**Design of a sectionalized MnO₂-Co₃O₄ electrode via selective
electrodeposition of metal ions in hydrogel for enhanced electrocatalytic
activity in metal-air batteries**

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Abstract

Tailored designing of highly active electrocatalysts plays a key role in determining the overall electrochemical performance of metal-air batteries for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). We report herein a facile agarose gel-mediated strategy for the selective electrodeposition of MnO_2 and Co_3O_4 onto 3D porous nickel foam, in an attempt to produce a sectionalized MnO_2 - Co_3O_4 electrode with low physical interference on catalytic function. The as-prepared agarose hydrogel with metal precursor ions allows the electrochemical deposition only onto the contact area between the gel and the substrate. The resulting electrodes are completely sectionalized by two different catalyst (MnO_2 and Co_3O_4) coating layers within the 3D porous nickel foam. This novel structure enhances both the ORR/OER catalytic activities compared to those of bare metal oxide catalyst electrodes and even after 400 h of operation (equivalent to ~ 100 cycles), the sectionalized MnO_2 - Co_3O_4 electrode shows excellent cycling performance and long-term stability in rechargeable Zn-air batteries. As such, this novel sectionalized electrode configuration has potential for wide applications in the fabrication of other electrode structures employing various metal oxides.

Keywords: agarose, gel-mediated electrodeposition, sectionalized electrode, electrocatalyst

1. Introduction

Rechargeable metal-air batteries based on oxygen reduction reaction and oxygen evolution reaction (ORR and OER) in alkaline media have received world-wide attention due to their high theoretical energy density, environmentally benign manufacturing process, and low operation risk [1-4]. Despite their enormous promise for commercialization, most metal-air batteries, including Zn-air batteries (ZABs), suffer from large overpotential and poor cycle life caused by sluggish ORR-OER kinetics at the air electrode during the charge-discharge process [5-7]. To circumvent this, noble-metal based catalysts, such as Pt/C, Ag/C, and Pd/C, have attracted considerable interests for their improved cell efficiency and stability, but the high cost and scarcity of these metals hamper their widespread use in practical applications [8-10]. In addition, the highly oxidative electrochemical potential encountered during OER can lead to severe carbon corrosion and catalyst oxidation/dissolution, reducing both the amount of catalytic material and electrocatalytic performance on the air electrode [11,12]. To date, a plethora of efforts have been focused on overcoming these issues by developing non-precious metal oxide catalysts to reduce production cost and by modifying cathode structures to improve the structural stability.

More recently, transition-metal oxides are being considered as promising candidates for metal-air battery cathodes, especially for ZABs, due to their reasonable catalytic activities [13-18]. Amongst the various metal oxides, MnO_2 is an attractive electrocatalyst for ORR in aqueous electrolyte due to its notable benefits such as natural abundance, low cost, environmental benignity, and high stability against corrosion [15,19,20]. Co_3O_4 is also another non-precious metal catalyst, which has been garnering attention due to its efficacy in aiding both ORR and OER [21,22]. Hence, we envisioned that a combination of MnO_2 as an effective ORR catalyst and Co_3O_4 as an effective OER catalyst could provide new insight for

the production of bifunctional electrocatalysts with enhanced catalytic activity. However, Du et al. demonstrated that although Co_3O_4 nanoparticle-modified MnO_2 nanotube exhibited improved OER catalytic activity, ORR activity of the electrode decreased due to partial occupation of MnO_2 by Co_3O_4 nanoparticles [23]. As such, from the view of catalyst configuration, a more efficient process for producing electrocatalysts with low physical interference on catalytic function is still required in order to maximize the combined merit of each electrocatalyst.

In this study, we demonstrate a novel sectionalized electrode configuration through the use of metal ions containing agarose gel as a model case for the fabrication of sectionalized MnO_2 - Co_3O_4 electrode by an electrodeposition method. The as-prepared electrode was employed as the air electrode for ZABs, and the present work focuses on the following issues: (1) synthesis of sectionalized MnO_2 - Co_3O_4 electrode on 3D interconnected porous substrate by electrodeposition, (2) improved ORR/OER catalytic activity of sectionalized electrode configuration, and (3) enhanced cycling performance and stability of the sectionalized MnO_2 - Co_3O_4 electrode. This electrode configuration was realized through electrodeposition, which facilitates for simple and precise control of mass, thickness, and morphology of electrocatalysts to be directly deposited onto the substrate without the aid of polymeric binders [24,25], and through agarose gel, allows for controlled dual coverage of MnO_2 and Co_3O_4 only onto the desired areas. To the best of our knowledge, a study on the feasibility of such a system for use in electrocatalysts has not been reported before, and the obtained results support our hypothesis that reducing the physical interference between MnO_2 and Co_3O_4 catalysts improves the catalytic activity for both ORR and OER. As such, the sectionalized MnO_2 - Co_3O_4 electrode differentiates itself with its simple synthesis process and electrochemical performance and provides insight into a new electrode configuration that

capitalizes on the strengths of both MnO_2 and Co_3O_4 without hampering the performance of the respective electrocatalysts.

2. Experimental methods

2.1 Preparation of agarose gel medium containing metal precursor ions

The agarose gel medium was initially prepared by dissolving 0.05 M of $\text{Co}(\text{NO}_3)_2$ and 0.075 M of NaNO_3 in deionized (DI) water (99 mL) with vigorous stirring at room temperature. Powdered agarose (1 g, bioreagent, Sigma-Aldrich) was added to the as-prepared solution and melted by heating and maintaining the solution at 120 °C in an oil bath. After the complete dissolution of agarose, the solution was then poured into a glass petri dish, followed by gelation at room temperature for 20 min. After cooling, agarose gel medium containing cobalt precursor ions (Agar-Co) was cut and separated (Figure S1a). The agarose gel medium containing manganese precursor ions (Agar-Mn) was made through the same procedure using 0.05 M $\text{Mn}(\text{NO}_3)_2$ and 0.075 M NaNO_3 (Figure S1b).

2.2 Preparation of a sectionalized MnO_2 - Co_3O_4 electrode

Sectionalized electrodes (SEs) were fabricated by the electrodeposition method. A high-purity nickel foam (purity > 99.99 %, porosity $\geq$ 95 %, MTI Inc.) was used as the substrate and working electrode. Prior to the electrodeposition, the nickel foam substrates (1 x 4 cm²) were cleaned by rinsing with acetone and deionized water. A Pt plate and Ag/AgCl were used as the counter electrode and reference electrode, respectively. First, the Agar-Co was cut into desirable shape and size (2 x 3 cm²) and attached onto one side of the nickel foam with Pt plate and reference electrode for sectionalized regions. The electrodeposition was performed at -1.0 V (vs Ag/AgCl) at room temperature with an electrochemical workstation (Autolab). After electrodeposition, the electrode was washed with deionized water and dried at room

temperature for 24 h and then calcined at 350 °C for 2 h under an argon atmosphere. Second, the Agar-Mn was also attached onto the opposite side of the resulting electrode and electrodeposition was conducted at 1.0 V (vs Ag/AgCl). The total mass loading was controlled to be 1.0 mg cm⁻² (0.5 mg cm⁻² MnO₂ and 0.5 mg cm⁻² Co₃O₄) by adjusting the deposition time; loading was confirmed by weighing the substrates before and after the electrodeposition. Finally, the as-synthesized electrodes were rinsed with deionized water and dried at room temperature for 24 h. For a comparison, bare MnO₂ and Co₃O₄ electrodes were electrodeposited, following a similar procedure by attaching the agarose gel medium containing metal precursor ions to both sides of the nickel foam to achieve a loading of 1.0 mg cm⁻².

2.3 Characterization

The surface morphology and elemental mapping analysis of the electrodeposited materials were obtained by scanning electron microscope (SEM, FEI, Quanta 650 ESEM) equipped with energy dispersive X-ray spectroscopy (EDS, Bruker). The crystallinity of the electrodes was investigated with X-ray diffraction (XRD, Rigaku, MiniFlex 600) with Cu K α radiation and the oxidation states of manganese and cobalt were examined by X-ray photoelectron spectroscopy (XPS, Kratos, Axis Ultra DLD) with Al K α radiation. All XPS spectra were calibrated to the line position of adventitious carbon at 285 eV and analyzed with CasaXPS software with Lorentzian function and a Shirley background.

2.4 Electrochemical measurements

All electrochemical experiments of the as-synthesized samples were performed at room temperature with a PGSTAT302N (Autolab) electrochemical workstation. A single glass cell

was set up in a standard three-electrode configuration with 0.1 M KOH aqueous solution, an Ag/AgCl reference electrode, a Pt counter electrode, and the as-prepared electrode as the working electrode. The electrochemical activities (ORR and OER) of the samples were evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹. The ORR activity was determined by cycling between -0.8 and 0.2 V vs. Ag/AgCl in an O₂-saturated electrolyte. Before the ORR study, all electrodes were cycled for background correction under the same conditions using N₂-saturated electrolyte until reproducible cyclic voltammograms were obtained. The OER activity was determined by LSV measurement in the potential range of 0.2 to 1.0 V vs. Ag/AgCl. Hereafter, the potentials measured vs. the Ag/AgCl reference electrode was normalized with respect to the potential of the reversible hydrogen electrode (RHE).

A home-made PTFE layered battery mold was designed to carry out the ZAB test. For the decoupled configurations, the air electrode for ORR was prepared, which consisted of the as-synthesized electrode ($0.76 \times 0.76 \text{ cm}^2$) with a hydrophobic carbon-fiber paper ($1.5 \times 1.5 \text{ cm}^2$). To make an air cathode, one side of the as-synthesized electrode was placed on the middle of the carbon-fiber paper and was pressed into a 0.5-mm-thick layer by a rolling machine. The OER electrode was made by the same sample electrode connected with a titanium wire, which acted as the current collector. A polished zinc plate was used as the anode and the electrolyte was 6 M KOH + 0.2 M ZnCl₂. For the decoupled cell configuration, the cycling performance was determined using two independent channels on an Arbin 2000 battery cycler at a current density of 1 mA cm⁻² in air atmosphere. Each charge and discharge period was set to be 2 h with a five-minute resting time. The conventional air electrode containing 1.0 mg cm⁻² Pt/C (20 wt.%, Johnson Matthey) was made of 80 wt.% catalyst and 20 wt.% LITH-ion binder as described in a previous report [17].

3. Results and discussion

The schematic diagram for the preparation of the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode through metal precursor ion agarose gel medium is illustrated in Scheme 1. The mixed solution of molten agarose and cobalt precursor ions was heated in an aqueous solution and upon cooling, the solution self-assembled into semi-flexible hydrogel possessing a 3-D interconnected porous structure generated through a series of cross-linking of hydrogen bonds [26-29]. This extensive porous network provides a metal precursor ion reservoir, but also facilitates transport of both electrons and Co^{2+} within the structure [27,30]. Deposition of the metal ions onto nickel foam was achieved through electrodeposition. By applying an electric current to the Agar-Co gel attached nickel foam, metal ions were able to migrate from the hydrogel and form a layer on the nickel foam and were subsequently reduced to Co(OH)_2 through a reduction process. The as-synthesized Co(OH)_2 was then converted into Co_3O_4 by heat treatment and MnO_2 was incorporated into the opposite side of the substrate using the same strategy. This strategy of electrodeposition through agarose gel medium is typically carried out in a solution-based electrolyte where metal ions freely move around in the immersed substrate, resulting in a randomly deposited layer. By employing an agarose gel, which acts as a medium for both a current flow channel and a metal precursor ion reservoir [27,30], selective electrodeposition can take place on desired areas of the substrate, thus preventing crossover of metal ions through the porous nickel foam structure. Furthermore, morphology control and preparation of the hydrogel is simple as agarose-gel synthesis is done through solution-mixing and casting onto various frames, and this technique can be applied to any conducting substrate such as stainless steel, nickel foam, and polymeric current collector [27,31,32]. Also, note that agarose-gel electrodeposition of metal ions

allows for dual co-deposition of anodically deposited metals (MnO_2) and cathodically deposited metals (Co_3O_4) [4,18,19,33].

The result of the agarose-gel electrodeposition strategy is a sectionalized bifunctional MnO_2 - Co_3O_4 electrode on each side of the nickel foam substrate, shown in Figure S2. MnO_2 and Co_3O_4 were uniformly coated onto each side of the substrate, each displaying distinctive colors (MnO_2 side; brown and Co_3O_4 side; black). Based on the side view optical image, it is apparent that the sectionalized electrode is divided into the two parts at the center of the electrode as seen in Figure S2. High-magnification observation (Figure 1a and c) reveals that both MnO_2 and Co_3O_4 are uniformly coated onto the nickel foam surface and electrodeposited MnO_2 exhibits a vertically aligned irregular nanoflower structure while the Co_3O_4 shows vertically grown and interconnected nanoflakes, which form a typical hierarchical structure. These deposited layers show well-developed porous structures and ensure that the surfaces of MnO_2 - Co_3O_4 electrode is highly accessible to electrolyte and O_2 , leading to increase active sites for OER and ORR for enhanced electrocatalytic activities [34]. Energy dispersive X-ray spectroscopy (EDS) mapping further confirmed the elemental distribution of cobalt and manganese on one side of the foam as seen in Figure 1d. Cobalt is very uniformly distributed over the surface of nickel foam while manganese signal is only sparsely detected. The reason why manganese signal appears could be ascribed to the high porosity of the substrate and due to the highly porous structure of the nickel foam; EDS beams pass through the open pores and detect manganese on the MnO_2 deposition side.

To validate that there is no MnO_2 crossover to the Co_3O_4 deposition, X-ray diffraction (XRD) patterns of each side of sectionalized MnO_2 - Co_3O_4 electrode are compared in Figure 2a. Co_3O_4 side of electrode, after calcination at 350°C under argon atmosphere, exhibit major diffraction lines at 31.5° , 36.9° , and 59.5° , which correspond, respectively, to the (220), (311),

and (511) planes of Co_3O_4 (JCPDS CARD No. 42-1467) [11]. On the other hand, the XRD pattern of MnO_2 side displayed only three nickel diffraction peaks without the detection of any discernable MnO_2 peaks, which indicates that the synthesized MnO_2 is amorphous in nature, as previously reported due to the absence of a heat treatment process [35,36]. Note that the three large nickel peaks also appear in Co_3O_4 XRD data. In this regard, it is apparent that the agarose gel medium not only provides metal precursor ions to be effectively deposited onto the substrate but also prevents the crossover of metal ions through the porous structure of nickel foam during the electrodeposition process, consequently resulting in the formation of a sectionalized MnO_2 - Co_3O_4 electrode.

X-ray photoelectron spectroscopy (XPS) was used to characterize both sides of the as-prepared electrode to elucidate the chemical states and the formation of sectionalized MnO_2 - Co_3O_4 electrode, as shown in Figure 2b and c. The Co 2p XPS spectrum of the Co_3O_4 deposited side shows two major peaks at 780.3 and 795.6 eV with a spin energy separation of 15.4 eV, which can be assigned to the Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks in Co_3O_4 [21]. These two main spin-orbital lines of the Co 2p peak are absent on the MnO_2 deposited side of electrode (Figure 2b). Mn 2p XPS spectrum of MnO_2 deposited side reveals two peaks at 654.1 and 642.4 eV corresponding to the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks of MnO_2 , respectively, and can be clearly seen with a spin-orbit splitting of 11.6 eV. Again, no distinct Mn 2p spectrum is observed on the Co_3O_4 side (Figure 2c) [23]. The XPS result is well consistent with the SEM and XRD results, suggesting that the agarose gel-mediated electrodeposition enables the formation of sectionalized and separate MnO_2 - Co_3O_4 layers within the porous substrate to be finely controlled.

To investigate the effect of the sectionalized configuration on the electrocatalytic activity, the sectionalized MnO_2 - Co_3O_4 electrode (labeled MnO_2 - $\text{Co}_3\text{O}_4/\text{NiF}$) was evaluated

as an integrated electrocatalytic electrode for ORR and OER in 0.1 M KOH solution with a typical three-electrode setup. As control experiments, three reference samples were also studied under the same conditions, including bare nickel foam (NiF), only MnO₂ deposited on NiF (MnO₂/NiF), and only Co₃O₄ deposited on NiF (Co₃O₄/NiF). The cyclic voltammetry (CV) curves of all the samples in an O₂ versus N₂-saturated electrolyte at a scan rate of 10 mV s⁻¹ are presented in Figure 3a. Although CVs in the presence of N₂ exhibits the typical behaviors of charge/discharge current from electrical double layers, significant cathodic currents appear under an O₂ atmosphere resulting from electrocatalytic oxygen reduction reaction. Figure 3b presents the expanded CV curves of MnO₂/NiF, Co₃O₄/NiF, and MnO₂-Co₃O₄/NiF under O₂ atmosphere. As seen in the image, MnO₂-Co₃O₄/NiF shows a much more positive ORR peak potential (~0.72 V vs. RHE), indicating higher ORR activity as compared to MnO₂/NiF and Co₃O₄/NiF. The ORR onset potential of the MnO₂-Co₃O₄/NiF is ~ 0.95 V, which is 40 mV more positive than Co₃O₄/NiF and 90 mV more positive than MnO₂/NiF. We postulate that this increase in ORR activity is caused by the synergetic effects of MnO₂ and Co₃O₄ [37]. Cobalt oxide has been reported to catalyze the disproportionation reaction of intermediates in oxygen reduction, giving rise to reduction of HO₂⁻ to OH⁻ [38]. Deng et al. stated that this in turn aids the decomposition of hydrogen peroxide ions as ORR of manganese oxide is achieved via 2 x 2e pathway, which plays a key role in the enhanced catalytic activity on the sectionalized MnO₂-Co₃O₄ electrode [39]. Additionally, Co₃O₄ has a high affinity towards oxygen and can facilitate better oxygen transport within the porous nickel foam substrate [38]. Still, Du et al. states in the Co₃O₄ nanoparticle-modified MnO₂ nanotube bifunctional catalyst report that concurrent use of Co₃O₄ and MnO₂ together as catalyst exhibits much lower ORR activity than pure MnO₂ nanotube due to the partial occupation of active sites on MnO₂ by Co₃O₄ nanoparticles [23]. This contradicts the

improved performance of sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode. However, what distinguishes the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode from Co_3O_4 nanoparticle-modified MnO_2 nanotube electrode is that the latter suffers from physical interference of Co_3O_4 while the former effectively overcomes this by separately incorporating MnO_2 and Co_3O_4 within the electrode through selective electrodeposition, which consequently contributes to the enhanced catalytic activity.

Apart from the ORR activity, the linear sweep voltammetry (LSV, not iR corrected) curves of OER for all the samples is shown in Figure 3c. The OER activities of MnO_2/NiF , $\text{Co}_3\text{O}_4/\text{NiF}$, and $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ all show anodic peaks at around 1.54 V, corresponding to either the oxidation of Co^{3+} to Co^{4+} or the adsorption process of OH^- to the surface of MnO_2 catalyst, followed by the onset of oxygen evolution at which the current density sharply increases [15,40]. The $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ displays an onset potential of 1.59 V, which is comparable to that of $\text{Co}_3\text{O}_4/\text{NiF}$ (1.58 V). Compared to that of the MnO_2/NiF electrode, the enhanced OER activity of the sectionalized electrode is even more strongly highlighted; the MnO_2/NiF exhibits ~ 0.05 V more positive onset potential than the $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ electrode. These results suggest that the sectionalized electrode could maximize the utilization of each MnO_2 and Co_3O_4 catalysts. The nickel foam structure further contributes to the OER activity as the 3D porous structure increases the active sites for OER and offers additional free space for providing reactants or product transfer pathways to the inner active sites [34]. Compared to the bifunctional activity of the previously reported precious metal and non-precious metal oxide catalysts, the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ electrode shows excellent oxygen electrode activities with a smaller separation between the ORR and OER voltages (Table S1). Interestingly, the current density values of $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ for both ORR and OER are found to be located between those of MnO_2/NiF and $\text{Co}_3\text{O}_4/\text{NiF}$. The

reason for this is likely due to the sectionalized configuration of the $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode, which would halve the deposit amounts of MnO_2 and Co_3O_4 , as compared to pure MnO_2 and Co_3O_4 electrode. This induces an intermediate current density value. Based on the above results, it should be noted that the physical configuration of the sectionalized bifunctional electrode has a significant effect on the electrocatalytic reaction. As such, the unique structure of the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode significantly contributes to the improved catalytic activity.

Another vital electrochemical aspect in ZABs is cycling performance and chemical stability. In order to further investigate the influence of the sectionalized electrode configuration on the electrochemical performance and stability, the as-prepared electrodes were tested in rechargeable ZABs (Figure 4). Note that to precisely monitor the efficacy of sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode on both ORR and OER, a decoupled design of electrodes with two independent channels was used where the ORR electrode was attached onto a hydrophobic carbon paper to maximize the three-phase boundary and the OER electrode was fully immersed in the electrolyte to ensure the full contact of the catalyst with the electrolyte (Figure S3) [17,41]. As shown in Figure 4a and b, the initial round-trip overpotentials of the $\text{Co}_3\text{O}_4/\text{NiF}+\text{MnO}_2/\text{NiF}$ and $\text{MnO}_2/\text{NiF}+\text{Co}_3\text{O}_4/\text{NiF}$ are, respectively, 0.78 and 0.79 V (voltaic efficiencies of 59.8 and 60.2 %). After 400 h of operation (95 cycles), these values increase to 0.90 and 0.91 V (voltaic efficiencies of 55.1 and 55.2 %). It should be noted that the final round-trip overpotentials are similar because despite a reduction in the ORR and OER overpotentials of the bare Co_3O_4 , the counter bare MnO_2 electrodes have larger overpotentials, culminating in similar round-trip overpotentials for the two systems (Figure S4). On the other hand, $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}+\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ (Figure 4c) exhibit initial charge and discharge potentials of ~ 1.96 and ~ 1.21 V and final values of ~ 1.99 and $\sim$

1.13 V after 95 cycles. Note that the difference between the initial and final potential values of $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}+\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ is an order of magnitude lower than the aforementioned configurations using bare metal oxides. Similarly, the initial and final round-trip overpotentials of $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}+\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ show relatively low values of 0.75 and 0.86 V, respectively, compared to those of bare metal oxides. These result indicates that the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode is effective in enhancing the catalytic activity for both ORR and OER as identified by the CV and LSV tests (Figure 4), consequently leading to a decrease in the overall overpotential.

For a clear comparison of electrocatalytic activity, the cycling performances of Zn-air batteries were also tested with sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ and a commercial Pt/C (20 wt.% Pt/C) catalyst using a conventional single air electrode. As shown in Figure 5a, the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ shows an initial discharge voltage of 1.18 V, which is significantly lower than that of Pt/C's 1.35 V, and an initial charge voltage of 1.96 V, which is lower than that of Pt/C's 2.02 V. The sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ also shows better stability compared to its commercial Pt/C counterpart; while the discharge and charge potential of $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ cathode varies by only 5 % in the first 90 h (21 cycles), the discharge and charge potentials of Pt/C cathode notably changes with time progression from 1.35 down to 1.22 V for discharge potential and 2.02 up to 2.15 V for charge potential. Such significant differences of initial and final potential are due to the corrosion of carbon support and the oxidation/dissolution of Pt nanoparticle under highly oxidizing OER condition during operation [11,12]. Based on these results, it can be concluded that the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ cathode outperforms commercial Pt/C catalyst by comparable ORR catalytic activity and higher OER catalytic activity. Even at an extended discharge-charge cycling of 400 h (equivalent to 95 cycles), the round-trip overpotential of Zn-air battery with

sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ cathode was 0.83 V, which is only 0.05 V more than its initial 0.78 V (Figure 5b). The high stability of the sectionalized electrode can be attributed to the strong connection between the catalyst and nickel foam matrix achieved through the electrodeposition process, which maintains the structural integrity by suppressing the pulverization of active materials that comes from the rising oxygen bubbles during cycling [34,40]. In addition, the directly grown catalysts on 3D porous nickel foam provides large contact areas for reactant and product transfer pathways to the inner active sites [34]. As such, the agarose-mediated electrodeposition represents a potentially powerful strategy for the fabrication of sectionalized bifunctional electrodes with two different metal oxides that simultaneously enhance chemical stability and reduce overall overpotential.

4. Conclusion

In summary, we have presented a sectionalized bifunctional $\text{MnO}_2\text{-Co}_3\text{O}_4$ catalyst layers deposited on 3D porous nickel foam through agarose gel-mediated electrodeposition. The agarose gel-mediated electrodeposition strategy has several advantages: it is simple, low-cost, and mechanically stable and allows for the control of shape and size of gel medium according to the casting frames and can facilitate the electrodeposition with any conducting substrates. Furthermore, electrodeposition can selectively deposit catalysts on the substrate and prevent crossover of metal ions in the interconnected nickel foam pores, thus minimizing physical interference of Co_3O_4 on functional MnO_2 active sites. These sectionalized electrodes display good bifunctional ORR/OER activity and can be directly used for ZAB cathodes without any additional ancillary materials. The sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrodes also show improved cycling performance and chemical stability compared to the commercial Pt/C catalyst. These auspicious results indicate that this strategy can be extended

to fabricating other high-performance transition-metal oxide-based catalyst electrodes with sectionalized bifunctional configuration for use in a wide variety of applications.

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FIGURES

Scheme 1. Schematic representation of the fabrication process used for the sectionalized bifunctional $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode.

Figure 1. Representative SEM images of the sectionalized bifunctional MnO₂-Co₃O₄ electrode: (a) MnO₂ deposited side of the electrode, (b) low-resolution SEM image of the sectionalized bifunctional electrode (MnO₂ side: upper left and Co₃O₄ side: lower right), and (c) Co₃O₄ deposited side of the electrode. (d) EDS atomic analysis results of the Co₃O₄ side of electrode.

Figure 2. (a) XRD pattern of the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode. High-resolution XPS spectra of each side of the sectionalized $\text{MnO}_2\text{-Co}_3\text{O}_4$ electrode: (b) Co 2p and (c) Mn 2p regions.

Figure 3. (a) CV curves of bare nickel foam (NiF), MnO₂/NiF, Co₃O₄/NiF, and MnO₂-Co₃O₄/NiF in O₂-saturated (solid line) and N₂-saturated (dash line) 0.1 M KOH solution and (b) corresponding cathodic current curves of MnO₂/NiF, Co₃O₄/NiF, and MnO₂-Co₃O₄/NiF for ORR catalytic activity. (c) LSV curves of bare NiF, MnO₂/NiF, Co₃O₄/NiF, and MnO₂-Co₃O₄/NiF for OER catalytic activity in 0.1 M KOH.

Figure 4. The discharge and charge voltage profiles of Zn-air batteries with (a) $\text{Co}_3\text{O}_4/\text{NiF} + \text{MnO}_2/\text{NiF}$, (b) $\text{MnO}_2/\text{NiF} + \text{Co}_3\text{O}_4/\text{NiF}$, and (c) $\text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF} + \text{MnO}_2\text{-Co}_3\text{O}_4/\text{NiF}$ decoupled catalysts at a current density of 1 mA cm^{-2} at room temperature.

Figure 5. (a) Cycling performance of Zn-air batteries with the single Pt/C (black) or MnO₂-Co₃O₄/NiF (red) air electrodes at room temperature. (b) First 10 and last 10 cycles of the rechargeable Zn-air battery using MnO₂-Co₃O₄/NiF electrode with a period of 400 h (96 discharge-charge cycles). The current density is 1 mA cm⁻², and the electrolyte is 6 M KOH added with 0.2 M ZnCl₂ solution.

Vitae

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