SUMMARY/GENERAL CONCLUSIONS

1. Introduction:

(i) Manganese oxides display a remarkable diversity of atomic architectures because Mn occurs in oxides in three different oxidation states: +2, +3 and +4, giving rise to a range of multivalent phases. The basic building block for most of the manganese oxides is the [MnO₆] octahedron. These octahedra can be assembled by sharing edges and/or corners into a large variety of different structural arrangements viz. Pyrolusite, nsutite, bixbyite, Octahedral Molecular Sieves (OMS), Octahedral layers (OL), etc.

OMS-2 materials are currently considered as ‘hot materials’ and find use in various areas from catalytic materials, detergents, to battery materials and sensors as well as ion exchangers. Their pore sizes are considered to be analogous to zeolites. Their acidities can be varied by altering the method of preparation, by specific activation, and by doping with transition metal cations either before or after crystallization. By inserting divalent cations into OMS it is possible to alter electronic, catalytic and structural properties. All this results in outstanding materials for various catalytic oxidation reactions.

(ii) Recent years has seen increased interest in fuel cells for a range of applications, including transport and small-scale static power, they being a fantastic source of clean alternative energy. Hydrogen the most promising fuel has storage, handling and transportation hazards. Liquid fuels like methanol, ethanol, etc. are better alternatives. Of the very few metals that are able to adsorb methanol in acidic medium, platinum is an excellent catalyst for the oxidation of methanol. But platinum poses CO poisoning as a major problem besides being very expensive. Thus, in general, the move is
(a) to reduce catalyst cost for direct methanol fuel cells by reducing noble metal content, and

(b) to identify potential non-noble metal catalytic systems.

2. Objectives of this work:

Manganese oxides are well known to have appreciable electrochemical activity. They are used as oxidation catalysts for preparation of a wide variety of specialty chemicals. Thus, in this work it was intended to test the OMS-2 materials:

(i) to improve the oxidation ability of these catalysts by modifying with cations,

(ii) as cathode materials for use in batteries, and

(iii) as anode catalysts for oxidation of methanol.

3. Contents of the Thesis:

The present work has been described in 5 chapters.

i. Chapter 1 — Introduction, has been divided into 2 sections — one introducing Octahedral Molecular Sieve (OMS-2), its applications in various fields especially catalysis and second - the current literature status in the area of anode catalysts in direct methanol fuel cells. Thus the salient features are as follows:

(a). Octahedral molecular sieves are currently ‘hot’ materials, which can find use in various applications.

(b). The ability to adjust their pore sizes and activities make them great materials for separation and sorption applications.

(c). Fine-tuning the valence states of the active sites gives the ability to perform selective catalytic reactions and conductivity changes for sensors.

(d). Fuel cells are in high demand in the area of energy/power generation.
(e). Various catalysts have been tried out so far with platinum and its alloys being the best.

(f). Thus the search is on for new materials, which will use lesser amount of expensive noble metals, but one which will not compromise on efficiency.

(g). This calls for a study of designing electrodes with specific structures using the catalytic material if one needs to develop high performance electrodes.

(h). Electrocatalyst studies are thus directed to establishing the nature of the species formed during adsorption, understanding the mechanism of the reaction, studying surface structural effects and invariably a search for new catalysts.

ii. Chapter II – deals with the synthesis of OMS-2 materials via a simple method using KCIO\(_3\) vis-à-vis the conventionally used KMnO\(_4\). OMS-2 is known to form in the presence of specific tunnel cations like K\(^+\), Ca\(^{2+}\), Pb\(^{2+}\), etc. In this work OMS-2 has been synthesized showing the importance of SO\(_4^{2-}\) in the phase formation. Some aspects regarding this have been discussed as follows;

(a). SO\(_4^{2-}\) ion has a crucial role in OMS-2 phase formation,

(b). OMS-2 could be synthesized without the presence of K\(^+\) ion,

(c). OMS-2 could be formed in a facile manner by use of chlorate as oxidizing agent in place of permanganate and

(d). OMS-2 samples could be successfully characterized both by IR and XRD techniques.

iii. Chapter III – describes the application of synthesized catalysts for oxidation of benzyl alcohol to benzaldehyde. Also activities of OMS-2 materials
modified with some transition metal cations have been studied. A mechanism has been proposed explaining the enhanced activity of these materials.

(a). Adding transition metal cations (Fe and Ti) has resulted in improved catalytic activity thus showing increasing % conversion with increase in transition metal content in the samples. The effect with Fe$^{3+}$ was found to be more as compared to that by Ti$^{4+}$.

(b). Corresponding increase in chemical reactivity and % weight loss in the three temperature intervals, with metal content is seen.

(c). The higher activity is associated with the extent of participation of lattice oxygen of the catalyst and a mechanism is proposed.

iv. Chapter IV — Cathodic reduction studies have been carried out on the OMS-2 materials and the results discussed in relation to other forms of manganese oxides. OMS-2 showed synergistic interactions with pyrolusite resulting in improved performance. Li$^+$ insertion behaviour of OMS-2 catalysts are also studied in comparison to a synthesized nsutite material.

v. Chapter V — For the first time OMS-2 is investigated as anode material for use in fuel cells. The activity of the materials has been discussed in comparison to some manganese oxides as well as in combination with carbon supported Ruthenium. Effect of temperature and reduction of OMS-2 composites have been studied. The results are as follows;

(a). Manganese octahedral molecular sieves have been found to be active for methanol electrooxidation.

(b). Pyrolusite in combination with manganese octahedral molecular sieves gave a higher current (more than twice) than the current produced by a combination of
pyrolusite with the international sample (IC8), thus suggesting that it produced a synergistic interaction with OMS-2 thus improving its activity towards methanol oxidation.

(c). In case of OMS-2 materials in combination with 5% Ru-C (whether *in situ* generated phase on the Ru-C or 1:1 mechanical mixture), Ru enhances oxidation of CO to CO$_2$ significantly.

(d). Methanol oxidation kinetics improved with temperature.

(e). Increasing amount of OMS-2 in a mixture with 5% Ru-C showed increase in exchange current density.

(f). Reduction studies revealed that OMS-2 shows maximum activity under reducing atmosphere by hydrogen up to 120 °C and is not stable beyond 300 °C.

(g). The high activity of the manganese oxide was associated with presence of Mn$^{4+}$/Mn$^{3+}$ redox couple. The extent of participation of lattice oxygen played an important role in methanol oxidation reaction.

(h). Cyclic voltammetry studies showed that active OMS-2 composites showed oxidation of methanol at a lower positive potential.