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,b Koichi Matsuzawa,a
Shigenori Mitsushimaa,b and Kenichiro Otaa

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-ish@ynu.ac.jp

Phone/Fax: +81 172 39 3559 E-mail: chisaka@eit.hirosaki-u.ac.jp
S1. The ORR selectivity of TaO\textsubscript{x}–MWCNT.

Rotating ring-disk electrode (RRDE) voltammograms were obtained to help evaluate the ORR selectivity of TaO\textsubscript{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\textsubscript{2}, 0.5% O\textsubscript{2} and 97.5% N\textsubscript{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\textsuperscript{-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\textsubscript{2} for 1800 s. Fig. S1 shows a RRDE voltammogram of the TaO\textsubscript{x}–MWCNT. The number of electrons transferred per unit oxygen molecule, \( n \), was calculated with the following equation:

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

(S1)

where \( I_{dx} \) and \( I_{x} \) 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\textsubscript{2} + 4H\textsuperscript{+} + 4e\textsuperscript{-} \rightarrow 2H\textsubscript{2}O) and 2-(O\textsubscript{2} + 2H\textsuperscript{+} + 2e\textsuperscript{-} \rightarrow H\textsubscript{2}O\textsubscript{2}) electron reaction pathways.

The \( -(I_{dO} - I_{dN}) \) m\textsuperscript{-1} was 25 mA g\textsuperscript{-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\textsuperscript{-1} under the identical conditions except that 0.1 mol dm\textsuperscript{-3} HClO\textsubscript{4} was used as an electrolyte solution for Pt-C. These results indicate that the activity of TaO\textsubscript{x}–MWCNT should be enhanced accompanied by improving the selectivity.
Fig. S1 A RRDE voltammogram of TaOₓ–MWCNT after pyrolysis at 1173 K for 3 h under flowing a gas mixture of 2% H₂, 0.5% O₂ and 97.5% N₂. Scans were performed under N₂ and O₂ 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 H₂SO₄. The TaOₓ–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$_2$O$_5$, 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.

![TG-DTA curves of TaOPc under flowing air. The heating rate was 10 K min$^{-1}$.](image)

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