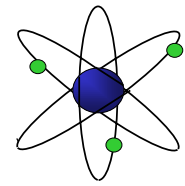




Electrochemical Synthesis of Manganese Dioxide Thin Films: Characterization of Electrocoloration and Electroinsertion Behavior

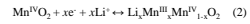
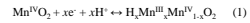


...where electrons and photons run naked and free...

Arash Shirvani, Todd McEvoy, Dr. Keith J. Stevenson

Introduction

Batteries and electrochemical capacitors are two of the main devices used to store electrical energy. Batteries contain a series of chemical reactions that produce electrons to provide electrical energy for everyday uses. Electrochemical capacitors are charge-storage devices that possess high power density, exhibit excellent reversibility, and have very long cycle life. Rechargeable batteries and capacitors have found use in electric vehicles aiding in all aspects of movement as well as in consumer parts such as cellular phones and camcorders. Much research in this area has been focused on the development of new electrode materials having high specific surface areas, in order to enhance the performance of batteries and capacitors. Transition metal oxides are one such material that shows great promise for use in batteries and capacitors. One particular example which shall form the topic of interest in this paper, is MnO₂. Its desirable properties of low cost and low toxicity (e.g. environmentally friendly) make it especially appealing as a charge-storage material. As with most electrically conductive metal oxides, manganese dioxide stores electrochemical charge by a double insertion of electrons and cations into the solid state. Typical insertion cations include protons and lithium ions:



These cation-insertion processes underlie many significant technological applications of the conductive metal oxides for use in many devices.

Electrochemical deposition techniques were carried out to create MnO₂ films. The resulting films were characterized using electrochemical techniques to study their ion/charge storage capabilities.

Energy Storage: Who cares and Why?

- We all do!!! If not, you should!
- Project Goals:
 - Synthesis of manganese dioxide thin films
 - Characterization structurally and electrochemically
 - Study associated energy storage performance
 - Can MnO₂ be used as an alternative battery material

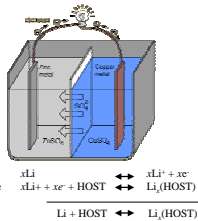


Toyota Prius
www.toyota.com

http://www.thkafmtech.com
www.magnopt-photon.gr

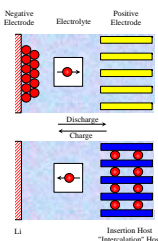
Primary

- One discharge battery
- Characterized by,
 - Good shelf life
- Example: Zinc/air battery



Secondary (Rechargeable)

- Recharged electrically after discharge
- Characterized by,
 - Re-usable numerous times
- Example: cell phone battery



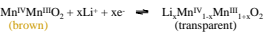
Rechargeable Lithium Batteries

- Energy density
- Power density
- Ion Storage Capacity
- Stability



Nanostructure

- porosity, surface area, particle-size, crystallinity, orientation



Classical Mechanism is simplified model.

Preparation of MnO₂ Electrodes

Why Electrodeposition?

Conventional methods (Vapor deposition, Sputtering):
High cost, energy consuming

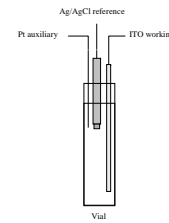
Electrodeposition:
Cheaper, low energy consumption, deposit onto materials of different shapes.

*MnO₂ is more environmentally friendly compared to CoO₂ – the currently utilized material for rechargeable lithium batteries.

Post deposition processing

A brown-colored manganese dioxide film forms on the ITO side of the glass with constant potential or constant current applied.

Typical electrodeposition set-up



4 M H₂SO₄ + .5 M MnSO₄

Electrochemical Characterizations with lithium and protons

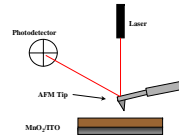
Lithium insertion was studied using films deposited at room temperature and films that were sintered following deposition. Lithium is simply inserted into the film as it is reduced, then lithium is desinserted as the film is oxidized. Theoretically, MnO₂ is involved in completely reversible reactions, thus the lithium should be fully inserted and desinserted. However, the results showed that MnO₂ was only quasi-reversible, as some lithium remained in the film at the end of the insertion process. This was visually noticeable as the region of the film exposed to the insertion became much lighter in color, due to reduction. Also, this becomes apparent on the graph of the lithium insertion since the areas above and below the zero mark should be equal for the reaction to have been completely reversible, but this is not the case

Three electrode cell



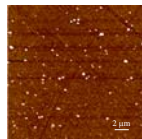
Pt Auxiliary

Structural Characterization of MnO₂ Thin Films

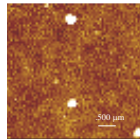


Structural characterization Using AFM on Thin Films Deposited at Room Temperature

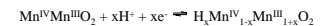
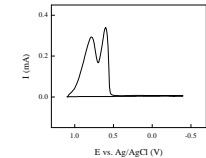
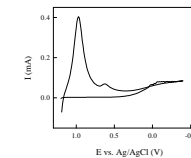
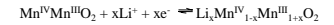
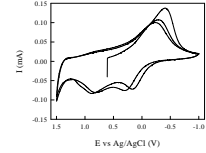
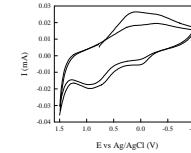
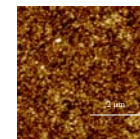
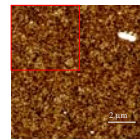
AFM Images on thin films deposited at elevated temperatures (~70 °C)



As-deposited



Sintered at 400 °C



Conclusions and Future Goals

Determine ways to produce more crystalline growth in the films

Compromise uniformity with crystalline growth

Seek protection against acid dissolution

MnO₂ can be utilized as a sufficient battery component if its reversibility can be fully attained and its full characteristics realized

Electrodeposition synthesis is practical and sufficient, especially at constant currents (chronopotentiometry)

Acknowledgements

Todd McEvoy

Dr. Keith Stevenson

Stevenson Research Lab

Welch Summer Scholar Program

