CHAPTER 8

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

8.1 SUMMARY

The research work done in this thesis is aimed to develop different structure tailored metal oxides for low temperature fuel cell applications. Some metal oxides such as Titanium dioxide nanotubes (TiO$_2$-NTs) and Tin dioxide nano facets (SnO$_2$ NFs) were used as non-carbon catalyst support materials in PEMFCs. Part of the thesis is dedicated to the evaluation of electrocatalytic performance of both commercial Pt/C and synthesized materials such as TiO$_2$-NTs and SnO$_2$-NFs before and after ADT. The other part of this thesis is dealt with the development of mixed transition spinel metal oxides as alternative non-noble metal electrocatalysts in alkaline fuel cells (AFCs). Two spinel mixed metal oxides such as CoMn$_2$O$_4$ and FeMn$_2$O$_4$ were analyzed for their activity and stability towards ORR. Conclusions related to each chapter are discussed below.

Morphological effect of two electrocatalyst supports such as TiO$_2$-NTs and SnO$_2$NFs on the electrocatalytic activity of Pt nanoparticles towards fuel cell reactions have been carried out. TiO$_2$-NTs were synthesized via anodization method and Pt deposition was carried out by impregnation reduction method. Pt deposited commercial TiO$_2$ NPs (Pt/TiO$_2$ NPs) and state of the art Pt/C catalyst was also used to compare the electrocatalytic activity. Hard X-ray photo emission spectroscopy (HAXPES) studies revealed the presence of intrinsic oxygen defects on the surface of TiO$_2$-NTs that could
improve the charge transfer between Pt nanoparticles and support. The ORR and MOR activity as well as stability studies were conducted on all the three catalysts such as Pt/TiO$_2$-NTs, Pt/TiO$_2$-NPs and Pt/C. The onset potential of ORR was better for Pt/TiO$_2$-NTs, where it showed positive onset potential of 0.69V vs Ag/AgCl compared to both Pt/TiO$_2$NPs (0.65V) and Pt/C (0.65V). The number of electrons transferred obtained from the slope of K-L plot was 3.8 for Pt/TiO$_2$-NT, indicate that it follows four-electron pathway by reducing O$_2$ directly to water without any intermediate H$_2$O$_2$ formation. The mass and specific activities of Pt/TiO$_2$-NTs are 17 times and 11 times higher than that of Pt/C and 3 times and 2 times higher than that of Pt/TiO$_2$-NPs respectively. The MOR activity was estimated to be 3 times higher than Pt/C and 2.4 times higher than that of Pt/TiO$_2$-NP. The current-voltage (I-V) profiles confirmed higher stability for Pt/TiO$_2$-NTs in terms of a stable current density compared to both Pt/TiO$_2$-NPs and Pt/C. Stability towards both ORR and MOR was better for Pt/TiO$_2$-NTs compared to both Pt/TiO$_2$-NPs and Pt/C.

A wide-gap semiconductor, SnO$_2$; band gap of 3.6 eV, was used as a model support for Pt NPs to demonstrate the role of surface defects on the electronic structure and electrocatalytic performance of supported catalysts. We have crystal-engineered SnO$_2$ via a hydrothermal route into single-crystalline nanoplates, which are surrounded by {113} facets containing surface-oxygen defects (SnO$_2$ nanofacets (NFS)), confirmed from transmission electron microscopy (TEM), HAXPES, low temperature photoluminescence (PL) and scanning probe microscopy (SPM) analysis. Pt nanoparticles were deposited onto the SnO$_2$ NFs via impregnation reduction method (Pt/SnO$_2$ NFs). SnO$_2$ nanoparticles were also synthesized by hydrothermal method and deposited Pt nanoparticles via impregnation reduction method to use as a control sample. EOR activity and stability of the catalysts have been evaluated for Pt/SnO$_2$ NFs, Pt/SnO$_2$ NPs and Pt/C. The Pt/SnO$_2$ NFs exhibited two-fold higher catalytic activity than Pt/C and
Pt/SnO$_2$ NPs towards EOR. The EOR current densities for the Pt/C and Pt/SnO$_2$ NPs decreased down to 54 and 48\% of the initial values, respectively, whereas the EOR current density for the Pt/SnO$_2$ NFs was retained more than 75\%. The Pt/SnO$_2$ NFs are superior to either the Pt/C or Pt/SnO$_2$ NPs in EOR activity over repeated electrochemical cycles. The surface-oxygen defects of the SnO$_2$ NFs are long-range ordered and give rise to a defect band (DB) in the band gap. This in-gap DB efficiently intermediates charge transport between the Pt NPs and the SnO$_2$ support, leading to an improved EOR performance of the Pt/SnO$_2$ NFs.

Pt/SnO$_2$ NFs were also analyzed towards ORR activity as well as stability. The onset potential for the ORR is 0.720 V for both Pt/SnO$_2$ NFs as well as Pt/SnO$_2$ NPs, whereas for Pt/C it is 0.650 V. There is a considerable positive shift of 0.030 V in the half-wave potential of Pt/SnO$_2$ NFs compared to Pt/SnO$_2$ NPs and 0.057 V compared to Pt/C which suggest that Pt/SnO$_2$ NFs are more active than the other two catalysts for ORR. The number of electrons transferred for ORR is 3.92 for Pt/SnO$_2$ NFs which suggest that the reduction occurred via four-electron pathway. The stability test in O$_2$ saturated 0.5 M H$_2$SO$_4$ has also been carried out and found that Pt/SnO$_2$ NFs showed an insignificant reduction (0.009V) in half wave potential compared to both Pt/SnO$_2$ NPs and Pt/C-which showed 0.018V and 0.087 V reduction in half wave potential after 10000 cycles of operation.

Summarizing the results obtained from ORR, MOR and EOR, Pt/TiO$_2$-NTs and Pt/SnO$_2$ NFs can be considered as active and stable electrocatalysts for both electro oxidation and ORR in PEMFCs.

In the next section of the thesis, two mixed metal spinel oxides such as Co substituted manganese oxide (CoMn$_2$O$_4$) and Fe substituted manganese oxide (FeMn$_2$O$_4$) have been evaluated for the oxygen reduction activity, methanol tolerance and stability in AFCs. A hybrid of CoMn$_2$O$_4$ and
graphene (CoMn\(_2\)O\(_4\)/G) and FeMn\(_2\)O\(_4\) and graphene (FeMn\(_2\)O\(_4\)/G) nanostructures were synthesized by a facile hydrothermal method. Both CoMn\(_2\)O\(_4\) and FeMn\(_2\)O\(_4\) nanoparticles had a close coupling with the graphene nanoflakes, which in turn reduced the charge transfer resistance in the interface between spinel metal oxide nanostructures and graphene. The improved interface charge transfer could help the betterment in the electrocatalytic activity of these two hybrid nanostructures towards ORR. The mesoporous nature of the nanomaterials leads to a higher specific surface area of 375 m\(^2\)g\(^{-1}\) and 393 m\(^2\)g\(^{-1}\) for CoMn\(_2\)O\(_4\)/G and FeMn\(_2\)O\(_4\)/G respectively. Both of these spinel compounds exhibited remarkable ORR performance and it was roughly equivalent to Pt/C. The onset potential, half wave potential and limiting current of CoMn\(_2\)O\(_4\)/G was better compared to the control samples such as CoMn\(_2\)O\(_4\)+G, CoMn\(_2\)O\(_4\), Co\(_x\)O\(_y\), Mn\(_x\)O\(_y\) and graphene. In the same way FeMn\(_2\)O\(_4\)/G also exhibited better activity compared to FeMn\(_2\)O\(_4\)+G, FeMn\(_2\)O\(_4\), Fe\(_x\)O\(_y\), Mn\(_x\)O\(_y\) and graphene. In the case of graphene, the ORR reduction was via two-electron pathway, whereas both CoMn\(_2\)O\(_4\)/G and FeMn\(_2\)O\(_4\)/G showed four-electron reduction pathway. The nanostructure morphology and strong interaction of spinel metal oxides with graphene, makes these classes of non-noble materials suitable for ORR in AFCs.

The results acquired in this thesis give insights into the effect of structure tuning of crystals for electrochemical applications. The surface structures of metal oxides play a major role in its electronic conductivity. Herewith we discussed the effect of oxygen defect on the structure tailored metal oxides as support materials for Pt nanoparticles for various fuel cell reactions such as ORR, MOR and EOR. It would be a great advantage for PEMFC’s development to replace carbon with these types of metal oxides in order to overcome the electro oxidation of carbon. We are reporting FeMn\(_2\)O\(_4\)/G for the first time as ORR catalyst in AFCs and its performance is competitive with that of Pt/C. It would encourage the researchers to replace Pt
based precious metal catalysts with these type of non-noble electrocatalysts for further development in AFC’s.

8.2 SUGGESTIONS FOR FUTURE WORK

i. Here we have addressed the support corrosion during electrocatalytic cycling by noticing the change in ECSA. Further study can be extended to the analysis of Pt agglomeration and/or dissolution from the surface of support materials as it is not addressed in the present work.

ii. We followed impregnation reduction method for Pt deposition on TiO$_2$-NTs and SnO$_2$-NFs. The effect of different methods of depositing Pt nanoparticles, which leads to controlled size and uniform dispersion on the electro catalytic activity, can be evaluated.

iii. High concentration of oxygen defects were observed on the surface of SnO$_2$ NFs. The thermal annealing could attribute to the oxygen vacancies on a metal oxide surface. A mechanistic understanding is required on the effect of annealing temperature on the formation of oxygen vacancies.

iv. From the three electrode cell experiment results, both Pt/TiO$_2$-NTs and Pt/SnO$_2$ NFs can be tested in PEM single cell under real fuel cell operation conditions.

v. The reason behind the ORR activity of mixed metal spinel oxides can be discussed more by studying the effect of crystal structure and cationic distribution of tetrahedral and octahedral sites.
vi. The strong coupling effect can be further evaluated with other carbonaceous materials which can provide better conductivity.

vii. These spinel metal oxides can be tested in single cell AFC’s under real fuel cell operation condition.

viii. Bi-functional oxygen electrode activity of these spinel metal oxides can be evaluated.

ix. The present strategy of structure tailoring can be implemented to other metal oxides and use for different electrochemical reactions.