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

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Received 26 August 2015; received in revised form 23 November 2015; accepted 23 November 2015
Available online 30 November 2015

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\textsubscript{x}Mn\textsubscript{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 IrO\textsubscript{2}, and comparable ORR activity to Pt/C with identical onset potential (0.96 V) in alkaline media. Furthermore, the NCNT/Co\textsubscript{x}Mn\textsubscript{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 +IrO\textsubscript{2}), respectively. Primary zinc-air battery tests show a gravimetric energy density of 695 W h kg\textsubscript{Zn}\textsuperscript{-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\textsuperscript{-2}.

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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 Co$_3$O$_4$/graphene [20], Co/CoO/graphene [21], CoO/NCNT [22], and Mn$_2$O$_3$/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 CoFe$_2$O$_4$ for the OER and Mn$_2$Fe$_{2-x}$O$_4$ (M=Fe, Cu, Co, 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 Co$_x$Mn$_{3-x}$O$_4$ at room temperature [27]. MnCo$_2$O$_4$/N-rGO or NCNTs hybrids were also prepared as bifunctional catalysts by Dai and Muhler’s groups [28,29]. Also, spinel MnCo$_2$O$_4$ and CoMn$_2$O$_4$ 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 Co$_x$Mn$_{1-x}$O is much simpler relative to spinel Co$_x$Mn$_{3-x}$O$_4$ because of its single oxidation state (Co$^{2+}$ and Mn$^{2+}$). To our best acknowledge, non-spinel Co$_x$Mn$_{1-x}$O compounds were not studied sufficiently relative to conventional spinel MnCo$_2$O$_4$ and CoMn$_2$O$_4$. Although mixed Mn$_x$Co$_{1-x}$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 Co$_x$Mn$_{1-x}$O has not been reported yet. There is also no any report about preparation of non-spinel Co$_x$Mn$_{1-x}$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 Fig. 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/Co$_{0.9}$Mn$_{1-x}$O cathode in primary zinc-air battery performs better relative to Pt/C cathode, showing specific capacities of 581 mA h g$^{-1}$ at a current density of 7 mA cm$^{-2}$, corresponding to gravimetric energy density of 695 W h kg$^{-1}$. 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/Co$_x$Mn$_{1-x}$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 Co(NO$_3$)$_2$·6H$_2$O (0.5 mmol, 145 mg), urea (5 mmol, 300 mg), NH$_4$F (2.5 mmol, 92.5 mg), and Mn (OAC)$_2$·4H$_2$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 autoclave reactor, which was subsequently heated at 150 °C for 12 h. During the synthesis, urea releases ammonia and provides carbonate ions through hydrolysis. The F$^-$ from NH$_4$F is a good chelating ligand that can prevent the formation of Co(OH)$_2$ and Mn(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 rCNT/Co$_x$Mn$_{1-x}$Co$_2$O$_3$ was annealed in a tube furnace at 500 °C for 2 h under 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 h was carried out to dope nitrogen into CNT. After cooling to room temperature, the resulting sample was labeled as NCNT/Co$_x$Mn$_{1-x}$O. The same procedure was used to prepare single Co- and Mn-based catalysts.

**Physcial characterization of catalysts**

X-ray diffraction (XRD, D/Max2000, Rigaku) was carried out by using Cu-K$_\alpha$ 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$^{-5}$ Torr using monochromatic Al K$_\alpha$ radiation (1486.6 eV). The scanning electron microscope (SEM) (S-4800, Hitachi) was operated at 10 kV, and high-resolution transmission electron microscope (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 RRe-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% Nafton 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$_2$ (~5 μm, 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 (Fig. 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 ~700 μm by an electrode pressing machine. The 250 μL ink similar to electrochemical measurements was carefully dropped onto the above air cathode and kept in a vacuum container for 30 min, followed by a mildly pressing procedure. The NCNT/Co$_x$Mn$_{1-x}$O- or (Pt/C + 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 NCNT/Co$_x$Mn$_{1-x}$O**

The scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) clearly show the formation of nanoparticles on the CNTs (Fig. 2(a)-(c)). 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
The elemental mapping of Co, Mn, O, and C atoms were carried out using HAADF–STEM (Fig. 2(d)). The elemental N was not 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 XRD patterns of rCNT/Co_{x}Mn_{1-x}O and NCNT/Co_{x}Mn_{1-x}O i.e. before and after the NH₃ annealing treatment, are shown in Fig. 2(e). The XRD patterns of precursor are similar to those of MnCO₃, CoCO₃, and Co_{x}Mn_{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_{x}Mn_{1-x}O (Fig. 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_{x}Mn_{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_{x}Mn_{1-x}O are obviously different to reported spinel Co_{x}Mn_{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_{x}Mn_{1-x}CO₃ and NCNT/Co_{x}Mn_{1-x}O. The full XPS surveys are recorded in Fig. 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 obtained by controlling the ratio of Co and Mn salts in the starting materials. Notable, both of Co2p and Mn2p spectra of NCNT/Co_{x}Mn_{1-x}O are found shifting to lower energy compared to those of rCNT/Co_{x}Mn_{1-x}CO₃ (Fig. S2b and c) because of the formation of Co–O and Mn–O bonds.
bonds. The high resolution XPS of O1s and N1s are shown in Fig. 52d-g. The appearance of the peak at 529.9 eV confirmed the formation of Mn–O or Co–O in the NCNT/Co$_x$Mn$_{1-x}$O (Fig. 52e), which is distinguished from that of the rCNT/Co$_x$Mn$_{1-x}$CO$_3$ precursor (Fig. 52d). After the annealing treatment under NH$_3$ atmosphere, the resulting NCNT/Co$_x$Mn$_{1-x}$O showed an increasing ratio of the pyridinic-N (398.3 eV)/pyrrolic-N (399.5 eV) relative to rCNT/Co$_x$Mn$_{1-x}$CO$_3$ (Fig. 52f and g). For Co2p spectrum of NCNT/Co$_x$Mn$_{1-x}$O, the peaks centered at 780.6 and 796.5 eV correspond to spin-orbit peaks of Co 2p$_3/2$ and 2p$_1/2$, respectively (Fig. S2c), which shift to lower energy compared to Mn2p of rCNT/Co$_x$Mn$_{1-x}$CO$_3$ due to the formation of Mn-O bond. They are similar to those of MnO for Mn$^{2+}$ in CoO–rGO and Co$_x$Ni$_{1-x}$O [40,41]. Meanwhile, Mn2p spectra of NCNT/Co$_x$Mn$_{1-x}$O centered at 641.4 and 653.3 eV that are ascribed to Mn 3d orbitals (Fig. 3(c)). The main edge peak at 6556 eV for NCNT/Co$_x$Mn$_{1-x}$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$_x$Mn$_{1-x}$CO$_3$ (Fig. 3(c)) 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$_x$Mn$_{1-x}$O at 1.70 and 2.67 Å correspond to Co–O and Co–Co bonding, respectively (Fig. 3(b)) [45]. The main peak for NCNT/Co$_x$Mn$_{1-x}$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$_x$Mn$_{1-x}$O between 4.0 and 10 Å are quite different from those of MnO (Fig. 3(d)) [44]. Furthermore, single NCNT/CoO and NCNT/MnO samples were also characterized by the XANES and EXAFS (Fig. S3a-d). Generally, the Co K-edge in NCNT/Co$_x$Mn$_{1-x}$O for Co K-edge of NCNT/Co$_x$Mn$_{1-x}$O is typically assigned to the transition of Co$^{2+}$ from Co 1s to Co 4p mixed state with O2p (Fig. 3(a)) that shows a slight shifting to high energy band relative to the rCNT/Co$_x$Mn$_{1-x}$CO$_3$, which is caused by an increased amount of O in the Co lattice for NCNT/Co$_x$Mn$_{1-x}$O compared to rCNT/Co$_x$Mn$_{1-x}$CO$_3$. Thus, the Co valence bands are attracted by the O ligands locating in Co lattice. As for Mn K-edge of NCNT/Co$_x$Mn$_{1-x}$O and rCNT/Co$_x$Mn$_{1-x}$CO$_3$, the pre-edge peak at 6541 eV is assigned to the quadruple transition from the 1s core level to unoccupied Mn 3d orbitals (Fig. 3(c)). The main edge peak at 6556 eV for NCNT/Co$_x$Mn$_{1-x}$O showed an increasing ratio of the pyridinic-N (398.3 eV)/pyrrolic-N (399.5 eV) relative to rCNT/Co$_x$Mn$_{1-x}$O [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

![Figure 3](image-url)
and NCNT/CoO are different. In particular, it can be split into two peaks at the range from 1.0 to 2.0 Å (1.29 and 1.70 Å) in NCNT/CoMn1−xO as shown in Fig. 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/CoMn1−xO, 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/CoMn1−xO is also different from that of NCNT/MnO, characterized by a peak shifting toward large interatomic distance (Fig. S3d). Therefore, these results indicate a strong interaction between Co and Mn in the mixed oxide.

Electrochemical activity of NCNT/CoMn1−xO

The electrochemical activities of NCNT/CoMn1−xO, 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 (Fig. 4(a)). Among these studied samples, the NCNT/CoMn1−xO 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/CoMn1−xO (40 mV dec−1) < NCNT/CoO (48) < IrO2 (67) < NCNT/MnO (110) < NCNT (240) (Fig. 4(b)). The NCNT/CoMn1−xO 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/CoMn1−xO 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,Mn1-x,O is indeed one of the best performing OER catalysts. The NCNT/Co,Mn1-x,O shows an onset potential as high as 0.96 V that is comparable to that of Pt/C. The half-wave potential (E1/2) determined in the mixed kinetic-diffusion control region for the NCNT/Co,Mn1-x,O is 0.84 V, showing positive shifts up to tens of millivolts relative to NCNT/Co and NCNT/MnO samples. The NCNT/Co,Mn1-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,Mn1-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) (Fig. 4(d)). The NCNT shows an insignificant activity, indicating the ORR activity of NCNT/Co,Mn1-x,O is mainly from a synergistic effect between NCNT and Co, which is from the synergistic effect between NCNT and Co. The linear scan voltamogram curves (LSV) of NCNT/Co,Mn1-x,O at different rotating rates were shown in Fig. S4 as well. The corresponding Koutecky-Levich (K-L) plots were recorded in Fig. 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,Mn1-x,O, we also prepared the catalysts using various Co/Mn ratios in the starting materials. Among studied rations, (Fig. S5a and b), NCNT/Co51Mn49O showed the highest performance. The ratio of Co/Mn (51/49) in NCNT/Co51Mn49O 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,Mn1-x,O and NCNT. In Fig. S5c and d, the NCNT/Co51Mn49O produced from 200, 100 and 25 mg CNT are also studied the catalytic activities for ORR and OER. NCNT/Co51Mn49O 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/Co51Mn49O 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 (Fig. S6a and b). The NCNT/Co51Mn49O showed much smaller charge transfer resistance (Rct) (~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 (Rct) (~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/Co51Mn49O was tested at a constant potential of 1.6 V (Fig. 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. Fig. S7b shows the loss of percentage of current density as function of testing time for NCNT/Co51Mn49O and Pt/C during the OER at the potential of 0.85 V. The change of current density is nearly negligible for NCNT/Co51Mn49O up to 20,000 s, while Pt/C loses 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 (Fig. 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/Co51Mn49O (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/Co51Mn49O was confirmed by its Co and Mn K-edge EXAFS (Fig. 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/Co51Mn49O, relative to NCNT/CoO and NCNT/MnO, further suggests the possible interaction between Co and Mn. (Fig. 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 (Fig. 4(a)). For OER evaluation, NCNT/CoO exhibits a similar activity to NCNT/MnO (Fig. 4(c)), indicating that both Co2++ and Mn2++ are important to catalyzing the OER. Although NCNT alone shows insignificant ORR and OER activity (Fig. S4), the hybridization of NCNT and Co,Mn1-x,O is indispensable due to enhanced electrical conductivity during the OER and the OER.

Zinc-air battery studies of NCNT/Co,xMn1-x,O cathodes

Thanks to the excellent ORR/OER activity of NCNT/Co,xMn1-x,O, 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 Fig. 5(a) clearly indicate that the voltage plateau of NCNT/Co,xMn1-x,O 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 Fig. 5(b). When normalized to the mass of consumed Zn in the anode, the NCNT/Co,xMn1-x,O-based batteries exhibited a specific capacity of 581 mAh gZn−1 at a current density of 7 mA cm−2, corresponding to a gravimetric energy density of 695 Wh kgZn−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 (Fig. 6(a)). The discharging and charging voltage profiles for both NCNT/Co,xMn1-x,O and Pt/C cathodes were.
and (Pt/C + IrO₂) cathode are compared in Fig. 6(b). The discharging overpotentials of the NCNT/CoₓMn₁₋ₓO 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/CoₓMn₁₋ₓO cathode are also lower than that of (Pt/C + IrO₂) in the whole current density range up to 90 mA cm⁻². Therefore, the sum of the charge-discharge overpotential for the NCNT/CoₓMn₁₋ₓO cathode in the rechargeable zinc-air battery is 1.18 V at the current density of 50 mA cm⁻². This value is lower than that of the Pt/C + IrO₂ cathode (1.29 V). Fig. 6(c) displays the charge-discharge...
cycling stability tests for the rechargeable zinc-air batteries using a constant current density of 7 mA cm\(^{-2}\). The NCNT/Co\(\text{Mn}_{1-x}\text{O}\) cathode demonstrated remarkable cycling stability with a negligible voltage change. The sum of overpotential (0.57 V) during the long term charge-discharge cycling (12 h) is lower than that of Pt/C+IrO\(_2\) cathode (0.60 V).

We also compared NCNT/Co\(\text{Mn}_{1-x}\text{O}\) 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 \(\sim 0.6\) V at a current density of 5 mA cm\(^{-2}\), which is larger than that of the NCNT/Co\(\text{Mn}_{1-x}\text{O}\) (0.57 V) at an even higher current density of 7 mA cm\(^{-2}\). Notable, we only used ambient air, rather than pure O\(_2\) for the rechargeable battery studies. In addition, the loading of 0.53 mg cm\(^{-2}\) for the NCNT/Co\(\text{Mn}_{1-x}\text{O}\) 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\(\text{Mn}_{1-x}\text{O}\) 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\(_{3}\)Co\(_3\)O\(_4\), NiCo\(_2\)O\(_4\), and core-corona-based bifunctional catalysts [30,51,52]. Therefore, the newly developed non-spinel NCNT/Co\(\text{Mn}_{1-x}\text{O}\) 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.

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\(\text{Mn}_{1-x}\text{O}\)) through a non-surfactant assistant hydrothermal method followed by annealing treatment in Ar and NH\(_3\). 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 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\(_{\text{Zn}}\)) 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\(\text{Mn}_{1-x}\text{O}\) are comparable to state-of-the-art Pt/C or Pt/C+IrO\(_2\) cathodes. This work provide 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.

Acknowledgments

This work is supported by the MSIP (Ministry of Science, ICT and Future Planning), South Korea, under the ITRC (Information Technology Research Center) support program (NIPA-2014-H0301-13-1009) supervised by the NIPA (National IT Industry Promotion Agency). G.W. is also grateful the financial supports from startup funds of University at Buffalo, SUNY along with U. S. Department of Energy, Fuel Cell Technologies Office (FCTO) Incubator Program (DE-EE0006960).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.11.030.

References

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