Supplementary Information

Monoclinic Hafnium Oxynitride Supported on Reduced Graphene Oxide to Catalyse the Oxygen Reduction Reaction in Acid Media

Mitsuharu Chisaka,[a,*] *Hirohito Sasaki*[a] *and Hirokazu Muramoto*[b]

[a] Department of Electronics and Information Technology, Hirosaki University,

3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan.

[b] Cooperative Research Facility Center, Toyohashi University of Technology,

1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan.

*Corresponding author

Phone/Fax: +81 172 39 3559

E-mail: chisaka@eit.hirosaki-u.ac.jp

S1. Effect of hydrothermal-treatment temperature on mass activity of HfO_xN_y-rGO.

Figure S1 shows mass activity versus potential $[(i_O - i_N)\ m^{-1} - E]$ curves of HfO_xN_y-rGO for four different hydrothermally-treated temperature, *T* followed by the pyrolysis under N_2 gas at a fixed condition of 1073 K for 2 h. The optimum *T* for the mass activity was 453 K, agree well with the results from Fig. 2.

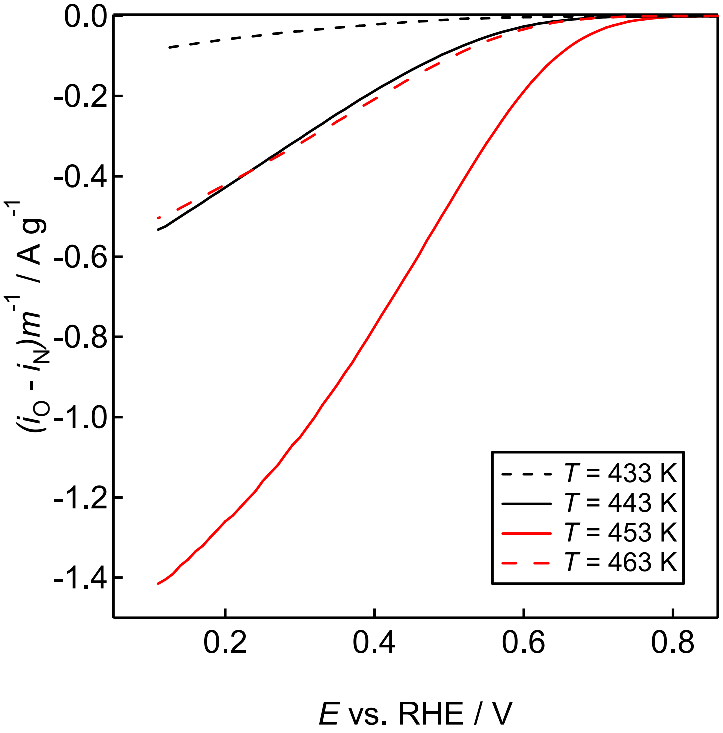

Fig. S1. Mass activity versus potential $[(i_O - i_N)\ m^{-1} - E]$ curves of HfO_xN_y-rGO hydrothermally-synthesized at four different *T* of 433 K, 443 K, 453 K, and 463 K and followed by the pyrolysis under flowing N_2 gas at a fixed condition of 1073 K for 2 h.

S2. The ORR selectivity of HfO_xN_y-rGO.

Rotating ring-disk electrode (RRDE) voltammograms were obtained to help evaluate the ORR selectivity of HfO_xN_y-rGO which showed the maximum activity. Using a glassy carbon (GC) disk (4 mm diameter)–platinum ring (5 mm inner diameter and 7 mm outer diameter) electrode as a working electrode, three electrode cells were prepared as described in the main body of the text. RRDE voltammograms were recorded in the disk potential range of 0.11–1.26 V at a scan rate of 5 mV s^{-1}, while keeping the ring electrode potential at 1.26 V, with a rotation speed of 1500 rpm after bubbling O_2 or N_2 for 1800 s. Fig. S2 shows a RRDE voltammogram of the HfO_xN_y-rGO. The n value was calculated with the following equation:

$$n = -4(I_{\mathrm{dO}} - I_{\mathrm{dN}})/[-(I_{\mathrm{dO}} - I_{\mathrm{dN}}) + (I_{\mathrm{rO}} - I_{\mathrm{rN}})/N] \qquad \text{(S1)}$$

where I_{dX} and I_{rX} denote disk and ring current obtained under X (X = O or N and corresponds to either oxygen or nitrogen, respectively) atmosphere, respectively, and N is the collection efficiency provided by the manufacturer, 0.424. At $E = 0.6$ V, n was 3.4 and gradually increased to 3.6 with decreasing E to 0.06 V.

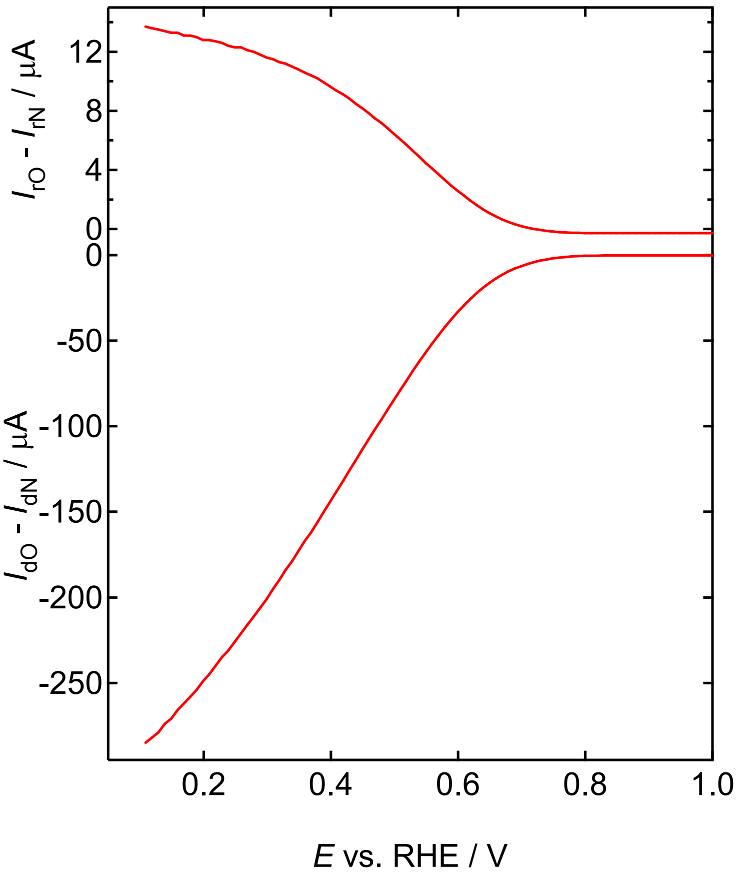

Fig. S2 A RRDE voltammogram of HfO_xN_y-rGO hydrothermally synthesized at 453 K after pyrolysis. Scans were performed under N_2 and O_2 with a rotation speed of 1500 rpm at a scan rate of 5 mV s^{-1} in 0.1 mol dm^{-3} H_2SO_4.

S3. Fitting results for a N 1s spectrum of HfO_xN_y-rGO.

The N 1s spectrum of HfO_xN_y-rGO which showed the maximum activity was deconvoluted into two peaks assigned to Hf-N bonding (~396 eV)[18] and C-N bonding (398–402 eV)[18,19] as shown in Fig. S3. This catalyst was hydrothermally synthesized at 453 K and followed by pyrolysis at 1073 K. It is noted that the aspect ratio (horizontal to vertical ratio) used in Fig. S3 is different from that shown in Fig. 5; however, the spectrum is the same. A weak peak assigned to Hf-N bonding is clearly seen in the spectrum. The result from XRD patterns (Fig. 4) and XPS analyses (Fig. 5 and Fig. S3) revealed that small amount of oxygen atoms in monoclinic HfO_2 phase were substituted by nitrogen atoms by the hydrothermal treatment. The nitrogen doping level, y in HfO_xN_y of this sample calculated from the peak assigned to Hf-N bonding in N 1s spectrum and Hf 4f spectrum is 0.08, one order of magnitude lower than that of HfO_xN_y nanoparticles synthesized using NH_3-gas pyrolysis.[11]

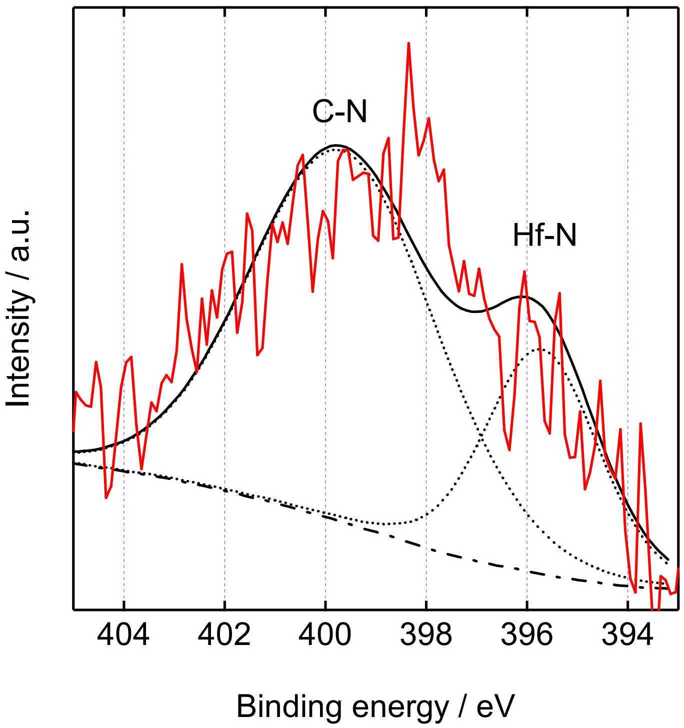

Fig. S3 A N 1s spectrum of HfO$_x$N$_y$-rGO hydrothermally synthesized at 453 K after pyrolysis shown in Fig. 5 (d) with overall fitting (solid line) and deconvolution into two peaks assigned to Hf-N bonding (~396 eV) and C-N bonding (398–402 eV) (dashed lines) after subtracting Shirley-type background (dash-dotted line).

S4. Reduction of GO.

Fig. S4 shows C 1s spectra of all HfO_xN_y-rGO samples, both from before and after pyrolysis. Although these spectra should contain contribution from the contaminants in spectrometer, they were used to evaluate the reduction degree of GO sheets with a rough assumption that the contaminant contribution to all the samples were almost the same. When T is the lowest value of 384 K, two clear peaks are observed from the spectrum before and after pyrolysis: the larger peak is centered at ~284.8 eV assigned to C-C/C=C bonding and the smaller one is at ~288.6 eV assigned to C=O bonding.[S1,S2] The smaller peak disappeared at $T \geq 433$ K, suggesting that GO surface was reduced to break the C=O bonding after the hydrothermal-treatment performed at this T range. The asymmetric peaks observed from the spectra at $T \geq 433$ K suggest that small peaks assigned to C-N bonding and/or C-O bonding are present. However, deconvolution is not possible as the peak binding energies for these bonding states are so close each other: 285.8 eV for C-N bonding[S3] and 285.9 eV for C-O bonding.[S1] All the C 1s spectra were not significantly changed by the pyrolysis indicating that the pyrolysis did not affect the bonding states of GO.

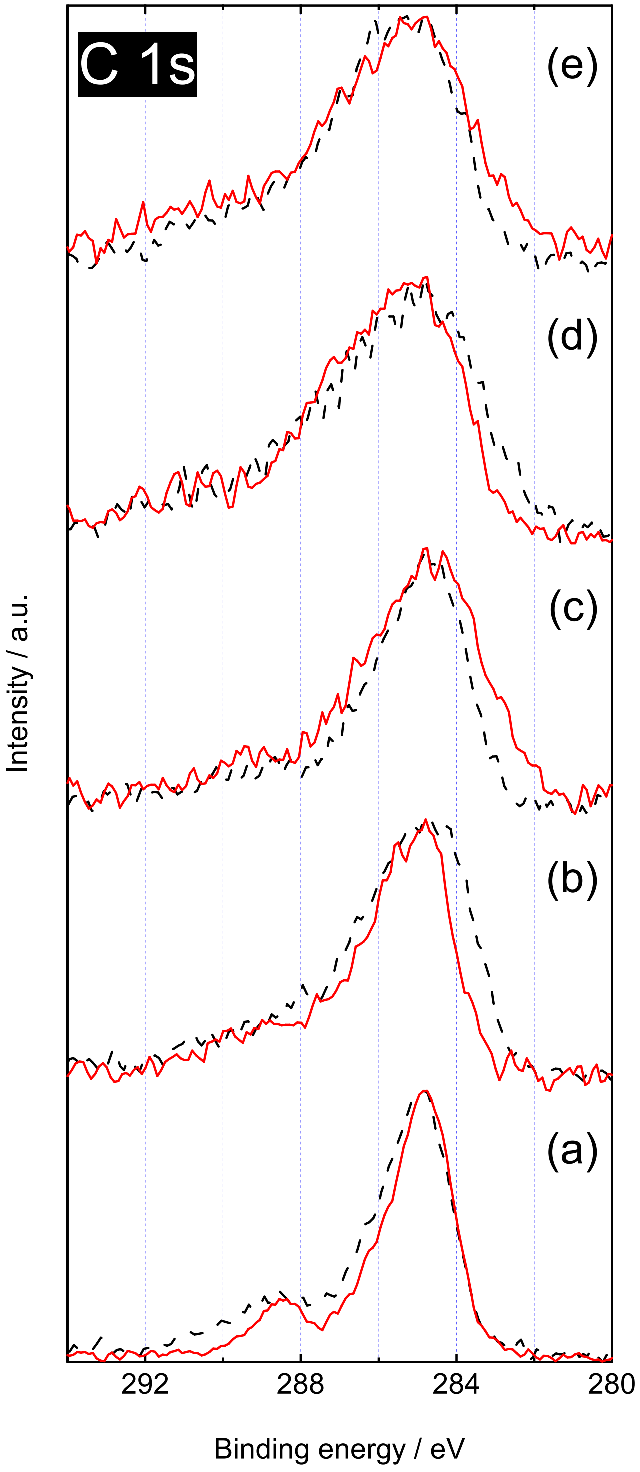

Fig. S4 C 1s spectra of HfO_xN_y-rGO hydrothermally synthesized at (a) 384 K, (b) 433 K, (c) 443 K, (d) 453 K, and (e) 463 K before (dashed line) and after (solid line) pyrolysis.

References

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