High-performance non-spinel cobalt-manganese mixed oxide-based bifunctional electrocatalysts for rechargeable zinc-air batteries

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Abstract

Development of efficient bifunctional electrocatalysts from earth abundant elements, simultaneously active for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), remains to be a grand challenge for electrocatalysis. Herein we firstly synthesized a new type of bifunctional catalyst (NCNT/Co_xMn_{1-x}O) consisting of non-spinel cobalt-manganese oxide supported on N-doped carbon nanotubes through a simple non-surfactant assistant hydrothermal method. This hybrid catalyst exhibits much higher OER activity than that of IrO₂, and comparable ORR activity to Pt/C with identical onset potential (0.96 V) in alkaline media. Furthermore, the NCNT/Co_xMn_{1-x}O catalyst was studied as a cathode in both primary and rechargeable zinc-air batteries demonstrating similar performance to commercial Pt/C or (Pt/C+IrO₂), respectively. Primary zinc-air battery tests show a gravimetric energy density of 695 Wh kg_{zn}⁻¹, and the rechargeable battery exhibits a high round-trip efficiency evidenced by a low discharge-charge voltage gap (0.57 V) at a current density of 7 mA cm⁻².

Keywords: Non-spinel cobalt-manganese oxide; Carbon nanotubes; Oxygen reduction and evolution reactions; Primary and rechargeable zinc air batteries

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Introduction

Rechargeable zinc-air batteries have recently attracted substantial attention as a potential alternative to lithium-ion batteries. A highly active bifunctional air cathode catalyst for the ORR and the OER is crucial for improving energy storage and conversion efficiency and cyclic durability [1-5]. Although Pt-, Ir-, and Ru-based materials are considered as the most active catalysts for either ORR or OER [6-10], such noble-metal-based materials are scarcity and high cost, which greatly hamper their widespread applications in these clean energy technologies. In addition, the single precious metal cannot serve as a bifunctional catalyst yet simultaneously to provide sufficient activity for both

the ORR and the OER [11]. Recently, some bifunctional catalysts consisting of non-noble-metal oxides show promise to be active for these oxygen reactions [12-15]. Previous studies demonstrated that pure metal oxides showed low catalytic activities due to self-passivity and low electrical conductivity, thereby decreasing active sites and hindering charge transports [16, 17]. The preparation of metal oxides/conductive nanocarbon hybrids is an efficient approach to enhancing catalytic activity [18, 19], such as Co₃O₄/graphene [20], Co/CoO/graphene [21], CoO/NCNT [22], and Mn_xO_y/NC [23]. The nanocarbons including graphene and carbon nanotubes are highly electrical conductive with large surface area, capable of improving utilization of dispersed oxide nanoparticles and providing facile electron transport channel [24, 25]. In addition, mixed metal oxides have demonstrated significant

advantages over the single metal oxides in terms of catalytic activity enhancement, such as $\text{CoFe}_2\text{O}_{3.6}$ for the OER and $\text{M}_x\text{Fe}_{3-x}\text{O}_4$ ($\text{M} = \text{Fe}, \text{Cu}, \text{Co}, \text{Mn}$) for the ORR [11, 26]. Among currently studied mixed metal oxide catalysts, spinel Mn-Co oxides were found to be highly active for both ORR and OER. Chen *et al.* developed a rapid synthesis method to prepare spinel $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ at room temperature [27]. $\text{MnCo}_2\text{O}_4/\text{N-rGO}$ or NCNTs hybrids were also prepared as bifunctional catalysts by Dai and Muhler's groups [28, 29]. Also, spinel MnCo_2O_4 and CoMn_2O_4 have been studied as air cathodes in rechargeable zinc-air batteries by Jung *et al* [30]. Although these spinel cobalt-manganese oxides exhibited good catalytic performance as the bifunctional catalysts, the complicated spinel structures make the study more complicated. Because spinel catalysts usually have multiple oxidation states for manganese and cobalt (Co^{2+} , Co^{3+} , Mn^{2+} , Mn^{3+} , Mn^{4+}), as well as different crystalline structures. Therefore, non-spinel $\text{Co}_x\text{Mn}_{1-x}\text{O}$ is much simple relative to spinel $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$ because of its single oxidation state (Co^{2+} and Mn^{2+}). To our best acknowledge, non-spinel $\text{Co}_x\text{Mn}_{1-x}\text{O}$ compounds were not studied sufficiently relative to conventional spinel MnCo_2O_4 and CoMn_2O_4 . Although mixed $\text{Mn}_x\text{Co}_{1-x}\text{O}$ oxides can be synthesized via a decomposition of metal carboxylate (manganese and cobalt acetic salts) with a surfactant assistance such as oleic acid, tri-n-octylamine, or 1-octadecene [31, 32], the synthesis procedure requires a complicated post-treatment to remove these surfactants. A simple hydrothermal synthetic route without surfactant assistance for non-spinel $\text{Co}_x\text{Mn}_{1-x}\text{O}$ has not been reported yet. There is also no any report about preparation of non-spinel $\text{Co}_x\text{Mn}_{1-x}\text{O}$ (Mn^{2+} , Co^{2+}) as bifunctional electrocatalysts for the

oxygen reactions.

In this report, for the first time, we synthesized a non-spinel cobalt-manganese oxide supported on highly stable nitrogen-doped carbon nanotubes (NCNT) as a highly efficient bifunctional electrocatalyst. The synthesis method includes a simple hydrothermal process in the absence of surfactant, followed by an annealing treatment under Ar and NH_3 as illuminated in **Figure 1**. This nanocomposite catalyst exhibits much higher OER activity than that of IrO_2 , and comparable ORR activity to Pt/C in alkaline media. In particular, when air is used as oxygen source, the NCNT/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$ cathode in primary zinc-air battery performs better relative to Pt/C cathode, showing specific capacities of $581 \text{ mAh g}_{\text{zn}}^{-1}$ at a current density of 7 mA cm^{-2} , corresponding to gravimetric energy density of $695 \text{ Wh kg}_{\text{zn}}^{-1}$. Rechargeable zinc-air battery studies also exhibited a high round-trip efficiency determined by a low discharge-charge voltage gap (0.57 V) with stable voltages up to 75 charging-discharging cycles at a current density of 7 mA cm^{-2} , which is very similar to the mixed Pt/C+ IrO_2 cathode.

Experimental Section

Synthesis of NCNT/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$

The mildly oxidized CNT (*moCNT*) used in this work was prepared using a commercial L-purified Multiwalled Nanotube (SES Research: outer diameter 10-30 nm) following a reported procedure [33]. In a typical procedure, the *moCNTs* (50 mg) was dispersed in 10 mL deionized water in a glass vial. Then $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 145 mg), urea (5

Figure 1 Schematic of the synthesis for NCNT/ $\text{Co}_x\text{Mn}_{1-x}\text{O}$.

mmol, 300 mg), NH_4F (2.5 mmol, 92.5 mg), and $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 122 mg) were dissolved in 10 mL deionized water in another vial. After being sonicated for 15 min, both solutions were transferred into a 50 mL Teflon-lined stainless steel auto-clave reactor, which was subsequently heated at 150°C for 12 hours. During the synthesis, urea releases ammonia and provides carbonate ions through hydrolysis. The F^- from NH_4F is good chelating ligand that can prevent the formation of $\text{Co}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$ [34]. The resulting dark solution was filtered, sonicated, and centrifuged at 4000 rpm for 5 min. The collected dark solid was dispersed in deionized water for lyophilization. The lyophilized precursor $\text{rCNT}/\text{Co}_x\text{Mn}_{1-x}\text{CO}_3$ was annealed in a tube furnace at 500°C for 2 hours under an Ar atmosphere with a gas flowing rate of 300 mL/min, following a natural cooling procedure for overnight at room temperature under Ar. An additional annealing procedure at 500°C under NH_3 atmosphere with a gas flowing rate of 500 mL/min for 1 hours was carried out to dope nitrogen into CNT. After cooling to room temperature, the resulting sample was labeled as $\text{NCNT}/\text{Co}_x\text{Mn}_{1-x}\text{O}$. The same procedure was used to prepare single Co- and Mn-based catalysts.

Physical Characterization of Catalysts

X-ray diffraction (XRD, D/Max2000, Rigaku) was carried out by using Cu-K α radiation. X-ray photoelectron spectroscopy (XPS) was obtained using an Escalab instrument (Escalab 250 xi, Thermo Scientific, England) with a base pressure of 5×10^{-9} Torr using monochromatic Al K α radiation (1486.6 eV). The scanning electron microscope (SEM) (S-4800, Hitachi) was operated at 10 kV, and high-resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F) was conducted at 200 kV. Co K-edge X-ray absorption spectra, X-ray absorption near edge structure (XANES) spectra, and extended X-ray absorption fine structure (EXAFS) spectra were collected on the BL10C beam line at the Pohang Light Source (PLS-II) in Korea with top-up mode operation under a ring current of 200 mA at 3.0 GeV.

Electrochemical measurements

OER and ORR activities of catalysts were measured using a standard three-electrode electrochemical cell filled with 1.0 M KOH electrolytes containing an HgO/Hg reference electrode, a Pt wire counter electrode, and a rotation glassy carbon disk (4 mm diameter) working electrode. The Hg/HgO reference electrode was calibrated with respect to reversible hydrogen electrode (RHE) in high-purity hydrogen saturated electrolyte solution using a Pt electrode.

The reported potentials in this work were not *iR*-corrected for both OER and ORR measurements because of negligible ohm resistance in 1.0 M KOH solution. High-purity O_2 gas was bubbled into the solution approximately 20 min before the electrochemical measurements and throughout the whole testing process. The catalysts (3.0 mg) and 60 μL of a 5 wt% Nafion solution were dispersed in 0.35 mL of ethanol and 0.15 mL of deionized water; the resulting mixture was sonicated to form a homogeneous ink. A loading of 0.21 mg cm^{-2} was applied on the surface of the glassy carbon disk electrode by the drop-addition of 5 μL of catalyst ink. The loading of Pt/C (20% Pt on Vulcan XC-72, Premetek Co) was 0.32 mg cm^{-2} . The commercial IrO_2 ($\sim 5 \mu\text{m}$, Sigma-Aldrich 99.9%) was used with a loading of 0.21 mg cm^{-2} .

Primary and rechargeable zinc-air battery tests

The construction of zinc-air batteries can be found in supporting information (**Figure S8**). The air cathodes were prepared by coating a mixture of the activated charcoal and PTFE (weight ratio = 7:3) on the nickel foam. The thickness of each air cathode was fixed to be $\sim 700 \mu\text{m}$ by an electrode pressing machine. The 250 μL ink similar to electrochemical measurements was carefully dropped onto the above air cathode and kept it in a vacuum container for 30 min, followed by a mildly pressing procedure. The $\text{NCNT}/\text{Co}_x\text{Mn}_{1-x}\text{O}$ - or $(\text{Pt}/\text{C} + \text{IrO}_2)$ -based air cathodes with the loading of 0.53 mg cm^{-2} were used to assemble primary and rechargeable zinc-air. Zinc plate was used as the anode that was separated by a nylon polymer membrane with the cathode and 6 M KOH electrolyte was filled between the cathode and anode for primary zinc-air batteries. Additional 0.2 M zinc oxides was added into the KOH solution as electrolyte for rechargeable zinc-air batteries. Nickel mesh was used as the current collector.

Results and Discussion

Structures of $\text{NCNT}/\text{Co}_x\text{Mn}_{1-x}\text{O}$

The scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) clearly show the formation of nanoparticles on the CNTs (**Figures 2a-2c**). The lattice fringe with *d*-spacing values of 2.08 Å and 2.63 Å are very similar to the (200) crystal plane of CoO and (111) crystal planes of cubic MnO, respectively. The local elemental mapping of Co, Mn, O, and C atoms were carried out using HAADF-STEM-EDS (**Figure 2d**). The elemental N was not

Figure 2 (a) SEM image of NCNT/Co_xMn_{1-x}O. (b, c) TEM images of NCNT/Co_xMn_{1-x}O. (d) HAADF-STEM-EDS images of NCNT/Co_xMn_{1-x}O and elemental maps of Co, Mn, O and C. (e) XRD patterns of NCNT/Co_xMn_{1-x}O.

detected due to its low content that will be discussed in XPS analysis. The atomic ratio of Co and Mn was determined to be 51/49 by inductively coupled plasma optical emission spectroscopy (ICP-OES). The X-ray diffraction (XRD) patterns of rCNT/Co_xMn_{1-x}CO₃ and NCNT/Co_xMn_{1-x}O i.e. before and after the NH₃ annealing treatment, are shown in **Figure 2e**. The XRD patterns of precursor are similar to those of MnCO₃, CoCO₃, and Co_xMn_{1-x}CO₃ [35-37]. The broad peak at 26.0° is attributed to CNT. XRD patterns of single metallic Co- and Mn-based samples (NCNT/CoO and NCNT/MnO) are also determined for a comparison with that of NCNT/Co_xMn_{1-x}O (**Figure S1**). The diffraction peaks of NCNT/CoO locate at 36.6°, 42.6°, 61.6°, 74.4°, and 77.8° corresponding to the (111), (200), (220), (311), and (222) crystal planes of CoO [38]. The

peaks of NCNT/MnO locating at 35.0°, 41.1°, 58.6°, 70.2° and 74.9° correspond to the (111), (200), (220), (311), and (222) crystal planes of MnO [35] have recently attracted. Thus, the diffraction peaks of NCNT/Co_xMn_{1-x}O locate at 35.8°, 41.7°, 60.1°, 72.4° and 75.9°, which are similar to those of CoO and MnO, suggesting a mixed oxide. It should be noted that the XRD patterns of NCNT/Co_xMn_{1-x}O are obviously different to reported spinel Co_xMn_{3-x}O₄ oxides [28-30], indicating an intrinsically different crystalline structure.

The XPS was employed to study oxidation states of the elements on surface layers of rCNT/Co_xMn_{1-x}CO₃ and NCNT/Co_xMn_{1-x}O. The full XPS surveys are recorded in **Figure S2a**. Elements including C, O, N, Mn and Co were detected. The optimized NCNT/Co_{0.51}Mn_{0.49}O with highest activity was

Figure 3 (a, b) The XANES and EXAFS spectra of NCNT/Co_xMn_{1-x}O and rCNT/Co_xMn_{1-x}CO₃ for Co-K-edge. (c, d) The XANES and EXAFS spectra of NCNT/Co_xMn_{1-x}O and rCNT/Co_xMn_{1-x}CO₃ for Mn-K-edge.

obtained by controlling the ratio of Co and Mn salts in the starting materials. Notable, both of Co2p and Mn2p spectra of NCNT/Co_xMn_{1-x}O are found shifting to lower energy compared to those of rCNT/Co_xMn_{1-x}CO₃ (**Figures S2b and S2c**) because of the formation of Co-O and Mn-O bonds. The high resolution XPS of O1s and N1s were shown in **Figures S2d-2g**. The appearance of the peak at 529.9 eV confirmed the formation of Mn-O or Co-O in the NCNT/Co_xMn_{1-x}O (**Figure S2e**), which is distinguished from that of the rCNT/Co_xMn_{1-x}CO₃ precursor (**Figure S2d**). After the annealing treatment under NH₃ atmosphere, the resulting NCNT/Co_xMn_{1-x}O showed an increasing ratio of the pyridinic-N (398.3 eV)/pyrrolic-N (399.5 eV) relative to rCNT/Co_xMn_{1-x}CO₃ (**Figure S2f and S2g**). For Co2p spectrum of NCNT/Co_xMn_{1-x}O, the peaks centered at 780.6 and 796.5 eV correspond to spin-orbit peaks of Co²⁺ (**Figure S2b**). In addition, there are two satellites found at 786.8 and 802.5 eV. The binding energies of these satellite peaks are ~ 6 eV higher than those of the major peaks. Since Co³⁺ species do

not give such strong shake-up peaks [39], this unambiguously confirms the presence of Co²⁺ species, which is consistent to the Co²⁺ in CoO-rGO and Co_xNi_{1-x}O [40, 41]. Meanwhile, Mn2p spectra of NCNT/Co_xMn_{1-x}O centered at 641.4 and 653.3 eV that are ascribed to Mn (II) 2p_{3/2} and 2p_{1/2}, respectively (**Figure S2c**), which shift to lower energy compared to Mn2p of rCNT/Co_xMn_{1-x}CO₃ due to the formation of Mn-O bond. They are similar to those of MnO@N-C [35]. Furthermore, the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were used to determine the local composition and bonding characteristics of these transition metals in the mixed oxide. At first, for XANES, the peak at 7726 eV for Co K-edge of NCNT/Co_xMn_{1-x}O is typically assigned to the transition of Co²⁺ from Co 1s to Co 4p mixed state with O2p (**Figure 3a**) that shows a slight shifting to high energy band relative to the rCNT/Co_xMn_{1-x}CO₃, which is caused by an increased amount of O in the Co lattice for NCNT/Co_xMn_{1-x}O compared to rCNT/Co_xMn_{1-x}CO₃.

Thus, the Co valence bands are attracted by the O ligands locating in Co lattice. As for Mn K-edge of NCNT/Co_xMn_{1-x}O and rCNT/Co_xMn_{1-x}CO₃, the pre-edge peak at 6541 eV is assigned to the quadruple transition from the 1s core level to unoccupied Mn 3d orbitals (**Figure 3c**). The main edge peak at 6556 eV for NCNT/Co_xMn_{1-x}O is attributed to purely electric dipole allowed transitions from the 1s core level to the 4p that is positively shifted by ~ 4 eV relative to rCNT/Co_xMn_{1-x}CO₃ (**Figure 3c**) that is also caused by the attraction of O in the Mn lattice. It should be noted that both Co and Mn K-edge are similar to those of CoO and MnO [40, 42-44].

In the case of EXAFS, the peaks of Co K-edge for NCNT/Co_xMn_{1-x}O at 1.70 and 2.67 Å correspond to Co-O and Co-Co bonding, respectively (**Figure 3b**) [45]. The main peak for NCNT/Co_xMn_{1-x}O at 2.73 Å corresponds to Mn-Mn interaction, and the peak at 1.75 Å to Mn-O interaction. However, the characteristics of peaks for NCNT/Co_xMn_{1-x}O between 4.0 and 10 Å are quite different from those of MnO (**Figure 3d**) [44]. Furthermore, single NCNT/CoO and NCNT/MnO samples were also characterized by the XANES and EXAFS (**Figures S3a-S3d**). Generally, the Co K-edge in NCNT/Co_xMn_{1-x}O and NCNT/CoO are different. In particular, it can be splitted into two peaks at the range from 1.0 to 2.0 Å (1.29 and 1.70 Å) in NCNT/Co_xMn_{1-x}O as shown in **Figure S3b**, corresponding to Co-O bonding. However, for NCNT/CoO, only single peak at 1.69 Å is shown. There is no obvious fine structure of peaks and valleys observed at the range of 4.0 to 8.0 Å for NCNT/Co_xMn_{1-x}O, instead of a broad peak, which is also different from NCNT/CoO, indicating a distinct local neighbor environment of Co atoms influenced by Mn. Likewise, the Mn K-edge of NCNT/Co_xMn_{1-x}O is also different from that of NCNT/MnO, characterized by a peak shifting toward large interatomic distance (**Figure S3d**). Therefore, these results indicate a strong interaction between Co and Mn in the mixed oxide.

Electrochemical activity of NCNT/Co_xMn_{1-x}O

The electrochemical activities of NCNT/Co_xMn_{1-x}O, NCNT/CoO, NCNT/MnO, NCNT, and commercial IrO₂ for the OER were evaluated in 1.0 M KOH solution by using linear sweep voltammetry at a scan rate of 10 mV s⁻¹ (**Figure 4a**). Among these studied samples, the NCNT/Co_xMn_{1-x}O exhibits the highest OER activity that is evidenced by the lowest overpotential at 0.34 V compared to NCNT/CoO (0.38), NCNT/MnO (0.48 V), and commercial IrO₂ (0.39 V) when a current density of 10 mA cm⁻² is generated. It is worth mentioning that the current density of 10 mA cm⁻² is the standard to evaluate

overpotential for the OER [46]. As expected, the NCNT alone shows poor OER activity with the highest overpotential (> 0.6 V). Furthermore, the Tafel behavior during the OER was studied for these catalysts. Log (j) against overpotential was re-plotted from the corresponding linear sweep voltammetric curves. The Tafel slopes were calculated following an order of NCNT/Co_xMn_{1-x}O (40 mV dec⁻¹) < NCNT/CoO (48) < IrO₂ (67) < NCNT/MnO (110) < NCNT (240) (**Figure 4b**). The NCNT/Co_xMn_{1-x}O exhibits the lowest Tafel slope among these samples that indicates a faster reaction rate [47]. The NCNT/MnO and pure NCNT show a sluggish reaction kinetics evidenced by their larger Tafel slopes. The activity of NCNT/Co_xMn_{1-x}O for the OER significantly outperforms that of IrO₂ nanoparticles. A current density of 4.6 mA cm⁻² is generated as the 0.3 V of overpotential is applied. **Table S1** summarized a comparison between the newly developed catalyst and other reported highly efficient metal oxides in terms of their OER activity. The non-spinel NCNT/Co_xMn_{1-x}O is indeed one of the best performing OER catalysts.

Figure 4c shows the ORR polarization curves for all of studied oxide catalysts and Pt/C (20% Pt on Vulcan XC-72) measured in an oxygen-saturated 1.0 M KOH solution at a rotating speed of 1600 rpm. The NCNT/Co_xMn_{1-x}O shows an onset potential as high as 0.96 V that is comparable to that of Pt/C. The half-wave potential (*E*_{1/2}) determined in the mixed kinetic-diffusion control region for the NCNT/Co_xMn_{1-x}O is 0.84 V, showing positive shifts up to tens of millivolts relative to NCNT/CoO and NCNT/MnO samples. The NCNT/Co_xMn_{1-x}O also exhibits the highest diffusion-limited current density among tested samples, suggesting the most facile mass transfer within catalyst layers. In addition, an increase in reaction kinetics for NCNT/Co_xMn_{1-x}O is indicated by its smaller Tafel slope (54 mV dec⁻¹) relative to NCNT/CoO (78 dec⁻¹) and NCNT/MnO (75 mV dec⁻¹) (**Figure 4d**). The NCNT shows an insignificant activity, indicating the ORR activity of NCNT/Co_xMn_{1-x}O is mainly from a synergistic effect between NCNT and Co_xMn_{1-x}O. The linear scan voltammogram curves (LSV) of NCNT/Co_xMn_{1-x}O at different rotating rates were shown in **Figure S4** as well. The corresponding Koutecky-Levich (K-L) plots were recorded in **Figure S4** (inset), in which inverse current is a function of the inverse square root of the rotation speed at varied potentials [48]. The average electron transfer number per oxygen molecule (*n*) for the ORR is determined to be 3.8 at various potentials of 0.4, 0.5, and 0.6 V by using the K-L equation, indicating a 4e⁻ reduction pathway during the ORR.

In order to optimize *x* value in Co_xMn_{1-x}O, we also prepared the catalysts using various Co/Mn ratios in

Figure 4 (a) Linear sweep voltammetric curves of NCNT/Co_xMn_{1-x}O, NCNT/CoO, NCNT/MnO, NCNT and IrO₂ for OER in 1 M KOH at the scan rate of 10 mV s⁻¹. (b) Derived Tafel plots from the corresponding OER linear sweep voltammetric curves at low current density region. (c) Linear sweep voltammetric curves of NCNT/Co_xMn_{1-x}O, NCNT/CoO, NCNT/MnO, NCNT and Pt/C for ORR in 1 M KOH at the scan rate of 10 mV s⁻¹. (d) Derived Tafel plots from the corresponding ORR linear sweep voltammetric curves at low current density region.

the starting materials. Among studied rations, (Figures S5a and 5b), NCNT/Co₅₁Mn₄₉O showed the highest performance. The ratio of Co/Mn (51/49) in NCNT/Co_xMn_{1-x}O was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). NCNT exhibits insignificant ORR and OER activities, indicating the synergistic effect of the Co_xMn_{1-x}O and NCNT. In Figures S5c and 5d, the NCNT/Co_xMn_{1-x}O produced from 200, 100 and 25 mg CNT are also studied the catalytic activities for ORR and OER. NCNT/Co_xMn_{1-x}O prepared from 50 mg CNT in starting material showed the highest catalytic activities, which indicates ratio of CNT in starting materials. Taking all of metrics, the NCNT/Co_xMn_{1-x}O represents one of the most active metal oxide ORR catalysts (Table S2). The charge transfer resistances for ORR and OER were further determined by using electrochemical impedance

spectroscopy (EIS) based on fitting results of an equivalent circuit (Figures S6a and 6b). The NCNT/Co_xMn_{1-x}O showed much smaller charge transfer resistance (R_{ct}) (~ 150 Ω) compared to those of NCNT/CoO (~ 400 Ω) and NCNT/MnO (~ 700 Ω) for the ORR. It also showed much smaller charge transfer resistance (R_{ct}) (~ 35 Ω) compared to those of NCNT/CoO (~ 60 Ω) and NCNT/MnO (~ 255 Ω) for the OER, indicating a fast reaction kinetics. The charge transfer resistance is directly correlated with the ORR and OER reactivity, indicating the synergistic effect of the Co and Mn.

The OER stability of NCNT/Co_xMn_{1-x}O was tested at a constant potential of 1.6 V (Figure S7a), the current densities remained constant for 7000 s. The stability measurement was also conducted on IrO₂ at the identical condition. The current densities were decreased to 50% in 7000 s. Figure S7b shows the

loss of percentage of current density as function of testing time for NCNT/Co_xMn_{1-x}O and Pt/C during the ORR at the potential of 0.85 V. The change of current density is nearly negligible for NCNT/Co_xMn_{1-x}O up to 20000s, while Pt/C losses 20% activity.

Generally, carbon blacks suffer catastrophic corrosion (thermodynamically favorable above 0.2 V in the presence of water) at very high potentials during the OER (>1.6 V). However, properly selected highly graphitized nanocarbon with optimal morphology and nanostructure would significantly mitigate carbon oxidation or corrosion [49]. Particularly, in this work, we have identified that carbon nanotube is much more stable relative to conventional carbon blacks (*e.g.*, BlackPearl 2000), evidenced by a potential cycling test at 0-1.9 V in O₂ saturated NaOH solution (**Figure S8**). Thus, use of CNT will provide a new opportunity to develop nanocarbon supported oxides for bifunctional catalyst application, as we demonstrated in this work.

Non-spinel NCNT/Co_xMn_{1-x}O ($x = 0.51$) exhibits much higher OER and ORR activities than those of NCNT/CoO and NCNT/MnO, which are mainly attributed to the synergistic effect of the Co and Mn. The interaction between Co and Mn in NCNT/Co_xMn_{1-x}O was confirmed by its Co and Mn K-edge EXAFS (**Figure S3**), in which are obviously different from those of single metal-based catalysts NCNT/CoO and NCNT/MnO. In addition, a smaller charge transfer resistance measured with the NCNT/Co_xMn_{1-x}O, relative to NCNT/CoO and NCNT/MnO, further suggests the possible interaction between Co and Mn. (**Figure S6**).

The linear sweep voltammetry indicates that Co²⁺ is a main active site for the OER because NCNT/CoO shows a much higher activity than NCNT/MnO (**Figure 4a**). For ORR evaluation, NCNT/CoO exhibits a similar activity to NCNT/MnO (**Figure 4c**), indicating that both Co²⁺ and Mn²⁺ are important to catalyzing the ORR. Although NCNT alone shows

insignificant OER and ORR activity (**Figure S4**), the hybridization of NCNT and Co_xMn_{1-x}O is indispensable due to enhanced electrical conductivity during the OER and the ORR.

Zinc-air battery studies of NCNT/Co_xMn_{1-x}O cathodes

Thanks to the excellent ORR/OER activity of NCNT/Co_{1-x}Mn_xO, we further explored the possibility to incorporate the catalyst into a real air cathode for homemade two-electrode zinc-air batteries. The galvanostatic discharge curves shown in **Figure 5a** clearly indicates that the voltage plateau of NCNT/Co_{1-x}Mn_xO cathode is similar to that of Pt/C cathode in the primary zinc-air battery at a current density of 7 mA cm⁻². Their specific discharging capacities is further compared in **Figure 5b**. When normalized to the mass of consumed Zn in the anode, the NCNT/Co_{1-x}Mn_xO-based batteries exhibited a specific capacity of 581 mAh g_{zn}⁻¹ at a current density of 7 mA cm⁻², corresponding to a gravimetric energy density of 695 Wh kg_{zn}⁻¹. These measured metrics of performance are similar to the Pt/C cathode-based batteries.

To fabricate rechargeable zinc-air batteries, the space between the anode and cathode was filled with a 0.2 M zinc oxide containing 6.0 M KOH solution (**Figure 6a**). The discharging and charging voltage profiles for both NCNT/Co_xMn_{1-x}O and (Pt/C+IrO₂) cathode are compared in **Figure 6b**. The discharging overpotentials of the NCNT/Co_xMn_{1-x}O cathode are lower than that of (Pt/C+IrO₂) at relatively low current densities up to 8.0 mA cm⁻². Importantly, during the more challenging charging process associated with the OER, overpotentials of NCNT/Co_xMn_{1-x}O cathode are also lower than that of (Pt/C + IrO₂) in the whole current density range up to 90 mA/cm². Therefore, the sum of the charge-discharge overpotential for the NCNT/Co_xMn_{1-x}O cathode in the rechargeable zinc-air battery is 1.18 V

Figure 5. Electrochemical performance of primary zinc-air batteries using NCNT/Co_xMn_{1-x}O and Pt/C-based cathodes in 6 M KOH. a) The galvanostatic discharge curves of the primary zinc-air batteries at the current density of 7 mA cm⁻². b) Specific capacities of the primary zinc-air batteries normalized to the mass of the consumed Zn at the current density of 7 mA cm⁻².

We also compared NCNT/Co_xMn_{1-x}O cathode with other reported bifunctional cathodes in rechargeable zinc-air batteries such as CoO/CNT + NiFe LDH/CNT cathode [50]. The sum of overpotentials for the CoO/CNT+NiFe LDH/CNT is ~ 0.6 V at a current density of 5 mA cm⁻², which is larger than that of the NCNT/Co_xMn_{1-x}O (0.57 V) at an even higher current density of 7 mA cm⁻². Notable, we only used ambient air, rather than pure O₂ for the rechargeable battery studies. In addition, the loading of 0.53 mg cm⁻² for the NCNT/Co_xMn_{1-x}O cathode in

our system is smaller than that of the CoO/CNT (1 mg cm⁻²) + NiFe LDH/CNT (5 mg cm⁻²) hybrid cathode. Because (CoO/CNT + NiFe LDH/CNT)-based zinc-air battery system is a beaker type rechargeable zinc-air battery, the large amounts of 6.0 M KOH electrolyte is required (~ 40 mL). However, only 2 mL electrolyte is needed in our system to generate sufficient current density. Importantly, the NCNT/Co_xMn_{1-x}O cathode-based battery demonstrated a negligible increase in the sum of overpotentials during a long term charge-discharge cycling tests, indicating significantly improved stability, relative to other reported mixed oxides including Mn_xCo_{3-x}O₄, NiCo₂O₄, and core-corona-based bifunctional catalysts [30, 51, 52]. Therefore, the newly developed non-spinel NCNT/Co_xMn_{1-x}O is one of the best performing nonprecious metal bifunctional catalysts for rechargeable zinc-air batteries, evidenced by its high round-trip efficiency alone with remarkable cycling stability with minimized sum of overpotential.

Figure 6. Rechargeable zinc-air battery performance using NCNT/Co_xMn_{1-x}O and Pt/C+IrO₂ as cathodes in 6 M KOH. a) Schematic illustration of a rechargeable zinc-air battery. b) Charge and discharge polarization curves of rechargeable zinc-air batteries. c) Charge/discharge cycling curves of two-electrode rechargeable zinc-air batteries at the current density of 7 mA cm⁻².

Conclusions

In this work, for the first time, we prepared a non-spinel cobalt-manganese oxide bifunctional electrocatalyst supported by nitrogen-doped carbon nanotubes (NCNT/Co_xMn_{1-x}O) through a non-surfactant assistant hydrothermal method followed by annealing treatment in Ar and NH₃. The hybrid cathode catalyst is highly active simultaneously for the ORR and the OER in alkaline media, likely due to the synergistic effect between CoO and MnO determined by X-ray absorption spectra. **Notable, a highly stable CNT with minimized carbon corrosion during the ORR and OER was selected as a nanocarbon support to well-disperse the oxide nanoparticles, which is a key factor during the catalyst design and synthesis.** The NCNT/Co_xMn_{1-x}O cathode demonstrated excellent performance in both primary and rechargeable zinc-air batteries. Particularly, a high discharge voltage plateau (1.22 V) and a high energy densities (~ 695 Wh kg_{zn}⁻¹) was achieved on a primary zinc-air battery when operated under ambient air. In addition, a high round-trip efficiency characterized by a low charge-discharge voltage gap (0.57 V) and stable charge-discharge cycling at a current density of 7 mA cm⁻² were achieved for two-electrode rechargeable zinc-air batteries. These exceptionally improved performance metrics of NCNT/Co_xMn_{1-x}O are comparable to state-of-the-art Pt/C or Pt/C+IrO₂ cathodes. This work provides a new approach to design and synthesis of advanced cobalt-manganese oxide catalysts for highly efficient ORR/OER bifunctional cathodes in high-performance rechargeable zinc-air batteries and other reversible utilized alkaline fuel cells.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at <http://>.

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