<h1 align="center">論 文 内 容 の 要 旨</h1>

In this thesis, model electrode studies were performed to explore the mechanism of enhanced durability of Pt/C modified by RuO$_2$ nanosheet (RuO$_2$ns). The electrostatic interaction between RuO$_2$ nanosheet and dissolved Pt ions and the strong metal-support interaction (SMSI) between RuO$_2$ nanosheet and metallic Pt are identified via model electrode studies. The main contents in each chapter are summarized below.

In Chapter 1, the background and significance of developing polymer electrolyte fuel cell (PEFC) and cathode catalyst are introduced. The existing problems such as high cost, durability of the cathode catalyst are also described. As an effective additive to enhance the durability of Pt/C, oxide nanosheet, especially RuO$_2$ nanosheet and its possible substitute TiO$_2$ nanosheet are introduced. Model electrode and its magnitude to the study of Pt/C catalyst are enlightened. The model electrode studies are expected to increase the understanding on the fundamental catalytic and lead to more efficient catalysts. It is therefore the purpose of this study, the clarification for enhanced durability of RuO$_2$ nanosheet modified Pt/C cathode catalyst using model electrode is performed.

In Chapter 2, the main experimental methods used in this study are introduced. The contents include the synthesis of RuO$_2$ nanosheet and TiO$_2$ nanosheet, fabrication and characterization of model electrode and the purpose of this study. As the important experimental methods in this study, vacuum evaporation, scanning tunneling microscopy and electrochemical atomic force microscopy are described in detail.

In Chapter 3, the electrostatic interaction between RuO$_2$ nanosheet and electrochemically dissolved Pt ions in sulfuric acid was investigated via model electrode studies. STM images showed that RuO$_2$ nanosheet had the same thickness either in air or in sulfuric acid solution. This indicated that the RuO$_2$ nanosheets did not drift away from the substrate in aqueous solution. Hence, it was possible to investigate the adsorption of dissolved Pt ions on the surface of RuO$_2$ nanosheets using surface analysis methods such as STM or AFM. The adsorbed hydrated Pt ions on RuO$_2$ nanosheet were detected by STM. Based on the geometries of the deposits, the amount of hydrated Pt ions adsorbed on RuO$_2$ nanosheet estimated from the STM images showed a close match to the estimated saturated adsorption amount of cationic Pt ions on RuO$_2$ nanosheet surface. After electrochemical reduction, AFM image showed numerous Pt nanoparticles appeared on the RuO$_2$ns surface. In addition, the reduced Pt nanoparticles showed activity towards oxygen reduction reaction. The electrostatic interaction between Pt ions and RuO$_2$ nanosheet should facilitate trapping and

re-deposition of the Pt ions on RuO_2 nanosheet, thereby impede loss of Pt during potential cycling in practical supported catalysts. The interaction behavior between TiO_2 nanosheet and dissolved Pt ions was investigated to evaluate TiO_2 nanosheet as a possible inexpensive substitute for RuO_2 nanosheet. AFM images showed that Pt ions were adsorbed on TiO_2 nanosheet surface and the adsorbed Pt ions could be reduced Pt nanoparticles easily. The results indicated that TiO_2 nanosheet showed electrostatic interaction for Pt ions like RuO_2 nanosheet.

In Chapter 4, the interaction behavior between RuO_2 nanosheet and metallic Pt, namely strong metal-support interaction (SMSI) was investigated by AFM. AFM images showed that the deposited Pt on HOPG aggregated obviously and tended to form 3-dimensional island deposits. While on the RuO_2 nanosheet surface Pt was likely to tend toward a 2-dimensional growth mode and form well-defined ultra-thin film. The two different growth modes revealed that RuO_2 nanosheet had a stronger adsorption or affinity for Pt compared to HOPG. A sequence of *in-situ* EC-AFM images showed that Pt supported on HOPG decreases while Pt on RuO_2 nanosheet increases with potential cycling. The driving force for this process was considered to be related to the stronger adsorption deriving from RuO_2 nanosheet compared to carbon material, which led to the re-deposited Pt was more than the dissolved Pt on RuO_2 nanosheet. This strong adsorption of Pt on RuO_2 nanosheet is considered as another significant factor for the enhanced durability of Pt/C modified with RuO_2 nanosheet. The results indicate that RuO_2 nanosheet supported Pt is likely more stable than HOPG supported Pt, which can yield a more stable catalyst by importing RuO_2 nanosheet compared to pure carbon supported Pt. Similar with the case of RuO_2 nanosheet, the deposited Pt on TiO_2 nanosheet also tended to form uniform over-layer. However, when immersed into sulfuric solution, the Pt over-layer on TiO_2 nanosheet changed to Pt nanoparticles. This revealed that TiO_2 nanosheet had a weaker interaction for Pt compared to RuO_2 nanosheet. *In-situ* EC-AFM images clearly showed that Pt nanoparticles on TiO_2 nanosheet surface increased with potential cycling. According this strong interaction behavior between TiO_2 nanosheet and Pt, it is believed that TiO_2 nanosheet can act as an anchor to stabilize Pt in practical catalyst.

Chapter 5 concludes this thesis by summarizing the main knowledge obtained from each chapter and the prospect about this study is discussed. The enhanced durability of RuO_2 nanosheet modified Pt/C is attributed to the strong electrostatic interaction between dissolved Pt ions and RuO_2 nanosheet, as well as the strong metal-support interaction (SMSI) of RuO_2 nanosheet for metallic Pt. As an important electrode material, RuO_2 nanosheet will be attracted more and more attention and much unknown knowledge about nanosheet will be explored in future. TiO_2 nanosheet may be an inexpensive substitute for RuO_2 nanosheet to enhance the durability of Pt/C. However, due to the poor conductivity of TiO_2 and the encapsulation of TiO_2 for Pt, excessive TiO_2 nanosheet added in Pt/C catalyst may yield an inverse effect such as the loss of electrochemically active surface area. In summary, TiO_2 nanosheet is a potential substitute for RuO_2 nanosheet to design new catalyst with high properties.