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High Performance Catalysts and Catalyts Layers for Polymer Electrolyte Fuel Cells

Polymer electrolyte fuel cells (PEFCs) including proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are highly expected to be used as power sources for the transportations, stationary applications as well as portable devices due to their high energy efficiency, low emission of poison gases and good portability. Until now, the most commonly used materials in catalyst layers are carbon supported catalysts prepared by distributing Pt nanoparticles onto carbon blacks, and organic proton conductive ionomers like perfluorosulfonic acids such as nafion. A catalyst layer structure with homogenous formation of three phase boundary between protons, electrons and reactant gases is always critically considered to maximize the utilization of precious metal catalyst and minimize the transportant resistances among three phases. However, the traditional catalyst materials and design of catalyst layer structure are always suffering from slow kinetics for electrode reactions, high amount but low utilization of precious metals as well as poor durability. Although continous efforts have been done in decades to improve cell perforamce from various approaches, there is still no reports of electrodes which could satisfy all the requirements for PEFCs. Consquently, to achieve the large-scale commercialization of PEFCs, the development of active, durable and low cost fuel cell electrode is aimed in this dissertation. The design of high performance catalyst materials and catalyst layer structures have been systematically focused aiming to prepare an “ideal” electrode to satisfy most of the requirements for PEFCs. The contents of this dissertation are shown as follows:

In chapter 1, the background of fuel cell technology, the components as well as the structure of fuel cell electrode followed by the determining factors for fuel cell performance are primarily introduced. In addition, a massive literature review on novel carbon supported catalysts in aspect of metal nanoparticles and carbon supports as well as the previous reports on catalyst layers regarding to proton conductors and fabrication methods will be also reviewed to address the importance of systematical consideration of both catalyst materials and catalyst layer structure.

In chapter 2, to achieve high temperature operation of PEFCs and maximize the utilization of noble metal catalysts, inorganic proton conductors are applied instead of traditional organic ionomers due to nano-sized structure for fabricating uniform nano-composite and good stability at high temperature. In this study, a novel catalyst layer structure consisted of carbon nanotube (CNT) supported Pt coated with zirconium sulfophenylphosphonate (ZrSPP), named ZrSPP-Pt-CNT is prepared via a two-step method. A novel catalyst layer structure consisted of a homogenous formation of three phase boundary and good thermal stability up to 200℃ are observed in the present material. In addition, membrane electrode assembly (MEA) consisted of ZrSPP-Pt-CNT is fabricated and its fuel cell performance is

investigated and compared with traditional design. According to electrochemical analysis, inorganic proton conductive layer must be carefully designed to avoid the large mass transport resistance.

In chapter 3, to establish a principle for preparing durable carbon supported catalysts, the correlation of various carbon supports (platelet carbon nanofiber, tubular carbon nanofiber and carbon black for commercial catalyst) with different structures to start-stop durability of carbon supported catalysts in fuel cell operation condition is investigated by examining Raman spectrum and changes of electrochemical active surface area (ECSA) values as well as I-V polarization curves before and after durability test. Carbon supports with higher degree of graphitization show significant enhancement in the better retention of ECSA value and cell performance due to the less amount of amorphous carbon or defects for carbon corrosion. Consequently, graphitization degree is proved to be effective index to evaluate durability of carbon supported catalysts.

In chapter 4, to prepare high performance carbon supported catalysts, a novel carbon support with three dimensional (3D) sandwich-like structure is synthesized and characterized to prevent graphene layers from restacking by intercalating graphene layers with effective carbon spacer of exfoliated carbon nanotubes (e-CNTs). The 3D carbon composite with enlarged surface area and expanded interlayer distance showed potential as a promising material for energy storage or catalyst support. In addition, 3D carbon is also applied as supporting materials for distributing active PtPd nanoparticles toward methanol oxidation reaction, a typical anode reaction for DMFCs. PtPd nanoparticles decorated on 3D carbon composite show homogenously distributed Pt-rich PtPd alloy nanoparticles with an enlarged ECSA value and mass activity toward methanol oxidation, which is superior to GO- or e-CNT- supported PtPd and state-of-the-art commercial catalysts.

In chapter 5, highly active carbon supported catalysts for oxygen reduction reaction (ORR) is prepared using 3D carbon supports developed in chapter 4. PtCo nanocrystals supported on 3D carbon with optimized carbon spacer ratio show enhanced ORR activity toward commercial catalyst as result of homogenous distribution of nanoparticles and synergic effects of secondary metal. In addition, 3D carbon supported PtCo also show high graphitization degree of carbon support with potential of high start-stop durability. Hence PtCo-GO+e-CNT is a promising catalyst with high activity and durability for PEFCs.

Finally, a summary of key findings in this study and prospective guidelines for future development of PEFCs are presented in chapter 6.