Strategies To Improve The Electrochemical Of Performance Transition Metal Compounds As Anode Materials For Li-Ion Batteries

Noemi Dominguez

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STRATEGIES TO IMPROVE THE ELECTROCHEMICAL OF PERFORMANCE TRANSITION METAL COMPOUNDS AS ANODE MATERIALS FOR LI-ION BATTERIES

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Dedication

To my family and friends who gave me inspiration to continuing pushing the boundaries of my knowledge and to never give up.
STRATEGIES TO IMPROVE THE ELECTROCHEMICAL PERFORMANCE 
OF TRANSITION METAL COMPOUNDS AS ANODE MATERIALS 
FOR LI-ION BATTERIES

by

NOEMI DOMINGUEZ RUIZ, M.S. MATERIALS ENGINEERING

DISSertation

Presented to the Faculty of the Graduate School of 
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Abstract

Nowadays, our society depends on fossil fuels as the main energy source. However, depletion, price fluctuations, and other concerns, such as global warming, have led to an exhaustive research for renewable energy resources. Here is where electrochemical energy systems play a critical role since they can provide power when renewable energy is not available. Among these electrochemical energy storage systems Li-ion batteries (LIBs) have shown higher volumetric, gravimetric, and power density capacities over other battery systems.

However, commercial LIBs are still relying on graphite base materials for the anode. However, graphite possesses a low specific capacity. Recently, transition metal compounds have reached great attention as anode materials due to their high theoretical capacity, i.e. 1230 mAh/g for MnO₂ vs 372 mAh/g for graphite. However, transition metal-based compounds suffer from low electric conductivity and poor cycling stability. Consequently, this dissertation primary focus was to improve cycling capabilities of the transition metal compounds investigated.

Here we present strategies to improve the electrochemical performance of transition metal compounds as anode materials for Li-ion Batteries. Particularly, CoMoS/bio-carbon composites, hollow MnO₂ spheres with a polyaniline coating, and porous iron sulfide/carbon composites were synthesized. Particularly, CoMoS/bio-carbon improved significantly with a ~60% charge capacity at the 200th cycle vs ~10% capacity at the 100th cycle for its control. MnO₂/PANI composite demonstrated a charge capacity of 200% at the 250th cycle vs 5% capacity of its control. For porous iron sulfide/carbon composites, sample 2X increased 30% its capacity from cycle 3 to the 450th, and retained ~65% its initial charge capacity vs ~12% capacity for sample 4X.
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Introduction

Nowadays, our society depends on fossil fuels as the main energy source. However, depletion, price fluctuations and the recent environmental concerns, such as global warming, have led to an exhaustive research to find cleaner and renewable energy resources\(^1\). For example, hydroelectric, wind, solar, and geothermal seem promising alternatives to meet our energy requirements\(^2\). Nevertheless, these energy sources generate electricity intermittently, therefore, an adequate energy storage system is required\(^3\). Here is where electrochemical energy systems play a critical role in sustainability since they can provide power when renewable energy is not available\(^4\).

Among these electrochemical energy storage systems Li-ion batteries (LIBs) has shown promising properties. For instance, Li-ion batteries have higher volumetric (mAh/cm\(^3\)) and gravimetric (mAh/g) capacities and power density over other battery rechargeable systems, such as lead-acid, nickel-cadmium (Ni-Cd) and nickel metal hydride (Ni-MH).

Since their introduction to the market in 1991 by Sony Corporation\(^5\), LIBs have modernized and revolutionized the communication media by making smaller, thinner and lighter electronic devices. However, current LIBs chemistry is still relying on carbon-base materials as the main component of the anode materials but they possess low specific capacities (e.g. 372 mAhg\(^{-1}\) for graphite).

This issue limits the application of LIBs to low power devices such as mobile phones, laptops, and digital cameras. Therefore, the development of advanced anode materials is necessary for the fabrication of competitive performance electric vehicles (EV), hybrid electric vehicles (HEV), smart electric grids\(^6\) and other applications that require higher power and energy density. Consequently, intensive research has been carried out worldwide to find alternative anode materials to replace the currently used graphite.
The general objective of this dissertation is the synthesis of based-transition metal compounds to investigate their electrochemical performance as anode materials for LIBs. Additionally, various strategies are carried out to improve the electrochemical performance of these compounds.


**Literature review**

2.1 **Li-on batteries**

LiBs have been extensively used in electronic devices and are considered the most promising green generation of energy storage technologies applied in EV, HEV because of their many advantages. First, Li has the most negative reduction potential of any element which allows Li-based batteries to hold the highest possible cell voltage potential. Additionally, Li is the third lightest element in the periodic table and owns one of the smallest ionic radii. These features permit Li-based batteries to have high gravimetric and volumetric capacities\(^7\).

![Volumetric and gravimetric densities of Li-ion battery compared with other type of secondary batteries\(^8\).](image-url)
A typical Li-ion battery mainly consists of a positive electrode or cathode made of layered LiCoO$_2$, the negative electrode or anode usually made of graphite, a polymer separator and electrolyte. The choice of the electrodes depends upon their electrochemical potential values ($\mu_A$ for the anode and $\mu_C$ for the cathode) as well as their positions relative to the HOMO-LUMO energy gap ($E_g$) of the electrolyte. In order to have a stable cell, $\mu_A$ must be lower in energy than the LUMO of the electrolyte to avoid the reduction of the electrolyte. On the other hand, $\mu_C$ has to be higher in energy than the HOMO of the electrolyte, otherwise the electrolyte will be oxidized$^9$, figure 2.

The electrolyte is typically a lithium salt (e.g., LiPF$_6$, LiBF$_4$, LiClO$_4$) dissolved in an organic solvent such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate$^{10}$. The electrolyte allows the movement of Li-ions between the electrodes, but at the same time works as an insulator for electrons. The electrons move between the electrodes by an external circuit. When the battery is charging, Li-ions, formed in the lithium metal oxide cathode, migrate to the anode through the electrolyte. During this Li-ion formation, the metal in the lithium metal oxide is reduced and the associated electrons are collected by the current collector (usually made of copper for anode). Frequently, a separator (porous membrane) is placed between the two electrodes to avoid a short circuit inside the battery but at the same time to allow diffusion of lithium ions. At this point, when the battery is charged, the Li-ions are stored on the anode as potential energy or voltage potential. When the battery starts to discharge, the lithium ions are transferred back to the cathode via the electrolyte, while the associated electrons are transferred through the current collector to generate power; current collectors are usually composed of aluminum for the cathode and copper for the anode. The half and overall reactions are shown in equations 1, 2 and 3, respectively.
Figure 2. Relative energy diagram of electrode potentials and electrolyte energy gap in LIBs (a) and diagram of lithium intercalation mechanism in LIBs (b). From reference⁹.

\[
\text{Cathode: } \text{LiCoO}_2 \leftrightarrow L_i,\text{CoO}_2 + x\text{Li}^+ + xe^- \quad (1)
\]

\[
\text{Anode: } 6\text{C} + x\text{Li}^+ + xe^- \leftrightarrow L_i,\text{C}_6 \quad (2)
\]

\[
\text{Overall reaction: } \text{LiCoO}_2 + C_6 \leftrightarrow L_i,\text{CoO}_2 + L_i,\text{C}_6 \quad (3)
\]

2.1.1 Battery Definitions

- **Battery:** A battery is the generic name for a unit that creates electrical energy from stored chemical energy. Strictly it consists of two or more cells connected in an appropriate series / parallel arrangement to provide the required operating voltage and capacity to meet its operating requirements. The term battery is also frequently used to refer to a unit consisting of a single cell, especially when it contains a battery management circuitry.

- **Capacity:** The capacity of a battery or cell is defined as the amount of energy that it can deliver in a single discharge. Battery capacity is normally specified in amp-hours (or milli-amp-hours) or as watt-hours.
- **Cell:** The definition of the cell is the basic electrochemical unit that is used to create electrical energy from stored chemical energy or to store electrical energy in the form of chemical energy. A basic cell consists of two electrodes with an electrolyte between them.

- **Charge rate or C-rate:** The definition of the charge rate or C-rate of a battery or cell is the charge or discharge current in Amperes as a proportion of the rated capacity in Ah. For example, in the case of a 500 mAh battery, a C/2 rate is 250 mA and a 2C rate would be 1 A.

- **Constant-Current Charge:** This refers to a charging process where the level of current is maintained at a constant level regardless of the voltage of the battery or cell.

- **Constant-Voltage Charge:** This definition refers to a charging process in which the voltage applied to a battery is held at a constant value over the charge cycle regardless of the current drawn.

- **Coulombic Efficiency (CE):** The ratio of the output of charge by a battery to the input of charge, Coulombic efficiency is determined by the internal resistance of a cell.

- **Current Density:** The current that is applied (or withdrawn in the case of discharge) to the battery by weight (units A/g or mA/g).

- **Cycle:** One sequence of charge and discharge.

- **Cycle Life:** The capacity of a rechargeable cell or battery changes over its life. The definition of the battery life or cycle life of a battery is number of cycles that a cell or battery can be charged and discharged under specific conditions, before the available capacity falls to a specific performance criteria - normally 80% of the rated capacity.

- **Cut-off voltage:** As a battery or cell is discharged it has a voltage curve that it follows - the voltage generally falling over the discharge cycle. The definition for a cell or battery of the cut-
off voltage cell or battery is the voltage at which the discharge is terminated by any battery management system. This point may also be referred to as the End-of-Discharge voltage.

- **Deep Cycle:** A charge discharge cycle in which the discharge is continued until the battery is fully discharged. This is normally take to be the point at which it reaches its cut-off voltage, typically 80% discharge.

- **Electrode:** The electrodes are the basic elements within an electrochemical cell. There are two in each cell: one positive and one negative electrode. The cell voltage is determined by the voltage difference between the positive and the negative electrode.

- **Electrolyte:** The electrolyte is the medium that provides the conduction of ions between the positive and negative electrodes of a cell, usually a liquid solvent.

- **Energy Density:** The volumetric energy storage density of a battery, expressed in Watt-hours per liter (Wh/l).

- **Power Density:** The volumetric power density of a battery, expressed in Watts per liter (W/l).

- **Rated Capacity:** Rated capacity or the nominal of capacity a battery (in Ah) is defined as the maximum Ah a fully charged battery can deliver under certain specified conditions.

- **Self-Discharge:** It is found that batteries and cells will lose their charge over a period of time, and need re-charging. This self-discharge is normal, but varies according to a number of variables including the technology used and the conditions. Self-discharge is defined as the recoverable loss of capacity of a cell or battery. The figure is normally expressed in a percentage of the rated capacity lost per month and at a given temperature. The self-discharge rate of a battery or cell is very dependent upon the temperature.

- **Separator:** This battery terminology is used to define the membrane that is required within a cell to prevent the anode and cathode shorting together. With cells being made more compact,
the space between the anode and cathode becomes much smaller and as a result the two electrodes could short together causing a catastrophic and possibly explosive reaction. The separator is an ion-permeable, electronically non-conductive material or spacer that is placed between the anode and cathode.

- **Specific Capacity**: Specific capacity, or gravimetric capacity density, defines battery capacity in weight (mAh/g); volumetric capacity density, reflects volume in liters (mAh/l).

- **Specific Energy**: The gravimetric energy storage density of a battery, expressed in Watt-hours per kilogram (Wh/kg).

- **Specific Power**: The specific power for a battery is the gravimetric power density expressed in Watts per kilogram (W/kg).

### 2.1.2 SEI formation

Solid electrolyte interphase (SEI) results from the irreversible electrochemical decomposition of the electrolyte. SEI is a solid layer that is formed at the surface of the negative electrode (anode) because of the instability of common electrolytes at the operating voltage.

Carbonaceous electrodes consists of many different materials including LiF, Li$_2$CO$_3$, LiCO$_2$-R, Li$_2$O, lithium alkoxides, nonconductive polymers and more. Based on x-ray photoelectron spectroscopy (XPS) measurements, SEI consists of several layers. Close to the lithium or LiC$_6$ the SEI consists of thermodynamically stable anions, such as O$^{2-}$, S$^{2-}$, and halides. Close to the solution the SEI also contains partially reduced materials such as polyolefins, semicarbonates, etc. These materials form simultaneously and precipitate on the electrode as a mosaic of microphases. These phases may, under certain conditions, form separate layers, but generally it is more appropriate to treat them as heteropoly microphases $^{11-15}$, see figure 3.
If the SEI layer is formed correctly, it works as a passivation layer to impede the further electrolyte decomposition. However, this film leads to a noticeable loss of capacity mainly in the first cycle since Li ions are consumed on the formation of the SEI during the battery’s first discharge. See figure 4. The suitable formation of SEI film is essential to the performance of LIBs since it has an effect on the capacity loss, cycle life, rate capability and safety characteristics of the battery. Therefore, a well formed SEI should be thin, mechanically stable, cover the entire surface of the anode as well as good adhesion to it.16,17
Figure 4. SEI live formation on a HOPG surface, during electrochemical potential sweep\textsuperscript{14}.

### 2.1.3 Cathode materials

Practical Li-ion batteries are based on intercalation compounds, also called insertion compounds for the cathode\textsuperscript{18}. An intercalation cathode is a solid host system which has the ability of storing guest ions. In Li ion batteries the guest is Li$^+$ ion and can be inserted and remove reversibly from the guest system. The host system compounds are metal chalcogenides, transition metal oxides and polyanion compounds. These compounds can be divided into various structures, such as layered (e.g., LiCoO$_2$), olivine (e.g., LiFePO$_4$), spinel (e.g., LiMn$_2$O$_4$) and favorite (e.g., LiFeSO$_4$F), see figure 5. Currently, intercalation cathode research is mainly focused on transition metal oxide and polyanion compounds due to their higher operating voltage window (3-5 V vs. Li$^+$/Li) and specific capacity (100-200 mAh/g)\textsuperscript{7}.
Anode materials

Typically, a commercial anode of a LIB is made of carbonaceous materials because of the flat voltage versus lithium, as well as a good structural stability during the cycling process. Nevertheless, to accommodate only one lithium ion, six carbon atoms are required. This results in low specific capacity for graphite\textsuperscript{20} of 372 mAh/g. This issue limits the utilization of carbonaceous materials as anode for LIBs applications where high capacity is essential as in the case of hybrid electrical vehicles (HEV), plug-in hybrids, and all-electric vehicles. Further information is presented in intercalation/de-intercalation pf anode materials.

In the search for new anode materials, diverse materials have been investigated. This compounds can be categorized in three main groups, according to their reaction mechanism: conversion materials, intercalation/de-intercalation (insertion/de-insertion) materials, and alloy-de-alloy materials.\textsuperscript{6}
2.1.4.1 Conversion anode materials

Conversion anode materials include transition metal oxides, such as Mn$_x$O$_y$, Fe$_x$O$_y$, CuO, Cu$_2$O, MoO$_2$ etc., metal sulfides, metal phosphides and metal nitrides (MX; where X=S,P,N). Several transition metal compounds exhibit conversion mechanism. According to eqn. (4), in the system MO, the metal oxide compound is reduced to its metallic state and Li$^+$ reacts with the oxygen part of the compound to form Lithium oxide (Li$_2$O) at the first lithiation which then returns to its initial state after delithiation, see figure 6. The number of electrons involved in the conversion mechanism depends on the oxidation state of the transition metal, which is usually more than one electron transferred per transition metal ion, in contrast to 0.5-1.0 for intercalation compounds.

The opportunity of using several oxidation states of transition metal leads to high specific capacities and high energy densities. Nevertheless, the conversion reaction mechanism presents some drawbacks. For example, the compounds with this mechanism exhibit low Columbic efficiency at the first cycle, unstable SEI film formation, large potential hysteresis and poor capacity retention.$^{21,22}$

Conversion reaction mechanism:

$$M_aX_b + 2bLi^+ + 2be^- \leftrightarrow aM + bLi_2X \quad (4)$$
Transition metal dichalcogenides with general formula MX\(_2\), where M= Mo, Ti, W, Nb, etc., X= S, Te, Se, have been deeply studied as electrode materials for lithium ion batteries due to the intrinsic property that they can host a diversity of guest atoms or molecules to form intercalation compounds. Among these materials, MoS\(_2\) have shown great interest because of the high specific theoretical capacity value (669 mAh/g).\(^{23,24}\) MoS\(_2\) possess a layer structure in which two sulfur atoms are linked to one molybdenum atom by covalent bonds within the plane whereas single layers are bound by weak van der Waals interactions, showing an analogous structure to graphite. It is this weak bond between single layers that makes MoS\(_2\) as an attractive material for LIBs anode. It can be easily broken to allow the intercalation of Li ions without a significant increase in volume expansion.
The reaction mechanism in LIBs for MoS$_2$ within the window potential of 3.0-1.1 V is governed by insertion reaction mechanism. Where Li ions are intercalated between the MoS$_2$ layers forming Li$_x$MoS$_2$ compound as directed in eqn. (5), whereas from 1.1-0 V is not well understood, despite several years of research. There are several studies$^{23,25-27}$ which claim that the mechanism within this voltage range is directed by the conversion reaction, where Li$_x$MoS$_2$ compound formed is converted into Li$_2$S and metallic molybdenum which is attributed to the plateau voltage around 0.5 V (eqn. 6).

\[
\begin{align*}
\text{MoS}_2 + x\text{Li}^+ + xe^- & \rightarrow \text{Li}_x\text{MoS}_2 \\
\text{Li}_x\text{MoS}_2 + (4 - x)\text{Li}^+ + (4 - x)e^- & \rightarrow \text{Li}_2\text{S} + \text{Mo}
\end{align*}
\] (5) (6)

**Cobalt Sulfides**

Cobalt sulfides (Co$_x$S$_y$) with different stoichiometric compositions, such as CoS$_2$, Co$_3$S$_4$, CoS, and Co$_9$S$_8$ are the most important type of metal chalcogenides.$^{28}$ They have shown great potential as anode materials for LIBs due to their good thermal stability, and high theoretical capacity.$^{29}$ For example, Co$_3$S$_4$ phase has theoretical capacity of $\sim 702 \text{ mAh/g}$. The reaction mechanism for cobalt sulfides is governed by the conversion mechanism (eq. 7).$^{31}$

\[
\begin{align*}
M^{n+}(X) + ne^- + n\text{Li}^+ & \leftrightarrow M^0 + n\text{Li}(X) \\
(X=S, O)
\end{align*}
\] (7)
Manganese Oxides (MnₙOₙ)

Manganese oxides, including MnO, Mn₃O₄, Mn₂O₃ and MnO₂ have been studied as alternative anode materials for LIBs because of their high theoretical capacities (756, 937, 1018, and 1232 mAh g⁻¹, respectively), low cost and environmentally benign natures. The Li storage behavior for most transition metal oxides is controlled by conversion reaction mechanism. However, for MnₓOᵧ compounds the reaction mechanism is not yet well understood. If the conversion reaction mechanism also works for MnₓOᵧ compounds it can be described as follows:

\[
\begin{align*}
MnO + 2Li^+ + 2e^- & \leftrightarrow Li_2O + Mn & \text{(for MnO)} \quad (8) \\
MnO_2 + 4Li^+ + 4e^- & \leftrightarrow 2Li_2O + Mn & \text{(for MnO}_2) \quad (9)
\end{align*}
\]

Iron Oxides

Iron oxides have been extensively studied as anode materials for LIBs because of their low cost, non-toxicity and high abundance. The main two phases of iron oxide, hematite (Fe₂O₃) and magnetite (Fe₃O₄) both show conversion reaction mechanisms (eqns. 10 and 11, respectively) and have high theoretical capacities (1007 and 926 mAh g⁻¹, respectively). However, LIBs comprised of iron oxides based anode materials are still far from commercialization due to several drawbacks, such as low electrical conductivity, low diffusion of Li-ions, high volume expansion/contraction and iron aggregation during charging and discharging.

\[
\begin{align*}
Fe_2O_3 + 6Li^+ + 6e^- & \leftrightarrow 3Li_2O + 2Fe & \quad (10) \\
Fe_3O_4 + 8Li^+ + 8e^- & \leftrightarrow 4Li_2O + 3Fe & \quad (11)
\end{align*}
\]
2.1.4.2 Intercalation/de-intercalation (insertion/de-insertion) anode materials

The materials for this group are classified in two main subgroups; carbonaceous materials (hard carbons, CNTS and graphene) and Titanium Oxides (LiTi$_4$O$_5$ and TiO$_2$). The mechanism in these materials involves the intercalation/de-intercalation of Li ions into/from a solid host without a significant change of the host structure $^{36}$, figure 8. The materials driven by this mechanism are attractive anode materials for rechargeable LIBs due to their low price and non-toxicity $^{21}$. The number of electrons involved in the insertion reaction is generally less than one per Li. Therefore, these materials have low specific capacity. Carbon and titanates (MOx where M= Ti) are the most common examples of insertion reaction materials. Graphite is the most used anode material in commercialized LIBs. The crystal structure of graphite is characterized by a stack of hexagonally sheets bonded together by van der Waals forces. The adjacent carbons in the same sheet are joined together by stronger bonds (sp$^2$ hybridized bonds) than carbon between the sheets. This characteristic makes graphite a suitable candidate for lithium intercalation between the planes or sheets. However, lithium ions can only combine with every second carbon hexagon in the graphite sheet which means that only one lithium ion can be inserted by 6 carbon atoms, figure 9. This fact leads to a low theoretical capacity of 372 mAh$^{-1}$ for graphite in LIBS.$^{37}$

Insertion reaction mechanism:

$$MO_x + yLi^+ + ye^- \leftrightarrow Li_yMO_x \quad Titanates \quad (12)$$

$$xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6 \quad Graphite \quad (13)$$
2.1.4.3 Alloy-de-alloy anode materials

Several elements M (M= Si, Sb, Ge, Bi, Sn, As, Pt, Ag, Au, Zn, Cd, Hg, Al, Ca, Mg, Pb, etc.) can form alloys with lithium(Li$_x$M) as is described in equation 14. 38. These materials exhibit high specific capacity (783–4211 mAh/g)\(^6\) by transferring multi-electrons. However, the major drawbacks are poor cycling life due to the high volume expansion/contraction and large irreversible capacity at the first cycles, figure 10. For example, silicon delivers a theoretical specific capacity of 4211 mAh/g\(^39\) but during the charging/discharging process the volume of the active material expands/contracts dramatically (over 300 %), leading to the pulverization of the electrode.
as well as the loss of the electronic interparticle contact and as a consequence failure of the battery in only few cycles.  

Li-alloy reaction mechanism:

\[
M + xLi^+ + xe^- \leftrightarrow Li_xM
\]  

2.1.5 Electrochemical measurements for LIBs

There are several techniques to evaluate the electrochemical performance of new electrodes for LIBs. In this project are described the most common methods that also form part of the characterization carried out in this research.

2.1.5.1 Galvanostatic measurements

This method measures the amount of charge stored within the electrodes under different experimental conditions, such as voltage window, current density along several cycles. With this technique the specific capacity, voltage profiles, rate capability, cycle life can be determined.

The charge behavior of a battery starts by applying a constant current density. The current density is held until the cut-off potential is reached. The current density is usually expressed in mAg\(^{-1}\), where the mass corresponds to the active material. Alternatively, the current density can be
measure in terms of C rate value, where 1 C is the theoretical amount of charge that can be extracted from a given material within one hour.

The voltage window, also called cut-off potential, is determined from the materials redox peak range to avoid side reactions like electrolyte decomposition. The ratio between the amounts of charge stored during the discharging/charging process is known as cycling Coulombic efficiency and indicates the reversibility of electrochemical process. Additional information can be obtained from galvanostatic measurements. For example, if the C-rate is held constant for several cycles, cycling life and cycling stability can be determined. On the other hand, if the battery is charged/discharged at different C-rates over several cycles, information about rate capability and the kinetics of the active material can be obtained. The performance of the anode material tends to decrease as the C-rate increases, this due to the higher C-rates reduces the time for lithium ions to diffuse deep into the material\textsuperscript{41}. Thus, reducing the capacity of the battery.

2.1.5.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) also known as AC impedance spectroscopy is a technique used to analyze the condition of a battery as well as the electrochemical behavior in the cell. Battery impedance is measured by applying a small AC potential to an electrochemical cell, where the analysis measures the internal dynamic response of the battery along a wide range of frequencies, usually from 1 mHz to 10 KHz. It is important to understand that a battery is a nonlinear, time-invariant system. Thus it needs enough resting time to reach electrochemical equilibrium\textsuperscript{42,43}. The battery’s frequency response, reveals the total impedance which constitutes the result of the following resistive components: Ionic transport resistance in the electrolyte. Charge transfer in the SEI layer. Solid-state diffusion of lithium ions into the solid electrode, known as mass transfer\textsuperscript{44,45}.
In figure 11 a, the X-axis represents the battery’s impedance (Re) and the Y-axis the imaginary impedance (Im). There are three main parts in a Nyquist plot over the full frequency range: (1) The low frequency range (1 mHz-1 Hz) in which a straight line at 45° is shown and it is attributed to the diffusion of lithium ions within the electrodes Zw, known as the Warburg slope. (2) Middle-high frequency range (1 Hz-10 KHz), where a semi-circle appears and it is attributed to the charge transfer resistance (Rct), porosity of the electrodes, and the double-layer effect of the electrode/electrolyte SEI interface (Cdl). (3) High frequency range >1 KHz, where a flat line appears and it is attributed to the battery’s ohmic resistance (Rs). The Nyquist plot is then analyzed with a matching electrical equivalent circuit (EEC), figure 11 b. With a matching ECC, it is possible to calculate the individual electrochemical components of the battery Rs, Rct, Cdl, and Zw.
2.1.5.3 Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a powerful and common electrochemical technique frequently used to investigate the reduction and oxidation processes of molecular species. A CV setup consists of a potentiostat, an electrochemical cell, a current-voltage converter and a data acquisition system. The electrochemical cell consists of an electrolytic solution as well as three electrode arrangement; the working electrode, counter electrode and the reference electrode\textsuperscript{47}, see figure 12.

The counter electrode (CE) is used to close the current circuit in the electrochemical cell. It does not participate in the electrochemical reaction and it is frequently made of inert materials, such as Pt, Au, graphite, glassy carbon, etc. The reference electrode (RE) has a constant and well-known potential and it is used as a reference point in the electrochemical cell for potential control and measurement. The working electrode (WE) is where the reaction of interest is occurring and the potential at this electrode is fluctuated linearly with time. The electrolytic solution provides ions to the electrodes during the oxidation-reduction reactions. As current is flowing between the WE and CE, it is important to have a higher surface area in the CE than that of the WE so that it will not be a limiting factor in the kinetics of the electrochemical reactions under investigation\textsuperscript{48}.

![Electrochemical cell diagram](image)
To analyze the WE a potentiostat produces a voltage differential with the equipment and the tested cell. Depending of the anodic or cathodic sweep, current is drawn into and out of the system. The data acquisition system collects and plots the data, resulting in a plot of current versus voltage.

The experimental CV is obtained by sweeping a fixed voltage potential per time (V/s) between two voltage values, $V_1$ and $V_2$. The initial cathodic trace is obtained from $A$ to $D$, where the potential is swept negatively from $V_1$ to $V_2$. The anodic trace is obtained when the scan direction is reversed from $D$ to $G$ and the potential $V_2$ is swept back to $V_1$. This triangular wave form represents one cycle and it can be repeated as many times are needed. A typical excitation signal is displayed in figure 13.

![Figure 13. Cyclic voltammetry excitation signal.](image-url)
The data acquisition system then collects and plots the data. As a result, a plot of current versus applied voltage is obtained and a cyclic voltammogram\textsuperscript{49} is produced, see figure 14. The current measured at the cathodic trace is known as the cathodic current ($I_{pc}$) and the current at the anodic trace is known as the anodic current ($I_{ap}$). During the cathodic sweep, the analyte is reduced and an increment in the current is observed at the cathodic peak potential ($E_{pc}$); this occurs at point C in figure 13. Shortly after, the current decreases as the concentration of reducible analyte is depleted; this process occurs from points $C$ to $D$ from figure 13. At the anodic sweep, the potential is scanned in the positive anodic direction where the analyte is re-oxidized if the reaction is reversible; points $D$ to $G$ in figure 13. The analyte oxidation is appreciated by the raise in current at the anodic potential peak ($E_{pa}$); point $F$ in figure 13\textsuperscript{50}.

![Cyclic voltammogram](image)

**Figure 14. Cyclic voltammogram.**
2.1.6 Electrode preparation and battery assembly

A battery half-cell is prepared by mixing active anode material with acetylene black and sodium carboxymethyl cellulose dissolved in deionized water (3 wt %) as binder. The materials are mixed with a mass ratio of 70:15:15, respectively. The obtained slurry is then coated onto a copper foil, using a wet film applicator rod and dried overnight under vacuum at 100°C. The battery’s electrodes are then cut with a diameter of 1.3 cm using a precision disc cutter. The process and anode materials used are further explained afterwards on the experimental section of the following chapters.

Figure 15. Electrode fabrication schematic
The coin cells (CR 2032) are then assembled inside an Argon filled glovebox with oxygen levels maintained below 0.1 ppm. Lithium foil is used as the counter/reference electrode, a ceramic-coated membrane is used as the separator, and 1.0 M LiPF6 inethylene carbonate/dimethyl carbonate (1:1 in volume) as electrolyte. The necessary springs and spacers are added to insure accurate material contact with the current collectors and the coin cell. The battery components are illustrated below, see figure 16. See appendix, section 8.1 for further assembly details.
Bimetallic CoMoS composite anchored to bio-carbon fibers as a high-capacity anode for Li-ion batteries

3.1 Introduction

To date, Li-ion batteries (LIBs) have been widely utilized for portable electronic devices due to their promising properties, including high energy density, long cycle lifetime, and low self-discharge. However, to meet nowadays energy demands for high power applications, as in the case of electric vehicles and smart grid systems, it is essential to find new anode materials with higher rate capacity, longer cycling lifetime and higher capacity to that of graphite (372 mAh\(^{-1}\))\(^{52}\), the anode material currently used for commercially available LIBs.

Recently, transition metal sulfides have reached great attention as anode materials for LIBs because of their high theoretical capacity\(^{53-55}\). For example, molybdenum sulfide (MoS\(_2\)) has a theoretical capacity value of 670 mA h/g\(^{25,56}\) (almost twice that of graphite). Additionally, MoS\(_2\) holds a layer structure that enables easy intercalation of Li ions within the (002) planes, hence proving a fast diffusion of ions during electrochemical processes\(^{57,58}\). However, this material suffers from low electric conductivity as well as poor cycling stability because of its inherent high volume change during the charging/discharging steps\(^{57}\). On the other hand, cobalt sulfides with different compositions (CoS\(_2\), CoS, and Co\(_9\)S\(_8\)) have shown encouraging results as anode materials for LIBs\(^{59-63}\). Moreover, cobalt sulfides possess higher electrical conductivity compared to other metal sulfides\(^{64,65}\) but also suffers from rapid capacity decay\(^{66}\).

Composites of MoS\(_2\) and cobalt sulfides, as well as CoMoS phases, have been investigated for other applications, including, catalysis in hydrodeoxygenation\(^{67,68}\), hydrodesulfurization\(^{57,69}\), and hydrogen evolution reaction\(^{70-73}\) among others. However, only a few reports of the combination
of molybdenum and cobalt sulfides for its application in LIBs have been reported\textsuperscript{58,74}. The combination of these two metal (Mo and Co) sulfides can offer synergistic advantages over single systems as it has been reported for other bimetallic sulfides for sodium-ion battery applications\textsuperscript{75,76}. Additionally, to improve the electrochemical performance of LIBs, transition metal compounds have been combined with carbon-based materials such as reduced graphene\textsuperscript{77,78} and carbon nanotubes,\textsuperscript{79,80} both of which are expensive materials and require elaborate methods for fabrication. On the other hand, promising results for LIB applications have been achieved from the combination of transition metal compounds and biomass-derived carbon\textsuperscript{81–83}. The use of biomass represents an easy and low-cost alternative to enhance the electrochemical performance of LIBs. Here, we present the synthesis of a bimetallic CoMoS composite by the hydrothermal method and the addition of cellulose fibers as a carbon source, followed by carbonization under argon atmosphere (CoMoS@C). The CoMoS@C composite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). To investigate its electrochemical properties as an anode material for LIBs, galvanostatic, cyclic voltammetry (CV), and electrochemical impedance spectroscopy measurements (EIS) were performed. The addition of carbon significantly enhanced the cycling stability retained a high specific capacity of $\sim$715 mA h/g after 200 cycles at a rate of 500 mA h/g compared to bare-CoMoS which retained $\sim$102 mA h/g after 100 cycles.

3.2 Experimental Section

Synthesis of CoMoS: The synthesis of CoMoS (cobalt–molybdenum sulfide) was carried out by hydro-thermal method in a high-pressure reactor (Par model 4540). The first step consisted the synthesis of ammoniumthiomolybdate (ATM) that was synthesized following the improved
method by Alonso et al. Next, ATM (19.2 mmol) was dispersed in a minimum amount of deionized water under constant stirring, followed by the addition of an equivalent molar amount (19.2 mmol) of NTA (nitriloacetic acid, Sigma-Aldrich) to this dispersion under stirring. Separately, 13.5 mmol of CoNO₃·6H₂O (Sigma-Aldrich) was dissolved in a minimum amount of deionized water and added to the ATM/NTA mixture. The reaction mixture was transferred to the reactor vessel and heated to 300°C for 2 h. It is important to mention that the pressure inside the reactor increased to 1200 PSI when the reaction reached 300°C

**Synthesis of CoMoS@Carbon:** First, 100 mg of CoMoS and 57 mg of medium-size cellulose fibers (cotton linters from Sigma-Aldrich) were placed in a vial and agitated for 5 min at 3000 rpm in a vortex machine. This mixture was placed in a ceramic boat, introduced into a tubular furnace (MTI Corporation, GSL-1100X-LD), and heated at 400°C for 1 h at a heating rate of 5°C/min under argon atmosphere. This sample was referred as CoMoS@C. For comparison purposes, CoMoS by itself was thermally treated under the same conditions and labeled as bare-CoMoS

**Characterization.** XRD (X-Ray Diffraction) measurements were performed on a D8 diffractometer from Bruker instruments (Cu Kα radiation, λ = 0.154 nm) with a scan rate of two degree/min. SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) images were obtained by using a Hitachi S-4800 machine. TEM (Transmission Electron Microscopy) images were acquired by a Hitachi H-7650 equipment. Image J software was used to measure the sizes of the particles and carbonized cellulose fibers from SEM images.

**Electrochemical measurements:** The working electrodes were prepared by mixing the active material (CoMoS@C), acetylene black, and a binder composed of sodium carboxymethyl cellulose dissolved in deionized water (3 wt %) in a weight ratio percentage of 70:15:15, respectively. The obtained slurry was then coated onto a copper foil and dried overnight under vacuum at 100°C.
The electrodes were cut with a diameter of 1.3 cm using a precision disc cutter from MTI Corporation. The coin cells (CR 2032) were assembled inside of an Ar-filled glovebox with oxygen levels maintained below 0.1 ppm. Li foil was used as the counter/reference electrode, a ceramic-coated membrane (16μm thick) from MTI Corporation was utilized as the separator (EQ-bsf-0016-500A), and the electrolyte employed was 1.0 M LiPF6inethylene carbonate/dimethyl carbonate (1:1 in volume) from Sigma-Aldrich. The specific capacity was calculated based on the active material weight. The galvanostatic charge/discharge measurements were performed in an eight-channel battery analyzer (MTI Corporation) with a voltage window of 0.01–3V. The EIS and CV studies were conducted in a CHI760D electrochemical workstation. EIS was measured in coin cells in a frequency range of 0.01−100 000 Hz at an ac amplitude of 0.05 V. The CV was evaluated in a three-electrode setup using an electrochemical cell (990-00343) from Gamry Instruments within the range of 3.0–0.01 V at a scan rate of 0.01 V.

3.3 Results and Discussion

3.3.1 Characterization

The crystal structures of CoMoS (before heat treatment), bare-CoMoS, and CoMoS@C were characterized by XRD, shown in figure17 b, c, and d curves. Most of the peaks from the three samples match the CoMoS4 phase registered in the COD (Crystallographic Open Database) no. 2106690, figure 17 a. However, bare-CoMoS and CoMoS@C X-ray spectrums, figure 1 c and d, show additional peaks corresponding to MoO3 and CoMoO4 phases with COD numbers 1011043 and 7205001, respectively.
We can see that most of the peaks corresponding to the oxide phases appeared after the compounds were subjected to heat treatment at 400°C. Therefore, these peaks were most likely formed by the accidental air exposure while the carbonization process was carried out. Additionally, bare-CoMoS and CoMoS@C presented similar XRD patterns. Nevertheless, bare-CoMoS displays sharper peaks than those found in CoMoS@C, figure 18, which shows broader peaks possibly because of the poorly crystalline nature of the carbonized cellulose fibers.
Figure 18. XRD patterns of carbonized cellulose fibers.

The SEM micrographs of three samples are presented in figures 19-24. Micron-sized particle clusters for the bare-CoMoS sample can be observed in figure 19. An elongated ribbon like morphology can be observed for cellulose fibers carbonized at 400°C for 1 h with diameter sizes ranging from 5 to 22 μm with an average size of ~10μm in figure 20. For sample CoMoS@C, carbonized cellulose fibers, with less than 10μm in diameter size, are decorated with CoMoS particle clusters with less than one micron in size, figure 21. However, there are larger CoMoS particle clusters standing apart from the fibers. A higher magnification image shows an individual microfiber with particle clusters anchored to its surface with diameter sizes ranging from 0.3 to 2 μm, figure 22. A seemingly uniform particle distribution was observed along the fiber.
Figure 19. SEM of CoMoS control image heat treated at 400°C.

Figure 20. SEM of cellulose fibers carbonized at 400 °C for 1 h
Figure 21. SEM of CoMoS/cellulose fibers composite carbonized at 400 °C for 1h.

Figure 22. SEM of CoMoS/cellulose fibers composite carbonized at 400 °C for 1h.
A more detailed perspective of the morphology can be appreciated in TEM images of bare-CoMoS and CoMoS@C, figure 23 and 24 respectively. Aggregates of nanosheets can be observed for both materials with no significant differences between the two samples, thus the material is preserved in CoMoS carbon fiber composite. Carbon micro fibers cannot be observed in image 24 due to the carbon fibers large size which completely blocks transmitted electrons.

Figure 23. TEM image of CoMoS heat treated at 400°C.
To obtain information about the chemical composition of the samples, EDS analysis was performed. Figure 25-a shows the SEM selected area of CoMoS@C for EDS analysis, the selected area is composed of both CoMoS particles and carbon fibers. The EDS spectrum of CoMoS@C confirms the sample composition of Mo, S, Co, and C elements, as well as some amount of oxygen coming from the carbonized cellulose fibers, figures 25-f and 26. From the elemental mapping images 25-b to 25-e, a homogeneous distribution of all the elements can be observed.
Figure 25. a) SEM image selected area for sample CoMoS@C, (b)-(e) elemental mapping images of C, S, Co and Mo. f) The EDS spectrum of CoMoS@C, elements detected are S, Mo, C, Co.

Figure 26. EDS spectrum of carbonized cellulose fibers, first and second peaks corresponds to carbon and oxygen, respectively. No other elements were detected.
To quantify carbon amount in CoMoS@C, TGA was performed from room temperature to 1000 °C under air atmosphere. The TGA curves of carbon fibers showed a large reduction of weight from 100 to 8% starting from ~ 350 °C up until 550 °C, figure 27. Afterward, the sample weight kept nearly constant up until 1000°C. The TGA results from CoMoS@C shows a weight reduction starting at ~350°C, this closely matches the weight loss of the carbon fibers. The CoMoS@C sample plateau at 550°C with 72% leftover weight was caused by the conversion of carbon to CO₂. At temperatures greater than 550°C, the oxidation of organic materials, Mo and Co, took place. Additionally, we can see that the weight drop from ~400 to 500 °C is absent for bare-CoMoS. Therefore, the carbon content in sample CoMoS@C is estimated to be ~28%.

Figure 27. TGA analysis samples CoMoS@C, bare-CoMoS and carbon fibers (cellulose fibers carbonized at 400 °C for 1h).
3.3.2 Electrochemical properties

The electrochemical performance of CoMoS@C was first evaluated by testing the charge/discharge galvanostatic measurements. Figure 28-b displays the 1st, 2nd, 3rd, and 25th cycles at a current density of 100 mA/g between 0.01 and 3 V versus Li+/Li for CoMoS@C sample. For comparison, we also present the charge/discharge results for bare-CoMoS under the same electrochemical conditions, figure 28-a. The discharge capacities for bare-CoMoS were 1043, 575, 519, and 396 mA h/g, respectively. By contrast, CoMoS@C, figure 28-b, showed significantly higher specific capacities of 1461, 925, 839, and 756 mA h/g, respectively. Furthermore, the CoMoS@C composite was evaluated at different discharge rates of 100, 200, 500, and 1000 mA/g, figure 28-c. After 40 cycles, a discharge capacity of ~425 mAh/g was observed. We also investigated the cycling performance of CoMoS@C for 200 cycles at a current rate of 500 mA/g, figure 28-d. CoMoS@C showed an initial high specific capacity of 1165 mA h/g and retained a high specific capacity value of ~715 mA h/g and a CE above 97% after 200 cycles. In contrast, bare-CoMoS maintained a low specific capacity of ~102 mA h/g after 100 cycles.
Figure 28. Charge-discharge voltage profiles at a current rate of 100 mAg⁻¹ for a) CoMoS-400°C and b) CoMoS@C. c) Rate capability of CoMoS@C from 0.1 to 1 Ag⁻¹. d) Cycling performance of CoMoS and CoMoS@C at a current rate of 500 mA/g.

To study the influence of the carbonized fibers in the cycling performance of CoMoS@C, an electrode of carbonized fibers was subjected to charge and discharge measurements for several cycles at a rate of 100 mA/g, figure 29-a and 29-b. The carbon fiber material showed only one discharge and does not have the ability of recharging, probably due to the low carbonization temperature. Therefore, the superior electrochemical performance of the CoMoS@C electrode is due to the synergistic effect of CoMoS and the carbonized fibers. CoMoS contributes to the high specific capacity value and the carbon fibers stabilize the cycling performance of the electrode.
Figure 29. Charging and discharging plots for carbonized cellulose fibers a) first discharge b) 2nd-30th cycles.

To further explore the electrochemical reactions of CoMoS@C and bare-CoMoS electrodes, CV measurements were performed for the first three cycles, and the results are shown in figures 30-a and 31-b, respectively. The first cathodic scan for sample CoMoS@C presents three peaks at 1.61, 0.86V, and another that ranges from $\sim$0.43 to $\sim$0.06 V. For the first anodic scan, only one big peak at $\sim$2.45 V is shown. In the following cycles, the cathodic peak in the range of $\sim$0.43 to 0.06 V disappears, the peak at 0.86 V stays at the same voltage position but the current decreased considerably, and the other peak becomes wider and slightly shifts from 1.61 to 1.69 V. Similarly, the peak at 2.45 V in the subsequent cycles for anodic scans stays in that potential and a new one appears at 1.7 V.
At the first cathodic scan, the peak at 0.86 V can be attributed to the intercalation of Li ions into the lattice of CoMoS₄ (LiₓCoMoS₄), whereas the peak in the range of 0.43–0.06 V can be ascribed to the further reduction of LiₓCoMoS₄ into metallic Mo and Co embedded into a LiS₂ matrix and also to the formation of a gel-like polymer resulting from the irreversible electrolyte degradation. The irreversible degradation is known as the solid electrolyte interface (SEI), as reported by a similar study⁷⁴ and other publications related to the intercalation of Li ions (lithiation) into molybdenum and cobalt sulfides²⁵,⁶¹,⁸⁶–⁸⁹. In the second and third cathodic scans, the peak at 1.69 V can be assigned to the intercalation of Li ions into cobalt and molybdenum sulfides⁵⁵,⁹⁰. In addition, the peak in the range of 0.43–0.06 V disappears. This fact coupled with the big reduction in capacity from the first to the second discharge, charge/discharge curves from figure 30-b, confirms the irreversibility of the SEI formation.

In contrast, the peaks at 1.7 and 2.45 V in the first anodic scan correspond to the conversion reaction of Mo and Co as well as LiS₂ to form molybdenum sulfide and cobalt sulfides, as suggested by some studies⁷⁴,⁹⁰, whereas other studies allude that this latter peak (2.45 V) corresponds to the formation of LiS₂ to S₈⁻².⁹¹ In the subsequent cycles (CoMoS@C), the CV curves almost overlap each other, indicating good reversibility of the electrode. On the other hand, for sample bare-CoMoS, figure 31-b, the redox peak intensity significantly decreases over cycling, indicating poor cycling performance. This result implies that the carbon matrix stabilizes the cycling performance for CoMoS@C electrode as is demonstrated by other studies which used cobalt sulfide and molybdenum sulfide with and without carbon addition⁶¹,⁸⁸,⁹²–⁹⁴.

To have a better understanding of the resistive behavior, electrochemical impedance spectroscopy (EIS) was conducted for bare-CoMoS, CoMoS@C figure 30-b, and carbonized fibers figure 31-a. Figure 30-b shows the raw experimental and fitted Nyquist plots for CoMoS@C and CoMoS (inset
of Figure 30-b) as well as the equivalent circuit used for fitting the plots. The EIS curves for the three electrode materials are composed of a depressed semicircle in the high–medium frequency region and a straight line in the low-frequency region. The high–medium frequency semicircle is composed of $R_s$ (Ohm resistance of the battery) and $R_{ct}$ (charge-transfer resistance). The inclined line represents the Warburg impedance ($W$) caused by the Li ions diffusion.

According to the equivalent circuit, the values for CoMoS and CoMoS@C are 72 and 40 $\Omega$, respectively, and 65 $\Omega$ for carbonized fibers. The charge-transfer resistance ($R_{ct}$) for CoMoS@C is 327 $\Omega$, 827 $\Omega$ for CoMoS, and 596 $\Omega$ for carbonized fibers. The CoMoS@C electrode presented the lowest charge-transfer resistance. Therefore, carbon fibers improved the composite’s electrical conductivity, as demonstrated in the Nyquist plots figure 30-b, as well as buffering the electrode volume changes and preventing the electrode material from pulverization, as previously reported by other publications\textsuperscript{95,96}.

Figure 30. a) Cyclic voltammetry and b) Nyquist plots for CoMoS@C (inset: bare-CoMoS).
Figure 31. a) Nyquist plots for carbon fibers and b) Cyclic voltammetry curves for bare CoMoS.

3.4 Conclusions

In summary, CoMoS@C composite was fabricated by the combination of CoMoS synthesized by hydrothermal method and cellulose fibers carbonized at 400 °C for 1 h. This composite showed significantly improved electrochemical performance when compared to bare-CoMoS. The carbonized bimetallic composite, CoMoS@C, retained a high specific discharge capacity of 715 mA h/g with a CE greater than 97% after 200 cycles at a current rate of 500 mA/g. The high specific discharge capacity and superior cycling stability can be accredited to the synergistic effect between the CoMoS and carbonized cellulose fibers. The use of biomass-derived carbon may offer an easy and cost-effective strategy to improve the electrochemical performance of metal and bimetallic sulfides and other metallic compounds.
Hollow MnO$_2$ microspheres with polyaniline coating as anode material for LIBs.

4.1 Introduction

Since their commercialization, Li ion Batteries (LiBs) have remained as the main rechargeable battery system to power our electronic portable devices and more recently electric vehicles (EVs). To fit the energy demands of the ever-increasing technology, the scientist community has done tremendous efforts to find novel active materials. Particularly, great attention has been paid to the development of better anode materials that can replace the graphitic anode with a low theoretical capacity of 372 mAh/g. Among these materials, transition metal oxides (TMOs), such as MnO$_2$, Iron Oxide (Fe$_2$O$_3$ and Fe$_3$O$_4$) and Co$_3$O$_4$ have been extensively studied because of their high theoretical capacity in comparison with graphite. Specially, MnO$_2$ has shown desirable properties, such as high theoretical capacity (1230 mAh/g), which is the highest value of all the TMOs. In addition, MnO$_2$ is a natural abundant material and environmentally benign. However, MnO$_2$ as anode material for LIBs is still facing rapid capacity fading and poor rate capability due to the volume change during the charge/discharge process as well as the lack of electrical conductivity.

Several approaches have been used to address these problems. For example, composites of MnO$_2$ and carbonaceous materials have been synthesized. The carbon material has a dual role, it works as a volume buffer to overcome the expansion/contraction of the active material while lithium uptake/release and as a conductive network to increase the electrical conductivity. On the other hand, hollow structures have demonstrated also good results when tested as anode materials for LIBs.
The use of conducting polymers (CPs) have shown great improvement in the performance of LIBs\textsuperscript{117–119}. Among them, polyaniline (PANI) is considered as one of the most promising CPs due to its facile synthesis, good electronic conductivity, low cost, environmental stability and forms a stable SEI film\textsuperscript{120–123}. A good SEI layer should prevent further electrolyte degradation by blocking the electron transport while allowing lithium ions to pass through it during cycling\textsuperscript{124,125}.

Herein, we propose a hierarchical assembly of hollow MnO\textsubscript{2} microspheres synthetized by templating of carbon spheres, the following removal of carbon core and finally a PANI coating to improve electronic conductivity.

4.2 Experimental Section

**Preparation of carbon spheres.** For the preparation of carbon spheres, 20.54 g (0.06 moles) of sucrose were dissolved in 60 ml of deionized water and then magnetically stirred until a clear solution is formed. Next, this solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and maintained at 180 ℃ for 9 h. The precipitate was collected and washed with deionized water and ethanol several times. Finally, the product was dried in a vacuum oven at 80 ℃ overnight.

**Preparation of hollow MnO\textsubscript{2} microspheres:** The hollow MnO\textsubscript{2} microspheres were prepared following this study\textsuperscript{126} with some variations. Firstly, 168 mg (14 mmol) of the as-prepared carbon microspheres were dispersed into distilled water (80 mL) by ultrasound for 30 min. The pH of the solution was adjusted to 2.5 by HCl. Then, 442.5 mg (2.8 mmol) of KMnO\textsubscript{4} was added into the solution. After stirring for 2 min, the solution was transferred into a Teflon-lined autoclave. The autoclave was sealed and then heated to 100 ℃ for 45 min in an electric oven. After that, it was naturally cooled to room temperature. The product, was collected by centrifugation, washed with
distilled water and ethanol several times, and then dried in vacuum at 70 °C for several hours. Then, the resultant brown powder was treated in air at 300 °C for 10 h to remove carbon.

**Preparation of MnO$_2$/PANI composite:** To prepare MnO$_2$/PANI composite 0.4 g of the hollow MnO$_2$ microspheres were ultrasonically dispersed in 40 mL of 0.1 M hydrochloric acid for 15 minutes. Then, the dispersion was placed in an ice bath until it was cooled down below 5 °C. Next, 82 µl of aniline monomer was added under constant magnetic stirring. Separately, 88 mg of APS (ammonium persulfate) was dissolved in 20 mL of 0.1 M HCl solution and then sonicated for 5 minutes. The APS solution was precooled to ~0 °C. At that point, the APS solution was slowly added into the MnO$_2$-aniline mixture under constant stirring in the ice bath. After polymerization for 6 h in the ice bath and under constant stirring, a dark green powder was collected by filtration and rinsed with water and methanol. Finally, the compound was dried in a vacuum oven at 70 °C overnight. A synthesis schematic is shown below in figure 32.

![Figure 32. Hollow MnO$_2$ synthesis schematic](image)

**Characterization.** XRD (X-Ray Diffraction) measurements were performed on a D8 diffractometer from Bruker instruments (Cu Kα radiation, λ = 0.154 nm) with a scan rate of two degree/min. SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) images were obtained by using a Hitachi S-4800 machine.
Electrochemical measurements: The working electrodes were prepared by mixing the active material (MnO$_2$/PANI), acetylene black, and a binder composed of sodium carboxymethyl cellulose dissolved in deionized water (3 wt %) in a weight ratio percentage of 70:15:15, respectively. The obtained slurry was then coated onto a copper foil and dried overnight under vacuum at 100°C. The electrodes were cut with a diameter of 1.3 cm using a precision disc cutter from MTI Corporation. The coin cells (CR 2032) were assembled inside of an Ar-filled glovebox with oxygen levels maintained below 0.1 ppm. Li foil was used as the counter/reference electrode, a ceramic-coated membrane (16μm thick) from MTI Corporation was utilized as the separator (EQ-bsf-0016-500A), and the electrolyte employed was 1.0 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (1:1 in volume) from Sigma-Aldrich. The specific capacity was calculated based on the active material weight. The galvanostatic charge/discharge measurements were performed in an eight-channel battery analyzer (MTI Corporation) with a voltage window of 0.01−3V. The EIS and CV studies were conducted in a CHI760D electrochemical workstation. EIS was measured in coin cells in a frequency range of 0.01–100 000 Hz at an AC amplitude of 0.05 V. The CV was evaluated in a three-electrode setup using an electrochemical cell (990-00343) from Gamry Instruments within the range of 3.0−0.01 V at a scan rate of 0.01 V.

4.3 Results

4.3.1 Characterization

The XRD patterns of the bare-MnO$_2$ and MnO$_2$/PANI are presented, figure 33. Both samples show amorphous patterns. Particularly, bare- MnO$_2$ trace presents weak peaks at 36.5° and 66°, most likely attributed to planes (211) and (002) of MnO$_2$\textsuperscript{126–128}. However, these peaks are most likely broadened by the weak crystallinity of the product. MnO$_2$/PANI peak as are fully attenuated due to the presence of PANI.
To obtain information about the chemical composition of the samples, EDS and elemental mapping analysis were performed. In figure 34, we can observe that MnO$_2$/PANI is comprised mainly of carbon (C), oxygen (O) and manganese (Mn). Also, a homogenous distribution is observed for all the elements. Figure 35, presents the EDS spectrum for MnO$_2$/PANI and the quantification in wt. % of the elemental composition. MnO$_2$/PANI is composed of 78% C, 18.8% O and 3% Mn. The C is mainly coming from PANI, O% is originated from the oxidation of manganese during the preparation process of MnO$_2$/PANI. Although we were not able to identify the phase of MnO$_2$/PANI from the amorphous XRD patterns, from the EDS analysis we can imply that the sample is comprised of polyaniline (PANI) and manganese oxide amorphous phase.
Figure 34. SEM image selected area for MnO$_2$/PANI and elemental mapping images of C, O and Mn.

Figure 35. EDS spectrum of MnO$_2$/PANI.
In contrast, figure 36 displays the selected area for bare- MnO$_2$ and elemental mapping images of carbon (C), oxygen O, potassium (K), aluminum (Al) and manganese (Mn). We can observe a homogeneous distribution for all the elements. Figure 37 shows the EDS spectrum and the quantification in wt. % of the elemental composition. Bare- MnO$_2$ is mainly composed of 50.9% C, 15.5% O and 29.3% Mn. Additional small amounts of K and Al are also present. The K is coming from the starting material KMnO$_4$ and aluminum might be coming from the aluminum-stage used for the EDS analysis, although the mass is ~0.1%.

Figure 36. SEM image selected area for bare- MnO$_2$ and elemental mapping images of C, O, K, Al and Mn.
SEM micrographs of carbon spheres, MnO$_2$ hollow spheres and MnO$_2$/PANI are presented below, figures 38-44. Figure 38, shows micron-sized carbon particles later used as template seed for the hollow MnO$_2$ spheres. Carbon spheres where sputter coated with Au/Pd to reduce particle charging and migration during image capture. The carbon particles average size was 4.35 µm with a size deviation of ±0.5 µm. Figure 39, shows hollow MnO$_2$ spheres after calcination at 300 °C for 10 h in air; MnO$_2$ spheres did not require Au/Pd sputtering for image acquisition. The average particle size is 5.76 µm with a size deviation of ±0.5 µm. Figure 40 shows a larger 18 µm hollow MnO$_2$ sphere where we can appreciate cracks forming on the surface and possibly debilitating the structure of the hollow sphere. Figure 41 demonstrates a broken hollow sphere. In order to obtain broken spheres, the material was loaded to a carbon tape and manually pressured with a fine spatula.

Figure 37. EDS spectrum of bare-MnO$_2$. 
Figure 38. Carbon spheres template.

Figure 39. MnO$_2$ hollow spheres after calcination at 300 °C for 10 h in air.
Figure 40. Large MnO$_2$ hollow sphere after calcination at 300 °C for 10 h in air.

Figure 41. Broken hollow spheres.
Due to the shallow depth of field available with SEM images a 3D oblique analysis was carried to determine if the apparent spheres were flat or spherical, figure 42. Here we can appreciate a 3D rendering demonstrating the spherical hollow nature of the MnO$_2$ spheres. Later, figure 43 demonstrates hollow MnO$_2$ microspheres now coated with PANI; no sputtering was needed for image acquisition of MnO$_2$/PANI spheres. The average particle size is 6.23 µm with a size deviation of ±0.9 µm. Furthermore, we can appreciate the PANI coating fully covering the MnO$_2$ spheres and no visible cracks were seen in the sphere, although, we can appreciate some spheres having small parts missing. Figure 44 shows a broken MnO$_2$/PANI sphere, produced in a similar manner as figure 41. Here we can appreciate that MnO$_2$/PANI spheres retained their hollow nature, after the PANI coating.
Figure 43. Hollow MnO$_2$/PANI spheres.

Figure 44. Hollow MnO$_2$/PANI microspheres, broken hollow sphere.
4.3.2 Electrochemical Properties

Figure 45 depicts the 1st, 2nd, 3rd and 250th cycle charge-discharge voltage profiles of MnO2/PANI at a current density of 500 mA\textsuperscript{g}^{-1} in the potential range from 0.01 to 3 V. The discharge capacities for cycles 1, 2, 3 and 250 were 118, 166, 156 and 237 mAh/g, respectively. In contrast, the discharge capacities of bare-MnO2 for cycles 1, 2, 3 and 250 were 917, 460, 432 and 49 mAh/g, figure 46. The discharge capacity for bare-MnO2 is higher for the first three cycles. However, at cycle 250 the discharge capacity for MnO2/PANI (237 mAh/g) is superior that that of bare-MnO2 (49 mAh/g). No capacity loss is observed from first to second discharge for MnO2/PANI electrode while for bare-MnO2 there is a high capacity loss (from 917, 460 mAh/g). This fact indicates that the SEI layer film formation for MnO2/PANI is very stable thanks to the addition of PANI as is stated in other publications\textsuperscript{124,129}. Interestingly, for MnO2/PANI, the capacity of the 250th cycle increased twice that of the first cycle capacity. However, for bare-MnO2, the capacity of the 250th cycle decreased to only 5% of the first cycle capacity.

![Figure 45. Charge-discharge voltage profiles at a current rate of 500 mA\textsuperscript{g}^{-1} for MnO2/PANI.](image-url)
Figure 46. Charge-discharge voltage profiles at a current rate of 500 mA/g for bare- MnO₂

Cycling performance of bare- MnO₂ and MnO₂/PANI at a current rate of 500 mA/g for 250 cycles is shown in figure 47. It can be seen that the capacity for bare- MnO₂ stars fading rapidly whereas the capacity for MnO₂/PANI kept rising over the cycles. It is important to mention the capacity for MnO₂/PANI became higher than that of bare- MnO₂ after cycle 50, even though the first cycle capacity of MnO₂/PANI was only 13% the capacity of bare-MnO₂. The coulombic efficiency of MnO₂/PANI was above 99% after 250 cycles.
Figure 47. Cycling performance of bare-MnO\(_2\) and MnO\(_2\)/PANI at a current rate of 500 mA/g for 250 cycles.

We also investigated the rate capability of MnO\(_2\)/PANI and bare-MnO\(_2\) from 500 to 1000 mA g\(^{-1}\), figure 47. Each of the current density values were kept for five consecutive cycles from cycle 1 to cycle 20. Afterwards, the current densities were repeated similarly from cycle 21 to 40. From cycle 41 to 130 (for MnO\(_2\)/PANI) and to cycle 105 for bare-MnO\(_2\), the current density was held at a constant value of 100 mA h/g. The capacity of MnO\(_2\)/PANI kept stable through the different current densities, whereas bare-MnO\(_2\) capacity varied significantly. Although the capacity of bare-MnO\(_2\) is superior to MnO\(_2\)/PANI, after cycle 105, the capacity of MnO\(_2\)/PANI equaled the capacity value of bare-MnO\(_2\) (227 mAh/g). After cycle 105, the capacity of MnO\(_2\)/PANI kept increasing while the tendency for bare-MnO\(_2\) decreased.
The electrochemical performance of MnO₂/PANI as anode material for LIBs was investigated by cyclic voltammetry (CV). The representative CV curves of MnO₂/PANI electrode, a scan rate of 0.1 mVs⁻¹ and a voltage window of 0.01-3.0 V, is presented in figure 49. In the first cycle, MnO₂/PANI showed two cathodic peaks at 1.8 and 0.25 V. The cathodic peak at 0.25 V could be ascribed to the conversion reaction of MnO₂ to metallic Mn and Li₂O formation which is commonly observed for manganese oxide electrode materials. The CV results are consistent with the plateau observed at ~0.25 V (first discharge) in the charge-discharge voltage profiles for MnO₂/PANI. In the first anodic sweep, only one peak at 2.16 V is present. This peak might be attributed to the oxidation of metallic manganese into MnO₂. In the following cycles, the behavior was similar to the first cycle, however, lower currents were observed in cycles 2 and 3.
To better understand the resistive behavior of MnO₂/PANI, electrochemical impedance spectroscopy (EIS) was conducted for bare- MnO₂ and MnO₂/PANI. The obtained Nyquist plots are shown below, figure 50. For MnO₂/PANI the high-frequency semicircle is composed of the constant phase element of the SEI film (CPE1), the charge-transfer impedance (R<sub>ct</sub>) and Z<sub>w</sub>, which is associated with the Warburg impedance corresponding to the lithium-diffusion process. R<sub>e</sub> represents the ohmic resistance of the battery. The R<sub>e</sub> and R<sub>ct</sub> values for MnO₂/PANI are 19.79 and 170.21 Ω, respectively. For bare-MnO₂, the high-frequency semicircle is comprised of the constant phase element of the SEI film (CPE1), and to the electrolyte resistance (R<sub>e</sub>). The semicircle in the medium-frequency region is assigned to the charge-transfer impedance (R<sub>ct</sub>) and constant phase
element of electrode/electrolyte interface (CPE2), and $Z_w$ is associated with the Warburg impedance corresponding to the lithium-diffusion process. The values of $R_e$, $R_f$ and $R_{ct}$ for bare-$\text{MnO}_2$ are, 44.72, 899.58 and 850.42 $\Omega$, respectively. The $R_e$ and $R_{ct}$ values were significantly lower for the $\text{MnO}_2$/PANI electrode, indicating an excellent improvement to the electric conductivity by the addition of PANI. The equivalent circuit models used for the EIS calculated values are shown in figure 51.

Figure 50. Nyquist plots for bare-$\text{MnO}_2$ and $\text{MnO}_2$/PANI.
Figure 51. Equivalent circuits for a) MnO$_2$/PANI and b) bare- MnO$_2$ spheres.

4.4 Conclusions

In summary, MnO$_2$/PANI composite was fabricated by a hierarchical assembly of hollow MnO$_2$ microspheres synthetized by templating carbon spheres, the following removal of the carbon core and addition of a PANI coating to improve the electronic conductivity of anode material. The MnO$_2$/PANI composite demonstrated excellent cycling performance when compared to bare-MnO$_2$ spheres. Interestingly, for MnO$_2$/PANI, the capacity of the 250$^{\text{th}}$ cycle increased twice that of the first cycle capacity. However, for bare-MnO$_2$, the capacity of the 250$^{\text{th}}$ cycle decreased to only 5% of the first cycle capacity. Despite MnO$_2$/PANI exhibited an initial 13% capacity vs its control, after the 50$^{\text{th}}$ cycle MnO$_2$/PANI outperformed its control with a final tested capacity 4.8 times larger than the control. Finally, the electrical conductivity of MnO$_2$/PANI improved dramatically, such as the R$_{ct}$ values which decreased to 20% its control.
Synthesis of a porous iron sulfide/carbon composite and its performance as anode material for LIBs.

5.1 Introduction

Intensive research has been conducted in order to find alternative anode materials for Li ion batteries (LIBs) to fulfill the energy requirements for applications demanding high energy storage, such as electric vehicles and smart grids. Transition sulfides are promising anode materials for LIBs owing to their high theoretical capacities. In particular, iron sulfides compounds have shown great interest due to their cost effectiveness, natural abundance and high theoretical capacities (609 mAh/g for FeS and 894 mAh/g for FeS$_2$). However, these materials are still facing some issues that are preventing them from commercialization. Firstly, iron sulfides suffers from limited electrical conductivity. Secondly, the large volume variation (~200%) achieved during the charging/discharging process leads to the pulverization of the electrode with a subsequent detachment from the current collector and consequently a quick fading of the capacity along the cycles. Lastly, the formation of lithium polysulfide intermediates (Li$_2$S$_n$) produced during the charge/discharge processes which are easily dissolved in the electrolyte, causing the degradation of the active material resulting in a poor electrochemical performance.

Numerous efforts have been dedicated to solve these problems. For example, several studies have reported that the use of a carbon coating or a carbon matrix can accommodate the volume change during the cycling process, help increase electrical conductivity, and promote the formation of a stable SEI (solid electrolyte interface) film. Thus, improving the long-term cycling performance. Moreover, a porous carbon matrix can offer additional Li ions sites to accommodate the large volume expansion during the charge-discharge process.
Herein we report a facile synthesis of a porous iron sulfide/carbon composite prepared by the mixture of D-(+)-Glucose, Zn, and Fe salts at room temperature and their subsequent carbonization at 1000 °C under argon atmosphere. SEM and EDS show porosity formed by the evaporation of zinc at 1000°C. Additionally, we investigated the electrochemical performance as anode material for LIBs.

5.2 Experimental Section

Chemicals and reagents. D-(+)-Glucose (ACS reagent), Zinc chloride (ZnCl₂), Iron(II) sulfate heptahydrate (FeSO₄.7H₂O) and iron chloride hexahydrate (FeCl₃.6H₂O) were all purchased and used as-is from Sigma Aldrich.

Preparation of iron sulfide/carbon composites. Three samples were prepared with different iron contents according to table 1. For the preparation of these samples, D-(+)-Glucose, ZnCl₂, FeSO₄.7H₂O and FeCl₃.6H₂O were dissolved in 15 mL of reverse osmosis (RO) water. The mixture was sonicated for 15 minutes and an orange solution was obtained. This solution was co-evaporated with reagent alcohol under reduced pressure until completely dry. Lastly, the obtained products were carbonized individually under Argon flow for two hours at 1000 °C with a ramp speed of 10 °C/min. The same procedure was followed for the control.

Table 1. Chemical amounts used for preparation of iron sulfide/carbon composites.
Characterization. XRD (X-Ray Diffraction) measurements were performed on a D8 diffractometer from Bruker instruments (Cu Kα radiation, λ = 0.154 nm) with a scan rate of two degree/min. SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectroscopy) images were obtained by using a Hitachi S-4800 machine. TEM (Transmission Electron Microscopy) images were acquired by a Hitachi H-7650 equipment.

Electrochemical measurements: The working electrodes were prepared by mixing the corresponding active material sample (1X, 2X, 4X, or control), with acetylene black, and a binder composed of sodium carboxymethyl cellulose dissolved in deionized water (3 wt %) in a weight ratio percentage of 70:15:15, respectively. The obtained slurry was then coated onto a copper foil and dried overnight under vacuum at 100°C. The electrodes were cut with a diameter of 1.3 cm using a precision disc cutter from MTI Corporation. The coin cells (CR 2032) were assembled inside of an Ar-filled glovebox with oxygen levels maintained below 0.1 ppm. Li foil was used as the counter/reference electrode, a ceramic-coated membrane (16μm thick) from MTI Corporation was utilized as the separator (EQ-bsf-0016-500A), and the electrolyte employed was 1.0 M LiPF6 in ethylene carbonate/dimethyl carbonate (1:1 in volume) from Sigma-Aldrich. The specific capacity was calculated based on the active material weight. The galvanostatic charge/discharge measurements were performed in an eight-channel battery analyzer (MTI Corporation) with a voltage window of 0.01−3V. The EIS and CV studies were conducted in a CHI760D electrochemical workstation. EIS was measured in coin cells in a frequency range of 0.1–100 000 Hz at an AC amplitude of 0.05 V. The CV was evaluated in a three-electrode setup using an electrochemical cell (990-00343) from Gamry Instruments within the range of 3.0−0.01 V at a scan rate of 0.01 V.
5.3 Results

5.3.1 Characterization

X-ray diffraction patterns for samples 1X, 2X and 4X are shown below, figure 52. Four diffraction peaks can be observed for sample 4X at 29.7°, 33.4°, 43.1°, and 52.9°, corresponding to (100), (101), (102) and (2-10) planes of FeS (COD No. 1009043), respectively. Two additional peaks were present in the diffractograms for sample 4X, one at 44.4° which can be assigned to metallic Fe phase (110) and another at 50.5°, which we were not able to identify. Sample 2X showed the same four peaks of FeS phase than sample 3 as well as the peak assigned to metallic iron. However, for sample 2X there are three more peaks located at 37.3°, 39.1° and 43.6° that match with the planes (111), (120) and (210) of FeS$_2$ phase (COD No. 1011013), respectively. On the other hand, sample 1X showed one peak of FeS (101), the same three peaks (111), (120), and (210) of FeS$_2$ phase that were observed in sample 2X and an additional peak (110) corresponding to metallic Fe phase. No peaks corresponding to iron oxide phases were observed in the XRD analysis.

![Figure 52. XRD diffractograms for the iron sulfide/carbon composites.](image-url)
The SEM images for the control, samples 1X, 2X and 3X are shown in figures 53-56. The control sample consists of large solid flakes with no evident porosity, see figure 53. Sample 2X showed flake-like shapes with some porosity, see figure 54. For samples 2X and 4X, smaller more porous flakes were observed, figures 55 and 56 respectively. From the SEM images, is evident that the addition of Zn lead to the formation of porous structures. In addition, it is possible that the size and the amount of the pores increases with additional amounts of Fe.

Figure 53. Control sample.
Figure 54. Sample 1X.

Figure 55. Sample 2X.
To obtain information about the chemical composition and elemental distribution of samples 1X, 2X, and 4X, energy-dispersive X-ray (EDX) analysis and element mapping were performed. A uniform elemental distribution of Fe, S, C, and a small percentage of oxygen was confirmed, shown in figures 57-59. Additionally, we can observe the amount of iron increases progressively from sample 1X through 4X, which is in accordance with the amount addition of iron during the synthesis of the samples. No evidence of Zn was observed in the EDS spectrum for any of the samples. This is in agreement with Wang et al. \textsuperscript{145}, which demonstrates Zn compounds reduce to metallic zinc consequently evaporating and leaving a porous structure in carbon.
Figure 57. a) SEM image selected area for Sample 1X, (b)-(e) elemental mapping images of C, Fe, O and S. f) The EDS spectrum of Sample 1X.

Figure 58. a) SEM image selected area for Sample 2X, (b)-(e) elemental mapping images of C, Fe, O and S. f) The EDS spectrum of Sample 2X.
Figure 59. a) SEM image selected area for Sample 3, (b)-(e) elemental mapping images of C, Fe, O and S. f) The EDS spectrum of Sample 3.

5.3.2 Electrochemical Properties

Figure 60 depicts the 1st, 2nd, 3rd and 286th cycle charge-discharge voltage profiles of sample 2X at a current density of 500 mA g⁻¹ in the potential range from 0.01 to 3 V. The discharge capacities for cycles 1, 2, 3 and 450 were 778, 467, 394 and 511 mAh/g, respectively. The initial capacity loss (from first to second discharge, 778 to 467 mAh/g), can be ascribed to the irreversible formation of the SEI layer on the electrode surface and the incomplete extraction of Li⁺ ions from the active material. The discharge capacity value (511 mAh/g) at cycle number 450 is higher than that of 2nd cycle (467 mAh/g), indicating that the stability of the electrode improves over cycling.

On the other hand, the charge-discharge voltage profiles for sample 4X under the same electrochemical conditions are displayed in figure 61. The discharge capacities for cycles number
1, 2, 3 and 450 were 1726, 648, 600 and 205 mAh/g, respectively. Sample 2X showed higher discharge capacity than sample 4X at cycle 450th.

Figure 60. Charge-discharge voltage profiles at a current rate of 500 mAg\(^{-1}\) for Sample 2X.

Figure 61. Charge-discharge voltage profiles at a current rate of 500 mAg\(^{-1}\) for Sample 4X.
We also investigated the cycling performance for sample 2X and 4X for 450 cycles at a current rate of 500 mA/g, figure 62. Sample 2X retained a high specific capacity value of 511 mAh/g and a CE above 99% after 450 cycles. In contrast, sample 4X retained a low specific capacity value of 205 mAh/g after 450 cycles. The cycling performance for sample 1X was studied at a current rate of 500 mA/g for 316 cycles, also figure 62. Sample 1X kept a specific capacity of 292 mAh/g which is the lowest capacity value for all the three samples at cycle 316. It is important to mention that the capacity kept increasing along the cycles for sample 2X whereas for sample 4X the capacity drastically decreased after 350 cycles. This demonstrated a superior cycling stability performance for sample 2X.

Figure 62. Cycling performance of sample 1X, 2X, and 4X at a current rate of 500 mA/g.
To investigate the rate performances of samples 2X and 4X, these were subjected to four different current densities (100, 200, 500 and 1000 mAh/g) for 80 cycles, figure 63. Each of the current density values was kept for five consecutive cycles from cycle 1 to cycle 20. Afterwards, the current densities were repeated in the same way from cycle 21 to cycle 40. From cycle 41 to cycle 80 the current density was held at a constant value of 100 mAh/g. The rate performance was found similar for both samples in these 80 cycles. However, sample 2X retained a final higher capacity value, 645 mAh/g, to that of sample 4X, 565 mAh/g, after 80 cycles. Therefore, sample 2X showed an enhanced rate performance.

Figure 63. Rate capabilities of samples 2X and 4X from 100 to 1000 mAh/g.
To have a better understanding of the resistive behavior, electrochemical impedance spectroscopy (EIS) was conducted for samples 2X, 4X, and the control, figure 64. Sample 1X was no longer investigated due to its low specific capacity. The equivalent circuit model of the studied samples is also shown in figure 64. In the equivalent circuit model, the $R_e$ represents the ohmic resistance of the half-cell battery. The high-frequency semicircle is composed of the constant phase element of the SEI film (CPE1), and the electrolyte resistance ($R_f$). The semicircle in the medium-frequency region is assigned to the charge-transfer impedance ($R_{ct}$) and constant phase element of electrode/electrolyte interface (CPE2), the $Z_w$ is associated with the Warburg impedance corresponding to the lithium-diffusion process$^{146}$.

Figure 64. Nyquist plots for samples 2X, 4X, and control and their equivalent electric circuit.
Table 2 shows the $R_c$, $R_f$ and $R_{ct}$ values for samples 2X, 4X, and the control. The SEI film resistance ($R_f$) and charge transfer resistance ($R_{ct}$) of sample 2X were significantly lower than those from sample 4X. Therefore, sample 2X has better rate performance due to the battery’s lower resistance, and improved Li ion diffusion. The sample’s 2X enhancement are most likely attributed to the porosity of the material, seen on figure 55.

Table 2. Impedance parameters derived using equivalent circuit model for Sample 2X, Sample 4X and Control (no zinc).

<table>
<thead>
<tr>
<th></th>
<th>Sample 2X</th>
<th>Sample 4X</th>
<th>Control (no zinc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_c$ (Ω)</td>
<td>15.65</td>
<td>48.5</td>
<td>45.38</td>
</tr>
<tr>
<td>$R_f$ (Ω)</td>
<td>124.85</td>
<td>147.5</td>
<td>316.32</td>
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<tr>
<td>$R_{ct}$ (Ω)</td>
<td>69.05</td>
<td>372.5</td>
<td>270.48</td>
</tr>
</tbody>
</table>

The electrochemical performance of sample 2X as anode material for LIBs was investigated by cyclic voltammetry (CV); sample 1X and 4X were not tested due to inferior performance. Figure 65 shows representative CV curves of sample 2X electrode at a scan rate of 0.1 mVs$^{-1}$ between 0.01 and 3 V versus Li$^+$/Li for the first three cycles. In the first cycle, sample 2X showed three cathodic peaks at 1.96, 1.5 and 1.03 V. The broad peak ~1.03 V might be due to the initiation of the formation of a solid electrolyte interface (SEI) layer. This can be observed in the charge-discharge voltage profile, figure 60, with the plateau around 1.09 V in the first discharge. The peak around 1.96 V could result from lithium ions insertion into the iron sulfide host ($\text{Li}_2\text{FeS}_2$, equation 14) while the peak located at 1.5 V is possibly due to the lithiation process of forming Li$_2$S and Fe (equation 15). Additionally, sample 2X shows two main anodic peaks in the first cycle located at 1.97 and 2.39 V. The anodic peak at 1.97 V is most likely due to the oxidation of Fe to transform into Li$_2$S$_x$FeS$_2^{134}$ according to equations 16 and 17$^{132,147}$. The anodic peak at 2.39 V might be due to the further formation of FeS$_y$ and S according to equation 18. In the second cathodic scan, the
peak at 1.96 V disappears, the peak at 1.5 V shifts to 1.41 V and the current decreases as well as the current of the broad peak located at 1.03 V drops considerably. The presence of the peak at 1.03 V in the second cathodic sweep is due to the incomplete formation of the SEI layer in the first cathodic sweep and therefore continues forming in the following cycles.

![Cyclic voltammetry for Sample 2X](Image)

Figure 65. Cyclic voltammetry for Sample 2X.

\[
FeS_2 + 2Li^+ + 2e^- \rightarrow Li_2FeS_2 \tag{14}
\]

\[
Li_2FeS_2 + 2Li^+ + 2e^- \rightarrow 2Li_2S + Fe \tag{15}
\]

\[
Fe + 2Li_2S \rightarrow Li_2FeS_2 + 2Li^+ + 2e^- \tag{16}
\]

\[
Li_2FeS_2 \rightarrow Li_{2-x}FeS_2 + XLi^+ + Xe^- \tag{17}
\]
\[ Li_{2-x}FeS_2 \rightarrow FeS_y + (2 - y)S + (2 - x)e^- + (2 - x)Li^+ \]  

(18)

### 5.4 Conclusions

In summary, a facile synthesis of a porous iron sulfide/carbon composite prepared by the mixture of D-(+)-Glucose, Zn, and Fe salts at room temperature and their subsequent carbonization at 1000 °C under argon atmosphere is presented. SEM images demonstrated porosity formed by the evaporation of zinc at 1000°C for samples 1X, 2X, and 4X. The composite’s porosity significantly improved electrochemical performance when compared to the non-porous control. Particularly, the sample 2X demonstrated improved cycling performance when compared to the control and other samples. Particularly, sample 4X initial capacity was more than twice the capacity of sample 2X, however, by the 450th cycle sample 2X retained capacity significantly better. Specifically, sample 2X retained ~65% its initial charge capacity vs ~12% capacity for sample 4X. The final capacity of sample 2X was 2.5 times larger than sample 4X (511/205 mAh/g). Finally, the electrical conductivity of the samples improved dramatically due to the samples porosity, where sample 2X exhibited a third of the resistance by the non-porous anode material.
Conclusion

During this research, we developed strategies to improve the electrochemical performance of transition metal compounds as anode materials for Li-ion Batteries. Particularly, we investigated the performance of bimetallic CoMoS/bio-carbon composites, hollow MnO2 spheres with polyaniline (PANI) coating, and porous iron sulfide/carbon composites. Due to the fact that transition metal compounds typically suffer from poor cycling capabilities, this dissertation primary focus was to improve the cycling capabilities of the transition metal compounds investigated.

Particularly, we combined CoMoS compounds with cellulose fibers as an easy and low-cost alternative biomass source to enhance the electrochemical performance of the transition metal compounds. This composite showed significantly improved electrochemical performance when compared to bare-CoMoS. Comparatively, CoMoS@C composite exhibited an initial capacity 40% higher than its control and a final tested capacity 90% higher than its control. Finally, CoMoS@C retained approximately 60% its charge capacity at its 200th cycle, whereas the control lost ~90% its capacity by the 100th cycle. Thus, CoMoS@C composite demonstrated a superior performance vs its control.

Thereafter, we synthesized MnO2/PANI composites by a hierarchical assembly of hollow MnO2 microspheres The MnO2/PANI composite demonstrated excellent cycling performance when compared to bare-MnO2 spheres. Interestingly, for MnO2/PANI, the capacity of the 250th cycle increased twice that of the first cycle capacity. However, for bare-MnO2, the capacity of the 250th cycle decreased to only 5% of the first cycle capacity. The MnO2/PANI composite outperformed its control with a charge capacity 4.8 times larger than the control by the 250th cycle. Finally, the
electrical conductivity of MnO\textsubscript{2}/PANI improved dramatically, such as the \( R_{ct} \) values which decreased to 20\% vs its control, thus improving the C-rate capabilities of the battery.

Finally, porous iron sulfide/carbon composites were prepared by the mixture of D-(+)-Glucose, Zn, and Fe salts at room temperature and their subsequent carbonization at 1000 \(^\circ\)C. SEM images demonstrated porosity for samples 1X, 2X, and 4X. The composite’s porosity significantly improved electrochemical performance when compared to the non-porous control. Particularly, the sample 2X demonstrated improved cycling performance when compared to the control and other samples. Particularly, sample 4X initial capacity was more than twice the capacity of sample 2X, however, by the 450\textsuperscript{th} cycle sample 2X retained capacity significantly better. Specifically, sample 2X retained ~65\% its initial charge capacity vs ~12\% capacity for sample 4X. The final capacity of sample 2X was 2.5 times larger than sample 4X (511/205 mAh/g).

Collectively, the superior cycling stability can be accredited to the synergistic effect between the transition metal compounds and their respective alloys. Where carbon sources was used for CoMoS and porous iron sulfide composites and a conductive polyaniline layer for the hollow MnO\textsubscript{2} spheres. Furthermore, the careful dimensional design and placement of the transition metal compounds greatly improves the battery’s conductivity of their respective compounds. Particularly, CoMoS was layered on top of carbon fibers instead of densely packed upon itself. Secondly, hollow MnO\textsubscript{2}/PANI spheres exhibited \( R_e \) and \( R_{ct} \) values ~80\% lower than its control. The electrical conductivity was likely improved by PANI’s effect on supporting the fragile and partially cracked MnO\textsubscript{2} spheres. Finally, the electrical conductivity of the porous Fe samples improved dramatically due to the samples porosity, where sample 2X exhibited a third of the resistance by the non-porous anode material.
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Maddipatla, R., Loka, C., Choi, W. & Lee, K.-S. Nanocomposite of Si/C Anode Material


Appendix

6.1 Battery Assembly

Assemble battery components:

- Negative case
- Spring
- Spacer x2
- Anode (lab synthesized)
- Separator (eq-bsf-0016-500A)
- Lithium foil cathode
- Positive case

Place cell with negative case up

Place the cell in the slot of crimping die.

Tighten pressure valve

Pressurize to 800-1000 psi by pumping lever

Higher pressures may seize crimper

Release pressure by loosening pressure valve
Remove battery
Inspect positive case edge
If successfully crimped, positive case will be rounded by the edges. Battery components are now sealed
Incorrect crimping results in straight positive case edges
Vita

Noemi Dominguez earned her Bachelor of Engineering degree in Physics Engineering from Universidad Autonoma de Ciudad Juarez (UACJ) in 2008. In 2011, she received her Master in Materials Science and Engineering from UACJ. During her master’s studies she worked as a lecturer at UACJ teaching classes of Statics and Dynamics. She joined UTEP’s doctoral program in Materials Science and Engineering in 2012.

During her doctoral studies Dr. Dominguez was a recipient of two scholarships, one from Chihuahua’s government and the other from CONACYT. She also had the opportunity to have the position of Teaching Assistant of General Chemistry lab I and General Chemistry lab II for two years. Also, she was awarded with a Research Assistant position from the NSF PREM (Partnership for Research and Education in Materials) program for one year. She published her work in several recognized journals such as ACS Omega.

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