Spinel-Type Metal Oxide Nanoparticles Supported on Platelet-Type Carbon Nanofibers as a Bifunctional Catalyst for Oxygen Evolution Reaction and Oxygen Reduction Reaction

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ABSTRACT

Development of highly active bifunctional electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) is required for air electrodes of zinc-air secondary batteries (ZAB). In this study, we synthesize spinel-type MnCo2O4 (MCO) nanoparticles on highly graphitized platelet-type carbon nanofibers (pCNF) via a solvothermal method. The pCNF is selected as carbon support in this study because of the excellent stability against anodic degradation under the OER condition. The MCO nanoparticles of 2–5 nm in diameter are uniformly dispersed on pCNF and the catalyst exhibits high activities for ORR due to strong interaction pCNF and MCO, in addition to the improvement of OER activities. The MCO/carbon hybrids show comparable electrocatalytic performances to state-of-the-art bifunctional electrodes for OER and ORR.

Keywords: Platelet-type Carbon Nanofiber, Spinel-type MnCo2O4, Zinc Air Battery, Bifunctional

1. Introduction

Zinc-air secondary battery (ZAB) is a promising candidate for the development of new generation of energy conversion systems due to its high theoretical energy density of 1370 Wh kg−1.1 The operation of an air-positive electrode in an alkaline ZAB is based on oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) via the following scheme:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad E^0 = 1.23 \text{ V vs. RHE} \quad (1)
\]

The four-electron reaction pathway described in (1) leads to large overpotentials in electrochemical terms, resulting in massive reduction of energy efficiency of batteries. Therefore, development of novel bifunctional electrode materials, which enable the decrease of overpotential for both ORR and OER with high durability in air electrode, is indispensable for commercialization of ZAB.

Carbon materials are one of the key components in the air electrode and used as promoting conductive supports of catalyst materials due to good electrochemical characteristics, lightweight, earth-abundant characteristics and a role as a cocatalyst for ORR.2,3 Many types of carbon materials, such as carbon nanotubes,2,3 graphene,4,5 carbon blacks,6,7 and carbon nanofibers,8,9 have been applied as electrode materials by loading electrocatalysts including metal and metal oxide nanoparticles. The carbon-containing hybrid materials have shown high activities for OER and ORR, but carbon materials are easily oxidized under OER conditions,7,9 leading to the degradation of battery performance.

Recently, platelet-type carbon nanofibers (pCNF) have an attracted increased attention as novel carbon materials for electrocatalysts and their supports.9,10,12 The pCNF with a high graphitization degree was formed by heat treatment at high temperatures >2000 °C.9,10,14 The high-temperature-treated pCNF has a unique structure with graphene layers stacked to the fiber axis without exposure of carbon edges by means of loop formation.10 Very recently, we have combined the highly graphitized pCNF with the state-of-the-art highly active Ca2FeCoO5 electrocatalysts by physical mixing and reported that the electrode exhibited high durability for OER in alkaline electrolyte for 1 month.13 In this durability test, the pCNF showed extremely slow anodic corrosion under the OER condition, whereas the conventional carbon materials were completely consumed within a few days.9 Therefore, pCNF with high graphitization degree is very promising as the anti-corrosive carbon material for ZAB.

Although the structural characteristics of the highly graphitized pCNF provide excellent stability in OER environment, there are shortcomings to limit the electrocatalytic activity of the pCNF when physically mixed with metal oxide electrocatalysts for ORR. Carbon materials work as the conductive support for the electrocatalysts on OER and ORR as mentioned above. Additionally, they provide co-catalyst effects for ORR electrocatalysis with metal oxides9,20 or hydroxides1,12 since carbon is catalytically active for ORR.1,7,15–18 This co-catalysis effect is an important factor to promote the ORR electrocatalysis for such platinum group metal-free (PGM-free) electrodes. Carbon edge sites and defect sites are commonly regarded as catalytic sites of carbon materials for ORR;15–18 however, edge sites and defect sites of highly graphitized pCNF are almost eliminated because of the loop formation on the sidewall. As a result, pCNF cannot provide the sufficient co-catalyst effect for the electrodes physically mixed with metal oxides as compared to conventional carbon blacks.19

To break the shortcoming, direct loading of the electrocatalyst particles onto the carbon surface could be an effective strategy,3,1 which enables to tune electronic states of electrocatalysts, for development of the electrocatalytic activities.21,24 Moreover, it is
often discussed that the interface between carbon material and metal oxide catalyst provides reasonable electrocatalytic centers for OER and ORR. Therefore, we suppose that construction of the hybrids of oxide electrocatalyst and pCNF can improve the ORR electrocatalysis of pCNF.

In this study, we tried to prepare a hybrid of electroactive oxide nanoparticles uniformly dispersed on highly graphitized pCNF for highly active bifunctional electrodes for ORR and OER in an alkaline environment. Spinel-type MnCo2O4 (MCO) nanoparticles, which are promising as a catalyst for OER and ORR, were supported on the pCNF via solvothermal synthesis, and their ORR and OER activities were examined. We compared the electrochemical properties of the pCNF/MCO with those of the MCO supported on commercial carbon black and physical mixtures of MCO and carbon materials to elucidate the importance of carbon and metal oxides interaction.

2. Experimental

2.1 Materials preparation

Commercially available pCNF (Sigma-Aldrich) was used in this study. Commercial carbon black (Denka black, DB, Denka Co.) was also used for comparison. Each carbon support was treated in concentrated HNO3 aqueous solution at 110 °C for the surface activation. MCO nanoparticles were loaded on each carbon support by a solvothermal synthesis method based on the previous report. The pCNF or DB (100 mg) was dispersed in ethanol (50 mL) ultrasonically for 30 min. After the addition of an aqueous solution (2.0 mL) containing 0.2 mol dm−3 manganese(II) acetate and 0.4 mol dm−3 cobalt(II) acetate, the amount of which corresponded to desired MCO content of 50 wt% in products, the mixture was stirred for 45 min at room temperature. Then, 0.75 mL of ultrapure water and 1.25 mL of 30% ammonia aqueous solution were added. After mixing all precursors, the mixture was refluxed at 80 °C with stirring for 20 h. The mixture was transferred to a 100 mL autoclave and the container was heated at 150 °C for 3 h. The products were filtered and dried in vacuum at 80 °C for 1 h. Carbon-free MCO nanoparticles were also prepared through the same procedure without adding carbon materials. Hereafter, MCO-loaded DB and pCNF hybrids synthesized by the solvothermal method are designated as DB/MCO and pCNF/MCO, respectively. The RuO2 and Pt/C were used as the reference materials to evaluate the electrocatalysis. The RuO2 powder (99.9%) was purchased from Sigma-Aldrich. The Pt/C catalyst were synthesized according to a procedure described elsewhere using commercial Ketjen black (Lion ltd., EC600JD) as a carbon support.

2.2 Characterizations

The morphology and structure of the carbon materials with and without MCO nanoparticles were characterized using the field-emission scanning electron microscope (SEM; ZEISS, Sigma-500) operated at 1.5 kV, and transmission electron microscopes (TEM; JEOL, JEM-2000FX and JEM-2100F) operated at 200 kV. Scanning transmission electron microscope (JEOL, JEM-ARM200F) with energy dispersive X-ray spectroscopy (EDS) facilities was also used to obtain compositional information. The phase purity and the graphization degree of the carbon materials were examined by Raman spectroscopy (Horiba Scientific, XploRA) using a 532 nm laser beam and X-ray powder diffraction (XRD; Rigaku, Ultima IV) using CuKα radiation (λ = 0.15418 nm). To estimate the crystallite size from XRD patterns, the following Scherrer equation is used:

\[ L_{c,\text{M}} = \frac{K \lambda}{\beta \cos \theta} \]                  

where λ, K and β are the X-ray wavelength (0.15418 nm), the shape factor and FWHM of the reflection used, respectively. The K value was used for carbon 002 reflection was 1.0, following the previous report, and that for MCO 311 reflection was 0.9. The BET surface areas of the carbon materials, pristine MCO and carbon/ MCO hybrids were determined by N2 gas adsorption isotherm measurements (for carbon materials; Bel Japan, Belsorp-mini instrument and for MCO and its hybrid; Yuasa Ionics, Autosorb 6AG) at −196 °C. The loading amounts of MCO on the carbon materials were evaluated by a thermogravimetric analyzer system (TGA; Netzsch, STA 2500 Regulus) in air at a heating rate of 10 K min−1.

2.3 Electrochemical measurements

The electrocatalytic activity was evaluated by the rotating disk electrode (RD; Pine Instrument Co. Ltd.) system using the catalyst-loaded glassy carbon disk electrodes (1.0 mg cm−2) and a Pt ring electrode. For the preparation of catalyst inks, 50 mg of carbon/MCO hybrids, or, pristine carbon, or physical mixtures of the pristine MCO and carbon materials with 1 : 1 mass ratio were dispersed ultrasonically in a mixture of 0.2 mL of 5 wt% Na2HPO4 exchanged Nafion solution and 4.8 mL of ethanol. Nafion was added as a binder and neutralized before dispersion to prevent MCO from undergoing acidic dissolution due to the lower pH of the Nafion binder. Physically mixed samples of carbon materials and MCO were designated as DB+MCO and pCNF+MCO. The RuO2 and Pt/C electrode were prepared based on the previous report. The electrochemical measurements were carried out in a three-electrode system using a potentiostat (Hokuto Denko, HZ-7000) and RRDE system. A carbon sheet and Hg/HgO/4 mol dm−3 KOH were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) was performed to investigate the electrochemical capacitance and redox reaction of the prepared electrode by applying 30 potential cycles between 1.3 and 0.4 V vs. RHE with a sweep rate of 50 mV s−1, prior to electrocatalysis evaluation. The 30th cycle of CV curve was adopted as the results. Linear sweep voltammetry (LSV) at 1600 rpm with a potential sweep rate of 1 mV s−1 was conducted at room temperature in a 4 mol dm−3 KOH aqueous solution with O2 saturation. The electron transfer number during ORR was evaluated by the RRDE method under the ring electrode potential of 1.4 V vs. RHE. The potential was converted from the Hg/HgO/4 mol dm−3 KOH reference scale to the RHE using the following equation:

\[ E \text{ vs. RHE} = E \text{ vs. Hg/HgO/4 mol dm}^{-3} \text{ KOH} + 0.9260 \]                  

Half-cell tests using the gas-diffusion air electrode were also performed. The hydrophobic gas-diffusion layer (GDL) was prepared from a mixture of 70 wt% carbon black (TOKAI CARBON, #3855) and 30 wt% PTFE, as reported previously. The resultant carbon/PTFE mixture was rolled in several steps to obtain 0.3 mm-thin sheets. The catalyst layer formed on the GDL also prepared from the catalyst ink with similar method described in elsewhere. The catalyst ink was prepared by ultrasonic mixing with the synthesized carbon/MCO hybrids or physical mixture of pCNF and MCO (1 : 1 mass ratio), water containing Triton X-100 (Kishida Chemical Co. Ltd.) and 6.0 wt% PTFE dispersion (D-210C, Daikin Industries, Ltd.). The ratio of catalyst to PTFE was controlled to be 83/17 in wt% in the resultant catalyst layer. The catalyst ink was assembled with the GDL with the loading amount of 20 mg cm−2, and then heated at 335 °C for 1 h under N2 flow, followed by pressing on to the nickel mesh (Niraco, 100 mesh) current collector. The electrochemical cell for the gas-diffusion air electrode test consisted of a Pt wire, a Hg/HgO electrode, and 8.0 mol dm−3 KOH aqueous solution as a counter electrode, a reference electrode, and electrolyte solution, respectively. The charge-discharge tests were conducted at 40 °C in the incubator (Espec, SU-221). The air electrode was exposed to ambient air without forced flow. Charge and discharge curves were obtained by
monitoring potential of the air electrode after applying each current density for 3 min using a galvanostat (Biologic, VSP). A charge-discharge cycle test was conducted by applying 20 mA cm\(^2\) for 1 h for each step.

3. Results and Discussion

3.1 Characteristics of the carbon materials

Figure 1 shows scanning electron micrographs and transmission electron micrographs of the pCNF and DB carbon materials. The pCNF used in this study has a nanorod-like morphology (Figs. 1a and 1b), and the diameter and length of the pCNF vary widely within 80–300 nm and 0.5–5 \(\mu\)m, respectively. This is contrast to the pCNF prepared using a porous anodic alumina template, in which the fiber diameter of the pCNF is well controlled to the pore size of the template.9,12–14,36 However, the pCNF used in this study has well-developed platelet-type structure with graphene layers being normal to the fiber axis. The well-developed (002) lattice clearly seen in Fig. 1c and its lattice spacing of 0.34 nm suggest the high degree of graphitization. Each carbon layer in highly graphitized pCNF has loop-shaped end, which is characteristic of pCNF thermally treated at \(>\)2000 °C,9,14 and each loop consists of concentrically laminated 6–10 carbon layers (Fig. 1c). In contrast, DB has granular morphology with the size of 40 ± 10 nm, as shown Figs. 1d and 1e. The (002) lattice fringes of DB (Fig. 1f) are less developed compared with those of pCNF, suggesting the lower graphitization degree of the former carbon. Figure 1f also shows that the carbon basal plane is mainly exposed on the surface of DB.

Raman spectroscopy was also used for structural characterization of carbon materials (Fig. 2a).9,14,37–39 Typically, three peaks are mainly observed in the Raman spectra of the present carbon materials. The G band peak around 1580 cm\(^{-1}\) is attributed to the stretching vibration in the aromatic layers, i.e., \(E_{2g}\) vibration mode of graphitic carbon.40 The D and \(D'\) bands at \(~\)1350 (\(A_{1g}\) vibration) and \(~\)1620 cm\(^{-1}\) (\(E_{1g}\) vibration), respectively, arise due to disordered graphite structure of carbon materials.41–43 The pCNF showed narrower peaks and higher intensity of the G band peak compared with the respective peaks for DB, suggesting that the pCNF has lower amounts of defects. The peak area ratio of the \(D\) band to the G band (\(I_{D}/I_{G}\)) is often used to evaluate the graphitization degree of carbon materials, which is inversely proportional to the size of graphitic crystals.38–40 Typically, carbon materials with well-developed graphic region show small \(I_{D}/I_{G}\) value. The results suggest that the pCNF (\(I_{D}/I_{G}=0.63\)) has lower defects number and well-developed graphite structure compared to DB (\(I_{D}/I_{G}=0.94\)) as summarized in Table 1.

The graphitization degree was also investigated by XRD (Fig. 2b). The XRD patterns showed 2\(\theta\) diffraction peaks at 25°, 43° and 45°. The (002) and (101) diffraction peaks at 25° and 43° are due to the graphene layer stacking in the carbon materials.41–43

Figure 1. (a, d) SEM images and (b, c, e, f) TEM images of the carbon materials used in this study; (a-c) pCNF and (d-f) DB.

Figure 2. (a) Raman spectra, (b) XRD patterns and (c) \(N_2\) adsorption/desorption isotherms of the carbon materials used in this study.
hybrid samples showed peaks at around 1320 cm$^{-1}$ due to those for DB, suggesting that pCNF has better graphitization degree compared to DB. The crystallite size, $L_c$, calculated from the Scherrer equation, suggests that the crystallite size of the pCNF is three times that of DB (Table 1). The (002) lattice spacing of the pCNF is smaller than that of the DB. Thus, both Raman spectroscopy and XRD measurements disclose the high graphitization degree of pCNF rather than DB.

The BET surface area of DB and pCNF was investigated by N$_2$ gas adsorption/desorption measurements. Type III isotherms in IUPAC classification are obtained for both carbon materials (Fig. 2c). Thus, micropores and mesopores are almost absent or limited in both carbon materials. Both carbon materials have similar BET surface areas of 40–60 m$^2$ g$^{-1}$ (Table 1).

### 3.2 Characterizations of carbon/MCO hybrid catalysts

Figure 3a shows the Raman spectra of carbon/MCO hybrid and carbon-free MCO samples. Each specimen was synthesized via solvothermal method described above. All samples showed peaks at around 473 and 609 cm$^{-1}$, which are assigned to vibration of E$_g$ mode and F$_{2g}$ mode of MCO, respectively.44,45 The carbon/MCO hybrid samples showed peaks at around 1320 cm$^{-1}$ and 1580 cm$^{-1}$ corresponding to the carbon D and G bands, respectively, in addition to peaks derived from MCO. Other peaks due to by-products were not observed for carbon/MCO hybrids. The carbon/MCO hybrid samples showed similar relative intensities of the peaks for G and D bands to those of pristine carbon materials, suggesting that no change in graphitic degree of carbon materials after the solvothermal synthesis.

Figure 3b shows XRD patterns of carbon/MCO hybrids and carbon-free MCO sample. The carbon-free MCO sample showed the XRD pattern of spinel-type MnCo$_2$O$_4$, which is similar to previous reports.2,44,45 The carbon/MCO hybrids also showed the pattern of MCO in addition to diffraction peaks around 25 and 40° assignable to 002 and 10 reflections of carbon, respectively. The XRD pattern of the pristine MCO is similar to those of the carbon/MCO hybrids apart from the reflections from carbon. We estimated the nanocrystal size of the MCO 311 diffraction peak (Table 2). The crystallite size of MCO does not change with the type of carbon, and also similar crystallite size of MCO was obtained under the carbon-free condition by the solvothermal method. Thus, MCO nanoparticles were successfully synthesized for carbon/MCO hybrids. The carbon peaks in the carbon/MCO hybrids are similar to those in the respective pristine carbon materials (Fig. 2b). The results suggest that structural changes of pCNF and DB hardly occurred during the solvothermal synthesis, being consistent with the results of Raman spectroscopy. Loading amount of MCO nanoparticles for the carbon/MCO hybrids was investigated by TG analysis. The MCO content on the pCNF (49 wt%) was similar to that on the DB (45 wt%) as shown in Table 2, well agreeing with the target content of metal resources applied for synthesis. As shown in Table 2, the carbon/MCO hybrids showed almost identical BET surface area, which is also similar to those of physically mixed samples (pCNF+MCO: 113 m$^2$ g$^{-1}$, DB+MCO: 118 m$^2$ g$^{-1}$). The results suggest that the size of MCO and carbon materials for the carbon/MCO hybrids were similar to that for the respective pristine ones.

We examined the distribution of MCO nanoparticles on the carbon materials by SEM and TEM observations (Fig. 4). Figures 4a and 4e show the scanning electron micrographs of pCNF/MCO and DB/MCO, respectively. Each carbon material is uniformly wrapped by the MCO nanoparticles after the solvothermal synthesis. Figures 4b–c and 4f–g show transmission electron micrographs of the carbon/MCO hybrids. MCO nanoparticles with average size around 5 nm were uniformly deposited on both carbon materials as illustrated in Figs. 4d and 4h. High resolution TEM observations (Figs. 4e and 4g) clearly reveal the formation of well-crystallized MCO nanoparticles on the carbon surfaces. The EDS analysis confirmed the Mn/Co ratio of 1/2 in both the hybrids (Table 2). Even after the solvothermal synthesis concentric loops are remained at the sidewall of pCNF, on which MCO nanoparticles are supported. Yamada et al. reported that exposed carbon edge planes were the preferred nucleation sites of oxide nanoparticles and Co$_3$O$_4$ nanoparticles were uniformly dispersed on pCNF that had exposed carbon edge plane at the side wall.32 They also found the difficulty of uniform dispersion of Co$_3$O$_4$ nanoparticles on multiwalled carbon nanotubes by a conventional supporting method. However, in the present study it is demonstrated that solvothermal synthesis is suitable to obtain uniformly dispersed carbon/MCO hybrids even though basal plane of carbon are exposed to surface in pCNF and DB.

### 3.3 Electrochemical performances for ORR and OER

Prior to the examination of ORR and OER activities, CV measurements were performed in Ar-saturated 4.0 mol dm$^{-3}$ KOH electrolyte (Fig. 5). Both pristine pCNF and DB carbon materials as well as physically mixed carbon and MCO nanoparticles (pCNF+MCO and DB+MCO) exhibit rather low current density, and only solvothermally prepared carbon/MCO hybrids show relatively high current density with a redox couple between 0.8–0.9 V vs. RHE. This redox is associated with the Co(II)/Co(III) redox in MCO.3 Despite almost identical BET surface area of the

| Table 1.  | Physicochemical properties of the carbon materials used in this study. |
|-----------|-----------------------------------------------------------------------|
| BET/m$^2$ g$^{-1}$ | $d$002/nm | $L_c$/nm | Raman I$_G$/I$_D$ |
| pCNF      | 40.3       | 0.336   | 26.8       | 0.63          |
| DB        | 59.4       | 0.346   | 7.9        | 0.94          |

| Table 2.  | Physicochemical properties of MCO nanoparticles with and without carbon formed by the solvothermal synthesis. |
|-----------|-----------------------------------------------------------------------|
| BET/m$^2$ g$^{-1}$ | $L_{221}$/nm | MCO content /wt% | Mn/Co ratio from EDS |
| pCNF/MCO | 118         | 4.56       | 49.5        | 0.46          |
| DB/MCO   | 115         | 3.99       | 45.3        | 0.48          |
| MCO      | 189         | 4.76       | 100         | 0.48          |

Figure 3. (a) Raman spectra and (b) XRD patterns of carbon/MCO hybrids and pristine MCO nanoparticles.
carbon/MCO hybrids and physically mixed electrodes, large difference of current density suggests that the MCO nanoparticles physically mixed with carbon may not be effectively used electrochemically as compared to those in the carbon/MCO hybrids.

The ORR activities were examined by LSV in O\textsubscript{2}-saturated 4.0 mol dm\textsuperscript{−3} KOH solution for pristine carbons, physically mixed samples of carbon materials and MCO and MCO/carbon hybrids (Fig. 6). The pristine pCNF showed a lower onset potential, defined as the potential at 0.1 mA cm\textsuperscript{−2} disk, than that of the pristine DB due to no exposed carbon edge structure.\textsuperscript{9,12,15,16} Physically mixed samples showed higher activities than those of the pristine carbon materials since MCO nanoparticles worked as the efficient ORR catalyst. The activities of pCNF+MCO sample were much lower than those of DB+MCO. This activity difference possibly reflected the co-catalyst effects of the carbon materials for ORR. The carbon/MCO hybrids showed higher activities compared with the physically mixed samples, indicating that higher dispersion of MCO nanoparticles on both carbon materials contributed to enhancement of ORR activities. It is worth noting that the pCNF/MCO exhibited comparable activities to those of the DB/MCO unlike the case of physically mixed samples. Many reports suggest that the interfaces between carbon materials and metal oxides play the important role for ORR electrocatalysis as the alternative of the carbon edge plane active sites.\textsuperscript{1,3,25,26} The carbon/MCO hybrids have the uniform and strong connection between the MCO and carbons as clarified by TEM observation. Therefore, ORR activities of the carbon/MCO...
hybrids were largely affected by such interfaces. We confirmed that
the carbon/MCO hybrids showed high electron transfer numbers
(\( n = 3.9 \)). The results indicate that construction of the interfaces
between pCNF and metal oxides could significantly enhance the
ORR activities for the pCNF even without exposed carbon edge
structure.

It was reported that the MCO hybrids with N-doped nano-
carbons, such as N-doped carbon nanotubes and N-doped reduced
graphene oxide are best in terms of ORR activity.\(^2\) Even without N
doping in carbon, the present study exhibits rather high ORR
activity of pCNF/MCO hybrid. Thus, the fabricated hybrid in this
study can be positioned as one of the promising electrocatalysts for
ORR in highly concentrated alkaline media.

Figure 7 shows the anodic polarization curves of pristine
carbons, physically mixed samples and carbon/MCO hybrids for
OER. Pristine pCNF and DB carbon materials show very low
activities for OER, indicating that OER activities of carbon materials
without MCO were negligible. Physically mixed samples showed
OER activities originated from MCO nanoparticles. The carbon/ MCO
hybrids showed higher activities than those of physically
mixed samples. The results indicate that higher dispersion of MCO
on carbon in the carbon/MCO hybrids led to more appropriated
electronic conductivity. The solvothermal synthesis also enabled to
improve OER activities as well as ORR activities. Therefore, it
could be considered that the carbon/MCO interface plays the
catalytic center for OER as similar to ORR. The onset potential
defined at a current density of 10 mAm\(^{-2}\) is higher than the
Ca\(_2\)FeCoO\(_3\)/carbon electrode which is one of the state-of-art OER
electrodes in 4.0 mol dm\(^{-3}\) KOH electrolyte (Table 3); however, the
current density at 1.7 V vs. RHE was over 100 mAm\(^{-2}\) and this can be
comparable with Ca\(_2\)FeCoO\(_3\)/carbon electrode.\(^{28\text{--}31}\) The
overpotential of pCNF/MCO at 100 mAm\(^{-2}\) is comparable to the
well-known RuO\(_2\) OER active electrocatalyst (Fig. 7).

The OOR and OER activities of the carbon/MCO hybrids are
compared with those of recently reported bifunctional electro-
catalysts (Table 3). The bifunctional activity has often been
evaluated by \( \Delta E \), which is the difference between the OER potential
at 10 mAm\(^{-2}\) (\( E_{\text{10}} \)) and the half-wave potential for ORR (\( E_{\text{1/2}} \)).\(^{16}\)
\( \Delta E \) value of the pCNF/MCO is as small as 0.68 V, being
comparable to the state-of-the-art bifunctional electrocatalysts.
Therefore, the fabricated pCNF/MCO electrode is a promising
bifunctional electrode. In particular, the pCNF is the unprecedented
non-consumption-resistant carbon material under OER in such media. Thus,
pCNF/MCO hybrid can be considered as a candidate of the air
electrode materials for ZAB.

### 3.4 Gas-diffusion electrode study

The performance of the electrocatalysts were further investigated
by preparing gas-diffusion-type air electrodes, which consisted of an
electrocatalyst layer and a gas-diffusion layer. Figure 8a shows the
charge-discharge performance of air electrodes of carbon/MCO
hybrids in 8.0 mol dm\(^{-3}\) KOH aqueous electrolyte at 40 °C. The
activity of OER decreases in the following order: DB/MCO >
pCNF/MCO > pCNF+MCO, which is the same as in Fig. 7. The activity difference of OER of the three electrocatalysts is relatively
small, but the ORR activities of the carbon/MCO hybrids were
markedly higher than that of the pCNF+MCO physical mixture. Thus, the strong carbon-MCO interaction is of importance for ORR
rather than OER in gas-diffusion air electrode. The deference in
activity enhancement is originated from the role of carbon materials
for OER and ORR.\(^{15,15}\) Since the activity of carbon materials were
negligible for OER, MCO and interface between MCO and carbon
materials work as catalytic site. On the other hand, carbon materials
work as catalysts for ORR and especially promote peroxide

discharge performance of air electrodes of carbon/MCO
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materials work as catalytic site. On the other hand, carbon materials
work as catalysts for ORR and especially promote peroxide
production through 2-electron ORR pathway. It was reported that metal oxides showed activities for the electrochemical reduction of peroxyde species as well as 4-electron ORR.1,32,51 The hybridization of carbon materials and metal oxide accelerates ORR due to the pseudo-4 electron ORR which is the combination of the 2-electron ORR on the carbon surface and further reduction of peroxyde species on the metal oxide surface. Direct loading of MCO on the carbon surface can be expected to omit the diffusion distance of peroxyde species produced on the carbon surface, and provides new catalytic center, i.e., the interface between the carbon materials and MCO.1,3,25,26 These two factors contributed to the effective enhancement of ORR electrocatalysis of the carbon/MCO hybrids. The charge-discharge cycle performance was examined at 20 mA cm$^{-2}$ and plotted in Fig. 8b. Stable charge and discharge potentials continues up to 10 cycles for both pCNF/MCO and DB/MCO hybrids. They showed similar charge-discharge curves. During further cycling, decrease of activities were observed for both electrodes, and the decrease was mainly caused by anodic corrosion of carbon in the gas-diffusion layer. This GDL corrosion would also relate to the difference of ORR degradation behavior for both electrodes and slight decrease of ORR potential for pCNF/MCO. Thus, for the examination of the long-term stability, the gas-diffusion layer must be constructed using a material with high oxidation resistance under the OER condition. In Fig. 8b, the potential difference between charging and discharging is less than 0.7 V. The difference of the onset potential for OER and the half-wave potential for ORR is also as small as 0.68 V for the pCNF/MCO (Table 3). The value suggests that the present pCNF/MCO hybrid is the top class bifunctional electrocatalyst in a range of electrocatalysts reported.36

4. Conclusions

We demonstrated to improve the ORR electrocatalysis for the pCNF by loading of MCO nanoparticles and developed the novel bifunctional electrocatalysts. Even under the low number edge exposure of carbon in pCNF, the solvothermal synthesis achieved to deposit MCO crystalline nanoparticles uniformly on the pCNF surface. The MCO/carbon hybrids showed comparable electrocatalysis with state-of-the-art bifunctional electrodes for ORR and OER. The activity of pCNF/MCO hybrid for both ORR and OER is considerably higher than that of the physical mixture of pCNF and MCO, because the strong interface connection between MCO and carbon provides the catalytic center for OER and ORR in highly concentrated alkaline media. The pCNF is the unprecedented corrosion-resistant carbon material under OER in alkaline media. Thus, our findings will contribute to provide highly active bifunctional electrocatalysts with superior corrosion resistance.

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