氏　　名	Santhosh Bukka
学位の種類	博士(マテリアルサイエンス)
学位記番号	博材第 458 号
学位授与年月日	平成 30 年 12 月 21 日
論文題目	Metal Nanoparticles on TiO_2 Based Supports as an Electrocatalysts for Oxygen Reduction Reaction
論文審査委員	主査　松見紀佳(北陸先端科学技術大学院大学　先端科学技術研究科　教授) 山口政之（同　教授） 高村禅（同　教授） 松村和明（同　准教授） 石田玉青（首都大学東京大学院都市環境科学研究科　准教授）

論文の内容の要旨

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 harm ful, 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 scenario 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, 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 temparature 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.

論文審査の結果の要旨

本論文においては、1）炭素材料と比較して電気化学的安定性に優れた TiO_2 ナノチューブ上に電気化学的に高速に金属ナノ粒子を担持させ、また、2）剥離アセチレンブラック/TiO_2 ナノチューブマトリックスにギ酸の存在下で白金ナノ粒子を光還元法で析出させ、それぞれ酸素還元反応における電気化学触媒活性に関して検討が行われた。いずれも酸素還元反応用電気化学触媒として好ましい特性を有することが見出された。

まず、TiO_2 ナノチューブに NaCl aq.中で $AuCl_3$ または H_2PtCl_6 を前駆体として電圧印加を行うことにより、TiO_2 ナノチューブ上への金ナノ粒子、白金ナノ粒子、及びコアシェル型ナノ

粒子の高速合成に成功した。これまでに合成手法が報告されている多くの系では数百分から千分程度の時間を要することが一般的であったが、電気化学安定性に優れた TiO_2 ナノチューブを基板とすることで高速合成が可能となった。TiO_2 ナノチューブ上の各金属ナノ粒子の構造、モルフォロジーは XPS スペクトル及び EDS 元素マッピングにより確認された。得られた各材料は塩基性水溶液中において顕著な酸素還元反応触媒活性を示した。回転ディスク電極を用いた反応メカニズムの解析においては、コア―シェル型ナノ粒子の構造により酸素還元反応のメカニズムが変化していることが分かった。XPS スペクトルとの関連から見られる構造―特性相関としては、金原子の電子密度が向上している系において酸素還元反応活性が向上することが明らかとなった。

次に、剥離アセチレンブラック/TiO_2 ナノチューブにギ酸の存在下、塩化白金酸を前駆体とした光還元法により擬似太陽光照射下で白金ナノ粒子を担持させたところ、粒径が 1.6 nm 程度の白金ナノ粒子が均一にマトリックスに分散した。XPS における Pt^0 ピークのシフトにより、強い金属―基板相互作用が示唆された。市販の Pt/C 系で 20 wt%の白金含量を有する系に対して、3.5 wt%の白金含量のみを有する本系は、市販の Pt/C 系と比較して約 5 倍の ECSA 値（電気化学活性表面積）を示し、大幅に優れた電気化学触媒活性を示した。回転ディスク電極を用いた反応メカニズムの解析により、4 電子移動による酸素還元が起きていることが示された。また、酸性水溶液中においてのみならず、非水系溶媒(TEGDME)のリチウム塩溶液中においてもリチウムイオンの酸化に伴う酸素還元反応触媒活性を顕著に示し、リチウム―空気電池への適用に関しても潜在的な有用性が示唆された。

以上のように、電気化学的安定性や光触媒機能に優れた TiO_2 ナノチューブを支持材料として金属ナノ粒子を担持させることにより、エネルギーデバイスの特性向上に新たな戦略を与えることができることが見出され、学術的にも博士学位に値すると認めた。