Supporting Information

Zirconium Oxynitride–Catalyzed Oxygen Reduction Reaction at Polymer Electrolyte Fuel Cell Cathodes

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S1. TEM images of ZrO$_x$N$_y$-MWCNTs

Figure S1 shows TEM images of ZrO$_x$N$_y$-MWCNTs after NH$_3$-pyrolysis at 973 K recorded at various locations. Black ZrO$_x$N$_y$ particles were deposited on both amorphous carbon layers and MWCNTs, appeared as grey area and tubes, respectively.

Figures S1. TEM images of different locations of ZrO$_x$N$_y$-MWCNTs after NH$_3$-pyrolysis at 973 K.
S2. XRD patterns of MWCNTs and ZrO$_x$N$_y$-MWCNTs

Figure S2 displays XRD patterns of MWCNTs and ZrO$_x$N$_y$-MWCNTs after NH$_3$-pyrolysis at five different temperatures, ranging from 973 to 1273 K. The tetragonal ZrO$_2$ phase observed at $T \leq 973$ K was converted to a rhombohedral Zr$_7$O$_8$N$_4$ phase at $1073 \leq T \leq 1173$ K, followed by transformation into a cubic Zr$_2$ON$_2$ phase at 1273 K. The base peak at $2\theta = 30.2\text{–}30.5^\circ$ features the contributions of tetragonal ZrO$_2$, Zr$_7$O$_8$N$_4$, and Zr$_2$ON$_2$ that are too close to each other to determine the crystal phase; however, we determined the phase from the peak at $2\theta = 21.4^\circ$ which is solely assigned to the (211) plane of Zr$_2$ON$_2$ as well as the peak shape at $2\theta = 34\text{–}36^\circ$ shown in the right.
Figure S2. XRD patterns of MWCNTs (a) and ZrO\textsubscript{x}N\textsubscript{y}-MWCNTs after pyrolysis at (b) 873 K, (c) 973 K, (d) 1073 K, (e) 1173 K, and (f) 1273 K under NH\textsubscript{3} gas (left). The enlarged (b)–(d) peaks at 2\theta = 34–36° are shown on the right.
S3. A XRD pattern and X-ray photoelectron spectra of ZrO$_x$N$_y$ powders

Commercial ZrO$_2$ powders were pyrolyzed at 1473 K for 5 h under NH$_3$ gas as a reference sample and the XRD pattern, X-ray photoelectron Zr 3d and N 1s spectra are shown in Figure S3.

Figure S3. A XRD pattern, X-ray photoelectron Zr 3d and N 1s spectra of ZrO$_x$N$_y$ powders.
S4. Optimization of pyrolysis conditions for ORR activity

Both $T$ and $t$ were optimized to maximize the ORR activity of ZrO$_x$N$_y$-MWCNTs, with their effects shown in Figures S4(i) and (ii), respectively. Mass activity ($j_M$) was evaluated at $E_d = 0.85$ V in order not to take the effect of oxygen diffusion into account, showing that $j_M$ exhibited a volcano-type dependence on $T$, with the optimum observed at 973 K. At optimum $T$, $j_M$ was almost unchanged for $t = 3$–6 h. The optimized activity was ~3 times higher than that observed before NH$_3$-pyrolysis, namely 33.5 mA g$^{-1}$. This activity, obtained before the NH$_3$-pyrolysis, has also been maximized by optimizing the O$_2$ content in the gas mixture to 0.05% (v/v) during the first pyrolysis. When the precursor mixture was pyrolyzed without adding O$_2$ gas, $j_M$ was one-order of magnitude lower which could be due to the large amount of remaining carbon species that covered ZrO$_x$N$_y$ particles. In contrast, the $j_M$ was 0 after increasing the O$_2$ content to 0.5%, which could be due to the removal of oxygen defects.

For comparison, the results for TaO$_x$N$_y$-MWCNTs synthesized using TaOPc are also shown. If the active sites on these catalysts originated from nitrogen-doped carbon species, the curves of two different oxynitrides should be identical, as they were pyrolyzed under NH$_3$ gas at identical conditions. However, the above catalysts exhibited clearly different performance at any $T$ and $t$, indicating that their activity was determined by oxynitrides and not carbon species.
Figure S4. (i) $j_{M|E=0.85\,V} - T|_{t=6\,h}$ curve and (ii) $j_{M|E=0.85\,V} - t|_{T=973\,K}$ curve of ZrO$_x$N$_y$-MWCNTs, with the corresponding curves of TaO$_x$N$_y$-MWCNTs shown for comparison. Scans were performed under N$_2$ and O$_2$ without rotation at a scan rate of 5 mV s$^{-1}$ in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. All $j_M$ values were background-corrected.
S5. Effect of HF treatment and following pyrolysis on the activity and chemical states of ZrO$_x$N$_y$-MWCNTs

Treatment by HF completely removed the tetragonal ZrO$_2$ phase of the as-synthesized catalyst, and only peaks of MWCNTs were observed from the XRD patterns, as shown in Figures S5A and B. The surface Zr-content was below the detection limit of X-ray photoelectron spectroscopy (XPS), ca. 0.1 atom % after the HF-treatment. The Fe-content was also below the detection limit of XPS regardless of the HF-treatment.
Figure S5. (Left top) RRDE voltammograms, (right top) XRD patterns, and (bottom) X-ray photoelectron Zr 3d and Fe 2p spectra of (A) ZrO$_x$N$_y$-MWCNTs after pyrolysis at 973 K for 6 h under NH$_3$ gas, (B) HF-treated (A), and (C) heat-treated (B) under Ar gas. The $m$ values for (A)–(C) was set to 1 mg cm$^{-2}$. Scans were performed under N$_2$ and O$_2$ at a rotation speed of 1600 rpm and a disk potential ($E_d$) scan rate of $-5$ mV s$^{-1}$ in 0.1 mol dm$^{-3}$ H$_2$SO$_4$. The ring potential ($E_r$) was kept at 1.2 V. Both geometrical disk and ring current densities, $j_d$ and $j_r$, were background-corrected.
S6. Stability of ZrO$_x$N$_y$-MWCNTs in a single cell

The stability of ZrO$_x$N$_y$-MWCNTs was evaluated in a single cell cathode using two protocols. The one is a simple constant current operation at $j = 0.1$ A cm$^{-2}$ for two weeks as shown in Figure S6a. The $V$ decreased sharply by 0.2 V during the first 100 h to yield 2 mV h$^{-1}$ of $-dV/dt_h$ but kept stable thereafter to decrease the rate to 0.3 mV h$^{-1}$. The other protocol is an accelerated degradation test (ADT) in a load cycle mode proposed by Fuel Cell Commercialization Conference of Japan (FCCJ)$^{63}$ and the scheme is shown in the inset of Figure S6b. The $j$ decreased by 50% during the first 1,000 cycles and kept more stable thereafter. This is the first to show high initial performance of MEAs employing oxynitride-based cathode catalyst and the precise mechanism for the degradation is not clear at this stage. Possible mechanisms for the degradations are at least two; oxidation of carbon species, especially for those derived from ZrOPc which connect ZrO$_x$N$_y$ particles and MWCNTs, and degradation of both carbon species and ionomer by H$_2$O$_2$ formed during ORR (Figure 2). The former, carbon oxidation has recently been experimentally confirmed to proceed even at low $V$ of 0.6 V in a single cell.$^{61}$ It should be the origin of several fatal factors such as loss of active sites, loss of pores in catalyst layers that cause water flooding. Carbon-free oxynitride-based catalyst layers will be one of the solutions to determine the degradation mechanism and to improve the stability of this catalyst type.
Figure S6. (a) Voltage versus time held at $0.1 \text{ A cm}^{-2}$ of constant current density ($V_{j=0.1\text{Acm}^{-2}} - t_h$) curve of a MEA fabricated using a ZrO$_x$N$_y$-MWCNT ($m = 8.9$ mg cm$^{-2}$, $T = 1073$ K, $t = 3$ h) cathode and a Pt-C anode (0.6 mg cm$^{-2}$, corresponding to a Pt loading of 0.3 mg cm$^{-2}$). (b) Normalized current density at 0.6 V of cell voltage versus number of voltage cycles ($jj_{0}^{-1}|_{V=0.6\text{V}} - N$) curve of a MEA fabricated using a ZrO$_x$N$_y$-MWCNT ($m = 8.3$ mg cm$^{-2}$, $T = 973$ K, $t = 3$ h) cathode and a Pt-C anode (0.6 mg cm$^{-2}$, corresponding to a Pt loading of 0.3 mg cm$^{-2}$). The $V$ was cycled between 0.6 and 1.0 V using a rectangular wave shown in the inset. Normalized current density is the $j$ divided by the initial value, $j_0$. 