CHAPTER I
INTRODUCTION

Crystalline molybdenum trioxide has a two-dimensional layered structure showing interesting lithium intercalation properties. Molybdenum oxide, especially MoO_3, is of interest for battery cathodes, catalysis, and electrochromic materials. The most common form of crystalline MoO_3 is the orthorhombic phase (*o*-MoO_3) where vertex-sharing chains of distorted MoO_6 octahedra share edges with other similar chains to form the layers. These two-dimensional layers are stacked in a staggered arrangement and weakly held together by van der Waals bonds. Molybdenum trioxide thus forms a very stable 2D layered oxide compound. These layers can be propped open by intercalated species, such as protons, solvated lithium and sodium ions, as well as larger molecules. Its open structure and the ease of creating oxygen vacancies in the structure make it an ideal candidate for lithium secondary batteries and electrochromic windows. Lithium capacity of up to 1.5 Li/Mo and discharge capacity of over 300 mA h/g have been reported.

Sol–gel synthesis of MoO_3 is desirable because the low synthesis temperatures can lead to the formation of amorphous or metastable phases not available through traditional synthesis methods. The low temperature phase can exhibit properties that are substantially different from the crystalline phase. Although it is often assumed that lithium intercalation occurs between the two-dimensional layers of the crystalline MoO_3, previous experiments have not been able to show a direct correlation between the degree of crystallinity and the Li capacity of MoO_3. Even more interest is that certain amorphous molybdenum oxides have exhibited better intercalation behavior compared to that of crystalline MoO_3.

BACKGROUND

Sol-gel process

The sol-gel process is a versatile solution process for making ceramic and glass materials. It generally refers to the transition of a system from a liquid (sol) into a solid (gel) phase, an more importantly produced better purity and high homogeneity at low temperature.

The sol–gel method has been attracting great interest as an excellent approach for the preparation of inorganic–organic hybrid materials. To date, this method has been applied in various fields, such as solid tunable lasers, nonlinear optics, other optical devices, and so on. In particular, the method has been recently employed for the preparation of organometallic complex-dispersed composite materials.

In the sol-gel process involving a preparation of the sol from metal-organic compounds, such as metal alkoxide, $M(OR)_n$, the precursors are dissolved in a suitable solvent. The precursors are subjected to a series of hydrolysis and condensation reactions: For example, metal alkoxide $M(OR)_n$ as a precursor involves two important reactions;

1. Hydrolysis

$$M(OR)_n + H_2O \longrightarrow M(OR)_{n-1}OH + ROH \quad (1.1)$$

2. Condensation

$$M(OR)_n + M(OR)_{n-1}OH \longrightarrow M_2(OR)_{2n-2} + ROH \quad (1.2)$$

or $$M(OR)_{n-1}OH + M(OR)_{n-1}OH \longrightarrow M_2OR)_{2n-2}OH + H_2O \quad (1.3)$$

The hydrolsis reaction is firstly initiated, followed by condensation reaction to give metal-oxygen-metal (M-O-M) bond and eventually extension to form network, or gel. The factors affecting hydrolysis and condensation reaction to form gel are:

a) The electronegativity of the metal atom to increase the coordinate number.

b) The steric hindrance of the alkoxy group (-MOR)

c) The molecular structure of the metal akoxiddes (monomeric or Oligomeric)

d) The amount of added water in the hydrolysis step and sequence of water addition.

e) pH