Supporting Information

Development of robust noble-metal free Lanthanum, Neodymium Doped $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$ as a bifunctional electrocatalyst for electrochemical water splitting

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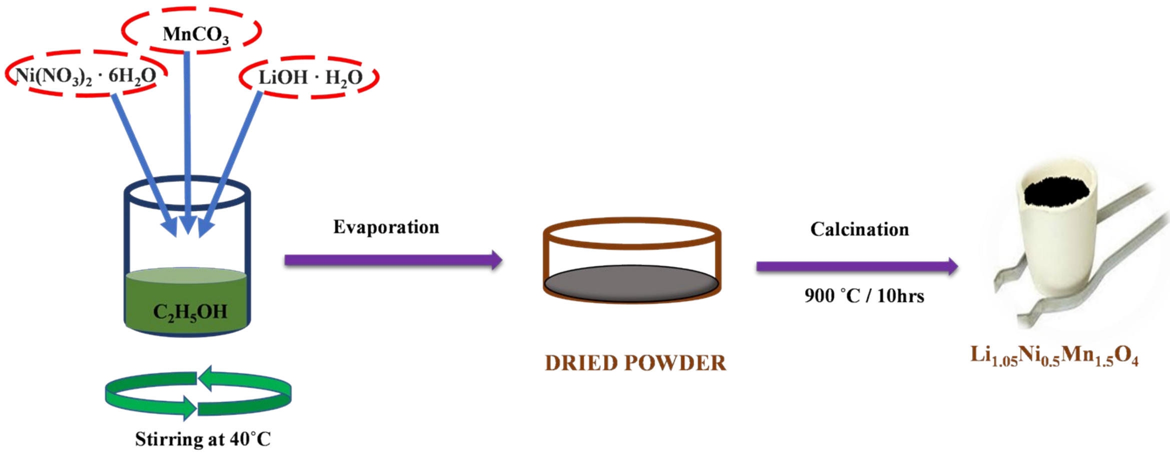
1. Synthesis method



1.1 Preparation of $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$

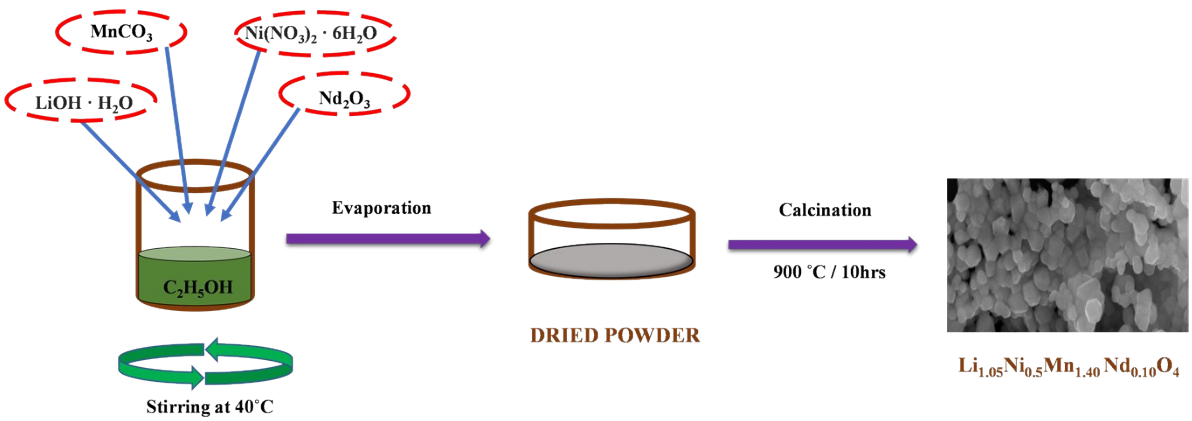
Figure. S1 Schematic represents the preparation of $Li_{1.05}Ni_{0.5}n_{1.5}O_4$

To synthesize $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, stoichiometric quantities of (1.05) lithium hydroxide monohydrate, (0.5) nickel nitrate hexahydrate, and (1.5) manganese carbonate in the proportions 1.05:0.5:1.5 of Li, Ni, and Mn were dissolved in ethanol. The ethanol was evaporated at 40 °C while stirring. After vaporization, the mixture was thermally treated at 900 °C for 10 h at a rate of 0.8 °C min^{-1} to achieve the final product presented in Figure S1.

1.2 Preparation of $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$

Figure. S2 Schematic represents the preparation of $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$

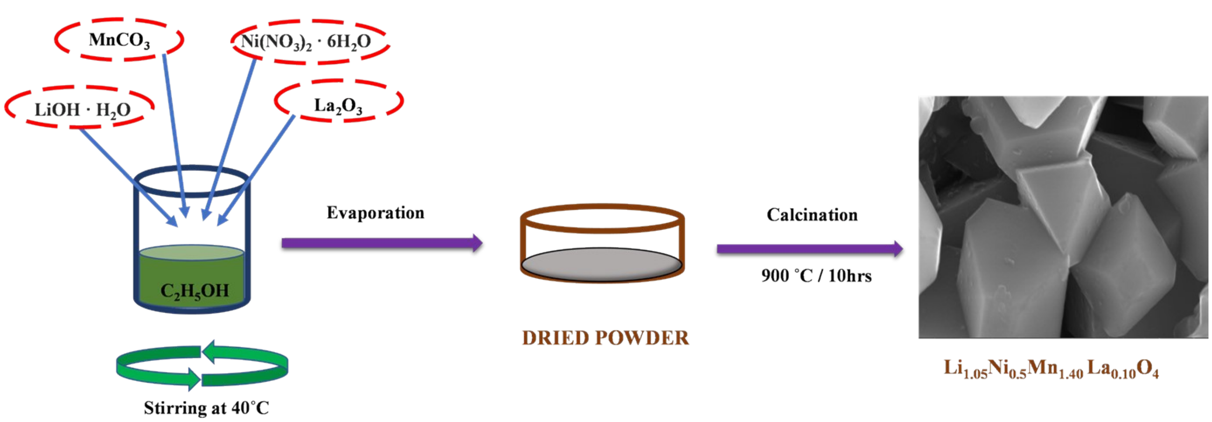
(1.05) Lithium hydroxide monohydrate, (0.5) nickel nitrate hexahydrate, (0.10) lanthanum oxide, and (1.40) manganese carbonate were dissolved in ethanol in the proportions 1.05:0.5:1.40 and 0.10 of Li, Ni, La, and Mn. To combine the reactants, the dispersion was mixed, and while stirring, the ethanol evaporated at 40°C. After volatilization, the mixture was calcined at 900 °C

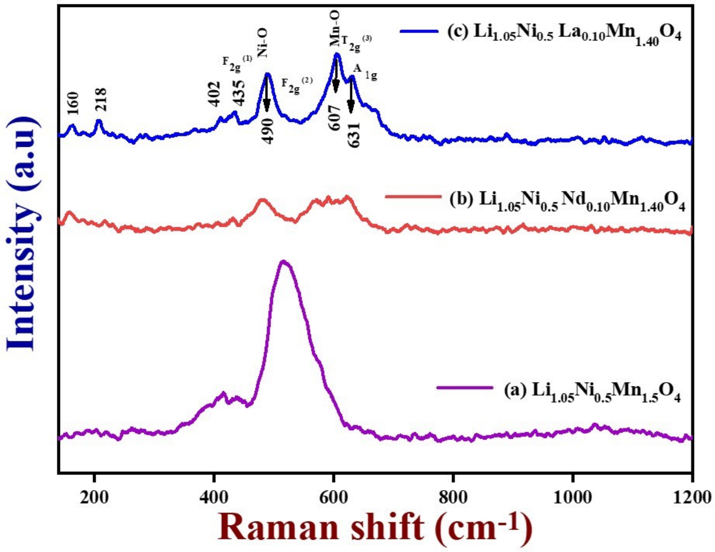


for 10 hours at a rate of 0.8 °C min^{-1} to yield $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$ is presented in Figure S2.

1.3 Preparation of $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$

Figure S3 Schematic represents the preparation of $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$





Stoichiometric quantities of (1.05) lithium hydroxide monohydrate, (0.5) nickel nitrate hexahydrate, (0.10) neodymium (III)oxide, and (1.40) manganese carbonate were dissolved in ethanol in the ratios 1.05:0.5:1.40 and 0.10 of Li, Ni, Nd, and Mn. To mix the reactants, the dispersion was stirred, and the ethanol evaporated at 40 °C while stirring the mixture. Following evaporation, the mixture was calcined at 900 °C for 10 hours at a rate of 0.8 °C min^{-1} to obtain $Li_{1.05}Ni_{0.5}$ $Nd_{0.10}Mn_{1.40}O_4$ is presented in Figure S3.

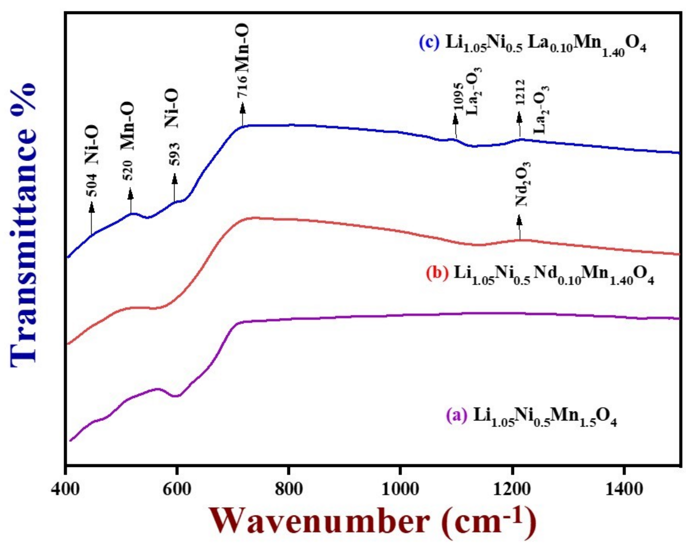


Figure S4 Raman spectra of (a) $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, (b) $Li_{1.05}Ni_{0.5}$ $Nd_{0.10}Mn_{1.40}O_4$ and (c) $Li_{1.05}Ni_{0.5}$ $La_{0.10}Mn_{1.40}O_4$

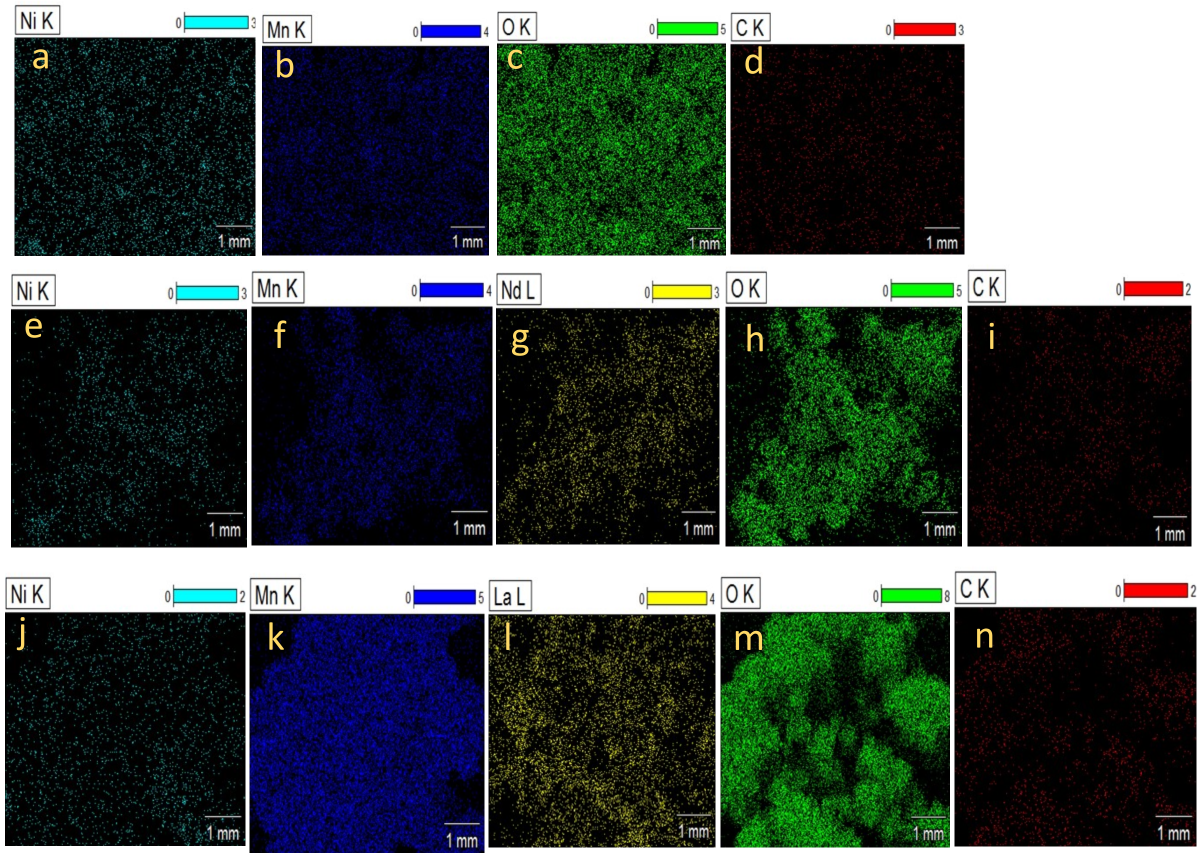
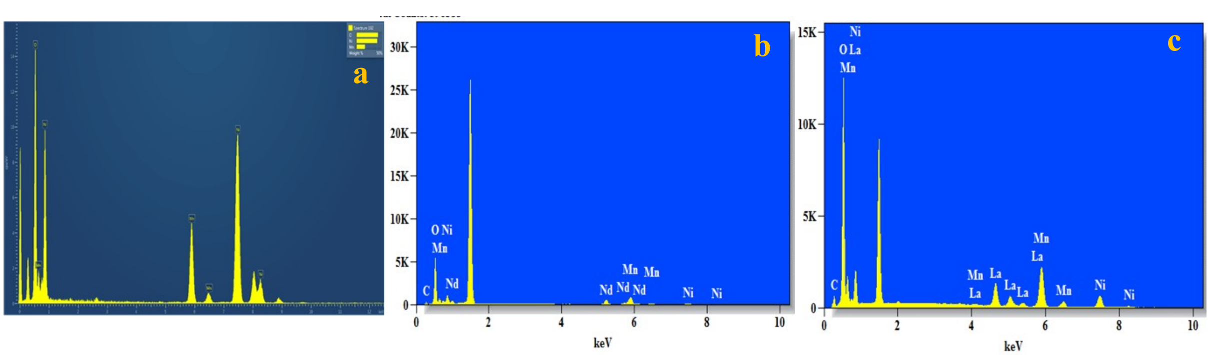


Figure S5 FT- IR spectra of (a) $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, (b) $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$ and (c) $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$.

Figure S6 Elemental mapping images of (a-d) $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, (e-i) $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$ and (j-n) $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$

Figure S7 EDAX images of (a) $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, (b) $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$ and (c) $Li_{1.05}Ni_{0.5}La_{0.10}Mn_{1.40}O_4$



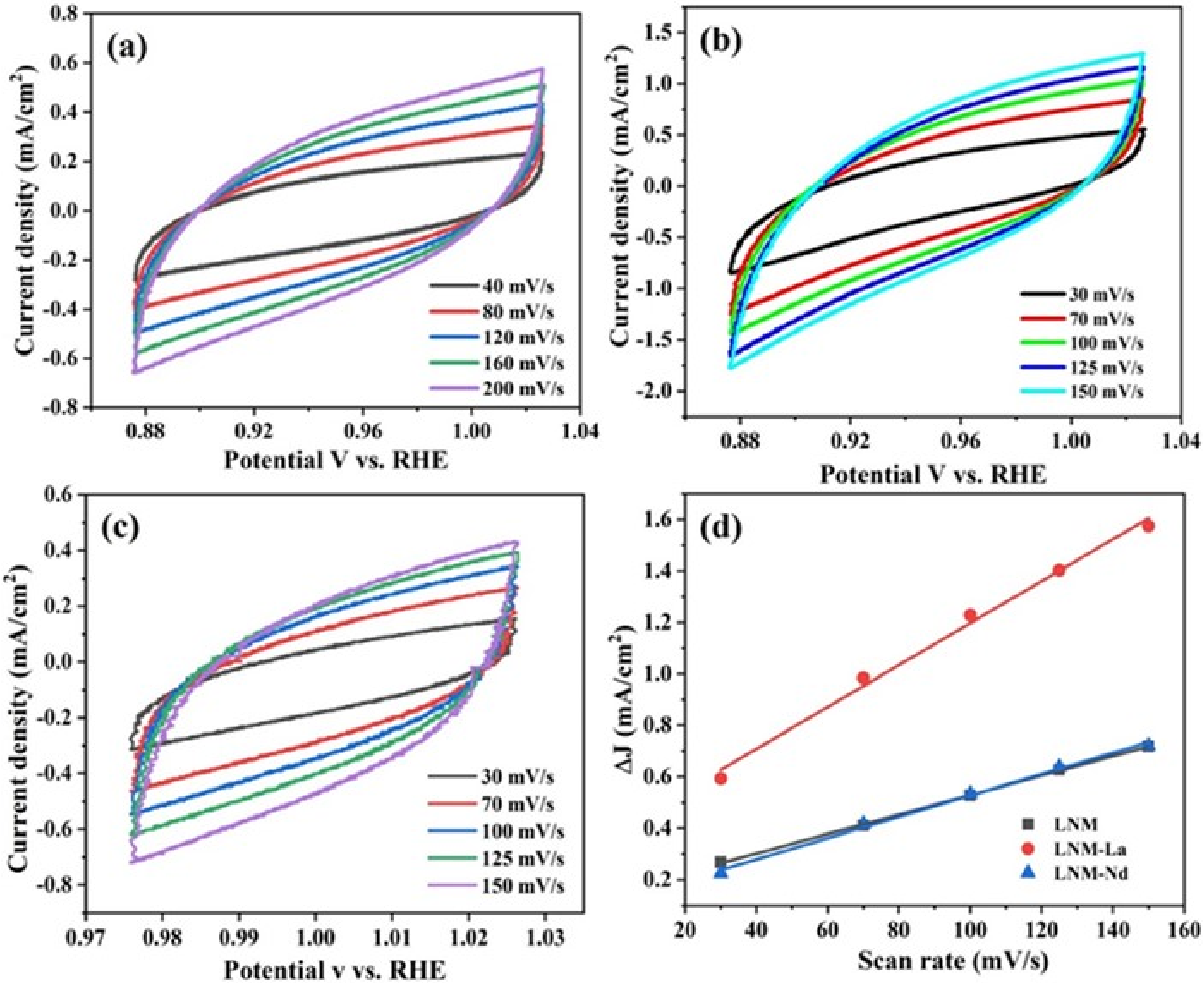


Figure S8 HER analysis: (a-c) Cyclic voltameteric analysis of at different scan rates of LNM, LNM-La, and LNM-Nd; (d) Plot of different scan rate vs. current density for LNM, LNM-La and LNM-Nd

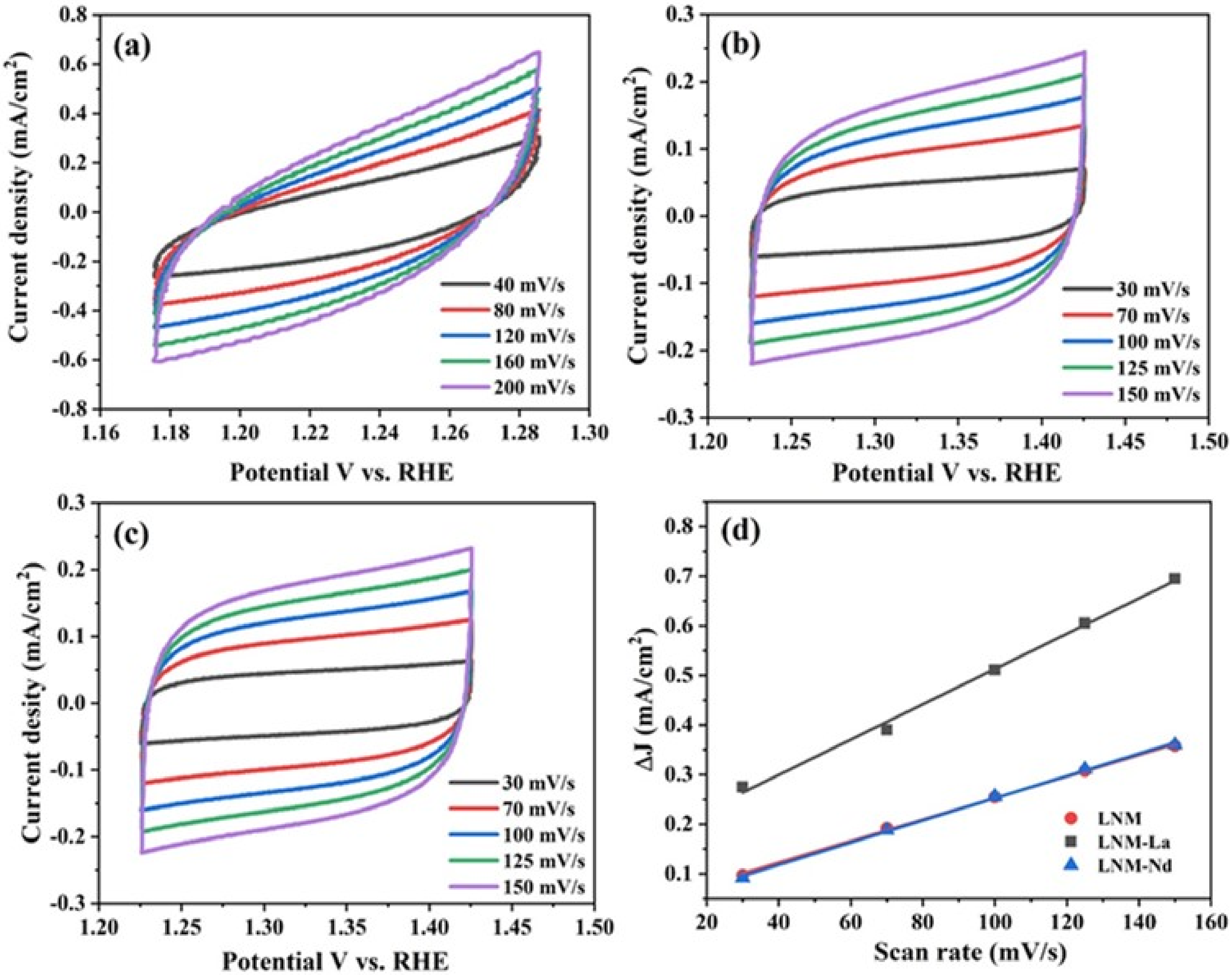
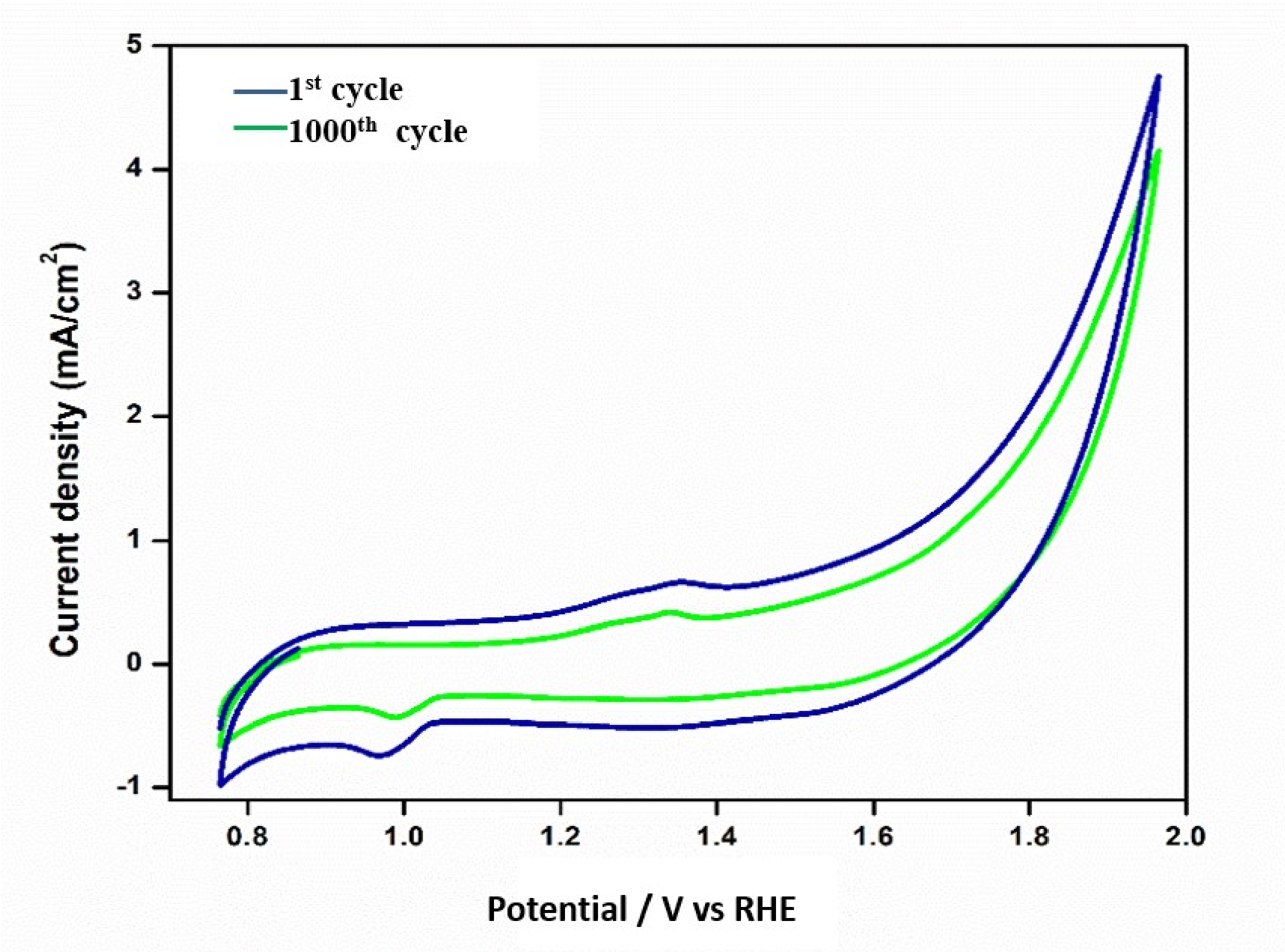
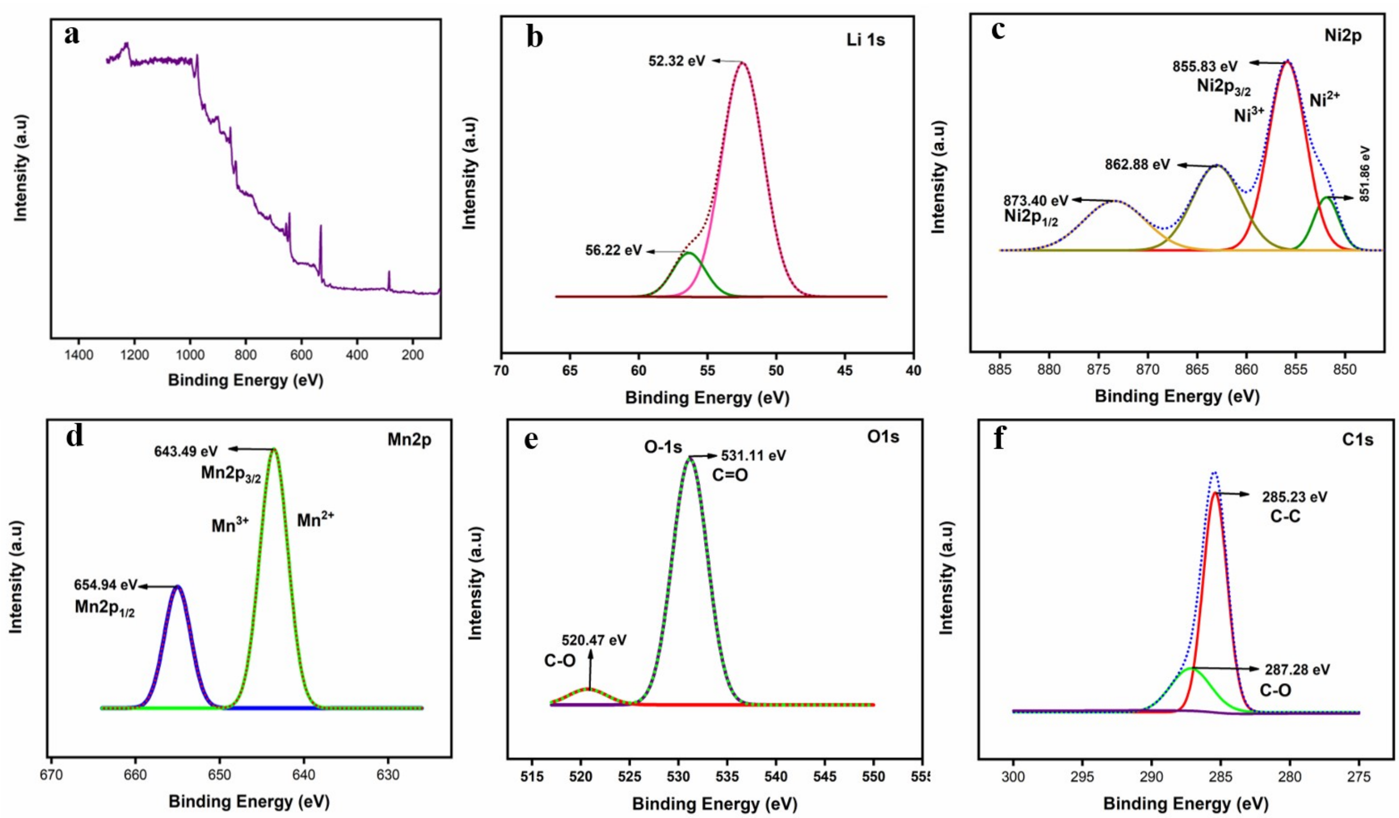

(a)
Current density (mA/cm^2)
Potential V vs. RHE
40 mV/s
80 mV/s
120 mV/s
160 mV/s
200 mV/s
(b)
Current density (mA/cm^2)
Potential V vs. RHE
30 mV/s
70 mV/s
100 mV/s
125 mV/s
150 mV/s
(c)
Current desity (mA/cm^2)
Potential V vs. RHE
30 mV/s
70 mV/s
100 mV/s
125 mV/s
150 mV/s
(d)
ΔJ (mA/cm^2)
Scan rate (mV/s)
LNM
LNM-La
LNM-Nd

Figure S9 OER analysis: (S9a-S9c) Cyclic voltameter analysis of LNM, LNM-La and LNM-Nd at different scan rates; (d) Plot of different scan rate vs. current density for LNM, LNM-La and



LNM-Nd

Figure S10 CV cycle stability test: Cyclic voltammograms measured at 1000 cycles at a scan rate of 50 mV/s were used to assess the stability of the $Li_{1.05}Ni_{0.5}$ $La_{0.10}Mn_{1.40}O_4$ catalyst.



a
Intensity (a.u)
Binding Energy (eV)
b
Li 1s
52.32 eV
56.22 eV
Intensity (a.u)
Binding Energy (eV)
c
Ni2p
855.83 eV
Ni2p3/2
Ni3+
Ni2+
862.88 eV
873.40 eV
Ni2p1/2
851.86 eV
Intensity (a.u)
Binding Energy (eV)
d
Mn2p
643.49 eV
Mn2p3/2
Mn3+
Mn2+
654.94 eV
Mn2p1/2
Intensity (a.u)
Binding Energy (eV)
e
O1s
O-1s
531.11 eV
C=O
520.47 eV
C-O
Intensity (a.u)
Binding Energy (eV)
f
C1s
285.23 eV
C-C
287.28 eV
C-O
Intensity (a.u)
Binding Energy (eV)

Figure S11 XPS spectra (a) XPS full survey spectra of $Li_{1.05}Ni_{0.5}Mn_{1.5}O_4$, (b) Li 1s, (c) Ni 2p, (d) Mn2p, (e) O1s, (f) C1s

Figure S12 XPS spectra (a) XPS full survey spectra of $Li_{1.05}Ni_{0.5}Nd_{0.10}Mn_{1.40}O_4$, (b) Li 1s, (c) Ni 2p, (d) Mn2p, (e) Nd 3d, (f) O1s, (g) C

Table S1 Comparison Table of the performance of LNM with recently reported catalysts.

S.No	**Catalyst**	**Overpotential (mv)**		**Tafel slope (mV dec^{-1})**		**Electrolyte**	**Reference**
		OER	**HER**	**OER**	**HER**		
1	NiMn-LDH	296	120	102	79	1M KOH	32
2	LSTN@NiMn-LDH	387	125	103	84	1M KOH	33
4	L						This work
5	L						This work
6	LNM-La	1.68	118	-0.41	73	1M KOH	This work