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Carbon-coated Single-phase Ti_4O_7 Nanoparticles as Electrocatalyst Support

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ABSTRACT

The unique structure of Magnéli phases TiO_x renders them effective for the electrochemical applications. This work demonstrates a synthesis of carbon-coated Magnéli phases TiO_x (TiO_x@C) nanoparticles from 3-aminophenol and rutile titania (TiO_2) nanoparticles as a support for platinum (Pt) electrocatalyst. 3-aminophenol was polymerized and carbonized on the surface of TiO_2 nanoparticles respectively in a microwave hydrothermal reactor and a tubular furnace. Reduction of the carbon-coated TiO_2 (TiO_2@C) into TiO_x@C was performed in hydrogen atmosphere at 800-1050 °C. The carbon coating effectively prevented TiO_2 nanoparticles from sintering, resulted in TiO_x@C sizes from 50 to 100 nm. Single-phase Ti_4O_7 core, which has the highest theoretical electrical conductivity among the Magnéli phases, was obtained from reduction of TiO_2@C at 1000 °C. for 10 min C/Ti_4O_7-supported Pt exhibited an electrochemical surface area of 46 $m^2\ mg_{Pt}^{-1}$ at 15% Pt loading, slightly higher than that reported for commercial TKK electrocatalyst with 20% Pt loading (44.13 $m^2\ mg_{Pt}^{-1}$).

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1. INTRODUCTION

Magneli phases titanium oxide with a chemical formula of Ti_nO_{2n-1}, or simply called Magneli phases TiO_x, are attractive because of their unique structure. The oxygen deficiencies form an ordered crystallographic shear of Ti_2O_3 corundum, which is continuously introduced throughout the rutile TiO_2 phase (Nörenberg, *et al.,* 1998). The interfacing Ti atoms between these two phases share electrons in the 3d orbital. The crystallographic shear enables a high theoretical electron conductivity, of which value depends on the crystal arrangement. It was reported that the highest theoretical electron conductivity may reach 1000 S cm^{-1} (Li, *et al.,* 2010). This value is achieved by Ti_4O_7 which consists of seven Ti-O bonds for every Ti-Ti bond with a very well-ordered crystallographic shear plane as the electron pathway (Phillips, *et al.,* 2013).

Development of Ti_4O_7 materials has been significantly improving in the recent years. This is consistent with the increasing demand for conductive materials. Besides having high electron conductivities, Magneli phases are generally stable under strongly oxidizing environment (Esfahani, *et al.,* 2015). This characteristic is favorable for electrochemical system involving acidic environment and potential cycling with a wide potential window. Ioroi, et al. demonstrated this material as a stable, durable, and highly efficient electrocatalyst support for platinum (Pt) (Ioroi, *et al.,* 2005 and Ioroi, *et al.,* 2008). Although the performance of Ti_4O_7 as electrocatalyst support has been proven, morphological structure of this material is still an issue. It is generally accepted that homogenous structure with small size is highly favored for this application.

Ti_4O_7 is mainly synthesized using a top-down approach, i.e. by reducing TiO_2 at high temperatures (> 1000 °C) in hydrogen or argon. The reduction temperatures exceed the sintering temperature of TiO_2, resulting in a big size of products which is unfavorable for most of the applications, including electrocatalyst support. Previous studies showed that Ti_4O_7 with small size could be synthesized using bottom-up approaches, i.e. by controlling the growth of Magneli phases. One good example of this approach is a study by Phillips, et al. which used atomic layer deposition to grow a single phase Ti_4O_7 (Phillips, *et al.,* 2012). However, this method required a substrate for the Ti_4O_7 phase to grow. Recently, Arif et al. introduced the first synthesis of nano-sized Magneli phases TiOx with chain-structure using induction thermal plasma method (Arif, *et al.,* 2017). Although this method did not require any substrate and successfully decreased the particle size down to ~20 nm, control of the crystal structure to form a single Ti_4O_7 phase was a challenging issue. The presence of Magneli phases other than Ti_4O_7, as well as some impurities, reduced the electrical conductivity far below the expected value. This is to say, that a synthesis of single phase Ti_4O_7 with nano size remains a challenge.

A possible approach to solve this challenge is using a top-down approach which features anti-sintering agent to encapsulate TiO_2 before reduction at high temperatures. Carbon is a good anti-sintering candidate for the production of Ti_4O_7 because of two reasons. First, carbon is conductive and therefore, is able to maintain high conductivity. Second, the structure of carbon can be controlled to be sufficiently porous. The porous structure enables the penetration of the reducing gas through carbon layer to reach and reduce TiO_2 core.

Based on this rationale, the present study demonstrates for the first time, a synthesis of single phase, nano-sized carbon-coated Ti_4O_7 (Ti_4O_7@C) from rutile TiO_2 and 3-aminophenol. TiO_2 was encapsulated with 3-aminophenol-derived carbon prior to the reduction at high temperatures. The encapsulation was assisted by microwave irradiation using a previously demonstrated method (Arif, *et al.,* 2016). After the successful reduction into single phase Ti_4O_7, Pt nanoparticles as electrocatalyst were deposited on Ti_4O_7@C using a microwave-assisted colloidal method. The electrochemical surface area (ECSA) of the Pt/Ti_4O_7@C electrocatalyst was then evaluated as the performance parameter. The results demonstrated in this study are expected to be the basis for further nanostructuration of Ti_4O_7@C for electrocatalyst support in the future.

2. METHODS

2.1. Synthesis of Ti_4O7@C nanoparticles

0.1 g of TiO_2 nanoparticles (Sakai Chemical Industry, Co., Ltd., Osaka, Japan), rutile phase, were dispersed in a mixture of ethanol (3.69 ml), ammonia (0.44 ml; Kanto Chemical Co. Inc., Tokyo, Japan), and ultrapure water (20.5 ml) in an ultrasonic bath. 0.1 g of 3-aminophenol (Sigma Aldrich, St. Louis, MO, USA) were added into the dispersion and stirred until dissolved. The mixture was then subjected to microwave irradiation in a microwave reactor (Initiator+, Biotage, Uppsala, Sweden) for 30 min at 150 °C after the addition of formaldehyde (Kanto Chemical Co. Inc., Tokyo, Japan). The obtained particles were separated from the remaining solution using centrifugation and washed several times with water and ethanol. After being dried at 40 °C, the particles were carbonized in a ceramic furnace for 2 hours at 1000 °C in nitrogen atmosphere. The resulting particles, TiO_2@C, was then placed in a quartz tube reactor for reduction in continuously flowing (2 L min^{-1}) hydrogen (H_2) for 10 min. Before the reduction started, the oxygen content in the reactor was kept minimum by evacuating the air and filling the reactor with high purity H_2. The effect of reduction temperature was studied at 800, 900, 1000, and 1050 °C.

2.2 Pt deposition on Ti_4O_7@C nanoparticles

Deposition of Pt on Ti_4O_7@C nanoparticles followed the procedure described in the previous report (Balgis, *et al.,* 2016). 10 mg of Ti_4O_7@C nanoparticles were dispersed in 20 ml ethylene glycol (Kanto Chemical Co. Inc., Tokyo, Japan) under ultrasonic. Chloroplatinic acid was added and the solution was further ultrasonicated for 30 min. The solution was subjected to microwave irradiation for 2 min at 150 °C. The obtained particles, Pt/Ti_4O_7@C, were washed several times with water and ethanol, and dried.

2.3 Characterization

Crystal structure of the prepared particles was analyzed using x-ray diffraction (XRD; Bruker D2 Phaser, Bruker AXS GmbH, Karlsruhe, Germany). The phase composition was evaluated semi-quantitatively in Diffrac EVA 3.0 software (Bruker AXS GmbH, Karlsruhe, Germany). The particle morphology was observed using a field-emission scanning electron microscope (SEM; S-5000, 20 kV, Hitachi High-Tech Corp., Tokyo, Japan) and transmission electron microscope (TEM; JEM-2010, 200 kV, JEOL Ltd., Tokyo, Japan). The ζ-potential of TiO_2 and the polymer was measured using a zetasizer (Zetasizer Nano ZSP, Malvern Instruments Ltd., Malvern, UK).

Electrochemical characteristic of the prepared particles was evaluated using a potentiostat (Hz-5000, Hokuto Denko Corp., Tokyo, Japan) in a 3-electrode configuration. The counter and reference electrode were respectively platinum wire and reversible hydrogen electrode (RHE). The catalyst ink was prepared by dispersing 2.64 mg of Pt/Ti_4O_7@C in 2-propanol (0.3 ml; Kanto Chemical Co. Inc., Tokyo, Japan), ultrapure water (0.95 ml) and Nafion (7 µl; Wako Pure Chemical Industries Ltd., Osaka, Japan) in an ultrasonic bath. The catalyst ink (10 µl) was transferred to a polished glassy carbon electrode and allowed to dry. Cyclic voltammetry was performed without rotation in a potential window between 0 and 1.2 V/RHE with a 50 mV s^{-1} potential sweep. The electrolyte was nitrogen-saturated 0.1 M $HClO_4$.

3. RESULTS AND DISCUSSION

The first part of the synthesis of Ti_4O_7@C nanoparticles was encapsulation of TiO_2 with carbon. The encapsulation mechanism was expected to be similar with that described in the previous report, except that TiO_2 was used as the foreign body the current study (Arif, *et al.,* 2016). Initially, 3-aminophenol monomer nucleated on the surface of TiO_2. The driving force for the nucleation was the electrostatic attraction due to the opposing ζ-potential. ζ-potential of TiO_2 was observed to be -30 mV. This value was contributed mainly by the OH- group on the particle surface. On the other hand, 3-aminophenol was positively charged (20 mV) which reflected the presence of amine group in the monomer.

Polymerization of 3-aminophenol was initiated immediately after the addition of formaldehyde (Zhao, *et al.,* 2012). The polymerization took place in the microwave reactor. At the end of the polymerization, TiO_2 nanoparticles were covered with 3-aminophenol polymer layer, creating a core-shell structure with the core being TiO_2 nanoparticle. The polymer was then converted to carbon after carbonization and the whole particle became TiO_2@C. The mechanism of TiO_2 encapsulation with carbon is illustrated in **Figure 1**.

The prepared TiO_2@C nanoparticles were then reduced in H_2 at high temperatures to form TiO_x@C. The morphology of the TiO_x@C synthesized using different reduction temperatures are shown in the SEM images in **Figure 2a-d**. The nanoparticles were dense and chain-structured with the sizes laid within a range between 50 to 100 nm and did not change with the increasing reduction temperature. The sizes were bigger than that of initial TiO_2, which was 20 nm for the longest axis (**Figure 2e**). However, they were significantly smaller than that of TiO_x synthesized using a reduction temperature of 1050 °C for the same reduction time without carbon encapsulation (**Figure 2f**). This indicated a successful suppression of TiO_2 sintering by carbon.

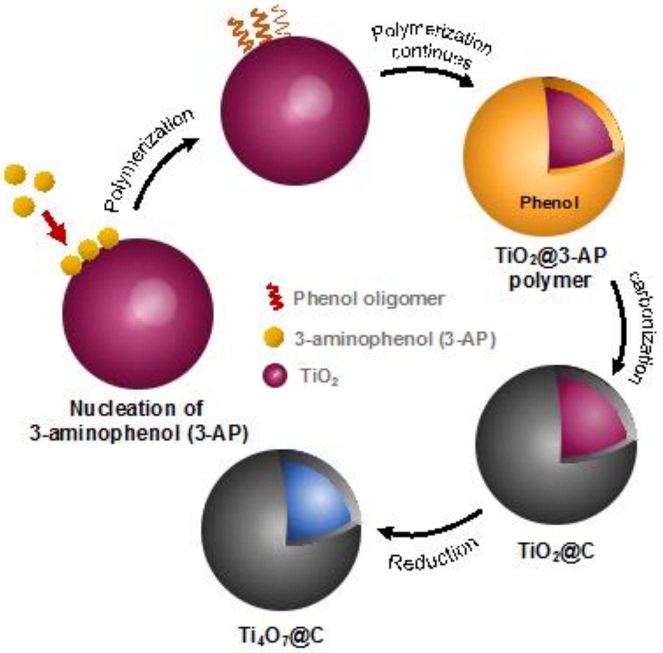

Figure 1. Illustration of the encapsulation mechanism of TiO_2 nanoparticles with carbon.

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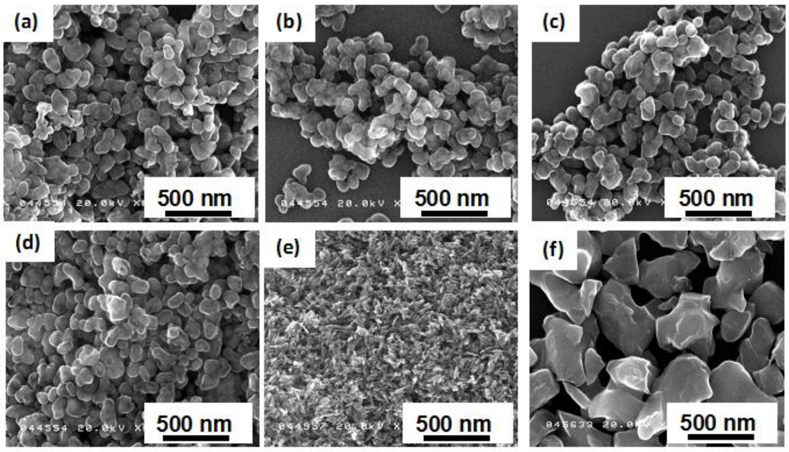

Figure 2. SEM image of Ti_4O_7@C nanoparticles synthesized using a reduction temperature of (a) 800, (b) 900, (c) 1000, and (d) 1050 °C, (e) rutile TiO_2 nanoparticles as the starting material, and (f) Ti_4O_7 particles synthesized by reducing TiO_2 at 1050 °C for 30 min without carbon encapsulation.

The core-shell structure of TiO_x@C was confirmed from the TEM images of the TiO_x@C sample reduced at 1000 °C in **Figure 3a-b**. **Figure 3a** shows carbon layer (light color) with a thickness of approximately 20 nm encapsulating the core particle (dark color). High resolution TEM image of the dark-colored core particle in **Figure 3b** shows highly crystalline TiO_x with clear lattices. The lattice space was 2.81 Å which corresponds to Ti_4O_7 [-1 0 4] plane. It is worth mentioning that the crystallographic shear plane – the main characteristic of Magneli phases TiOx – is clearly visible in **Figure 3b**. The shear planes were neatly ordered as they belong to Ti_4O_7 phase.

A further increase in the reduction temperature to 1050 °C excessively reduced the TiO_2, indicated by the presence of less conductive Ti_2O_3 phase in the XRD spectrum. It is interesting that the temperature required for reducing TiO_2 to Ti_4O_7 in this study was slightly less than that reported by other researchers which was usually 1050 °C or higher (Kitada, *et al.,* 2012 and Zhang, *et al.,* 2013). In the current study, the reducing agents were H_2 and carbon. The small TiO_2 size inside the carbon layer and the good contact between carbon and TiO_2 surface were believed to facilitate an efficient reduction process.

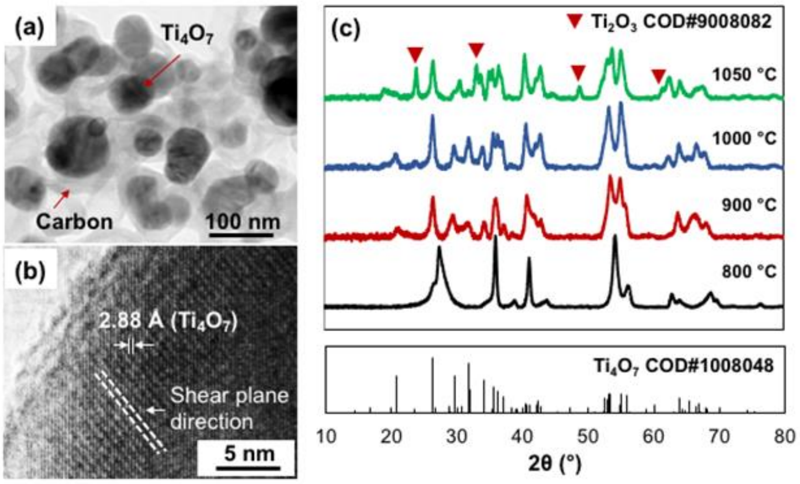

Figure 3. (a) TEM and (b) high resolution (HR) TEM of TiO_x@C synthesized using a temperature of 1000 °C for the reduction, (c) X-ray diffraction spectra of the sample prepared using various reduction temperatures.

Pt nanoparticles were deposited onto the surface of Ti_4O_7@C with a Pt loading of 15 wt%. As shown in the SEM image in **Figure 4a**, the average Pt size was 3 nm, which was preferred for the electrocatalysis application. However, the dispersion of Pt nanoparticles was not exceptional compared with the literatures which used the same Pt deposition method, indicated by the wide size distribution and the presence of area with vacant Pt. The formation of big-sized Pt suggested Pt agglomeration because of two possible reasons. First, the dense and chain structure of Ti_4O_7@C nanoparticles could not facilitate a good hydrodynamic of ethylene glycol as the dispersant for Pt precursor during Pt deposition. Therefore, some parts of Ti_4O_7@C could not be wetted by the Pt precursor. The second possible reason would be the limited available surface for Pt deposition. The same tendency was shown in a study by Balgis, et al. which also involved a computational fluid dynamic simulation (Balgis, *et al.,* 2016).

Cyclic voltammogram of Pt/Ti_4O_7@C electrocatalyst shows a typical voltammogram shape of Pt. The ECSA was calculated using the H_2 adsorption charge limited by the potential just above the hydrogen generation (~0.05 V/RHE) and 0.3 V/RHE. The ECSA was calculated to be 46 m^2 mg_{Pt}^{-1}. This value was comparable with the ECSA of commercial TKK catalyst with 20% Pt loading, which was reported to be 44.13 m^2 mg_{Pt}^{-1}. Further analysis is required to investigate the reason for the good performance despite the low Pt loading. Speculatively, the good performance may be attributed to the good electron transfer through the Ti_4O_7@C structure. Although the 3-aminophenol-derived carbon was reported to be amorphous, the good electron transfer was made possible by the highly crystalline Ti_4O_7 in the core of the Ti_4O_7@C.

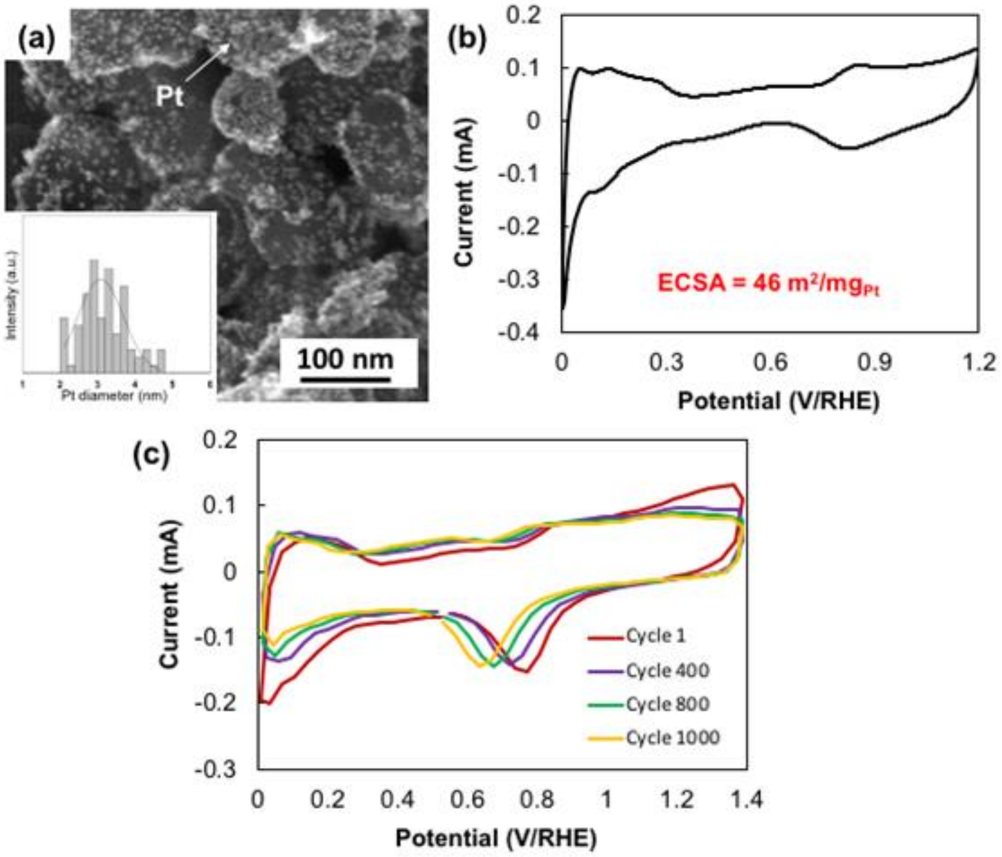

Figure 4. (a) SEM images of Pt/Ti_4O_7@C, (b) cyclic voltammogram of Pt/Ti_4O_7@C in 0.1 M $HClO_4$ solution, and (c) cyclic voltammogram of Pt/Ti_4O_7@C after several potential cycles from 0 to 1.4 V/RHE.

Durability of Pt/Ti_4O_7@C electrocatalyst was evaluated by performing 1000 cycles from 0 to 1.4 V/RHE. This condition is considered to be highly severe because the normal theoretical operating potential of a fuel cell does not exceed 1.2 V/RHE. Pt/Ti_4O_7@C electrocatalyst showed low durability after 1000 cycles, that the ECSA decreased from 46 to 15 m^2 mg_{Pt}^{-1}. A durability study on pure Magneli phases TiO_x demonstrated excellent results (Arif, *et al.,* 2017). Therefore, the low durability in the current study is attributed to the carbon oxidation at high potential. This issue can be overcome by using graphitic carbon to encapsulate Ti_4O_7 from other carbon sources, for example sucrose.

4. CONCLUSION

A method to synthesize single phase, nano-sized Ti_4O_7 with carbon layer as electrically conductive anti-sintering agent has been demonstrated in this study. 3-aminophenol-derived carbon encapsulated the surface of TiO_2 prior to the reduction, through a microwave-assisted hydrothermal method and followed with carbonization. The resulting particles after reduction, TiO_x@C core-shell, were dense and chain-structured. Ti_4O_7 phase was formed using a reduction temperature of 1000 °C. Pt-deposited Ti_4O_7@C electrocatalyst exhibited an ECSA of 46 m^2 mg_{Pt}^{-1}. This value was slightly higher than that reported for TKK commercial electrocatalyst (44.13 m^2 mg_{Pt}^{-1}) and was attained using lower Pt loading (15% versus 20%). The high performance was speculatively attributed to the highly crystalline Ti_4O_7 core which promoted good electron transfer. A room for improvement in the future is available, especially in the catalyst durability, which can be attained by using graphitic carbon for the encapsulation using the same method demonstrated in this study.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

7. REFERENCES

Arif, A. F., Balgis, R., Ogi, T., Iskandar, F., Kinoshita, A., Nakamura, K., and Okuyama, K. (2017). Highly conductive nano-Sized magnéli phases titanium oxide (TiO_x). *Scientific Reports*, *7*(1), 1-9.

Arif, A. F., Kobayashi, Y., Balgis, R., Ogi, T., Iwasaki, H., and Okuyama, K. (2016). Rapid microwave-assisted synthesis of nitrogen-functionalized hollow carbon spheres with high monodispersity. *Carbon*, *107*(2016), 11-19.

Balgis, R., Arif, A. F., Mori, T., Ogi, T., Okuyama, K., and Anilkumar, G. M. (2016). Morphology-dependent electrocatalytic activity of nanostructured Pt/C particles from hybrid aerosol–colloid process. *AIChE Journal*, *62*(2), 440-450.

Esfahani, R. A. M., Videla, A. H. M., Vankova, S., and Specchia, S. (2015). Stable and methanol tolerant Pt/TiO_x-C electrocatalysts for the oxygen reduction reaction. *International Journal of Hydrogen Energy*, *40*(42), 14529-14539.

Ioroi, T., Siroma, Z., Fujiwara, N., Yamazaki, S. I., and Yasuda, K. (2005). Sub-stoichiometric titanium oxide-supported platinum electrocatalyst for polymer electrolyte fuel cells. *Electrochemistry Communications*, *7*(2), 183-188.

Ioroi, T., Senoh, H., Yamazaki, S. I., Siroma, Z., Fujiwara, N., and Yasuda, K. (2008). Stability of corrosion-resistant magnéli-phase Ti_4O_7-Supported PEMFC catalysts at high potentials. *Journal of The Electrochemical Society*, *155*(4), B321-B326.

Kitada, A., Hasegawa, G., Kobayashi, Y., Kanamori, K., Nakanishi, K., and Kageyama, H. (2012). Selective preparation of macroporous monoliths of conductive titanium oxides Ti_nO_{2n-1} (N= 2, 3, 4, 6). *Journal of The American Chemical Society*, *134*(26), 10894-10898.

Li, X., Zhu, A. L., Qu, W., Wang, H., Hui, R., Zhang, L., and Zhang, J. (2010). Magneli phase Ti4O7 electrode for oxygen reduction reaction and its implication for zinc-air rechargeable batteries. *Electrochimica Acta*, *55*(20), 5891-5898.

Nörenberg, H. and Briggs, G. A. D. (1998). Surface structure of the most oxygen deficient magnéli phase–an STM study of Ti_4O_7. *Surface Science*, *402*(15), 738-741.

Phillips, R., Hansen, P., and Eisenbraun, E. (2012). Atomic layer deposition fabricated substoichiometric TiO_x nanorods as fuel cell catalyst supports. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, *30*(1), 01A125.

Phillips, R., O'Toole, A., He, X., Hansen, R., Geer, R., and Eisenbraun, E. (2013). Processing and functionalization of conductive substoichiometric TiO_2 catalyst supports for PEM fuel cell applications. *Journal of Materials Research*, *28*(3), 461-467.

Zhang, L., Kim, J., Zhang, J., Nan, F., Gauquelin, N., Botton, G. A., He, P., Bashyam, R., and Knights, S. (2013). Ti_4O_7 supported Ru@Pt core–shell catalyst for CO-tolerance in PEM fuel cell hydrogen oxidation reaction. *Applied Energy*, *103*(2013), 507-513.

Zhao, J., Niu, W., Zhang, L., Cai, H., Han, M., Yuan, Y., Majeed, S., Anjum, S., and Xu, G. (2012). A template-free and surfactant-free method for high-yield synthesis of highly monodisperse 3-aminophenol–formaldehyde resin and carbon nano/microspheres. *Macromolecules*, *46*(1), 140-145.