The Effect of Nickel Salt on OMS-2 Nanorods in Oxygen Reduction Reaction

Xinyu Zhang^{1,2} · Jun Zhang² · Yaya Sun¹ · Xiang Liu¹ · Dong-Sheng Li^{1,3}

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Abstract

The practical applications of Pt-based nano-catalysts in oxygen reduction reaction (ORR) have been seriously restricted by their high cost and poor durability. Therefore, it is significantly desirable to explore high active, non-noble metal and low-cost electrocatalysts for ORR. Herein, a series of nickel salts [NiNH₂SO₃, Ni(NO₃)₂, NiSO₄, NiAc₂, NiCl₂, and Ni(acac)₂] doped MnO₂ octahedral molecular sieves (Ni-OMS-2) nanomaterials are successfully synthesized by a simple hydrothermal reaction and used as cathodic ORR electrocatalyst. We also demonstrate that nickel salt has a significant influence on the porous structure, morphology and ORR performance. Notably, comparing with other nickel salts-doped Ni-OMS-2 catalysts, the resulting Ni-OMS-2 with NiNH₂SO₃ dopant exhibits impressive electrocatalytic performance toward ORR in alkaline (0.1 M KOH), with a more positive E_{onset} (0.866 V) and $E_{1/2}$ (0.792 V), as well as high limited diffusion current (5.03 mA/ cm²), respectively. Moreover, it displays superior long-term stability and methanol tolerance than that of commercial Pt/C, and the ORR process follows an ideal 4e⁻ transfer pathway. Such outstanding ORR performance primarily contributes to the well-defined one-dimensional nanorods and nickel salts doping, which are in favor of promoting electron transfer, active sites exposure and intermediates absorption during the catalytic process.

Graphical Abstract



Keywords OMS-2 · Ni dopants · Electrocatalyst · ORR · Nanorod

Jun Zhang junzhang@cqust.edu.cn

- Xiang Liu xiang.liu@ctgu.edu.cn
- ¹ Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, Hubei, China
- ² College of Metallurgy and Materials Engineering, Chongqing Key Laboratory of Nano/Micro Composites and Devices, Chongqing University of Science and Technology, Chongqing 401331, China
- ³ Hubei Three Gorges Laboratory, Yichang 443002, Hubei, China



1 Introduction

As human being enters the twenty-first century, it is of significant theoretical importance and practical meaning to develop green and renewable energy storage technologies and conversion devices due to the increasing concerns about the global traditional energy shortage issue and a series of associated environmental contamination [1, 2]. Among them, metal-air batteries and fuel cells, as the common electric energy storage and conversion devices, have been widely deemed as the most potential portable and auxiliary power generators because of their merits of green, low cost, simple structure, wide operating temperature range, high specific energy and high energy conversion efficiency [3-6]. The electric energy storage and conversion at the fuel cells and metal-air batteries provides a very practical solution for the storage, distribution, transmission and supply of electricity [7-10]. However, the industrial applications of both fuel cells and metal-air batteries have been severely limited by the thermodynamically sluggish kinetics and high polarization of oxygen reduction reaction (ORR) on the cathode [11–15]. In general, the noble metal Pt or Pt-based cathode catalysts have been widely regarded as the most high-efficiency electrocatalysts for ORR [16], however the practical applications have been seriously restricted by their high cost, limited abundance and poor durability [17–19]. Therefore, it is significantly desirable to explore high active, non-noble metal and low-cost electrocatalysts for ORR. [20, 21] Currently, manganese oxides (MnO_x) have been attracted considerable attention in alkaline media toward ORR due to their low cost, abundance, environmental friendliness, and outstanding catalytic performance [22]. Numerous researches have revealed the ORR performance of MnO_x catalyst are strong dependence on the size, morphology, crystal structure and phase [23]. For example, the MnO_x catalyst with Mn³⁺/Mn⁴⁺ redox couple in the octahedral sites and vacancy in solid phase usually possesses excellent electrocatalytic performance toward ORR [24]. On the one hand, the Mn³⁺/Mn⁴⁺ species are regarded as electrochemical mediator for ORR. A larger amount of Mn³⁺ ions are beneficial to increase the Jahn-Teller lattice distortions and regulate the electronic structure, which coud result in an enhanced oxygen adsorption ability and elongated the O–O bond located in adsorbed oxygen [25]. On the other hand, introducing native oxygen defects could manipulate the interaction between oxygen species and catalyst surface, and could enhance O₂ absorption [26]. However, MnO_x as a semiconductor material, the lower electrical conductivity significantly hampered its widespread applications. Therefore, it is highly desired to design advanced



Scheme 1 The synthesis of Ni-OMS-2-1

strategy to improve the electrocatalytic activity of MnO_x catalyst.

To mitigate this drawback, a large number of strategies, such as conductive polymer or carbon introduction, morphology modification and cation doping, have been proposed to achieve outstanding ORR performance [27–32]. Currently, MnO₂ octahedral molecular sieves (OMS-2), with a 4.6×4.6 Å tubular structure, has received special attention in the fields of oxidation reaction, polluted water treatment and ORR [33-35], due to its highly porous structure, high abundance availability, high stability and coexistence of Mn²⁺/Mn³⁺/Mn⁴⁺. [36–39] Especially, the unique OMS-2 material with well-defined one dimensional (1D) nanorod and tunable pore size are considerably conducive to improve the electrical conductivity and enhance the amount of surface active sites for ORR. Furthermore, research has also shown that incorporated cations (e.g., Co, Ni, Cu) appropriately into the lattice matrix of MnO_x are beneficial to achieve superior electrocatalytic performance [40, 41]. Miao group first reported the synthesis of Ni and Co-doped MnO₂ nanomaterials for the efficient ORR, with $E_{1/2}$ at 0.780 V [42]. In 2020, Yang group first reported the synthesis of OMS-2 nanorods filled with different concentrations of Co ions toward ORR via a simple hydrothermal reaction and exhibit outstanding ORR activity. The excellent ORR performance is the result of the following reasons: (i) incorporating cations into tunnel structure tailored the electronic structures and interconversion of Mn⁴⁺/Mn³⁺ redox pair improved the inherent conductivity [43], (ii) as a regulatory substance, cations could effectively manipulated the coordination geometry and oxidation state of MnO₆ octahedron, for stabilizing Mn³⁺ by enhancing Mn–O covalency and increasing the O₂ adsorption ability for next conversion between oxygen and hydroxide [44]. Notably, enormous efforts have been devoted to designing cations doping and constructing OMS-2 nanomaterials for obtain efficient ORR performance, while rarely research has explored the influence of anion doping on the morphology, porous structure as well as ORR activity and durability of OMS-2.

Herein, we report a series of nickel salts doped MnO_2 octahedral molecular sieves Ni-OMS-2 **1–6** nanomaterials by a hydrothermal reaction of KMnO₄, MnSO₄ and various nickel salts (including nickel sulfaminate, nickel nitrate, nickel sulfate, nickel acetate, nickel chloride, and nickel acetylacetonate) for cathodic oxygen reduction reaction

under alkaline condition for the first time (Scheme 1). The effect of nickel salts on the crystal and porous structure, morphology and ORR performance have systematically investigated in this study. Then the optional Ni-OMS-2–1 nanocomposite, which was doped with nickel sulfamate, exhibits the highest catalytic activity in ORR, with an onset and $E_{1/2}$ at 0.866 V *resp.* 0.792 V *vs.* RHE. Meanwhile, the resulting Ni-OMS-2–1 catalyst shows outstanding stability and methanol tolerance relative to commercial Pt/C. These measurements are required for exploring the effect of nickel salts on OMS-2 nanorods in ORR.

2 Experimental

The synthesis of Ni-OMS-2–1: In briefly, Ni-OMS-2–1 was prepared by following these steps: Potassium permanganate (1.8 mmol), manganese sulfate (0.6 mmol), and nickel sulfamate (0.8 mmol) were dissolved in 15 mL deionized water. After Stirring for 30 min, then transferred to a polytetrafluoron-lined reactor, which reacted at 180 °C for 12 h. Finally, the resulting precipitation was centrifuged and washed with deionized water for three times to obtain Ni-OMS-2–1. Other Ni-OMS-2 were synthesized under the same condition.

3 Results and Discussion

As shown in Scheme 1, a series of Ni-OMS-2 nanocomposites have been designed and prepared by a hydrothermal method from KMnO₄, MnSO₄ and various Ni salts with different anion [including Ni(NH₂SO₃)₂, Ni(NO₃)₂, NiSO₄, Ni(Ac)₂, NiCl₂, and Ni(acac)₂]. The final products are denoted as Ni-OMS-2 1-6 corresponding to the Ni salt (Table 1). Then these Ni-OMS-2 1-6 have been characterized by the powder X-ray diffraction (XRD), which were obtained from θ at 5° to 80° at 40 kV and 44 mA. As displayed in Fig. 1a, the crystal phase of only Ni-OMS-2-1 prepared by this hydrothermal method is attributed to OMS-2 (JCPDS 44-0141) [45]. Ni-OMS-2 2 and 3 retained most of the crystal phase of OMS-2, but a small part of crystal phase had been damaged by the doping of $Ni(NO_3)_2$ and NiSO₄, while a majority of OMS-2 phase of Ni-OMS-2 4 and 5 had been destroyed by the doping of $Ni(Ac)_2$ and NiCl₂. Surprisingly, OMS-2 crystal phase of Ni-OMS-2-6 had been totally destroyed by the doping of Ni(acac)₂, due to the super strong coordination ability of acetyl acetone with Mn^{2+,3+} ions. As shown in Fig. 1b and c, these Ni-OMS-2 **1–6** nanocomposites have also been measured by the N_2 sorption isotherm to determine their BET surface areas, pore sizes and pore volumes, as summarized in Table 1. Except for Ni-OMS-2-2 (23.6 m^2/g), their BET surface area has

Table 1 The surface area, pore volume, pore size, E_{onset} , $E_{1/2}$ and limiting current density of Ni-OMS-2 1–6

Examples	Ni salts	Surface area (m ² /g)	Pore vol- ume (cm ³ /g)	Pore size (nm)	E _{onset} (V)	$E_{1/2}\left(V\right)$	$J_L (mA/cm^2)$
Ni-OMS-2–1	$Ni(NH_2SO_3)_2$	43.8	0.38	34.5	0.866	0.792	5.03
Ni-OMS-2-2	$Ni(NO_3)_2$	23.6	0.44	75.3	0.848	0.764	5.66
Ni-OMS-2-3	$NiSO_4$	47.9	0.36	29.8	0.856	0.755	5.21
Ni-OMS-2-4	Ni(Ac) ₂	49.0	0.26	20.8	0.836	0.73	5.31
Ni-OMS-2-5	NiCl ₂	48.7	0.35	28.4	0.842	0.725	5.32
Ni-OMS-2–6	Ni(acac) ₂	32.4	0.07	9.0	0.832	0.635	4.96



Fig. 1 a XRD, b BET and c pore diameter distribution of Ni-OMS-2 1-6

increased a lot in comparison to OMS-2 (26.45 m^2/g). The pore volume and size of Ni-OMS-2–6 are only $0.07 \text{ cm}^3/\text{g}$ and 9.0 nm, suggesting tunnel structure of OMS-2 had been totally destroyed. Moreover, the morphology and microstructure of these Ni-OMS-2 1-6 nanocomposites have also been characterized by TEM. In Fig. 2, only Ni-OMS-2-1 remains the well-defined nanorods-shaped morphology like pure OMS-2 nanorods (Fig. 2a). Unfortunately, as shown in Fig. 2b-e, the nanorods-shaped structure of Ni-OMS-2 2-5 have been partially destroyed by doping Ni salts, especially that of Ni-OMS-2-6 have been completely destroyed into nanoparticles (Fig. 2f), which are consistent with XRD results. The above results demonstrated that the Ni salts doping has an important influence on the morphology structure of Ni-OMS-2 catalysts, and the NiNH₂SO₃ is more conducive to construct 1D nanorods shapes, which favors the electronic transfer to obtain high ORR activity.

To investigate why Ni-OMS-2–1 is so efficient in ORR, its SEM, HRTEM, energy dispersive X-ray spectrometry (EDX) and Raman spectrum have been further measured. Scanning electron microscope (SEM) images of Ni-OMS-2–1 are further displayed in Fig. 3. It is clear that Ni-OMS-2–1 possesses a nanorods-shaped structure, with a mean diameter and length of approximately 40 nm and 250 nm, respectively. Then, the lattice fringes of Ni-OMS-2–1 have been provided from high-resolution TEM (HRTEM) images.

In Fig. 4, the crystal planes spaces of 0.220 nm, 0240 nm, 0304 nm and 0.488 nm are assigned to OMS-2 (420), (211), (340) *resp.* (200), suggesting Ni-OMS-2–1 still remains the nanorods-shaped structure as pure OMS-2 [43]. For investigating the accurate localization of Ni in Ni-OMS-2–1, its EDX elemental mapping is also recorded in Fig. 5. Figure 5b shows that the homogeneous distributions of K (Fig. 5c), Mn (Fig. 5d), N (Fig. 5e), O (Fig. 5f), Ni (Fig. 5g) and S



Fig. 3 SEM images of Ni-OMS-2-1

(Fig. 5h) throughout Ni-OMS-2–1. In Fig. 5g, the element of Ni is homogeneously dispersed onto the surface of OMS-2, suggesting that Ni atoms have been successfully doped into OMS-2. As illustrated in the Raman spectrum of Ni-OMS-2–1 (Fig. 6), the peaks of Mn–O bond of MnO₆ octahedral in OMS-2 are placed at 496.88 cm⁻¹, 572.09 cm⁻¹ and 628.98 cm⁻¹, being consistent with pure OMS-2 [46].

To investigation of the electrocatalytic ORR performance of different anion doping Ni-OMS-2 catalyst, the electrocatalytic properties of Ni-OMS-2 **1–6** have been evaluated by CV, LSV, stability test and methanol resistance test. As shown in Fig. S1, it can be seen a rectangular-like disappearance and then an obvious cathodic oxygen reduction peaks appearance when the electrolyte changes from N₂-saturated to O₂-saturated, which is evidenced all Ni-OMS-2 based catalysts has positive ORR performance [47]. Additionally, the NiNH₂SO₃ doped Ni-OMS-2 exhibits the most positive

Fig. 2 TEM images of Ni-OMS-2 **1–6** nanocomposites





Fig. 5 a HAADF-STEM image, **b** Combined (S, Ni, K, O, Mn and N), **c** K, **d** Mn, **e** N, **f** O, **g** Ni and **h** S EDX compositional mapping of Ni-OMS-2–1





Fig. 6 Raman spectra of Ni-OMS-2–1 nanocomposite

oxygen reduction peak potential compared with other anions doped Ni-OMS-2, indicating that Ni-OMS-2–1 possesses more ORR activity (Fig. S1) [48]. The compared catalytic

activities of these Ni-OMS-2 1-6 nanocomposites for ORR in O₂ saturated 0.1 M KOH solution at 1600 rpm have been further measured in Fig. 7. All Ni-OMS-2 1-6 nanocomposites exhibit the typical sigmoidal wave (Fig. 7a). As shown in Table 1, it is clear that Ni-OMS-2-1 presents the highest catalytic activity toward ORR with E_{onset} of 0.866 V, $E_{1/2}$ of 0.792 V and J_L of 5.03 mA/cm² in a range of Ni-OMS-2 nanocomposites. The order of half-wave potential of Ni-OMS-2 1-6 nanocomposites in ORR as follow: Ni-OMS-2-1 (0.792 V) > Ni-OMS-2-2 (0.764 V) > Ni-OMS-2-3 (0.755 V)>Ni-OMS-2-4 (0.73 V)>Ni-OMS-2-5 (0.725 V) > Ni-OMS-2-6 (0.635 V). This result is highlighting the dominant factor of Ni salts doping and nanorodsshaped structure in facilitating ORR in our system. To order to study the ORR pathway of Ni-OMS-2 1-6 nanocomposites, LSV curves have also measured at various rotation rates from 800 to 2500 rpm (Figs. 7b and S2). It is obvious that dissolved O₂ is the first-order kinetic, based on the K–L plots [49]. The number of electron transfer for Ni-OMS-2–1 is determined as 4.0 at a potential range of 0.3-0.5 V. Furthermore, Tafel slopes of Ni-OMS-2 1-6 nanocomposites have been calculated in Fig. 7c, Ni-OMS-2-1 exhibits an



Fig.7 a LSV curves of Ni-OMS-2–1-6 recorded in O_2 -saturated 0.1 M KOH solution at 1600 rpm; b LSV curves of Ni-OMS-2–1 tested under various rotation speeds; c Tafel plots of Ni-OMS-2 1–6 nanocomposites; d Chronoamperometric response of the commercial

Pt/C and Ni-OMS-2–1 at 0.5 V and e Chronoamperometric current density of the commercial Pt/C and Ni-OMS-2–1 against operation time after adding CH₃OH. \mathbf{f} H₂O₂ yield and electron transfer number vs. potential of Ni-OMS-2–1

Tafel slope of 99 mV/dec, which is lower than that of Ni-OMS-2–2 (103 mV/dec), Ni-OMS-2–3 (105 mV/dec), Ni-OMS-2–4 (125 mV/dec), Ni-OMS-2–5 (130 mV/dec) and Ni-OMS-2–6 (100 mV/dec). According to the above analysis, the NiNH₂SO₃ doped Ni-OMS-2 catalyst demonstrates the most excellent ORR performance, which is may be ascribe to (i) the reserved MnO₆ octahedral in well-defined Ni-OMS-2–1 nanorods could provide the excellent charge transfer performance [49], (ii) Ni-OMS-2–1 also provides a good condition for stabilizing the Mn³⁺ active site, which is favor of ORR [50], (iii) the Ni atom introduced in Ni-OMS-2–1 exhibit the superior interaction with OH⁻ species, which is contributing to the remarkable ORR activity [51, 52]. Therefore, the optimized Ni-OMS-2–1 catalyst is used for further physical and electrochemical characterizations.

To further explore the stability and anti-methanol penetration, the stability of Ni-OMS-2–1 has been further tested by the chronoamperometry process in Fig. 7d. The result reveals that the Ni-OMS-2–1 still remains 85.2% current density after 10,000 s, which is remarkably higher than that of commercial Pt/C (69%). Meanwhile, the methanol resistance of Ni-OMS-2–1 has also been studied under O₂-saturated KOH solution (0.1 M) in Fig. 7e. The current density of Pt/C catalyst reduces to 45.2% suddenly when the addition of 0.5 M CH₃OH solution, and then the current density will be returns to 72.3% until 1000 s. More interestingly, there is not obvious current density loss for Ni-OMS-2–1 catalyst after the CH₃OH solution added, indicating that Ni-OMS-2–1 exhibited the excellent methanol resistance for ORR [53]. As displayed in Fig. 7f, the calculated H₂O₂ yield and electron transfer number of Ni-OMS-2–1 is 18% and 3.7, respectively, indicating the Ni-OMS-2–1 catalyst follows a predominant four-electron transfer ORR pathway for the reduction of O₂ to OH⁻ [54].

To confirm surface chemical compositions and their valence states of Ni-OMS-2-1, its XPS has further been measured in Fig. 8. As shown in Fig. 8a, Ni, Mn, O, and K elemental signals have obviously recorded in the full XPS spectrum of Ni-OMS-2-1. As displayed in Fig. 8b, Mn 2p spectra of Ni-OMS-2-1 with six peaks centered at 653.35 & 642.19 eV, 654.11 & 642.56 eV and 654.95 & 643.5 eV are corresponding to Mn²⁺, Mn³⁺ and Mn⁴⁺, respectively, the coexistence of Mn²⁺/Mn³⁺/Mn⁴⁺ redox couple could facilitate transferring electrons from Mn^{3+} ion to $O_2(ad)$ to obtain Mn⁴⁺-O_{2(ad)} [24, 55–58]. In Fig. 8c, Ni 2p spectra of Ni-OMS-2-1 is deconvoluted into four peaks located at 872.66 & 849.81 eV and 874.12 & 855.27 eV, which are fitted to Ni (0) and Ni (II), respectively. Interestingly, as shown in Fig. 8d, O 1s spectra of Ni-OMS-2-1 with two peaks placed at 531.88 eV and 530.09 eV are lattice oxygen



Fig.8 XPS of a full spectrum, b Mn 2p, c Ni 2p and d O 1s in Ni-OMS-2–1



Fig. 9 FT-IR of Ni-OMS-2–1 and NiNH₂SO₃

and oxygen vacancy, respectively, which is further increases the oxygen absorption.

In addition, Fourier Transform infrared spectroscopy (FT-IR) of Ni-OMS-2–1 and NiNH₂SO₃ have been recorded in Fig. 9. It is clear that the characteristic peaks of NH₂SO₃^{2–} did not appear in Ni-OMS-2–1, suggesting that only Ni²⁺ had been doped into OMS-2.

4 Conclusion

In summary, a series of nickel salts doped MnO_2 octahedral molecular sieves Ni-OMS-2 **1–6** nanomaterials, via a hydro-thermal reaction of KMnO₄, MnSO₄ and various nickel salts

(including nickel sulfaminate, nickel nitrate, nickel sulfate, nickel acetate, nickel chloride, and nickel acetvlacetonate) have been developed for cathodic oxygen reduction reaction under alkaline condition for the first time. Detailed physical characterizations have verified that Ni-OMS-2-1 exhibits a uniform nanorods-shaped structure with a mean diameter and length of approximately 40 nm and 250 nm, while the tunnel structure of other Ni-OMS-2 nanocomposites had been destroyed by the doping of Ni salts. Then the optional Ni-OMS-2-1 nanocomposite, which was doped with NiNH₂SO₃, exhibits the highest catalytic activity in the ORR, with an E_{onset} and $E_{1/2}$ at 0.866 V resp. 0.792 V vs. RHE. Meanwhile, it displays a good electrochemical stability and methanol tolerance compared with Pt/C, and exhibits a predominant 4e⁻ transfer pathway. It seems that Ni embedded Ni-OMS-2-1 not only provides a good condition for stabilizing the Mn³⁺ active site, but also exhibits the superior interaction with OH⁻ species, which is favor of ORR.

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Declarations

Conflict of interest The authors declare no competing financial interest.

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