# First-row transition metal carbonates catalyze the electrochemical oxygen evolution reaction: Iron is master of them all

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## **Experimental Section:**

AR-grade chemicals were purchased from Alfa Aesar and used without any further purification process. All the solutions were prepared using Millipore water (final resistivity of > 10 M $\Omega$ ·cm). Prior to the electrochemical experiments, the Ni foam (0.5 ×1 cm<sup>2</sup>) was cleaned ultrasonically to remove oxides and other impurities from its surface with 10 % HCl, Acetone, deionized water, and ethanol for 30 min, respectively. The electrochemical synthesis and characterizations were performed in a three-electrode cell setup consisting of Ag/AgCl (3.0 M KCl solution) electrode as a reference and platinum as a counter electrode under N<sub>2</sub> inert atmosphere using a PalmSens4 Instrument. The electrodeposition of Mn<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> on the NF was done with the help of chronoamperometry at 1.1 V vs. Ag/AgCl in a solution containing 0.30 mM MnCl<sub>2</sub> and 0.10 M NaHCO<sub>3</sub> for 1.0 hour. Similarly, 0.50 mM of Co(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, NiSO<sub>4</sub> were used for respective deposition of  $Co_2(CO_3)_3$ ,  $Cu(CO_3)$ ,  $Ni_2(CO_3)_3$  on the NF electrode. 0.40 mM FeSO<sub>4</sub> was used for the deposition of  $Fe_2(CO_3)_3$  on the NF surface. With respect to the geometrical area, the current density values have been calculated. Upon successful deposition, the electrodes were rinsed thoroughly with deionized water and later subjected to drying under air before being utilized for their further analysis and electrochemical measurements.

#### **Electrode Characterizations**

The morphology of the electrodeposited metal carbonates on the NF electrode was determined by scanning electron microscopy using a TESCAN MAIA3 scanning electron microscope (SEM). The functional groups' evaluation in the metal carbonates on the NF were determined using Bruker Alpha 2 FT-IR instrument. Further, X-ray photoelectron spectroscopy (XPS) recorded the oxidation states of the elements in the metal carbonates deposited on the NF electrode, using an ESCALAB 250 ultrahigh vacuum ( $1 \times 10^{-9}$ ) apparatus with an Al K $\alpha$  X-ray source and a monochromator. All spectra were calibrated with respect to the C1s peak positioned at 284.8 eV. Gauss function helped in the fitting of the XPS spectra.

### **Electrochemical Measurements**

The oxygen evolution reactions were performed in a three-electrode cell setup to evaluate the catalytic behavior of metal carbonates deposited on the NF electrodes comprising 1.0 M KOH and subjected to deaeration by purging N<sub>2</sub> for 30 min. Additionally, different techniques, namely, cyclic voltammetry, linear sweep voltammetry, chronoamperometry, and impedance techniques, were used to study the oxygen evolution reaction. The obtained potentials vs. Ag/AgCl (in 3.0 M KCl) were converted to the Reversible Hydrogen Electrode (RHE) scale. Where  $E_{\text{RHE}}$  is the converted potential vs. RHE,  $E_{\text{Ag/AgCl}}$  (in 3.0 M KCl) is the measured potential against Ag/AgCl reference electrode,  $E^{\circ}_{\text{Ag/AgCl}}$  (in 3.0 M KCl) is the standard potential of Ag/AgCl (in 3.0 M KCl) at 25 °C. Electrochemical impedance spectra were measured with an applied amplitude of 0.0010 V under oxygen evolution conditions in the frequency range of 100 kHz to 0.1 Hz. Chronoamperometric experiments were carried out to elucidate the long-term stability of the oxygen evolution activity.



Fig. S1. ATR spectrum of  $Co_2(CO_3)_3/NF(a)$ ,  $Ni_2(CO_3)_3/NF(b)$ ,  $Cu(CO_3)/NF(c)$ .

The determination of oxidation states of the elements present in  $Co_2(CO_3)_3/NF$  and  $Mn_2(CO_3)_3/NF$  catalysts, along with the chemical composition, was determined by the XPS analysis. Additionally, all the metal carbonates showed the presence of metals, C, and O in their complex structure, which was as expected from the metal carbonates. The XPS spectra of  $Co_2(CO_3)_3/NF$  and  $Mn_2(CO_3)_3/NF$  showed the presence of Co and Mn in 2+, 3+ and 3+, 4+ oxidation states, respectively. The peaks of the Co 2p spectrum showed the presence of two peaks at 780.6 and 795.3 eV relative to the presence of Co  $2p_{3/2}$  and Co  $2p_{1/2}$  (Fig. S2b).<sup>1</sup> In addition, the Mn peaks were correlated to the presence of Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  at 642.1 eV and 653.6 eV (Fig. S2a).<sup>2</sup> Correspondingly, the O 1s spectrum was split into three components with peaks appearing at 531.9 eV, 531.2 eV, and 529.2 eV related to  $CO_3^{2-}$  lattice O, O attached to  $CO_3^{2-}$  groups and O of M-O bond, respectively (Fig. S2c). Along with the O 1s spectrum, the C 1s spectrum was also studied, and the data obtained displayed peaks at 285 eV and 289 eV relative to the bonding of C and O in the  $CO_3^{2-}$  for C-O and C=O (Fig. S2d).<sup>2</sup> The Ni 2p spectrum was also determined, and the peaks correspond to Ni 2p3/2 and Ni 2p1/2 at 856 and

873 eV, indicating the presence of Ni<sup>2+</sup> after the deposition of metal carbonates on the NF surface (Fig. S2e).<sup>2</sup> Moreover, the survey spectra for the metal carbonates on the NF electrodes were determined; the results are presented in Fig. S2 (f-j). Apart from the evaluation of oxidation states, the elemental composition of metal carbonates was also determined by the XPS. It was found that  $Mn_2(CO_3)_3/NF$  showed the atomic percentage of Mn- 5.86 %, C- 35.3 %, O- 56.5 % and Ni- 2.36 %. The Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>/NF revealed the atomic percentage of Fe- 2.92 %, C-29.21 %, O- 60.48 %, and Ni- 7.39, respectively. Followed by  $Co_2(CO_3)_3/NF$ , which had the elements Co, C, O, and Ni with the atomic percentage evaluate to 7.8 %, 21.6 %, 61.3 %, and 9.3 %, respectively followed by  $Ni_2(CO_3)_3/NF$  had the elemental atomic percentage composition as follows, Ni- 9.20 %, C- 30.42 % and O- 60.38%, respectively. Cu(CO<sub>3</sub>)/NF had an atomic composition of Cu, C, O, and Ni evaluated to 10.7 %, 23.2 %, 65.7 %, and 0.4 %, respectively.





Fig. S2. XPS analysis spectra of (a) Mn2p (b) Co2p (c) O1s (d) C1s (e) Ni2p, XPS survey spectra of (f)  $Mn_2(CO_3)_3/NF$ , (g)  $Fe_2(CO_3)_3/NF$ , (h)  $Co_2(CO_3)_3/NF$ , (i)  $Ni_2(CO_3)_3/NF$ , (j)  $Cu(CO_3)/NF$ .

### Linear Sweep Voltammetry study

In order to compare the effect of substrate and metal carbonates for OER,  $Fe_2(CO_3)_3$  and  $Ni_2(CO_3)_3$  were deposited by chronoamperometry on carbon cloth (CC) and stainless-steel (SS) surface at 1.1 V vs. Ag. These experiments were performed to determine whether, NF played a role in enhancing the activity of metal carbonates during OER. Fig S3 (a & b) shows the LSV curves for CC,  $Fe_2(CO_3)_3$ ,  $Ni_2(CO_3)_3$ , deposited on CC and SS,  $Fe_2(CO_3)_3$ ,  $Ni_2(CO_3)_3$  deposited on SS, respectively. The electrochemically deposited  $Fe_2(CO_3)_3/CC$  achieved an overpotential of 410 mV (1.64 V vs. RHE) with 10 mA·cm<sup>-2</sup> current density in 1.0 M KOH medium, the  $Ni_2(CO_3)_3/CC$  and CC achieved the overpotential of 440 mV (1.67 V vs. RHE) and 550 mV (1.78 V vs. RHE), respectively. Additionally, the electrochemical deposited  $Fe_2(CO_3)_3/SS$  achieved the overpotential of 340 mV (1.57 V vs. RHE) with 10 mA·cm<sup>-2</sup> current density in 1.0 M KOH mediust in 1.0 M KOH medium compared to  $Ni_2(CO_3)_3/SS$  with overpotential of 360 mV (1.59 V vs. RHE) and SS with overpotential of 440 mV.





Fig. S3. Linear sweep voltammogram graphs at a scan rate of 20 mV·s<sup>-1</sup> in 1.0 M KOH

# Cyclic Voltammetry study

CV studies were performed to determine the redox behavior of the metal carbonates towards the oxygen evolution reaction. It was observed that prior to the appearance of a sharp peak representing the catalytic oxygen evolution, the metal carbonates showed the presence of multiple oxidation peaks. Fig. 3b displays the CV curves of the redox activity of  $Mn_2(CO_3)_3/NF$ ,  $Fe_2(CO_3)_3/NF$ ,  $Co_2(CO_3)_3/NF$ ,  $Ni_2(CO_3)_3/NF$ ,  $Cu(CO_3)/NF$ ,  $CO_3/NF$  and NF at an anodic scan rate of 1.38 V to 1.55 V vs RHE. Bare NF shows redox peaks with a low current density. The appearance of redox peaks with the oxidation peak at 1.41 V vs. RHE and reduction peak 1.32 V vs. RHE corresponded to  $Ni^{III/II}$ .<sup>3</sup> Following this, the  $Ni_2(CO_3)_3/NF$  electrode displayed two broad redox peaks in the potential range of 1.25 V – 1.56 V vs. RHE, corresponding to  $Ni^{IV/III}$  and  $Ni^{III/II}$ , respectively.<sup>4</sup> The Fe<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>/NF electrode exhibited two redox peaks at a potential range of 1.1 V – 1.45 V vs. RHE. These peaks were related to the presence of Fe<sup>IV/III</sup> and  $Ni^{III/II}$ . The peak for Fe<sup>IV/III</sup> overlapped with the peak of  $Ni^{III/II}$ . Similarly,

the Cu(CO<sub>3</sub>)/NF electrode displayed redox peaks, but these peaks correspond to the redox behavior of the Ni surface. There is a slight indication of state change at 1.58 V vs. RHE for Cu<sup>II</sup> to Cu<sup>III</sup>, which suggests that Cu<sup>III</sup> is the active water oxidizing agent.<sup>5</sup> Similarly, there was no change in the redox behavior of Co<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>/NF and only peaks corresponding to the redox nature of surface Ni were observed. The results relating to Mn<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>/NF and CO<sub>3</sub>/NF have been previously reported in a recent publication.<sup>2</sup>



Fig. S4. Nyquist plot of  $Mn_2(CO_3)_3/NF$ ,  $Fe_2(CO_3)_3/NF$ ,  $Co_2(CO_3)_3/NF$ ,  $Ni_2(CO_3)_3/NF$ ,  $Cu(CO_3)/NF$ ,  $CO_3/NF$  and NF.

Electrocatalyst	R <sub>s</sub>	<b>R</b> <sub>ct</sub>	$\mathbf{Q}_{dl}$
Mn <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	2.226	3.014	0.750
Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	1.700	3.23	0.700
Co <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	1.775	7.982	0.815
Ni <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	1.925	3.900	0.700
Cu(CO <sub>3</sub> )/NF	1.95	6.520	0.800
CO <sub>3</sub> /NF	2.714	8.650	0.797
NF	2.831	13.19	0.730

**Table S1**: The fitting results of the impedance electrochemical element parameters of  $Mn_2(CO_3)_3/NF$ ,  $Fe_2(CO_3)_3/NF$ ,  $Co_2(CO_3)_3/NF$ ,  $Ni_2(CO_3)_3/NF$ ,  $Cu(CO_3)/NF$ ,  $CO_3/NF$  and NF

**Table S2**: The oxygen evolution of  $Mn_2(CO_3)_3/NF$ ,  $Fe_2(CO_3)_3/NF$ ,  $Co_2(CO_3)_3/NF$ ,  $Ni_2(CO_3)_3/NF$ ,  $Cu(CO_3)/NF$ ,  $CO_3/NF$  and NF overpotentials, Tafel slope and Impedance parameters.

Electrocatalyst	E vs RHE / V	Tafel slope	R <sub>s</sub>	<b>R</b> <sub>st</sub>
Mn <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	360 mV	106 mV·dec <sup>-1</sup>	2.226	3.014
Fe <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	310 mV	86 mV·dec <sup>-1</sup>	1.700	3.23
Co <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	390 mV	96 mV·dec <sup>-1</sup>	1.775	7.982
Ni <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> /NF	350 mV	110 mV·dec <sup>-1</sup>	1.925	3.900
Cu(CO <sub>3</sub> )/NF	400 mV	112 mV·dec <sup>-1</sup>	1.95	6.520
CO3/NF	460 mV	112 mV·dec <sup>-1</sup>	2.714	8.650
NF	520 mV	122 mV·dec <sup>-1</sup>	2.831	13.19

## **Electrochemical impedance spectroscopy (EIS):**

After the durability test, the EIS for the  $Fe_2(CO_3)_3/NF$  was performed to check the electron transfer kinetics for the OER. Fig. S5 shows the EIS-Nyquist plot of the  $Fe_2(CO_3)_3/NF$ . The experiments relating to EIS were carried out at constant potential for OER (The potential used was similar to the potential used for the durability test). The  $Fe_2(CO_3)_3/NF$  exhibited smaller charge transfer resistance ( $R_{ct}$ ). From Fig S4 and Fig S5, it can be observed that there is no much change in the charge transfer resistance.



Fig. S5. Nyquist plot of  $Fe_2(CO_3)_3/NF$ .

#### **References:**

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