CHAPTER 7

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

7.1 SUMMARY

Facile syntheses of a few layered (4 to 5 layers) graphene oxide were done by chemical method. The lattice defects and functional groups including carbonyls, epoxides, hydroxyls, etc., on graphene oxides act as strong anchoring sites for Pt nanoparticles. These graphene oxide sheets showed improved electronic properties. Although the morphology and physical characteristics of these graphene materials are similar, considerable change in the electrical conductivity, graphitization and stability were observed due to the variation in the amount of oxygen functionalities.

Pt/Graphene has been prepared by polyol method using pre-functionalized graphene and Pt salt solution, hexachloroplatinic acid. Electrochemical studies of the Pt supported onto graphene showed improved performance for Hydrogen Oxidation Reaction (HOR) and Methanol Oxidation Reaction (MOR) compared to state of the art Pt/C catalyst. A thermal treatment (Ar/H₂, 100°C, 3 hours) applied to the catalysts improved the catalytic activity and stability of Pt/Graphene catalyst showing an electrochemical surface area of 58m².g⁻¹ and the stability was found 3 fold higher than the Pt/C conventional catalyst. After 4,000 cycles, the cyclic voltammetry measurements showed that the Pt/Graphene catalyst lost only 20% of the Pt initial ECSA, whereas the degradations of Pt /C catalyst was quite high showing 65% loss.
The Pt/Graphene catalyst also exhibited a higher performance in the methanol electrooxidation for the promotion of C–H breaking and CO\textsubscript{ad} tolerance and good stability as well. The electrochemical activity towards methanol oxidation of Pt/Graphene was found 2 fold higher than Pt/C and can be attributed to the uniform dispersion of Pt particles on the graphene and the accessibility of these sites for hydrogen adsorption and desorption reactions. The results also indicate better mass transport in the catalyst layer. This study suggested a bi-functional effect of both graphitization and the oxygenated groups on the catalytic activity.

The use of unsupported catalysts also provided improved stability during electrochemical reactions and high durability due to their non-corrosive component Carbon. Advanced mesoporous architectures were created in which the pore and metal composition are controlled at the nanoscale level. Hard template assisted synthesis, which create periodic porosity in the solid, are used to create mesoporous platinum and platinum bimetallic catalyst. The ability to control the composition, shape and porous architecture of Pt and Pt bimetallic combinations, eliminating the carbon corrosion problem improved the activity of catalyst. Hence, synthesis of 3D bicontinuous mesoporous silica KIT-6 and 2D mesoporous silica SBA-15 were done. Ordered mesoporous silica prepared has uniform mesopores (7.9 and 7.3nm for KIT-6 and SBA-15 respectively) and high specific surface areas 772 m\textsuperscript{2}.g\textsuperscript{-1} (for KIT-6) and 943 m\textsuperscript{2}.g\textsuperscript{-1} (for SBA-15). These hard silica templates were used for the synthesis of mesoporous metal particles for fuel cell electrocatalyst.

Well-ordered mesoporous Pt particles and several Pt bimetallic (Pt-Ru, Pt-Co, Pt-Ni) self-supporting catalysts with uniform shapes are synthesized using SBA-15 and KIT-6 as a hard template through controlled chemical reduction using Pt salt and ascorbic acid. The Pt replicas from
KIT-6 showed polyhedral morphology and periodically arranged Pt nanowires were observed for 2D hexagonally ordered mesoporous silica (SBA-15). The BET surface areas were found to be 39 and 37 m$^2$.g$^{-1}$ for mesoporous Pt prepared from KIT-6, and SBA-15, respectively. The single crystallinity of the Pt fcc structure coherently extended over the whole particle. The present facile synthesis showed high controllability in the particle size without breakdown of well-ordered mesostructure.

Synthesis and characteristics of mesoporous Pt-Ru, Pt-Co and Pt-Ni bimetallic catalyst with low contents of the secondary metals (Ru or Co or Ni) by using SBA-15 and KIT-6 as hard templates were studied. The ratio of the primary metal (Pt) and the secondary metal were changed and evaluated for their electro-catalytic activity. The size and shape of the mesoporous Pt-Co and Pt-Ni materials were found to be uniform with particle size. Inside the particles of mesoporous Pt-Ru, Pt-Co and Pt-Ni, periodically arranged nanowires replicated from SBA-15 were observed clearly. In the case of the KIT-6 system, sponge-like Pt nanostructures were observed. The replication of mesoporous bimetallic from KIT-6 and SBA-15 retaining the original symmetry were confirmed by small angle X-ray scattering measurements. The porous Pt bimetallic catalyst exhibited well defined structure of pore size ranging between 2.1 and 3.2nm, uniform shape and well developed crystallinity. The surface area of all the mesoporous Pt bimetallic catalyst falls in the range of 34 to 42m$^2$.g$^{-1}$. Wide-angle X-ray diffraction (WAXRD), HRTEM and elemental mapping clearly proved that both primary metal (Pt) and secondary metal (Ru or Co or Ni) were atomically distributed in the frameworks without any phase segregation.

The electrochemical activity and stability of mesoporous Pt-Ru, Pt-Co and Pt-Ni bimetallic catalyst towards hydrogen oxidation (PEMFC) and methanol oxidation (DMFC) was relatively higher than that of mesoporous Pt
and Pt black catalyst. The ECSA of mesoporous bimetallic catalyst (87 m².g⁻¹ for Pt-Ru), (74 m².g⁻¹ for Pt-Co), (81 m².g⁻¹ for Pt-Ni) while Pt black showed 38 m².g⁻¹ and mesoporous Pt showed ECSA of 61 m².g⁻¹. Porous Pt-Ru showed ECSA loss of 10% and about 5% ECSA loss was observed for porous Pt-Co, Pt-Ni. They were found to be more durable than mesoporous Pt (15% loss) and Pt black (45% loss), suggesting that the unique geometry of these pores effectively improves catalytic activity, easing the loss of ECSA.

Alloying Pt with Ru or Co or Ni substantially improves its catalytic performance by reducing the CO poisoning and required noble metal. The mass-normalized current density of mesoporous Pt-Ru (598 mA.mg⁻¹) was approximately 2 times higher than that of mesoporous Pt (298 mA.mg⁻¹) and around 8 times higher than Pt black (72 mA.mg⁻¹). The electrochemical activity towards methanol oxidation of Pt-Co was found to be 7 times higher than Pt black. The mass normalized current density of Pt-Ni was found to be 5 times higher than Pt black. The results revealed that mesoporous Pt bimetallics serve the purpose of effective electrocatalyst in fuel cell applications together with the superiority of mesoporous structure.

The alloying element modifies the electronic properties of the Pt and helps enhancing the electrocatalytic activity of the bimetallic catalyst. The highly enhanced activity of the mesoporous Pt and Pt bimetallic catalyst, compared with Pt black, can be attributed to the porous structure that eases the reaction kinetics and electron transport and also improves the diffusion of reactants to Pt surface. In addition less surface defects on the particles, have a closer resemblance to the bulk catalyst surface that have been proved to exhibit much higher specific activities, than the Pt/C catalysts in PEMFCs.
7.2  SUGGESTIONS FOR FUTURE WORK

Based on the present results, the future perspectives for PEM fuel cell electrocatalysts are:

i. The design of corrosion resistant support materials which enable a well dispersion of nanoparticles with high conductivity and graphitization.

ii. The design of Pt based catalyst with different morphology using different silica templates which increases the electrochemical activity.

iii. The particle size of the metal clusters can be varied by changing the deposition time for improvement in the activity.

iv. The transfer/scale-up of the present results established by electrochemical measurements to single MEA and stack experiments under typical PEM fuel cell conditions.

v. The investigation of the present catalyst concepts and/or components for other chemical reactions and application to other fuel cells.