Cu₆Sn₅-TiC-C Nanocomposite Anodes for High-performance Sodium-ion Batteries

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Abstract

Cu₆Sn₅ alloy nanoparticles dispersed in a TiC and C conductive matrix have been developed via high energy mechanical milling (HEMM), and the resulting Cu₆Sn₅-TiC-C nanocomposite has been assessed as anodes for sodium-ion batteries. Composite anodes of Sn-C exhibit poor cyclic performance even with the introduction of 2 vol. % fluoroethylene carbonate (FEC) additive into the electrolyte. In contrast, Cu₆Sn₅-TiC-C nanocomposite anodes exhibit stable cycle life corresponding to a capacity retention of ~80% at 40 cycles and high-rate performance with a capacity retention of ~ 62% at 3,000 mA g⁻¹. These superior performance metrics is ascribed to the well-developed electrochemically active nanocrystalline material (Cu₆Sn₅) as well as a hybrid conductive matrix (TiC and C). The incorporation of 2 vol. % FEC additive into the electrolyte further improves the performance of Cu₆Sn₅-TiC-C nanocomposite to display a capacity retention of ~94% at 250 cycles and high-rate capacity retention of ~ 82% at 5,000 mA g⁻¹, which are attributed to the formation of a thin and stable SEI layer in presence of FEC.

Keywords: sodium-ion batteries, copper-tin alloy anodes, titanium carbide, electrolyte additives

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1. Introduction

To date, the high-performance characteristics, including high energy density, long cycle life, and high-rate capability, of Li-ion batteries have led to the revolution of the portable electronics industry [1-3]. Nevertheless, the future prospects of Li-based energy storage technologies for large-scale applications, such as electric vehicles and grid storage, are not always optimistic due to the high cost and restricted abundance and availability of lithium. Therefore, it is necessary that a more sustainable energy-storage technology with a more stable material supply is developed as we progress. Based on this scenario, sodium-ion batteries are becoming attractive as a potential electrochemical energy storage system due to their favorable characteristics such as high abundance, low cost, easy recycling, and oxidation potential only ~ 0.3 V lower than that of lithium [4-6]. Even though there are many limitations with sodium-ion battery technology, much groundwork for further research and development is being established. In particular, researchers have focused on the advanced cathode materials for sodium-ion batteries [7-10]. By comparison, the investigation of anode materials for sodium-ion batteries has been making slow progress. Among the anode materials, carbonaceous materials including amorphous carbon and hard carbon, which have charge capacities of $200 \sim 250 \text{ mAh g}^{-1}$, have been vigorously explored [11-15]. However, carbon materials have serious problems including limited reversibility and the risk of sodium plating, resulting from their operating voltage close to that of Na/Na^+ , similar to what is observed in lithium-ion cells. Due to the low theoretical capacity as well as safety problems, it is essential to explore new anode materials beyond carbon for sodium-ion batteries.

Metallic/intermetallic alloy compounds could be a promising alternate anode for sodium-ion cells. Various alloy systems have been extensively developed so far [16-20]. Certain alloy

systems have potential advantages such as the suppression of solid-electrolyte interphase (SEI) layer, elimination of sodium-plating (resulting in better safety) due to higher operating voltages, and high volumetric capacity due to high tap density values relative to graphite ($< 1 \text{ g cm}^{-3}$). A variety of metallic/intermetallic materials including germanium (Ge), antimony (Sb), tin (Sn), and so on are able to react with sodium-ions and form an alloy during discharge. However, sodium alloy systems face a significant problem of large volume expansion/contraction with the uptake or removal of sodium-ions: Sn-Na and Sb-Na alloy formations generate large volume changes of, respectively, $\sim 424\%$ for $\text{Na}_{15}\text{Sn}_4$ and $\sim 390\%$ for Na_3Sb [18]. To overcome these limitations, it is necessary to develop buffering against the volume expansion by utilizing nanostructured materials and active-inactive nanocomposite materials. Thus, much research utilizing alloy compounds consisting of active-inactive components as anodes for sodium-ion cells have been conducted; however, there still remain various problems to be solved, including the ratio between active and inactive materials, composition of the composite materials, and optimized size of the active materials in inactive materials.

We present here a novel $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ nanocomposite, which is prepared by a facile high energy mechanical milling (HEMM) synthesis process. The incorporation of a hybrid conductive matrix of TiC and carbon and conductive metal framework (Cu) supporting the electrochemically active material Sn leads to much better electrochemical performance. Meanwhile the similarly prepared Sn-C composite lacking the TiC and Cu frameworks displays inferior electrochemical performance. In addition, $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ nanocomposite exhibits a high tap density (2.2 g cm^{-3}) compared to that of carbon; thus offering high volumetric capacity as well.

2. Experimental

2.1. Preparation of Cu₆Sn₅-TiC-C nanocomposite

Required amounts of Sn (99.8%, < 45 μm , Aldrich), Cu (99%, 45 μm , Acros Organics), and Ti (99.99%, ~325 mesh, Alfa Aesar) powders were mixed and heat-treated at 900 °C for 12 h in argon atmosphere. The formed Cu-Sn-Ti phases were then mixed with 20 wt.% of acetylene black and placed in an 80 cm³ capacity hardened steel vial with steel balls (diameter 0.5 and 0.25 inch at a ball to powder mass ratio of 20 : 1). The HEMM process was conducted at a speed of 500 rpm for 40 h under argon atmosphere with a Fritsch Pulverisette 6 planetary mill, which generated the Cu₆Sn₅-TiC-C nanocomposite. For the preparation of tin-carbon (Sn-C) nanocomposite, Sn powder was mixed with 20 wt.% acetylene black and subjected to HEMM for 40 h under the same conditions.

2.2. Materials Characterization

The as-prepared Cu₆Sn₅-TiC-C samples were characterized with a Rigaku RINT 2000 diffractometer and Cu K α radiation in the range of 20 – 70° with a scan rate of 0.03° s⁻¹. To examine the sodium-ion storage mechanism, *ex situ* XRD measurements were carried out with cycled electrochemical cells at different states of charge/discharge. Specifically, the tested electrodes were disassembled, rinsed with anhydrous dimethyl carbonate to remove the residual salts, and dried in an argon-filled glove box. The developed nanostructure and composition of the powder samples were characterized with a JEOL 2010F transmission electron microscope (TEM).

2.3. Electrochemical Characterization

Electrodes were prepared on Cu foils with slurries consisting of 70 wt.% active material, 15 wt.% polyvinylidene fluoride (PVDF) as a binder, 15 wt.% Super P carbon as a conductive

medium, and N-methyl-pyrrolidone (NMP) as a solvent. The electrodes were then dried at 60 °C for 3 h in an air oven and at 120 °C overnight in a vacuum oven. The coin-type (CR 2032) cells were assembled with sodium metal as the counter electrode, a sample electrode as the working electrode, 1 M NaClO₄ in a mixture of ethylene carbonate (EC)/propylene carbonate (PC) (1:1 by volume) as the electrolyte, and a glass separator (APFA from Millipore). Two vol. % fluoroethylene carbonate (FEC) was also introduced as an electrolyte additive for a comparison of the electrochemical performance. The prepared electrodes had an active material (Cu₆Sn₅) content of 1 – 1.5 mg, but the capacity values were calculated based on the total weight of the composite (Cu₆Sn₅ + TiC + C). The theoretical capacity of Cu₆Sn₅ for sodium-ion batteries is 516 mAh g⁻¹[21]. The galvanostatic charge/discharge experiments were conducted at a constant current density of 100 mA g⁻¹ (~ C/5 rate) at 0.0 – 2.0 V vs. Na/Na⁺. Electrochemical impedance spectroscopy (EIS) analysis was carried out with a Solartron SI 1260 instrument with an applied amplitude of 10 mV in the range of 100 kHz to 0.1 Hz at 2.0 V vs. Na/Na⁺.

3. Results and Discussion

Fig. 1 shows the XRD pattern of the Cu₆Sn₅-TiC-C composite material. The starting powder materials were Cu, Sn, Ti, and C. After the HEMM process, the XRD pattern reveals the peaks of Cu₆Sn₅ and TiC without any peaks of pure Cu, Sn, and Ti, illustrating that the reactions to form Cu₆Sn₅ and TiC are completed during the HEMM. All the peaks could be designated to the Cu₆Sn₅ and TiC based on the JCPDS card No. 00-045-1488 and JCPDS No. 00-032-1383, respectively.

TEM images of the as-prepared Cu₆Sn₅-TiC-C composite are shown in Fig. 2. In Fig. 2a, individual nanoparticles corresponding to Cu₆Sn₅ and TiC are observed, which have particle

sizes of 8 – 12 nm, and the crystalline nature of Cu_6Sn_5 and TiC could be confirmed with the high-resolution TEM image as shown in Fig. 2b in addition to the amorphous carbon matrix. The inset in Fig. 2b displays the selected-area electron diffraction (SAED) pattern, where the dot patterns resulting from the Cu_6Sn_5 and TiC nanocrystallines could be observed as well.

Fig. 3 depicts the initial voltage profiles of the Cu_6Sn_5 -TiC-C composite. For a comparison, the voltage profile of the Sn-C composite is also shown in Fig. 3a. The Sn-C composite anode reveals discharge and charge capacities of, respectively, 639 mAh g^{-1} and 445 mAh g^{-1} , which corresponds to an initial Coulombic efficiency of $\sim 70\%$. In the case of Cu_6Sn_5 -TiC-C composites, the electrode without FEC additive shows discharge and charge capacities of, respectively, 373 mAh g^{-1} and 225 mAh g^{-1} , corresponding to an initial Coulombic efficiency of $\sim 61\%$. The electrode with 2 vol. % FEC additive shows discharge and charge capacities of, respectively, 146 mAh g^{-1} and 261 mAh g^{-1} , which correspond to an initial Coulombic efficiency of $\sim 56\%$. The electrode with the FEC additive shows lower capacity values, which is discussed later. Both electrodes exhibit similar sodiation/desodiation voltage profiles except for the occurrence of the decomposition of FEC at $\sim 0.8 \text{ V}$ as seen in Fig. 3b. These initial Coulombic efficiencies are frequently observed in the case of alloy anodes due to the irreversible reduction of the electrolyte to form the solid-electrolyte interphase (SEI) layer. Specifically, when comparing other initial Coulombic efficiencies reported in the literature, our values (70% for Sn-C and $56 \sim 61\%$ for Cu_6Sn_5 -TiC-C) are relatively higher than the average values; for example, SnSb-C anodes [22] have an initial Coulombic efficiency of $\sim 75\%$, mesoporous Sn/C anode [23] has $\sim 40\%$, Sn-graphite anode [24] has $\sim 51\%$, $\text{Sn}_{0.9}\text{Cu}_{0.1}$ anode [25] has 35% , SnS-Sn-C anode [26] has $\sim 60\%$, and electrospun Sb/C anode [27] has $\sim 55\%$. It is noted that the Sn-C anode exhibits more distinct voltage plateaus compared to that of the Cu_6Sn_5 -TiC-C anode.

The voltage profile of Sn-C shown in Fig. 3a clearly shows three discharge and four charge plateaus, reflecting the stepwise sodium-tin (Na-Sn) alloy phase transition processes [22]. The Cu_6Sn_5 -TiC-C composite anode has somewhat less apparent voltage plateaus as shown in Fig. 3b. The voltage plateaus are reflected as peaks in the differential capacity plots (DCP) presented in Fig. 4. It is noted that the Cu_6Sn_5 -TiC-C composite exhibits DCP profile similar to that of Sn-C even though the alloying/dealloying reaction voltages with Na-ion are a bit different. In addition, when observing the discharge scan of Cu_6Sn_5 -TiC-C composite, the peak intensity of the alloying reaction is not prominent as compared to those of Sn-C composite, which could be related to a partial alloying reaction between Sn in Cu_6Sn_5 -TiC-C composite and Na-ion, due to limited Na-ion diffusion within the primary electrode particle (Cu_6Sn_5) [21]. This supposition can be further explained with the *ex-situ* XRD patterns.

Fig. 5 shows the *ex-situ* XRD patterns of Cu_6Sn_5 -TiC-C composite at different stages of discharge-charge. During discharge (*i.e.* 0.4 V and 0.1 V), additional peaks at 30.6° , 32.0° , 43.9° , and 44.9° are observed, which correspond to pure Sn. In addition, Cu_6Sn_5 peaks are detected during discharge even though the peak intensity corresponding to them becomes weak. Therefore, it can be concluded that the whole of each Cu_6Sn_5 primary electrode particle does not react with Na-ion to generate new Na-Sn alloy. Furthermore, when the Cu_6Sn_5 -TiC-C composite is discharged, a peak appears at around 35.5° and the peak disappears at fully discharged state (*i.e.* 0 V). This peak may correspond to an intermediate $\text{Na}_x\text{Cu}_{6-y}\text{Sn}_{5-z}$ phase. At the fully discharged state, two peaks at 31.9° and 37.5° corresponding to the $\text{Na}_{15}\text{Sn}_4$ phase can be observed. The peaks corresponding to the TiC phase are persistent throughout the discharge-charge conditions, illustrating little electrochemical activity [18]. During the charge, the Sn peaks increase in intensity and the intermediate $\text{Na}_x\text{Cu}_{6-y}\text{Sn}_{5-z}$ phase can be observed again, while the $\text{Na}_{15}\text{Sn}_4$

peaks disappear. At the fully charged state (*i.e.* 2 V), the Cu₆Sn₅, Sn, and TiC phases coexist.

Fig. 6 shows the cyclic performance of the as-prepared Cu₆Sn₅-TiC-C at a current of 100 mA g⁻¹ (C/5 rate) and compares it to that of Sn-C composite. In the case of Sn-C composite anode, very unstable cyclability is seen. For example, its charge capacity is about 225 mAh g⁻¹ at only 10 cycles, which corresponds to a capacity retention of 50%. When 2 vol. % of FEC additive is incorporated into the electrolyte, although it shows better cyclability at the beginning, fast capacity fade occurs as shown in Fig. 6a. The Cu₆Sn₅-TiC-C composite anode exhibits much better cycle performance compared to Sn-C composite as seen in Fig. 6b. After 40 cycles, it maintains a capacity retention of 80%. This can be ascribed to both the conductive metal framework (Cu) supporting Sn and the incorporation of a hybrid conductive matrix composed of TiC and carbon, resulting in lower impedance. On introducing the FEC additive (2 %), it exhibits lower charge capacity than those without FEC additive as shown in Fig. 6b due to the decomposition of FEC at ~ 0.8 V in the first discharge for the formation of a stable SEI layer, resulting in a lower discharge capacity, and no significant difference in the initial Coulombic efficiency before and after FEC addition [18]. In addition, the capacity values are observed to increase at the beginning stages of cycling (*i.e.* from first cycle to 30th cycle), which could be related to an enhanced reaction of Cu₆Sn₅ with Na-ion. As discussed in the *ex-situ* XRD section, there is no full reaction of all Cu₆Sn₅ material with Na-ion in the initial stages. However, a greater portion of Cu₆Sn₅ active material may participate in the reaction with Na⁺ ions during extended cycling. Therefore, the capacity value increases during the beginning cycles as observed in Fig. 6b. The Cu₆Sn₅-TiC-C with FEC additive exhibits very stable cyclability even at 100th cycle. Furthermore, when considering the tap density of Cu₆Sn₅-TiC-C (2.2 g cm⁻³), it offers a good volumetric capacity as shown in Fig. 6c. After 250 cycles, it still maintains a

capacity retention of ~94%. This outstanding cyclic performance could be attributed to a stable and thin SEI layer formation on the electrode surface during long cycle test in addition to the incorporation of a hybrid conductive matrix and a conductive metal framework.

The cyclic performance of the as-prepared $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ composites with and without FEC additive was further investigated by electrochemical impedance spectroscopy (EIS). Fig. 7 shows the EIS data of $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ composite with and without the FEC additive after 100 cycles, which exhibit two semicircles and one slope. The inset in Fig. 7 illustrates the equivalent circuit, where R_e represents the electrolyte resistance, R_{SEI} the surface resistance, C_{SEI} the capacitance, R_{ct} and C_{ct} the charge-transfer resistance and double layer capacitance for sodiation, respectively, and Z_w the diffusion impedance of sodium-ion in the solid phase. The semicircle at the high-frequency region corresponds to sodium-ion diffusion through the surface and the other at the high-to-medium frequency region represents the charge-transfer reaction between the electrochemically active-anode mass and sodium at the electrode surface, while the slope in the low-frequency region is ascribed to the sodium-ion diffusion through the bulk material. The diameter of the first semicircle represents the SEI film resistance (R_{SEI}) and the diameter of the second semicircle corresponds to the charge transfer resistance (R_{ct}). When comparing the R_{SEI} and R_{ct} of the $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ composite anodes without and with the 2 vol. % FEC additive at 100 cycles, the impedances are $R_{\text{SEI}} = 0.073 \text{ ohm g}$ and $R_{\text{ct}} = 0.328 \text{ ohm g}$ for the electrode without the additive, and $R_{\text{SEI}} = 0.039 \text{ ohm g}$ and $R_{\text{ct}} = 0.212 \text{ ohm g}$ for the electrode with the FEC additive. Therefore, the $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ nanocomposite with 2 vol. % FEC demonstrates smaller semicircle areas corresponding to a smaller surface and charge-transfer resistance, due to the suppression of the formation of thick solid-electrolyte interphase (SEI) layer on the anode surface, than the $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ composite anode without FEC additive. This result confirms that

the Cu₆Sn₅-TiC-C composite with FEC additive exhibits better electrochemical performance as discussed in the previous section.

The rate performance of the as-prepared Cu₆Sn₅-TiC-C nanocomposite is described in Fig. 8. First, it was cycled at 100 mA g⁻¹ for 30 cycles and then the current rate was increased incrementally from 500 mA g⁻¹ to 5,000 mA g⁻¹. In the case of Cu₆Sn₅-TiC-C nanocomposite without 2 vol. % of FEC additive into electrolyte, a noticeable decrease in capacity is seen when increasing the current rate compared to those of Cu₆Sn₅-TiC-C with FEC additive. The relative percent capacity retention values based on the capacity obtained at 100 mA g⁻¹ are shown in Fig. 8b. At a high-current rate of 3,000 mA g⁻¹, Cu₆Sn₅-TiC-C without FEC additive has a percent capacity retention of 62%. On the other hand, Cu₆Sn₅-TiC-C with FEC additive demonstrates a superior capacity retention of 92% at 500 mA g⁻¹, 89% at 1,000 mA g⁻¹, 84% at 3,000 mA g⁻¹, and 82% at 5,000 mA g⁻¹. This high-rate cycle performance could be ascribed to the formation of more stable and thin SEI layer when introducing 2 vol. % of FEC additive into the electrolyte along with the smaller electrode impedance as shown previously in Fig. 7.

4. Conclusions

Cu₆Sn₅-TiC-C nanocomposite synthesized by HEMM has been examined as an anode material for Na-ion batteries. The incorporation of both a metal framework supporting the electrochemically active component Sn and a hybrid conductive matrix consisting of TiC and carbon leads to much better electrochemical performance compared to a Sn-C composite anode. The Sn-C composite anode exhibits inferior cycle performance even when an FEC additive is introduced into the electrolyte. The Cu₆Sn₅-TiC-C composite anode displays good cyclic life with a capacity retention of ~ 80% after 40 cycles without the FEC additive and ~ 94% at 250

cycles with 2 vol. % of FEC additive in the electrolyte. Furthermore, Cu₆Sn₅-TiC-C with FEC additive shows superior rate performance with a normalized capacity retention of 82% at 5,000 mA g⁻¹ compared to that found without FEC additive (~53%) at the same high-current rate. This enhanced electrochemical performance could be related to a stable and thin SEI layer formation together with the conductive metal framework, smaller charge-transfer resistance, and better dispersion of the electrochemically active material in a hybrid conductive matrix consisting of TiC and carbon. Even though the as-prepared Cu₆Sn₅-TiC-C nanocomposite demonstrates good electrochemical performance, it is necessary to facilitate a more complete reaction between Cu₆Sn₅ and Na⁺ ions by controlling the nanoparticle size of Cu₆Sn₅ and/or optimizing the molar ratio of the reactants (*i.e.*, Cu, Sn, Ti, and C) to achieve an increase in specific and volumetric capacity values with long cyclic life.

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Figure captions

Figure 1. XRD patterns of the as-synthesized Cu_6Sn_5 -TiC-C nanocomposite. The vertical lines represent the reference peaks of, respectively, Cu_6Sn_5 and TiC.

Figure 2. (a) TEM image of Cu_6Sn_5 -TiC-C nanocomposite. The yellow circles indicate the nanoparticles of Cu_6Sn_5 and TiC dispersed in the amorphous carbon matrix. (b) High-resolution TEM image of Cu_6Sn_5 -TiC-C nanocomposite, with the inset showing the electron diffraction pattern over the selected region.

Figure 3. Initial voltage profiles of (a) Sn-C and (b) Cu_6Sn_5 -TiC-C electrodes at 100 mA g^{-1} .

Figure 4. Differential capacity plots (DCP) of (a) Sn-C and (b) Cu_6Sn_5 -TiC-C electrodes between 0.0 and 1.5 V vs. Na/Na^+ .

Figure 5. *Ex-situ* XRD patterns of Cu_6Sn_5 -TiC-C nanocomposite anodes before cycling, at various states of discharge (0.4, 0.1, and 0 V), and at various states of charge (0.5, 0.7, and 2 V). The various alloy phases are identified with different symbols.

Figure 6. Comparison of the cyclic performances of (a) Sn-C and (b) Cu_6Sn_5 -TiC-C with and without 2 vol. % of FEC additive at 100 mA g^{-1} . (c) Long cyclic life of Cu_6Sn_5 -TiC-C nanocomposite displayed with volumetric capacity.

Figure 7. Electrochemical impedance spectra (EIS) of $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ electrodes with and without 2 vol. % of FEC additive in the electrolyte at 100 cycles. The inset depicts the equivalent circuit.

Figure 8. (a) Rate performances of $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ with and without 2 vol. % of FEC additive at various current rates. (b) Normalized % charge capacity retention values of $\text{Cu}_6\text{Sn}_5\text{-TiC-C}$ composite anodes with and without 2 vol. % of FEC additive.

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Graphical Abstract