Supplementary Information

Synthesis of Nano-TaO_x Oxygen Reduction Reaction Catalysts on Multi-Walled Carbon Nanotubes Connected via a Decomposition of Oxy-tantalum Phthalocyanine

Akimitsu Ishihara,[a,b,*] *Mitsuharu Chisaka,*[c,*] *Yoshiro Ohgi,*[‡a] *Koichi Matsuzawa,*[a]

Shigenori Mitsushima[a,b] *and Kenichiro Ota*[a]

[a] Green Hydrogen Research Centre, [b] Institute of Advanced Sciences, Yokohama National University,

79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan.

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

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

‡ Present address: Kumamoto Industrial Research Institute, 3-11-38 Azuma-cho, Azuma-ku, Kumamoto, Kumamoto 862-0901, Japan.

*Corresponding authors

Phone/Fax: +81 45 339 4021 E-mail: a-ishi@ynu.ac.jp

Phone/Fax: +81 172 39 3559 E-mail: chisaka@eit.hirosaki-u.ac.jp

S1. The ORR selectivity of TaO_x–MWCNT.

Rotating ring-disk electrode (RRDE) voltammograms were obtained to help evaluate the ORR selectivity of TaO_x–MWCNT that showed the maximum activity. The catalyst was synthesized as follows: 0.6 g of TaOPc (Dainichiseika Color & Chemicals Mfg. Co., Japan) and 0.256 g of MWCNT powder (VGCF-X, SHOWA DENKO K.K., Japan) were mixed using a planetary ball mill. The mixed powders were heated at 1173 K for 3 h under flowing a gas mixture of 2% H_2, 0.5% O_2 and 97.5% N_2 in a rotary furnace. Using a glassy carbon (GC) disk (6 mm diameter)–platinum ring (7 mm inner diameter and 9 mm outer diameter) electrode as a working electrode, three electrode cells were prepared as reported in reference 16. RRDE voltammograms were recorded in the disk potential range of 0.2–1.2 V at a scan rate of 5 mV s^{-1} in the cathodic direction, while keeping the ring electrode potential at 1.2 V, with a rotation speed of 1600 rpm after bubbling O_2 for 1800 s. Fig. S1 shows a RRDE voltammogram of the TaO_x–MWCNT. The number of electrons transferred per unit oxygen molecule, n, was calculated with the following equation:

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

where I_{dX} and I_{rX} denote the disk and ring current obtained under X atmosphere, respectively, where X = O or N and corresponds to either oxygen or nitrogen; N is the collection efficiency (0.337). At E = 0.6 V, n was 3.3 and gradually increased to 3.6 with decreasing E to 0.2 V suggesting that ORR proceeded via both 4-($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) and 2-($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) electron reaction pathways.

The $-(I_{dO} - I_{dN})\ m^{-1}$ was 25 mA g^{-1} at E = 0.8 V, similar to the maximum value reported in the main body of the text. Commercial 50% (w/w) Pt-C catalysts (TEC10E50E, Tanaka Kikinzoku Kogyo K.K., Japan) showed three orders of magnitude higher $-(I_{dO} - I_{dN})\ m^{-1}$ under the identical conditions except that 0.1 mol dm^{-3} $HClO_4$ was used as an electrolyte solution for Pt-C. These results indicate that the activity of TaO_x–MWCNT should be enhanced accompanied by improving the selectivity.

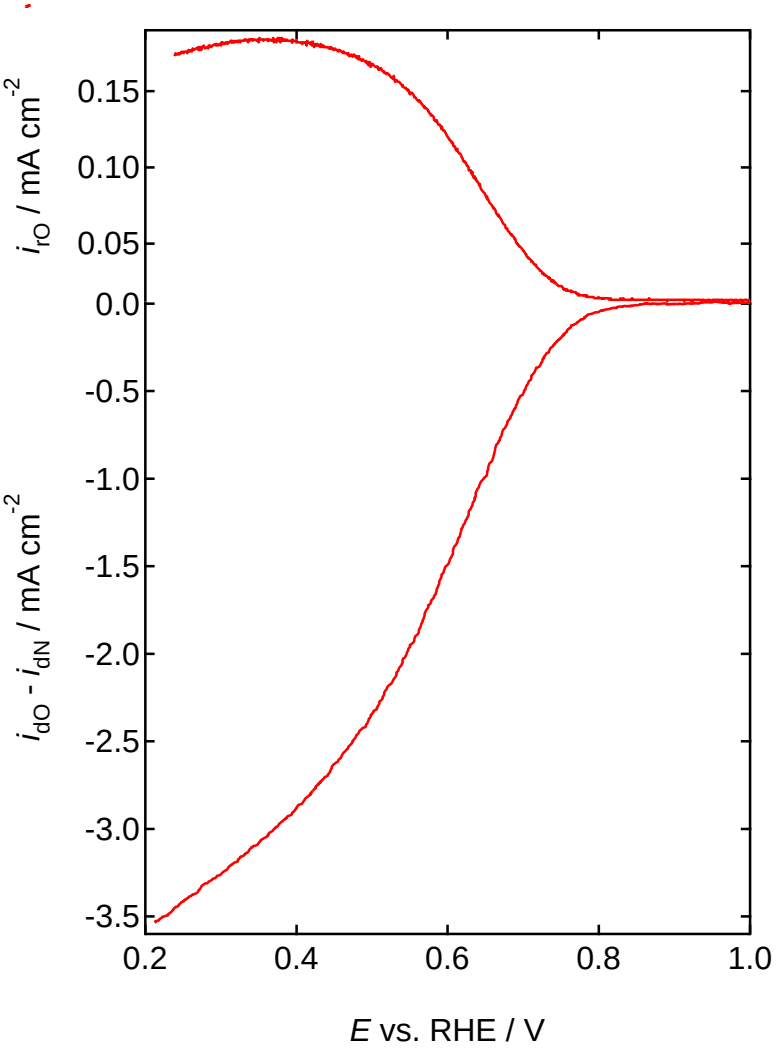

Fig. S1 A RRDE voltammogram of TaO_x–MWCNT after pyrolysis at 1173 K for 3 h under flowing a gas mixture of 2% H_2, 0.5% O_2 and 97.5% N_2. Scans were performed under N_2 and O_2 with a rotation speed of 1600 rpm at a scan rate of 5 mV s^{-1} in the cathodic direction in 0.1 mol dm^{-3} H_2SO_4. The TaO_x–MWCNT loading was 1.6 mg cm^{-2}.

S2. Elemental analysis of TaOPc precursor.

The TG-DTA curves of TaOPc under flowing air are shown in Fig. S2. The DTA curve shows a sharp peak at around 800 K and TG curve reaches plateau at around 850 K indicative of the burning off of carbon and nitrogen species in TaOPc. When the stoichiometric TaOPc was oxidized to form Ta_2O_5, the mass loss should be 69% whereas observed value from Fig. S2 is only 37% indicating that the used TaOPc precursor is non-stoichiometric; it contained less carbon and nitrogen and thus more tantalum atoms compared with stoichiometric TaOPc. The powders after the TG-DTA test were completely white, ruling out the presence of the remaining carbon and nitrogen species.

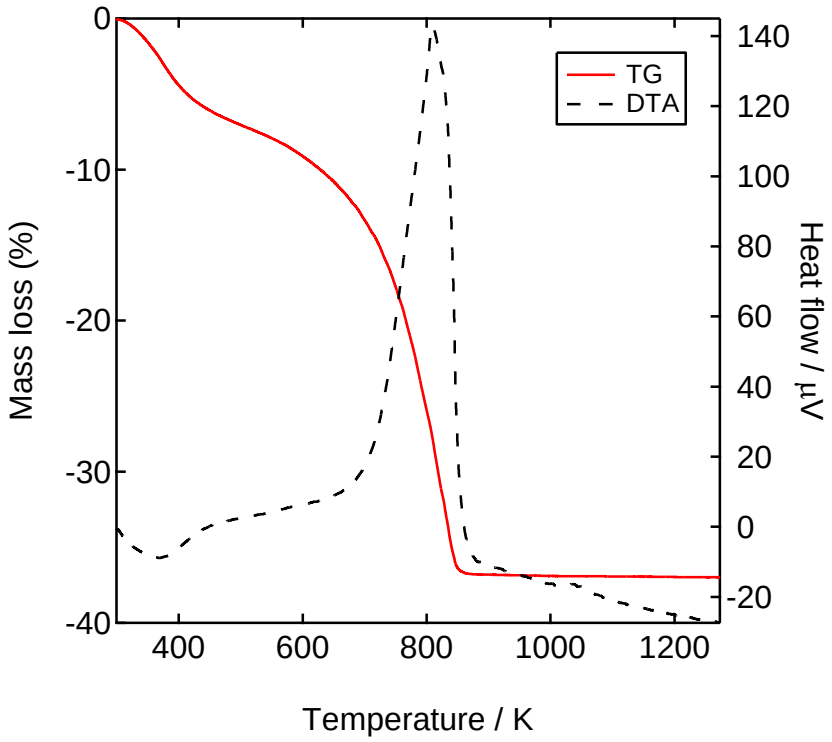

Fig. S2 TG-DTA curves of TaOPc under flowing air. The heating rate was 10 K min^{-1}.