Abstract

An efficient oxygen reduction reaction (ORR) offers the potential to fulfil the energy demand of the world in Polymer Electrolyte Membrane Fuel Cells (PEMFCs). However, the cost of the PEMFC which mainly arises from the Pt based catalyst hinders its widespread applications. Efforts are underway for reducing the total cost by increasing the Pt utilization or by the use of non-noble metal catalysts. In the advent of nanomaterials, the electrocatalyst performance has been considerably benefited and satisfactory performance has been obtained so far. Some of the advances in this direction include low Pt catalysts like core-shell or alloy type materials with various binary and ternary combinations and Pt-free catalysts like nitrogen doped carbon materials, nitrogen containing macrocyclic complexes, transition metal chalcogenides etc. However, still, there are some major challenges to be addressed for their extensive applications. If we consider durability and reliability issues along with the catalyst activity, till now, the best catalyst for ORR is Pt supported on carbon materials. It is interesting to note that the performance and Pt utilization in a fuel cell catalyst is determined by many factors like active catalyst size and shape, dispersion of the catalyst on support material, surface area of support, catalyst-support interaction, proper mass transfer rate, balanced electron and proton conductivity, ionomer-catalyst-gas pore triple-phase boundary (TPB) etc. Therefore, the best way to effectively meet the requirements for an efficient ORR electrocatalyst is to design advanced electrode materials with high level of catalyst utilization by carefully considering all the above mentioned key parameters.

In view of overcoming some of the above mentioned issues, one-dimensional (1D) nanostructures of carbon such as nanotubes (CNTs) and nanofibers (CNFs) have triggered wide interest, mainly due to their exciting features such as anisotropy, unique structure, and surface properties. However, the inherently low surface area possessed by many of these materials restricts the amount of active component such as Pt that can be dispersed on these materials. A catalyst with higher carbon to catalyst ratio leads to a thick layer of catalyst with high mass transfer and electric resistances. A strategic approach to obviate these
issues is to develop Membrane Electrode Assembly (MEA) with thin electrodes by using catalysts possessing high Pt loading and dispersion. Tubular morphologies of some carbon nanomaterials with open tips are interesting in the context of developing low-carbon-loaded, metal-rich catalysts because the morphology offers the possibility to access both inner and outer surfaces of carbon support for metal dispersion.

The genesis of my work is inspired by this concept where the immense scope for the utilization of both the inner and outer walls of a 1-D carbon nanostructure with peculiar morphological characteristics will be unfolded. Since the materials confined inside are expected to show different chemical and electrochemical behaviour due to the change in the intermolecular interactions, first part of my research is focusing on the decoration of catalyst particles, both monometallic and bimetallic, along the inner and outer walls of CNF support. A suitable process is developed by carefully optimizing the surface tension, polarity and surface wettability of the solvent to achieve this goal. As the establishment of TPB around the catalyst nanoparticles with the provision for proton, electron and gaseous reactants is needed to facilitate the electrode reactions, introduction of proton conductivity along the inner cavity as well as the outer wall is also a major issue. Nafion®, which is a perfluorosulfonic acid polymer with high proton conductivity, has proved to be the best binder in forming a TPB in PEMFCs. However, due to its high molecular weight and fibrillar structure, Nafion cannot be incorporated in the inner cavity of CNFs. Therefore, the next goal of my research is to incorporate a low molecular weight proton conducting polymer in the inner cavity as well as on the outer walls of CNF to provide effective pathways for proton conduction and reactant distribution.

Recently, nitrogen doped (N-doped) carbon nanostructures have been demonstrated as low cost alternatives to Pt with their comparable electrocatalytic activity and improved durability. However, there has not been any attempt to induce N-doping along the inner cavity as well as on the outer surfaces of hollow carbon morphologies. Hence, another goal of this thesis is to develop N-doped CNFs with active sites along the inner and outer walls of CNF.
The thesis is presented in eight chapters, a brief summary of which is given here.

The first chapter is a general introduction to fuel cells, describing the history, working principle and the classification. A detailed review about PEMFCs is included with special emphasis on ORR mechanism, electrocatalysts and catalyst supports. General introduction to the field of nanostructured multifunctional materials and their scope as electrocatalysts for PEMFCs are also included. Finally, the importance of nanoconfinement in modulating the electrochemical properties of materials is also discussed.

Chapter 2 presents different methods employed for the synthesis of various electrocatalysts. The basic principle and experimental details of different characterization techniques employed in the present research are also described.

Chapter 3 describes a novel strategy for the selective decoration of Pt nanoparticles only in the inner wall or along both the walls of CNF by a modified polyol process. The pristine CNF, which possesses inherently active inner wall surface and inactive outer surface, led to selective Pt deposition along the inner wall (C-Pt), whereas activation of the outer wall with chemical functionalization resulted into excellent dispersion of Pt along both the inner and outer walls (F-Pt). Structural and morphological characterizations of these materials revealed that when Pt could be dispersed along the inner as well as the outer walls of CNF, the Pt particle size reduces to almost half as compared to the one with Pt decoration only along a single wall. Further, electrochemical studies using CV and RDE measurements revealed enhanced ORR and methanol oxidation properties of F-Pt as compared to the conventional CNT supported catalyst.

In Chapter 4, we discuss the synthesis of a Pt thin layer catalyst supported on an in-situ prepared ‘RuO$_2$-Carbon-RuO$_2$’ sandwich type hybrid support. While the selective exposure of Pt on the hybrid support surface is confirmed from the HRTEM analysis, the electronic changes effected in the CNF support are evident from the XPS and XRD analyses. Electrochemical evaluation of this catalyst revealed its exceptionally high activity for ORR with three times increase in the
electrochemically active surface area (ECSA) and four times improvement in the limiting current density coupled with 80 mV gain in onset potential. Apart from this, a drastic reduction in the CO poisoning is observed for methanol oxidation reaction.

In Chapter 5, we demonstrate the importance of surface functionalization in the design of bimetallic electrocatalysts. When pristine CNF is used to decorate Pt and RuO$_2$ nanoparticles, mainly phase-separated nanoparticles rich in RuO$_2$ characteristics is obtained (C-PtRuO$_2$). In contrast to this, when CNF activated by a simple H$_2$O$_2$ treatment to create oxygen-containing surface functional groups are used, a material rich in Pt features on the surface is obtained (F-PtRuO$_2$). This is achieved because of the preferential adsorption of RuO$_2$ by the functionalized surface of CNF. Evaluation of the electrochemical properties of these materials indicated that C-PtRuO$_2$ exhibits a charge storage property whereas F-PtRuO$_2$ shows an oxygen reduction property. Thus, the results of this study show how important it is to have a clear understanding of the nature of surface functionalities in the processes involving dispersion of more than one component on various carbon materials.

In Chapter 6, we discuss the synthesis of a novel electrocatalyst system with unique multifunctional characteristics originated by the presence of proton conducting polybenzimidazole (PBI-BuI) bound layer and electron conducting hollow CNF substrate with catalytically active Pt nanoparticles. This is achieved by decorating Pt nanoparticles along the inner cavity as well as on the outer walls of the hollow CNF support (F-Pt). In a further extension, the low molecular weight polymer, PBI-BuI is incorporated into the inner cavity and along the outer surfaces of F-Pt. Electrochemical studies using CV and RDE revealed the high activity of this hybrid material with improved ECSA, 70 mV shift in the onset potential and higher current density.

Chapter 7 describes a simple polymer mediated strategy for N-doping along the inner and outer surfaces of CNF and its electrocatalytic activity for ORR. This is achieved by the high temperature treatment (700-1000 °C) of the
PBI-BuI incorporated CNFs. The initial PBI-BuI content and the annealing temperature are also systematically varied to choose the right combination of starting precursors and heat-treatment conditions. These materials are characterized by a host of techniques and electrochemical characterizations of this material using CV, RDE studies and durability analysis demonstrated that this material can act as a metal-free ORR electrocatalyst with improved oxygen reduction kinetics and stability.

Chapter 8 presents an overall conclusion and comparison of the work reported in the earlier chapters on the synthesis and characterization of monometallic, bimetallic and even non-metal (N-doped CNF) electrocatalysts and their electrocatalytic activities for oxygen reduction reaction. The role of surface functionalization and the need for a proper process modification to access the inner cavity as well as the outer surfaces are discussed in detail. Further work required to be carried out to enhance the electrocatalytic activity of these materials, in comparison with the present work as well as the work reported in the literature are also discussed.