

Title	TiO <sub>2</sub> 系支持材料上への金属ナノ粒子の合成と酸素還元 反応用電気化学触媒としての応用
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## Abstract

Fuel cells and Li air batteries are foreseen to be the future sustainable energy sources to mitigate the problem of global warming. Since the byproducts of these two sources are not harmful, research community is focussing to undertake a paradigm shift from petroleum based energy sources to fuel based systems. But to come into market there are many issues that need to be solved. Generally an electrocatalyst will be employed to catalyze the two main reactions that occur towards the anode side and cathode side. Pt based metal catalyst supported on carbon will be employed as electrocatalyst for enhancing the reactions. But the major problem lies towards the cathode side where oxygen reduction reaction occurs (ORR). This reaction is highly sluggish with slow kinetics. So in order to improve this reaction, catalyst loading will be increased because of which the cost is booming and almost 50% of fuel cell cost is from Pt based catalyst. Apart from this problem of high cost, another major problem is the stability of the catalyst. During the continuous cycling of fuel cells, carbon on which Pt nanoparticles were supported gets corroded as a result Pt nanoparticles will aggregate and efficiency of the catalyst comes down. So chapter 1 focusses on the current scenerio of research is focussing on two main important problems of research i.e, to design electrocatalyst in such a manner that the amount of Pt utilization is minimized and to replace the carbon as support material either as partially or completely.

So far many Pt free metal based electrocatalysts and metal free electrocatalysts were designed and used. But none of them could replace Pt based electrocatalysts. So the focus is specifically oriented towards the minimization of Pt content. This can be achieved by designing core shell nanoparticles. In this core shell nanoparticles, inner material, acting as core, is made of any other metal other than Pt and outer material acting as shell, is made of Pt. There are wide variety of metals that can be utilized as core materials such as Ni, Co, Fe, Pd and Au. But of all the metals Au is most preferred as it has an extra advantages when compare to other metals such as high resistance to corrosion. Hence Au is most preferred core material. In order to synthesize core shell nanoparticles, wide variety of methods were designed. These include physical methods, wet chemical methods and electrodeposition techniques. Literature provides volumes and volumes of different core shell nanoparticles that were synthesized by using any of the forementioned methods. But all those methods involves huge experimental setup, tedious process, expensive chemicals, high temperature and above all, time and energy consuming aspects are making the process cumbersome. Hence there is a need to shift the focus in designing core shell nanoparticles

in the easiest method. Since the carbon undergoes corrosion during long term cycling of fuel cell, it is even more desirable to replace this carbon as support materials. Many semiconducting materials can act as support in place of carbon for holding the nanoparticles. But of all,  $\text{TiO}_2$  with tube morphology is superior because it is low cost, environmentally friendly and possessing high resistance to corrosion.

Hence keeping in view of above required demands, chapter 2 focusses on a new method of depositing the core shell nanoparticles of Pt and Au over titania nanotubes. The synthesis was achieved through electrodeposition by applying potential of -2.0 V for 60 sec. The novelty of this method lies in the fact that the synthesis was achieved without long reaction time, high temperature and without any reducing agent. The as synthesized core shell nanoparticles were tested for electrochemical activity towards ORR and were found to be active.

Chapter 3 focusses on the cost reduction and enhancing durability of the catalyst. Hence to attain this, a composite made of titania nanotubes and functionalized acetylene black was used as support material for Pt decoration. In this Pt nanoparticles were decorated over this composite through photoreduction method by utilizing the spill over of electrons from titania. The successful formation of composite and decoration of Pt nanoparticles was characterized by various morphological techniques and found that Pt content was 3.5 wt%. As prepared material showed excellent ORR activity and found to have high electrochemical active surface area (ECSA) than commercially available Pt Vulcan XC-72.

**Key words:** Oxygen Reduction Reaction, Titania Nanotubes, Metal Nanoparticles, Electrochemical Deposition, Photochemical Reduction.