Sn/SnO₂ embedded in mesoporous carbon nanocomposites as negative electrode for lithium ion batteries

Fathy M. Hassan a, Zhongwei Chen a, Aiping Yu a, Zhu Chen a, Xingcheng Xiao b

a Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada
b General Motors Global Research and Development Center, 30500 Mound Road, Warren, MI 48090, USA

A R T I C L E   I N F O

Article history:
Received 12 June 2012
Received in revised form 31 August 2012
Accepted 7 September 2012
Available online 16 September 2012

Keywords:
Tin and tin oxides
Mesoporous carbon
Composites
Negative electrode
Lithium ion battery

A B S T R A C T

Mesoporous Sn/SnO₂/carbon composites with uniformly Sn/SnO₂ embedded within the carbon pore walls have been rationally designed and synthesized. These nanocomposites have been characterized by XRD, SEM, TEM, XPS and tested as negative electrodes in a cell using lithium foil as the counter electrode. The inclusion of metallic Sn in SnO₂/CMK-3 resulted in a unique, ordered structure and provided a synergistic effect which resulted in an impressive initial reversible capacity of 799 mAh g⁻¹. In addition, at a higher current of 800 mA g⁻¹, the heterostructure was able to provide a stable capacity of 350 mAh g⁻¹. Furthermore, a retention capacity of ~670 mAh g⁻¹ was obtained after 60 cycles.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Fossil fuel supply limitations and concerns of climate change due to steadily increasing greenhouse gas emissions has drawn public attention toward the development of eco-friendly technologies such as hybrid electric vehicles (HEVs) and electric vehicles (EVs). Among various energy storage systems, lithium (Li) ion batteries currently present the best performances to meet the applications’ demands because of its high gravimetric and volumetric energy density, long cycle life and low self-discharge rate. However, it remains a significant technical challenge to increase the capacity, rate capabilities and durability of Li ion batteries in order to meet the steadily increasing energy density demands for large-size applications.

Metallc tin (Sn) is one of the best candidates as a negative electrode material for next generation Li ion batteries because it is capacity is more than two times higher than that of conventional graphite electrodes. According to the mechanism of the reaction between Sn and Li, up to 4.4 Li atoms can associate with each Sn atom, leading to a theoretical capacity of 994 mAh g⁻¹ [1–3]. Nevertheless, large volume change during alloying/de-alloying of Sn with Li causes mechanical degradation in the form of pulverization and cleavage of the electrode materials, inevitably resulting in poor cycle stability. An alternative candidate to Sn-based materials is SnO₂, which has a two-step energy storage mechanism occurring during battery operation. First, the irreversible formation of Li₂O will occur, followed by the reversible formation of a Li-Sn alloy. The first reaction provides a buffer matrix of the materials to improve the cycle stability and contributes to the irreversible capacity. Conversely, the second reaction contributes to the reversible capacity which is maintained due to mitigated mechanical degradation owing to the buffer matrix remaining from the first reaction. Because of the initial formation of Li₂O, SnO₂ gives a lower theoretical capacity (782 mAh g⁻¹) than that of metallic Sn (994 mAh g⁻¹) [3].

Although SnO₂ provides improved long-term cycle stability compared to metallic Sn, after only a few cycles of alloying/de-alloying reactions with Li, aggregation of Sn may occur which can break down the Li₂O buffer matrix and eventually show the same mechanical degradation problems as that of metallic Sn. Various research efforts to improve the capabilities of SnO₂ materials have been reported, including the incorporation of SnO₂ into carbon-based material composites such as carbon nanotubes (CNTs) [4–8], graphene [9–13] and porous carbon [14], which have been demonstrated to provide remarkable improvements. The carbon-based materials provide high surface areas and a rigid structure to maintain mechanical integrity of the SnO₂ based composites, and conductive pathways to facilitate electron transport during the alloying/de-alloying cycles.

Ordered mesoporous carbon [15] provides host site for nano-sized metal oxide to be formed and its 3-dimensional conductive structure enhances conductivity of the metal oxide based electrode. In addition, it can be suggested that confining the metal oxide particles in the rigid skeleton can suppress large volume
change during alloying/de-alloying cycles. Herein, we report the synthesis of Sn-based mesoporous carbon composites as a negative electrode material for Li ion batteries. We initially prepared SnO₂ embedded in CMK-3, then after controlled heat treatment we were able to partially reduce SnO₂ to form Sn/SnO₂/CMK-3 or completely reduce it to Sn/CMK-3. These materials were investigated as electrode material for Li ion battery. Based on the results from the study, Sn/SnO₂/CMK-3 composite introduced the best performances regarding capacity and cycle stability (Fig. 1).

2. Experimental

2.1. Synthesis of CMK-3

First of all, mesoporous SBA-15 as a silica template was prepared using the triblock copolymer, EO₂₀PO₇₀EO₂₀ (Pluronic P123), as the surfactant and tetraethylorthosilicate (TEOS) as the silica source based on the procedure described by Zhao et al. [16]. Then 1 g of SBA-15 was mixed with a solution containing 1.25 g of sucrose and 0.14 g of H₂SO₄ in 5 g of H₂O, following the method reported by Jun et al. [17]. The mixture was put in a drying oven for 6 h at 373 K, and subsequently the oven temperature was increased to 433 K and maintained there for 6 h. After collecting the sample, the sample was treated again with 0.8 g of sucrose, 0.09 g of H₂SO₄ and 5 g of H₂O followed by another heat treatment at 373 and 433 K as previously stated. The sample was carbonized at 1173 K under a nitrogen gas. The product was washed with 5 wt% HF aqueous solutions at room temperature to remove the silica template. Lastly, CMK-3 was filtered, washed with distilled water and dried at 393 K.

2.2. Synthesis of Sn-based materials/CMK-3

Initially, 100 mg of CMK-3 were dispersed in 250 ml of 0.13 M HCl (prepared using deionized water and concentrated HCl). Then 800 mg of SnCl₂·2H₂O were dissolved in 150 ml DI H₂O and this solution was added to the dispersed CMK-3 solution drop wise while magnetic stirring. After that, the solution was kept stirring for 4 h at room temperature (298 K). Finally the composite SnO₂/CMK-3 was separated by filtration and subsequent washing with DI several times. The residue was dried in an oven at 373 K for 1 day. The composite powder was separated into 3 parts. The first and the second parts were subjected to annealing at 673 and 823 K for 5 h under flowing Ar atmosphere (100 sccm). The third part was annealed at 1073 K for 5 h in a mixture of Ar and 10% H₂ gas.

2.3. Characterization

X-ray powder diffraction (XRD) was conducted to confirm the CMK-3 structure and Sn-based materials’ phases in the CMK-3. The structural properties and morphology of Sn-based/CMK-3 were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). N₂ adsorption–desorption isotherms were used to analyze pore sizes and surface areas by the Brunauer–Emmett–Teller (BET) method. Thermal gravimetric analysis (TGA) was carried out to investigate the ratio of Sn-based materials and CMK-3. X-ray photoelectron spectroscopy (XPS) was also conducted to support the composition of Sn-based/CMK-3 products. The electrochemical performances were conducted with coin type cells. For the working electrode, a slurry consisting of 70% of active material, 10% super-p as a conductive material and 20% polyvinylidene fluoride (PVdF) as a binder was prepared in N-methyl-2-pyridolone (NMP) and was coated on Cu foil. The electrode was dried in the drying oven at 373 K for 1 h, followed by being placed in the vacuum oven at 373 K for overnight. The coin cells were fabricated in an argon-filled glove box with the working electrode and the Li metal as the reference and counter electrode. A polypropylene separator was employed to separate the two electrodes and 1 M LiPF₆ in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC) (Novolyte, USA) was used as the electrolyte. Galvanostatic charge/discharge test was carried out at the voltage range of 0.01–3.00 V (except SnO₂ powder, 0.01–1.50 V) with current density of 100 mA g⁻¹ based on Sn-based materials/CMK-3 mass. For rate capability test the current densities were varied from 100 to 800 mA g⁻¹.

3. Results and discussion

In this study, SnO₂/CMK-3 was first prepared as a reference of the study and then treated by alteration of annealing temperature and atmosphere to transform into metallic Sn. It was confirmed that the amount of SnO₂ in CMK-3 is 58.2% by TGA (Fig. S1 in the supporting information). Fig. 2 shows nitrogen adsorption–desorption isotherms and pore size distributions of pure CMK-3, SnO₂/CMK-3 which was annealed at 673 K and SnO₂ which was obtained from SnO₂/CMK-3 after burning CMK-3 away in air atmosphere at 773 K. Distinct step for pure CMK-3 Between 0.4 and 0.5 of
relative pressure \((P/P_0)\) was observed indicating typical mesoporous material characteristics. After incorporation of SnO\(_2\) into CMK-3, the distinct step in the relative pressure curve disappeared because synthesized SnO\(_2\) into CMK-3 blocks the pore of CMK-3 (Fig. 2a). Another evidence is introduced by pore size distribution curves. SnO\(_2\)/CMK-3 composite shows lower intensity and smaller pore size in the materials (Fig. 2b). The Brunauer–Emmett–Teller (BET) specific surface areas of pure CMK-3, SnO\(_2\)/CMK-3 composite and SnO\(_2\) from SnO\(_2\)/CMK-3 were calculated based on Fig. 2a. The BET surface areas decreased from 1556 m\(^2\) g\(^{-1}\) for pure CMK-3 to 536 m\(^2\) g\(^{-1}\) for SnO\(_2\)/CMK-3 composite suggesting that SnO\(_2\) is successfully formed into the pore of CMK-3 and reduced the surface area. On the other hand, the surface area of the SnO\(_2\) nanoparticles is 136.6 m\(^2\) g\(^{-1}\), which is reasonable value for nano-sized SnO\(_2\) particles.

In addition, TEM images in Fig. 3 exhibit direct evidence of SnO\(_2\) particles formed inside CMK-3. The SnO\(_2\) particles can be found at the channels of CMK-3 in the SnO\(_2\)/CMK-3 composite (Fig. 3b) while pure CMK-3 shows ordered spotless channels in Fig. 3a even though the image is not clear because of the weak resolution between the CMK-3 skeletons. The ordered structure was confirmed by a low angle XRD pattern (inset in Fig. 3a), introducing three peaks of \(\{100\}\), \(\{110\}\) and \(\{200\}\) which agree with two dimensional hexagonal structure (P6\(_{3}\)mm) [17]. Furthermore, a low angle XRD pattern for SnO\(_2\)/CMK-3 (inset in Fig. 3b) suggest that the ordered structure is maintained after incorporation of SnO\(_2\) which is also supported by the TEM image of SnO\(_2\)/CMK-3 in Fig. 3b. The particle size can be estimated to \(\sim 2.5\) nm which is less than the channel size of CMK-3 without aggregation of the particles.

Fig. 4 introduces HRTEM for Sn/SnO\(_2\)/CMK-3 composite material. The image (Fig. 4a) reveals detailed intrinsic nanostructure of these mixed Sn-based materials. The nanoparticles were evenly distributed inside the mesoporous carbon matrix. Several lattice spacing correspond to SnO\(_2\) nanoparticles, e.g. 0.33 nm for the \(\{110\}\) plane, 0.26 nm for \(\{101\}\), and 0.24 nm for \(\{200\}\) were successfully elucidated by selected area electron diffraction (SAED) pattern. It was difficult to detect any lattice spacing correspond to metallic Sn, even though it was confirmed by XRD (cf Fig. 8). This suggests that metallic tin is formed by reduction of carbon in a small fraction in the deep pores of the CMK-3. These buried nanoparticles of Sn, which are overlayered by several carbon and SnO\(_2\), were difficult to be detected by HRTEM. Furthermore, the element analysis performed by EDS mapping of the Sn/SnO\(_2\)/CMK-3 sample was displayed in Fig. 4c. It shows that the Sn/SnO\(_2\) nanoparticles were homogeneously distributed and clearly confirm that there is no agglomeration inside the material. The EDS elemental analysis (Fig. 4b) showed that the molar ratio of Sn to O is slightly less than 1:2, which suggest that there is a small portion of metallic Sn is embedded in the material.

Fig. 5 shows the TEM for SnO\(_2\)/CMK-3 after being subjected to annealing at 1073 K in a mixture of Ar and 10% H\(_2\) gases. This environment was suitable to reduce all SnO\(_2\) to metallic Sn. Because of the low melting point of tin and large surface energy, the particles tend to diffuse on the surface of carbon forming larger particles, or tiny droplets, which eventually coalesce forming large islands of metallic Sn. The islands of metallic Sn are clearly shown by TEM images (Fig. 5a), and TEM dark field (Fig. 5c). Elemental mapping of the elements C, O and Sn, which was detected based on Fig. 5c is also a strong evidence for Sn agglomeration. The process of agglomeration did not lead to collapse of the mesoporous carbon skeleton (Fig. 5b). However, it may have caused some local break for parts of the nano carbon rods. Fig. 6 compares the SEM images of pure CMK-3 (Fig. 6a), and SnO\(_2\)/CMK-3 composite (Fig. 6b). It can be noted that there is no distinct change between pure CMK-3 and SnO\(_2\)/CMK-3 composite. It is indicating that most SnO\(_2\) is formed interior of CMK-3 and the SnO\(_2\) do not destroy the framework of the CMK-3. Fig. 7 introduces SEM images of the SnO\(_2\) particles after burning CMK-3 from SnO\(_2\)/CMK-3 composite. The aggregated particles are found in Fig. 7a because high surface energy of nano-sized SnO\(_2\) cannot be kept without the CMK-3’s frameworks. However, on the surface of the SnO\(_2\) particles the trace of nano-sized SnO\(_2\) particles can be found and that morphology is attributed to the high surface area (Fig. 7b).

To confirm the phases of Sn-based materials, an X-ray diffraction (XRD) analysis was carried. Fig. 8 shows the XRD patterns for the materials with different annealing conditions. The XRD patterns of the SnO\(_2\)/CMK-3 treated by 673 K in Ar atmosphere and pure SnO\(_2\) obtained from the SnO\(_2\)/CMK-3 are corresponding to the tetragonal SnO\(_2\) with cassiterite structure (JCPDS No. 41-1445) [18]. Based on the peak broadness, it is assumed that the SnO\(_2\) particles are made up nanocrystalline size. The particle size can be estimated to \(\sim 2.5\) nm, which is comparable with channel size of CMK-3 without aggregation of the particles, by using Scherrer equation [18] (see the Supporting information). With the increase in temperature up to 823 K in Ar, the XRD pattern suggests some SnO\(_2\) was reduced to metallic Sn (JCPDS No. 86-2265) [18] in the carbon matrix resulting in coexistence of SnO\(_2\) and Sn in the CMK-3. By further reduction of SnO\(_2\) at higher temperature and hydrogen gas, it is confirmed by XRD pattern that all of SnO\(_2\) were reduced to metallic Sn and the XRD pattern also suggests that Sn is agglomerated to become larger particles. X-ray photoelectron spectroscopy (XPS) was conducted to examine the chemical composition of the surface of SnO\(_2\)/Sn/CMK-3 composite. XPS spectrum proved that the material is composed of tin, oxygen and carbon elements (Fig. 9a).
Fig. 3. TEM images of the (a) pure CMK-3 and (b) SnO₂ incorporated CMK-3, inset: low angle X-ray diffraction (XRD) patterns.

Fig. 4. (a) High resolution TEM image (inset: SAED patterns), (b) EDS spectrum and (c) dark field TEM image of the Sn/SnO₂/CMK-3 composites and the corresponding C, O, and Sn EDS elemental mapping.
Fig. 5. (a) and (b) TEM images of different area of Sn/CMK-3 and (c) dark field TEM image and the corresponding C, O and Sn EDS elemental mapping.

Fig. 6. SEM images of (a) CMK-3 and (b) SnO$_2$/CMK-3 composite.
High resolution spectrum for Sn element presents around 487 (Sn 3d5/2) and 496 eV (Sn 3d3/2) peaks for Sn^4+ (Fig. 9b). Another high resolution spectra shows peaks at around 531 and 285 eV are attributed to the O1s from SnO2 and C1s from CMK-3, respectively (Fig. 9c and d) [13]. Based on those series characterization techniques, SnO2 and (or) Sn materials were successfully incorporated into CMK-3 and Sn-based materials can be controlled by the annealing conditions. In addition, EDS and XPS proposed strong evidences of chemical composition of CMK-3.

Electrochemical performances were carried out by galvanostatic discharge and charge processes (Fig. 10). Fig. 10b demonstrates number of cycle with retention capacity of the series products that were synthesized in this work. Fig. 10a exhibits voltage and capacity curves of initial, 2nd and 3rd cycles of SnO2/Sn/CMK-3 electrode which shows superior cycle stability among the products. The electrode, consisting of SnO2/Sn/CMK-3 with carbon black and PVdF in a weight ratio of 70:10:20, is casted on a Cu current collector (Fig. 11).

The initial cycle in Fig. 10a shows large irreversible capacity which is caused by conversion reaction of SnO2 with Li ion into Sn and Li2O, a solid–electrolyte interface (SEI) layer formation and some irreversible reaction of Sn and CMK-3 during Li insertion and extraction. The SnO2 reaction mechanism has been proposed in other reports as below [3,19,20].

\[
\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \quad \text{(irreversible reaction)} \tag{1}
\]

\[
\text{Sn} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{Sn} \quad \text{where} \quad 0 \leq x \leq 4.4 \quad \text{(reversible reaction)} \tag{2}
\]

According to the curves of subsequent cycles, irreversible capacity sharply decreased, indicating that most of irreversible reactions occurred during 1st discharge. The Sn/SnO2/CMK-3 shows first cycle Coulombic efficiency of about 58%. This is attributed to the irreversible decomposition of SnO2 into active metallic tin surrounded by an inactive Li2O matrix, in addition to SEI formation. Subsequently, the cycle efficiency is maintained at almost 100% as the cycle number increases up to 100 cycles (see Fig. 10b, and Fig. S2 in the Supporting information). The initial charge capacities are 799, 616, 636, and 392 mAh g\(^{-1}\) for the SnO2/Sn/CMK-3, SnO2/CMK-3, Sn/CMK-3 and SnO2, respectively. As expected, metallic Sn contained materials give higher capacity based on their theoretical capacity [18,21]. However, the capacity of Sn/CMK-3 is lower than SnO2/Sn/CMK-3. This is attributed to the fact that increasing the Sn content resulted in larger Sn particle sizes which provide less reactivity for Li alloying/de-alloying process [22].

After 30 cycles, retention capacities are about 88.6, 76.4, 49.6, and 22.7% for the SnO2/Sn/CMK-3, SnO2/CMK-3, Sn/CMK-3 and SnO2, respectively. In particular, SnO2/Sn/CMK-3 exhibits the best performances in terms of initial capacity and cycle stability, indicative of a synergistic effect existing in mixed phase Sn-based materials. This is consistent with a recent report by Wen et al. [13] who observed improved capacity and cycle performance for graphene based composites in the presence of both Sn and SnOx. It is assumed that metallic Sn contributes increase capacity and Li2O matrix from SnO2 during 1st discharge suppresses Sn particles from agglomeration among the particles during Li alloying/de-alloying processes [21,23]. Moreover, CMK-3 plays critical role for the electrochemical performances. CMK-3 provides 3-dimensional electron pathway and large contact sites for the Sn-based materials [24]. Additionally, its 3-dimensional frameworks maintain electrical contact with Sn materials which are likely agglomerated and then severely changed in their volume as Li alloying/de-alloying proceeds and not only provide buffer space for the large volume change of Sn-based.
Fig. 9. (a) Low resolution XPS spectrum of SnO2/Sn/CMK-3; high resolution XPS of (b) Sn3d, (c) O1s and (d) C1s in SnO2/Sn/CMK-3.

materials but also suppress the volume change. It is also worth noting that CMK-3 work as active material in the composite, partially contributing the specific capacity. These roles of CMK-3 can be directly supported by measuring the performance of Pure CMK-3 (see Fig. S3 in the supporting information). The initial cycle for pure CMK-3 shows a first charge capacity of 430 mAh g\(^{-1}\), the subsequent cycles shows stable reversible capacity at about 390 mAh g\(^{-1}\) for more than 60 cycles. Additionally, referring to Fig. 10b, SnO2/CMK-3 composite demonstrates high initial capacity and acceptable cycle stability which is attributed to the functions of CMK-3 in the composite. However, Sn/CMK-3 composite does not present good cycle stability. It is assumed during the reduction of SnO\(_2\) to metallic Sn, the particles were agglomerated to become bigger size and then could destroy the frameworks of CMK-3 during cycles. The growth of the size after conversion of SnO\(_2\) into Sn was confirmed by the TEM image (Fig. 5) and XRD patterns (Fig. 8). The rate performance along with cycle stability of SnO\(_2\)/Sn/CMK-3 composite was tested and shown in Fig. 10. The test was conducted from 100 to 800 mA g\(^{-1}\) of the current density with 5 cycles to investigate cycle stability. At the highest current density of 800 mA g\(^{-1}\) the composite exhibits around 350 mAh g\(^{-1}\) with good stability which is close to the theoretical capacity of conventional graphite (372 mAh g\(^{-1}\)) that can be achieved at the current density of 30 mA g\(^{-1}\)[25]. Furthermore, it has been

Fig. 10. Galvanostatic (a) discharge and charge curves of SnO\(_2\)/Sn/CMK-3 composite, (b) charge capacity of SnO\(_2\), SnO\(_2\)/CMK-3, Sn/SnO\(_2\)/CMK-3 and Sn/CMK-3 composites, and the Columbic efficiency of Sn/SnO\(_2\)/CMK-3, at current rate of 100 mA g\(^{-1}\) with respect to the cycle number.
reported that at the similar current density, lower than 50 mAh g⁻¹ was obtained for the conventional graphite [25].

In order to clarify the hybrid effect on the electrochemical performance of SnO₂/CMK-3, we calculated theoretically the capacity of physical mixture of SnO₂/CMK-3. We considered the theoretical capacity of SnO₂ as 782 mAh g⁻¹ and for CMK-3 as 430 mAh g⁻¹ (estimated from Fig. S3 and the maximum charge capacity). Considering the mass ratio of 58.2% SnO₂ and 41.8% CMK-3 (as computed from TGA result Fig. S1), the theoretical capacity of the hypothetical mixture can be calculated as follow:

\[ C_{\text{theoretical for SnO}_2/\text{CMK-3}} = (C_{\text{SnO}_2} \times \text{mass}\% \ of \ SnO_2) + (C_{\text{CMK-3}} + \text{mass}\% \ of \ CMK3) = 782 \times 0.582 + 430 \times 0.418 = 634.86 \text{ mAh g}^{-1} \]

(3)

Interestingly the observed capacity for SnO₂/CMK-3 is 616.23 mAh g⁻¹ (based on the maximum charge capacity observed in Fig. 10b). This value is comparable to the estimated theoretical capacity of the hybrid SnO₂/CMK-3 material. On performing similar calculation for the hybrid Sn/SnO₂/CMK-3 material, assuming after annealing there is minimal change in mass ratio of tin to carbon and assuming both Sn and SnO₂ contribute 1:1 of their theoretical capacity which mean \( C_{\text{theoretical for Sn/SnO}_2} = 888 \text{ mAh g}^{-1} \), then:

\[ C_{\text{theoretical for Sn/SnO}_2/\text{CMK-3}} = (C_{\text{SnO}_2/Sn} \times \text{mass}\% \ of \ SnO_2/Sn) + (C_{\text{CMK-3}} + \text{mass}\% \ of \ CMK3) = 888 \times 0.582 + 430 \times 0.418 = 696.56 \text{ mAh g}^{-1} \]

(4)

This value is less than the observed, for this material, in Fig. 10b which is 798.64 mAh g⁻¹. This result points to a synergistic effect caused by embedding Sn nanoparticles along with SnO₂ into the nanochannels of CMK-3. For the above estimated value, we assumed a Sn to SnO₂ ratio of 1:1; however in reality, the actual value of Sn is less. This means that the theoretical value should be less than 696.56 mAh g⁻¹ calculated for Sn and SnO₂ present in unity, and greater than 634.86 mAh g⁻¹ corresponding to only SnO₂ with CMK-3. This emphasizes the synergistic effect that exists between these components, with a capacity observed in excess of those predicted herein.

It is not unexpected that the CMK-3 under unseen structure conditions could show high specific capacity. Reference [26] showed that CMK-3 may have a reversible capacity level up to LiₓC₆, where \( x = 2.3–3 \). However, a satisfactory explanation for this high capacity has not been yet developed. In order to account for the high specific capacity for Sn/SnO₂/CMK-3, we have to think about the synergistic effect of the inclusion of Sn nanoparticles into SnO₂ where both are embedded into the nanochannels of the CMK-3. This unique structure is believed to enable less activation over-potential for the Li intercalation into CMK-3 leading to more usable sites and consequently increasing the overall charge capacity of the composite material.

Based on the rate capability and cycle stability results, it is proposed that the SnO₂/Sn/CMK-3 composite is an excellent negative electrode material for Li ion battery over the conventional negative electrode material.

4. Conclusions

In conclusion, SnO₂ and/or Sn embedded in CMK-3 was prepared to investigate the electrochemical performances for Li ion batteries. Initially, Sn ion precursor was incorporated into CMK-3 and then annealed at different temperature under variable environmental conditions to obtain SnO₂/Sn/CMK-3 and Sn/CMK-3. In terms of initial capacity, cycle stability and rate capability, SnO₂/Sn/CMK-3 demonstrated the best performances which are superior to the conventionally used graphite. It is proposed that metallic Sn contributes to the higher initial specific charge capacity of 799 mAh g⁻¹ compared to other previously reported [11,27] Sn-based composites, meanwhile the promising cycle stability and rate capability is attributed to the 3-D structure of the mesoporous carbon, CMK-3. The specific capacity of 350 mAh g⁻¹ was achieved at the current density of 800 mAh g⁻¹ and the retention capacity of 670.9 mAh g⁻¹ was obtained at 50 cycles. With the remarkable rate capability and cycle stability, the SnO₂/Sn/CMK-3 composite is considered as highly promising negative electrode materials for next generation Li ion batteries.

Acknowledgments

The University of Waterloo, the Natural Sciences and Engineering Research Council of Canada (NSERC), the Waterloo Institute for Nanotechnology and General Motors are gratefully acknowledged for their financial support for this work. The authors also wish to thank Dr. Linda Nazar and Mr. Hey Woong Park for their kindness.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2012.09.015.

References

C. L.S. 852
F.M. 10.1039/c2jm14999k.


