Electronic Supplementary Information

Electrode Surface Embedded Manganese(III)-Pincer Complexes: Efficient Electrocatalysts for Oxygen Evolution Reaction

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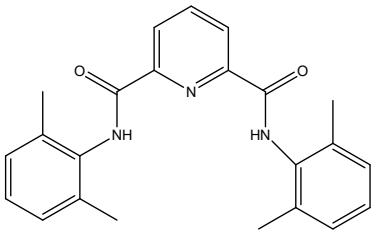
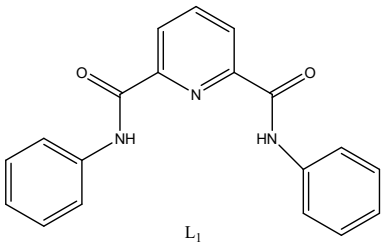
Synthesis of N,N′-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide (L)

The ligand N,N′-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide (L) is prepared by using a reported procedure with slight modification. 363.54 mg, 3.0 mmol 2,6-dimethyl aniline was dissolved in dichloromethane (DCM) and added 0.626 mL Et_3N added dropwise with stirring at 0^{o}C under inert atmosphere. Thereafter, a DCM solution of pyridine dicarbonyl dichloride (306.02 mg, 1.5 mmol) was added drop wise and stirred with heating at around 40 ^{0}C under inert atmosphere for 4 hours. The resulting solution was washed with 10% HCl, water and dried over Na_2SO_4. After drying, the crude product was recrystallized by using petroleum ether/DCM mixture. Yield: 453.6 mg, 81%.

Similar procedure was adopted for the synthesis of N,N′-(diphenyl)-2,6-pyridinedicarboxamide) (L_1) using aniline instead of 2,6-dimethyl aniline. Yield: 395.08 mg, 82.98%



L



L_1

Characterization

N,N′-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide (L):

High resolution mass spectra: Chemical formula: $C_{23}H_{23}N_3O_2$, (m/z) $[M+H]^+$ (Calculated) 374.1863,(m/z) $[M+H]^+$ (Experimental): 374.1871.

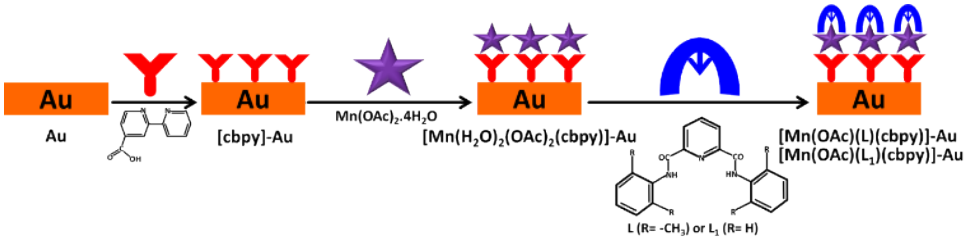
^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.07 (s, NH), 8.53 (d, $1H^{Py}$), 8.17 (t, $1H^{Py}$), 7.19-7.14 (m, $2H^{Bz}$), 2.32 (s, 3H).

N,N′-(diphenyl)-2,6-pyridinedicarboxamide) (L_1) :

High resolution mass spectra: Chemical formula: $C_{19}H_{15}N_3O_2$, (m/z) $[M+H]^+$ (Calculated): 318.1243, (m/z) $[M+H]^+$ (Experimental): 318.3004.

^{1}H-NMR: (400 MHz, $CDCl_3$): δ 9.13 (s, NH), 8.59 (d, $1H^{Py}$), 8.22 (t, $1H^{Py}$), 7.24-7.19 (m, $2H^{Bz}$).

High resolution mass spectra and ^{1}H-NMR spectra supports the formation of ligand N,N′-(2,6-dimethylphenyl)-2,6-pyridinedicarboxamide (L) and N,N′-(diphenyl)-2,6-pyridinedicarboxamide) (L_1).



Scheme S1 Electrode modification process

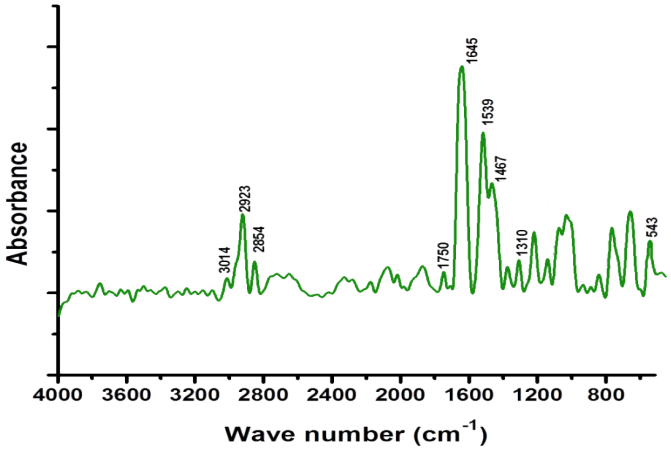


Fig. S1 ATR-FTIR of [Mn(OAc)(L)(cbpy)]-Au

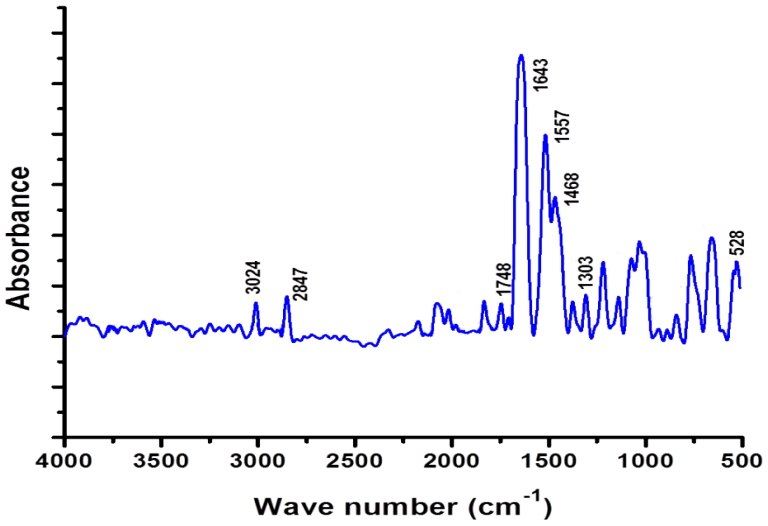


Fig. S2 ATR-FTIR of [Mn(OAc)(L_1)(cbpy)]-Au

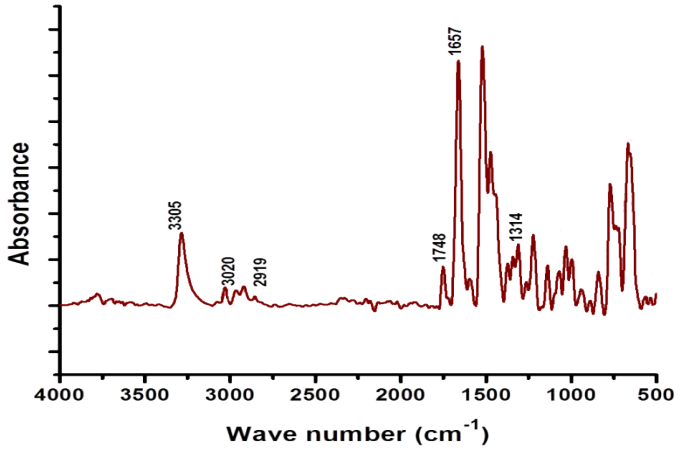


Fig. S3 ATR-FTIR of pincer ligand, L

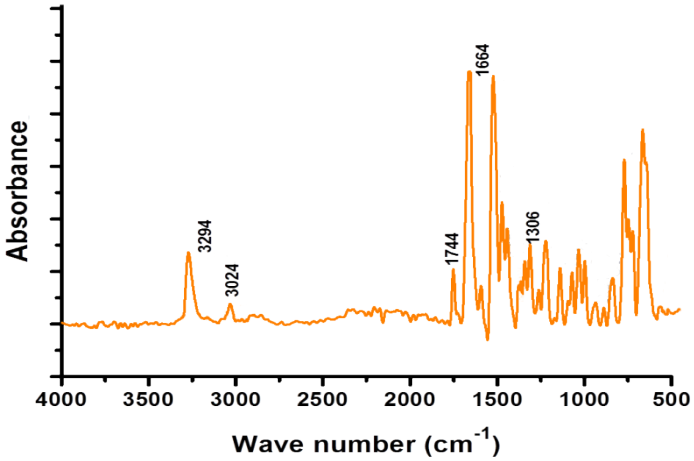


Fig. S4 ATR-FTIR of pincer ligand, L_1

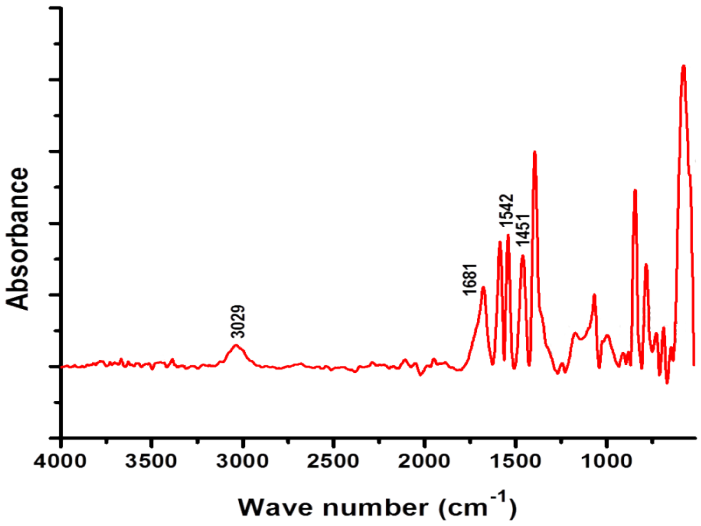


Fig. S5 ATR-FTIR of cbpy-Au

Table S1. ATR-FTIR spectral data

Compounds	C=O	N-H	C=N	C-N	-COO^- (sym.)	-COO^- (asym.)	CH str. of -CH_3	CH_3 of CH_3COO-	Aromatic CH str.	Mn-N
Ligand L	1748	3305	1657	1314	-	-	2919		3020	-
[Mn(OAc)(L)(cbpy)]-Au	1750	-	1645	1310	1467	1539	2923	2854	3014	543
Ligand L_1	1744	3294	1664	1306	-	-	-	-	3024	-
[Mn(OAc)(L_1)(cbpy)]-Au	1748	-	1643	1303	1468	1557	-	2847	3024	528
cbpy-Au	-	-	1681	-	1451	1542	-	-	3029	-

Table S2. SERS spectral data

Complexes on gold electrode surface	δ $(COO^-)_{sym}$	δ $(COO^-)_{asym}$	C=N / C=C	C-N	-CH_3COO^-				Au-O	Mn-O	Mn-N
					CH	γCOO	γCO	CH_3 rock			
Mn(OAc)(L)(cbpy)]-Au	1388	882	1548	1152	2949	2880, 1388	1252	1015	253	573	645
Mn(OAc)(L_1)(cbpy)]-Au	1385	893	1532	1137	2951	2872	1258	1016	246	566	664

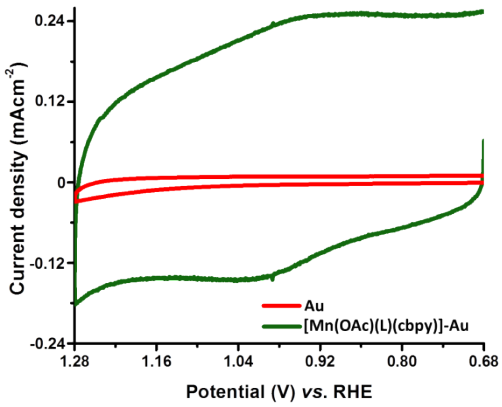
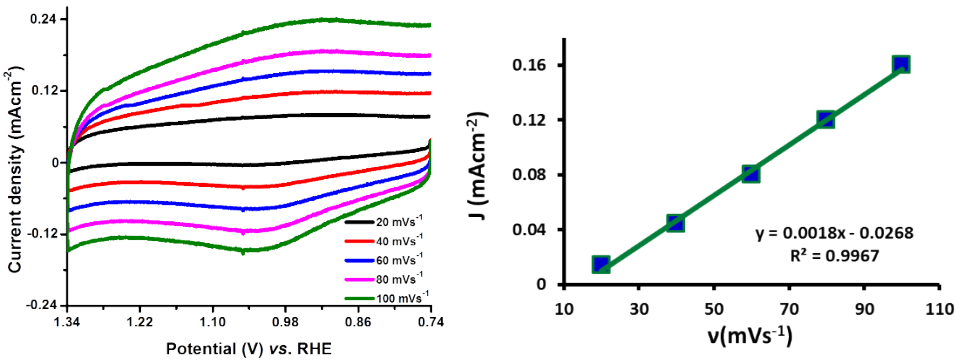


Fig. S6 Overlaid CVs obtained at bare Au and [Mn(OAc)(L)(cbpy)]-Au electrodes in 0.1 M PBS at pH 7.0 (scan rate 1000 mVs^{-1}).



(a) (b)

Fig. S7 CVs of [Mn(OAc)(L)(cbpy)]-Au electrode in 0.1 M PBS at pH 7.0 at different scan rate (20-100 mVs^{-1}) (a), A plot of current density *versus* scan rate (b).

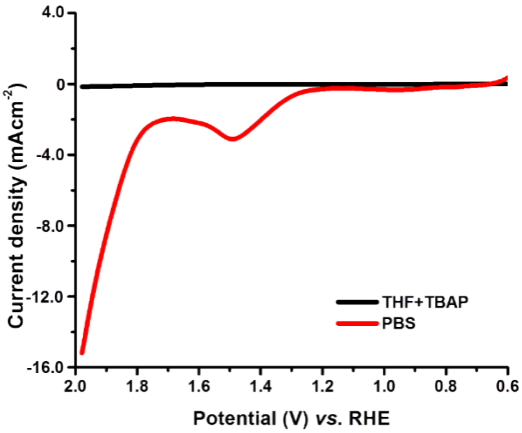


Fig. S8 Overlaid LSV taken in aqueous (red curve) and non-aqueous solvent (black curve) at [Mn(OAc)(L)(cbpy)]-Au electrode.

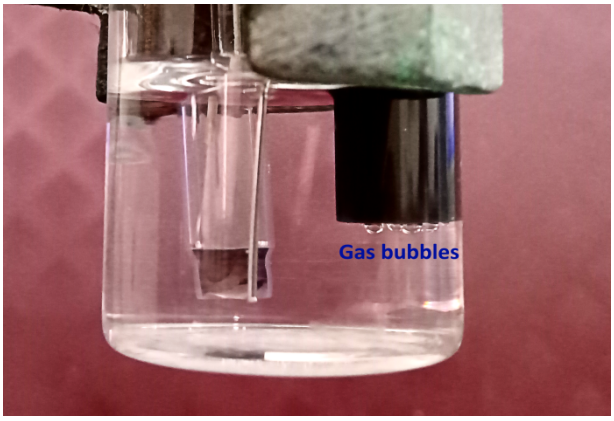


Fig. S9 Formation of O_2 gas bubbles on the [Mn(OAc)(L)(cbpy)]-Au electrode after 25 repetitive runs.

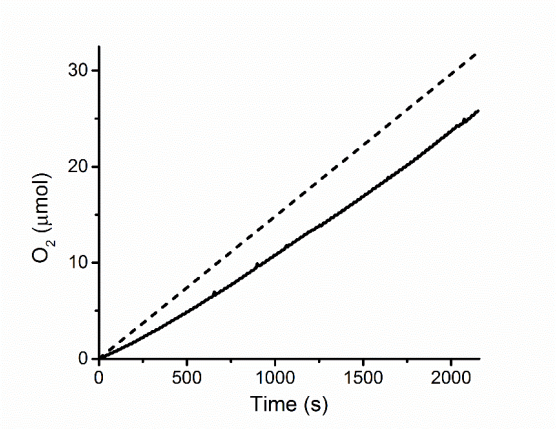


Fig. S10 Oxygen evolution during the controlled potential electrolysis of water in a gas tight electrochemical cell under N_2 atmosphere (0.1 M PBS, pH 7.0) with [Mn(OAc)(L)(cbpy)]-Au electrode at an applied potential of + 1.48 V *versus* RHE. Dotted line denotes the theoretical oxygen evolution with 100 % efficiency.

Faraday efficiency (%) = (Amount of O_2 × Number of electron needed to produce O_2) / Amount of charge passed to the solution.

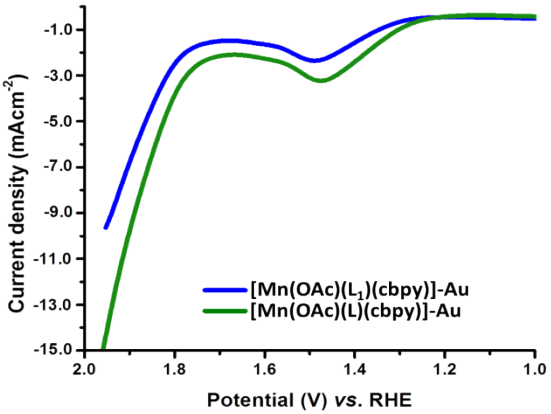


Fig. S11 Overlaid LSV in 0.1 M PBS using [Mn(OAc)(L)(cbpy)]-Au and [Mn(OAc)(L_1)(cbpy)]-Au electrode.

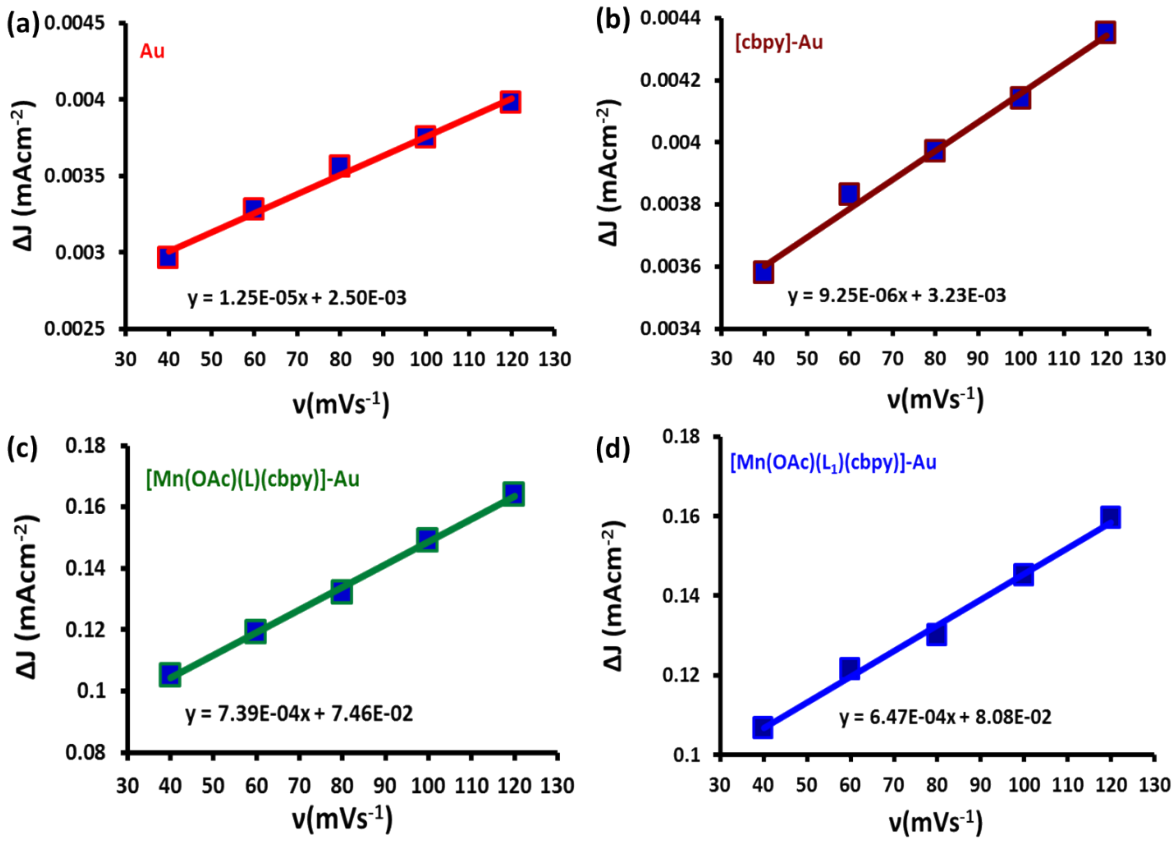


Fig. 12 Plot of ΔJ (J_a-J_c) *versus* scan rate (ν) for bare Au (a), cbpy-Au (b), [Mn(OAc)(L)(cbpy)]-Au (c) and [Mn(OAc)(L_1)(cbpy)]-Au electrode. The slope ($2C_{dl}$) were used to represent ECSA.

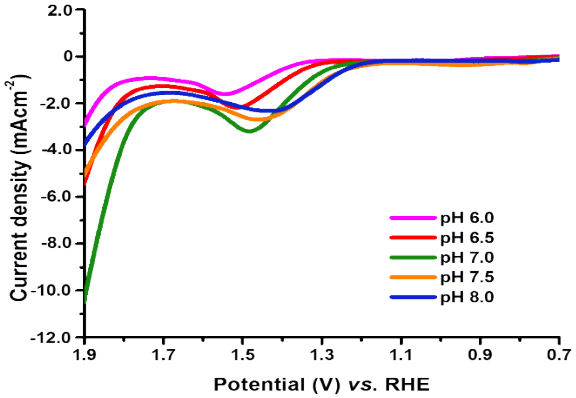
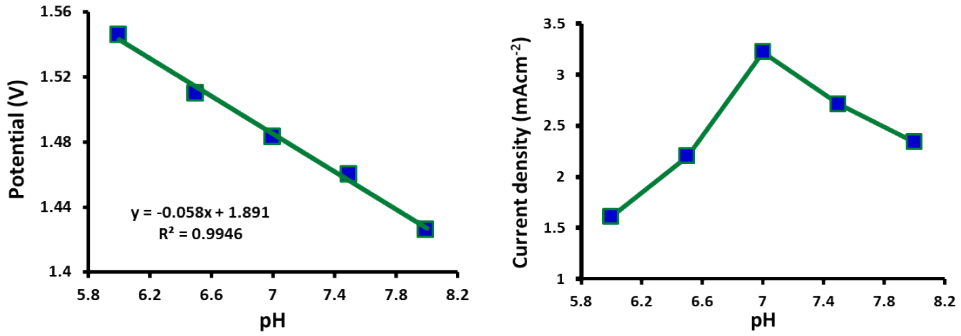


Fig. S13 Overlaid LSV obtained at [Mn(OAc)(L)(cbpy)]-Au electrode with increasing pH from 6.0 to 8.0.



(a) (b)

Fig. S14 Plot of potential *versus* pH of the medium (a). Plot of current density *versus* pH of the medium (b).

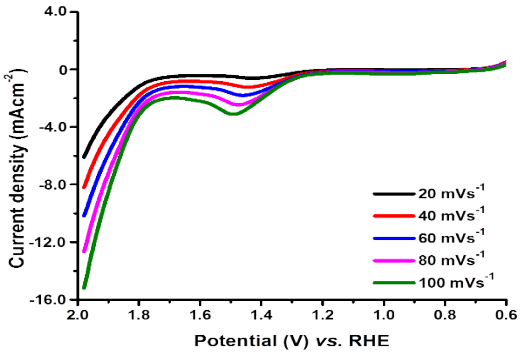


Fig. S15 Overlaid LSV in 0.1 M PBS (pH 7.0) with increasing scan rate (20-100 mVs-1) at [Mn(OAc)(L)(cbpy)]-Au electrode.

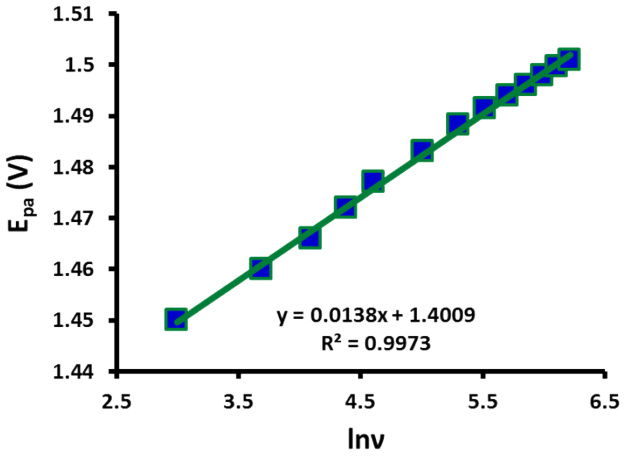


Fig. S16 Plot of E_{pa} *versus* ln ν

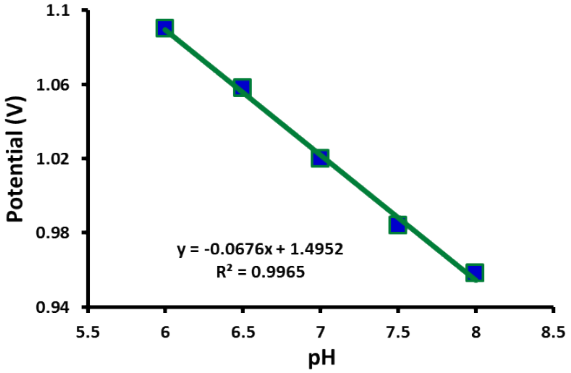


Fig. S17 Plot of potential versus pH

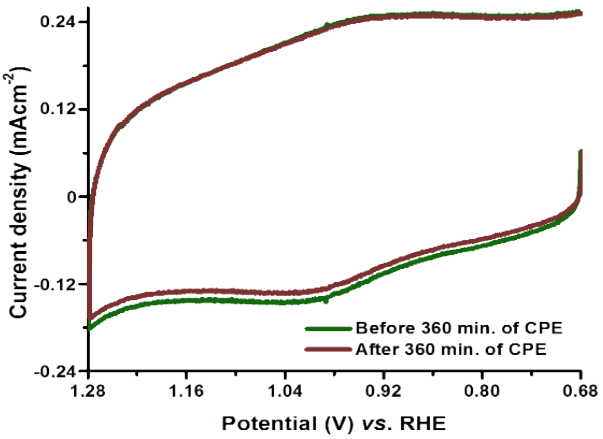
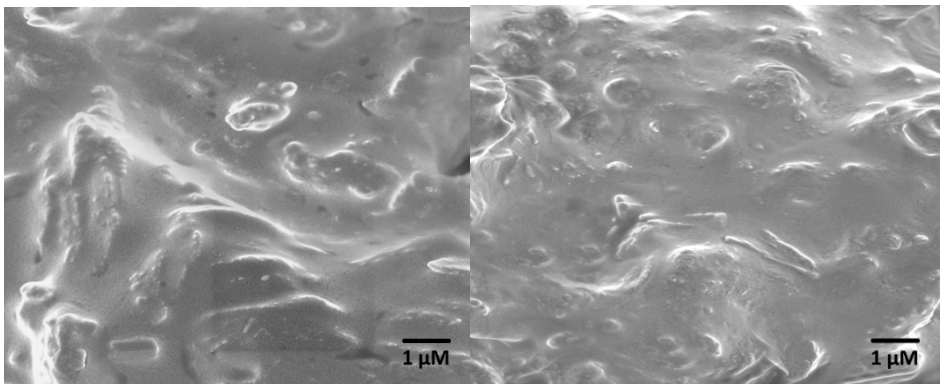
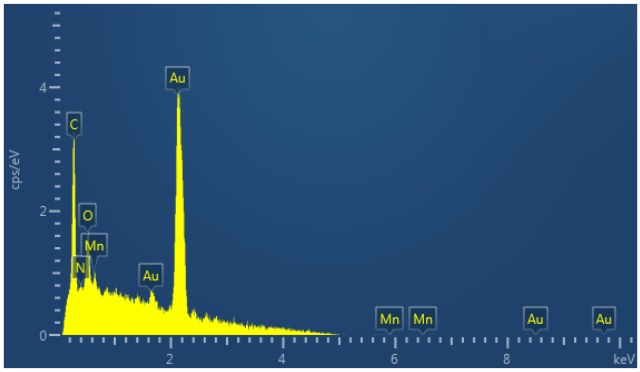


Fig. S18 Overlaid CVs before and after CPE using [Mn^{III}(OAc)(L)(cbpy)]-Au electrode (scan rate 100 mVs^{-1})

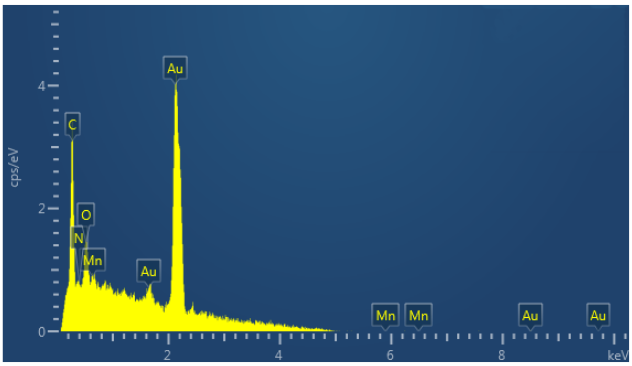


(a) (b)

Fig. 19 FE-SEM of [Mn^{III}(OAc)(L)(cbpy)]-Au electrode before (a) and after (b)after six hours of CPE

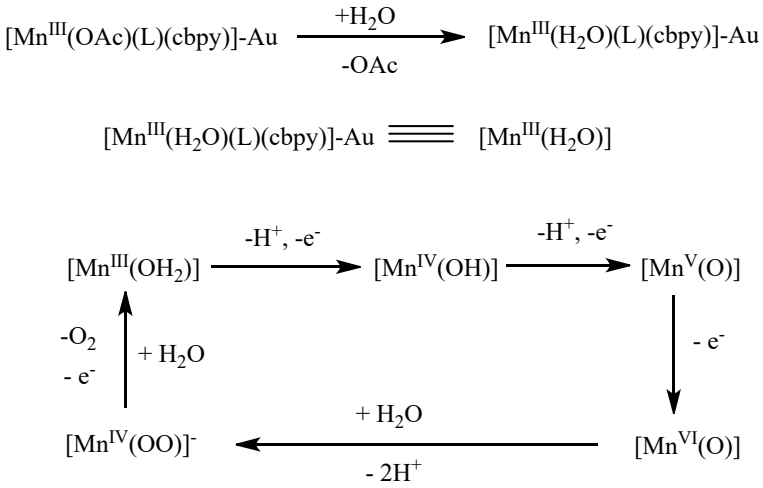


(a)



(b)

Fig. S20 EDX spectra of [Mn(OAc)(L)(cbpy)]-Au electrode before (a) and after (b) CPE.



Scheme S2. Plausible mechanism of OER at the [Mn(OAc)(L)(cbpy)]-Au electrode