Contents lists available at ScienceDirect

Journal of Colloid And Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

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Charge redistribution engineering in $Mn_{5.64}P_3$ /CePO₄ heterostructure enhances oxygen reduction for advanced zinc-air battery

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GRAPHICAL ABSTRACT

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HIGHLIGHTS

- A Mn_{5.64}P₃/CePO₄@Cs is synthesized *via* hydrothermal and phosphating strategy.
- Fermi level gap triggers electron transfer, forming a BEF to adjust the electronic structure.
- The catalyst shows good ORR performance with high peak power density and durability for ZAB.
- Interface electron redistribution optimizes O-intermediate adsorption/ desorption, boosting reaction kinetics.

ARTICLE INFO

Keywords: Heterostructure Built-in electric field Oxygen reduction Zinc-air batteries Theoretical calculation



ABSTRACT

Tailoring the electronic structure via charge redistribution is a promising strategy for constructing oxygen reduction reaction (ORR) catalysts to accelerate reaction kinetics for metal-air batteries. Herein, an approximately 3.9 nm thin-layer of $Mn_{5.64}P_3/CePO_4$ heterostructure stabilized on mesoporous carbon spheres ($Mn_{5.64}P_3/CePO_4@Cs$) was synthesized *via* mild hydrothermal and high-temperature phosphating approaches. The resultant $Mn_{5.64}P_3/CePO_4@Cs$ demonstrates superior ORR performance in 0.1 M KOH with a kinetic current density of 5.2 mA cm⁻² at 0.8 V, increasing 2.4- and 5.8-fold compared to CePO_4@Cs and $Mn_{5.64}P_3@Cs$, respectively. Moreover, the zinc-air battery (ZAB) incorporating $Mn_{5.64}P_3/CePO_4@Cs$ showcases a peak power density of 168 mW cm⁻² and robust durability of 400 h, surpassing the advanced Pt/C. Experiments and density functional theory (DFT) calculations indicate that the built-in electric field (BEF)-induced charge asymmetry regulates the *d*-band center of $Mn_{5.64}P_3/CePO_4@Cs$ and reduces the energy barrier of oxygen intermediates, thereby improving ORR catalystic performance. This work provides a promising avenue to rationally manipulate the electronic structure of ORR catalysts by constructing heterostructure driven BEF strategy.

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https://doi.org/10.1016/j.jcis.2025.138141

Received 16 April 2025; Received in revised form 1 June 2025; Accepted 8 June 2025 Available online 9 June 2025 0021-9797/© 2025 Elsevier Inc. All rights are reserved, including those for text and data mining, AI training, and similar technologies.





1. Introduction

Zinc-air batteries (ZABs) are recognized as one of the most promising high-energy density conversion devices due to their competitive advantages of zero emissions, high efficiency, and low initial costs [1–3]. The oxygen reduction reaction (ORR) is a critical process in ZABs, characterized high overpotentials and kinetic retardation caused by difficulties in activating O_2 and regulating the adsorption/desorption of intermediates [4,5]. Although platinum group metal catalysts are considered the benchmark for ORR, their high cost and inferior stability severely impede their large-scale application [6]. Therefore, exploring accessible and efficient non-precious metal alternatives is imperative in expediting reaction kinetics [7,8].

The ORR catalytic activity is primarily influenced by the electronic structure distribution of the active center, with an ideal catalyst requiring a moderate binding strength of the intermediate to the active site [9]. Therefore, modulating the electronic structure of the metal center emerges as an effective strategy for enhancing catalytic performance [10]. Generating a built-in electric field (BEF) through interface engineering is a promising strategy for tailoring electronic structures [11]. This is achieved by integrating two components with distinct Fermi energy levels at heterointerface [12]. This energy difference drives electrons to migrate spontaneously from the substrate with a lower work function (WF) to one with a higher WF, resulting in charge redistribution [13,14]. This process stabilizes the local electrophilic and nucleophilic regions, fine-tuning the electronic structure of the active sites and balancing the adsorption strength of reaction intermediates, thus promoting the catalytic kinetics [15]. In addition, the ORR performance is influenced by conductivity and dispersion [16]. Carbonbased materials have emerged as prominent catalyst supports due to their high electrical conductivity, porosity, and large specific surface area [17]. In this case, coupling two components with different Fermi energy levels to construct heterostructures anchored on carbon materials is a viable strategy for elevating ORR activity. Mn-based compounds, with the multiple valence states of Mn, hold considerable potential for catalyzing ORR [18,19]. Moreover, rare earth cations, with their unsaturated 4f orbital valence electron configuration and abundant coordination sites, can participate in regulating and optimizing electrocatalytic performance [20]. The high-temperature phosphating process facilitates the formation of abundant defects and disordered structures at the heterointerface, expediting the charge transfer rate and furnishing numerous electrocatalytic active sites [21].

In this work, we leveraged the effective coupling between rare earth metal (Ce) and transition metal (Mn) to create a carbon-loaded $Mn_{5.64}P_3/CePO_4$ catalyst demonstrating significant ORR activity and stability. The optimized $Mn_{5.64}P_3/CePO_4$ @Cs exhibits a half-wave potential of 0.8 V, comparable to commercial Pt/C. Strikingly, the catalyst endows the ZAB with an ideal power density of 168 mW cm⁻² and superior stability exceeding 400 h, outperforming the standard Pt/C-based battery. The experimental results indicate that the well-dispersed mesoporous carbon spheres architecture enhances the specific surface area and electrical conductivity, facilitating rapid electron transfer. Moreover, the superhydrophilicity of $Mn_{5.64}P_3/CePO_4$ @Cs ensures optimal contact between the reactants and active sites. Density functional theory (DFT) calculations confirm the critical role of the BEF generated by the fabricated heterostructure in tuning the *d*-band center, optimizing intermediate adsorption, and reducing reaction energy barriers.

2. Experimental Section

2.1. Chemicals and reagents

Glucose (C₆H₁₂O₆, \cdot 6H₂O, specific spectral index = $+52.5^{\circ} \sim 53.0^{\circ}$), manganese(II) chloride tetrahydrate (MnCl₂·4H₂O, \geq 99.0 %), and absolute ethanol (C₂H₅OH, 99.7 %) were sourced from Xilong chemical Co., Ltd. Cerium (III) nitrate hexahydrate (Ce(NO₃)₂·6H₂O, 99.9 %), zinc acetate (Zn(Ac)₂, 99.0 %) and commercial Pt/C (20.0 wt% Pt) were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Potassium hydroxide (KOH, 95.0 %) was procured from Macklin Biochemical Co., Ltd. Nafion (5.0 % solution) was purchased from Alfa Aesar. All reagents employed were of analytical grade and required no further purification. The RuO₂ powder was derived by calcinating RuCl₃·xH₂O (99.0 %, Ru 37.0–40.0 %) at 400 °C in an oxygen-rich environment.

2.2. Preparation of catalysts

2.2.1. Synthesis of Mn-Ce precursor on carbon spheres (Cs)

Carbon spheres (Cs) were synthesized following the same procedure as we reported previously [22]. Subsequently, a mixture of 100 mg of Cs, 6 mmol of $Ce(NO_3)_2 \cdot 6H_2O$, and 6 mmol of $MnCl_2$ was dissolved in a solution comprising of 60 mL of deionized water and ethanol (v/v = 2/ 1). The resulting mixture was stirred at ambient temperature for 8 h, followed by centrifugation. The obtained product was dried overnight at 70 °C, resulting in the formation of the brown Mn-Ce precursor (Mn-Ce@Cs). In addition, the Ce/Mn ratio was precisely adjusted while keeping the total amount of 12 mmol of substance, and the ratios of Ce/ Mn metal salts were varied as 0:4, 1:3, 1:1, 3:1, and 4:0, respectively.

2.2.2. Synthesis of Mn_{5.64}P₃/CePO₄@Cs

The specified 50 mg of the aforementioned Mn-Ce@Cs was mixed well with 100 mg of red phosphorus, and then thoroughly ground for 10 min. The resultant powder was calcined in a tube furnace at 1000 °C (900 and 1100 °C) for 2 h at an elevated temperature rate of 5 °C min⁻¹ under an N₂ atmosphere.

2.3. Materials characterization

X-ray diffraction (XRD) was measured on the Rigaku D/Max-3c with Cu K α ($\lambda = 0.15418$ nm) radiation. Raman spectroscopy (Renishaw, Via Quotation) was employed to elucidate the composition and level of graphitization across all samples. Scanning electron microscope (SEM) images were taken on Quanta FEG 200 (Holland). Transmission electron microscopy (TEM) was conducted using a Talos F200S equipped with an energy-dispersive X-ray spectroscopy (EDS) analyzer. The metallic components in the various catalysts were precisely quantified through the utilization of inductively coupled plasma mass spectroscopy (ICP-MS) with the FLexar-NexION300X instrument provided by PerkinElmer Corporation. For the determination of the Brunauer-Emmett-Teller (BET) surface area and pore size distribution, a Quantachrome instrument (3H-2000PS4) was employed. To assess the relative intensity of vacancies, Electron paramagnetic resonance (EPR) spectroscopy was conducted using a Bruker A300 instrument. The wetting behavior was evaluated using the Dataphysics OCA20 instrument for contact angle (CA) tests. X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250Xi system to investigate the elemental composition and surface valence states of the materials.

2.4. Electrochemical measurements

All electrochemical measurements were performed in a conventional three-electrode configuration using a CHI 760E electrochemical work-station. A rotating ring disk electrode (RRDE, diameter = 5.61 mm, Paine Instruments, USA) and a rotating disk electrode (RDE, diameter = 5 mm, Paine Instruments, USA) loaded with catalyst ink were used as working electrodes, and Ag/AgCl (saturated potassium chloride solution) electrode and graphite rod were used as the working electrode, reference electrode, 2 mg catalyst was dispersed in 200 μ L isopropyl alcohol, 100 μ L deionized water and 5 μ L of a 5 wt% Nafion solution, ultrasonic for 30 min to form a uniform ink. Then, the prepared ink 20 μ L is dropped on the working electrode and dried naturally. All tests were

performed in a 0.1 M KOH electrolyte, with oxygen or nitrogen passing through the electrolyte for 30 min prior to measurement. In linear sweep voltammetry (LSV), the hydrogen peroxide yield is tested using a rotating ring disk electrode (RRDE) with a potential range of 0.1–1.1 V (relative to RHE) and a sweep rate of 5 mV s⁻¹. More detailed description of the test and calculation approaches are provided in the supplementary data.

3. Results and discussion

3.1. Synthesis and structural analysis

Fig. 1a presents a concise schematic diagram illustrating the fabrication process of the well-dispersed Mn_{5.64}P₃/CePO₄ heterostructure on mesoporous carbon spheres (Cs). Initially, the glucose-derived Cs were synthesized according to our previous work. Subsequently, Mn and Ce species were physically adsorbed onto the Cs through stirring at room temperature, forming the Mn-Ce precursor (Mn-Ce@Cs), which was then subjected to high-temperature phosphating to produce the phosphide/phosphate composite (Mn_{5.64}P₃/CePO₄@Cs). X-ray diffraction (XRD) analysis characterized the crystal structure of the obtained catalysts. The XRD patterns of Mn₅₆₄P₃@Cs, CePO₄@Cs, and Mn₅₆₄P₃/ CePO₄@Cs display peaks attributed to Mn_{5.64}P₃ (JCPDS: 30-0823) and CePO₄ (JCPDS: 04–0632) [23], except for the carbon peak at 26.0° (Fig. 1b and Fig. S1) [24]. The weak peak intensity suggests a low content of the synthesized metal phosphides/phosphates. Electron paramagnetic resonance (EPR) spectroscopy (Fig. 1c) reveals distinct signals in the synthesized samples, indicating the presence of P vacancies, primarily due to the escape of P during high-temperature pyrolysis [25,26]. Intriguingly, the g value of $Mn_{5.64}P_3$ @Cs is 2.01, while CePO₄@Cs and $Mn_{5.64}P_3$ /CePO₄@Cs present a slight increase to 2.04, suggesting variations in the binding capacities of the surrounding atoms in these samples [27,28]. The formation of P vacancies, due to the unsaturated coordination environment, promotes electron delocalization,

enhances carrier mobility and accelerates charge transfer [29,30]. Meanwhile, the vacancies facilitate the exposure of more active sites [31]. The specific surface area and porosity of catalysts were evaluated using the nitrogen adsorption-desorption technique (Fig. 1d and Fig. S2). The Mn_{5.64}P₃/CePO₄@Cs catalyst exhibits a larger Brunauer-Emmett-Teller (BET) surface area of 783.88 $m^2 g^{-1}$, surpassing that of $Mn_{5.64}P_3@Cs$ (432.07 m² g⁻¹) and CePO₄@Cs (601.90 m² g⁻¹) [32]. The large BET surface area and mesoporous structure (inset in Fig. 1d) augment the extensive exposure of the active sites and comprehensive interaction with the reactants, thereby increasing the efficiency of mass transfer [33,34]. The degree of graphitization and defect features within the samples were assessed using Raman spectroscopy [35]. As illustrated in Fig. S3, the ratio of peak intensities in the D- and G-band (I_D/I_G) is approximately 1.18, 0.98, and 1.24 for Mn_{5.64}P₃/CePO₄@Cs, Mn_{5.64}P₃@Cs, and CePO₄@Cs, respectively. This suggests that Mn_{5.64}P₃/CePO₄@Cs achieves a suitable balance between defect formation and graphitization, ensuring a favorable number of active sites and commendable electrical conductivity [36,37]. The highly porous structure ensures exceptional permeability and effective contact with reactants and electrolytes. Therefore, contact angle tests were conducted to evaluate the hydrophilicity of the synthesized samples. As depicted in Fig. 1e, the contact angle of $Mn_5 {}_{64}P_3/CePO_4@Cs$ is 47.1° , smaller than that of Mn_{5.64}P₃@Cs (54.3°) and CePO₄@Cs (48.2°). This indicates that the integration of Mn_{5.64}P₃ and CePO₄ results in the formation of more hydrophilic surfaces, facilitating the penetration of the electrolyte and ion transport, thereby significantly enhancing the electrochemical ORR efficiency [38].

The scanning electron microscopy (SEM) images reveal that the synthesized Cs assumes a spherical configuration with a smooth surface (Fig. S4). After loading the Mn-Ce species, the surface of Mn-Ce@Cs becomes slightly rougher than the original Cs (Fig. S5). Following high-temperature phosphating, the synthesized $Mn_{5.64}P_3$ /CePO₄@Cs retains the spherical microstructure of Cs without any agglomeration, confirming the highly dispersed nature of the spherical structure



Fig. 1. (a) Schematic illustration of the synthesis of $Mn_{5.64} P_3$ /CePO₄ @Cs. (b) XRD pattern of $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of the as-prepared $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of $Mn_{5.64} P_3$ /CePO₄ @Cs. (c) EPR spectra of



Fig. 2. (a) SEM, (b) TEM, (c-e) HR-TEM, (f) the lattice spacing profiles of Mn_{5.64} P₃ and CePO₄, (g) HAADF-STEM and the corresponding elemental mapping images of Mn_{5.64} P₃ /CePO₄ @Cs.

(Fig. 2a). Transmission electron microscopy (TEM) images further display the spherical structure (Fig. 2b), with a clear observation of the compact internal structure and an average diameter of approximately 500 nm. Fig. 2c distinctly shows that the thickness of Mn_{5.64}P₃/CePO₄ on the Cs is approximately 3.9 nm, indicating a relatively low content of metal phosphide/phosphate in the synthesized samples. High-resolution TEM (HR-TEM) images (Fig. 2d-e) and the corresponding lattice spacing profiles (Fig. 2f) of the optimized $Mn_{5.64}P_3/\text{CePO}_4@\text{Cs}$ demonstrate a distinct interface between Mn_{5.64}P₃ and CePO₄, with lattice spacings of 0.354 and 0.199 nm corresponding to the (110) and (210) planes of CePO₄ and Mn_{5.64}P₃, respectively. The discontinuous lattice fringes and structural aberrations, supported by EPR results, indicate the presence of vacancies, consistent with findings reported in previous studies [39,40]. Significantly, TEM, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and the corresponding elemental mapping images of Mn_{5.64}P₃@Cs and CePO₄@Cs are presented in Figs. S6-7, which further verify the successful synthesis of these compounds. Meanwhile, the HR-TEM image of Cs shows no obvious lattice spacing of carbon features on its surface (Fig. S8), further confirming that the lattice spacing of 0.354 nm pertains to CePO₄. HAADF-STEM and elemental mapping images clearly showcase the uniform distribution of Mn, Ce, C, O and P elements in $Mn_{5.64}P_3/CePO_4@Cs$ (Fig. 2g). Moreover, energy dispersive X-ray spectroscopy (EDS) further supports this observation (Fig. S9). These results indicate the successful synthesis of Mn_{5.64}P₃/CePO₄ on the carbon sphere support. Additionally, inductively coupled plasma mass spectrometry (ICP-MS) was employed to accurately quantify the Mn and Ce contents in the proposed catalysts (Table S1). The Mn and Ce contents in $Mn_{5.64}P_3/CePO_4@Cs$ are determined to be 5.2 wt% and 3.6 wt%, respectively.

Ultraviolet photoelectron spectroscopy (UPS) was utilized for indepth analysis of the electronic properties of synthetic samples to elucidate their enhanced intrinsic activity. As shown in Fig. 3a-b, the work function ($\Delta \Phi$) of Mn_{5.64}P₃/CePO₄@Cs, Mn_{5.64}P₃@Cs and CePO₄@Cs are 4.41, 4.54 and 4.30 eV, respectively. Moreover, the valence band maxima (E_v) of Mn_{5.64}P₃@Cs and CePO₄@Cs are 2.60 and 3.43 eV, respectively, while $Mn_{5.64}P_3$ /CePO₄@Cs exhibits a moderate band gap of 3.19 eV. According to the *d*-band center (ε_d) theory, the proximity of the *d*-band center to the Fermi energy level (E_f) indicates a higher density of empty antibonding states, resulting in stronger adsorption of reaction intermediates [41]. In this regard, the interfacial structure of Mn_{5.64}P₃/CePO₄@Cs, with a moderate band gap, is conducive to providing optimized active sites for adsorption and desorption of oxygen-containing intermediates. An electron transfer diagram was plotted based on the UPS results (Fig. 3c). Since the work function of CePO₄@Cs is lower than that of Mn_{5.64}P₃@Cs, electrons spontaneously stream from CePO₄ to Mn_{5.64}P₃, resulting in charge redistribution at the interface. Positive charge accumulates in the vicinity of CePO₄, while electron enrichment occurs close to Mn_{5.64}P₃, resulting in a BEF. The formation of BEF provides a heightened driving force for electron flow, which is beneficial in regulating the electron density of active center [42]. X-ray photoelectron spectroscopy (XPS) was performed to elucidate the surface chemical valence states and elemental composition of the designed catalysts. The XPS survey spectra further confirm the existence of Mn, Ce, P, O and C in Mn_{5.64}P₃/



Fig. 3. (a) UPS spectra, (b) band structure alignment of Mn_{5.64} P₃ /CePO₄ @Cs, Mn_{5.64} P₃ @Cs, and CePO₄ @Cs. (c) Schematic diagram of band structure of Mn_{5.64} P₃ /CePO₄ @Cs. High-resolution XPS spectra of (d) Ce 3*d*, (e) Mn 2*p*, (f) P 2*p*, and (g) O 1 *s* in the synthesized catalysts.

CePO₄@Cs (Fig. S10). The C 1 s spectra exhibit four peaks associated with C=C (284.0 eV), C-C (284.5 eV), C-O (286.4 eV) and C=O (289.8 eV) (Figs. S11-12) [43]. In the Ce 3d XPS spectra (Fig. 3d), µ and v denote the spin-orbit coupling of Ce $3d_{5/2}$ and Ce $3d_{3/2}$, respectively. The peaks of μ_1 (882.2 eV)/ ν_1 (901.0 eV), μ_3 (887.1 eV)/ ν_3 (906.4 eV) and μ_4 (898.3 eV)/ ν_4 (916.4 eV) correspond to Ce⁴⁺, while μ_2 (885.1 eV)/ v_2 (903.9 eV) indicate Ce³⁺ [15]. The presence of Ce⁴⁺ may be due to the surface oxidation of CePO₄. Apparently, the μ_2/μ_3 peaks of Ce 3d in Mn_{5.64}P₃/CePO₄@Cs show positive shifts of 0.45 eV and 0.56 eV, respectively, compared with CePO₄@Cs. For the Mn 2p XPS spectra (Fig. 3e), the peaks can be deconvoluted into two paired peaks corresponding to Mn²⁺ (641.8 and 653.1 eV) and Mn³⁺ (645.8 and 658.0 eV [44,45]. The Mn 2p peak of Mn_{5.64}P₃/CePO₄@Cs exhibits a negative shift (~0.28 eV) relative to Mn_{5.64}P₃, revealing that the CePO₄ modulation enhances the electron density of Mn at the interface [13]. These results corroborate the electron transfer from CePO₄ to Mn_{5.64}P₃, consistent with the UPS results. As shown in Fig. 3f, the core-level XPS spectra of P 2p display two prominent peaks at binding energies of 129.5 and 130.5 eV, corresponding to P $2p_{3/2}$ and P $2p_{1/2}$ in M–P bond (M = Mn/Ce). A weak band at 132.6 eV is also observed, indicative of P-O bonding resulting from surface oxidation [46-48]. As illustrated in Fig. 3g, the high-resolution O 1 s spectra exhibits three distinct types of peaks at 529.7, 531.4, and 533.1 eV, corresponding to metal-oxygen (M-O) bonds, O-C=O bond, and surface adsorbed oxygen (H₂O_{ads}), respectively.

3.2. ORR activity in alkaline media

The ORR performance of the developed catalysts was evaluated using a conventional three-electrode configuration in 0.1 M KOH solution. Initially, the impact of varying Mn/Ce ratios on catalyst performance was investigated (Fig. S13), revealing that the catalyst achieves optimum oxygen reduction activity at a Mn/Ce molar ratio of 1/1. Subsequently, polarization curves were obtained for the synthesized Mn_{5.64}P₃/CePO₄@Cs in O₂-saturated electrolyte at different phosphating temperatures (Fig. S14). Impressively, the catalyst synthesized through phosphatization at 1000 °C exhibits superior ORR performance. evident from its high limiting current density (J_L) and $E_{1/2}$. These results clearly indicate that the ORR catalytic activity of catalysts can be effectively optimized by precisely regulating the Mn/Ce molar ratio and phosphating temperature. Using CV to evaluate the catalytic activity of the samples (Fig. 4a), Mn_{5.64}P₃/CePO₄@Cs shows a more positive peak cathodic current, aligning with the ORR activity. Based on the LSV curves (Fig. 4b), Mn_{5.64}P₃/CePO₄@Cs showcases superior ORR activity, outperforming that of Mn_{5.64}P₃@Cs, CePO₄@Cs, and even commercial Pt/C. The Tafel slope can be determined by analyzing the LSV curve in proximity to the onset potential, providing insight into the ORR reaction kinetic rate of the catalysts. The Tafel slope of $Mn_{5.64}P_3$ /CePO₄@Cs is 143 mV dec⁻¹, significantly lower than that of CePO₄@Cs (161 mV $dec^{-1}\mbox{)},$ but higher than that of $Mn_{5.64}P_3@Cs$ (84 mV $dec^{-1}\mbox{)},$ signifying that coupling $Mn_{5.64}P_3$ is favorable for accelerating the reaction kinetic rate of CePO₄, thereby driving the ORR progress (Fig. 4c). As presented in Fig. 4d, $Mn_{5.64}P_3@C$ exhibits inferior catalytic activity, with an $E_{1/2}$ of 0.74 V and a kinetic current density (J_k) of 0.9 mA cm⁻². In contrast, CePO₄@Cs exhibits higher ORR activity ($E_{1/2}=$ 0.76 V, $J_k=$ 2.2 mA cm⁻²). Remarkably, Mn_{5.64}P₃/CePO₄@Cs delivers the highest E_{1/2} (0.80 V) and J_k (5.2 mA cm⁻²). The collaborative synergy of CePO₄ and Mn_{5.64}P₃ considerably enhances the catalytic activity, underscoring their joint efforts to elevate overall ORR performance. The Cdl was determined in the non-Faraday region by performing CV tests at various scan rates to assess the electrochemically active surface area (ECSA), as outlined in Fig. S15. The results show that Mn_{5.64}P₃/CePO₄@Cs exhibits a higher C_{d1} value (4.2 mF cm⁻²) compared to Mn_{5.64}P₃@Cs (1.4 mF cm^{-2}) and CePO₄@Cs (2.3 mF cm^{-2}), suggesting that Mn_{5.64}P₃/ L. Wang et al.

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Fig. 4. Electrochemical performance of different catalysts. (a) Cyclic voltammetry (CV) curves in N₂ or O₂ -saturated 0.1 M KOH solution. (b) Linear sweep voltammetry (LSV) polarization curves in O₂ -saturated 0.1 M KOH electrolyte, (c) Tafel plots, (d) the corresponding half wave potential ($E_{1/2}$) and kinetic current densities (J_k). (e) double layer capacitance (C_{dl}) values. (f) Overviewing of the onset potential (E_{onset}) and $E_{1/2}$ for Mn_{5.64} P₃ /CePO₄ @Cs and the recently reported ORR catalysts. (g) H₂ O₂ yield (%) and electron transfer number (*n*) from various catalysts. (h) Methanol tolerance test of Mn_{5.64} P₃ /CePO₄ @Cs and Pt/C (20 wt%) in 0.1 M KOH with the addition of 3 M methanol at around 400 s. (i) The corresponding stability test in O₂ -saturated 0.1 M KOH solution at a rotating speed of 1600 rpm.

CePO₄@Cs offers a greater number of accessible active sites (Fig. 4e). Electrochemical impedance spectroscopy (EIS) discloses that Mn_{5.64}P₃/ CePO₄@Cs presents a relatively low charge transfer resistance (Fig. S16a), further illustrating that the coupling of Mn₅₆₄P₃ and CePO₄ can efficiently accelerate the charge transfer process [49]. The impedance fitting results depicted in Fig. S16b indicate that the electrode process is primarily attributed to both charge transfer and diffusion processes. The Mn_{5.64}P₃/CePO₄@Cs exhibits satisfactory ORR catalytic activity (E1/2 and Eonset), surpassing recently reported catalysts and other Mn/Ce-based composites (Fig. 4f and Table S3). The Rotating Ring Disk Electrode (RRDE) measurements (Fig. 4g) indicate that the number of electrons transferred (n) for Mn_{5.64}P₃/CePO₄@Cs is precisely 3.95 within the voltage range of 0.2–0.8 V, confirming a direct four-electron pathway from O_2 to H_2O [50]. Methanol tolerance is crucial for the practical application of ORR electrocatalysts. Hence, a methanol tolerance test was performed (Fig. 4h). Remarkably, upon the injection of methanol at 400 s, the current density of Pt/C undergoes a significant decline, while the $Mn_{5.64}P_3$ /CePO₄@Cs electrocatalyst demonstrates negligible sensitivity to methanol, signifying the incredible methanol tolerance of Mn_{5.64}P₃/CePO₄@Cs. Long-term stability is also another crucial indicator of an ideal ORR catalyst. As expected, Mn_{5.64}P₃/ CePO₄@Cs exhibits an impressive current retention of 97 % after the chronoamperometric response for 18 h (Fig. 4i). In contrast, CePO₄@Cs and Mn_{5 64}P₃@Cs only retained 90 % and 73 % after 9 h, respectively. These results unveil that the coupling of earth phosphate CePO₄ greatly

improves the stability of Mn_{5.64}P₃. Consequently, Mn_{5.64}P₃/CePO₄@Cs shows considerable promise for practical applications in methanol fuel cells and metal-air batteries. Post-stability characterization of the Mn_{5.64}P₃/CePO₄@Cs catalyst confirmed the preserved structural integrity of both Mn₅₆₄P₃ and CePO₄ phases via XRD, albeit with a slight reduction in peak intensity (Fig. S17). In addition, the Mn_{5.64}P₃/ CePO₄@Cs catalyst was characterized by XPS after ORR stability testing. The post-reaction C 1 s spectrum (Fig. S18) illustrates the presence of a π - π * bond at 292.1 eV, in contrast to the pristine sample. Additionally, a K 2p peak was observed at 295.1 eV, which can be attributed to the adsorption of K ions by the catalyst during the ORR conducted in 0.1 M KOH. Notably, the other XPS spectra remain predominantly consistent with their initial states (Fig. S19), indicating not only the exceptional corrosion resistance of the carbon matrix but also underscoring the pivotal role of the synergy between $\mathrm{Mn}_{5.64}\mathrm{P}_3$ and CePO_4 in achieving high stability [51].

3.3. DFT calculation

The above results elucidate the charge transfer tendency in $Mn_{5.64}P_3$ /CePO₄, suggesting the form of an interfacial energy barrier arising from the BEF, with electrons migrating from CePO₄ to $Mn_{5.64}P_3$ (Fig. 5a) [12]. To gain deeper insights into the effect of BEF on the electronic structure of the interface and the *d*-band center, DFT calculations were conducted. We acknowledge that vacancies can influence



Fig. 5. (a) Schematic illustration of the electron transfer mechanism in $Mn_{5.64} P_3$ /CePO₄ induced by the BEF. (b) Differential charge density of $Mn_{5.64} P_3$ /CePO₄. (c) The calculated DOS of for the synthesized samples. (d) Free energy diagrams of $Mn_{5.64} P_3$ /CePO₄ , $Mn_{5.64} P_3$ and CePO₄ towards ORR. (e) Corresponding overpotential for of $Mn_{5.64} P_3$ /CePO₄ , $Mn_{5.64} P_3$ and CePO₄ , $Mn_{5.64} P_3$ and CePO₄ . (f) Schematic of the ORR catalytic mechanism for $Mn_{5.64} P_3$ /CePO₄ .

ORR mechanisms. However, our study focuses on the dominant oxygen adsorption mechanism, which is consistent with existing theoretical research. For instance, Wang et al. utilized this mechanism in Fe-N-C catalysts [52], and Zhang et al. demonstrated its significance in CoO oxides despite varying vacancy levels [53]. Our findings align with this established understanding in the literature. Therefore, the Mn_{5.64}P₃ (210)-CePO₄ (110) plane was chosen as the optimization model for the Mn_{5.64}P₃/CePO₄ heterostructure based on HR-TEM analysis. In addition, a comparative model of $Mn_{5.64}P_3$ (210) and CePO₄ (110) was established for reference (Fig. S20). It is widely recognized that metal sites serve are active centers in electrochemical reactions. Thus, all calculations were performed based on the Mn and Ce sites. The differential charge density results reveal a notable depletion of electrons around CePO₄, accompanied by a substantial accumulation of electrons surrounding $Mn_{5.64}P_3$ (Fig. 5b, where yellow areas indicate electron accumulation and cyan areas indicate electron depletion). This indicates that local charge redistribution occurs at the Mn_{5.64}P₃/CePO₄@Cs interface, facilitating the migration of electrons from CePO₄ to Mn_{5.64}P₃, which aligns with the UPS and XPS results. Bader charge analysis (Table S2) discloses that Mn_{5.64}P₃ acquires electrons and exhibits a Bader charge of -0.34 e⁻, whereas CePO₄ undergoes electron loss and manifests a Bader charge of 0.34 e⁻. These observations are consistent with the differential charge density analysis results. The density of states (DOS) results indicated that the ε_d value for Mn_{5.64}P₃/CePO₄@Cs is -1.01 eV, while the ε_d values for Mn_{5.64}P₃@Cs and CePO₄@Cs are -0.85 eV and -1.33 eV, respectively (Fig. 5c). This observation implies that the construction of the heterointerface between Mn_{5.64}P₃ and CePO₄ facilitates the formation of a beneficial BEF, optimizing the adsorption/desorption strength of the intermediates and thereby accelerating the ORR kinetics [54]. As shown in Fig. 5d, the fundamental steps of all models reveal thermodynamic downhill behavior at U = 0 V, suggesting that the reactions tend toward instantaneous exothermicity

[55]. When U = 1.23 V, the rate-determining step (RDS) (*OH + $e^- \rightarrow *$ + OH⁻) for Mn_{5.64}P₃/CePO₄-Ce presents an energy barrier of 0.43 eV, lower than the 0.48 eV at the Mn site, as well as the $Mn_{5.64}P_3$ (*OOH + $e^- \rightarrow O + OH^-$, -1.36 eV) and CePO₄ (*O + H₂O + $e^- \rightarrow *OH + OH^-$, 0.63 eV). This reduced barrier expedites the refreshment of the active site. These results substantiate that Mn_{5.64}P₃/CePO₄ demonstrates superior intrinsic activity, with Ce serving as the primary active site for promoting the ORR process [56]. DFT calculations indicate that the overpotential (\eta) at the Ce site of $Mn_{5.64}P_3/\text{CePO}_4$ is 0.43 V, which is lower than that at the Mn site ($\eta = 0.48$ V), as well as that of Mn_{5.64}P₃ (η = 0.63 V) and CePO₄ (η = 1.07 V) (Fig. 5e). Fig. 5f illustrates the optimized adsorption structures and evolution of the ORR intermediates (including *OOH, *O, and *OH) on the active Ce sites in $Mn_{5.64}P_3/$ CePO₄. In summary, the BEF formed in $Mn_{5.64}P_3$ /CePO₄ promotes interfacial charge redistribution and reduces the energy barrier of RDS, thus enhancing the ORR activity [57].

3.4. Test for performance of assembled ZABs

Inspired by the exceptional ORR performance of $Mn_{5.64}P_{3/}$ CePO₄@Cs, we constructed a lab-made ZAB, as illustrated in Fig. 6a. The $Mn_{5.64}P_{3/}$ CePO₄@Cs-based ZAB exhibits a superior open-circuit voltage (OCV) compared to the platinum-based alternative (Fig. 6b). Interestingly, it can also illuminate an LED screen (the inset of Fig. 6b). The polarization curves and power densities of the assembled ZABs (Fig. 6c) unveil that $Mn_{5.64}P_{3/}$ CePO₄@Cs achieves a maximum power density of 168 mW cm⁻², outstripping that of Pt/C (129 mW cm⁻²). This advancement can be credited to the synergistic interplay between $Mn_{5.64}P_3$ @Cs and CePO₄@Cs, supported by a large specific surface area and highly conductive carbon sphere carriers, facilitating efficient oxygen diffusion and electrolyte infiltration into the heterostructure phosphide/phosphate electrocatalytic center. Additionally, at a current



Fig. 6. (a) Schematic configuration of assembled aqueous ZAB. (b) OCV of the ZABs (inset: digital image of LED panel lit by an assembled $Mn_{5.64} P_3$ /CePO₄ @Cs-based ZAB). (c) Discharge polarization curves and the corresponding power densities of the ZABs. (d) Specific capacity plots. (e) Discharge curves at various current densities. (f) Comparison of $Mn_{5.64} P_3$ /CePO₄ @Cs as air cathode with other recently reported excellent catalysts. (g) Charge-discharge cycle curves at a current density of 5 mA cm⁻².

density of 5 mA cm⁻², the Mn_{5.64}P₃/CePO₄@Cs-based battery achieves a specific capacity of up to 708 mAh g_{Zn}^{-1} , surpassing the Pt/C-based battery (702 mAh g_{Zn}^{-1}), as illustrated in Fig. 6d. The multiplicative performance of ZABs at discharge current densities ranging from 2 to 50 mA cm^{-2} was investigated. As shown in Fig. 6e, the discharge voltage declines with increasing current density. Notably, the discharge voltage remains above 0.8 V even at the elevated current density of 50 mA cm $^{-2}$. When the current density is reverted to 2 mA cm^{-2} , the voltage exhibits only a slight decay of 0.04 V compared to the initial current density, demonstrating the stability of the system. As depicted in Fig. 6f and Table S4, the Mn_{5.64}P₃/CePO₄@Cs-based ZAB exhibits superior power density and specific capacity compared to recently reported Mn/Cebased and phosphide-based ZABs. Considering the poor OER performance observed in Fig. S21, with an overpotential of 676 mV at a current density of 20 mA cm⁻², Mn_{5.64}P₃/CePO₄@Cs + RuO₂ (mass ratio = 2:1) was used as the air cathode to evaluate the charge-discharge stability of the ZAB. For comparison, Pt/C + RuO₂ was also prepared. Moreover, the Mn_{5.64}P₃/CePO₄@Cs + RuO₂-based ZAB operates continuously for 400 h with a voltage retention of up to 90 % (Fig. 6g). Contrarily, the Pt/C + RuO₂-assembled ZAB demonstrates limited cycling stability, functioning for only 120 h with voltage retention of merely 82 %, underscoring the superior stability of the Mn_{5.64}P₃/ CePO₄@Cs-based ZAB.

4. Conclusions

In summary, Mn_{5.64}P₃/CePO₄ catalyst with abundant heterointerface is synthesized and immobilized on carbon sphere supports via hightemperature phosphorylation of Mn-Ce species. As anticipated, the meticulously engineered Mn_{5.64}P₃/CePO₄@Cs exhibits encouraging durability and methanol tolerance, overmatching the Pt/C benchmark. The Mn_{5.64}P₃/CePO₄@Cs-based ZAB achieves a peak power density of 168 mW cm^{-2} , surpassing that of the Pt/C counterpart (129 mW cm $^{-2}$). Moreover, the catalyst demonstrates remarkable stability during the discharge-charge cycling, maintaining operation for 400 h with a retained round-trip efficiency of 90 %. The satisfactory ORR performance arises from forming BEF at the Mn_{5.64}P₃/CePO₄ heterointerface, which modulates the electronic structure and lowers the reaction energy barrier. Simultaneously, the highly dispersed mesoporous spherical structure enhances electrical conductivity and increases the availability of active sites, thereby facilitating mass and electron transport. This work sheds new light on the optimization of electronic structure through the strategic construction of BEF to enhance the catalytic ORR performance.

CRediT authorship contribution statement

Lixia	Wang:	Writing	_	original	draft,	Investigation,

Conceptualization. Jiasui Huang: Investigation. Bowen Yao: Data curation. Zhiyang Huang: Methodology. Aling Zhou: Data curation. Haoran Yin: Methodology. Tayirjan Taylor Isimjan: Writing – review & editing. Bao Wang: Writing – review & editing. Xiulin Yang: Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been supported by the National Natural Science Foundation of China (no. 52363028, 21965005), Natural Science Foundation of Guangxi Province (2021GXNSFAA076001. 2018GXNSFAA294077), Guangxi Technology Base and Talent Subject (GUIKE AD23023004, GUIKE AD20297039), Guangxi Training Program of Innovation and Entrepreneurship for Undergraduates (S202410602135).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2025.138141.

Data availability

Data will be made available on request.

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