

## Supplementary Information

*for*

### Ta and Nb co-doped TiO<sub>2</sub>, and Its Carbon-Hybrid Materials for Supporting Pt-Pd Alloy Electrocatalysts for PEM Fuel Cells Oxygen Reduction Reaction

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## EXPERIMENTAL SECTION

### *(1) Preparation of the support.*

The synthesis of TaNbTiO<sub>2</sub> was done via an acidic catalyzed thermal hydrolysis process as described below. In a 250 ml beaker with a magnetic stirrer, niobium (V) ethoxide (Alfa, 0.066 ml, 0.261mmol) was added to 12M hydrochloric acid (Aldrich, 80 ml, 965 mmol), and stirred for 15 minutes. To this solution, we added titanium (IV) isopropoxide (Alfa, 2.33 ml, 7.60mmol) and kept stirring for 15 minutes to form a niobium (V) and titanium (IV) precursor solution. Subsequently, Tantalum (V) butoxide (Aldrich, 0.38 ml, 0.92 mmol) was added to the prior solution. The solution was stirred for 15 minutes and then heated at 120 oC for 20 hs under stirring with an evaporation speed of 20 ml/h. After that, a dry product was obtained and moved to the furnace for the heat treatment at 700°C for 10 h under pure H<sub>2</sub> gas at a flow rate of 300 ml/min. Finally, the Ta<sub>0.01</sub>Nb<sub>0.03</sub>Ti<sub>0.96</sub>O<sub>2</sub> product was confirmed by both the X-ray diffraction (XRD) and energy dispersive X-ray (EDX) measurements. For other compositions of Ta<sub>x</sub>Nb<sub>y</sub>Ti<sub>1-x-y</sub>O<sub>2</sub> (x = 0.01 to 0.08, and y = 0.08 to 0.20, respectively), the appropriate amount for various metal precursors were used in the synthesis procedure above. For the preparation of the C-TaNbTiO<sub>2</sub> (TKKE is the E-type carbon black of Tanaka Kikinokoku International (America) Inc.) hybrid support, the calculated amount of carbon was added to the mixture solution containing niobium (V) ethoxide, titanium (IV) butoxide and Tantalum (V) butoxide under stirring as described above. The subsequent steps of the synthesis were carried out in the same way as in the previous procedure. According to the weight ratio of carbon to Ta<sub>0.01</sub>Nb<sub>0.03</sub>Ti<sub>0.96</sub>O<sub>2</sub>, two hybrid support samples were obtained, i.e. C<sub>75wt%</sub>-(Ta<sub>0.01</sub>Nb<sub>0.03</sub>Ti<sub>0.96</sub>O<sub>2</sub>)<sub>25wt%</sub> and C<sub>25wt%</sub>-(Ta<sub>0.01</sub>Nb<sub>0.03</sub>Ti<sub>0.96</sub>O<sub>2</sub>)<sub>75wt%</sub>.

## **(2) Preparation of catalyst.**

The content of the Pt-Pd catalyst alloy in the supported catalysts was fixed at 20 wt%. All of catalysts were synthesized by a microwave assisted polyol method. Firstly, 90 mg of support material was ultrasonicated in 20 ml ethylene glycol for 1h to get a support mixture. Separately a mixed Pt and Pd-precursor solution was prepared by mixing a  $(\text{NH}_4)_2\text{PdCl}_6$  solution (18.9 mg in a mixture solvents of 0.5ml DI water and 1 ml ethylene glycol) with a  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution (45.25 mg  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in 0.5ml DI water). This mixed Pt-Pd solution was added dropwise into the support ink and the final solution was stirred for 1 h to form the precursor solution. After pH was adjusted to 10 using 0.1 M NaOH solution, the final solution was kept for another additional 1 h under stirring and reduced at the ethylene glycol boiling point ( $T=196-198^\circ\text{C}$ ) for 120 seconds in a Panasonic microwave (Sonicator 3000, Misonix). The resulting catalyst suspension was filtered and the residue was washed out with DI water till the washed-out water achieved pH 7. A final catalyst powder was dried in the oven at  $60^\circ\text{C}$  in air for 16 h. In this paper, three synthesized catalysts are expressed as:  $20\text{wt}\%\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{Ta}_{0.01}\text{Nb}_{0.03}\text{Ti}_{0.96}\text{O}_2$ ,  $20\text{wt}\%\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{C}_{75\text{wt}\%}-\text{(Ta}_{0.01}\text{Nb}_{0.03}\text{Ti}_{0.96}\text{O}_2)_{25\text{wt}\%}$ , and  $20\text{wt}\%\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{C}_{25\text{wt}\%}-\text{(Ta}_{0.01}\text{Nb}_{0.03}\text{Ti}_{0.96}\text{O}_2)_{75\text{wt}\%}$ , respectively.

## **Characterization**

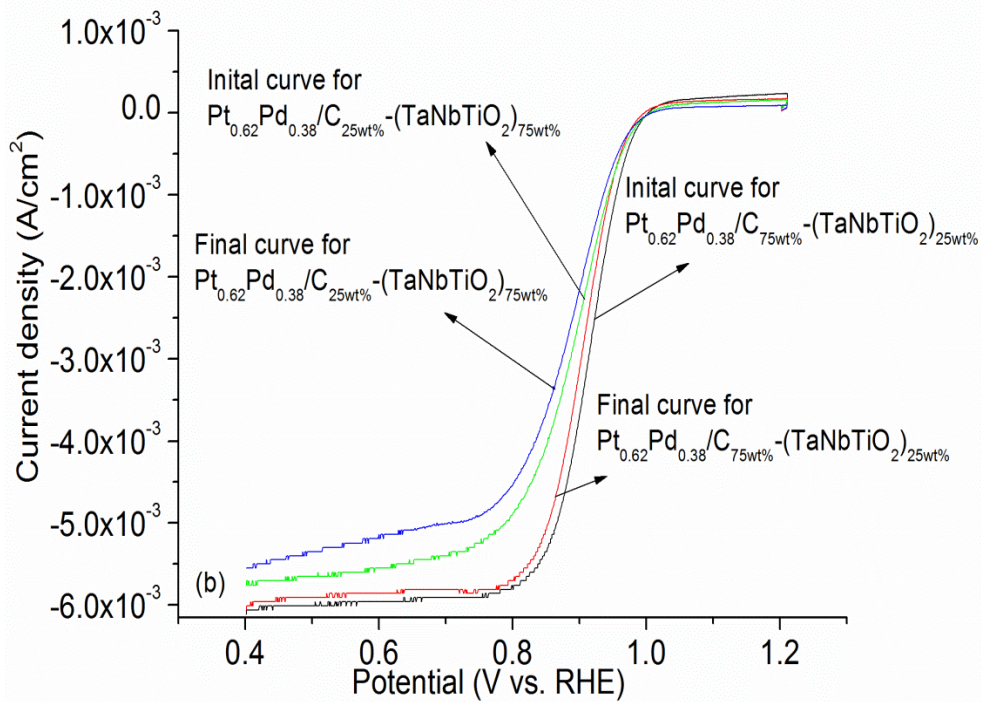
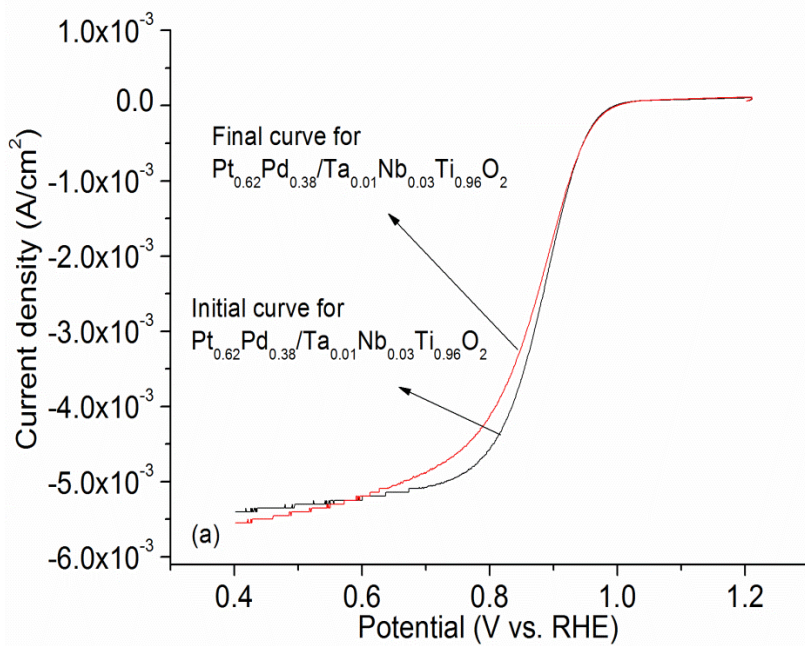
X-ray diffraction (XRD), was conducted using a Bruker D8 Advanced X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) at a scan rate of  $0.02^\circ/\text{Sec}$  over the  $2\theta$  range of  $10^\circ-90^\circ$ . A Brunauer-Emmet-Teller (BET) spectrometer was used with an analyzer (SA3100, Beckman Coulter) to determine the specific surface area of samples. The morphology and dispersion of the catalyst nanoparticles on the support were examined using a conventional transmission electron

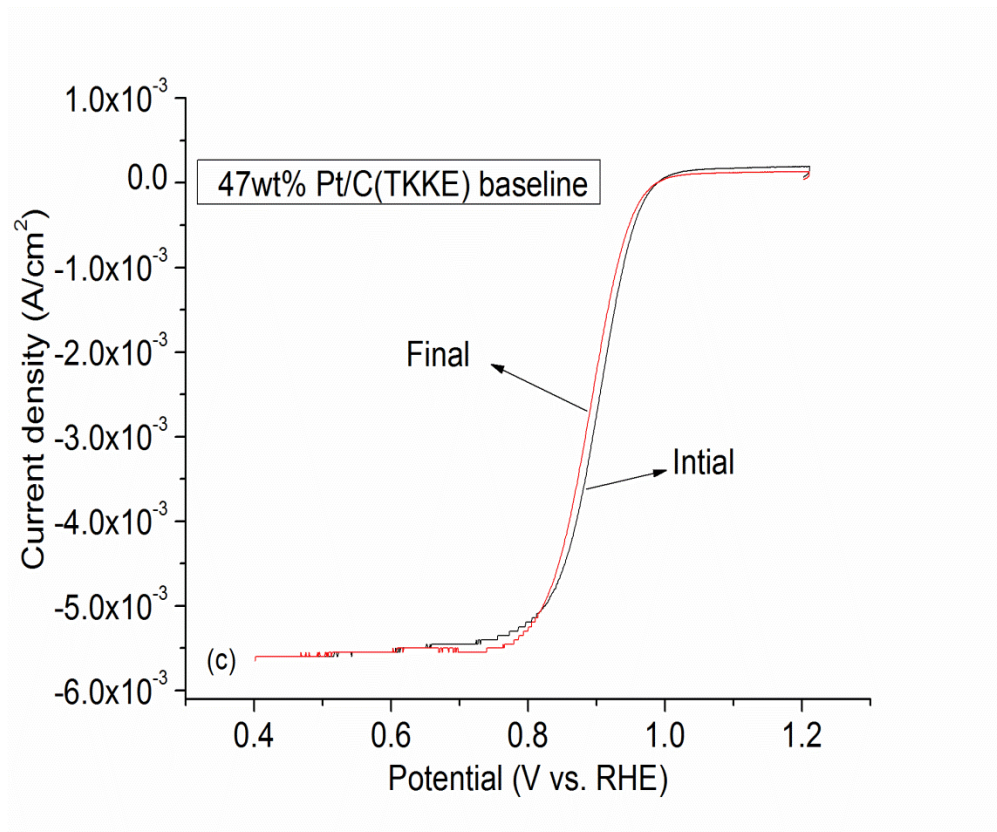
microscope (TEM, Philips CM12) and scanning transmission electron microscopy (STEM) observation/characterization were performed on a JEOL-2010F operated at 200 KV and equipped with an energy dispersive X-ray spectrometer (EDX). Samples for TEM/STEM observations were directly supported on a copper mesh with a carbon support film. The electronic conductivity of samples was determined using the electrochemical impedance spectroscopy (EIS) method at room temperature. The EIS measurements were carried out using a Solartron 1260 frequency response analyzer (FRA) connected to the Solartron 1480A Multistat at the frequency range of 100 KHz to 0.1 Hz with a 10 mV AC perturbation. The electrochemical surface area and ORR mass activity of synthesized catalysts were measured using the cyclic voltammetry (CV) and linear sweep voltammetry (LSV) methods. CVs and LSVs were recorded on Solartron multichannel potentiostat 1480A (controlled with Corrware software, Scribner Associates Inc., USA). The catalyst coating was deposited on the polished and precleaned gold rotating disk electrode (Au RDE, Pine Research Instrumentation). The catalyst ink was prepared by mixing 18.9 mg of the catalyst powder with 9.5 ml of distilled water and 0.5 ml of isopropyl alcohol under sonication for one hour. Then 24 $\mu$ l of this ink was carefully placed onto the Au rotating disk electrode (RDE) surface. The geometric surface area of RDE is 0.196 cm<sup>2</sup>. After solvent evaporation, the deposited coating layer was impregnated by 7  $\mu$ l of Nafion<sup>®</sup> ionomer solution (5wt%, Dupont) in order to fix the particles on the Au electrode surface. This coated Au RDE was dried in air for 0.5 h. A three-electrode cell (Pine Research Instrumentation) with a working Au RDE and a reversible hydrogen reference electrode (RHE), and a Pt mesh counter electrode were used for all electrochemical measurements. The electrochemical surface area of supported Pt-Pd catalysts was estimated by a cyclic voltammograms (CVs) (20th cycles at a potential scan rate of 20 mV/s in the potential range of 0.05- 1.2 V (RHE)) recorded in a N<sub>2</sub>-

purged 0.1 M HClO<sub>4</sub> electrolyte. For ORR mass activity measurements, linear sweep voltammograms were measured at a potential scan rate of 5 mV/s and an electrode rotation rate of 1600 rpm in an O<sub>2</sub>-saturated 0.1M HClO<sub>4</sub> electrolyte solution. All electrochemical experiments were performed at 30°C and ambient pressure.

**Table S1.** Mass activity and mass activity loss for various  $Ta_xNb_yTi_{1-x-y}O_2$  ( $x=0.01$  to  $0.08$ , and  $y=0.03$  to  $0.20$ ).

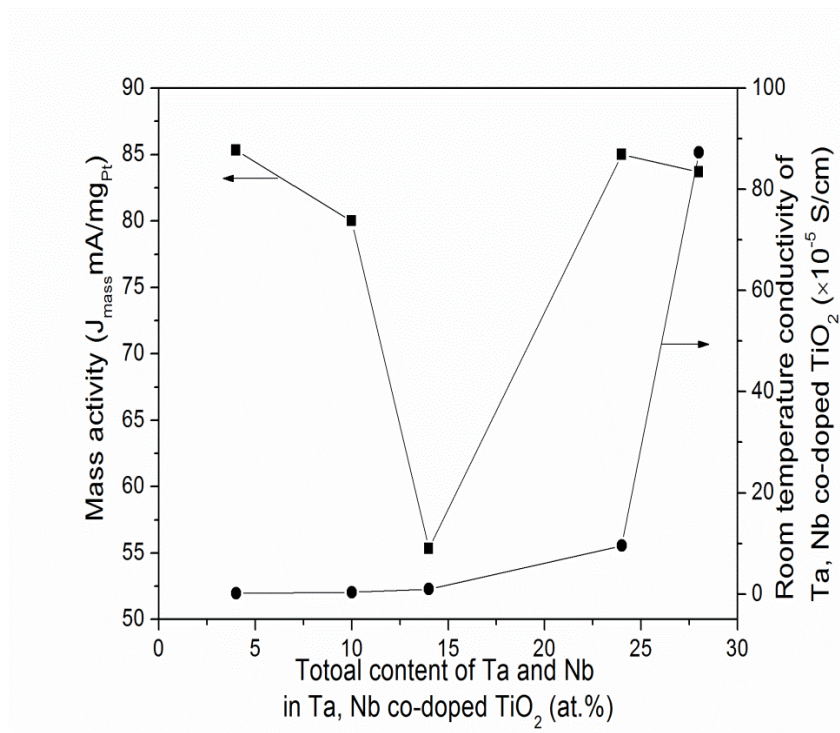
Sample	Total content of Ta and Nb (at%)	Ta content (at%)	Nb content (at%)	Mass activity (mA/mg <sub>Pt</sub> )	Mass activity loss (mA/mg <sub>Pt</sub> )
20wt%Pt <sub>0.62</sub> Pd <sub>0.38</sub> / Ta <sub>0.01</sub> Nb <sub>0.03</sub> Ti <sub>0.96</sub> O <sub>2</sub>	4	1	3	85.3	12.5
20wt%Pt <sub>0.62</sub> Pd <sub>0.38</sub> / Ta <sub>0.04</sub> Nb <sub>0.06</sub> Ti <sub>0.9</sub> O <sub>2</sub>	10	4	6	80	25
20wt%Pt <sub>0.62</sub> Pd <sub>0.38</sub> / Ta <sub>0.08</sub> Nb <sub>0.06</sub> Ti <sub>0.9</sub> O <sub>2</sub>	14	8	6	55.3	20
20wt%Pt <sub>0.62</sub> Pd <sub>0.38</sub> / Ta <sub>0.04</sub> Nb <sub>0.2</sub> Ti <sub>0.76</sub> O <sub>2</sub>	24	4	20	85	26
20wt%Pt <sub>0.62</sub> Pd <sub>0.38</sub> / Ta <sub>0.08</sub> Nb <sub>0.2</sub> Ti <sub>0.72</sub> O <sub>2</sub>	28	8	20	83.7	24



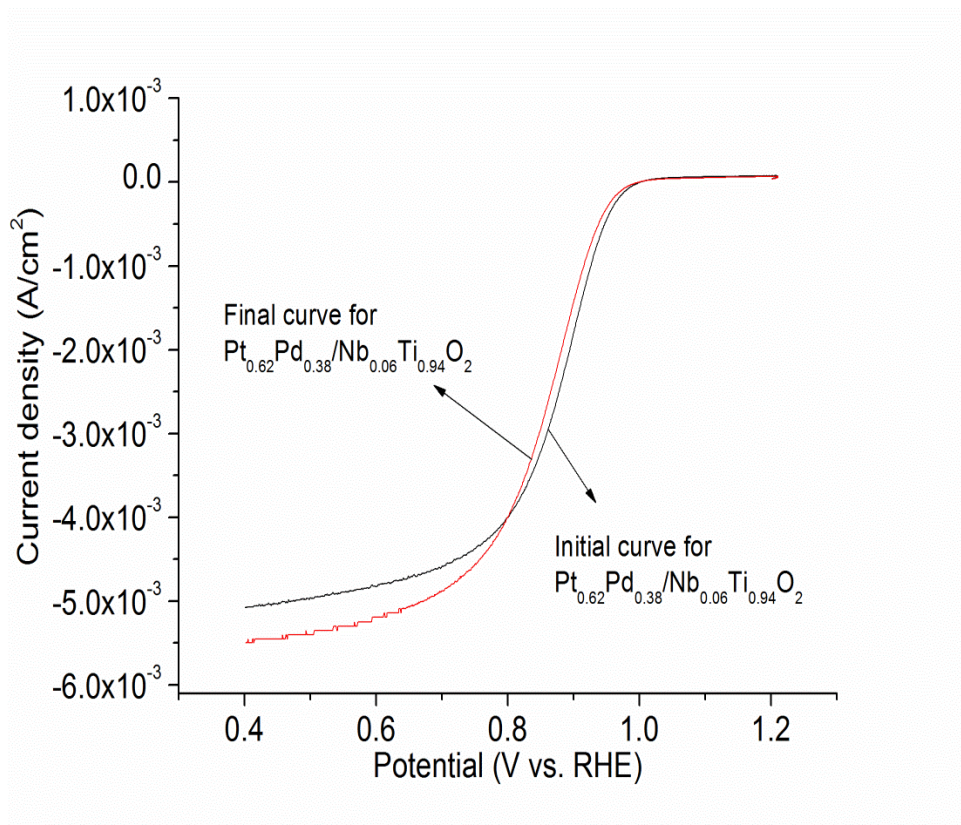


**Figure S1.** Initial and final ORR curves for three catalysts at PtPd loading of 20wt%.: (a)  $\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{Ta}_{0.01}\text{Nb}_{0.03}\text{Ti}_{0.96}\text{O}_2$ , (b)  $\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{C}(\text{TKKE})_x(\text{Ta}_{0.01}\text{Nb}_{0.03}\text{Ti}_{0.96}\text{O}_2)_{1-x}$  ( $x=25\text{wt\%}$  and  $75\text{wt\%}$ ), and (c)  $\text{Pt}/\text{C}(\text{TKKE})$ .





**Figure S2.** Pt mass activity of 20wt%Pt<sub>0.62</sub>Pd<sub>0.38</sub>/Ta<sub>x</sub>Nb<sub>y</sub>Ti<sub>1-x-y</sub>O<sub>2</sub> (x=0.01 to 0.08, and y= 0.03 to 0.20) and electronic conductivity of Ta<sub>x</sub>Nb<sub>y</sub>Ti<sub>1-x-y</sub>O<sub>2</sub> support materials as function of the total content of Ta and Nb in Ta, Nb co-doped TiO<sub>2</sub> (at.%)



**Figure S3.** Initial and final ORR curves for the  $\text{Pt}_{0.62}\text{Pd}_{0.38}/\text{Nb}_{0.06}\text{Ti}_{0.94}\text{O}_2$  catalysts at the PtPd loading of 20wt%.