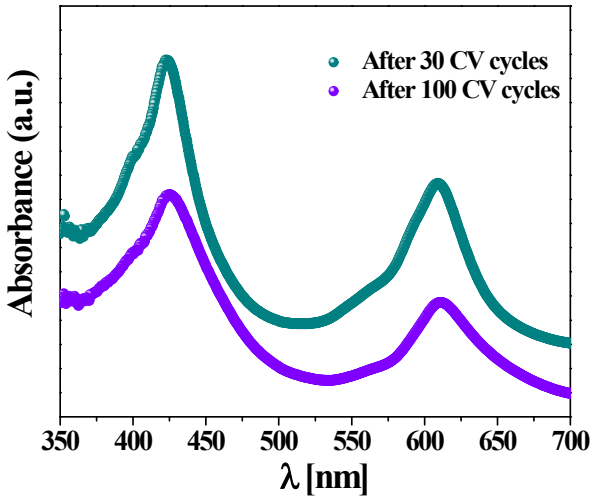


Fig. S17 UV-visible spectra showed the peaks corresponding to the Ni(O)(OH)/Ni-corrole after 30 CV cycles and 100 CV cycles activation.[7]

Reference:

5. S. Eulberg, N. Schulze, J. Krumsieck, N. Klein and M. Bröring, *Angew. Chemie Int. Ed*. 2023, **62**, e202306598.

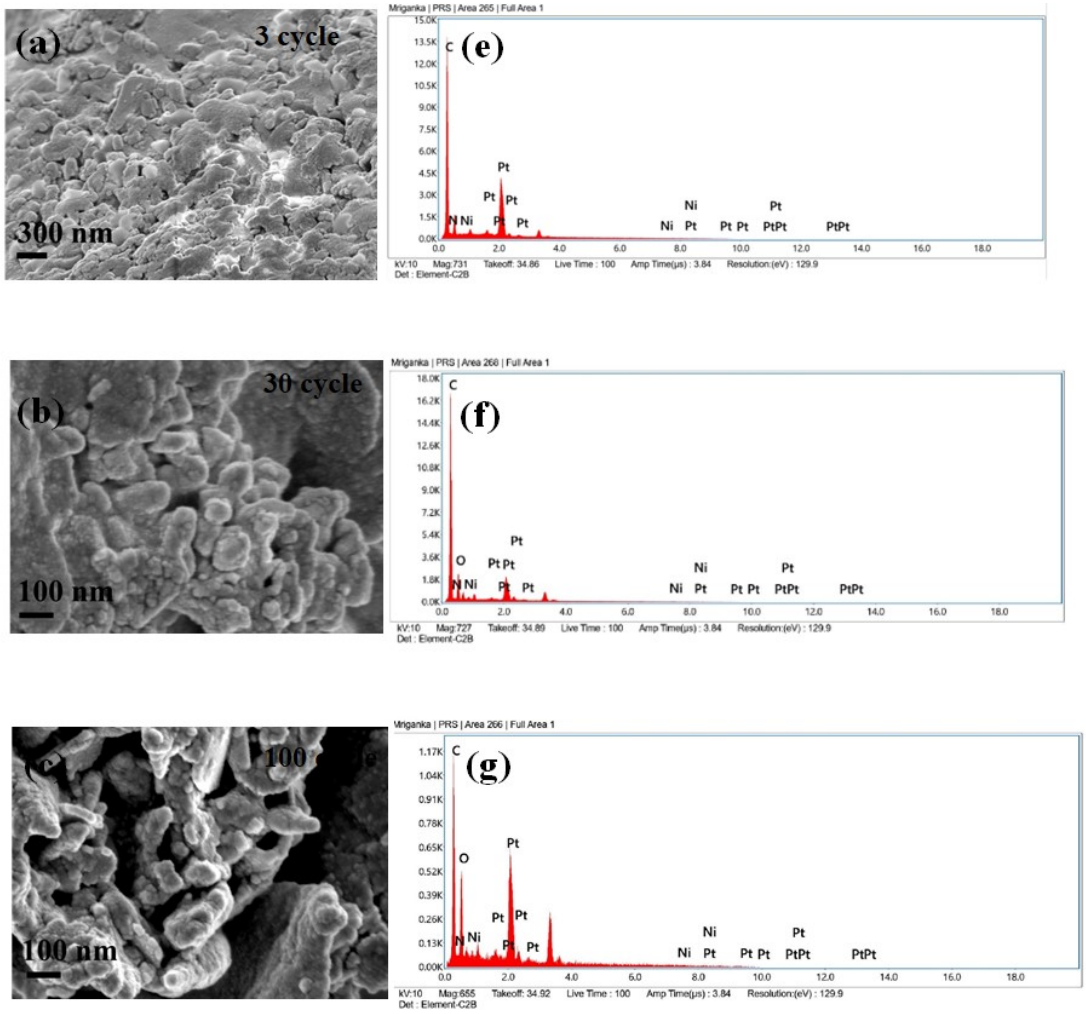


Fig. S18 (a-c) The SEM and EDX studies of Ni(O)(OH)/Ni-corrole after the different CV cycle-activation showed a change in the morphological feature. **(**e-g) The EDX data of the catalyst after 3 cycles, 30 cycles, and 100 cycles of CV activation showed that Ni, C, N, O, and S but with a varying amount.

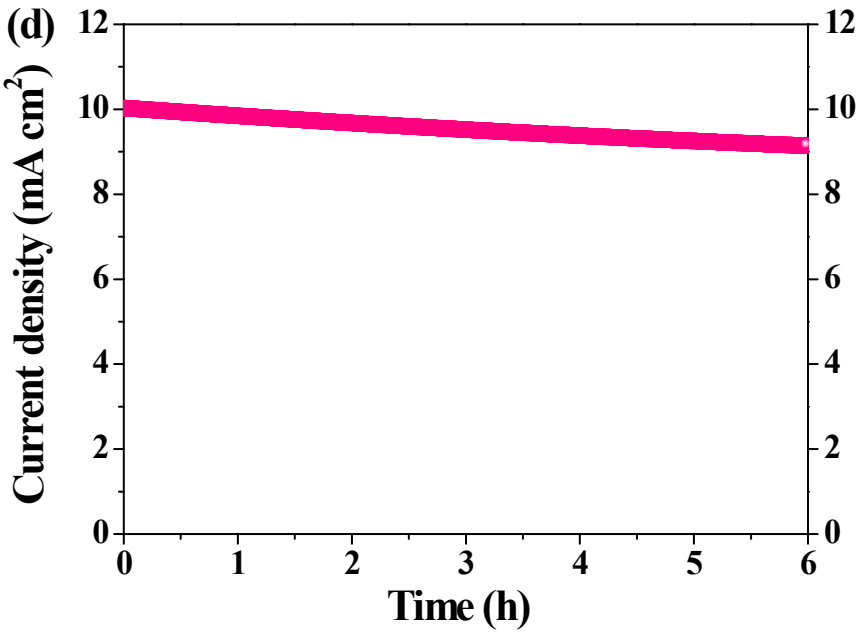


Fig. S19 The chronoamperometric study of Ni(O)(OH)/Ni-corrole demonstrates the stability of the catalyst for 6 hours.

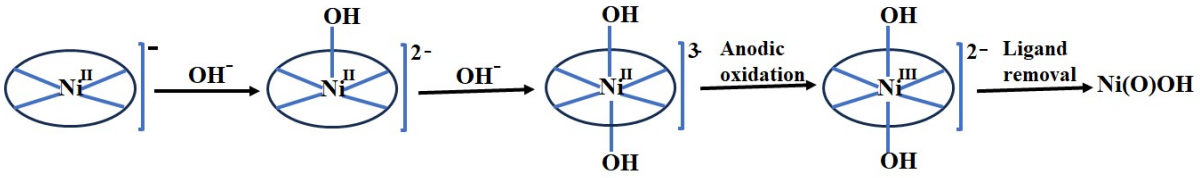


Fig. S20 The plausible mechanism for the formation of Ni(O)OH from the Ni-corrole complex by the anodic activation in the alkaline medium.