To develop a long-lifetime metal-air battery, oxygen reduction electrodes with improved mass-transfer routes are designed by adjusting the mass ratio of the hydrophobic polytetrafluoroethylene (PTFE) to carbon nanotubes (CNTs) in nickel foam. The oxygen reduction catalyst MnO₂ is grown on the nickel foam using a hydrothermal method. Scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Brunauer–Emmett–Teller analysis are employed to characterize the morphology, crystal structure, chemical composition, and pore structure of the electrodes, respectively. The air electrodes are evaluated using constant-current tests and electrochemical impedance spectroscopy. A PTFE:CNT mass ratio of 1:4–2:1 with 3-mm-thick nickel foam yields the optimal performance due to the balance of hydrophilicity and hydrophobicity. When the electrodes are applied in primary zinc–air batteries, the electrode with a PTFE:CNT mass ratio of 1:4 achieves the maximum power density of 95.7 mW cm⁻² with a discharge voltage of 0.8 V at 100 mA cm⁻², and completes stable discharge for over 14400 s at 20 mA cm⁻².

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Despite the efforts made in the development of integrative oxygen electrodes,\textsuperscript{35,37–48} most of these studies have focused on the exploitation of new catalysts, whereas efforts to investigate the mass-transfer structure of the porous electrode are currently lacking. Oxygen reduction is a typical triphase reaction process, involving oxygen from the gas phase, hydroxide from the aqueous solution, and electron conduction in the solid, with charge transfer occurring at the triphase interfaces (liquid–gas–solid interfaces). Compared with hydroxide ion diffusion and electron conduction, oxygen transfer is usually the “bottleneck” because of the low solubility of oxygen in aqueous solution. Flooding in the cathode impedes oxygen transport to reaction sites and seriously blocks the surface of the catalysts, thereby resulting in a significant, sometimes catastrophic, decrease in battery performance. For this reason, fabrication of a gas diffusion route through the ORR cathode becomes a critical issue in theoretical investigations.\textsuperscript{50–52} To prevent flooding of the oxygen diffusion route, balance is required between hydrophilicity and hydrophobicity. The hydrophilic channels in the electrode must be appropriately wetted to provide access to the liquid electrolyte, and the hydrophobic channels must be designed to facilitate oxygen transfer from the atmosphere to the active sites and to avoid leakage. To our knowledge, there is little research on the effect of the cathode structure and oxygen transfer route on zinc–air battery performance or a guide to help maintain the balance of the 3D interfacial surface for ORR cathode design.

In this study, the oxygen reduction catalyst MnO\textsubscript{2} was directly grown on nickel foam using hydrothermal method. As reported in literature, MnO\textsubscript{2} exhibits considerable electrocatalytic activity and possesses advantages such as low toxicity, low cost, and environmental friendliness.\textsuperscript{53–58} Recently, Meng studied the structure-property relationship of manganese oxides with different crystal structures, and found that α-MnO\textsubscript{2} was more active than other structures for ORR.\textsuperscript{59} Cheng discovered a facile strategy to enhance the activity of β-MnO\textsubscript{2} by introducing native oxygen defects into the manganese oxides, which enabled larger current, and lower peroxide yield for the ORR electrocatalysis.\textsuperscript{60} Among different manganese oxides, layered manganese dioxide (δ-MnO\textsubscript{2}), consisting of edge sharing MnO\textsubscript{6} octahedra, demonstrates excellent water oxidation and oxygen reduction reaction performance, as can be seen in many investigations.\textsuperscript{55,56,61,62}

To achieve a balance of hydrophilic/hydrophobic interaction, the hydrophobic components PTFE and carbon nanotubes (CNTs) were added to Ni foam coated with MnO\textsubscript{2} using hydrothermal synthesis. Oxygen transfer channels were fabricated by adjusting the mass ratio of PTFE to CNTs (FT9000, Cnano Technology Ltd. Beijing, China). The electrochemical performance of the electrodes was tested using a three-electrode system for the zinc–air battery discharge process. Finally, the enhanced oxygen transfer effects with an appropriate ratio of hydrophilic to hydrophobic components were discussed in detail.

Experimental

Synthesis of MnO\textsubscript{2} nanospheres on Ni foam.—All chemical reagents were of analytical purity and used without any further purification. MnO\textsubscript{2} nanospheres were directly grown on nickel foam via a modified hydrothermal method.\textsuperscript{63} The Ni foam (3 × 7 cm, 5-mm thick, Shenzhen Lifexin Environmental Protection Co., Ltd) was soaked in 3 M HCl (Beijing Modern Oriental Fine Chemistry Co., Ltd.) for 30 min and rinsed with deionized water and ethanol under ultrasonication for several minutes. Five pieces of Ni foam were placed against the wall of a 200-mL Teflon-lined autoclave containing a homogenous solution of K\textsubscript{2}MnO\textsubscript{4} (1 g, Beijing Modern Oriental Fine Chemistry Co., Ltd.) in 120 mL of deionized water. After reaction at 160°C for 24 h, the substrates coated with MnO\textsubscript{2} nanospheres were removed and washed with deionized water under ultrasonication and rinsed with ethanol to remove physisorbed and loosely attached MnO\textsubscript{2}, followed by drying at 80°C overnight. The loading density of MnO\textsubscript{2} was calculated to be approximately 4.0 mg cm\textsuperscript{−2}.

Fabrication of Ni/MnO\textsubscript{2} air electrodes.—The Ni/MnO\textsubscript{2} electrodes were coated with a gas diffusion layer, which was prepared using CNTs (0.5 g, FT9000, Cnano Technology Ltd. Beijing, China) and a PTFE emulsion (60 wt%, Shanghai Hesen Electric Co., Ltd) with PTFE/CNT mass ratios of 0:1, 1:2, 1:1, 2:1, 4:1, 6:1, 8:1, and 10:1 in 15 mL of absolute ethanol. This mixture was stirred for approximately 30 min, ultrasonically separated for 30 min, and heated in a water bath for approximately 10 min at 80°C. The gas diffusion layer was fitted on one side of Ni/MnO\textsubscript{2}, and a Teflon membrane was attached to the back side of the electrode. Finally, the air electrode was pressed into a 0.4-mm-thick layer under a pressure of 30 MPa and then dried at 80°C for 12 h. The schematic diagram of the air electrode structure is shown in Fig. 2.

Material characterization.—Morphological investigation was performed using scanning electron microscopy (SEM, Merlin, Carl Zeiss, Germany). The chemical compositions of the electrodes were determined using energy-dispersive X-ray spectroscopy (EDS, Merlin, Carl Zeiss, Germany), and X-ray diffraction (XRD, Bruker D8 Advance, Bruker, Germany) was used to analyze the crystal structure of the catalysts with continuous scanning in the diffraction angle range (2θ) of 10°–80°. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi (Thermo Fisher, English) using Al Kα radiation as the radiation source. All the binding energies are referenced to the C 1 s peak at 284.8 eV. N\textsubscript{2} adsorption-desorption isotherms were measured at 77 K with an IQ2 sorptometer (Quantachrome Instruments, USA). The specific surface area was
calculated using the Brunauer–Emmett–Teller (BET) equation, and the pore size distribution was calculated from the adsorption curve using the Barrett–Joyner–Halenda (BJH) method.

Electrochemical measurements.—Electrochemical activity.—
Electrochemical tests were performed in 6 M KOH using an electrochemical workstation (VersaSTAT-3, Princeton Applied Research, USA) with a three-electrode set-up. A saturated calomel electrode and platinum mesh were used as the reference electrode and counter electrode, respectively. The Ni/MnO2 cathode coated with a mixture of PTFE and CNT was directly used as the working electrode with a geometric working area of 1 cm². The electrochemical activity was evaluated using galvanostatic discharge and charge-discharge impedance spectroscopy (EIS). The electrodes were tested at current densities of 0, 5, 10, 20, and 30 mA cm⁻². Potentiostatic EIS was conducted at an ORR potential of ~0.3 V vs. Hg/HgO with an amplitude of 10 mV in the frequency range of 100 kHz to 0.1 Hz to obtain Nyquist plots. The electrochemical active surface area was analyzed using double-layer capacitance (Cdl) tests. Cyclic voltammetry (CV) curves were measured in a potential window nearly without any faradaic processes at scan rates of 1, 1.5, 2, 2.5, and 3 mV s⁻¹ for oxygen reduction electrodes with different mass-transfer structures.

Zinc–air battery.—A polished zinc plate (Institute of Metal Research, Beijing, China) and air electrode were used as the anode and cathode, respectively. The geometric area of the cathode exposed to air was approximately 1 cm², and the same area of the catalyst layer was exposed to the electrolyte (6 M KOH). Constant-current discharge measurements were conducted to estimate the electrochemical performance of the air electrode applied in a zinc–air battery. The measurement was performed using the same electrochemical workstation as the three-electrode system under the ambient air atmosphere.

Results and Discussion

Morphology, crystal structure, and chemical composition.—
The morphology of the MnO2 nanospheres directly grown on Ni foam was examined using SEM. Figs. 3a and 3b present representative SEM images of the Ni foam and MnO2 nanospheres on the Ni foam, respectively. The 3D grid structure with hierarchical macroporosity of the pristine Ni foam was still observed for the MnO2 nanospheres grown on Ni foam. The insets in Figs. 3a and 3b present magnified SEM images of the Ni foam and MnO2 nanospheres on Ni foam, respectively, further revealing their microstructures. For the MnO2 grown on Ni foam, the skeleton of the Ni foam was generally completely and uniformly covered by MnO2 nanosheets assembled into nanospheres. This structure was considerably different from that of the pristine Ni foam, which exhibited no surface covering. Here, the Ni foam serves as both the current collector and catalyst substrate. The 3D network structure formed by the MnO2 nanospheres and Ni foam substrate, with micro open cages and zigzag flow channels, provided the electrode with a mass transport property for the diffusion of O₂ and facilitated ion diffusion during the catalytic process. The MnO2 on the Ni foam contained Ni, Mn, and O as the main components according to the EDS analysis. The elemental mappings revealed that Mn and O mainly occupied the positions of the nanospheres, with Ni primarily distributed in the crevices, and these elements had a relatively homogeneous distribution throughout the electrode. The 3D grid structure with hierarchical macroporosity contributed to the EDS analysis. The elemental mappings revealed that Mn and O mainly occupied the positions of the nanospheres, with Ni primarily distributed in the crevices, and these elements had a relatively homogeneous distribution throughout the electrode. The 3D grid structure with hierarchical macroporosity contributed to the EDS analysis. The elemental mappings revealed that Mn and O mainly occupied the positions of the nanospheres, with Ni primarily distributed in the crevices, and these elements had a relatively homogeneous distribution throughout the electrode. The 3D grid structure with hierarchical macroporosity facilitated ion diffusion during the catalytic process. The MnO2 on the Ni foam contained Ni, Mn, and O as the main components according to the EDS analysis. The elemental mappings revealed that Mn and O mainly occupied the positions of the nanospheres, with Ni primarily distributed in the crevices, and these elements had a relatively homogeneous distribution throughout the electrode.
Figure 3. (a) SEM images of Ni foam and (b) MnO$_2$-coated Ni foam. The insets present high-magnification images. (c) SEM image used for EDS analysis and EDS elemental mappings of (d) Mn, (e) Ni, and (f) O distributions. (g) XRD pattern of MnO$_2$-coated Ni foam. The inset presents a magnified view of the range of 10–40$^\circ$. XPS spectra of (h) Mn 2p and (i) O 1 s.
ratios of 1:2 and 2:1, 6:1, and 8:1 consisted of only agglomerates of CNTs, agglomerates of CNTs and spherical PTFE particles, and mostly spherical PTFE particles, respectively.

Surface morphology of Ni/MnO₂ with different mass transfer structures.—The surface morphologies of Ni/MnO₂ coated with different mass ratios of PTFE to CNTs are displayed in Figs. 4e, 4f, 4g, 4h, 4i, 4j. Figs. 4e, 4f, 4j presents SEM images of Ni/MnO₂ with PTFE:CNT mass ratio of 1:2 (Ni/MnO₂-1:2). The 3D porous structure of the Ni foam can still be observed in Fig. 4e, and the CNTs have intimate contact with the MnO₂ nanospheres. The sample with the PTFE:CNT mass ratio of 8:1 had a more compact surface than that with the mass ratio of 1:2, as observed in Figs. 4i, 4j. The surface of this sample mainly consisted of MnO₂ nanospheres, with no visible CNTs. MnO₂ is known to exhibit poor conductivity; therefore, the intimate contact with the CNTs can improve the electrical contact. The Ni/MnO₂-1:2 sample contained more CNTs on the surface, which increased its conductivity. In addition, the large area of interfaces between MnO₂ nanospheres and CNTs generated a high population of active sites, promoting the ORR activity of the electrode via a synergistic effect.45,70–72

Stabilization of ORR electrode performance with addition of PTFE/CNT mixtures.—The stabilization of ORR electrode performance was investigated by the electrochemical behaviors of the Ni foam electrode with or without the mixture of PTFE/CNTs. Using oxygen from ambient air in atmosphere, Fig. 5 shows the potential variation with time measured with two Ni foam electrodes, i) composed of MnO₂ covered on Ni foam; ii) covered by the mixture of PTFE/CNT (ratio 1:2) above MnO₂ layer. The latter gives better stability as showed in the different potential step corresponding to various current densities at 5, 10, 20 mA cm⁻². As a contrast, the former provides continuous decreasing potential, it can be ascribed to oxygen concentration decrease with time due to water clogging in the microspores of the electrode. This result illustrates the importance of appropriate balance of hydrophobic/hydrophilic force in the porous structure of air electrode, the addition of PTFE/CNTs mixture offers a simple method to adjust hydrophobic/hydrophilic performance, which plays a critical role for oxygen transfer through porous diffusion layer.
Figure 5. Comparison of ORR activity of MnO$_2$-coated Ni foam with PTFE:CNT (1:2) and without the mixture.

After the hydrothermal process, the surface of nickel foam electrode covered by MnO$_2$ becomes hydrophilic, thus is easily wetted by water. The mixture of PTFE/CNTs has proper hydrophobicity and porosity, which ensure oxygen transfer through micro pores inside the electrode, and the liquid–gas–solid triphase reaction can be carried out smoothly. In contrast with the conventional ORR electrode, in which catalytic active layer is usually composed of the mixture of electrocatalyst and PTFE/carbon fine powder, this novel fabrication method provides a structure that MnO$_2$ directly grows on the porous nickel foam, and then the mixture of PTFE/CNTs is filled into nickel foam to form gas diffusion layer, thus leading to successfully increased active surface area, decreased dead volume and controlled multiphase interfaces. Therefore, this novel air electrode is fundamentally favorable for electron conductivity and triphase electrochemical reaction.

Effect of mass transfer behaviors on oxygen reduction performance.—To determine the relationship between the mass-transfer structure and oxygen reduction performance, galvanostatic discharge tests were conducted in a three-electrode half cell. Fig. 6a shows the potentials measured at different current densities for the MnO$_2$-coated Ni foam with different mass ratios of PTFE to CNTs. The sample with a PTFE:CNT mass ratio of 0:1 exhibited a low ORR activity compared with the samples with mass ratios of 1:2–4:1 because the electrode was easily flooded without PTFE, which can increase the hydrophobicity of the microstructure inside the electrode. With increasing PTFE content, the electrochemical activity decreased because ohmic resistance became the main barrier after the quantity of PTFE exceeded the optimum content. The potential difference increased with increasing current density from 5 to 30 mA cm$^{-2}$, as observed in the mass ratio range of 4:1–10:1. This finding can be explained by the mass-transfer restriction of oxygen and ohmic resistance increase with increasing current densities.

The different mass ratios of PTFE to CNTs result in different transfer structures, which affect the ORR activity. A pore size distribution diagram (Fig. 6b) was used to analyze the structure in more depth. The sample with a PTFE:CNT mass ratio of 1:2 contained more micropores than the sample without PTFE, with an increase in the quantity of catalyst and PTFE/carbon fine powder, this novel fabrication method provides a structure that MnO$_2$ directly grows on the porous nickel foam, and then the mixture of PTFE/CNTs is filled into nickel foam to form gas diffusion layer, thus leading to successfully increased active surface area, decreased dead volume and controlled multiphase interfaces. Therefore, this novel air electrode is fundamentally favorable for electron conductivity and triphase electrochemical reaction.

Figure 6. (a) Electrochemical activity of air cathodes using different mass ratios of PTFE to CNTs in 6 M KOH under ambient air atmosphere at 5, 10, 20, and 30 mA cm$^{-2}$. (b) Pore size distribution of air cathodes with different mass ratios of PTFE to CNTs (0:1, 1:2). FE-SEM images of cross-sections of air cathodes using mass ratios of PTFE to CNTs of (c) 1:2, (d) 4:1, and (e) 8:1.
The cross-sectional images show the high-magnification structures. As observed in Figs. 6c, 6d, 6e, the samples with PTFE:CNT mass ratios of 1:2, 4:1, and 8:1 consisted of mainly CNTs, a mixture of PTFE and CNTs, and more spherical PTFE, respectively. The inclusion of PTFE affected the hydrophobicity of the electrode and provided channels for gas transport around PTFE that promoted oxygen diffusion. However, for excessive PTFE contents, the catalyst particles could be coated with PTFE, resulting in decreased electron conductivity and low catalyst utilization.

Moreover, the BET results indicate that the Ni/MnO$_2$ with a PTFE:CNT mass ratio of 1:2 had the highest specific surface area of 26.81 m$^2$ g$^{-1}$ (Table I), which is consistent with the trend observed in Fig. 6a. Here, PTFE acts as a spacer between different CNT agglomerates. Consequently, PTFE played an important role in this process, such as modifying the pore structure inside the electrode, altering the pore size in the micro system, and increasing the hydrophobicity.

**EIS analysis and electrochemical active surface area.**—The EIS indicated that a suitable composition of PTFE was beneficial for oxygen transfer and reduction of the charge-transfer process. According to the Nyquist plots, the impedance spectra consisted of two semicircles in the high- and low-frequency regions. The first semicircle was related to the surface process between the electrode and electrolyte, and the second semicircle was related to the charge-transfer resistance of the electrode, which was directly related to the electrocatalytic activity of the air electrode. The impedance data were fitted using five elements, $R_s$, $Q_{int}$, $R_{int}$, $Q_{dl}$, and $R_{ct}$, and the equivalent circuit is shown in Figure 7. A similar equivalent circuit has been proposed by other researchers for investigating the resultant equivalent circuit is shown in Figure 7. A similar equivalent circuit was related to the charge-transfer resistance of the electrode, and provided channels for gas transport around PTFE that promoted oxygen diffusion. However, for excessive PTFE contents, the catalyst particles could be coated with PTFE, resulting in decreased electron conductivity and low catalyst utilization.

Moreover, the BET results indicate that the Ni/MnO$_2$ with a PTFE:CNT mass ratio of 1:2 had the highest specific surface area of 26.81 m$^2$ g$^{-1}$ (Table I), which is consistent with the trend observed in Fig. 6a. Here, PTFE acts as a spacer between different CNT agglomerates. Consequently, PTFE played an important role in this process, such as modifying the pore structure inside the electrode, altering the pore size in the micro system, and increasing the hydrophobicity.

**Effect of Ni foam thickness on oxygen reduction performance.**—The effect of the thickness of the primary Ni foam on the performance of the oxygen reduction electrode is shown in Figs. 9a, 9b. As observed in Fig. 9a, the air electrode with 3-mm-thick primary Ni foam exhibited the optimal oxygen reduction activity. The electrochemical activity was reduced upon further increasing the Ni foam thickness. This result was observed because the final thickness of the air electrode increased with increasing initial thickness of the primary Ni

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### Table I. Surface area, pore volume, and average pore diameter (N$_2$ adsorption–desorption isotherm) of air cathodes with different mass ratios of PTFE to CNTs.

<table>
<thead>
<tr>
<th>PTFE:CNT</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>13.80</td>
<td>0.076</td>
<td>2.756</td>
</tr>
<tr>
<td>1:2</td>
<td>26.81</td>
<td>0.170</td>
<td>1.436</td>
</tr>
<tr>
<td>4:1</td>
<td>16.38</td>
<td>0.120</td>
<td>1.440</td>
</tr>
<tr>
<td>8:1</td>
<td>14.97</td>
<td>0.082</td>
<td>2.475</td>
</tr>
</tbody>
</table>

*PTFE:CNT is the mass ratio of the PTFE emulsion to CNTs.

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### Table II. Values of equivalent circuit elements based on EIS analysis of Ni/MnO$_2$ air electrodes with different mass ratios of PTFE to CNTs.

**PTFE:CNT**

<table>
<thead>
<tr>
<th>Element</th>
<th>0:1</th>
<th>1:2</th>
<th>1:1</th>
<th>2:1</th>
<th>4:1</th>
<th>6:1</th>
<th>8:1</th>
<th>10:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$(Ω)</td>
<td>1.12</td>
<td>0.832</td>
<td>0.848</td>
<td>0.86</td>
<td>1.098</td>
<td>1.194</td>
<td>1.095</td>
<td>0.833</td>
</tr>
<tr>
<td>$R_{int}$(Ω)</td>
<td>0.62</td>
<td>1.87</td>
<td>1.35</td>
<td>1.64</td>
<td>1.16</td>
<td>1.54</td>
<td>2.56</td>
<td>1.97</td>
</tr>
<tr>
<td>$R_{ct}$(Ω)</td>
<td>11.19</td>
<td>2.97</td>
<td>3.64</td>
<td>3.4</td>
<td>4.46</td>
<td>8.04</td>
<td>8.35</td>
<td>14.94</td>
</tr>
<tr>
<td>$Q_{int}$(C m$^{-2}$)</td>
<td>0.0046</td>
<td>0.0261</td>
<td>0.0127</td>
<td>0.02</td>
<td>0.0085</td>
<td>0.011</td>
<td>0.0135</td>
<td>0.2341</td>
</tr>
<tr>
<td>$Q_{dl}$(C m$^{-2}$)</td>
<td>0.2111</td>
<td>0.2203</td>
<td>0.2463</td>
<td>0.1864</td>
<td>0.0876</td>
<td>0.0543</td>
<td>0.0514</td>
<td>0.0661</td>
</tr>
</tbody>
</table>

*PTFE:CNT is the mass ratio of the PTFE emulsion to CNTs.

---

### Figure 7. (a) EIS analysis of air cathodes using different mass ratios of PTFE to CNTs.
Figure 8. (a) CV curves of Ni/MnO₂ with mass ratio of PTFE to CNTs of 1:2 at scan rates of 1, 1.5, 2, 2.5, and 3 mV s⁻¹. (b) Linear relationship between current density and scan rate.

Table III. Cdl values of Ni/MnO₂ with different mass ratios of PTFE to CNTs.

<table>
<thead>
<tr>
<th>PTFE:CNT</th>
<th>0:1</th>
<th>1:4</th>
<th>1:2</th>
<th>1:1</th>
<th>4:1</th>
<th>6:1</th>
<th>8:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cdl (mF cm⁻²)</td>
<td>182.8</td>
<td>225.8</td>
<td>223.1</td>
<td>260.5</td>
<td>170.1</td>
<td>93.3</td>
<td>75.1</td>
</tr>
</tbody>
</table>

PTFE:CNT is the mass ratio of PTFE emulsion to CNTs.

Figure 9. (a) Electrochemical activity of air cathodes for different thicknesses of Ni foam in 6 M KOH under ambient air atmosphere at 5, 10, and 20 mA cm⁻². (b) EIS analysis of air cathodes using different Ni foam thicknesses with a mass ratio of PTFE to CNTs of 1:1.

Table IV. Values of equivalent circuit elements based on EIS analysis of Ni/MnO₂ air electrodes with different Ni foam thicknesses.

<table>
<thead>
<tr>
<th>The thickness of Ni foam</th>
<th>1.7 mm</th>
<th>3 mm</th>
<th>5 mm</th>
<th>10 mm</th>
<th>15 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs (Ω)</td>
<td>0.918</td>
<td>1.028</td>
<td>0.848</td>
<td>0.76</td>
<td>0.65</td>
</tr>
<tr>
<td>Rct (Ω)</td>
<td>4.94</td>
<td>3.50</td>
<td>3.64</td>
<td>6.82</td>
<td>8.54</td>
</tr>
<tr>
<td>Qdl (S⁻¹)</td>
<td>0.0151</td>
<td>0.0043</td>
<td>0.2463</td>
<td>0.0404</td>
<td>0.0310</td>
</tr>
</tbody>
</table>

of charge and greater active material utilization during the electrochemical reaction. In addition, Rint of the 3-mm-thick electrode was 0.31 Ω, which is much lower than that for the other thicknesses, indicating much lower interfacial resistance between the electrode and electrolyte. The 3-mm-thick Ni foam with the appropriate hydrophilic catalyst loading exhibited a better balance between the hydrophilicity...
and hydrophobicity than the Ni foams of other thicknesses. It can thus be concluded that with increasing Ni foam thickness, the loading of the catalyst increases, contributing to improved performance. However, for thicknesses greater than the optimal thickness, the increase in the mass-transfer resistance causes poor performance. Therefore, the electrode with optimal thickness is one that can achieve the best balance between the catalyst loading and mass-transfer resistance.

**Zinc–air battery performance.**—Ni foam with the optimal thickness of 3 mm was used as the substrate of the air electrode for zinc–air battery tests. Fig. 10 shows the performance of air electrodes with PTFE:CNT mass ratios of 1:4 and 1:2 used in zinc–air batteries. The discharge curves and power density curves are presented in Fig. 10a. Ni/MnO$_2$-1:4 had a 0.8-V discharge voltage at a current density of 100 mA cm$^{-2}$, with a power density of more than 80 mW cm$^{-2}$ at a current density of 100 mA cm$^{-2}$. The peak power density of Ni/MnO$_2$-1:4 was 95.7 mW cm$^{-2}$, which is better than that of other Mn catalyst-based electrodes in the literature$^{41,57,77,78}$ (Table V). Fig. 10b shows the stability of two types of electrodes at a current density of 20 mA cm$^{-2}$, which was attributed to the three-dimensional design of the electrode with smooth electron transport, sufficient access to catalytically active sites, and more efficient gas transport. Based on the time efficiency, ease of preparation, and high activity and stability of this novel air cathode, it has great potential for application in long-lifetime metal-air batteries and other electrochemical devices.

**Conclusions**

Oxygen reduction electrodes were improved by the design of the oxygen transfer route inside Ni foam coated with MnO$_2$ electrocatalysts using hydrothermal synthesis. To enhance the oxygen transport, optimal PTFE:CNT mass ratios in the range of 1:4–2:1 were adopted, which achieved the most efficient balance between the hydrophilic/hydrophobic interface with relatively larger electrochemical active area, low resistance, and small pore size. Moreover, PTFE not only served as a hydrophobic agent but also helped modify the pore structure inside the gas diffusion electrode. This novel structure used in zinc–air batteries resulted in a peak power density of 95.7 mW cm$^{-2}$, which was attributed to the three-dimensional design of the electrode with smooth electron transport, sufficient access to catalytically active sites, and more efficient gas transport.

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