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# Engineering built-in electric fields in oxygen-deficient MnO-CeO<sub>2</sub>@Cs catalysts: enhanced performance and kinetics for the oxygen reduction reaction in aqueous/flexible zinc–air batteries†

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Deliberate engineering of built-in electric fields (BEFs) can facilitate electron transfer and promote asymmetrical charge distribution, thereby regulating the adsorption/desorption of reaction intermediates. Herein, an oxygen-deficiency-rich MnO-CeO<sub>2</sub> is synthesized supported on a carbon sphere (MnO-CeO<sub>2</sub>@Cs), adeptly crafted with a prominent work function difference ( $\Delta\Phi$ ) and robust BEF, targeting the electrocatalytic oxygen reduction reaction (ORR). Empirical and theoretical results substantiate that the BEF triggers interfacial charge redistribution, fine-tuning the adsorption energy of oxygen intermediates and hastening reaction kinetics. Consequently, the MnO-CeO<sub>2</sub>@Cs showcases commendable performance ( $E_{1/2} = 0.80$  V and  $j_L = 5.5$  mA cm<sup>-2</sup>), outshining its single-component counterparts. Impressively, the MnO-CeO<sub>2</sub>@Cs-based zinc–air batteries (ZABs) boast an exemplary power density of 202.7 mW cm<sup>-2</sup> and enduring stability of 297 h. Additionally, the solid-state ZAB commands a peak power density of 67.4 mW cm<sup>-2</sup>, underscoring its potential in flexible ZAB applications. This work delineates a strategic avenue to harness interfacial charge redistribution, aiming to enhance the catalytic performance and longevity of energy conversion/storage apparatuses.

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## 1. Introduction

Achieving zero-emission goals, critical for tackling climate change, demands the introduction of energy storage and conversion technologies.<sup>1</sup> In this regard, various groundbreaking electrocatalytic devices have been crafted to capture intermittent renewable energy sources and reach carbon neutrality.<sup>2</sup> Notably, zinc–air batteries (ZABs) stand out due to their high theoretical energy density, cost-effectiveness, environmental sustainability, and safety features.<sup>3,4</sup> However, their utility is hampered by the slow kinetics of the cathodic oxygen reduction reaction (ORR), impacting their energy efficiency and power density.<sup>5</sup> Historically, platinum-based materials

have been the leading ORR electrocatalysts.<sup>6,7</sup> Regrettably, their high cost, limited availability, and durability issues hinder their widespread adoption.<sup>8</sup> Consequently, crafting affordable and efficient ORR electrocatalysts is pivotal for ZAB advancement.<sup>9</sup>

Transition metal oxides are gaining traction as potential oxygen electrocatalysts, with Mn-based oxides drawing attention for their cost-effectiveness and abundant supply.<sup>10–12</sup> These oxides exhibit excellent capability in facilitating charge transfer and accelerating the decomposition of intermediates.<sup>13</sup> Moreover, the rare-earth metal oxide CeO<sub>2</sub> is widely employed in various catalytic domains, attributed to its superb catalytic activity and resilience.<sup>14</sup> The reversible redox switch between Ce<sup>3+</sup> and Ce<sup>4+</sup> in CeO<sub>2</sub> ensures facile electron flow without affecting its structure integrity.<sup>15</sup> To address the limitations of individual components, heterostructure engineering is a powerful tactic, offering more active sites at their interface.<sup>16</sup> Therefore, melding MnO with CeO<sub>2</sub> offers a logical step in ORR catalyst design.

Additionally, a well-orchestrated built-in electric field (BEF), established by merging components with differing Fermi levels, can adeptly modify the electronic configuration of the

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active site and balance the adsorption/desorption kinetics of reactants and intermediates.<sup>17</sup> Significantly, the work function variance between these components creates an inherent driving force and imparts directionality for charge transfer at the interface.<sup>18</sup> Hence, understanding the relation between interfacial BEF and the intermediate adsorption behavior is critical to decoding the core catalytic mechanism of ORR. Introducing vacancies, engineering heterogeneous interfaces, and employing heteroatom doping are powerful strategies for efficiently inducing charge redistribution within electrocatalysts, effectively promoting the formation of a BEF.<sup>19</sup> Moreover, merging heterojunction catalysts with carbon aids enhances electron transfer, invoking mutual benefits from the catalyst-carbon interaction and spatial restrictions of the carbon matrix.<sup>20</sup> This can enhance conductivity and catalytic prowess, thus accelerating electron transfer rates and overall catalytic performance.<sup>21</sup> Besides, introducing oxygen vacancies can serve as active centers in the catalytic reaction, thereby facilitating the reaction kinetics.<sup>8</sup> For instance, Wang *et al.* adeptly engineered Co<sub>3</sub>O<sub>4</sub> through thermal annealing with controllable oxygen vacancies.<sup>22</sup> These introduced vacancies triggered the formation of BEF, showcasing remarkable electrochemical performance in Li-ion batteries. Nevertheless, excessive oxygen vacancies can result in morphological changes and structural damage, leading to a reduction in catalytic performance.<sup>23</sup> Thus, balanced oxygen vacancy content in catalysts typically exhibit superior electrocatalytic activity.<sup>24</sup>

Inspired by these insights, exploring the profound impact of the BEF on ORR catalysts and zinc-air batteries, this study employs DFT calculations to unveil BEF's role in optimizing oxygen intermediate adsorption. Experimental results reveal that the prepared catalyst possessed a pronounced energy difference, prompting electron transfer from MnO to CeO<sub>2</sub>, resulting in a stable BEF at the interface. MnO-CeO<sub>2</sub>@Cs demonstrate enhanced ORR activity compared to MnO@Cs and CeO<sub>2</sub>@Cs, excelling in current density, kinetic density, and half-wave potential. The BEF further improves reaction kinetics, reflected in the smaller Tafel slope. MnO-CeO<sub>2</sub>@Cs-based zinc-air batteries showcase exceptional performance with accelerated reaction kinetics.

## 2. Experimental section

### 2.1. Materials

Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>·6H<sub>2</sub>O), potassium permanganate (KMnO<sub>4</sub>, 99.5%), and absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.7%) were acquired from xilong chemical Co., Ltd. Dopamine hydrochloride ((HO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>·HCl, 98%), polyvinylpyrrolidone (PVP), cerium(III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.95%), zinc acetate ((CH<sub>3</sub>COO)<sub>2</sub>Zn, 99%), and commercial Pt/C (20 wt% Pt) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Nafion (5 wt%) was acquired from Alfa Aesar, and potassium hydroxide (KOH, 90%) was obtained from Macklin Biochemical Co., Ltd. All reagents were analytical grade and were used without any further purification.

### 2.2. Synthesis of carbon spheres (Cs)

Highly dispersed carbon spheres (Cs) were acquired following procedures outlined in previously reported work.<sup>25</sup> In a typical synthesis process, 25 μL of 1 M KOH was added to 40 mL of 0.5 M glucose solution under vigorous stirring, until a colorless and transparent solution was obtained. Subsequently, the resulting solution was transferred to a Teflon-lined stainless-steel autoclave at 180 °C for 6 h. The dark brown product was collected by centrifugation, washed multiple times with deionized water and ethanol, and finally dried at 60 °C overnight.

### 2.3. Synthesis of Mn<sub>3</sub>O<sub>4</sub> particles

50 mg of the above Cs were dispersed in 10 mL of 0.01 M KMnO<sub>4</sub> solution, stirred in air for 30 min to form a uniform purple slurry which was then centrifuged and dried. The resulting powder was oxidationba0093354Tm(1r)191i400°Cfor 3h.

### 2.4. Synthesis of Mn<sub>3</sub>O<sub>4</sub>/PVP

100 mg Mn<sub>3</sub>O<sub>4</sub> was dispersed in 20 mL of deionized water, 0.1 g dopamine hydrochloride and 0.5 g PVP were dis-

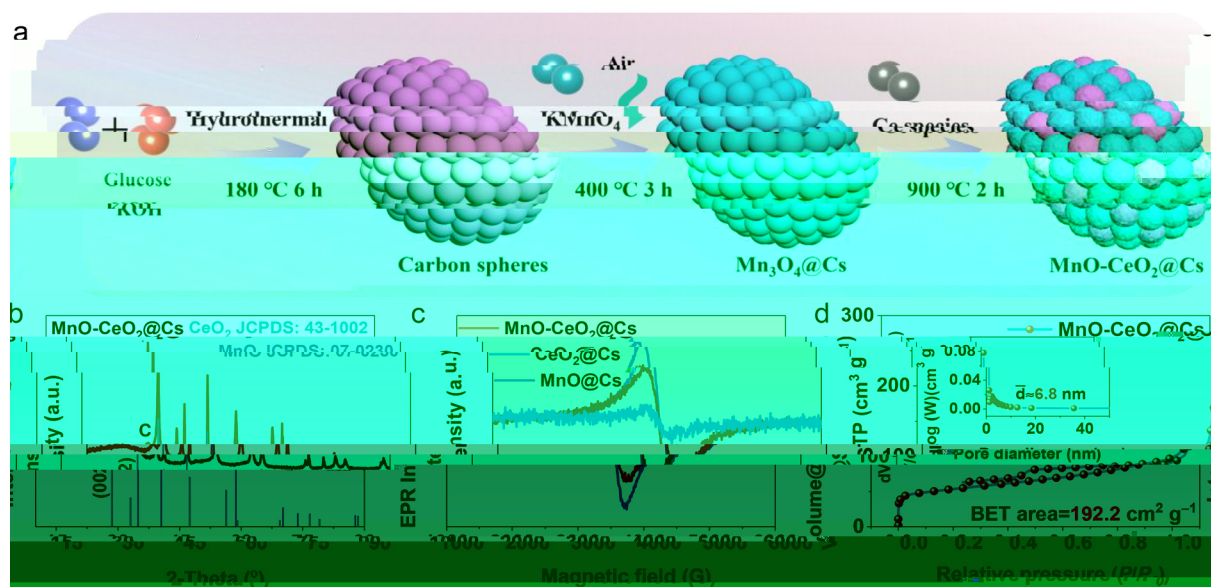


Fig. 1 (a) Schematic illustration of the synthesis process. (b) XRD pattern of  $\text{MnO-CeO}_2$ @Cs. (c) EPR spectra of as-synthesized samples. (d)  $\text{N}_2$  adsorption-desorption isotherm with the inset showing the corresponding pore size distribution of  $\text{MnO-CeO}_2$ @Cs.

(JCPDS: 07-0230) and  $\text{CeO}_2$  (JCPDS: 43-1002), respectively. After coating the Ce species on the  $\text{Mn}_3\text{O}_4$ @Cs precursor, the dominant diffraction peaks align with  $\text{MnO}$  and  $\text{CeO}_2$ , with a distinct diffraction peak at  $26^\circ$  attributed to the (002) crystal plane of graphitic carbon (Fig. 1b).<sup>27</sup> The D band ( $1350 \text{ cm}^{-1}$ ) and G band ( $1586 \text{ cm}^{-1}$ ) in the Raman spectra (Fig. S4†) are used to reflect the defects and disorder of  $\text{sp}^3$  carbon, as well as the graphitization degree of  $\text{sp}^2$  hybrid carbon in the graphite structure, respectively.<sup>28</sup> Importantly, graphitized carbon enhances electrical conductivity, and defective carbon provides numerous active sites.<sup>29</sup> The  $I_D/I_G$  ratios for  $\text{MnO-CeO}_2$ @Cs,  $\text{MnO}$ @Cs and  $\text{CeO}_2$ @Cs were 1.03, 1.12 and 0.97, respectively. This suggests that coupling  $\text{CeO}_2$  to  $\text{MnO}$ @Cs delivers an optimal balance of carbon defects and graphitization, ensuring an optimal number of active sites and commendable electrical conductivity.<sup>30</sup> Moreover, fine-tuning the quantity of Ce elements (0.25, 0.50, and 0.75 mmol) and the calcination temperature (800, 900, and 1000 °C), we successfully synthesized  $\text{MnO-CeO}_2$ @Cs catalysts with varying crystallinity and  $I_D/I_G$  values. Remarkably, the catalyst synthesized with 0.50 mmol of Ce species, and pyrolyzed at 900 °C demonstrated the best crystallinity alongside an optimal level of defects and graphitization (Fig. S5 and 6†). These results underscore the substantial impact of the quantity of Ce species and the precise control of calcination temperature on the crystallinity and defect level of  $\text{MnO-CeO}_2$ @Cs catalysts. Additionally, Fig. 1c displays the electron paramagnetic resonance (EPR) spectra of the samples, with peak intensity positively correlated with the oxygen vacancy content ( $g = 2.002$ ).<sup>31</sup> Remarkably,  $\text{MnO}$ @Cs exhibits the highest concentration of oxygen vacancies, attributable to the formation of vacancies during the oxidation with potassium permanganate and calcination processes. Conversely,  $\text{CeO}_2$ @Cs displays the lowest

concentration of oxygen vacancies, possibly due to the loading of Ce species stabilizing the lattice structure of  $\text{CeO}_2$ . Interestingly, the coupling  $\text{CeO}_2$  in  $\text{MnO}$  decreases the oxygen vacancy concentration. This phenomenon can be attributed to the interfacial effect between  $\text{MnO}$  and  $\text{CeO}_2$ , where the introduction of  $\text{Ce}^{4+}$  replaces some of the  $\text{Mn}^{2+}$  and occupies the oxygen vacancies.<sup>32</sup> Intriguingly, the EPR signals displayed similarity for Ce species added at 0.25 and 0.50 mmol (Fig. S7†). However, increasing the amount to 0.75 mmol led to the strongest EPR signal but suboptimal performance. These findings underscore the significance of fine-tuning the ratio to control the oxygen vacancy concentration, emphasizing the advantage of maintaining a moderate oxygen vacancy concentration for enhancing the electrocatalytic ORR performance.  $\text{N}_2$  adsorption-desorption isotherm analysis on the samples revealed reversible type IV curves with a significant hysteresis loop (Fig. 1d and Fig. S8†).<sup>33</sup> Specifically, the specific surface area of  $\text{MnO-CeO}_2$ @Cs is  $192.2 \text{ m}^2 \text{ g}^{-1}$ , slightly lower than that of  $\text{MnO}$ @Cs ( $309.4 \text{ m}^2 \text{ g}^{-1}$ ) and  $\text{CeO}_2$ @Cs ( $377.8 \text{ m}^2 \text{ g}^{-1}$ ). This result is attributed to the incorporation of  $\text{MnO}$  and  $\text{CeO}_2$  onto the carbon spheres, leading to the formation of inherent agglomerates during the high temperature calcination process.<sup>34</sup> Importantly, all three catalysts showcase a mesoporous structure with a pore size in the range of 5.0–7.7 nm. This mesoporous architecture not only fosters favorable electrolyte-active site interactions but also expedites ion transportation during the ORR process.<sup>35,36</sup>

The morphology and structural of the catalysts were assessed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 2a, the synthesized glucose carbon spheres which exhibit the spheres structure with a smooth surface. In Fig. 2b, the SEM images of  $\text{MnO-CeO}_2$ @Cs depicts a consistent spherical design even

after high-temperature calcination. However, a noticeable alteration is the evolution of its surface to a lychee-like rough and textured appearance. TEM images (Fig. 2c) further illustrated the litchi-like morphology, with the intricate distribution of CeO<sub>2</sub> nanoparticles within the MnO matrix. This embedding process is facilitated during calcination. We have clarified the structural features revealed by the high-resolution TEM (HR-TEM) image, as indicated by the green dashed line in Fig. 2d. This image exposes a well-defined heterostructure between MnO and CeO<sub>2</sub>, emphasizing a robust interfacial coupling. The discernible lattice fringes within the heterostructure provide insight into the (111) planes of MnO and CeO<sub>2</sub>, with respective spacings of 0.257 and 0.328 nm. Additionally, Fig. 2e offers an energy-dispersive X-ray spectroscopy (EDS) spectrum for MnO-CeO<sub>2</sub>@Cs, confirming the presence of C, O, Mn, and Ce elements. Moreover, high-angle annular dark-field STEM (HAADF-STEM) and corresponding elemental mapping disclosed the uniform distribution of C, O, Ce, and Mn across the nanosphere (Fig. 2f). Basic and above, it is plausible that interdiffusion occurs between MnO and CeO<sub>2</sub> rather than the formation of a solid solution. XRD analysis definitively confirms the identical phase composition of MnO-CeO<sub>2</sub>@Cs to that of MnO@Cs and CeO<sub>2</sub>@Cs. Furthermore, the crystal structure and lattice parameters of MnO-CeO<sub>2</sub>@Cs remain consistent with those of the individual material phases. Both SEM and TEM observations reveal an alternating arrangement of the two substances, strongly suggesting interdiffusion between MnO and CeO<sub>2</sub>.

Ultraviolet photoemission spectroscopy (UPS) is a pivotal technique for determining the work function of a catalyst. It sheds light on the synergy between a material's electronic pro-

perties and its electrocatalytic activity.<sup>37</sup> Essentially, UPS reveals the minimum energy required for electrons to transition from the Fermi level to the vacuum level, suggesting

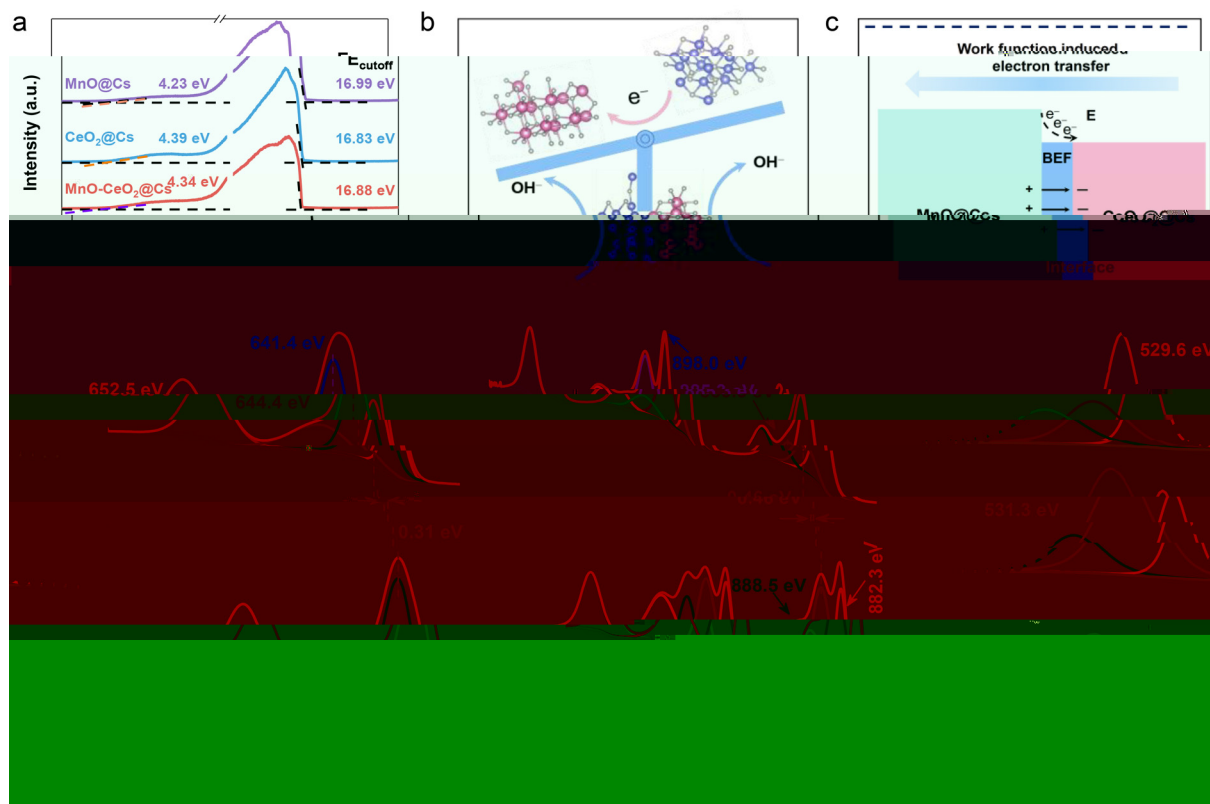


Fig. 3 (a) UPS spectra of MnO@Cs, CeO<sub>2</sub>@Cs and MnO-CeO<sub>2</sub>@Cs. (b) Proposed ORR process and regulated mechanism of electronic structure in MnO-CeO<sub>2</sub>@Cs. (c) Charge transfer process in MnO-CeO<sub>2</sub>@Cs. High-resolution XPS spectra of (d) Mn 2p, (e) Ce 3d, and (f) O 1s in MnO-CeO<sub>2</sub>@Cs, MnO@Cs and CeO<sub>2</sub>@Cs.

2p<sub>3/2</sub> at 644.4 eV.<sup>42</sup> The binding energies of Mn<sup>2+</sup> in MnO-CeO<sub>2</sub>@Cs were positively shifted by 0.31 eV compared to MnO@Cs, signifying that the inclusion of CeO<sub>2</sub> leads to a lower valence state of the Mn ion.<sup>43</sup> The Ce 3d XPS spectra of MnO-CeO<sub>2</sub>@Cs and CeO<sub>2</sub>@Cs is presented in Fig. 3e, where  $\mu$  and  $\nu$  represent the spin-orbit coupling of Ce 3d<sub>5/2</sub> and Ce 3d<sub>3/2</sub>, respectively. Specifically, three sets of peaks at  $\mu_1$  (882.3 eV)/ $\nu_1$  (900.6 eV),  $\mu_3$  (888.5 eV)/ $\nu_3$  (907.2 eV), and  $\mu_4$  (898.0 eV)/ $\nu_4$  (916.4 eV) correspond to three different states of Ce(IV). Meanwhile, a unique peak set at  $\mu_2$  (885.3 eV)/ $\nu_2$  (903.9 eV) indicative of Ce(III).<sup>44</sup> The existence of Ce(III) may be attributed to the reduction of CeO<sub>2</sub>, resulting in the release of oxygen and the formation of oxygen vacancies in CeO<sub>2</sub>.<sup>45</sup> Significantly, the  $\mu_2$  peak of Ce 3d in MnO-CeO<sub>2</sub>@Cs exhibits a negative shift of 0.46 eV compared to CeO<sub>2</sub>@Cs, providing further evidence for electron transfer from MnO to CeO<sub>2</sub>, echoing the findings from the UPS analysis. As well, the high-resolution O 1s spectra (Fig. 3f) exhibited three main peaks at 529.6 eV, 531.3 eV and 533.1 eV, which were attributed to lattice oxygen (O<sub>L</sub>), oxygen vacancies (O<sub>V</sub>) and adsorbed oxygen (O<sub>A</sub>), respectively.<sup>46</sup>

### 3.2. t t

Considering the profound BEF, the ORR electrocatalytic activity of the various electrocatalysts was appraised in a 0.1 M

KOH solution. Through optimization processes, the prime catalyst was pinpointed and formulated with a Ce species molar count of 0.5 and a calcination temperature of 900 °C, termed MnO-CeO<sub>2</sub>@Cs (Fig. S10, 11 and Table S1†). As depicted in Fig. 4a, the cathodic peaks of MnO-CeO<sub>2</sub>@Cs is favorably positioned at more electropositive potentials in contrast to MnO@Cs, CeO<sub>2</sub>@Cs, and Pt/C, indicating that the constructed BEF conferred its preeminence in ORR activity. Furthermore, MnO-CeO<sub>2</sub>@Cs showcases exceptional ORR activity (Fig. 4b), with an onset potential ( $E_{\text{onset}}$ ) and limiting current density ( $j_L$ ) outclassing its contemporaries and aligning closely with Pt/C, even besting several advanced catalysts (Table S2†). Half-wave potential ( $E_{1/2}$ ) and kinetic current density ( $J_k$ ) are crucial parameters for assessing ORR performance. As portrayed in Fig. 4c, MnO-CeO<sub>2</sub>@Cs demonstrates the highest  $E_{1/2}$  value (0.8 V), surpasses both CeO<sub>2</sub>@Cs (0.69 V) and MnO@Cs (0.67 V). Moreover, the  $J_k$  value of MnO-CeO<sub>2</sub>@Cs robustly outperforms its peers, emphasizing its distinguished ORR capabilities. The Tafel slope, indicative of ORR reaction kinetics in electrocatalysts, for MnO-CeO<sub>2</sub>@Cs is 37.4 mV dec<sup>-1</sup>, considerably lower than that of MnO@Cs (81.8 mV dec<sup>-1</sup>), CeO<sub>2</sub>@Cs (62.8 mV dec<sup>-1</sup>), and Pt/C (65.0 mV dec<sup>-1</sup>), emphasizing the superior reaction kinetics of MnO-CeO<sub>2</sub>@Cs (Fig. 4d).<sup>47</sup> The electrochemical behavior of MnO-CeO<sub>2</sub>@Cs was meticulously scrutinized using ORR polar-

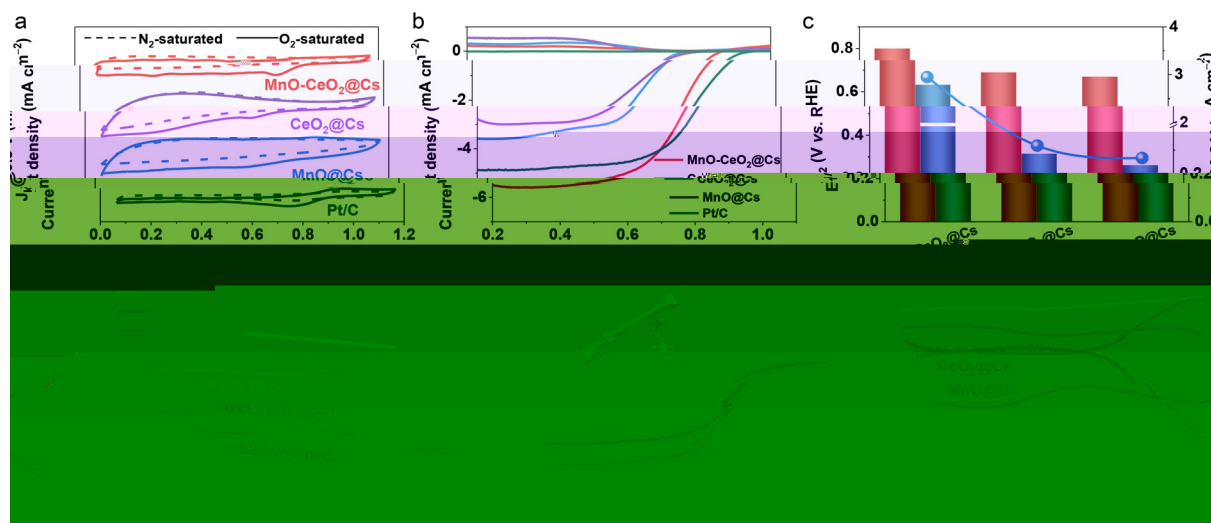


Fig. 4 (a) CV curves in  $\text{N}_2$  or  $\text{O}_2$ -saturated 0.1 M KOH solutions. (b) LSV polarization curves in  $\text{O}_2$ -saturated 0.1 M KOH electrolyte, (c) the corresponding half-wave potential ( $E_{1/2}$ ) and kinetic current density ( $J_k$ ) at 0.8 V, and (d) Tafel plots of different catalysts. (e) Polarization curves of  $\text{MnO-CeO}_2@\text{Cs}$  with various rotating speeds from 400 to 1600 rpm, and the corresponding K–L plots (inset). (f)  $\text{H}_2\text{O}_2$  yield (%) and electron transfer number ( $n$ ) from various catalysts.

ization curve tests over various rotation speeds (400–1600 rpm), displayed in Fig. 4e. The corresponding Koutechy–Levich (K–L) plot indicates an electron transfer number ( $n$ ) nearing 4, proving a predominant four-electron transfer reaction (inset of Fig. 4e).<sup>48</sup> As illustrated in Fig. 4f,  $\text{MnO-CeO}_2@\text{Cs}$  exhibits a low  $\text{H}_2\text{O}_2$  yield (<20%) and a high electron transfer number (>3.9) in the potential range of 0.2–0.8 V, underscoring its predilection for a direct four-electron ( $4e^-$ ) reduction pathway.<sup>49</sup>

Delving deeper into the electrochemical active surface area (ECSA), CV scans were taken for each catalyst across varied scan rates (Fig. S12<sup>†</sup>). The ECSA of  $\text{MnO-CeO}_2@\text{Cs}$  is  $201.7 \text{ cm}^2$ , surpassing  $\text{CeO}_2@\text{Cs}$  ( $33.3 \text{ cm}^2$ ), and showing a slight increase compared to  $\text{MnO}@\text{Cs}$  ( $195.0 \text{ cm}^2$ ). Despite a small improvement in surface area,  $\text{MnO-CeO}_2@\text{Cs}$  performed better than  $\text{MnO}@\text{Cs}$  in ORR, showing the importance of the BEF (Fig. S13<sup>†</sup>).<sup>50</sup> This dominance was further echoed in CV tests using a  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution (Fig. S14<sup>†</sup>). When evaluating methanol tolerance,  $\text{MnO-CeO}_2@\text{Cs}$  demonstrated unparalleled resilience against methanol interference, a feat not mirrored by the commercial Pt/C (Fig. S15a<sup>†</sup>).<sup>51</sup> In durability tests spanning 40 000 s (illustrated in Fig. S15b<sup>†</sup>),  $\text{MnO-CeO}_2@\text{Cs}$  retained a staggering 99.4% of its initial activity, overshadowing Pt/C. This finding indicates the superior durability of  $\text{MnO-CeO}_2@\text{Cs}$ , primarily attributed to its porous carbon sphere structure, which facilitates mass charge transport and effectively prevents the aggregation of metal ions during the electrochemical process.<sup>52</sup> Collectively, the performance of  $\text{MnO-CeO}_2@\text{Cs}$  metrics solidify its considerable potential in practical electrocatalytic endeavors.

The  $\text{MnO-CeO}_2@\text{Cs}$  catalyst was characterized after stability testing, revealing that it maintained its composition of MnO and  $\text{CeO}_2$ , as validated by XRD analysis. SEM images revealed

that the  $\text{MnO-CeO}_2@\text{Cs}$  catalyst retained its lyotropic rough appearance, with minimal agglomeration observed (Fig. S16<sup>†</sup>), in agreement with the TEM results. Notably, EDS elemental mapping exhibited a uniform distribution of C, O, Ce, and Mn throughout the entirety of the catalyst, providing compelling evidence for the impressive structural stability displayed by  $\text{MnO-CeO}_2@\text{Cs}$ .

### 3.3. ZAB performance

Given the impressive electrocatalytic performance of  $\text{MnO-CeO}_2@\text{Cs}$ , we constructed an aqueous ZAB to assess its potential applications in energy storage and conversion devices. In light of the suboptimal OER performance observed in Fig. S17<sup>†</sup>, the charge–discharge stability of ZAB was assessed using  $\text{MnO-CeO}_2@\text{Cs} + \text{RuO}_2$  (mass ratio = 2 : 1) as the air cathode. Simultaneously, Pt/C +  $\text{RuO}_2$  was prepared for comparison. As illustrated in Fig. 5a, the ZAB was equipped with a zinc plate anode,  $\text{MnO-CeO}_2@\text{Cs}$  as the cathode, and 6.0 M KOH containing 0.2 M  $\text{Zn}(\text{AC})_2$  as the electrolyte. The ZAB built with  $\text{MnO-CeO}_2@\text{Cs}$  displayed a commendable open-circuit voltage (OCV) of 1.53 V, outpacing the OCV of the Pt/C (1.41 V) ZAB and other comparative samples (Fig. 5b and Fig. S18a<sup>†</sup>). Notably, the ZAB even powered a “Mn–Ce” LED screen (inset of Fig. 5b).  $\text{MnO-CeO}_2@\text{Cs}$  delivered a specific capacity of  $802 \text{ mA h g}_{\text{Zn}}^{-1}$ , higher than that of Pt/C based ZAB ( $699 \text{ mA h g}_{\text{Zn}}^{-1}$ ), further affirming its exemplary efficiency (Fig. 5c). Encouragingly, the  $\text{MnO-CeO}_2@\text{Cs}$  reached a peak power density of  $202.7 \text{ mW cm}^{-2}$  (Fig. 5d), considerably outperforming the Pt/C ( $127.6 \text{ mW cm}^{-2}$ ),  $\text{CeO}_2@\text{Cs}$  ( $159.1 \text{ mW cm}^{-2}$ ) and  $\text{MnO}@\text{Cs}$ -based ( $99.8 \text{ mW cm}^{-2}$ ) counterparts (Fig. S18b<sup>†</sup>). When benchmarked against recent advancements in oxide ORR catalysts for ZABs,  $\text{MnO-CeO}_2@\text{Cs}$  stands out in both power density and capacity (Fig. 5e and Table S3<sup>†</sup>).

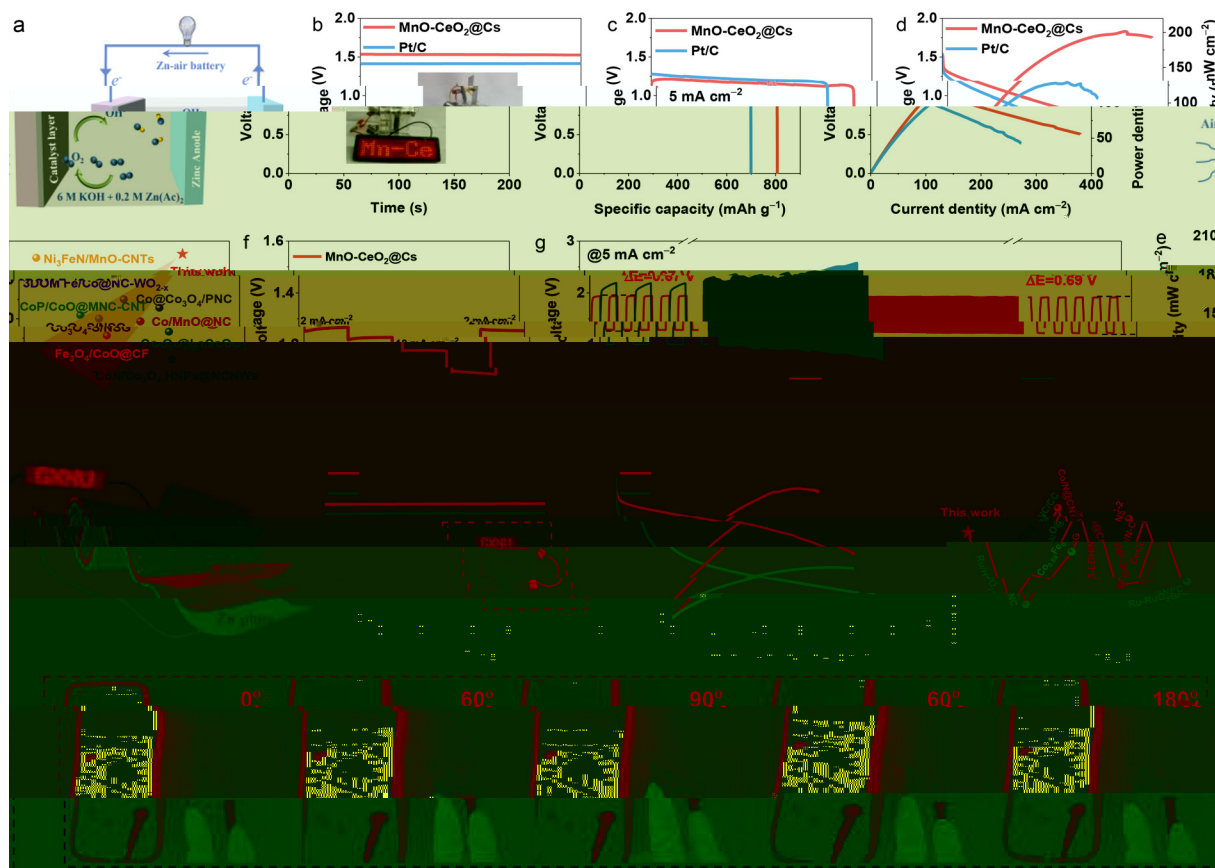


Fig. 5 (a) Schematic configuration of assembled ZAB. (b) Open-circuit voltage (OCV) plots (inset: digital image of LED panel lit by an assembled ZAB). (c) Specific capacity plots. (d) Discharge polarization curves and the corresponding power densities of the catalysts. (e) Comparison of MnO-CeO<sub>2</sub>@Cs as air cathode with other recently reported oxide ORR catalysts, in terms of power density and specific capacity. (f) Discharge profiles at various current densities. (g) Galvanostatic cycling at 5 mA cm<sup>-2</sup> (20 min for each cycle). (h) Schematic diagram of the flexible ZAB. (i) OCV of MnO-CeO<sub>2</sub>@Cs and Pt/C based flexible ZAB with (inset) LED lighting demonstration of MnO-CeO<sub>2</sub>@Cs based flexible ZAB. (j) The discharge polarization and corresponding power density profiles of MnO-CeO<sub>2</sub>@Cs and Pt/C based flexible ZAB. (k) Comparison of MnO-CeO<sub>2</sub>@Cs as flexible ZAB with other recently reported catalysts. (l) OCV at different bending angles of MnO-CeO<sub>2</sub>@Cs based flexible ZAB.

Subsequent electrostatic discharge tests underscored its exceptional rate performance comparable to Pt/C, showing minimal voltage drop during varied current densities (Fig. 5f and Fig. S19†). The long-term stability test is vital for practical applications, the MnO-CeO<sub>2</sub>@Cs exhibited a negligible voltage gap decay of only 0.02 V after continuous operation for 297 h, while the Pt/C, CeO<sub>2</sub>@Cs, and MnO@Cs alternative began faltering much sooner (Fig. 5g and Fig. S18c†). In light of these impressive aqueous ZAB results, a flexible solid-state ZAB was devised, incorporating carbon cloth laden with MnO-CeO<sub>2</sub>@Cs as the cathode, zinc foil anode, and a polyvinyl alcohol (PVA) hydrogel electrolyte (Fig. 5h). The solid-state battery exhibited admirable performance, achieving an OCV of 1.45 V, surpassing Pt/C and other comparable flexible batteries (Fig. 5i and Fig. S20a†). Simultaneously, the flexible ZAB illuminated a red “GXNU” LED panel, emphasizing its practicality (inset of Fig. 5i). The MnO-CeO<sub>2</sub>@Cs-based flexible ZAB exhibits an impressive peak power density of 67.4 mW cm<sup>-2</sup>, overshadowing the Pt/C variant and most contemporary alternatives (Fig. 5j, k and Fig. S20b, Table S4†). Furthermore, the

MnO-CeO<sub>2</sub>@Cs-based flexible ZAB maintained consistent voltage across varying bending angles (0, 90, 180°), reinforcing its adaptability and robustness in flexible configurations (Fig. 5l). The primary factor contributing to the performance improvement is the generation of an optimally oriented BEF by MnO-CeO<sub>2</sub>@Cs, which promotes ion/electron migration, thereby accelerating the reaction kinetics at the air cathode.<sup>53</sup> Consequently, the MnO-CeO<sub>2</sub>@Cs-based ZAB exhibits improved power density and greater cycling stability. Overall, these assessments distinctly highlight the great potential of MnO-CeO<sub>2</sub>@Cs for practical energy storage application (from conventional ZAB to flexible battery configurations).

### 3.4. Density functional theory

To better understand the impact of BEF on the interfacial electronic structure and d-band center ( $\epsilon_d$ ), we performed density functional theory (DFT) calculations, shedding light on the heightened ORR activity of MnO-CeO<sub>2</sub>. According to HRTEM results, the MnO (111) and CeO<sub>2</sub> (111) planes were selected as optimized structural models (Fig. S21†). The MnO-CeO<sub>2</sub>

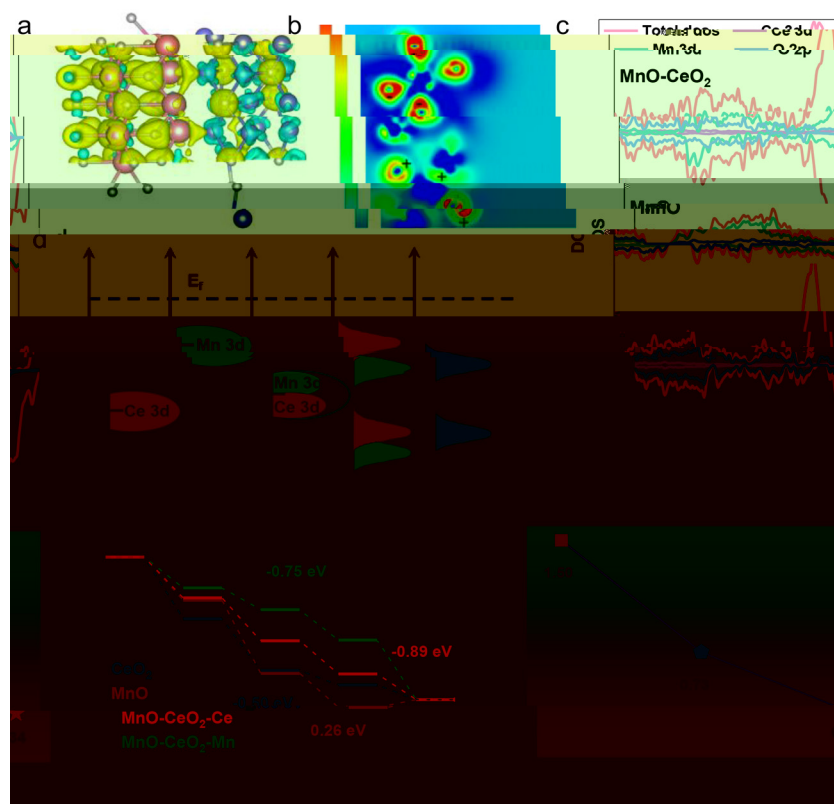


Fig. 6 (a) Differential charge density of MnO-CeO<sub>2</sub>. (b) Charge density distribution of MnO-CeO<sub>2</sub>, where + and – represent gained and lost electrons, respectively. (c) DOS calculations of MnO, CeO<sub>2</sub> and MnO-CeO<sub>2</sub>. (d) Corresponding schematic illustration of bond formation between the reaction surface and the adsorbate (Ads.) and d-band center. (e) Free energy diagrams of MnO, CeO<sub>2</sub> and MnO-CeO<sub>2</sub> towards ORR. (f) Corresponding overpotential for MnO, CeO<sub>2</sub> and MnO-CeO<sub>2</sub>.

charge density variation highlights electron transfer dynamics, with regions colored in yellow and cyan indicating electron accumulation and depletion, respectively (Fig. 6a). Evidently, electron loss is pronounced around MnO while being markedly concentrated around CeO<sub>2</sub>'s periphery (Fig. 6b). This observation suggests that the coupling of CeO<sub>2</sub> triggers localized charge redistribution at the interface, bolstering electron mobility from MnO to CeO<sub>2</sub>, a notion supported by XPS and UPS results. Based on the density of states (DOS) results depicted in Fig. 6c, it is observed that neither electrocatalyst presents a band gap at the Fermi level. Notably, MnO-CeO<sub>2</sub> manifests a heightened DOS adjacent to the Fermi level, indicating its enhanced conductivity and electrocatalytic prowess compared to its MnO and CeO<sub>2</sub> counterparts.<sup>54</sup> Remarkably, the  $\epsilon_d$  values for MnO and CeO<sub>2</sub> were  $-0.32$  eV and  $-3.75$  eV, respectively (Fig. 6d), implying that the adsorption of reaction intermediates at these respective sites may be either excessively weak or overly intense. In stark contrast, the  $\epsilon_d$  of MnO-CeO<sub>2</sub> is  $-1.95$  eV, signifying a balanced adsorption strength. The results suggested that amalgamating CeO<sub>2</sub> with MnO effectively modulated the adsorption strength of ORR intermediates, thereby accelerating the ORR kinetics.<sup>27</sup> Notably, the DOS of MnO-CeO<sub>2</sub> in proximity to the  $E_f$  predominantly arises from the Mn 3d orbitals, underscoring that MnO plays a pivotal role

in amplifying the overall catalytic conductivity within the reaction matrix.<sup>55</sup> The Gibbs free energy diagrams for the ORR process were calculated for four configurations (MnO, CeO<sub>2</sub>, Mn site in MnO-CeO<sub>2</sub>, and Ce site in MnO-CeO<sub>2</sub>), as shown in Fig. 6e. The limiting potential ( $U$ ) is defined by the minimum free energy change in the rate-determining step (RDS) during the ORR process.<sup>39</sup> At zero electrode potential, all models consistently present a downward trajectory in their free energy pathway, signifying a near-instantaneous exothermic reaction. The only exception is MnO in the transformation from OH\* to OH<sup>-</sup>, which is also the rate-determining step (RDS) in its ORR process. The calculated barrier for the RDS in MnO-CeO<sub>2</sub> (Mn) (OOH + e<sup>-</sup> → O + OH<sup>-</sup>) is  $-0.75$  V, exceeding the barrier on MnO-CeO<sub>2</sub> (Ce) ( $\eta = -0.89$  V). This indicates that MnO-CeO<sub>2</sub> (Ce) has a lower RDS barrier compared to MnO-CeO<sub>2</sub> (Mn), and even lower than MnO (0.26 V) and CeO<sub>2</sub> ( $-0.50$  V). This suggests that the coupling of CeO<sub>2</sub> is crucial for enhancing the ORR activity of MnO, thereby underscoring the likelihood of Ce serving as the active site. Encouragingly, the calculated overpotential ( $\eta$ ) of MnO-CeO<sub>2</sub> is 0.34 V, which is more positive than that of MnO ( $\eta = 1.50$  V) and CeO<sub>2</sub> ( $\eta = 0.73$  V) (Fig. 6f). Collectively, the above results suggest that the formation of the BEF between MnO and CeO<sub>2</sub> led to the interfacial electron redistribution, which effectively fosters optimized adsorption



of oxygen intermediates, ultimately leading to the superior ORR activity of MnO-CeO<sub>2</sub>.<sup>56</sup>

## 4. Conclusions

In summary, we successfully synthesized an oxygen-deficient spherical MnO-CeO<sub>2</sub>@Cs electrocatalyst using a high-temperature pyrolysis strategy. The MnO-CeO<sub>2</sub>@Cs catalyst exhibits satisfactory ORR activity ( $E_{1/2} = 0.80$  V,  $j_L = 5.5$  mA cm<sup>-2</sup>) in alkaline conditions. Additionally, the ZAB assembled with MnO-CeO<sub>2</sub>@Cs showcases an elevated peak power density of 202.7 mW cm<sup>-2</sup>, and displays remarkable stability over 297 h. Experimental results and theoretical calculations unequivocally validate a unique interfacial electronic structure driven by the harmonious synergy between MnO and CeO<sub>2</sub>. This distinctive BEF at the MnO-CeO<sub>2</sub>@Cs interface fosters a conducive environment for charge redistribution, optimizing the adsorption energy of oxygen intermediates and amplifying the ORR kinetics. Specifically, MnO plays a critical role, particularly through its 3d orbitals, significantly enhancing the overall electrical conductivity and reaction efficiency of the catalyst. This work not only signifies a monumental stride in electrocatalyst development but also paves the way for a novel paradigm in designing interfacial BEFs. This is anticipated to provide a nuanced control over charge distribution on catalyst surfaces, heralding a new era in electrocatalyst design and applications.

## Author contributions

Lixia Wang: investigation, conceptualization, writing-original draft. Xinran Hu: investigation. Huatong Li: data curation. Zhiyang Huang: methodology. Jia Huang: data curation. Tayirjan Taylor Isimjan: writing-review & editing. Xiulin Yang: supervision, writing-review & editing.

## Conflicts of interest

There are no conflicts to declare.

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