



## Short communication

## Preparation of reduced tantalum pentoxide by electrochemical technique for oxygen reduction reaction



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## HIGHLIGHTS

- An electrochemical reductive treatment was successfully applied to reduce Ta<sub>2</sub>O<sub>5</sub> deposited on a glassy carbon.
- The electrochemical treatment also resulted in morphological changes of the deposits.
- The treated TaO<sub>x</sub> exhibits a high ORR activity in acidic solutions.
- The reduced oxide possesses a four-electron ORR electrocatalysis at potential above 0.8 V.

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## ABSTRACT

A non-Pt based electrocatalyst, tantalum oxide (TaO<sub>x</sub>) deposited on glassy carbon, for oxygen reduction reaction (ORR) in acidic solutions was prepared by electrochemical technique. The tantalum pentoxide (Ta<sub>2</sub>O<sub>5</sub>) formed on the as-prepared deposits was electrochemically reduced to generate its reduced species which conventionally need a heat treatment under H<sub>2</sub> atmosphere. The reduced Ta<sub>2</sub>O<sub>5</sub> shows a fairly high onset potential of ORR (0.87 V vs. RHE) in comparison with that (0.98 V) at a commercially available Pt/C catalyst. The ORR performance of the TaO<sub>x</sub> was investigated using a rotating ring-disk electrode voltammetry showing that a four-electron ORR takes place actually at potential above ca. 0.8 V and a two-electron ORR becomes significant gradually as the potential is increased negatively.

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## 1. Introduction

In the light of changing of energy policy which turns to renewable resources and in order to reduce greenhouse gas effects, the emergence of clean technologies has been an important issue. One of their examples is proton exchange membrane fuel cells (PEMFCs) which have still a major problem for commercialization due to the scarcity and high price of Pt used as electrocatalysts. Particularly at the cathode where oxygen reduction reaction (ORR) takes place, it is even more challenging because the poor stability of Pt nanoparticles supported carbon (Pt/C) catalysts at a high potential (>0.8 V) demands a huge amount of them to keep the performance for a long period of operation [1]. Therefore, the development of non-Pt catalysts for the cathode has been rapidly increased in the last decade. For instance, tantalum oxide (TaO<sub>x</sub>)–

based materials would be promising alternatives since they can sustain in acidic environments and have been found as active electrocatalysts for ORR [2–5]. The presence of oxygen vacancies in the oxides is strongly suggested to play a pivotal role in the electrocatalytic reaction because they may enhance the electrical conductivity as well as serve as the active sites for O<sub>2</sub> adsorption [4–10].

Oxygen vacancies of metal oxide are well known to determine the chemical and electronic properties of the oxide and are associated with oxygen-deficient *d*<sup>0</sup> or reduced oxides with a low number of electrons filled in the *d* bands [9–11]. Conventionally, to produce such oxide phases, the oxides which are usually in their stoichiometric forms, e.g., Ta<sub>2</sub>O<sub>5</sub>, are calcined under a reduced atmosphere, e.g., pure H<sub>2</sub> or at extremely high temperature with the absence of O<sub>2</sub>. These techniques have been routinely used, for example by Ota et al. [4,5] and Domen et al., [3], to prepare active metal oxides-based electrocatalysts (TaO<sub>x</sub>, NbO<sub>x</sub>, ZrO<sub>x</sub>, etc.) for ORR with highly positive onset potentials (>0.8 V vs. RHE). However, a high temperature of calcination particularly under pure H<sub>2</sub> gas not

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only results in a high cost and safety issues but also usually causes a sintering of nanoparticles leading to a loss in their active surface area and nature. Moreover, because of the technical difficulties arising from this conventional method [3], the rotating-ring disk electrode (RRDE) voltammetric measurements are difficult actually, although the obtained results are very useful in clarifying ORR mechanism, typically on whether a four-electron ORR process takes place or not.

In this communication, we demonstrate a new technique for fabrication of  $\text{TaO}_x$ -based electrocatalyst for ORR in which the  $\text{TaO}_x$  was electrodeposited on a glassy carbon (GC) electrode ( $\text{TaO}_x/\text{GC}$ ). Instead of using calcination techniques as mentioned above, we attempted to employ an electrochemical reductive treatment to generate a reduced species of the  $\text{Ta}_2\text{O}_5$ . This facile, inexpensive and simple method has successfully produced an active  $\text{TaO}_x$  for ORR electrocatalysis and easily allowed us to investigate its activity using RRDE voltammetric measurements. To the best of our knowledge, this is the first attempt to apply the electrochemically reduced  $\text{Ta}_2\text{O}_5$  as ORR electrocatalyst.

## 2. Experimental

For fabricating the  $\text{TaO}_x/\text{GC}$  electrode, there are only two required steps. The first one is the electrodeposition of  $\text{TaO}_x$ , and the detailed procedure basically follows our previous work [12]. Briefly, a cleaned RRDE electrode (GC disk: 6 mm in diameter) was connected into a conventional three-electrode electrochemical cell which contains Ta solution. An Ag wire was used as a quasi-reference electrode, and a GC plate as a counter electrode to avoid Pt contamination. The solution was prepared by firstly dissolving 0.179 g of  $\text{TaCl}_5$  (Alfa Aesar) and then 1.06 g of  $\text{LiClO}_4$  (Wako Pure Chemicals) in 10 mL of propylene carbonate (PC, Kanto

Chemicals) solution. The bath solution was vigorously degassed by Ar bubbling for 15 min. A cyclic voltammetry (CV) technique was utilized for the deposition of Ta in which the potential was scanned between 0.3 and  $-2.0$  V vs. Ag wire at scan rate of  $20 \text{ mV s}^{-1}$  for 2 cycles giving about  $\sim 29 \mu\text{g cm}^{-2}$  of Ta. Immediately after the deposition, the electrode was successively immersed in methanol and water for 1 min each to remove the remaining solution. As the second step, to mimic the heat treatment under  $\text{H}_2$  atmosphere in producing the reduced  $\text{Ta}_2\text{O}_5$  species, we introduced an electrochemical reductive treatment in which the Ta-deposited electrode was potentiostatically poised at potential of  $-0.6$  V for 12 h (as the optimum condition). This was then followed by performing a CV in the potential range of  $-0.2$  and  $1.3$  V at  $50 \text{ mV s}^{-1}$  for 10 cycles for electrochemical treatment before ORR measurements. As a control experiment for anticipating the contribution of (if any) impurities deposited during electrolysis, the same electrochemical procedure was also carried out for the bare RRDE at which the ORR performance was examined for comparison.

All the electrochemical experiments were performed using a three-electrode electrochemical cell by operating ALS/CHI Electrochemical Analyzer (Model 760 Ds) at room temperature (set at  $25^\circ\text{C}$ ). For electrochemical characterizations including RRDE voltammetric measurements, a Pt wire was used as a counter electrode and an  $\text{Ag}|\text{AgCl}|\text{KCl}_{(\text{sat})}$  was served as a reference electrode and all the potentials reported here are given with respect to a reversible hydrogen electrode (RHE). For ORR comparison, a good quality of thin film of a commercially available Pt/C (Pt: 46.6 wt. %) purchased from Tanaka Kikinzoku Kogyo Corp., Japan (TKK) with loading of  $10 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$  was used and the details of its preparation were given in our previous report [13]. Briefly, a 30 mg of the Pt/C was weighted and poured into a 25 mL vial. A 21 mL of 67% isopropanol solution was prepared and then it was transferred into the

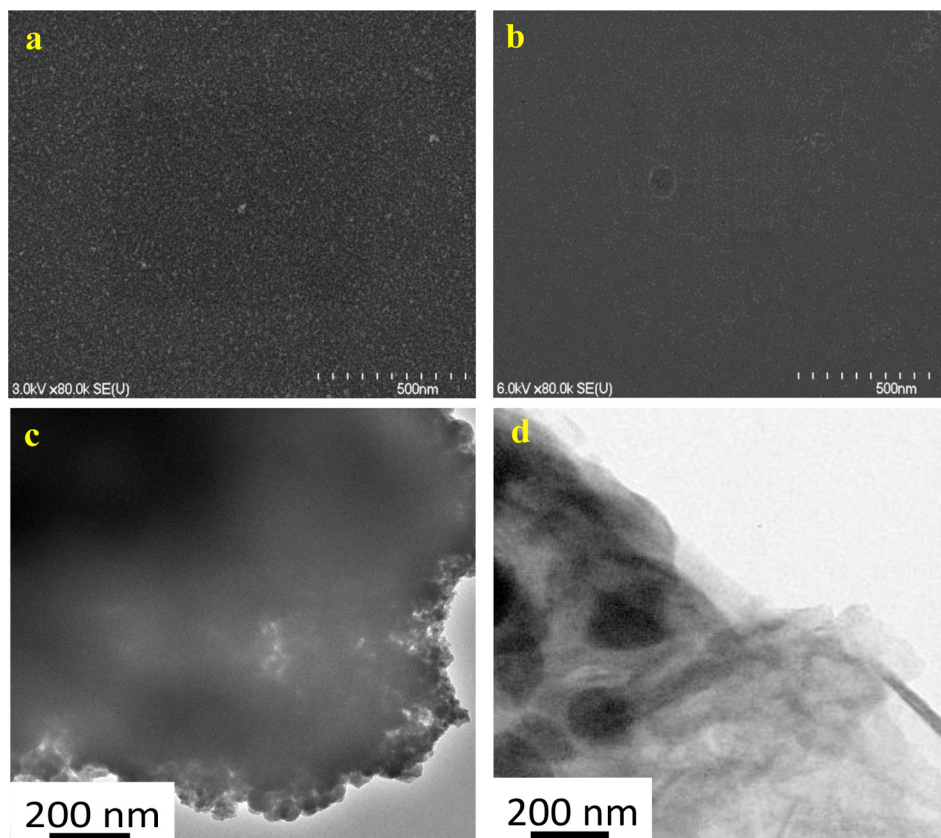


Fig. 1. (a and b) SEM and (c and d) TEM images taken at the  $\text{TaO}_x/\text{GC}$  electrodes (a and c) before and (b and d) after the electrochemical reductive treatment.

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