Composites of a Prussian Blue Analogue and Gelatin-Derived Nitrogen-Doped Carbon-Supported Porous Spinel Oxides as Electrocatalysts for a Zn–Air Battery

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To date, most studies have focused only on the interaction between oxygen and the catalyst, with the intention of minimizing the mass-transfer resistance by using the rotating disk electrode (RDE) method, which is based on the forced-convection theory. To begin with, in order to increase the reaction rate, the oxygen should be able to reach the active sites of the catalyst readily (mass transfer). Next, a moderate (i.e., not too strong or weak) interaction (kinetics) should be maintained between the oxygen molecules and the catalyst, in order to allow for better adsorption and desorption. Therefore, these two factors should be taken into consideration when designing electrocatalysts for oxygen reduction. Further, there is bound to be a demand for large-scale metal-air batteries in the future. With these goals in mind, in this study, a facile and scalable method is developed for fabricating metal-air batteries based on the fact that the Prussian blue analogue Mn$_2$[Co(CN)$_6$]$_2$·nH$_2$O and gelatin-coated Ketjenblack carbon thermally decompose at 400 °C in air (i.e., without requiring high-temperature pyrolysis under inert conditions) to form porous spinel oxides and N-doped carbon materials. The intrinsic kinetics characteristics and the overall performance of the resulting catalysts are evaluated using the RDE method and a Zn-air full cell, respectively.

1. Introduction

Conventional rechargeable batteries such as Li-ion batteries are closed systems in which energy storage and conversion occur in the same compartment. As a result, they are not suitable for meeting the ever-increasing demands for higher energy densities. On the other hand, a notable characteristic of metal–air batteries is their open-cell structure, which allows oxygen to diffuse through the porous electrode and participate in the oxygen reduction reaction (ORR) at the cathode. Therefore, metal–air batteries can have higher energy densities than those of Li-ion batteries, as the former do not need to store oxygen. A significant overpotential, however, is required to reduce oxygen, resulting in a decrease in the overall cell performance, especially at high current discharges. Therefore, increasing the ORR rate is a critical issue. However, most attempts to do so, which usually involve the thin-film rotating disk electrode (RDE) method, have focused on electrocatalysts such as precious metals as well as nonprecious metal-free catalysts. In general, in the case of metal–air batteries, the ORR can be considered to consist of the following two processes. First, the oxygen molecules must reach the surface of the catalyst through a porous electrode in the air. They then have to form chemical bonds with the catalyst surface, resulting in their activation. Therefore, when designing electrocatalysts for such batteries, the following factors should be taken into consideration: how to transfer oxygen to the active sites effectively (mass transfer) and how to ensure that the binding energy is moderately high (kinetics). In this regard, the RDE method, which is based on the forced-convection theory, is not very useful, especially when it comes to the oxygen-transfer process (Figure S1, Supporting Information).

For example, the concentration of oxygen in 6 m KOH in a Zn–air single cell is ≈10 times lower than that in 0.1 m KOH in an RDE (the concentrations in 0.1 m KOH and 6 m KOH are ≈10⁻³ and ≈10⁻⁴ mol L⁻¹, respectively, at 25 °C). Hence, the three-phase ORR is of far greater significance under ambient conditions (i.e., when the ORR takes place in air), because gas-phase oxygen can be utilized more efficiently than can dissolved oxygen during Zn–air full cell operation. Therefore, greater efforts should be devoted to developing electrocatalysts that increase the rate of utilization of gas-phase oxygen. To meet this goal, it is crucial to design electrocatalysts that have a highly interconnected and porous architecture, exhibit hydrophobicity for better gas-phase oxygen transfer, and have a large surface...
area and suitable high electrical conductivity. Spinel oxides, which are inexpensive, have been used widely as alternative electrocatalysts for the reduction of oxygen in alkaline solutions,\(^\text{[9]}\) as the kinetics for the ORR are better in alkaline media than in acidic ones.\(^\text{[10]}\) Furthermore, metal–organic frameworks (MOFs), which can be synthesized readily, have been used as precursors for porous spinel oxides.\(^\text{[11]}\) Finally, derived metal oxides are more porous and have rougher surfaces; this makes them hydrophobic and thus better suited as catalysts. However, these materials also exhibit a few limitations, such as poor electrical conductivity and a low surface area.\(^\text{[12]}\)

In this study, we designed a facile and scalable strategy for synthesizing electrocatalysts for metal–air batteries based on the fact that the Prussian blue analogue \(\text{Mn}_x\text{[Co(CN)\(_6\)]}_2\cdot\text{nH}_2\text{O}\) and gelatin-coated Ketjenblack carbon thermally decompose at 400 °C in air to form porous spinel oxides and N-doped carbon materials, respectively. The obtained catalysts exhibited performances better than that of even a Pt/C electrode when used in a Zn–air battery at a high current density. This should aid in the development of practical Zn–air batteries.

2. Results and Discussion

Highly porous spinel oxides can be synthesized readily by thermally decomposing Prussian blue analogues through calcination; this is because of the Kirkendall effect.\(^\text{[13]}\) For example, when \(\text{Mn}_x\text{[Co(CN)\(_6\)]}_2\cdot\text{nH}_2\text{O}\) is heated at 400 °C in air, the C–N group is oxidized into gases such as \(\text{CO}_2\) and \(\text{N}_2\)\(_\text{O}_y\), resulting in the formation of a highly porous tetragonal spinel oxide, \(\text{Mn}_3\text{Co}_{1.2}\text{O}_4\) (JCPDS Card No. 77-0471, see Figures S1 and S2, Supporting Information), with a nanocubic architecture; the obtained catalysts exhibited performances better than that of even a Pt/C electrode when used in a Zn–air battery at a high current density. This should aid in the development of practical Zn–air batteries.

\[\begin{align*}
\text{Mn}_3\text{Co}_{1.2}\text{O}_4 \rightarrow \text{Mn}_3\text{Co}_{1.2}\text{O}_4 + x\text{H}_2\text{O} & \quad \text{at temperatures lower than 450 °C (Figure S3, Supporting Information).} \\
\text{Mn}_3\text{Co}_{1.2}\text{O}_4 + 3\text{H}_2\text{O} \rightarrow \text{Mn}_3\text{Co}_{1.2}\text{O}_4 \cdot 3\text{H}_2\text{O} & \quad \text{at temperatures higher than 450 °C.}
\end{align*}\]

In addition, commercial Ketjenblack carbon remains thermally stable till ≈550 °C without undergoing oxidation (Figure 1). Thus, gelatin-coated Ketjenblack can be transformed into N-doped carbon materials that can function as both catalysts for oxygen reduction and conducting agents and can thus improve the applicability of porous \(\text{Mn}_x\text{Co}_{1-x}\text{O}_4\). Therefore, it is possible to decompose both gelatin-coated Ketjenblack and Prussian blue analogues through a single heat treatment at 400 °C in air. During this thermal-decomposition process, two types of active sites, namely, those on the porous spinel oxides and the N-doped carbon materials, are generated simultaneously, allowing for an increase in the mass transfer of oxygen (Figure 1). In addition, this process can be scaled with ease by using a commercial mixer to prepare the slurry for the electrodes (Figure S4, Supporting Information).

As expected, X-ray diffraction (XRD) analysis confirmed that the as-prepared hybrid electrocatalysts (referred to as \(\text{Mn}_x\text{Co}_{1-x}\text{O}_4/\text{N-Ketjenblack}\)) had a tetragonal spinel structure (Figure 2a). Further, the broad nature of the XRD peaks indicated that these oxides were composed of small-sized grains (Figure S2c, Supporting Information).

The microstructures of the hybrid catalysts were examined using transmission electron microscopy (TEM) (Figure 2b). As shown in the figure, the catalysts had a porous, foam-like structure composed of a large number of sub-nanosized particles, which resulted in a high surface roughness. In addition, selective area electron diffraction (SAED) patterns revealed that the hybrid catalysts were polycrystalline; their spinel structure was also confirmed (inset of Figure 2b). Furthermore, the results of

Figure 1. a) TGA curves of Ketjenblack, gelatin, and \(\text{Mn}_x\text{[Co(CN)\(_6\)]}_2\cdot\text{nH}_2\text{O}\) and b) schematic illustration of the synthesis of the electrocatalysts derived from Ketjenblack, gelatin, and \(\text{Mn}_x\text{[Co(CN)\(_6\)]}_2\cdot\text{nH}_2\text{O}\).
element mapping indicated that the porous manganese–cobalt oxides were homogeneously distributed in the gelatin-functionalyzed Ketjenblack carbon (Figure S5, Supporting Information). Finally, X-ray photoelectron spectroscopy (XPS) measurements further confirmed their chemical compositions (Figure 2c).

It was found that, in particular, nitrogen atoms were better dispersed in the Ketjenblack carbon than were those of the Prussian blue-derived oxides. This was probably because of the strong interaction between the gelatin and the carbon powder. The scanning electron microscopy images also confirmed that the obtained catalysts did not contain any free, large-sized gelatin-derived carbon materials, indicating that the gelatin solution had been coated uniformly onto the surfaces of the Ketjenblack carbon particles (Figures S3 and S5, Supporting Information). It is known that N-doped carbon materials can also function as electrocatalysts for oxygen reduction, and that the type of doped nitrogen and its concentration affect their catalytic activity. In the case of the hybrid catalysts, the high-resolution N1s XPS data indicated that the gelatin had decomposed into N-doped carbon materials and that the dominant nitrogen species were pyrrolic and pyridinic nitrogen (Figure 2d). This finding is in keeping with what is observed in the case of gelatin powder heated in air (Figure S3d, Supporting Information). However, the obtained N-doped carbon materials were completely different from a previously reported N-doped carbon material containing pyridinic and graphitic N species and prepared at 800 °C under inert conditions. This difference is probably attributable to the thermal instability of the pyrrolic N species, which experiences structural strain at temperatures greater than 800 °C.

The electrical conductivity of a catalyst is also an important factor affecting the overall electrochemical performance of the catalyst. Gelatin carbonized at 400 °C in air undergoes a relatively lower degree of graphitization than does commercial Ketjenblack carbon; this observation is based on the fact that it exhibits unsymmetrical peaks at ~285 eV and is supported by its Raman spectrum (Figure S6, Supporting Information). This result suggested that the conductivity of the as-prepared hybrid catalysts was sufficiently high because of Ketjenblack and not the gelatin-derived carbon materials. This hypothesis is supported by the results of a previous study, in which we found that gelatin powder pyrolyzed at 900 °C in Ar exhibited catalytic activity lower than that of pristine Ketjenblack carbon, indicating that the electrical conductivity cannot be improved by using only gelatin and that another conducting carbon material is necessary. Therefore, it can be concluded that a cost-effective way of synthesizing efficient N-doped carbon-based electrodes that exhibit sufficiently high electrical conductivity is through the pyrolysis of organic materials in nitrogen at temperatures greater than 800 °C.

To determine the intrinsic catalytic activity (kinetic part, Figure S1, Supporting Information) of the Mn_{x}Co_{3−x}O_{4}/N-Ketjenblack electrocatalysts with respect to the ORR, we performed RDE measurements in an O_{2}-saturated electrolyte (0.1 m KOH) at room temperature; this was done to minimize the mass-transfer resistance as much as possible (Figure 3a). It is noted that Mn_{x}Co_{3−x}O_{4} has the best ORR performance among other Prussian blue analogues derived metal oxides (Figure S7, Supporting Information).

To begin with, the presence of a distinct oxygen reduction current was confirmed on the basis of the differences

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**Figure 2.** a) XRD, b) TEM images (inset: corresponding SAED), c) XPS survey spectrum, and d) high-resolution N1s spectra of the as-prepared electrocatalysts.
of the results of the cyclic voltammetry (CV) experiments performed in O2- and Ar-saturated electrolytes. In addition, the hybrid catalysts (Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4}/N-Ketjenblack) exhibited higher capacitive currents than did a physical mixture of Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} and Ketjenblack, indicating that the gelatin-derived carbon materials increased the electrochemically active surface area. As a result, electrodes of the hybrid catalysts had greater half-wave potentials (E\textsubscript{1/2}) than did an electrode of the physical mixture, indicating that the composite catalysts were comparable to Pt/C in terms of performance. Furthermore, the fact that the cathodic currents of the hybrid catalysts were higher than that of the physical mixture indicated that the hybrid catalysts were active enough to reduce all the oxygen molecules. This result suggested that the active sites in the hybrid catalysts corresponded to the pyridinic and pyrrolic N species derived at a low temperature of 400 °C (these are known to decrease the overpotential\cite{6b}). Thus, the Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} and the N-doped Ketjenblack carbon in the hybrid catalysts had a synergistic effect on the catalytic activity with respect to the ORR.

We also determined the rotation speed-dependent polarization curves for the hybrid catalysts and the physical mixture, in order to estimate the reaction pathways for the ORR process (Figure 3b). After the capacitive current had been corrected for, the Koutecky–Levich (K–L) plots for the hybrid and mixture electrodes, which were nearly parallel, suggested that the reaction kinetics were of the first order with respect to the concentration of dissolved oxygen and resulted in similar electron transfer numbers with respect to the ORR at different potentials. In the case of Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4}/N-Ketjenblack, the electrons transfer number (n) was calculated to be ~4.1 for −0.2 to −0.5 V (vs Hg/HgO in 0.1 m KOH) from the slopes of the K–L plots (see inset of Figure 2b), suggesting that the hybrid catalysts favored a direct 4e oxygen reduction pathway; in contrast, the physical mixture had an n value of ~2.88 and favored an indirect pathway. These first-order reaction relationships made it possible to construct mass-transfer-corrected Tafel plots.\cite{18}

That the activity of the Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4}/N-Ketjenblack carbon hybrid catalysts was high with respect to the ORR was also confirmed from the fact that their Tafel slope (≈56 mV dec\textsuperscript{−1}) in 0.1 m KOH was much smaller than that of the physical mixture of Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4} and Ketjenblack and Pt/C (≈83 mV dec\textsuperscript{−1}) (Figure 2d). These results indicated that the rate-determining step (rds) of the hybrid catalysts was different from that of Pt/C as well as the physical mixture and that the pyrrolic and pyridinic N species formed in situ determined the rds in the case of the hybrid catalysts. Significantly, the Mn\textsubscript{x}Co\textsubscript{3−x}O\textsubscript{4}/N-Ketjenblack catalysts showed a better tolerance to methanol crossover than commercial Pt/C, enabling our electrode to be applied to DMFC (direct methanol fuel cell) (Figure S8a, Supporting Information) and also has more stable chronoamperometric (i–t) response than Pt/C (Figure S8b, Supporting Information).

In practical Zn–air batteries, the concentration of KOH is normally much higher (≈6 m) than that during RDE measurements (0.1 m); this is to ensure a high ionic conductivity and
suppress the hydrogen gas onto the Zn metal surface. It is worth noting that, at higher KOH concentrations, the solubility of oxygen is generally lower. For example, the concentration of oxygen in 6 m KOH in a Zn–air single cell is ≈10 times lower than that in 0.1 m KOH in an RDE.[8] Thus, the three-phase ORR is of greater significance in ambient air than in pure oxygen, because gas-phase oxygen can be utilized much more efficiently than can dissolved oxygen during Zn–air full cell operation. Using the RDE technique, during which the mass-transfer resistance can be minimized by forced convection, only kinetic parts can be estimated. Thus, it is not suitable for describing the entire conversion process related to the mass transfer of oxygen molecules (Figure S1, Supporting Information). Therefore, to elucidate the entire process, we assembled Zn–air batteries with porous air electrodes catalyzed by the MnₓCo₃₋ₓO₄/N-Ketjenblack carbon hybrids, the physical mixture, and Pt/C; zinc powder was used as the anode. This was done to demonstrate the potential of the hybrid catalysts for use in practical applications and to show that they improved the mass transfer of oxygen. To ensure that the comparison was reliable, all the catalyzed air electrodes had the same thickness and contained the catalysts in the same concentrations. Further, they were tested under the same conditions.[19]

Figure 4a,b shows the polarization curves of the Zn–air single cells and their discharge profiles corresponding to changes in the current density from low to high. At the low current density, the Pt/C-catalyzed cell had a higher voltage than did the cell catalyzed by MnₓCo₃₋ₓO₄/N-Ketjenblack; this was in keeping with the results obtained using the RDE. However, at a higher current density, the voltage drop rate of the cell catalyzed by MnₓCo₃₋ₓO₄/N-Ketjenblack was lower than that of the cell catalyzed by Pt/C; this was the case even at 0.8 V when the power density of the cell was 16% higher than that of the Pt/C-catalyzed cell (Figure 4a). Finally, the cell catalyzed by MnₓCo₃₋ₓO₄/N-Ketjenblack also exhibited excellent rate capability and a fast dynamic response (Figure 4b and Figure S9, Supporting Information). Therefore, testing a Zn–air full cell in ambient air yields information regarding mass transfer within the entire air electrode and not just the catalyst, in contrast to the RDE method. Thus, using full and half cells in combination should allow newly developed ORR catalysts to be characterized in depth.

3. Conclusion

In conclusion, we revisited the ORR and determined that the widely used RDE characterization method, which is used to characterize newly developed catalysts, yields limited information about oxygen transfer in ambient air, resulting in a bottleneck with regard to the use of metal–air batteries. To overcome this issue, we successfully synthesized N-doped carbon-supported porous metal oxides through a single heat treatment at 400 °C in air. The highly porous nature and rough surfaces of the spinel oxides increased both the number of available active sites and the mass-transfer rate of oxygen molecules. In addition, the gelatin-coated Ketjenblack-derived pyrrolic and pyridinic N species afforded additional types of active sites while also increasing the electrical conductivity. Owing to these factors, the as-prepared hybrid catalysts exhibited better performance in a Zn–air single cell at high current densities than did a Pt/C electrode. Given that the synthesis method is readily scalable and that the hybrid catalysts exhibited noticeably better performance in single cells, these catalysts should aid the development of practically usable Zn–air batteries.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by the next-generation battery R&D program of MOTIE/KEIT, Korea (10042575), and was also funded by the 2016 Research Fund (1.160033.01) of UNIST (Ulsan National Institute of Science and Technology). Y.C. acknowledges the support from Stanford GCEP.

Received: May 19, 2016
Revised: June 21, 2016
Published online: