Fe–Mn bimetallic oxides-catalyzed oxygen reduction reaction in alkaline direct methanol fuel cells

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Two Fe–Mn bimetallic oxides were synthesized through a facile solvothermal method without using any templates. \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3 \) is made up of \( \text{Fe}_2\text{O}_3 \) and \( \text{Mn}_2\text{O}_3 \) as confirmed via XRD. TEM and HRTEM observations show \( \text{Fe}_2\text{O}_3 \) nanoparticles uniformly dispersed on the \( \text{Mn}_2\text{O}_3 \) substrate and a distinct heterojunction boundary between \( \text{Fe}_2\text{O}_3 \) nanoparticles and \( \text{Mn}_2\text{O}_3 \) substrate. \( \text{MnFe}_2\text{O}_4 \) as a pure phase sample was also prepared and investigated in this study. The current densities in CV tests were normalized to their corresponding surface area to exclude the effect of their specific surface area. Direct methanol fuel cells (DMFCs) were equipped with bimetallic oxides as cathode catalyst, PtRu/C as the anode catalyst and PFM as the electrolyte film. CV and DMFC tests show that \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(3:1) \) exhibits higher oxygen reduction reaction (ORR) activity than \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(1:1), \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(1:3), \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(5:1) \) and \( \text{MnFe}_2\text{O}_4 \). The much superior catalytic performance is due to its larger surface area, the existence of numerous heterojunction interfaces and the synergistic effect between \( \text{Fe}_2\text{O}_3 \) and \( \text{Mn}_2\text{O}_3 \), which can provide numerous catalytic active sites, accelerate mass transfer, and increase ORR efficiency.

1. Introduction

The rapid depletion of fossil fuel and the increase in environmental pollution have driven us to search for sustainable and clean energy resources. Fuel cells have been considered promising power sources owing to their advantage of transforming chemical energy directly into electrical energy. At present, direct methanol fuel cells (DMFCs) are obtaining great attention in virtue of their high energy density, environment friendliness and comparatively lower operating temperature. Furthermore, methanol is convenient and safe for transport and storage, swift to refuel and available at a low price. At present, DMFCs have great potential application as a portable power supply or electric vehicle power supply. Nevertheless, the inertial oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) dynamics and the high cost of noble-based catalysts and proton exchange membrane (PEM) hinder the commercial application of DMFCs.

Recently, polymer fiber membranes (PFMs) have been demonstrated to be an excellent alternative to PEMs for higher performance liquid fuel cells at a reduced cost in our previous study. The fibers in PFMs are neutral and possess pores and gaps, which allow molecules, ions, and liquid fuel to transport or move through the PFM freely. Consequently, the cathode catalysts should have both outstanding tolerance for methanol poisoning and excellent stability. The widely used cathode catalysts are Pt or Pt-based metal alloy catalysts, such as Pt–Co, Pt–Pd, Pt–Ni, and Pt–Fe. However, these catalysts have both ORR and MOR catalytic activity, leading to a mixed potential at the cathode and poisoning by methanol. In terms of lower cost, a variety of non-Pt catalysts, such as Ru–Se, Pd–Ni, Pd–Fe, Co–Se, Fe–N–C, Cu–Fe–S, and Co–O, display ORR catalytic activity and better methanol tolerance than Pt-based catalysts, also have been researched.

Among them, transition metal (Fe, Co, Ni, Mn, etc.) oxides have gained increasing interest as ORR catalysts in virtue of their high activity, low cost and environmental friendliness. In recent years, numerous studies have focused on binary and ternary metal oxides because of their good synergistic effects and good cycle stability. NiCo\(_2\)O\(_4\), KMn\(_2\)O\(_7\), MnFe\(_2\)O\(_4\), and Co–Ni–Te–O have higher ORR catalytic activities and methanol tolerance. For example, the catalytic activity of MnFe\(_2\)O\(_4\) is higher than that of Fe\(_2\)O\(_3\) (ref. 26) and Mn\(_2\)O\(_3\). Nevertheless, the catalytic activity of the mixed compound of Fe\(_2\)O\(_3\) and Mn\(_2\)O\(_3\) has not been discussed.

In this study, we prepared two Fe–Mn bimetallic oxides, namely, Fe\(_2\)O\(_3)/Mn\(_2\)O\(_3\) and MnFe\(_2\)O\(_4\) by a simple solvothermal method. Fe\(_2\)O\(_3)/Mn\(_2\)O\(_3\) is made up of Fe\(_2\)O\(_3\) and Mn\(_2\)O\(_3\) as confirmed via XRD. MnFe\(_2\)O\(_4\) is a pure phase sample. The as-prepared Fe\(_2\)O\(_3)/Mn\(_2\)O\(_3\) exists in the form of porous nanosheets-self-assembled globular structure. The
microspheres are 3–4 μm in diameter and the pore size is about 30 nm. The TEM and HRTEM images show Fe₂O₃ nanoparticles uniformly dispersed on the Mn₂O₃ substrate and a distinct heterojunction boundary between Fe₂O₃ nanoparticles and Mn₂O₃ substrate. MnFe₂O₄ has a hierarchical structure, in which the nanoparticles are 20–30 nm in diameter and create self-assembled globular shapes with diameters of 300–500 nm. The alkaline DMFCs were assembled using Fe₂O₃/Mn₂O₃ or MnFe₂O₄ as cathode catalyst, PtRu/C as anode catalyst, and PFM instead of PEM. CV and DMFC performance tests indicate that the ORR catalytic activity of Fe₂O₃/Mn₂O₃ is superior to that of MnFe₂O₄.

2. Experimental section

2.1 Synthesis of Fe₂O₃/Mn₂O₃ and MnFe₂O₄ catalysts

All reagents were analytical grade and used without further purification. All the reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. The anode catalyst PtRu/C (HiSpec 3000) was bought from Johnson Matthey (UK). Multiwalled carbon nanotubes (TMN7, >95%, OD: 30–50 nm, length: 10–20 mm) were obtained from Chengdu Organic Chemicals Co. Ltd (Chengdu, China). They were produced by natural gas catalytic decomposition over a nickel-based catalyst and purified with dilute hydrochloric acid at 80 °C. The PFM (thickness 1/4 159.3 μm) was purchased from the Nippon Kodoshi Corporation.

In the synthesis of Fe₂O₃/Mn₂O₃, first, 25 mL ethylene glycol (EG) and 0.14 g Tween 80 were dissolved into 25 mL ultrapure water to form a transparent solution. Then, 3 mmol MnSO₄·H₂O, 9 mmol Fe(NO₃)₃·9H₂O and 30 mmol urea were added to the solution, which was then magnetically stirred at 25 °C for 1 h, forming a red-brown solution. Next, the solution was put into a 100 mL Teflon-lined stainless-steel autoclave, which was then heated at 200 °C for 24 h with continuous rotation. The precipitate was washed by centrifugation with anhydrous ethanol and ultrapure water several times until the pH was 7 and the precursor of Fe₂O₃/Mn₂O₃ was obtained by drying it at 80 °C for 12 h. The resultant product was calcined at 800 °C in air for 5 h in a muffle furnace to obtain the Fe₂O₃/Mn₂O₃ sample. Fe₂O₃/Mn₂O₃ with different Fe/Mn ratios of 1 : 1, 1 : 3, 3 : 1 and 5 : 1 were prepared for comparison, which were controlled by altering the molar ratio of MnSO₄·H₂O and Fe(NO₃)₃·9H₂O. The samples were designated as Fe₃O₃/Mn₂O₃(1 : 1), Fe₃O₃/Mn₂O₃(1 : 3), Fe₂O₃/Mn₂O₃(3 : 1) and Fe₂O₃/Mn₂O₃(5 : 1), respectively.

The precursor of MnFe₂O₄ was synthesized following the same solvolithmic method except the raw materials were 2.5 mmol Mn(CH₃COO)₂·4H₂O, 5.0 mmol FeCl₃·6H₂O, 1.0 g polyethylene glycol (PEG), 3.6 g CH₃COONa and 40 mL ethylene glycol (EG). The MnFe₂O₄ catalyst sample was obtained after calcination at 500 °C in air for 4 h.

2.2 Materials characterization

The structures and compositions of the as-prepared Fe₂O₃/Mn₂O₃ and MnFe₂O₄ were characterized via X-ray diffraction (XRD, D/Max 2200PC, Japan) and high-resolution TEM (HRTEM). The morphological properties were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, FEI company Tecnai G2 F20) equipped with energy-dispersive spectrometer (EDS). The Brunauer–Emmett–Teller (BET) method was carried out to determine the pore volumes, pore size and the specific surface area distribution of the samples using a surface area and porosimetry system (ASAP 2460, Micromeritics Instrument Corporation, USA). X-ray photoelectron spectroscopy (XPS) measurements (VG Thermo ESCALAB 250 spectrometer) were used to quantitatively analyze the chemical compositions of samples.

2.3 Electrochemical measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical workstation (CHI 660E, Chenhua Instruments, Shanghai, China). A standard three-electrode system consisted of the catalyst-modified glassy carbon electrode as the working electrode, Hg/HgO electrode as the reference electrode and the Pt network as the counter electrode. The glassy carbon electrode was modified as follows: 4 mg catalyst, 1 mg CNTs, 0.2 mL distilled water, 0.5 mL absolute ethyl alcohol and 50 μL Nafion solution (5 wt%) were ultrasonically dispersed into a homogeneous suspension for about 1 h; then, the suspension was poured on the glassy carbon electrode surface and dried at room temperature.

2.4 Electrode preparation and DMFC measurements

The cathode electrode was a sandwich structure, including catalyst layer, current accumulating matrix and gas diffusion layer. The gas diffusion layer was obtained by mixing 60 wt% acetylene black and 40 wt% polytetrafluoroethylene (PTFE, 30 wt% solution) with ethanol under ultrasonication and pressing the slurry into a thin layer of 0.3–0.5 mm and then treating at 350 °C for 1 h. The catalyst layer was obtained first through mixing 24 mg catalyst, 6 mg CNTs and 6.7 mg 30 wt% PTFE solution into slurry with addition of a certain amount of absolute ethanol; the slurry was pasted on nickel foam (porosity > 95%) and then dried at 80 °C for 2 h. Finally, the cathode was obtained by pressing the catalyst layer on nickel foam and the gas diffusion layer under 2 MPa.

The anode was obtained via mixing PtRu/C (60 wt%) and Nafion solution (5 wt%) at a mass ratio of 1 : 1. The anode preparation process is consistent with that of the cathode without the gas diffusion layer. The loading of PtRu/C was 5 mg cm⁻².

The cathode, PFM and anode were assembled into a fuel cell. At the cathode, the oxygen flow rate was 20 cubic centimeters per minute; the anode aqueous solution was 4 M KOH and 5 M methanol. The structure of PFM-DMFCs was introduced and described in our previous study. A battery testing system (Neware Technology Co., Ltd., Shenzhen, China) was used to measure the performance.
formation of nanopores is due to the release of CO2, which
analysis results shown in Fig. 1(a), it can be inferred that the
diameter and the pore size is about 30 nm. From the XRD
bulk, while the Fe2O3/Mn2O3(3 : 1) catalyst exists as sub-sized
morphologies, which are nanoparticles and nanostructured
Fe2O3 and the formation of Mn2O3 is due to the decomposition
MnFe2O4 and their precursors. The precursor of Fe 2O3/
Mn2O3(3 : 1) (Fig. 2(c)) can be well indexed to Fe2O3 (JCPDS no. 33-0664) and MnCO3 (JCPDS no. 44-1472). However, the diffraction peaks of Fe2O3/Mn2O3(3 : 1) agree with the standard patterns of Fe2O3 (JCPDS no. 33-0664) and Mn2O3 (JCPDS no. 24-0508). It can be illustrated that Fe2O3/Mn2O3(3 : 1) is composed of Mn2O3 and Fe2O3, and the formation of Mn2O3 is due to the decomposition of MnCO3 in its precursor. Moreover, the diffraction peaks of MnFe2O4 and its precursor can be well assigned to the standard patterns of MnFe2O4 (JCPDS no. 10-0319).

FESEM was applied to describe the morphology of Fe2O3/
Mn2O3(3 : 1), MnFe2O4 and their precursors. Fig. 2(a) shows that the precursor of Fe2O3/Mn2O3(3 : 1) exhibits two morphologies, which are nanoparticles and nanostructured bulk, while the Fe2O3/Mn2O3(3 : 1) catalyst exists as sub-sized porous nanosheets-self-assembled globular structure (Fig. 2(b)). The microspheres of Fe2O3/Mn2O3(3 : 1) are 3–4 μm in diameter and the pore size is about 30 nm. From the XRD analysis results shown in Fig. 1(a), it can be inferred that the formation of nanopores is due to the release of CO2, which comes from MnCO3 decomposition during the calcination process. In particular, mesoporous structure is profitable for the rapid transmission of O2, fuel and electrolyte, which can accelerate the redox reaction rate and improve electrochemical performance.

Further, the EDS elemental mappings of MnFe2O4 clearly indicates that the Fe, Mn and O elements are uniformly distributed (Fig. 3(c)–(f)).

The TEM image of Fe2O3/Mn2O3(3 : 1) (Fig. 4(a)) shows that numerous nanoparticles with diameters of 10–30 nm are uniformly dispersed on the substrate. To better characterize the microstructure, a HRTEM image of Fe2O3/Mn2O3(3 : 1) was obtained (Fig. 4(b)). The nanoparticle has a clear lattice fringe with d-spacing of 0.37 nm and 0.22 nm, corresponding to the Fe2O3 phase (104) and (113) plane, respectively, while that of the substrate is 0.38 nm and 0.31 nm, corresponding to the (211) and (122) plane of Mn2O3, respectively. Therefore, Fe2O3/Mn2O3(3 : 1) consists of Fe2O3 and Mn2O3, which is consistent with the XRD results. As shown in Fig. 4(b), a distinct hetero-junction boundary between Fe2O3 nanoparticles and Mn2O3 substrate could be detected as shown by the red line. Fig. 4(c) shows that MnFe2O4 exists as nanospheres with diameters of 300–500 nm. The lattice fringe with d-spacing is 0.25 nm, which can be well indexed to the (311) plane of MnFe2O4 phase (Fig. 4(d)).

XPS was used to measure the surface chemical composition and confirm the Fe/Mn ratio of the as-prepared Fe2O3/Mn2O3 samples. As shown in Fig. 5(a), the common peaks of Fe 2p, Mn 2p and O 1s are present. The element contents are calculated and summarized in Table 1, illustrating that the results of Fe/Mn ratios are approximately equal to the corresponding experimental values. The N2 adsorption–desorption technique at 77 K was used to investigate specific surface areas and pore structures of the as-prepared samples. The nitrogen adsorption–desorption curves (Fig. 5(b)) manifest a type IV isotherm line with a delay loop-line in the P/P0 range of 0.9–1.0 for Fe2O3/Mn2O3 samples and 0.8–1.0 for MnFe2O4, indicating porous structures. The BET surface areas are 12.390, 19.889, 21.73 and 18.165 m2 g–1 for Fe2O3/Mn2O3(1 : 1), Fe2O3/Mn2O3(1 : 3), Fe2O3/Mn2O3(3 : 1) and Fe2O3/Mn2O3(5 : 1), while their pore sizes are 55.7, 32.8, 32.8, and 43.7 nm, respectively. MnFe2O4 illustrates the BET surface area and pore size of 3.05 m2 g–1 and 14.4 nm, respectively.

3. Results and discussion
3.1 Structural and morphological characterization

Fig. 1 displays the XRD patterns of Fe2O3/Mn2O3(3 : 1), MnFe2O4 and their precursors. The precursor of Fe2O3/Mn2O3(3 : 1) can be well indexed to Fe2O3 (JCPDS no. 33-0664) and MnCO3 (JCPDS no. 33-0664). However, the diffraction peaks of Fe2O3/Mn2O3(3 : 1) agree with the standard patterns of Fe2O3 (JCPDS no. 33-0664) and Mn2O3 (JCPDS no. 24-0508). It can be illustrated that Fe2O3/Mn2O3(3 : 1) is composed of Mn2O3 and Fe2O3, and the formation of Mn2O3 is due to the decomposition of MnCO3 in its precursor. Moreover, the diffraction peaks of MnFe2O4 and its precursor can be well assigned to the standard patterns of MnFe2O4 (JCPDS no. 10-0319).

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3.2 ORR activity and DMFC performance

CV tests were performed to describe ORR catalytic activity. The current densities were normalized to their corresponding surface area. Capacitance correction was acquired by subtracting the measured current densities under N₂ from those measured under O₂ under the same condition. Fig. 6(a) shows the CV curves of Fe₂O₃/Mn₂O₃ with different Fe/Mn ratios and MnFe₂O₄ modified glassy carbon electrodes in O₂-saturated 1 M KOH solution. Oxygen reduction peaks of these samples are

Fig. 2 FESEM images of (a) the precursor of Fe₂O₃/Mn₂O₃(3 : 1) and (b) Fe₂O₃/Mn₂O₃(3 : 1); EDS elemental mapping images of Fe₂O₃/Mn₂O₃ ((c) to (f)).

Fig. 3 FESEM images of (a) the precursor of MnFe₂O₄ and (b) MnFe₂O₄ catalyst; EDS elemental mapping images of MnFe₂O₄ catalyst ((c) to (f)).
distinct, demonstrating their ORR catalytic activities. Their oxygen reduction peak current densities and corresponding potentials are summarized in Table 2. The oxygen reduction peak current densities are \( \frac{i}{C_0} = 58.43 \), \( \frac{i}{C_0} = 61.21 \), \( \frac{i}{C_0} = 86.7 \) and \( \frac{i}{C_0} = 47.9 \) mA m\(^{-2} \) for \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(1 : 1) \), \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(1 : 3) \), \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(3 : 1) \) and \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(5 : 1) \), respectively, while the corresponding peak potentials are \( \frac{E}{C_0} = 0.246 \), \( \frac{E}{C_0} = 0.267 \), \( \frac{E}{C_0} = 0.348 \) and \( \frac{E}{C_0} = 0.257 \) V. Clearly, \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(3 : 1) \) has the highest oxygen-reduction peak current density. As compared \( \text{MnFe}_2\text{O}_4 \), although the reduction peak potential of \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(3 : 1) \) is  

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**Fig. 4** (a) TEM and (b) HRTEM images of \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3(3 : 1) \); (c) TEM and (d) HRTEM images of \( \text{MnFe}_2\text{O}_4 \).

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**Fig. 5** (a) XPS survey spectra of \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3 \) with different Fe/Mn ratios; (b) nitrogen adsorption–desorption isotherms and pore size distributions of \( \text{Fe}_2\text{O}_3/\text{Mn}_2\text{O}_3 \) with different Fe/Mn ratios and \( \text{MnFe}_2\text{O}_4 \).
slightly more negative than that of MnFe$_2$O$_4$ (−0.237 V), the oxygen-reduction peak current density is much greater than that of MnFe$_2$O$_4$ (−26.26 mA m$^{-2}$). CV results indicate Fe$_2$O$_3$/Mn$_2$O$_3$ exhibits higher ORR activity than MnFe$_2$O$_4$, which have excluded the effect of their specific surface area, demonstrating Fe$_2$O$_3$/Mn$_2$O$_3$ has more active sites probably introduced by heterojunction boundary between Fe$_2$O$_3$ and Mn$_2$O$_3$.

The polarization and power density curves of Fe$_2$O$_3$/Mn$_2$O$_3$ with different Fe/Mn ratios and MnFe$_2$O$_4$ used as cathode catalysts in DMFCs are shown in Fig. 6(b). The maximum power densities ($P_{\text{max}}$) for these catalysts are 17.09, 15.54, 20.29, 12.88 and 12.15 mW cm$^{-2}$ for Fe$_2$O$_3$/Mn$_2$O$_3$(1 : 1), Fe$_2$O$_3$/Mn$_2$O$_3$(1 : 3), Fe$_2$O$_3$/Mn$_2$O$_3$(3 : 1), Fe$_2$O$_3$/Mn$_2$O$_3$(5 : 1) and MnFe$_2$O$_4$, respectively. These data indicate that the Fe$_2$O$_3$/

Table 1 Elemental composition of Fe$_2$O$_3$/Mn$_2$O$_3$ with different Fe/Mn ratios

| Fe/Mn ratio | Fe 2p (at%) | Mn 2p (at%) | O 1s (at%) | Binding energy |
|-------------|-------------|-------------|------------|----------------|
| 1 : 1       | 708.00 eV   | 639.00 eV   | 528.00 eV  | Fe/Mn          |
| 1 : 3       | 3.77        | 4.03        | 92.2       | 0.94           |
| 3 : 1       | 2.43        | 7.63        | 89.94      | 0.32           |
| 5 : 1       | 9.81        | 2.84        | 87.36      | 3.45           |
|             | 12.10       | 2.34        | 85.56      | 5.17           |

Fig. 6 (a) CV curves of Fe$_2$O$_3$/Mn$_2$O$_3$ with different Fe/Mn ratios and MnFe$_2$O$_4$ modified glassy carbon electrodes in O$_2$-saturated 1 M KOH solutions under ambient conditions. Scan rate: 50 mV s$^{-1}$. Counter electrode: Pt wire. Reference electrode: Hg/HgO. (b) performance of DMFCs with Fe$_2$O$_3$/Mn$_2$O$_3$ with different Fe/Mn ratios and MnFe$_2$O$_4$ cathode catalysts at room temperature; (c) performance of the Fe$_2$O$_3$/Mn$_2$O$_3$(3 : 1) and MnFe$_2$O$_4$-based DMFCs at 40 °C and 60 °C; (d) stability tests at the constant current density of 10 mA cm$^{-2}$. Fe$_2$O$_3$/Mn$_2$O$_3$(3 : 1) and MnFe$_2$O$_4$ were employed as the cathode catalysts at room temperature.
MnO₂-based DMFC is superior to MnFe₂O₄-based DMFC. As shown in Table 2, Fe₂O₃/MnO₂(3 : 1) shows the largest peak current density, BET surface area and P_max, illustrating its superior ORR activity. Therefore, Fe₂O₃/MnO₂(3 : 1) was assigned as Fe₂O₃/MnO₂ and used for further studies. Fig. 6(c) shows the temperature effects on the DMFCs’ performances. The P_max of Fe₂O₃/MnO₂- and MnFe₂O₄-based DMFCs are 32.4 and 22.5 mW cm⁻² at 40 °C and 45.6 and 27.9 mW cm⁻² at 60 °C, respectively. Table 3 compares the P_max of DMFCs in the literature. In particular, the Fe₂O₃/MnO₂-based DMFC achieves the highest P_max among noble and non-noble metal cathode catalysts of DMFCs.

Stability tests were conducted in galvanostatic discharge by monitoring the voltage of Fe₂O₃/MnO₂- and MnFe₂O₄-based DMFCs. As shown in Fig. 6(d), at a constant current of 10 mA cm⁻² at room temperature, the Fe₂O₃/MnO₂-based DMFC has much higher cell voltage than MnFe₂O₄-based DMFC for 75,000 s. In about 50,000 seconds, the voltage of MnFe₂O₄-based DMFC decreases sharply. For the Fe₂O₃/MnO₂-based DMFC, no distinct attenuation phenomenon is found, indicating that this cell is quite stable.

3.3 ORR mechanism of Fe₂O₃/MnO₂

In conclusion, Fe₂O₃/MnO₂(3 : 1) exhibits higher ORR activity and superior DMFC performance than MnFe₂O₄. The first reason is that Fe₂O₃/MnO₂(3 : 1) has a much larger specific surface area (21.73 m² g⁻¹) than MnFe₂O₄ (3.05 m² g⁻¹), which plays a key role in enhancing ORR activity, providing numerous active sites and accelerating mass-transfer. It is worth noting that although current densities are normalized to their corresponding surface area in the CV tests, Fe₂O₃/MnO₂ still demonstrates higher ORR activity than MnFe₂O₄. The second reason is due to the existence of the numerous heterojunctions between Fe₂O₃ and MnO₂, which provides an intensive internal electric field at the interface of the two oxides and increases the catalytic active sites, electron transfer and ORR efficiency.

EIS was applied to describe the internal resistance of Fe₂O₃/MnO₂(3 : 1) and MnFe₂O₄. As shown in Fig. 7(a), the Nyquist plots of the Fe₂O₃/MnO₂(3 : 1)- and MnFe₂O₄-based DMFCs exhibit similar trends. The ohmic resistances (R_s) of the Fe₂O₃/MnO₂(3 : 1)- and MnFe₂O₄-based DMFCs are 0.2 U cm⁻² and 0.4 U cm⁻², respectively.
are the ohmic resistances of the total cell from the anode to cathode, including the solution, electrodes and membrane resistances. These two cells differ only in the cathode catalysts; they have the same solution (4 M KOH and 5 M methanol), membrane and anode. Therefore, it is speculated that the lower resistance of Fe2O3/Mn2O3 is owing to the heterojunction providing an intensive internal electric field and increasing the electron transfer. Moreover, the content of heterojunctions between Fe2O3 nanoparticles and Mn2O3 matrix is proportional to the number of Fe2O3 nanoparticles. In other words, with an increase in the Fe/Mn ratio, the density of heterojunctions gradually increases. As shown in Fig. 7(b), on increasing the quantity of heterojunctions, \( P_{\text{max}} \) is gradually improved.

However, when the Fe/Mn ratio reaches 5 : 1, \( P_{\text{max}} \) decreases sharply because numerous Fe2O3 nanoparticles wrap in the Mn2O3 matrix, impeding the Mn2O3 catalytic sites from contacting with O2 and electrolyte. In addition, Fe2O3/Mn2O3(1 : 1) has smaller specific surface area but higher power density than Fe2O3/Mn2O3(1 : 3), indicating the ORR activity follows the order of Fe/Mn ratio instead of its specific surface area.

The third reason is the synergistic effect between Fe2O3 and Mn2O3 in Fe2O3/Mn2O3. The Fe2O3 particles not only enhance the dispersity of Mn2O3, but also increase the O2 storage capability. Fe2O3 is an n-type semiconductor with a large number of oxygen vacancies. Many reports suggest that Fe2O3 has the outstanding ability of reversibly exchanging O2 through the transformation of Fe3+ and Fe2+. 31,32 As shown in Fig. 7(c), Fe2O3 acts as an O2-storage and release site owing to the Fe3+/Fe2+ redox couple. It can store O2 in O2-surplus condition and release it under oxygen deficiency condition. When O2 concentration is sufficient, Fe2O3 captures the surrounding O2 molecules on its surface by oxidation reaction from Fe2+ to Fe3+ as shown in Fig. 7(c1). Moreover, when O2 is insufficient, such as at high current density, the adsorbed O2 on the Fe2O3 surface can release and obtain electrons, thus forming HO2-/C0, which rapidly transfers to adjacent catalytic sites of the Mn2O3 matrix via reduction reaction from Fe3+ to Fe2+ as illustrated in Fig. 7(c3). The rapid supply of excess O2 and HO2− can increase O2 transfer and ORR efficiency in Fe2O3/Mn2O3. Therefore, the synergistic coupling between Fe2O3 and Mn2O3 greatly promotes its superior ORR ability over MnFe2O4. However, excess Fe2O3 will reduce ORR ability owing to its poorer intrinsic ORR activity compared to Mn2O3. Above all, the larger specific surface area, large number of heterojunction interfaces, and excellent synergistic effect of Fe2O3 and Mn2O3 play key roles in the enhanced ORR activity of Fe2O3/Mn2O3.

4. Conclusions

(1) Fe2O3/Mn2O3 and MnFe2O4 were synthesized via a facile template-free solvothermal method. Fe2O3/Mn2O3 exists as sub-size porous nanosheets-self-assembled globular structures. The
microspheres are 3–4 μm in diameter and the pore size is about 30 nm. The formation of nanopores is due to the release of CO₂, which comes from MnCO₃ decomposition during the calcination process. The TEM and HRTEM images show Fe₂O₃ nanoparticles uniformly dispersed on the Mn₂O₃ substrate and a distinct heterojunction boundary between Fe₂O₃ nanoparticles and Mn₂O₃ substrate. MnFe₂O₄ has a hierarchical structure, in which the nanoparticles are 20–30 nm in diameter and the self-assembled globular shapes have diameters of 300–500 nm.

(2) CV and DMFC performance tests show that Fe₂O₃/Mn₂O₃(3 : 1) exhibits higher ORR activity than Fe₂O₃/Mn₂O₃(1 : 1), Fe₂O₃/Mn₂O₃(1 : 3), Fe₂O₃/Mn₂O₃(5 : 1) and MnFe₂O₄. The Pₓmax of Fe₂O₃/Mn₂O₃(3 : 1)-based DMFCs are 32.4 and 45.6 mW cm⁻² at 40 and 60 °C, respectively. The results indicated that the as-prepared Fe₂O₃/Mn₂O₃ catalysts achieved the highest Pₓmax among noble and non-noble metal cathode catalysts of DMFCs.

(3) The much superior catalytic performance of Fe₂O₃/Mn₂O₃ is due to its larger surface area, the existence of numerous heterocontact interfaces and the synergistic effect between Fe₂O₃ and Mn₂O₃, which can provide numerous catalytic active sites, accelerate mass transfer, and increase ORR efficiency. It is worth noting that Fe₂O₃ acts as an O₂-storage and release site owing to the Fe³⁺/Fe²⁺ redox couple. In addition, the synergistic effect between Fe₂O₃ and Mn₂O₃ greatly promotes its ORR properties.

Conflicts of interest

There are no conflicts to declare.

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