Hydrothermally Grown Dual-Phase Heterogeneous Electrocatalysts for Highly Efficient Rechargeable Metal-Air Batteries with Long-Term Stability

Chandran Balamurugan, Changhoon Lee, Kyusang Cho, Jehan Kim, Byoungwook Park, Yusin Pak, Jaemin Kong, and Sooncheol Kwon

Metal-air batteries as alternatives to the existing lithium-ion battery are becoming increasingly attractive sources of power due to their high energy-cost competitiveness and inherent safety; however, their low oxygen evolution and reduction reaction (OER/ORR) performance and poor operational stability must be overcome prior to commercialization. Herein, it is demonstrated that a novel class of hydrothermally grown dual-phase heterogeneous electrocatalysts, in which silver-manganese (AgMn) heterometal nanoparticles are anchored on top of 2D nanosheet-like nickel vanadium oxide (NiV$_2$O$_6$), allows an enlarged surface area and efficient charge transfer/redistribution, resulting in a bifunctional OER/ORR superior to those of conventional Pt/C or RuO$_2$. The dual-phase NiV$_2$O$_6$/AgMn catalysts on the air cathode of a zinc-air battery lead to a stable discharge–charge voltage gap of 0.83 V at 50 mA cm$^{-2}$, with a specific capacity of 660 mAh g$^{-1}$ and life cycle stabilities of more than 146 h at 10 mA cm$^{-2}$ and 11 h at 50 mA cm$^{-2}$. The proposed new class of dual-phase NiV$_2$O$_6$/AgMn catalysts are successfully applied as pouch-type zinc-air batteries with long-term stability over 33.9 h at 10 mA cm$^{-2}$.

1. Introduction

Considerable demand and progress in alternatives to conventional lithium-ion batteries have led to the aim of commercialization, as such materials would provide an environmentally compatible and sustainable source of electricity.$^{[1]}$ Zinc-air batteries (ZABs) consisting of a non-precious zinc electrode (anode), alkaline electrolytes, membrane separators, and an air-permeable carbon sheet (cathode) have been considered the most promising alternative battery technology that could satisfy the above requirements, with a high specific energy density of up to 1218 Wh kg$^{-1}$. In addition, ZABs can ensure a flat discharge voltage, safety and environmental benefits, and high volumetric energy density compared to most primary batteries at low cost.$^{[3]}$ However, their commercialization has not yet been fully realized because the reaction mechanism of oxygen-based
electrochemistry on the air cathode is sluggish, which causes large overpotentials during the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) and thereby deteriorates the energy efficiency of ZABs.

Because the slow ORR and OER on the air cathode involve four electron transfer reactions, introducing a precious metal-based or metal compound-based bifunctional electrocatalyst (i.e., Ir, Ru, Pt, IrO2, and RuO2) into the air cathode has been demonstrated to improve oxygen catalysis processes.[4] In addition, earth-abundant catalyst materials, such as iron oxides (FeO), manganese oxides (MnO2), cobalt oxides (Co3O4), and nickel oxides (NiO),[5] are also emerging as promising ORR/OER bifunctional electrocatalysts because they are environmentally safe and low cost, and they readily modulate the composition conditions to achieve high catalytic activity for oxygen reactions.[6,7] The catalytic efficiency of metal oxides/metals for the ORR/OER can be further improved by employing defect sites, surface/nanostructure modifications and the formation of composite materials.[8] However, single-phase electrocatalysts are not generally sufficient to simultaneously perform both the ORR and OER, resulting in an imbalance of the ORR/OER during charge and discharge processes, respectively, and thus poor operational stability in alkaline electrolytes.[9]

One desirable approach for securing dual catalytic functions is to develop a dual-phase heterogeneous electrocatalyst by incorporating ORR- and OER-active elements into advantageous nanostructures.[10] For example, promising ORR elements (typically metals such as silver (Ag) and manganese (Mn)) can be physically or chemically bound to OER elements (typically metal oxides such as NiO and Co3O4).[11] A dual-phase heterogeneous configuration can promote further benefits, such as an increased interfacial area and charge transfer/redistribution, which are not present in conventional single-phase electrocatalytic nanostructures. Although several studies have been proposed to derive dual-phase electrocatalytic materials using electrospinning/calcination processes, wet chemistry and sequential electrodeposition, they still suffer from time-consuming and rigorous synthetic steps, thus decreasing the reproducibility, cost competitiveness and operational stability.[12] Therefore, it has long been desired to establish a simple but efficient binding strategy for ORR and OER elements to derive a new class of dual-phase heterogeneous electrocatalysts without sacrificing any catalytic efficiency.

Here, we report a new class of hydrothermally grown dual-phase heterogeneous electrocatalysts consisting of ORR and OER elements that can be used to achieve bifunctional activities and operational stability superior to those of conventional Pt/C or RuO2. By employing a hydrothermal synthesis process with high-purity precursor solutions, AgMn heterometal nanoparticles as ORR elements are homogeneously dispersed on top of a nickel vanadium oxide (NiV2O6) nanostructure as the OER element to form desirable dual-phase bifunctional electrocatalysts. The resultant NiV2O6/AgMn bifunctional electrocatalysts allow an efficient charge transfer/redistribution and increased surface area, leading to a half-wave potential of 0.83 V for the ORR and an OER overpotential of 1.39 V at 10 mA cm−2. The potential gap, ΔE (ΔE = E1/2,ORR − E1/2,OER), of NiV2O6/AgMn is 0.56 V. The use of the NiV2O6/AgMn catalyst as an electrode in a zinc (Zn)-air battery also shows an excellent discharge–charge voltage gap of 0.83 V at 50 mA cm−2, with a specific capacity of 660 mAh g−1 and life-cycle stabilities of more than 146 h at 10 mA cm−2 and 11 h at 50 mA cm−2, thus outperforming the other previously reported dual-phase catalysts. Furthermore, the NiV2O6/AgMn catalyst is successfully applied to the realization of a zinc-air pouch cell with long-term stability for more than 33.9 h at 10 mA cm−2.

2. Results and Discussion

2.1. Preparation of a NiV2O6/AgMn Nanostructure via a Sequential Hydrothermal Process

The dual-phase NiV2O6/AgMn nanostructure was prepared via a sequential hydrothermal reaction process (Figure 1a). Initially, a high-purity precursor solution of nickel nitrate hexahydrate (Ni(NO3)2·6H2O) and ammonium metavanadate (NH4VO3) was heated to 150 °C for 12 h in a sealed autoclave, producing a highly crystalline NiV2O6 nanostructure on top of a fluorine-doped tin oxide (FTO) substrate. Then, the subsequent hydrothermal process with silver nitrate hexahydrate (AgH12NO9) and manganese nitrate hexahydrate (Mn(NO3)2·6H2O) precursor was conducted using the sealed autoclave and NiV2O6/FTO substrate (for more details, see Experimental Section). Figures S1 and S2, Supporting Information show the XRD patterns of the prepared catalysts. The corresponding high-resolution scanning electron microscopy (SEM) image of the films after the initial and subsequent hydrothermal processes (Figure 1b,c, respectively) showed that a number of AgMn heterometal nanoparticles were successfully dispersed on top of a distinctive NiV2O6 2D sheet-like structure, indicating the formation of a dual-phase NiV2O6/AgMn heterogeneous nanostructure (for more details, see Figures S3–S7, Supporting Information).

In contrast to the single-phase NiV2O6 electrocatalyst, which favors the OER process (4OH− → O2 + 4e− + 2H2O), the dual-phase NiV2O6/AgMn heterogeneous nanostructure was hypothesized to be highly beneficial to both the OER and ORR (O2 + 2H2O + 4e− → 4 OH−) processes by i) facilitating fast interfacial electron transfer from AgMn to NiV2O6, ii) increasing the number of active sites and the surface binding energy, and iii) minimizing the ORR/OER overpotentials required for the above-mentioned reactions (Figure 1d,e).

2.2. Structural and Morphological Analysis of the NiV2O6/AgMn Nanostructure

To investigate the structure of the dual-phase NiV2O6/AgMn obtained by the sequential hydrothermal process, transmission electron microscopy (HRTEM) measurements were performed on the single-phase NiV2O6 and dual-phase NiV2O6/AgMn samples. The TEM image of NiV2O6 exhibited a 2D nanosheet structure, which is consistent with the SEM analysis described above (Figure 2a). The high-magnification TEM image of NiV2O6 clearly indicated a high crystallinity of the primary nanoparticles, and the observed lattice fringes with interplanar distances of 0.220 and 0.247 nm corresponded to the (210) and (013) crystal planes (ICCD card No: 98-015-8112) of NiV2O6 (Figure 2b). The selected area electron diffraction (SAED) ring patterns on NiV2O6 showed a polycrystalline feature with (111), (12-2), (030), (20-2), and (311) facets (ICCD card No: 98-015-8112) (Figure 2c).
Figure 1.  a–c) A schematic representation of facile hydrothermal synthesis with high-purity metal ion precursors for producing the single-phase NiV\(_2\)O\(_6\) 2D nanosheet structure and dual-phase NiV\(_2\)O\(_6\)/AgMn nanosheets. d,e) Schematic illustration of OER and ORR processes across the single-phase NiV\(_2\)O\(_6\) and dual-phase NiV\(_2\)O\(_6\)/AgMn nanosheet surfaces.

The electron dispersive X-ray spectroscopy (EDX) measurement on NiV\(_2\)O\(_6\) provided a vivid elemental color mapping image confirming the surface distributions of Ni, V, and O elements (Figure 2d).

Interestingly, Figure 2e–g show a series of TEM images in which AgMn heterometal nanoparticles are homogeneously anchored on top of the NiV\(_2\)O\(_6\) nanosheets; the AgMn metal nanoparticles are thought to be precipitated in their metal oxide form, similar to AgMnO\(_x\). The obtained images indicated that the lattice spacing of 0.271 nm was associated with the (120) plane (ICDD card No: 98-015-8112) of NiV\(_2\)O\(_6\), whereas the interplanar spacings of 0.210 and 0.237 nm corresponded to the (221) plane (ICDD card No: 00-001-1234) of Mn and the (111) plane (ICDD card No: 00-001-1164) of Ag, respectively (see more details in Figures S8 and S9, Supporting Information). Additionally, the TEM images also indicated that the NiV\(_2\)O\(_6\) spherical particles in the 2D nanosheet structure are strongly interconnected with the AgMn heterometal nanoparticles, implying an increase in the surface area and improvement of charge transport/redistribution during the electrocatalytic process (Figure 2g). The corresponding EDX elemental color mapping distribution showed a uniform distribution of Ag (magenta) and Mn (green) metal nanoparticles across the entire surface of NiV\(_2\)O\(_6\), confirming successful hydrothermal metal particle decoration on the catalyst surface (Figure 2h). Therefore, the overall SEM and TEM analysis strongly supported the idea that our proposed sequential hydrothermal approach was successfully applied to the formation of dual-phase NiV\(_2\)O\(_6\)/AgMn heterogeneous nanostructures.

2.3. Probing the Electrocatalytic OER and ORR Activity of NiV\(_2\)O\(_6\)/AgMn

To clarify the impact of AgMn on the electrocatalytic activity of NiV\(_2\)O\(_6\), various electrocatalysts, including single-phase NiV\(_2\)O\(_6\), dual-phase NiV\(_2\)O\(_6\)/Ag, NiV\(_2\)O\(_6\)/Mn, and NiV\(_2\)O\(_6\)/AgMn, were
evaluated using linear sweep voltammetry (LSV) at a scan rate of 5 mV s$^{-1}$ in a 1 m KOH solution. We found that the single-phase NiV$_2$O$_6$ exhibits oxygen evolution overpotentials ($\eta_{10}$) at 360 mV @ 10 mA cm$^{-2}$, which signifies a more positive overpotential than that of the commercial RuO$_2$ electrode ($\eta_{10}$ to 330 mA cm$^{-2}$) (Figure 3a). However, significant improvements (295 and 260 mV @ 10 mA cm$^{-2}$) in the OER activity were observed for the dual-phase NiV$_2$O$_6$/Ag and NiV$_2$O$_6$/Mn electrodes compared with those of the single-phase NiV$_2$O$_6$. Moreover, the dual-phase NiV$_2$O$_6$/AgMn electrode showed a much better OER performance and further reduced overpotential (\eta) at 10 mA cm$^{-2}$ (160 mA), and a 345 mV overpotential was needed to obtain a current density of 100 mA cm$^{-2}$. Notably, the LSV polarization curves (brown dotted lines) for the NiV$_2$O$_6$/AgMn catalyst after continuous OER electrolysis (189.6 h) exhibited only a slight anodic shift in the potential of 0.019 V versus RHE, indicating that the NiV$_2$O$_6$/AgMn structures are stable electrocatalysts for the OER. These excellent results mainly originated from
a strong electronic interaction\textsuperscript{[12b]} between AgMn and NiV\textsubscript{2}O\textsubscript{6}, which tunes the electronic structure of the catalyst to facilitate Ni\textsuperscript{2+} to Ni\textsuperscript{4+} or Ni\textsuperscript{4+}\textsuperscript{[13–17]} (Figure S10, Supporting Information). The amount of O\textsubscript{2} generated during the OER process of the NiV\textsubscript{2}O\textsubscript{6}/AgMn electrocatalysts was assessed using a gas chromatographic technique. Chronopotentiometry was performed in 1.0 M KOH with a constant current density of 10 mA cm\textsuperscript{-2} at 5 h. The time dependence of oxygen evolution in NiV\textsubscript{2}O\textsubscript{6}/AgMn catalysts (Figure S11, Supporting Information) showed that the Faradaic efficiency for the OER reached nearly 100%.

The reaction kinetics of the OER process in various electrocatalysts, including conventional RuO\textsubscript{2}, NiV\textsubscript{2}O\textsubscript{6}, NiV\textsubscript{2}O\textsubscript{6}/Ag, NiV\textsubscript{2}O\textsubscript{6}/Mn, and NiV\textsubscript{2}O\textsubscript{6}/AgMn, were also evaluated using Tafel analysis (Figure 3b). The Tafel slopes of the above materials were calculated to be 52.1, 53.2, 48.4, 43.2, and 39.1 mV dec\textsuperscript{-1}, respectively. Among all of the samples, the NiV\textsubscript{2}O\textsubscript{6}/AgMn catalyst
exhibited the fastest kinetics and the smallest Tafel slope, implying that AgMn anchored on top of NiV2O6 can modulate the catalytic activity by tuning the intrinsic kinetics. The turnover frequencies (TOFs) of NiV2O6/AgMn for the OER are superior to those of the individual NiV2O6, NiV2O6/Mn, and NiV2O6/Ag catalysts. At an overpotential of 320 mV versus RHE (details of the calculation are given in the Supporting Information), the TOF of NiV2O6/AgMn was calculated to be 0.344 s⁻¹, which was 28-fold, 53-fold, and 138-fold those for the OER on NiV2O6/Mn (0.0123 s⁻¹), NiV2O6/Ag (0.0065 s⁻¹), and NiV2O6 (0.0025 s⁻¹), respectively. The higher TOF value of NiV2O6/AgMn is consistent with the improved OER process rate. In addition, the electrochemical operational durability of the OER was assessed using chronomperometric techniques at an overpotential of 400 mV versus RHE (1 m KOH) for NiV2O6 (≥185 h) and 190 mV versus RHE (1 m KOH) for NiV2O6/AgMn for 189.6 h, resulting in reductions in the current density of 13% and 5%, respectively (Figure 3c).

In parallel, the ORR catalytic activity of the NiV2O6, NiV2O6/Ag, NiV2O6/Mn, NiV2O6/AgMn catalysts was evaluated using a rotating disc electrode (RDE) at 1600 rpm in an O₂-saturated 0.1 m KOH electrolyte (Figure 3d). The optimized NiV2O6/AgMn catalysts exhibited a larger diffusion-limited current density of 13% and 5%, respectively (Figure 3c).

2.4. Chemical Interactions Among the Components of NiV2O6/AgMn

To understand the origin of the excellent dual catalytic activity of NiV2O6/AgMn, we performed X-ray photoemission spectroscopy (XPS) to analyze the electronic interactions of the elements on the catalyst surface (see XPS survey and C 1s XPS spectra of NiV2O6, and NiV2O6/AgMn catalysts in Figures S16 and S17, Supporting Information). The XPS survey for NiV2O6/AgMn showed peaks corresponding to NiV2O6, NiV2O6/Mn, NiV2O6/Ag, and Ni(OH)2, respectively (Figure 4b). The high-resolution V 2p spectrum (Figure 4b) showed that the Ni 2p peaks with binding energies of 517.0/524.5 eV corresponding to the V 2p3/2 and V 2p1/2 spin orbitals were attributed to V4⁺ oxidation state, providing sufficient bond strength for intermediate reactions at the catalyst surface, leading to optimized OER performance. [32–34] However, after a second annealing process of NiV2O6/AgMn at 400 °C, two distinct metal peaks of Ni were detected at 853.9 (Ni 2p3/2) and 871.3 eV (Ni 2p1/2). [26] In addition, the Ni 2p binding energies of NiO (854.9/872.6 eV) [23,24] and Ni(OH)2 (856.2/874.9 eV) [25] in NiV2O6/AgMn were negatively shifted compared to that of pristine NiV2O6 (Figure 4b). Interestingly, after a second annealing process of NiV2O6/AgMn at 400 °C, two distinct metal peaks of Ni were detected at 853.9 (Ni 2p3/2) and 871.3 eV (Ni 2p1/2). [36] In addition, the Ni 2p core level XPS spectrum in Figure 4b shows a peak at 858.0 eV [20–23] suggesting the formation of Ni³⁺ on the NiV2O6/AgMn surface after AgMn decoration. The oxidation peak associated with Ni³⁺ corresponds to an active site for the OER, and consequently, the enhanced Ni³⁺ oxidation state provides sufficient bond strength for intermediate reactions at the catalyst surface, leading to optimized OER performance. [32–34]
Figure 4c. The binding energies of the V 2p\textsubscript{3/2} spin orbital peaks of 515.8 and 517.8 eV were also associated with V\textsuperscript{5+} and V\textsuperscript{4+}, respectively.\cite{35,36} However, for NiV\textsubscript{2}O\textsubscript{6}/AgMn, the peak of V\textsuperscript{5+} (516.9 eV) and the peak of V\textsuperscript{4+} (516.1 and 523.7 eV)\cite{37} shifted to lower binding energies, implying an electronic connection with adjacent metal particles. Indeed, we found that the Mn 2p core level of NiV\textsubscript{2}O\textsubscript{6}/AgMn showed distinct metallic Mn\textsuperscript{0} peaks at 637.2 and 651.8 eV for the Mn 2p\textsubscript{3/2} spin orbital due to the reduction of some of the MnO\textsubscript{x} to the metallic state Mn\textsuperscript{0} (Figure 4d)\cite{38} (a detailed view of the XPS spectrum of the AgMn nanoparticles is shown in Figure S18, Supporting Information). For the core-level Ag spectrum, two distinct metal (Ag\textsuperscript{0}) peaks corresponding to Ag 3d\textsubscript{5/2} and Ag 3d\textsubscript{3/2} and a splitting energy of 6 eV for NiV\textsubscript{2}O\textsubscript{6}/AgMn were located at 368.1 and 374.1 eV\cite{39} (Figure 4e). Additional fitting peaks for the Ag 3d\textsubscript{5/2} and Ag 3d\textsubscript{3/2} spin orbitals at 367.2, 373.5, and 368.7 eV corresponded to the Ag\textsuperscript{2+} and Ag\textsuperscript{3+} states, respectively.\cite{40,41}
oxygen species (530.6 eV for O$_{2}^{2-}$, O$^{-}$), hydroxyl species or surface adsorbed oxygen (531.6 eV for OH or O$_{2}$) and adsorbed water molecules (532.6 eV for H$_{2}$O). The relative amounts of the four oxygen species in the NiV$_{2}$O$_{6}$ and NiV$_{2}$O$_{6}$/AgMn catalysts were calculated as the sum of the relative areas of the various peaks, and the results are listed in Table S4, Supporting Information. The relative amount of 35.89% highly oxidative oxygen species (surface peroxides O$_{2}^{2-}$ and O$^{-}$) on the NiV$_{2}$O$_{6}$/AgMn catalyst surface has been reported to strongly correlate with the concentration of surface oxygen species contributing to superior ORR and OER activity.

Furthermore, the negative shift of the Ni and V binding energies of NiV$_{2}$O$_{6}$/AgMn suggests rapid electron transfer from AgMn metal particles to NiV$_{2}$O$_{6}$ and an increase in the electron density around NiV$_{2}$O$_{6}$. These core-level shifts are substantially more sensitive to the modulated electronic properties of NiV$_{2}$O$_{6}$/AgMn, which can result in partial loss of oxygen in the NiV$_{2}$O$_{6}$ lattice, resulting in oxygen vacancies. The presence of oxygen vacancies (OVs) was confirmed by a strong signal at g = 2.004 in the electron paramagnetic resonance (EPR) spectrum, which was strongly correlated with the presence of unpaired electrons (Figure 4g). Therefore, the presence of AgMn metal and oxygen vacancies was confirmed in NiV$_{2}$O$_{6}$/AgMn, which is very beneficial for tuning the surface catalytic activity and electronic properties and thus enhancing their OER/ORR activity.

In addition, the confirmed AgMn metal and oxygen vacancies generated an excess electron density in the catalyst to enhance electrical conductivity and improve charge transfer during electrolysis of the OER and ORR. This conclusion was further substantiated by Nyquist plot analysis. Figure 4h shows the Nyquist plots obtained from fitting the electrochemical impedance spectroscopy (EIS) results of the NiV$_{2}$O$_{6}$, NiV$_{2}$O$_{6}$/Ag, NiV$_{2}$O$_{6}$/Mn, and NiV$_{2}$O$_{6}$/AgMn samples using the simplified Randles equivalent circuit (Figure S19 and Table S5, Supporting Information). The charge transfer resistance ($R_{ct}$) values for NiV$_{2}$O$_{6}$, NiV$_{2}$O$_{6}$/Ag, NiV$_{2}$O$_{6}$/Mn, and NiV$_{2}$O$_{6}$/AgMn were 6996, 4300, 1172, and 539, respectively, exhibiting the lower internal resistance and faster charge transfer ability of NiV$_{2}$O$_{6}$/AgMn. Furthermore, type III N$_{2}$ isotherm curves with H$_{3}$ hysteresis loops were also observed for all of the catalysts, indicating the presence of pores in the samples (Figure 4i and Figure S20a, Supporting Information). The Barrett–Joyner–Halenda pore size distribution curve of the sample shows that the mesopore size diameter was 3–50 nm (Figure S20b and Table S6, Supporting Information). The specific surface area of NiV$_{2}$O$_{6}$/AgMn was 196 m$^{2}$ g$^{-1}$, which was more than twice that of NiV$_{2}$O$_{6}$ (c.f., 90, 120, and 135 m$^{2}$ g$^{-1}$ for NiV$_{2}$O$_{6}$/Ag, NiV$_{2}$O$_{6}$/AgMn, and NiV$_{2}$O$_{6}$/Mn, respectively).

2.5. Understanding the Phenomenon of the Presence of AgMn Metal and Oxygen Vacancies Using DFT Calculations

To clarify the reason for the presence of AgMn metal and the formation of oxygen vacancies on top of NiV$_{2}$O$_{6}$, we performed calculations based on density functional theory (DFT) with a simple crystal structure of AgMnO$_{2}$, which has a trigonal symmetry [SG(space group): R-3m] (R1), as revealed by grazing incident wide-angle X-ray scattering (GIWAXS) measurements (see Figure S21 and Table S7, Supporting Information). Figure S5a shows that Ag$^{+}$ (d$^{10}$) forms a triangular net in the ab plane and that Mn$^{3+}$ (d$^{4}$) forms a MnO$_{2}$ layer by sharing the edge of MnO$_{6}$ octahedra in the ab plane, while the MnO$_{2}$ layer is sandwiched between Ag triangular nets along the c direction. For the Ag triangular net of AgMnO$_{2}$, the Ag$^{+}$ ions interact with the nearest O$^{2-}$ of the MnO$_{6}$ layer along the c direction (Figure 5b). The interaction between Ag$^{+}$ (d$^{10}$) ions causes instability in the AgMnO$_{2}$ system because the fully occupied antibonding level increases their instability. To relieve this instability, AgMnO$_{2}$ undergoes a phase transition by distorting its structure or developing Ag vacancies. For this reason, the experimental Ag-deficient Ag$_{0.9}$MnO$_{2}$ structure is distorted from the ideal R-3m structure, inducing crystallization of monoclinic C2/m. Indeed, a negative frequency indicating the dynamical instability of the structure was observed in the R-3m structure, while the negative frequency disappeared in the monoclinic C2/m structure, implying that there is a possibility of
Figure 6. a) Discharge polarization plots and the corresponding power density curves for NiV2O6, NiV2O6/Ag, NiV2O6/Mn, and NiV2O6/AgMn catalyst-based Zn-air battery cells. b) Galvanostatic voltage-specific capacity discharge curves of Zn-air battery cells with different catalysts when discharged at 10 mA cm\(^{-2}\). c) NiV2O6/AgMn catalyst-based Zn-air battery cell when discharged at 20 and 50 mA cm\(^{-2}\). d,e) Comparison of the galvanostatic discharge–charge voltage cycling profiles for NiV2O6 and NiV2O6/AgMn catalyst-based Zn-air battery cells at 10 mA cm\(^{-2}\). f) A photograph of a two-electrode liquid homemade rechargeable battery. g) Discharge–charge voltage cycling stabilities of the NiV2O6/AgMn catalyst-based Zn-air battery cell at 50 mA cm\(^{-2}\).
The NiV$_2$O$_6$/AgMn Zn-air battery cell exhibited a power density of 119 mW cm$^{-2}$ at 180 mA cm$^{-2}$, which is significantly higher than the density of 108 mW cm$^{-2}$ for the NiV$_2$O$_6$/Mn-based Zn-air battery cell at 164 mA cm$^{-2}$, and it also far exceeds those of the NiV$_2$O$_6$/Ag-based Zn-air battery (100 mW cm$^{-2}$ at 152 mA cm$^{-2}$) and the NiV$_2$O$_6$-based Zn-air battery (80 mW cm$^{-2}$ obtained at 154 mA cm$^{-2}$). The open circuit voltages (OCVs) of Zn-air batteries with NiV$_2$O$_6$/AgMn, NiV$_2$O$_6$/Mn, NiV$_2$O$_6$/Ag, and NiV$_2$O$_6$ catalysts are ≈1.53, ≈1.36, ≈1.51, and ≈1.34 V, respectively, as determined from the polarization profiles.

Galvanostatic discharge polarization curves are shown in Figure 6b. When the current density was 10 mA cm$^{-2}$, the Zn-air battery catalyzed by the NiV$_2$O$_6$/AgMn sample delivered a specific capacity of 795.3 mAh g$^{-1}$, surpassing those of the NiV$_2$O$_6$/Mn, NiV$_2$O$_6$/Ag, and NiV$_2$O$_6$-based Zn-air cells, which were 681.6, 603.4, and 461.2 mAh g$^{-1}$, respectively. Notably, the zinc-air battery catalyst with the NiV$_2$O$_6$/AgMn sample can withstand high current densities of 20 and 50 mA cm$^{-2}$ and provide specific capacities of 734.4 and 660 mAh g$^{-1}$, respectively (Figure 6c).

Charge–discharge cycle tests of NiV$_2$O$_6$- and NiV$_2$O$_6$/AgMncatalyzed Zn-air batteries were also performed by galvanostatic measurement conducted with 20 min cycles. In each cycle, the cell was charged for 10 min and then discharged for 10 min. At room temperature and a constant current density of 10 mA cm$^{-2}$, the NiV$_2$O$_6$/AgMn-catalyzed Zn-air battery displayed cyclic discharge and charge potentials of 1.14 and 2.02 V, corresponding to a small voltage gap (ΔV) of 0.88 V. In addition, the superior performance of NiV$_2$O$_6$/AgMn-catalyzed Zn-air batteries was advantageous compared to that of NiV$_2$O$_6$-catalyzed Zn-air batteries, with discharge and charge potentials of 1.06 and 2.01 V, leading to a voltage gap (ΔV) of 0.95 V. Therefore, the lower charge–discharge voltage gap and stable performance with rechargeability obtained for 146.8 h (as shown in Figure 6d, e) in the Zn-air battery with the NiV$_2$O$_6$/AgMn catalysts were much better than those in the NiV$_2$O$_6$-catalyzed zinc-air battery (94.8 h). The cycling performance of the catalyst was evaluated using the Zn-air battery cell shown in Figure 6f. We further tested the stability of NiV$_2$O$_6$/AgMn, as shown in Figure 6g. The individual cycle involved charging for 30 min and then discharging for 30 min, and the performance of the Zn-air battery with the NiV$_2$O$_6$/AgMn catalyst remained almost unchanged (ΔV = 0.83 V) for more than 11 h, even at a high current density of 50 mA cm$^{-2}$, demonstrating that the NiV$_2$O$_6$/AgMn structure is stable and practical.

Moreover, we designed a special structure in the form of pouch cells to drive zinc-air batteries. A polypropylene-coated aluminum pouch was used as a package, and a pinhole was drilled at the catalyst reaction side to allow air to enter and exit. In addition, a polytetrafluoroethylene (PTFE) film was attached to prevent leakage and evaporation of the electrolyte through the pinhole so that it could be operated for a long time. A catalyst-coated gas diffusion layer (GDL), glass fiber separator, and zinc metal plate were prepared inside, and aluminum lead tabs were attached to each electrode. After setting the interiors, both sides were sealed by a thermal press machine. Finally, a zinc-air battery was completed by injecting electrolyte into the pouch cell and sealing it. Photographs of the NiV$_2$O$_6$/AgMn catalyst-based rechargeable Zn-air battery pouch cell are shown in Figure 7a–c. A demonstration of lighting an LED house continuously for 33 h was also conducted by connecting three prepared pouch cells (OCV of 4.22 V, while a single battery is 1.40 V) in series to match the voltage (Figure 7d). To connect each cell, ultrasonic welding was used to minimize the electrical resistance. As shown in Figure 7e, f, the Zn-air battery pouch cell catalyzed by NiV$_2$O$_6$/AgMn shows a small charge–discharge voltage gap of 0.81 V, and after 33.9 h of continuous operation, there was no obvious voltage drop (ΔV = 0.808 V), indicating the excellent durability. In contrast, the Zn-air battery pouch cell catalyzed by NiV$_2$O$_6$ presented limited stability of only 25 h, as seen in (ΔV 0.98 V initial to 1.023 V final). For comparison, NiV$_2$O$_6$ and NiV$_2$O$_6$/AgMn catalysts with Zn-air coin cells were also constructed with and without PTFE film (Figure 7g–i). Zn-air batteries with NiV$_2$O$_6$/AgMn catalysts and PTFE film exhibited very stable cyclic discharging and charging for 7.1 h with a smaller voltage gap of 0.87 V than Zn-air batteries with the NiV$_2$O$_6$ catalyst (6.4 h, ΔV = 0.96 V). These results further reveal that NiV$_2$O$_6$/AgMn is a potential candidate for efficient rechargeable Zn-air battery applications.

3. Conclusion

In conclusion, we demonstrated that the proposed new class of dual-phase NiV$_2$O$_6$/AgMn heterogeneous electrocatalysts can be obtained by a sequential hydrothermal method. The strong electronic interactions between highly active NiV$_2$O$_6$ and AgMn catalysts resulted in superior bifunctional electrocatalytic activity for both the ORR and the OER compared to conventional Pt/C or RuO$_2$. By employing TEM and advanced electrochemical analysis methods, we confirmed that the excellent bifunctional electrocatalytic activity of NiV$_2$O$_6$/AgMn was attributed to the synergistic interplay of NiV$_2$O$_6$ with abundant Ag and Mn metal active centers, which can accelerate the catalytic activity due to the increase in active surface sites. In addition, we found that the formation of oxygen vacancies in AgMnO$_2$ and the favorable electronic structure of NiV$_2$O$_6$/AgMn not only lowered the charge transfer resistance but also provided a fast charge transfer rate in the ORR/OER process. The formation of the active intermediate Ni$_{3+}^{2-}$ and highly oxidative oxygen species (O$_2$/$O^-$) on the NiV$_2$O$_6$/AgMn surface also contributed to the additional catalytic support to further enhance the bifunctional activity. The derived NiV$_2$O$_6$/AgMn catalyst was used as an air cathode for highly efficient and stable Zn-air batteries, resulting in an excellent charge–discharge voltage gap of 0.83 V at 50 mA cm$^{-2}$, with a specific capacity of 660 mAh g$^{-1}$ and life cycle stability of more than 146 h at 10 mAc$^{-2}$ and 11 h at 50 mA cm$^{-2}$. Thus, the NiV$_2$O$_6$/AgMn catalyst was successfully applied to the practical application of zinc-air pouch cells with long stability of over 33.9 h at 10 mA cm$^{-2}$. These results provide an example of the successful combination of dual-phase catalysts as a new class of ORR/OER bifunctional electrocatalysts and the prospect of practical applications in the field of Zn-air batteries and energy conversion.

4. Experimental Section

Synthesis of NiV$_2$O$_6$ Nanosheets: NiV$_2$O$_6$ nanosheets were prepared on FTO substrates by a hydrothermal method. Before preparing the NiV$_2$O$_6$ nanosheets, the FTO-coated glass surface (2 cm × 2 cm) was cleaned sequentially with acetone, ethanol, and deionized water in an ultrasonic bath for 10 min each to remove surface impurities. To fabricate
the NiV₂O₆ microsheets, a seed layer of NiV particles was coated on the substrate. Then, 0.01 m nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O and 0.01 m ammonium metavanadate NH₄VO₃ (Sigma-Aldrich, 97%) were mixed with 50 mL of isopropanol and stirred at 45 °C for 35 min to form a homogeneous solution. The FTO substrate was vertically immersed in the solution for 5 min. After rinsing with a mixture of ethanol and deionized water (1:1), the samples were dried at 100 °C under air for 30 min.

To prepare NiV₂O₆ nanosheets in FTO, 0.01 mol of Ni(NO₃)₂·6H₂O and 0.01 mol of NH₄VO₃ together with 50 mL of 0.02 mol of aqueous citric acid solution were vigorously stirred until a homogeneous solution was formed. ≈18 mL of an ethylene glycol (EG) dispersant, 2.6 mmol of a polyvinyl alcohol polymerization agent, and 0.85 mmol of a cetyltrimethylammonium bromide (CTAB)-based surfactant were added to the solution, followed by further stirring at 35 °C for 2 h. The mixed solution was then poured into a Teflon-lined autoclave containing a NiV seed layer-coated FTO plate, sealed in a stainless steel tank, and heated at 120 °C for 10 h. After the hydrothermal reaction, the samples were collected and washed with a mixed solvent of deionized water and ethanol (1:1 v/v ratio) to remove residual ions and excess surfactant. The resulting final sample was calcined in a muffle furnace at a heating rate of 5 °C min⁻¹ for 2 h at 500 °C to successfully obtain mesoporous hierarchical NiV₂O₆ nanosheets.

**Synthesis of AgMn Heterometal Nanoparticles:** Ag/Mn metal nanoparticles were prepared by reacting stoichiometric amounts of the two metal precursors. Briefly, 18 mmol of manganese(II) nitrate hexahydrate Mn(NO₃)₂·6H₂O was mixed in 50 mL (8.4 g, 40 mmol) of weak triprotic citric acid. After that, 20 mg of a mild reducing agent, polyvinylpyrrolidone (2.0 μmol) metal stabilizer, 12 mmol EG (a dispersant and reducing agent), and 2 mmol of a CTAB surfactant were added to the reaction solution, and the mixture was stirred for 1 h to obtain a homogeneous solution. Then, 5 mL of sodium borohydride (NaBH₄) and 16 mmol of silver nitrate hexahydrate (AgNO₃) source mixture were added to the solution, and stirring was continued in a reflux condenser at 40 °C for 30 min to obtain a homogeneous solution. The resulting solution was transferred to a Teflon-lined autoclave and heated at 150 °C for 1 h. After the hydrothermal reaction was completed, the AgMn metal precursor was recovered from the liquid by centrifugation, followed by repeated washing with acetone. The resulting...
A three-electrode assembly in 0.1 m KOH solution used a sample-coated RDE (BioLogic Science Instruments) connected to a DY2300 potentiostat. The potentiometer was equipped with a Nova impedance spectrum analyzer. EIS measurements were performed on a standard module of the ohmic drop electrochemical workstation tested with ohmic drop compensation. The sample pore size distribution was characterized using the prepared NiV2O6 nanosheets, sealed in a stainless steel tank, placed in an electric oven, and heated at 120 °C for 1 h. The collected sample was heat treated at 400 °C for 1 h to obtain a final NiV2O6/AgMn electrode material.

Characterizations of Dual-Phase NiV2O6/AgMn: X-ray diffraction analysis was performed on an X’Pert PRO operated at 40 kV using Cu Kα radiation (λ = 1.5406 A). The nitrogen adsorption and desorption isotherms of the prepared samples were investigated with a Micromeritics ASAP 2020 analyzer. The sample pore size distribution was characterized using the Barrett–Joyner–Halenda model. The chemical composition and valence state of the metal elements in the sample were investigated using XPS (ESCALAB-MKII) (hv = 1486.6 eV). Morphological and elemental mapping of the samples were analyzed by field emission SEM (Hitachi). The incident angle of each X-ray beam was set as 0.1°, and the scattering angles were determined from the positions of the reflected X-ray beam from the silicon substrate using precalibrated silver behenate.

Electrochemical OER and ORR Activities of Dual-Phase NiV2O6/AgMn: The electrocatalytic OER experiments were conducted with an electrochemical workstation (Interface1010 potentiostat/galvanostat/ZRA) with a three-electrode setup. The sample prepared on a substrate was used as a working electrode (active area of 0.2 cm²). A graphite rod and Hg/HgO (NaOH, 1 m) were used as the counter and reference electrodes, respectively. The potential was measured relative to the Hg/HgO electrode followed by the calibration to the RHE according to the Nernst equation: E_RHE = E_Hg/HgO + 0.059 × pH + 0.5 × log i. LSV and Tafel plots were recorded using an Autolab electrochemical analyzer coupled with a vacuum chamber (p = 10⁻¹³ Torr). The samples were 0.201 m away from the CCD detector. The incident angle of each X-ray beam was set as 0.1°, and the scattering angles were determined from the positions of the reflected X-ray beam from the silicon substrate using precalibrated silver behenate.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

AgMn, dual-phase electrocatalysts, nickel vanadium oxide (NiV2O6), sequential hydrothermal reaction, Zn-air batteries

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Decoration of AgMn Heterometal Nanoparticles over the NiV2O6 Nanosheets: To decorate the NiV2O6 surface with AgMn metal nanoparticles, AgMn metal nanoparticles were directly deposited on the NiV2O6 surface by a hydrothermal method. 30 mg of AgMn metal nanoparticles was continuously sonicated in 50 mL of acetyl acetone nanoparticle capping agent for 10 min to ensure uniform dispersion. Then, the AgMn metal nanoparticle dispersion was transferred to a Teflon-lined autoclave containing the prepared NiV2O6 nanosheets, sealed in a stainless steel tank, placed in an electric oven, and heated at 120 °C for 1 h. The collected sample was heat treated at 400 °C for 1 h to obtain a final NiV2O6/AgMn electrode material.

References

1. Davari, D. G. Ivey, Sustainable Energy Fuels 2018, 2, 39.
2. J. Fu, R. Liang, G. Liu, A. Yu, Z. Bai, L. Yang, Z. Chen, Adv. Mater. 2018, 31, 1805230.
3. a) Z. P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. Chen, Nat. Energy 2018, 3, 279; b) B. Nykvist, M. Nilsson, Nat. Clim. Change 2015, 5, 329.
4. a) J. Chen, B. Lim, E. P. Lee, Y. Xia, Nano Today 2009, 4, 81; b) V. Petrykin, K. Macounova, O. Shlyakhutin, P. Kriti, Angew. Chem., Int. Ed. 2010, 49, 4813; c) Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, J. Phys. Chem. Lett. 2012, 3, 399; d) Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, M. Jarosnec, S. Z. Qiao, J. Am. Chem. Soc. 2016, 138, 16174; e) S. Chevertko, S. Goiger, O. Kasian, N. Kulyk, J.-P. Gratzel, A. Savan, B. R. Shrestha, S. Merzlikin, B. Breitbach, A. Ludwig, K. J. J. Mayrhofer, Catal. Today 2016, 262, 170.
5. a) D. M. Morales, M. A. Kazakova, S. Dieckhofer, A. G. Selyutin, G. V. Golubtsov, W. Schulmann, J. Masa, Adv. Funct. Mater. 2020, 30, 1905992; b) M. A. Kazakova, D. M. Morales, C. Andronescu, K.
[59] J. Yi, D. Ya-Ping, L. Ruilin, F. Jing, G. Rui, L. Dan, B. Zhengyu, H. Yongfeng, Y. Aiping, C. Zhongwei, Nat. Commun. 2020, 11, 5858.

[60] C. Haixin, G. Dongqi, C. Junwei, L. Ruchun, Z. Xiaofeng, Y. Tongwen, W. Yi, S. Shuqin, Chem. Commun. 2020, 56, 10529.