学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Fabrication and Characterization of Pt and CeOx Nanowire Interface for
Improvement of Methanol Electro-oxidation Activity and Oxygen Reduction Reaction Activity on Pt
（白金のメタノール酸化活性及び酸素還元反応活性の改善に資する白金–セリアナノワイヤ界面の作製と評価）

Energy shortage and environmental pollution are crucial challenges in the world. To solve these problems, the development of high performance fuel cells is required. Especially, the design of interface on electrodes in fuel cell is key in this challenge. Recently, the promotion effect of oxide on Pt electrode was reported in previously reported papers. Ceria (CeO_x) has been used as promoter of methanol electro-oxidation reaction and oxygen reduction reaction on Pt. However, its promotion effect for enhancement of aforementioned activities on Pt is not sufficient. The design concept of functional interface on Pt has to be developed.

In **chapter 1**, first we described types of fuel cell, kinetics and thermodynamics of fuel cell. Effect of synthesis methods on the features of CeO_x nanomaterials was introduced in this chapter 1. Also, the limitation of previously reported nanomaterial catalysts including Pt-CeO_x nanoparticle/C was mentioned. In **chapter 2**, the experimental techniques were explained in detail with brief introduction of principle of experimental methods. Finally, outline of simulation technique which was helpful for conclusion of novelty and uniqueness of Pt-CeO_x nanowire interface which was fabricated in the present thesis work was described.

Synthesis route of CeO_x nanowire by using simple alcohothermal process was examined in **chapter 3**. The effect of experimental factors on the synthesis of CeO_x nanowire was discussed. Also, the interface of Pt and CeO_x nanowire was fabricated and characterized for fabrication of unique Pt loaded CeO_x nanowire/C electro-catalysts. After the growth process of CeO_x nanowire was examined by using XRD, SEM and so on, the influence of electro-chemical pre–treatment process on enhancement of electrochemical active surface area (EASA) was summarized. Then, the uniqueness in the measurement of EASA observed for Pt-CeO_x nanowire/C was discussed. EASA observed for Pt-CeO_x nanowire/C was approximately 4 times higher than the Pt-CeO_x nanoparticle/C, even though average particle sizes of Pt in both electro-catalysts were almost same each other. Based on all experimental results in this chapter 3, I made conclusion that large amount of Pt-CeO_x nanowire interface was formed around Pt on CeO_x nanowire as compared with the case of previously reported Pt-CeO_x nanoparticle/C electro-catalysts. Also, this suggests that the fabricated Pt-CeO_x nanowire interface with high EASA contributes to the improvement of the representative electrocatalytic activities for fuel cell reactions such as electro-oxidation of methanol and oxygen reduction reaction (ORR) on Pt. To develop my idea for fabrication of high quality Pt with Pt-CeO_x nanowire interface, the methanol electro-oxidation properties

and ORR activities on Pt in Pt-CeO_x nanowire/C were examined **in chapter 4 and in chapter 5**, respectively. In the chapter 4, the influence of Pt-CeO_x nanowire interface formation on improvement of activity in methanol electro-oxidation reaction on Pt surface was examined by using analyses of onset potential of methanol electro-oxidation reaction and I_f/I_b peak intensity ratio. In-situ FT-IR analysis which is direct observation of desorption process of adsorbed CO on Pt surface agreed with the measurement results of onset potential of electro-oxidation of methanol in chapter 4. Those results suggest that activity in methanol electro-oxidation reaction on Pt in Pt-CeO_x nanowire/C is higher than the conventional Pt/C. The onset potential observed for Pt-CeO_x nanowire/C became close to PtRu/C, even though aforementioned onset potential observed for Pt-CeO_x nanoparticle/C is higher than PtRu/C. Based on the results in chapter 4, it is concluded that activity of methanol electro-oxidation on Pt can be effectively improved by formation of two Pt-CeO_x interfaces (i.e. One is previously reported Pt-CeO_x nanoparticle interface and another one is Pt-CeO_x nanowire interface). In the chapter 5, to develop this idea in chapter 4, ORR activities on Pt-CeO_x nanowire/C were compared with Pt-CeO_x nanoparticles/C and conventional Pt/C. Tafel plot and Kotecky-Levich plot analyses also suggest that ORR activity was enhanced by formation of large amount of Pt-CeO_x nanowire interface. To characterize aforementioned conclusion, the kinetic current density which was estimated from Kotecky-Levich plot dependence of potential was examined by using Pt-CeO_x nanowire/C, Pt-CeO_x nanoparticle/C and previously reported Pt/C electro-catalysts. Based on all experimental results, I made conclusion that the formation of large amount of Pt-CeO_x nanowire interface around Pt in Pt-CeO_x nanowire/C promoted the surface activity on Pt cathode and contributed to the improvement of the ORR activity on Pt at lower potential region such as less than 0.87 V (vs. RHE). To develop the conclusion in the present thesis work, the defect simulation for characterization of uniqueness of Pt-CeO_x nanowire interface between Pt and CeO_x nanowire was performed in **chapter 6**. Also, the defect structural feature of Pt-CeO_x nanowire interface was compared with the simulation results of previously reported Pt-CeO_x nanoparticle/C. The defect simulation clearly indicated that the Frenkel type defect plays key role for formation of unique Pt-CeO_x nanowire interface, although Pt-CeO_x nanoparticle interface mainly consists of Schotkky type defect. Also, this result would suggest that the charge transfer between Pt and Pt-CeO_x nanowire interface around Pt is easier than that in Pt-CeO_x nanoparticle/C case. Then, high promotion effect for enhacemrent of activities on Pt was observed in the present work.

In **chapter 7,** I summarized highlited points of experimental results in each chapter, and concluded that the formation of Pt-CeO_x nanowire interface around Pt on CeO_x naowire is key for improvement of activities of metahnol electro-oxidation reaction and ORR on Pt in the Pt-CeO_x nanowire/C. Also, I made conclusion that less Pt amount electrocatalysts can be developed by using the design paradigm for fabrication of functional interface around Pt based electrocatalyts shown in the present thesis.