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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.1 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.2-5 Furthermore, methanol is convenient and safe for transport and storage, swift to refuel and available at a low price.6 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.4,7,8

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.^{9,10} The fibers in PFMs are neutral and possess pores and gaps, which allow molecules, ions, and liquid fuel to transport

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. Fe₂O₃/Mn₂O₃ is made up of Fe₂O₃ and Mn₂O₃ as confirmed *via* XRD. TEM and HRTEM observations show Fe₂O₃ nanoparticles uniformly dispersed on the Mn₂O₃ substrate and a distinct heterojunction boundary between Fe₂O₃ nanoparticles and Mn₂O₃ substrate. MnFe₂O₄ 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 Fe₂O₃/Mn₂O₃(3 : 1) exhibits higher oxygen reduction reaction (ORR) activity than Fe₂O₃/Mn₂O₃(1 : 1), Fe₂O₃/Mn₂O₃(1 : 3), Fe₂O₃/Mn₂O₃(5 : 1) and MnFe₂O₄. The much superior catalytic performance is due to its larger surface area, the existence of numerous heterojunction interfaces and the synergistic effect between Fe₂O₃ and Mn₂O₃, which can provide numerous catalytic active sites, accelerate mass transfer, and increase ORR efficiency.

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,¹¹ Pt-Pd,⁴ Pt-Ni,¹² and Pt-Fe.¹³ 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,¹⁴ Pd–Ni,¹⁵ Pd–Fe,¹⁶ Co–Se,¹⁷ Fe–N–C,¹⁸ Cu–Fe–S,¹⁹ and Co–O,²⁰ which 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.²¹ In recent years, numerous studies have focused on binary and ternary metal oxides because of their good synergistic effects and good cycle stability. NiCo₂O₄,²² KMn₈O₁₆,²³ MnFe₂O₄,²⁴ and Co–Ni–Te–O²⁵ have higher ORR catalytic activities and methanol tolerance. For example, the catalytic activity of MnFe₂O₄ is higher than that of Fe₂O₃ (ref. 26) and Mn₂O₃.²⁷ Nevertheless, the catalytic activity of the mixed compound of Fe₂O₃ and Mn₂O₃ has not been discussed.

In this study, we prepared two Fe–Mn bimetallic oxides, namely, Fe_2O_3/Mn_2O_3 and $MnFe_2O_4$ by a simple solvothermal method. Fe_2O_3/Mn_2O_3 is made up of Fe_2O_3 and Mn_2O_3 as confirmed *via* XRD. $MnFe_2O_4$ is a pure phase sample. The asprepared Fe_2O_3/Mn_2O_3 exists in the form of porous nanosheets-self-assembled globular structure. The

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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 Fe_2O_3/Mn_2O_3 and $MnFe_2O_4$ 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 (TNM7, >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 μ m) 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. Fe_2O_3/Mn_2O_3 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 $MnSO_4 \cdot H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$. The samples were designated as $Fe_2O_3/$ $Mn_2O_3(1:1)$, $Fe_2O_3/Mn_2O_3(1:3)$, $Fe_2O_3/Mn_2O_3(3:1)$ and $Fe_2O_3/Mn_2O_3(5:1)$, respectively.

The precursor of $MnFe_2O_4$ was synthesized following the same solvothermal method except the raw materials were 2.5 mmol $Mn(CH_3COO)_2 \cdot 4H_2O$, 5.0 mmol $FeCl_3 \cdot 6H_2O$, 1.0 g polyethylene glycol (PEG), 3.6 g CH₃COONa and 40 mL ethylene glycol (EG). The $MnFe_2O_4$ 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 Fe_2O_3/Mn_2O_3 and $MnFe_2O_4$ 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 catalystmodified 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 μ L 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.⁹ A battery testing system (Neware Technology Co., Ltd., Shenzhen, China) was used to measure the performance.



Fig. 1 XRD patterns of (a) $Fe_2O_3/Mn_2O_3(3:1)$ and its precursor; (b) $MnFe_2O_4$ and its precursor.

3. Results and discussion

3.1 Structural and morphological characterization

Fig. 1 displays the XRD patterns of $Fe_2O_3/Mn_2O_3(3:1)$, MnFe₂O₄ and their precursors. The precursor of $Fe_2O_3/Mn_2O_3(3:1)$ can be well indexed to Fe_2O_3 (JCPDS no. 33-0664) and MnCO₃ (JCPDS no. 44-1472). However, the diffraction peaks of $Fe_2O_3/Mn_2O_3(3:1)$ agree with the standard patterns of Fe_2O_3 (JCPDS no. 33-0664) and Mn_2O_3 (JCPDS no. 24-0508). It can be illustrated that $Fe_2O_3/Mn_2O_3(3:1)$ is composed of Mn_2O_3 and Fe_2O_3 and the formation of Mn_2O_3 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/ $Mn_2O_3(3:1)$, $MnFe_2O_4$ and their precursors. Fig. 2(a) shows that the precursor of $Fe_2O_3/Mn_2O_3(3:1)$ exhibits two morphologies, which are nanoparticles and nanostructured bulk, while the $Fe_2O_3/Mn_2O_3(3:1)$ catalyst exists as sub-sized porous nanosheets-self-assembled globular structure (Fig. 2(b)). The microspheres of $Fe_2O_3/Mn_2O_3(3:1)$ 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.²⁸ Further, the EDS elemental mappings of Fe₂O₃/ $Mn_2O_3(3:1)$ (Fig. 2(c)-(f)) were recorded to obtain elemental distribution of Fe, Mn and O in the structure and it could be observed that the three elements are distributed homogeneously. As shown in Fig. 3(a) and (b), MnFe₂O₄ catalyst and its precursor have similar hierarchical structures. The nanoparticles are 20-30 nm in diameter and exhibit self-assembled globular shapes with diameters of 300-500 nm. Moreover, the EDS elemental mapping of $MnFe_2O_4$ clearly indicates that the Fe, Mn and O elements are uniformly distributed (Fig. 3(c)–(f)).

The TEM image of $Fe_2O_3/Mn_2O_3(3:1)$ (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 $Fe_2O_3/Mn_2O_3(3:1)$ 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 Fe_2O_3 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/ $Mn_2O_3(3:1)$ consists of Fe_2O_3 and Mn_2O_3 , which is consistent with the XRD results. As shown in Fig. 4(b), a distinct heterojunction 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 adsorptiondesorption curves (Fig. 5(b)) manifest a type IV isothermal line with a delay loop-line in the P/P_0 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), $Fe_2O_3/Mn_2O_3(3:1)$ and $Fe_2O_3/Mn_2O_3(5:1)$, 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 $3.05 \text{ m}^2 \text{ g}^{-1}$ and 14.4 nm, respectively.



Fig. 2 FESEM images of (a) the precursor of $Fe_2O_3/Mn_2O_3(3:1)$ and (b) $Fe_2O_3/Mn_2O_3(3:1)$; EDS elemental mapping images of Fe_2O_3/Mn_2O_3 ((c) to (f)).

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. 3 FESEM images of (a) the precursor of MnFe₂O₄ and (b) MnFe₂O₄ catalyst; EDS elemental mapping images of MnFe₂O₄ catalyst ((c) to (f)).



Fig. 4 (a) TEM and (b) HRTEM images of $Fe_2O_3/Mn_2O_3(3:1)$; (c) TEM and (d) HRTEM images of $MnFe_2O_4$.

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 -58.43, -61.21, -86.7 and -47.9 mA m⁻² for Fe₂O₃/Mn₂O₃(1 : 1), Fe₂O₃/Mn₂O₃(1 : 3), Fe₂O₃/

 $Mn_2O_3(3:1)$ and $Fe_2O_3/Mn_2O_3(5:1)$, respectively, while the corresponding peak potentials are -0.246, -0.267, -0.348 and -0.257 V. Clearly, $Fe_2O_3/Mn_2O_3(3:1)$ has the highest oxygenreduction peak current density. As compared $MnFe_2O_4$, although the reduction peak potential of $Fe_2O_3/Mn_2O_3(3:1)$ is



Fig. 5 (a) XPS survey spectra of Fe_2O_3/Mn_2O_3 with different Fe/Mn ratios; (b) nitrogen adsorption–desorption isotherms and pore size distributions of Fe_2O_3/Mn_2O_3 with different Fe/Mn ratios and $MnFe_2O_4$.

Table 1	Elemental	composition	of Fe ₂ O	₃ /Mn ₂ O ₃	with	different	Fe/Mn	ratios
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	Composition			
	Fe 2p (at%)	Mn 2p (at%)	O 1s (at%)	Fe/Mn
	Binding energy			
Fe/Mn ratio	708.00 eV	639.00 eV	528.00 eV	
1:1	3.77	4.03	92.2	0.94
1:3	2.43	7.63	89.94	0.32
3:1	9.81	2.84	87.36	3.45
5:1	12.10	2.34	85.56	5.17

slightly more negative than that of MnFe₂O₄ (-0.237 V), the oxygen-reduction peak current density is much greater than that of MnFe₂O₄ (-26.26 mA m⁻²). CV results indicate Fe₂O₃/Mn₂O₃ exhibits higher ORR activity than MnFe₂O₄, which have excluded the effect of their specific surface area, demonstrating Fe₂O₃/Mn₂O₃ has more active sites probably introduced by heterojunction boundary between Fe₂O₃ and Mn₂O₃.

The polarization and power density curves of Fe_2O_3/Mn_2O_3 with different Fe/Mn ratios and $MnFe_2O_4$ used as cathode catalysts in DMFCs are shown in Fig. 6(b). The maximum power densities (P_{max}) for these catalysts are 17.09, 15.54, 20.29, 12.88 and 12.15 mW cm⁻² for $Fe_2O_3/Mn_2O_3(1:1)$, $Fe_2O_3/Mn_2O_3(1:3)$, $Fe_2O_3/Mn_2O_3(3:1)$, $Fe_2O_3/Mn_2O_3(5:1)$ and $MnFe_2O_4$, respectively. These data indicate that the $Fe_2O_3/$



Fig. 6 (a) CV curves of Fe_2O_3/Mn_2O_3 with different Fe/Mn ratios and $MnFe_2O_4$ 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_2O_3/Mn_2O_3 with different Fe/Mn ratios and $MnFe_2O_4$ cathode catalysts at room temperature; (c) performance of the $Fe_2O_3/Mn_2O_3(3:1)$ - and $MnFe_2O_4$ -based DMFCs at 40 °C and 60 °C; (d) stability tests at the constant current density of 10 mA cm⁻². $Fe_2O_3/Mn_2O_3(3:1)$ and $MnFe_2O_4$ were employed as the cathode catalysts at room temperature.

Table 2 Comparison of the ORR activities and DMFCs performance of the as-prepared samples

Catalysts	Peak current density (mA m $^{-2}$)	Peak potential (V)	BET surface area $(m^2 g^{-1})$	$P_{ m max} (m mW cm^{-2})$	
$Fe_2O_3/Mn_2O_3(1:1)$	-58.43	-0.246	12.390	17.09	
$Fe_2O_3/Mn_2O_3(1:3)$	-61.21	-0.267	19.889	15.54	
$Fe_2O_3/Mn_2O_3(3:1)$	-86.7	-0.348	21.73	20.29	
$Fe_2O_3/Mn_2O_3(5:1)$	-47.9	-0.257	18.165	12.88	
MnFe ₂ O ₄	-26.26	-0.237	3.05	12.15	

Mn₂O₃-based DMFC is superior to MnFe₂O₄-based DMFC. As shown in Table 2, Fe₂O₃/Mn₂O₃(3 : 1) shows the largest peak current density, BET surface area and P_{max} , illustrating its superior ORR activity. Therefore, Fe₂O₃/Mn₂O₃(3 : 1) was assigned as Fe₂O₃/Mn₂O₃ and used for further studies. Fig. 6(c) shows the temperature effects on the DMFCs' performances. The P_{max} of Fe₂O₃/Mn₂O₃- 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/Mn₂O₃-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 Fe_2O_3/Mn_2O_3 - and $MnFe_2O_4$ -based DMFCs. As shown in Fig. 6(d), at a constant current of 10 mA cm⁻² at room temperature, the Fe_2O_3/Mn_2O_3 -based DMFC has much higher cell voltage than $MnFe_2O_4$ -based DMFC for 75 000 s. In about 50 000 seconds, the voltage of $MnFe_2O_4$ based DMFC decreases sharply. For the Fe_2O_3/Mn_2O_3 -based DMFC, no distinct attenuation phenomenon is found, indicating that this cell is quite stable.

3.3 ORR mechanism of Fe₂O₃/Mn₂O₃

In conclusion, $Fe_2O_3/Mn_2O_3(3:1)$ exhibits higher ORR activity and superior DMFC performance than $MnFe_2O_4$. The first reason is that $Fe_2O_3/Mn_2O_3(3:1)$ has a much larger specific surface area (21.73 m² g⁻¹) than $MnFe_2O_4$ (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, Fe_2O_3/Mn_2O_3 still demonstrates higher ORR activity than $MnFe_2O_4$.

The second reason is due to the existence of the numerous heterojunctions between Fe_2O_3 and Mn_2O_3 , 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.^{29,30} EIS was applied to describe the internal resistance of $Fe_2O_3/Mn_2O_3(3:1)$ and $MnFe_2O_4$. As shown in Fig. 7(a), the Nyquist plots of the $Fe_2O_3/Mn_2O_3(3:1)$ - and $MnFe_2O_4$ -based DMFCs exhibit similar trends. The ohmic resistances (R_s) of the $Fe_2O_3/Mn_2O_3(3:1)$ - and $MnFe_2O_4$ -based DMFCs are $0.2 \Omega \text{ cm}^{-2}$ and $0.4 \Omega \text{ cm}^{-2}$, respectively. R_s values

Table 3 Comparison of DMFCs performance						
Cathode (catalyst loading/mg $\rm cm^{-2}$)	Anode (catalyst loading/mg cm ⁻²)	Solution	Electrolyte	Temperature/°C	Power density/mW cm ⁻²	
$Pt/C(8)^{33}$	PtRu(5)	КОН	Nafion 211	25	15	
$Pt(1)^{34}$	Pt(1)	КОН	PVA-KOH	90	10	
$Pt(1)^{35}$	PtRu(2)	КОН	PBI/KOH	90	31	
$Pt(5)^{36}$	PtRu(5)	КОН	PVA/FS	60	39	
$Pt/C(10)^{22}$	PtRu(6)	KOH	Nafion 211	26	16	
Pt black $(1)^{37}$	Pt(0.5)	КОН	Nafion 117	60	15	
				90	77	
$\text{Fe-AApyr}(7.4)^{38}$	PtRu(1)	H_2SO_4	Nafion 115	30	6.5	
				60	18	
				90	35	
$Fe-N-C(4.5)^{39}$	PtRu(1)	H_2SO_4	Nafion 115	90	48	
Fe-ABZIM(3) ⁴⁰	PtRu(1)	H_2SO_4	Nafion 115	60	17	
$MnO(4)^{41}$	PtRu(4)	KOH	Q-PVA/PECH	25	17	
$MnO_2/C(4)^{42}$	PtRu black(4)	КОН	PVA/HAP	25	11	
$MnO_2(4)^{43}$	PtRu(4)	KOH	PVA/HAP	25	11	
$MnFe_2O_4(24)$ (this work)	PtRu/C(5)	КОН	PFM	20	12	
				40	22	
				60	28	
$Fe_2O_3/Mn_2O_3(3:1)$ (24) (this work)	PtRu/C(5)	КОН	PFM	20	20	
				40	32	
				60	46	

Paper



Fig. 7 (a) Nyquist plots of the DMFCs with Fe_2O_3/Mn_2O_3 and $MnFe_2O_4$ cathode catalysts. (Inset: corresponding Nyquist plot in the high-frequency range); (b) P_{max} and BET surface area of Fe_2O_3/Mn_2O_3 with different Fe/Mn ratios; (c) schematic diagrams of ORR mechanism with Fe_2O_3/Mn_2O_3 as the cathode catalysts; (c₁) the microstructure of Fe_2O_3/Mn_2O_3 ; (c₂) ORR mechanism under O_2 surplus; (c₃) ORR mechanism under O_2 deficiency; (c₄) illustration of the Fe^{2+}/Fe^{3+} ORR mechanism.

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_{max} is gradually improved. However, when the Fe/Mn ratio reaches 5:1, P_{max} decreases sharply because numerous Fe₂O₃ nanoparticles wrap in the Mn₂O₃ matrix, impeding the Mn₂O₃ catalytic sites from contacting with O_2 and electrolyte. In addition, $Fe_2O_3/Mn_2O_3(1:1)$ has smaller specific surface area but higher power density than $Fe_2O_3/Mn_2O_3(1:3)$, 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 Fe_2O_3 and Mn_2O_3 in Fe_2O_3/Mn_2O_3 . The Fe_2O_3 particles not only enhance the dispersity of Mn_2O_3 , but also increase the O_2 storage capability. Fe_2O_3 is an n-type semiconductor with a large number of oxygen vacancies. Many reports suggest that Fe_2O_3 has the outstanding ability of reversibly exchanging O_2 through the

transformation of Fe^{3+} and Fe^{2+} .^{31,32} As shown in Fig. 7(c), Fe_2O_3 acts as an O_2 -storage and release site owing to the Fe^{3+}/Fe^{2+} 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(c_2). Moreover, when O_2 is insufficient, such as at high current density, the adsorbed O2 on the Fe2O3 surface can release and obtain electrons, thus forming HO₂⁻, which rapidly transfers to adjacent catalytic sites of the Mn₂O₃ matrix via reduction reaction from Fe^{3+} to Fe^{2+} 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) Fe_2O_3/Mn_2O_3 and $MnFe_2O_4$ were synthesized *via* a facile template-free solvothermal method. Fe_2O_3/Mn_2O_3 exists as subsize porous nanosheets-self-assembled globular structures. The

microspheres are $3-4 \mu m$ 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 $P_{\rm max}$ 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 $P_{\rm max}$ 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 heterojunction 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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Paper

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