Performance of Hybrid SnO$_2$/Li$_2$FeMn$_3$O$_8$ Nanostructured Electrode for Efficient Li-ion Storage Application

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Abstract

Li$_2$FeMn$_3$O$_8$ (LFMO) nanocomposite material for Li-ion battery is synthesized using the chemical combustion method. To fabricate a hybrid nanostructure electrode, LFMO is coated on tin oxide (SnO$_2$) nanorods (NR), which is grown using a vapor-liquid-solid (VLS) technique on a steel substrate. The surface morphology of the hybrid nanostructure electrode confirms that single-crystalline SnO$_2$ nanorods are grown vertically with spine-like structures, a few microns in length, as evident from field emission scanning electron microscope image. The electrochemical performance of SnO$_2$/LFMO shows very interesting characteristic with enormous charge storage capability. The coin cell shows improved capacity with a higher number of charging and discharging cycles. This SnO$_2$/LFMO hybrid composite electrode shows better specific capacitance value as compared to the pristine SnO$_2$ electrode.

Introduction

Compared to the various types of batteries, lithium-ion batteries (LIBs) are one of the most currently used energy storage devices. Due to their high energy density and long cycle stability, they are used in numerous applications such as consumer electronics, electric vehicles, and power grids to name a few. The quest to improve the performance of LIBs has sparked a lot of research interest in the field of energy storage, especially the search for new electrode materials and optimization of already existing electrodes materials.

The performance of LIBs relies greatly on the properties and structure of the electrode material for lithium storage (Wang et al., 2013; Wang et al., 2012; Wang et al., 2013). Nanostructured electrodes are of great importance in lithium-ion storage because of their large surface area for lithium insertion channels as well as quick lithium-ion diffusion (Wang et al., 2013; Liu et al., 2012; Xu et al., 2012). Also, carbonaceous materials have been used to serve as a volume change buffers and good electron conductors to enhance the electrochemical performance of SnO$_2$ nanocomposites (Wang et al., 2015). One such electrode material is tin dioxide (SnO$_2$) nano-
rods because of its high theoretical capacity of (~782 mAhg-1), low cost, abundance and relatively low charge-discharge plateau compared to other metal oxides (Wang et al., 2015; Poizot et al., 2000; Tarascon et al., 2001; Arico et al., 2005). Besides, SnO₂ is a semiconductor with good lithium storage properties, exhibits nontoxic and nonreactive behaviors owing to its excellent electrical conductivity. Desirable properties of SnO₂ are believed to improve the electrochemical performance of cathode materials when applied as a coating (Carvajal et al., 2017; Guan et al., 2014; Hudaya et al., 2014). Besides these advantages, SnO₂ electrodes also encounter a few issues such as (i) severe electrode pulverization and capacity fading during the cycling process as a result of 200% volume expansion, which occurs during lithiation and de-lithiation process; (ii) relatively low discharging capability due to low electrical conductivity, which reduces the electron transport; and (iii) poor Coulombic efficiency due to irreversible conversion reaction during initial lithiation process resulting in additional cathode material consumptions. There is a myriad of research efforts to provide solutions to problems that affect the surface area and the lithium-ion kinetics in a positive direction. This is achieved via the use of surface modification such as nanorods, nanowires, and nanotubes (Wang et al., 2015).

LFMO is a lithium-rich cathode material with a high atomic ratio of extractable lithium to the transition metal, which is noted to provide a high discharge capacity (Penki et al., 2016). The LFMO is one of the efficient cathode materials that deliver a specific capacity of 103 mAhg-1, which is 70% of its theoretical capacity value with 83% of Coulombic efficiency during the first cycle. Also, the LFMO exhibits two groups of distinct plateaus at 4.0 V and 4.9 V for discharge and 4.1 V and 5.0 V for charge (Penki et al., 2016). Furthermore, the LFMO contains the majority of iron and manganese without cobalt, which makes it environmentally friendly, and less expensive than Co and Ni-based cathodes (Zhao et al., 2016; Tabuchi et al., 2005). Nevertheless, LFMO cathode materials, reported in the literature, exhibit low rate capabilities due to their low electronic and ionic conductivities, which limit their practical application (Zhao et al., 2016; Pan et al., 2018; Si et al., 2015). Cation-doping and surface modifications, by coating with carbon, have been modified to improve the electrochemical performances of LFMO (Yuge et al., 2016; Wu et al., 2015; Wang et al., 2016). Considering the properties of the SnO₂ nanorods and the LFMO stated above, there would be a trade-off, if the composite material can be prepared out of these two materials. Therefore, the incorporation of LFMO into the SnO₂ nanorods forming a composite electrode, could potentially enhance the electrochemical performance of the battery for better energy storage application. Hudaya et al. reported on SnO₂ thin film coating on LiCoO₂ cathode material. The SnO₂ coating increases the initial discharge capacity of pristine LiCoO₂ from 172 to 183 mAhg-1 at 1C (Hudaya et al., 2014). Furthermore, other researchers used insulating materials or semiconductive materials such as ALF₃, Al₂O₃, TiO₂, ZnO, Li₂SiO₃, LiAlO₂, and SnO₂ as effective coating materials for cathode electrode in the lithium-ion battery. These coatings do not only prevent the active substances from diffusion and dissolution in electrolyte but also improve the electronic conductivity as well as structural stability (Wang et al., 2019; Yang et al., 2012; Lee et al., 2013; Wang et al., 2015; Dai et al., 2016; Lai et al., 2016; He et al., 2017; Srur-Lavi et al., 2017; Liua et al., 2018; Zheng et al., 2018; Xie et al., 2019). The advantage of the vapor-liquid-solid (VLS) technique, used in growing the SnO₂, compared to the other SnO₂ coating is that you can grow highly oriented vertically dense nanorods with easy size tunability and no sophisticated or expensive equipment, such as chemical vapor deposition (CVD).

### Materials and Methods

The synthesis procedure and the chemicals used to fabricate the SnO₂ nanorods as well as the LFMO composite is shown in Figure 1. SnO₂ is synthesized on a cleaned stainless-steel disc substrate using ZnCl₂ and SnCl₂ powders in a ratio of 4:1 as source materials. The ZnCl₂ and SnCl₂ were mixed thoroughly in an alumina boat and the cleaned stainless-steel disc substrate is placed on top of a glass slide at approximately 1.6 cm from the bottom of the alumina boat. The alumina boat with the mixture of ZnCl₂ and SnCl₂ is put inside a furnace in the presence of oxygen under controlled temperature. The furnace is allowed to cool down to room temperature naturally after it stayed constant at 510 °C for 10 minutes before the removal of the sample. The ZnO grown dur-
The annealed LFMO is mixed with carbon black (good electron conductor), polyvinylidene fluoride (PVDF binder) in a mass ratio percentage of 80:10:10, after which N-methyl-2-pyrrolidone (NMP) is added to obtain slurry in a ratio of 1:2 by weight of solids to liquids. The surface area of the powders greatly affects the viscosity of the slurry. Therefore, the larger the surface area, the thicker the slurry. A slurry is placed on the stirrer overnight for thorough mixing. The resulting slurry is coated on SnO₂ nanorods deposited on the stainless-steel substrate using the doctor blade technique to form the electrode and allowed to dry in air overnight. Furthermore, the electrode on the steel substrate is dried in a vacuum oven at 90 °C for 12 hours. The stainless steel is pre-weighed and post-weighed to determine the active mass of the electrode. The SnO₂ and SnO₂/LFMO composite are used as a cathode electrode to construct an individual coin cell for this work.

Lithium foil is used as an anode electrode and 1 M of lithium hexafluorophosphate (LiPF₆) in 1:1 ratio of propylene carbonate (PC) and dimethyl carbonate (DMC) as the electrolyte. The coin cell is left to sit for three days to allow the liquid electrolyte to diffuse via the separator before the electrochemical testing. BST8-WA (MTI corp.) eight-channel battery analyzer is used to analyze the coin cell to determine the cycling performance and its capacity. The channel of the analyzer has independent constant-current and constant-voltage source in a range of 0.005 mA-1.0 mA up to 5 V that is programmed and controlled by computer software.

The discharge specific capacity is calculated by the
battery analyzer system from the discharge curves using the following equation:

Discharge Specific Capacity = \[
\frac{I(mA) \times t(h)}{m(g)}
\]

Where \(I(mA)\) is the discharge current, \(t(h)\) is the discharge time consumed in the voltage range and \(m(g)\) is the mass of active materials of the electrode (Jiang et al., 2011). While Coulombic efficiency of any battery is the ratio of charge output to charge input. The calculation of the Coulombic efficiency is given by the formula below:

Coulombic Efficiency = \[
\frac{\text{Discharge Capacity}}{\text{Charge capacity}} \times 100\%
\]

Thermogravimetric analysis (TGA) is performed to assess the thermal stability of the LFMO raw material since the electrical resistance of conductors could be influenced by temperature (Lacy, 2011). Approximately 5 mg of the sample is placed in a platinum crucible and then placed into a thermogravimetric analyzer. Nitrogen gas of flowrate (30 mL) is allowed into the pyrolyzing unit to ensure an oxygen-free atmosphere. The sample is heated from room temperature to 900 °C at a heating rate of 10 °C/min. It is relevant to know the performance of LFMO as it could be disposed off in the incineration waste plant, which will in turn affect the environment.

The Brunauer-Emmett-Teller (BET) surface area, the pore volume, and the pore size of the new and used catalysts are measured using Quantachrome (NOVA 200e) surface area analyzer having degassed at 300 °C for 3 hours, adsorbed, and desorbed with \(N_2\) at -196 °C. The surface area is evaluated using a multi-point BET model. The pore size distribution is obtained from the desorption isotherm using Barret-Joyner-Halenda (BJH) model (Asiedu et al. 2019; Lowell et al., 2006) while the total pore volume is calculated at a relative pressure \((P/P_0)\) range of 0.0-1.0.

Results and Discussion

FESEM technique is used to verify the morphology of \(\text{SnO}_2\) nanorods before the coating of the LFMO onto it. The images, shown in Figure 2(a-b), reveal that \(\text{SnO}_2\) is single crystalline in nature and grew vertically with spine-like structures in the range of few microns in length. The FESEM images of the LFMO electrode, Figure 2(c-d), did not exhibit any distinctive shapes or particular arrays, however, it forms an aggregate with particles growing on top of each other. Although LFMO aggregates, when the size is decreased from 5 µm to 2 µm, the pores within the LFMO electrode are still visible. LFMO spread evenly on the \(\text{SnO}_2\) nanorods, via doctor blade technique, exhibiting high porosity, as seen in Figure 2(e-f). However, the \(\text{SnO}_2\) nanorods are not noticeable in the images. This might be due to the large surface area of LFMO. In addition, the increase in porosity of LFMO/\(\text{SnO}_2\) will help to improve the surface area.

Figure 2. Surface morphology at different magnifications of (a-b) pristine \(\text{SnO}_2\), (c-d) pristine LFMO, and (e-f) \(\text{SnO}_2/\text{LFMO}\) composite electrodes.
Figure 3. (a) TGA curve for LFMO powder, (b) Adsorption-desorption isotherm curves of LFMO and (c) pore size distribution of LFMO.

Figure 4. (a) XRD pattern of SnO$_2$ nanorods and (b) XRD pattern of LFMO powder. (c) XRD pattern of SnO$_2$/LFMO composite.
for the lithiation and the delithiation process.

Figure 3 (a) highlights the TGA of LFMO as it is heated from room temperature to 900 °C. It is observed that LFMO remained stable between 25-220 °C. It could, therefore, be inferred that the electrical or internal resistance of the material remains unchanged at ambient conditions where the battery is tested. Between 220 °C and 900 °C, LFMO lost nearly 6% of its original mass, which could be traceable to the PVDF binder. The maximum rate of decomposition is experience at 800 °C, which is close to the normal incineration temperature of batteries (D3242-11, 2017; Ebin et al, 2017). This means even if the LFMO ends up at an incineration plant, its environmental emissions would be insignificant compared to the emission of a conventional battery, which loses approximately 80% of its mass into the atmosphere during incineration (Patel et al., 2016).

Figure 3(b) shows the adsorption and desorption of N₂ on the LFMO. It can be observed that as the pressure increased, the volume of N₂ adsorbed increase until the pores in the LFMO became saturated, as indicated by the desorption curve. Decreasing the pressure resulted in the evaporation of the adsorbed N₂ and the decrease in the amount of N₂ in the pores, as shown by the desorption isotherm. This type of hysteresis depicts a type 1 and 4 isotherm, according to the International Union of Pure and Applied Chemistry [19]. It is also observed that the surface area and pore volume for LFMO are 2.018 m²/g and 4×10⁻³ cm³/g, respectively. The modal pore width is registered to be 35.5 Å (Figure 3c), which shows that the LFMO is microporous (Asiedu et al., 2019).

To further study the phase composition of the SnO₂ nanorods and the LFMO material, X-ray diffraction is performed with Cu K-alpha radiation at 40 kV and 40 mA. Figure 4 (a) shows XRD patterns of SnO₂ nanorods on a glass substrate. The diffraction peaks reveal that the SnO₂ has a strong peak on the (101) plane. In addition, the nanorods are well crystalized as results of the enhanced (002) peaks, which grows the crystals on the (001) direction. The XRD pattern also matched with the JCPDS Card #41-1445, which is in an agreement with the results of Sharma et al. (Sharma et al., 2018). In addition, the SnO₂ exhibited a rutile structure, which is associated with tetragonal
crystal systems. Figure 4 (b) shows the XRD patterns of the LFMO powder. The peaks revealed the LFMO powder as being in a phase pure spinel structure. The diffraction peaks matched the cubic phase of $\text{Li}_2\text{FeMn}_3\text{O}_8$, which agrees with Kawai et al. (Kawai et al., 1998). While figure 4(c) depicts the XRD pattern of the SnO$_2$/LFMO composite. Most of the XRD diffraction peaks of the composite material are well matched with the LFMO, as a result of a very thick slurry of LFMO covering the entire surface of the SnO$_2$ nanorods beneath it. However, a distinct peak of the SnO$_2$ nanorods orientated along the (10\(\bar{1}\)) direction is visible in the composite XRD pattern.

Figure 5 (a) shows the galvanostatic charge and discharge curves of multiple cycles Li-ion coin cell battery made up of SnO$_2$ electrode at the voltage window between 0.5 V and 3 V. The cell showed a specific capacity of 250 mAh/g during the first charge and discharge cycles. However, it did not maintain significant stability with time at that performance. The charging and discharging capacity decreases as the number of cycles increases, as shown in figure 5 (a). This capacity decrease could be the result of the pulverization of SnO$_2$ due to severe volume expansion impeding the lithium-ion during the intercalation and de-intercalation process. Furthermore, galvanostatic charge and discharge curves of multiple cycles of the SnO$_2$/LFMO composite at the voltage window between 0.5 V and 3 V as shown in Figure 5 (b). The coin cell showed a specific capacity of 325 mAh/g initially and gradually lowered its value as the number of cycles increased. However, the specific capacity (mAh/g) of the composite electrode improved significantly compared to the pristine SnO$_2$, as shown in Figure 5(b).

Figure 6 (a) shows the Coulombic efficiency of SnO$_2$ and SnO$_2$/LFMO composite. The pristine SnO$_2$ is approximately 95% whiles the SnO$_2$/LFMO composite Coulombic efficiency is steady at 100%. Figure 6 (b) shows the specific capacity vs. cycle number of SnO$_2$ and SnO$_2$/LFMO composite electrode. The initial discharge capacity of the pristine SnO$_2$ is 250 mAh/g and the capacity decreases significantly during the first 100 cycles. On the other hand, the
SnO$_2$/LFMO composite electrode material exhibits interesting capacitance behavior with a specific discharging capacity of 325 mAh/g. In addition, the battery shows the capacitance value of 325 mAh/g during the 100th cycle of operation, which is an indication that the SnO$_2$/LFMO composite improved the discharging rate of the pristine SnO$_2$. This improvement could be attributed to the carbonaceous material, which is added to the LFMO, acting as an ideal volume change buffer as well as a good electron conductor (Wang et al., 2015). According to Hudaya et al., carbonaceous material plays an essential role in the prevention of aggregation of SnO$_2$ nanoparticles during the lithiation and delithiation process (Hudaya et al., 2015). Figure 6 (c) shows the relations of cycle number with a capacity retention of SnO$_2$ and SnO$_2$/LFMO composite electrode.

**Conclusion**

The preparation and the electrochemical characterization of pristine SnO$_2$ nanorods and SnO$_2$/LFMO composite electrodes are investigated systematically. The as-prepared electrode is used to fabricate a coin cell Li-ion battery. The electrochemical characterization of the constructed coin cell is used to determine the specific capacity of the electrodes and their behavior as a function of current density. The results show that the addition of the LFMO to SnO$_2$ to form the composite electrode, increases the discharging capacity of the SnO$_2$/LFMO to 325mAh/g, an increase of ~30% than that of the SnO$_2$ electrodes. In addition, we can improve the retention rate of the SnO$_2$ nanorods by forming a composite with the LFMO.

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