Title	燃料電池及びリチウム一空気電池用高効率酸素還元反応触媒としての新たな炭素ナノ構造体の設計
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Abstract

The importance of Oxygen Reduction Reaction (ORR) as a principle reaction in various elelctrochemical applications have been well understood over the years. Fuel cells and Li-air battery working on the basis of ORR, which project a high energy density, prolonged durability with low emission of global warming gases have gained greater significance among plethora of electrochemical energy devices. Electrocatalyst plays an important role in realization of both these devices by enhancing the sluggish kinetics of ORR. The two interconnected materials forming the ORR catalyst are the porous & conducting carbon support and the active metal nanoparticles as ORR centres. A careful and strategic optimization in their designing of the substrate for enhanced activity, increased durability, simple preparation method for immediate commercialization and reduction of overall cost. In this view, the present work details the importance of substrate modification in enhancing above attributes of the catalytic activity of Pt/carbon based catalysts by tuning a) surface area of carbon based support b) ability to support the catalyst c) pore size d) charge transfer resistance and e) the ability to anchor Pt nanoparticles. The chapters in this thesis, include strategies to tune one, more or all of the above mentioned intrinsic properties of the catalyst with very simple, facile and in some cases green processes which can possibly see the light of commercialization.

Chapter 2 deals with a novel single-pot method to exfoliate and functionalize acetylene black. The deliberate functionalization was found to enhance the intrinsic oxygen reduction efficiency along with the nucleation and growth of platinum nano-particles on the surface. The prepared material was well characterized to understand the morphology, elemental composition and electrocatalytic behaviour. The resulting material showed enormously high oxygen reduction reactivity compared to its commercial counterparts. The mass activity evaluated from the rotating disc electrode (RDE) techniques was found to be higher than the target set by the department of energy (DOE), USA. The material also showed very encouraging results when

employed as cathode material for PEMFC and Li air batteries.

Electrocatalytic materials for oxygen reduction reaction, currently dominated by platinum/carbon catalyst is marred by drawbacks such as, use of copious amount of Pt and use of “non-green” sacrificial reducing agent (SRA) during the synthesis. A single stroke remedy for these two problems has been achieved through an *in-situ* aqueous photoreduction void of even trace amounts of SRA with an enhanced activity. Reduction of $PtCl_6^{2-}$ salt to Pt nano particles on carbon substrate was achieved solely using solar spectrum as the source of energy and TiO_2 as photocatalyst. In chapter 3, it was demonstrated that this new procedure of photoreduction, decorates Pt over different types of conducting carbon allotropes with the distribution and the particle size primarily depending on the conductivity of these allotrope. The $Pt/C/TiO_2$ composite unveiled an ORR activity on par with the most efficient Pt based electrocatalyst prepared through the conventional sacrificial reducing agent aided preparation methods.

The development of novel substrates possessing high durability, strong anchoring to catalytic metal nanoparticle and low charge transfer resistance that can replace conventional carbon is of great importance. In order to improve the durability and reduce the cost of various energy devices, new methodologies are necessary. In this regard, chapter 4 highlights the preparation of a macroporous hybrid material containing a foam like polythiophene electropolymerized on to TNT. The prepared hybrid material showed very low charge transfer resistance and was further modified with novel and green photo-generated Pt nanoparticles. The material exhibited very strong metal substrate interaction which makes it highly durable during the ORR. This chapter proposes a novel macroporous organic/inorganic hybrid material as a candidate material that has a great probability to replace the conventional carbon substrates for ORR catalysts.

Keywords: Carbon Nano-Architectures, Metal Nanoparticles, Oxygen Reduction reaction, Photo-Reduction, Fuel Cell, Li-Air Battery.