# CHAPTER II

# LITERATURE SURVEY

In 1996, Guzman et al synthesized hydrated molybdenum trioxides $MoO_3$ $nH_2O$ via the condensation of molybdic acid in aqueous solutions. These hydrated oxides are studied by thermal analysis, X-ray diffraction and FTIR spectroscopy. The electrochemical properties, i.e. thermodynamics and kinetics, of lithium-intercalated $MoO_3 \cdot nH_2O$ cathodes were investigated in relation to their structure and morphology. These compounds show good charge-discharge cyclic behaviour at a capacity of below 1.5 $e^{-1}$/Mo. The electrochemical features of these materials are compared with those of other molybdic acids, i.e. $MoO_3 \cdot (2/3)H_2O$, $MoO_3 \cdot 1H_2O$ and $MoO_3.2H_2O$. The chemical diffusion coefficient of $Li^+$ ions reaches a value $3 \times 10^{-9}$ $cm^2 \ s^{-1}$ in $MoO_3 \cdot (1/2)H_2O$ materials.

Thin films of $MoO_3$ for gas sensing application have been deposited by reactive sputtering using a metallic molybdenum target. After annealing at 500°C in air, the layer cosmists of rhombic molybdenum trioxide with a (010) texture occurred. The morphology of the layers considerably depends on the film thickness (Mutschall et al, 1996).

Monolithic molybdenum oxide aerogels and xerogels were synthesized by sol–gel methods using a variety of sol compositions from the system of $Mo(OC_3H_7)_5/MoCl_3(OC_3H_7)_2$/acetonitrile/nitric acid/$H_2O$. The aerogels were found to have a density of 0.1–0.2 g/cm³ with surface areas between 150–180 m²/g. The xerogels had densities between 1.5–2.0 g/cm³ and surface areas less than 10 m²/g. The as-prepared gels are amorphous materials with compositions corresponding to $MoO_3 \cdot 1H_2O$:0.3$CH_3NH_2$. Crystallization to the orthorhombic phase occurs at 350°C. Electrochemical measurements demonstrate that lithium can be intercalated reversibly into the aerogel structure. An ambient pressure drying method based on the use of low surface tension solvents produced monolithic gels with high surface areas (250–270 m²/g) and densities between 0.7–0.9 g/cm³ (Dong and et. al, 1998).

In 2000, Lopez et al reported the relationship between structure and morphology of amorphous molybdenum oxide $MoO_3$ evaporated onto polycrystalline cadmium sulfide (CdS) substrates synthesized on glass slide substrates using the chemical bath deposition technique (CBD). Molybdenum oxide films were deposited onto glass and glass/CdS substrates by vacuum thermal evaporation, with film thickness of about 350 nm.

In 2001 Dong et al prepared molybdenum oxide aerogel and studied the structural and electrochemical properties of amorphous and crystalline molybdenum oxide aerogel. The structure and chemical different among amorphous, crystalline and nanocrystalline molybdenum oxide aerogels were determined using extended X-ray absorption fine structure (EXAFS), fourier transform infrared (FTIR) analysis and powder X-ray diffraction (XRD). These different forms of the same nominal material were produced by heat treatment. The most interesting material was the $MoO_3$ aerogel heated to 300°C. The material was found to be nanocrystalline; there are no XRD peaks but the EXAFS were virtually identical to orthorhombic $MoO_3$.

In the same year, Li et al prepared $MoO_3$–$TiO_2$ nanocomposite thin films using the sol–gel process. The $MoO_3$–$TiO_2$ thin films were prepared by $Mo(OC_2H_5)_5$ and $Ti(OC_4H_9)_4$ precursor solutions. Different atomic ratios of the two compounds were investigated. The thin films were deposited on silicon, quartz and sapphire substrates annealed at temperatures of 400°, 450°, 500° and 600°C for 1 h. The XRD patterns revealed the structure of the molybdenum dominated films consisted mainly of an orthorhombic $MoO_3$ phase with preferential orientation along the (0 1 0) plane. The TEM selected area diffraction patterns revealed the presence of orthorhombic $MoO_3$ and anatase and brookite $TiO_2$ phases. The XPS characterization indicated the films are stoichiometric ($MoO_3$ and $TiO_2$). The SEM analysis showed that the films annealed at 400°C were smooth and uniform with 20–100 nm sized grains. The $MoO_3$ dominated films annealed at high temperatures ($T$>500°C) have relatively large micrometer particles grown out of the film. The AFM images showed that the $MoO_3$ dominated thin films possess a high surface roughness and the $TiO_2$ dominated films have smooth and uniform nanosized grains. The TEM results showed that the $TiO_2$ dominated films had an average grain size of 6 nm with a narrow distribution. The $MoO_3$ dominated films had an average size of 5 nm with a

broad distribution. The morphological and physical properties of the $MoO_3$–$TiO_2$ nanocomposite can be tailored by altering the ratio of the two compounds, and hence, enhanced thin films for gas-sensing could be achieved.

In the same year Galatsis et al studied oxygen gas sensing properties of molybdenum trioxide and tungsten trioxide ($MoO_3$–$WO_3$) mixed metal oxide thin-films. Various $MoO_3$–$WO_3$ ratio thin-film samples are deposited onto silicon (1 0 0) and sapphire substrates via the sol–gel route. SEM analysis showed the presence of $MoO_3$ orthorhombic phase, abating as $WO_3$ dominated the mixed system. $MoO_3$–$WO_3$ sensors exhibited a linear response to $O_2$ concentrations varying from 10 to 10,000 ppm. The $MoO_3$–$WO_3$ film response was stable and reproducible operating at an optimal temperature of 420°C.

In 2001, Galatsis et al used the sol-gel technique to prepare titanium dioxide ($TiO_2$), $WO_3$, and $MoO_3$ single metal oxide based gas sensors was conducted. Process variables, such as, solution concentration, deposition parameters, gelling time, annealing time and temperature, remained constant.

A novel procedure for the synthesis of molybdenum oxide nanoparticles has been developed. Mo nanoparticles were prepared on Au (1 1 1) by dissociation of $Mo(CO)_6$ molecules at 500 K. These Mo nanoparticles were found inactive towards oxygen according to results of synchrotron-based high-resolution photoelectron spectroscopy (PES). There was no sign of molybdenum oxide formation after an exposure to 150 L of oxygen at 300–850 K. However, these Mo nanoparticles can be oxidized by reaction with $NO_2$ at 500 K to form molybdenum oxides, $MoO_2$ or $MoO_3$. The stability of the $MoO_3$ particles upon annealing was further investigated by PES. The fully oxidized $MoO_3$ clusters do not react with ethylene (Chang and et al 2002).

In 2003, Ramirez et al successfully prepared $\beta$-$MoO_3$ free of $\alpha$-$MoO_3$ through soft chemistry methods. The formation of $\beta$-$MoO_3$ with high purity was determined by the formation of the precursor $MoO_3 \cdot 2H_2O$ when a solution of $Na_2MoO_4 \cdot 2H_2O$ was passed through a cation-exchange resin. A structural,

spectroscopic and thermal study of the polymorph synthesised was made by XRD, electron dispersion spectroscopy (EDS), FTIR and TGA/DTA techniques, respectively, in order to make a study about the possibilities of $\beta$-MoO$_3$ as active material in a lithium battery. Electrochemical experiments showed a high ability of the $\beta$-MoO$_3$ to form lithium molybdenum bronzes via a lithium insertion reaction.

In 2004, Cruz and Ramirez followed the route of $\beta$-MoO$_3$ synthesis through soft chemistry methods. A new amorphous material with composition of MoO$_3$·2H$_2$O was detected. The hydrated molybdenum oxide showed the capacity for electrochemical lithium insertion.