



Faculty of Resource Science and Technology

**PREPARATION AND CHARACTERIZATION OF MANGANESE
OXIDE NANOPARTICLES AND THIN FILMS FOR
ELECTROCHEMICAL APPLICATIONS**

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**Preparation and Characterization of Manganese Oxide
Nanoparticles and Thin Films for Electrochemical
Applications**

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DECLARATION

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.



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Preparation and Characterization of Manganese Oxide Nanoparticles and Thin Films for Electrochemical Applications

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ABSTRACT

Stable colloidal suspension of tetramethylammonium manganese oxide (TMAMnO_x) was synthesized by the reduction of tetramethylammonium permanganate salt with 2-butanol at room temperature. TMAMnO_x thin films were prepared by electrochemically deposition of TMAMnO_x colloidal suspension directly onto clean stainless steel plates followed by heat treatment. The capacitive behavior of TMAMnO_x films was studied using cyclic voltammetry (CV). The studies observed by cyclic voltammetry showed that the charge capacity of TMAMnO_x thin films were strongly affected by the deposition duration of TMAMnO_x colloidal suspensions onto stainless steel plates, annealing temperatures and various aqueous electrolytes and its concentrations. These thin films exhibited high capacitive behavior with a specific capacitance of 338 F/g. The manganese oxide concentrations of TMAMnO_x colloidal suspension and total manganese oxide loading of TMAMnO_x thin films determined by AAS were about 16.46 mg/L and 0.51 mg/cm² respectively. SEM micrographs showed that the manganese oxide thin films were nanoparticulate and porous in nature. Consistent with quantum confinement effects and particle growth of manganese oxide, UV-Visible spectroscopy of the colloids showed two absorbance bands with higher energy band near 210 nm while the other near 310 nm both of which were shifted to higher wavelength and lower energy.

Key words: Tetramethylammonium Manganese Oxide, CV, Charge Capacity, AAS, SEM, UV-Visible

ABSTRAK

Tetramethylammonium mangan oksida (TMAMnO_x) yang stabil disintesis dengan penurunan TMAMnO_x oleh 2-butanol pada suhu bilik. Filem nipis TMAMnO_x disediakan dengan menggunakan teknik elektrokimia yang menyalutkan TMAMnO_x ke atas kepingan logam tidak berkarat yang bersih diikuti dengan perawatan pemanasan. Kelakuan kapasitif filem nipis TMAMnO_x diujikan dengan menggunakan kitaran voltameter (CV). Penentuan dengan menggunakan CV menunjukkan kapasiti cas TMAMnO_x yang amat dipengaruhi oleh masa penyalutan TMAMnO_x ke atas kepingan logam tidak berkarat, suhu pemanasan dan pelbagai elektrolit akeus dan kepekatan. Filem nipis ini memberi kelakuan kapasitif yang tinggi dengan kapasiti spesifik adalah 338 F/g. Kepekatan mangan dalam TMAMnO_x larutan dan mangan amaun dalam TMAMnO_x filem nipis yang dikaji dengan menggunakan AAS adalah kira-kira 16.46 mg/L dan 0.51 mg/cm² masing-masing. SEM mikrograf menunjukkan bahawa mangan oksida filem nipis adalah zarah-zarah nanosaiz dan berliang-liang kecil. Konsisten dengan kesan batasan kuantum dan perkembangan partikel mangan oksida, UV-Visible spectra TMAMnO_x menunjukkan dua keluk penyerapan, iaitu satu keluk tenaga yang lebih tinggi menghampiri 210 nm manakala keluk yang satu lagi menghampiri 310 nm dengan beralihan ke kedua-dua gelombang yang lebih panjang dan tenaga yang lebih rendah.

Kata kunci: Tetramethylammonium mangan oksida, CV, kapasiti cas, AAS, SEM, UV-Visible

CHAPTER 1

INTRODUCTION

Manganese oxide is the most important manganese compound. It is widely distributed in the earth crust. Manganese oxide can be found naturally as pyrolusite (MnO_2) and hausmannite (Mn_2O_4). Pyrolusite is widely being used as a chemical oxidant in organic synthesis. Manganese oxide is an all-around material. It is widely used in the preparation of dry-cell batteries, in the chemical industry as a catalyst and in the medical industry.

Manganese oxide crystallizes into different arrangements such as layered, tunnel and channel structures which are called birnessite and buserite respectively (Jones *et al.*, 2004). Each of these structures contributes to specific applications since the application depends on their sizes, morphology and porosity. According to Jones *et al.* (2004), the birnessite manganese oxide is made up of a single sheet of edge-sharing MnO_6 octahedral, the small overall negative charge on which is balanced by hydrated interlayer, ion-exchangeable cations. Birnessite is an important precursor for the transformation to tunnel structure materials (Cai *et al.*, 2002).

Much studies has been done on lithiated manganese oxide, LiMn_2O_4 . According to Li *et al.* (2006), MnO_2 spinel-based electrodes are the most favorable for Li^+ -intercalation batteries when considering a combination of specific energy, cost, availability, toxicity, and electrode potential. Lithium-ion, like lithium manganese oxide is designed to solve the safety problem of the highly reactive properties of lithium metal. Lithiated manganese oxide cells

have no memory effect. They have good discharge ability. LiMn_2O_4 provides a higher cell voltage than cobalt based chemistry at 3.8 to 4.0 volts (Otsuji *et al.*, 2005).

Manganese oxide mixtures in the form of nanoparticles, prepared by co-precipitating with additive(s) or mechanically mixed with the additives(s), are able to lower the amount of carbon monoxide and nitric oxide in the mainstream smoke of cigarette. Manganese oxide mixtures are able to convert carbon monoxide to carbon dioxide and nitric oxide to nitrogen. The amount of carbon monoxide and nitric oxide in the mainstream smoke of cigarette which will reach the smoker and give off in secondhand smoke can be reduced (Li *et al.*, 2004).

According Ressler *et al.* (1999), mixed valent manganese oxide materials are of interests due to their range of electrical, magnetic and catalytic properties. Malinger *et al.* (2006) noted that the presence of small dopant levels of various transition metal ions in Octahedral Molecular Sieves (OMS) and Octahedral Layered (OL) manganese oxide materials could influence the conductivity of these materials. The particle size of these materials can be controlled in order to investigate their physical and chemical characteristics. Specific surface area of manganese oxide can be enhanced by preparing small, nanometer particle sizes and can be used to influence the reaction rate in catalytic reactions.

In recent years, much interest has been focused on developing the synthesis and characterization of manganese oxide. Jones *et al.* (2004) reported that the manganese oxide can be applied as a faradaic electrochemical capacitor using mild aqueous electrolytes. The low cost of manganese oxide compared with other electrode materials of supercapacitors including ruthenium and iridium oxides attracts many researchers.

Studies of Chin *et al.* (2002) and Brock *et al.* (1999) have shown that MnO_2 thin films derived from sol-gel method are a promising electrode material for supercapacitors due to their high reversibility, good stability of cycling and their high capacitive behavior. But, this useful device is practical only if low concentration of 10^{-3} M of MnO_2 colloidal suspension is employed in the preparation of coatings. It is because the strong tendency of manganese oxide to agglomerate or coagulate at high concentrations of manganese oxides. Thus, incorporating of tetraalkylammonium cations such as tetramethylammonium, tetraethylammonium, tetrapropylammonium and tetrabutylammonium, to manganese oxides during synthesis can be employed to prevent agglomeration of negatively charged manganese oxide particles.

Amorphous or nanocrystalline structures of manganese oxide have attracted much attention as electronic devices where a long discharge time is desired. Yang *et al.* (2005) reported that manganese oxides exhibit very high intercalation capacities over a wide voltage range corresponding to more than one electron reduction of Mn (IV) ions. However, manganese oxide produced will give low cycling performance which is not suitable as electrode materials in rechargeable lithium ion batteries if the processing temperature is low through aqueous routes. Therefore more researches are needed to develop methods for preparing better material with improved cycling performances.

In this study, stable colloidal of tetramethylammonium manganese oxide (TMAMnO_x) was prepared and TMAMnO_x thin films were deposited on the stainless steel substrate by electrophoretic deposition technique. The electrochemical characteristics of TMAMnO_x thin

films under various conditions such as deposition duration, heat-treatment, different aqueous electrolyte and electrolyte concentration were investigated.

The objectives of this study are:

1. To prepare various manganese oxide nanoparticles in the form of colloidal suspension using different precursor materials and synthesis conditions.
2. To prepare nanostructured manganese oxide thin films from manganese oxide colloidal suspension prepared.
3. To characterize the physical and electrochemical properties of these nanostructured manganese oxide thin films.

CHAPTER 2

LITERATURE REVIEW

Many methods have been employed for preparing manganese oxide, its structural investigation and characterization. The methods for synthesizing manganese oxide materials are the sol-gel method, air oxidation method and reflux method. The powder X-ray Diffraction is employed for structural investigation and characterization.

Cai *et al.* (2002), reported an air oxidation method to synthesize manganese oxide materials by air oxidation of Mn^{2+} . This is the reaction between permanganate ion, MnO_4^- and manganous sulfate, MnSO_4 in the presence of nitric acid. Parameters such as conditions of airflow, the concentration of OH^- , and the aging time were altered to study the effect of synthesis conditions on properties of manganese oxide synthesized.

Brock *et al.* (1999), had employed the sol-gel method for the synthesis of manganese oxide nanocrystals with a tunnel structure and birnessite layered materials. These materials were prepared by reacting MnO_4^- solution such as potassium permanganate with fumaric/maleic acid or sucrose to form a gel and heating the xerogel at an effective temperature. Brock *et al.* (1999), also reported that this sol-gel method gave many advantages, including high thermal stabilities of products than other methods. Besides, Yang *et al.* (2005) reported two different sol-gel routes to prepare a nanostructured amorphous manganese oxide cryogel. The cryogel produced exhibits very high lithium intercalation capacity and excellent rate capability. Yang and Xu (2003) reported that, the higher the precursor concentration used for the preparation of the hydrogel, the higher the specific capacity of the resultant cryogel.

Such enhanced properties could be attributed to the specific surface area and the local structure of the cryogels.

The reflux method had been employed to prepare manganese oxide microporous materials. Xiao *et al.* (1998) reported that a metal-doped material with a 2 x 2 tunnel structure and high surface area of 279 m²/g was prepared. Manganese oxide materials with the surface area of more than 200 m²/g should be outstanding catalytic materials for oxidative reactions and ionic/electronic conductors for high energy storage.

Besides, manganese oxide can also be prepared by the intercalation of organic ammonium ions in OL-1. Birnessite structure K-OL-1 was prepared using this method. K-OL-1 was ion-exchanged with ion H⁺ to form H-OL-1, which was being used in further intercalating reactions. The tetraalkylammonium hydroxides such as Me₄NOH, Et₄NOH, Pr₄NOH and Bu₄NOH and diamines such as ethylenediamine, 1,6-diaminohexane and 1,10-diaminooctane were used to intercalate H-OL-1. Elemental analyses, x-ray diffraction, FTIR spectroscopy, SEM and energy-dispersive x-ray anal., UV-visible spectroscopy, and TEM were employed to characterize these samples (Gao *et al.*, 2001).

Malinger *et al.* (2006) reported that manganese oxide-based solids with nanostructure of channels, layers, and pillars can be used for applications which vary from detergents to sensors. According to Malinger *et al.* (2006) octahedral molecular sieves (OMS) comprise infinite 3-D crystalline frameworks with molecule-sized tunnels similar to the naturally occurring zeolites while octahedral layered (OL) materials have interlayer spacings similar to clay-type materials. Malinger *et al.* (2006) reported that the interlayer spacing of OL-1 is

approximately 7Å and it contains exchangeable cations and water molecules. Navrotsky *et al.* (1998) showed that the layered materials have the lowest heat of formation among all the manganese oxide systems.

Octahedral molecular sieves (OMS) and octahedral layered (OL) manganese oxide materials exhibit good conductivity, high porosity, and good thermal stability. Various dimensions of the channels and interlayer spacings in OMS and OL manganese oxide materials can be adjusted to fit various applications. Chemical reactions that take place at the active sites can be varied by substituting different metals into the structure or by altering the valence of the manganese ions. Such flexibility gives potential applications in many areas, such as adsorbents, batteries, catalysts, catalyst supports, detergents, protective coatings, and sensors Malinger *et al.* (2006).

According to Nakayama *et al.* (2004), manganese oxides stores electrical charge by simultaneous electrons injection and charge-compensating cations such as alkylammonium cations into the solid which is useful for applications of charge storage. The application can be as cathodes in secondary lithium batteries, electrochromic devices and lately electrochemical supercapacitors in aqueous electrolytes. Charge storage characteristics of manganese oxides are associated with electrical conductivity in the solid phase and ionic transport within the pores.

Manganese oxide can be doped with metal cations such as Fe, Co, Ni, Ca, and Cd. According to Cai *et al.* (2002), these metal cations were added to the initial reactant solution as framework dopant to investigate their effect on the synthesized materials and to alter the

characteristics of the materials. The crystal phases, average oxidation states, surface areas, particle size, and thermal properties of manganese oxide at different synthesis conditions were studied by Cai *et al.* (2002).

Malinger *et al.* (2006) found that amorphous manganese oxide materials were able to photochemically and thermally decompose phosphine oxide materials that are model complexes for chemical warfare agents. Upon preparing all the catalyst by Malinger *et al.* (2006), cryptomelane (OMS) material are the most active catalyst they prepared for oxidation of cyclohexane (Xia *et al.*, 1998; Wang *et al.*, 1998), H_2O_2 decomposition (Zhou *et al.*, 1998), and the oxidative dehydrogenation of ethanol.

OMS and OL materials can be used as adsorbents. According to Malinger *et al.* (2006), various researchers have observed the ability of porous manganese oxides to adsorb metals in high concentration. Natural occurring manganese oxides contain many impurities oxide phases, including SiO_2 , Fe_2O_3 , Al_2O_3 and P_2O_5 (Xiao *et al.*, 1998). This situations cause difficulties of characteristic analysis. Approaches were employed to prepare pure materials are ion-exchange reactions, hydrothermal synthesis, electrolytic synthesis and chemical synthesis methods (Xiao *et al.*, 1998).

CHAPTER 3

METHODOLOGY

3.1 Preparation of Tetramethylammonium Permanganate Salt (TMAMnO₄)

In this study, the tetramethylammonium permanganate salt (TMAMnO₄) was prepared from tetramethylammonium bromide, (CH₃)₄NBr, and potassium permanganate (KMnO₄). 15.5 mmol of tetramethylammonium bromide, TMABr (2.3878g) was weighed and dissolved in 20 mL of ultrapure water whereas 13.9 mmol of potassium permanganate (2.197g) was weighed and dissolved in 50 mL of ultrapure water. TMABr solution was poured into a burette and added to the KMnO₄ solution drop by drop. The mixtures were stirred using magnetic stirrer for one hour. The solution mixture was then filtered by vacuum filtration and Whatman No. 1 filter paper to obtain the product (TMAMnO₄ salt) in the form of purple precipitate. The TMAMnO₄ salt was air-dried at room temperature and stored in desiccators to avoid oxidation and contamination by the polluted air.

3.2 Preparation of Manganese Oxide Colloidal Suspension (TMAMnO_{x(x<2)})

Various manganese oxide samples have been prepared through the reduction of tetramethylammonium permanganate salts with 2-butanol. In order to prepare TMA-manganese oxide colloidal suspension of 0.04 mol/L manganese concentration, TMAMnO₄ was being added into a stirred (1:1) mixture of ultrapure water and 2-butanol. Typically, 2 mmol of TMAMnO₄ (0.3862g) was dissolved in 50 mL of ultrapure water. Then 50 mL of 2-butanol was being added into the solution. After being stirred for two hours at room

temperature, the resulting mixture was then poured into a separating funnel. Dark-red-brown aqueous colloidal suspension of TMA-manganese oxide (TMAMnO_x) was formed as the lower aqueous layer while the 2-butanol layer was formed on the upper layer since they were not miscible. Using the separating funnel, the 2-butanol layer was separated from the aqueous layer of colloidal suspension of TMAMnO_x . All the reactions were carried out under ambient temperature and atmospheric pressure.

3.3 Preparation of Stainless Steel Plates

About 200 pieces of stainless steel plates (4 cm x 1.5 cm) were being prepared. Every stainless steel plate was being polished using sand paper no. 1000 to remove the oxidized surface layer and then being cleaned with detergent. The stainless steel plates were placed in a beaker containing detergent solution and sonicated for 15 minutes. They were subsequently cleaned by sonicating in ultrapure water for another 15 minutes. This step was followed by sonicating with HNO_3 acid and acetone. Sonicating with ultrapure water has to be carried out in between these steps and each sequence took 15 minutes. Finally, the stainless steel plates were being dried in oven at 105 °C. All of the stainless steel plates were individually labeled and weighed. All these cleaning steps were deemed necessary in order to obtain clean stainless steel plates so that pure and uniform coatings would be formed on them and the charge capacity of these coatings would not be affected.

3.4 Preparation of Manganese Oxide Thin Films

The TMA manganese oxide colloidal suspension (TMAMnO_x) were being well dispersed by sonication and used to prepare thin films by electrochemical deposition onto precleaned and preweighed stainless steel plates. The deposition current was being keep constant at 30 mA throughout the deposition process while the deposition voltage was allow to vary over the range of 4.0 - 8.0 V. The duration used for the deposition of colloidal suspension onto stainless steel plates was being varied between 5 sec and 75 sec. The longer the duration of deposition, the thicker were the film being deposited onto the stainless steel plates. All depositions were done in triplicate to obtain average results. A flow chart showing the steps in the preparation of manganese oxide suspension, thin films and their characterization is shown in Figure 3.1.

3.5 Characterization of Manganese Oxide Nanoparticles and Thin Films

All manganese oxide nanoparticles and thin films samples were characterized to determine their physical and electrochemical properties using established methods as follow:

3.5.1. Atomic Absorption Spectrophotometer (AAS)

The concentrations of manganese in TMAMnO_x colloidal suspensions and thin films were determined by using Perkin-Elmer model 3110 Flame Atomic Absorption Spectrophotometer (AAS).

1 mL of freshly prepared TMAMnO_x colloidal suspension was digested with 2 mL of concentrated nitric acid (HNO_3) and then diluted to 250 mL with ultrapure water. Freshly coated TMAMnO_x thin films were digested with 2 mL of concentrated nitric acid and then diluted to 100 mL with ultrapure water. Triplicates of each type of samples were being analyzed to determine the average concentration of manganese. Standard manganese of concentration range between 1 ppm to 16 ppm solutions were prepared from 1000 ppm metal stock solution by dilution.

3.5.2. Scanning Electron Microscope (SEM)

The morphology and the particle size distribution of manganese oxide thin films were investigated using SEM (JOEL model JSM-5300 LV) available at The Timber Research Centre Kuching. Thin films samples analyzed by SEM include samples as deposited at room temperature, and samples that had been calcined at 150 °C and 300 °C. SEM micrographs were obtained for electrode areas that had been exposed to electrolytes during CV cycling as well as electrode areas that had not been exposed to electrolytes, in order to study the effect of voltammetric cycling.

3.5.3. Fourier Transformed Infrared Spectrometer (FTIR)

The presence of TMA cations in the permanganate salts were examined by the FTIR spectrometer. The TMAMnO_4 salt was being grounded with KBr and then being pressed into a pellet. It was being placed in the light beam of the spectrometer to obtain the FTIR spectrum. The ratio of KBr to sample used was 1:10.

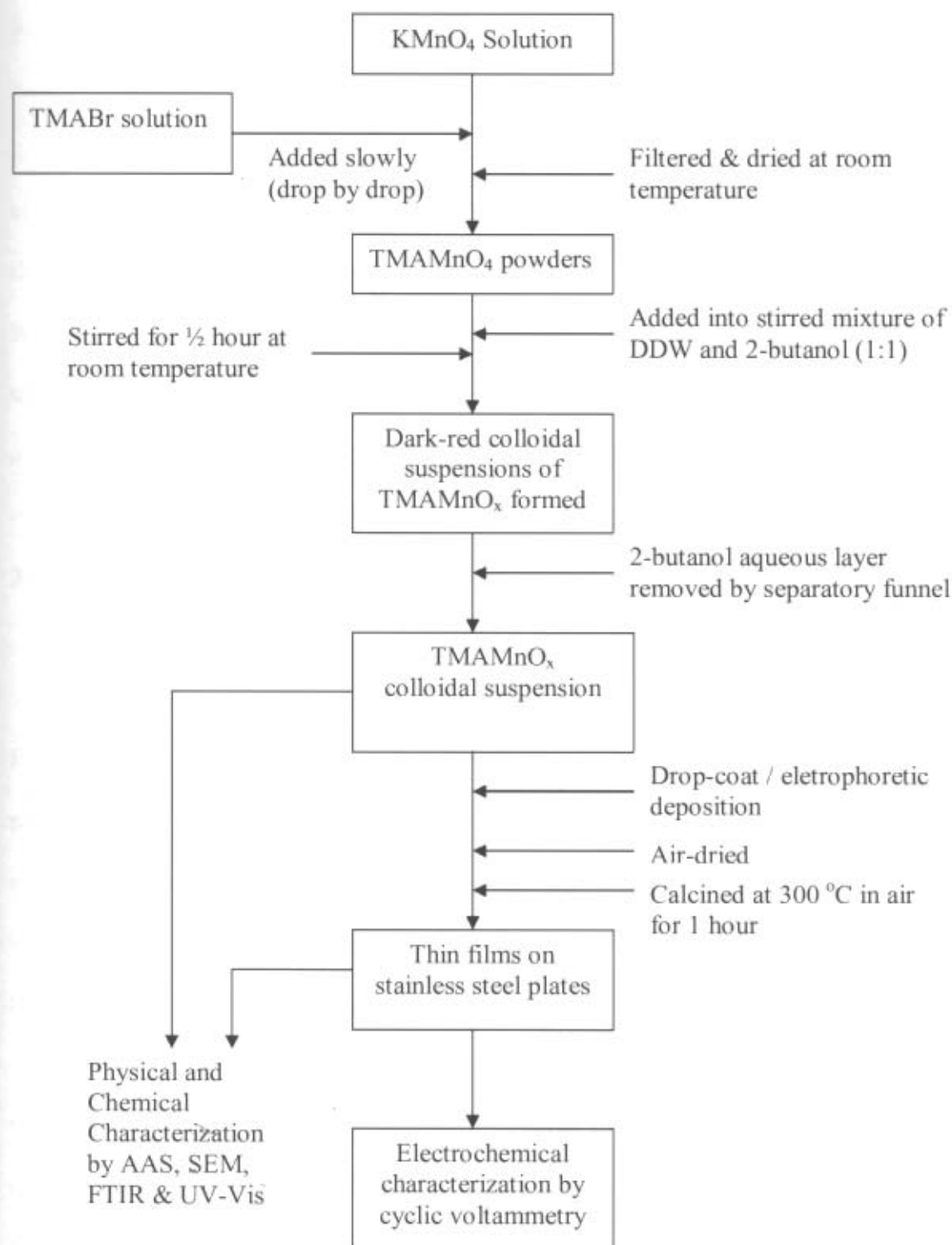


Figure 3.1: Flow chart showing steps in the preparation of manganese oxide suspension, thin films and their characterization.

3.5.4. Scanning UV-Visible Spectrometer

The aggregation and stability of manganese oxide nanoparticles in the form of colloidal suspensions were studied using Scanning UV-Visible Spectrometer by measuring the absorbance of the suspensions over a predetermined range of wavelength from 200 nm to 900 nm. Prior to each measurement, these suspensions were being diluted to 2×10^{-4} M using ultrapure water. The UV-Visible absorption spectra of these suspensions were being acquired over a total of 38 days of aging time.

3.5.5. Advanced Electrochemical Analyzer

The electrochemical properties of manganese oxide thin films were studied using the Potentiostat/Frequency Response Analyzer (PARSTAT 2263). The electrochemical properties were studied by cyclic voltammetry using a standard three-electrode cell configuration. Cyclic voltammetry was conducted by scanning over the potential range of 0.0 - 1.0 V at a scan rate of 50 mV/s in various mild aqueous electrolytes. The electrochemical test cell consists of a saturated calomel electrode (SCE) (Saturated KCl) fitted with a bridge of Vycor frit as reference electrode and a platinum foil (0.025 mm thick and 25 x 25 mm) was used as the counter electrode. Thin-film samples deposited on stainless steel plates were used as the working electrodes. Each manganese oxide thin films were being cycled for 50 cycles. In this study, the effects of the deposition duration between 5 to 75 seconds on the charge capacity of deposited TMAMnO_x thin films were investigated with 1 M Na_2SO_4 aqueous electrolyte. Besides, the effects of calcination temperatures on the charge capacity of TMAMnO_x thin films were studied by cyclic voltammetry with 1 M Na_2SO_4 aqueous as