FeSn₂-TiC nanocomposite alloy anodes for lithium ion batteries

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ABSTRACT

FeSn₂-TiC nanocomposite alloy anodes for lithium-ion batteries have been synthesized by a mechanochemical process involving high-energy mechanical milling of Fe/Ti, Ti/Sn, and carbon black. Characterization of the nanocomposites formed with x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) reveals that this alloy is composed of crystalline nanoparticles of FeSn₂ dispersed in a matrix of TiC. The FeSn₂-TiC alloy shows an initial gravimetric capacity of 511 mAh g⁻¹ (1073 mAh cm⁻³) with a first-cycle coulombic efficiency of 77 % and a tap density of 2.1 g cm⁻³. The TiC buffer matrix in the nanocomposite anode accommodates the large volume change occurring during the charge-discharge process and leads to good cyclability compared to similar Sn-based anodes.

Keywords: lithium-ion batteries; alloy anodes; nanocomposites; mechanochemical reaction; electrochemistry

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Introduction

Lithium ion batteries have been instrumental in the growth of the personal electronics industry due to their high energy storage capacity relative to other battery systems. Efforts to extend the application of lithium-ion technology to the fields of transportation and stationary storage have led to much research in this area in recent years. Significant incremental strides have been made in Li-ion batteries but the use of new and innovative materials and structures offers an avenue for a dramatic enhancement in performance. This is especially true on the anode side where the limited capacity, low density, limited rate capability, and safety issues of graphitic carbon have led to extensive investigation into Sn-based anode materials [1-3]. These efforts are already yielding fruitful results as the Sony Corporation has released a Sn/Co/C composite anode material as part of their Nexelion battery system offering improved capacity, cycle life, and charge rates when compared to systems employing the conventional carbon anode.

In terms of reaction and performance, Sn anodes vary significantly from their graphite counterparts. Graphite anodes undergo an intercalation reaction in which Li^+ ions are reversibly transported and stored in between 2-D carbon planes forming a final stoichiometry of LiC_6 and yielding a theoretical capacity of 372 mAh g^{-1} . This reaction is desirable in that it occurs at low potentials, granting maximum open-circuit voltage for the cell, and causes only a very small volume change in the graphite structure, maintaining good electrode integrity [4-5]. However, the low reaction potential has a negative aspect as it leads to significant solid-electrolyte interphase (SEI) layer formation, a contributor to first cycle irreversibility, and presents a risk of dangerous lithium plating on the electrode surface, especially under conditions of fast charge [2,6-7]. The 2-D transport mechanism in graphite serves to further limit the rate capability of the electrode and the low material density limits the practical volumetric capacity of graphite

electrodes [8]. The reaction of Sn with lithium is a reversible electrochemical alloying reaction which allows for much greater lithium storage capacity with a final stoichiometry of $\text{Li}_{22}\text{Sn}_5$ and a theoretical capacity of 993 mAh g^{-1} , as elucidated in reactions 1 and 2 [3].

In addition, a slightly higher average reaction potential of $\sim 0.5 \text{ V}$ means that the possibility of lithium plating and its associated dangers are essentially eliminated and that the electrodes are, therefore, more safely subjected to fast charging conditions [6-7,9]. Tin also possesses a high density, allowing for high volumetric capacity electrodes. However, the mobility of Li^+ within tin is quite poor, which limits the actual rate capability of the material, and as with all alloying anodes, the reaction with lithium results in an extremely large volume change, which causes significant mechanical strain and eventual structural failure of the electrode with the end result of a short cycle life [8,10-14].

The material investigated in this study is a Sn-based composite electrode utilizing an active material of intermetallic FeSn_2 combined with an inactive reinforcing phase of TiC . FeSn_2 has been previously studied as a negative electrode in lithium-ion systems and shown to operate via the conversion mechanism shown in reactions 3 and 4 [15-18].

This reaction yields a theoretical capacity of 804 mAh g^{-1} , which is slightly lower than the capacity of pure Sn due to the inclusion of the electrochemically inactive Fe. The inactive Fe in this material, which is extruded from the structure during lithiation as shown in reaction 3, provides structural reinforcement against the large volume change of Sn and provides additional

conductive enhancement to the otherwise poorly conductive Li-Sn system [19-21]. This serves to enhance the material cycle life beyond that of pure Sn. However, the cycle life of FeSn_2 alone is still insufficient for practical purposes, so combinations with additional reinforcing phases are implemented. Different types of composites are commonly implemented in an effort to extend the cycle life of alloying anodes: carbon-based composites in which the reinforcing phase is a softer carbon material that coats the active phases and maintains electronic connectivity throughout the volume change of the lithiation/delithiation process, and ceramic-based composites that rely on the high strength and toughness of the reinforcing phase to absorb the strain of the large active material volume change and thereby prevent active material crumbling [10,17,22]. While carbon has demonstrated success in enhancing the cycle life of alloying anodes, there are some significant drawbacks to the approach. Carbon is a low density material and has a reactive surface with respect to the organic electrolyte employed in lithium-ion cells, which leads to lower volumetric capacity for the composite electrode and higher first cycle losses to fully passivate the carbon [18,23-26]. Ceramics employed in these composites are frequently oxides such as Al_2O_3 or carbides such as TiC [24-25,27-29]. The reinforcing ceramic of TiC was selected for this study for a number of reasons: it has demonstrated the capability to effectively increase the cycle life of alloying anodes; it is a highly conductive ceramic material, so it can also aid in electrical conductivity of the electrode; it has a higher density that can yield greater volumetric electrode capacity; it has produced composites with lower first cycle losses than competing carbon composites [24-25].

Accordingly, the synthesis and performance characterization of FeSn_2 - TiC is reported here. The synthesis is carried out with a high energy mechanical milling (HEMM) process because of its ability to yield nano-scale products, which is beneficial to electrode performance, as well as

high-density products to enable high volumetric capacity of the final electrode [18-19,23,27-30]. The synthesized $\text{FeSn}_2\text{-TiC}$ is characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), while its electrochemical performance is measured and compared to baseline electrodes in which (i) the reinforcing phase is substituted for carbon black in the form of an $\text{FeSn}_2\text{-C}$ composite or (ii) the intermetallic FeSn_2 active phase is replaced with pure Sn in a Sn-TiC composite.

Experimental

The $\text{FeSn}_2\text{-TiC}$ composite electrode is synthesized by a two-step method. The first step is the preparation of the precursors of Fe/Ti and Ti/Sn by heating. The second step is the milling of the Fe/Ti and Ti/Sn precursors with carbon black to yield the final $\text{FeSn}_2\text{-TiC}$ material

In step one, a 4 : 3 atomic mixture of Fe (Alfa Aesar, 98 %, -325 mesh) and Ti (Alfa Aesar, 99.99 %, -325 mesh) and a 2 : 1 atomic mixture of Ti and Sn (Alfa Aesar, 99.8 %, -325 mesh) are separately heated in a flowing argon atmosphere at 800 °C for 6 h. This precursor preparation process facilitates inter-atomic mixing of the metallic elements, which is necessary for the HEMM step to yield the desired products under the synthesis conditions.

In step two, the Fe/Ti and Ti/Sn are mixed together such that the atomic ratio of Fe : Sn is 1 : 2 so that the final desired phase of FeSn_2 will be formed. A stoichiometric amount of carbon black (Alfa Aesar, acetylene black, 99.99 %, -200 mesh) to facilitate the full conversion of Ti to TiC is also added to the precursors. This full mixture is then subjected to HEMM under an argon atmosphere at room temperature for 48 h at a speed of 500 RPM and a ball to powder ratio of 20 : 1. This HEMM process drives a mechanochemical reaction to form the final products of FeSn_2 and TiC based on reaction 5 and due to the free energy reduction from the formation of TiC from Ti and carbon ($\Delta G^\circ_{\text{TiC}} = -206 \text{ kJ mol}^{-1}$) and the alloying of Fe with Sn to form FeSn_2 ($\Delta G^\circ_{\text{FeSn}_2} =$

-58 kJ mol⁻¹) [31-32]. Based on precursor ratios, the final FeSn₂-TiC electrode powder has a phase composition of 51 % FeSn₂ and 49 % TiC, assuming complete reaction.

Baseline electrode powders of FeSn₂-C and Sn-TiC were also synthesized via HEMM for comparative analysis of FeSn₂-TiC. FeSn₂-C was synthesized from precursors of metallic Fe, metallic Sn, and carbon black with a 1 : 2 atomic ratio of Fe : Sn and 20 wt. % carbon black. The formation of FeSn₂ was again induced by HEMM due to the lowering of free energy to form FeSn₂. However, in this case, the reinforcing material of carbon black was only mixed mechanically with the active phase instead of being formed *in situ* as was the case with TiC. Sn-TiC utilized precursors of metallic Sn, metallic Ti, and carbon black balanced to yield a final composition of 60 wt. % TiC. For both materials, the precursor powder mixtures were unheated and subjected to HEMM with similar conditions as described above. XRD of these electrode powders can be seen in Figure S1.

The phase constituency of the synthesized electrode powder was characterized with XRD using a Philips X-ray Diffractometer with Cu-K α radiation. The morphology of the composite powder was analyzed with a JEOL JSM-5610 SEM and a JEOL 2010F high-resolution TEM operating at 300 kV. Tap density measurements were carried out with a Quantachrome AT-4 Autotap machine.

To analyze the electrochemical properties of the FeSn₂-TiC and FeSn₂-C materials, electrodes were prepared by first mixing a slurry with 70 wt. % active material, 15 wt. % conductive carbon (Super P), and 15 wt. % polyvinylidene fluoride (PVDF) binder dissolved in N-methyl pyrrolidone (NMP). Electrodes were made by casting this slurry onto a Cu foil with

the doctor blade method and subsequently drying the electrodes in a vacuum oven at 120° C for 24 h. Individual electrodes with areas of 1 cm² and active mass loading of ~ 2.5 mg were punched from the cast electrode. These electrodes were assembled into CR2032 coin cells in an Ar-filled glovebox with the cast electrode as the working electrode, lithium foil as the counter electrode, a Celgard polypropylene separator, and 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1 : 1 v/v) as the electrolyte. The discharge/charge cycling analysis was performed over a voltage range of 0 – 2.0 V vs. the lithium reference at a constant current density of 100 mA g⁻¹ with an Arbin battery cycler.

Results and Discussion

Figure 1 shows the XRD patterns of the as-synthesized FeSn₂-TiC sample. The FeSn₂-TiC sample is shown to contain active material particles of FeSn₂ (JCPDS File: 01-071-8402) with a lattice constant of $a = 6.545 \text{ \AA}$. The reaction for the formation of FeSn₂ appears to have progressed to completion as there are no residual precursor peaks. The pattern also shows peaks corresponding to crystalline TiC (khamrabaevite phase, JCPDS File: 00-031-1400), with lattice constant of $a = 4.33 \text{ \AA}$. No peaks for carbon are seen in the sample, suggesting that it is mostly incorporated into the titanium carbide phase as desired.

SEM micrographs were taken of the FeSn₂-TiC powder, shown in Figure 2. The powder is composed of roughly spherical particles, with sizes ranging from 5 microns to nanometer-scale particles. Figure 3 shows the higher magnification HRTEM images of the same FeSn₂-TiC material. Figure 3a shows what would be viewed in Figure 2 as a single particle roughly 100 nm in diameter to actually be an agglomerate of smaller crystallites. The crystalline nature is evidenced by the mildly crystalline diffraction pattern shown in the inset but closer examination in Figure 3b enables the observation of atomic lattice fringes measured to match to lattice

spacings for both FeSn₂ and TiC. This agrees with the measured XRD results of crystalline phases for both active FeSn₂ and reinforcing TiC and further elucidates that the morphology is indeed a well inter-mixed nanocomposite of the two phases. This is a very attractive morphology for two reasons: (i) the nano-scale active particles yield the previously discussed benefits of greater strain accommodation during volume change and shorter Li⁺ ion diffusion distances that lead to enhanced cycle life and rate capability; (ii) the intermixing with the TiC reinforcing phase allows it to reinforce the active material more uniformly throughout the composite and serves to separate regions of active material into smaller domains, mitigating the agglomeration of these active particles to keep them on the nano-scale [33-34]. The BET surface area of FeSn₂-TiC was also measured as described in the supplementary information (see Figure S2) to be 0.975 m² g⁻¹, meaning the small active material particles are retained in larger agglomerates that allows the material to retain low surface area and minimize SEI-layer losses.

The voltage vs. capacity curves for the first 5 cycles of FeSn₂-TiC in half-cells are shown in Figure 4. In the initial discharge, shown with a dashed line, a bump in the curve is observable beginning at roughly 0.6 V corresponding to the irreversible formation of an SEI layer on the electrode surface. The primary plateau associated with the lithiation of FeSn₂ begins at approximately 0.3 V and slopes slightly to just above 0.0 V vs. Li/Li⁺. Upon discharge there is a single primary plateau observed centered at 0.5 V. Subsequent cycles show similar primary plateau location with heavy overlap from cycles 2 through 5, meaning good reversibility. In addition, after the first cycle, there is no bump in the region initially identified with SEI layer formation, further confirming this reaction in the initial discharge cycle to be SEI layer formation. Overall, the voltage vs. capacity curves of this material are very attractive, with low reaction potential allowing for a maximized cell voltage and relatively flat plateaus with minimal

hysteresis between charge and discharge. In addition, though the reaction potential remains low, it is still higher than that of graphite, allowing for a degree of safety enhancement especially as it relates to lithium plating.

The differential capacity plot (DCP) shown in Figure 5 gives a more detailed account of the reaction potentials for FeSn₂-TiC. Figure 5a shows for a comparison the reaction peaks of active Sn incorporated with reinforcing TiC. The strongest peak during discharge falls at about 0.4 V while on charge it is at roughly 0.6 V [35]. Figure 5b shows the DCP of FeSn₂-TiC to be in agreement with those observed in the literature and similar to Sn-TiC in terms of peaks present [16-17,22,35]. However, in general, the peaks are much wider for the FeSn₂-TiC material. The wider peaks are most likely due to the smaller Sn active particle sizes after the initial cycling step in which metallic Fe is extruded from the structure [36]. Smaller particle sizes leads to sloping of the reaction plateau, and therefore, widening of the differential capacity peak because as the particle size decreases, the surface effects play a larger role relative to the bulk crystalline effects, allowing for a larger solid solubility range before phase-change reactions progress as part of the lithiation process [37]. Figure 5b also shows the DCP curve for FeSn₂-TiC after 30 cycles to be very similar to that of the second cycle, highlighting the good reversibility of the reaction. A small increase in the polarization can be seen with cycling as the anodic peaks are shifted to higher voltages, possibly associated with the increasing impedance caused by SEI-layer formation.

The quantitative electrochemical capacity values for the initial cycles of Sn-TiC, FeSn₂-C, and FeSn₂-TiC are summarized in Table 1. FeSn₂-TiC demonstrates an initial discharge capacity of 511 mAh g⁻¹ and a second cycle reversible capacity of 398 mAh g⁻¹, yielding an irreversible capacity loss of 113 mAh g⁻¹. As described in the experimental section, the FeSn₂-TiC precursors

were measured such that the final makeup of the electrode composite is 49 wt. % TiC and 51 wt. % FeSn₂. Assuming the lithiation of FeSn₂ occurs as shown in reaction 3, the theoretical capacity of pure FeSn₂ is 804 mAh g⁻¹. In addition, although it does not undergo phase change during cycling, Figure S3 shows that TiC synthesized by HEMM has demonstrated a capacity of ~ 100 mAh g⁻¹ in half cell testing, possibly as a result of unreacted carbon black precursor. This yields a total theoretical capacity of 460 mAh g⁻¹ for FeSn₂-TiC, slightly above the observed reversible capacity, meaning there may be some non-participating active material present. The higher capacity in the initial cycle is likely a result of the irreversible losses associated with SEI layer formation and the first cycle losses of milled TiC, which inflate the initial capacity but are not reversible. When performances are compared between FeSn₂-TiC, FeSn₂-C, and Sn-TiC conclusions can be drawn regarding the effects of the components within the various composites. Neither FeSn₂-TiC nor Sn-TiC have carbon black as a final component in their composite structure and they exhibit much lower first cycle losses than FeSn₂-C, which has carbon black. This is in agreement with previous studies attributing higher first cycle irreversibility to carbon black in composite electrodes [25]. In addition, the use of FeSn₂ intermetallic instead of Sn as the active material results in significant increase in capacity retention as demonstrated by the higher capacity values at 100 cycles for both FeSn₂-TiC and FeSn₂-C relative to Sn-TiC.

A cycle life performance comparison is shown for the same three materials in Figure 6, highlighting the benefits of combining the FeSn₂ intermetallic with a TiC reinforcing phase. The importance of the FeSn₂ active phase is demonstrated by the performance of Sn-TiC, which shows good early cycling but suffers dramatic capacity loss after about 30 cycles. This short cycle life is attributed to in part to the lack of an intermetallic phase, the cycle life extending benefits of which are discussed previously [19-21]. In addition, the active Sn was incorporated

into the reinforcing TiC structure by an *in situ* formation process during HEMM as was the case for FeSn₂-containing materials in which the active material formed in tandem with the reinforcing TiC, allowing for more intermixed morphology.

The FeSn₂-C composite, which lacks the TiC reinforcing phase in favor of carbon black secondary phase, shows very large initial capacity loss due to the carbon black inclusion and subsequently has a consistent capacity fade as the carbon phase is unable to adequately mitigate the capacity loss effects of the active material volume change. Similar capacity fade has been observed in previous studies of alloying anode materials where carbon black was the reinforcing phase [25]. The FeSn₂-TiC material demonstrates both good early cycling as well as stable capacity for 100 cycles. This is due to the greater accommodation of the volume change by the TiC reinforcing phase. Figure 7 shows this effect through *ex situ* SEM observation of cycled electrode surfaces of FeSn₂-C and FeSn₂-TiC. The FeSn₂-C electrode is much rougher, with some particles at the surface having appeared to physically broken free from the electrode. The FeSn₂-TiC surface, on the other hand, still appears quite smooth with the active particles still bound within the binder material. Figure S4 shows Nyquist plots arising from the EIS measurements of FeSn₂-C and FeSn₂-TiC, showing similar SEI-layer resistance values and enhanced Li⁺ ion diffusion in the bulk FeSn₂-TiC material.

The early specific capacity of FeSn₂-TiC in Figure 6 due to the greater content of TiC, but as elucidated in Figure 8 below, this is made up for by the high density of FeSn₂-TiC. The practical tap density of FeSn₂-TiC was measured to be 2.1 g cm⁻³, more than twice that of commercial graphite powder and nearly twice the 1.1 g cm⁻³ measured for FeSn₂-C. Figure 8 shows the effects this has on the electrode when capacity values are represented volumetrically. FeSn₂ shows an early volumetric capacity of over 800 mAh cm⁻³ and retains well over 600 mAh cm⁻³

after 100 cycles. This is a roughly two-fold increase over the volumetric capacity demonstrated by graphite. The coulombic efficiency of the electrode is also shown in Fig. 7 to be 71 % on the first cycle and it quickly rises to greater than 99 % by the 10th cycle. After this point, the coulombic efficiency levels out to a final value of 99.2 %.

Conclusion

FeSn₂-TiC nanocomposite anodes have been synthesized via a HEMM method and characterized by XRD, SEM, and TEM. The characterization revealed that the FeSn₂-TiC sample is composed of FeSn₂ and TiC mixed together at the nano-scale. The FeSn₂-TiC nanocomposite shows excellent cyclability to 100 cycles and demonstrates the benefits of combining the use of an FeSn₂ active intermetallic together with TiC reinforcing phase relative to using pure Sn active material or carbon black reinforcing phase. The FeSn₂-TiC sample possesses an initial capacity of 511 mAh g⁻¹ (1073 mAh cm⁻³) with a tap density of 2.1 g cm⁻³ and is able to retain a capacity of over 325 mAh g⁻¹ (683 mAh cm⁻³) for 100 cycles. In addition, the material possesses an attractive electrochemical profile with low reaction potentials, flat reaction plateaus, and minimal hysteresis.

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Tables

Table 1. Capacity data of synthesized composite electrodes.

Electrode	Initial Capacity (mAh g ⁻¹)	Reversible Capacity (mAh g ⁻¹)	Irreversible Capacity (mAh g ⁻¹)	Capacity at 100 Cycles (mAh g ⁻¹)
Sn-TiC	432	350	82	41
FeSn ₂ -C	883	657	226	284
FeSn ₂ -TiC	511	398	113	328

Figure Captions

Figure 1. XRD pattern of the as-synthesized FeSn₂-TiC electrode powder with peaks of FeSn₂ and TiC identified.

Figure 2. SEM image of the as-synthesized FeSn₂-TiC electrode powder.

Figure 3. HRTEM images of the as-synthesized FeSn₂-TiC electrode powder showing (a) a lower magnification image of a ~ 100 nm agglomerate with the inset showing the diffraction pattern and (b) a high magnification image of adjacent crystallites of FeSn₂ and TiC with identified lattice fringe planes labelled.

Figure 4. Voltage vs. capacity plot for the first five cycles of FeSn₂-TiC at a constant current of 100 mA g⁻¹ over a potential window of 0 – 2.0 V vs. lithium.

Figure 5. Differential capacity plot (DCP) of the second cycle of (a) Sn-TiC and (b) FeSn₂-TiC as well as the 30th cycle of FeSn₂-TiC.

Figure 6. Cycle life performance of various synthesized electrodes cycled at a constant current of 100 mA g⁻¹ over a potential window of 0 – 2.0 V. vs. lithium for 100 cycles.

Figure 7. *Ex situ* XRD of electrode surface after 50 charge/discharge cycles of (a) FeSn₂-C and (b) FeSn₂-TiC

Figure 8. Volumetric capacity performance of FeSn₂-TiC compared to that of graphite with the coulombic efficiency of FeSn₂-TiC identified on the secondary axis.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Highlights

- FeSn₂-TiC nanocomposite anode was synthesized via high-energy mechanical milling (HEMM)
- Crystalline nanocomposites of FeSn₂ and TiC are identified after HEMM.
- Use of conductive TiC yields higher density and lower first cycle losses.
- Incorporation of TiC into the electrode structure enhances cycle life.
- High tap density yields a volumetric capacity of greater than 1070 mAh cm⁻³ for FeSn₂-TiC

FeSn₂-TiC nanocomposite alloy anodes for lithium ion batteries

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Experimental

After the synthesis process described in the primary manuscript experimental section, the synthesized electrode powders of Sn-TiC and FeSn₂-C were analyzed by X-ray diffraction (XRD) using a Rigaku Miniflex 600 with Cu-K α radiation. The resulting patterns reveal that for Sn-TiC, shown in Figure S1a, the only crystalline phases are metallic Sn and TiC, as expected. For FeSn₂-C, shown in Figure S1b, there are strong peaks relating to both FeSn₂ and Sn, meaning the precursors did not fully react to form FeSn₂, leaving residual Sn in the sample that may affect performance.

In order to determine the surface area of the synthesized FeSn₂-TiC electrode powder, nitrogen adsorption-desorption curves were measured with a Quantachrome Autosorb iQ2 instrument and used to determine the Brunauer-Emmett-Teller (BET) surface area of the sample. Figure S2 shows these isotherms as well as the determined BET surface area of 0.975 m² g⁻¹.

As TiC is a major component of FeSn₂-TiC, its electrochemical performance was also measured in half-cell configuration to determine its contribution to the overall electrode performance. The TiC analyzed here was synthesized by subjecting stoichiometric amounts of Ti and carbon black to HEMM under an argon environment and at room temperature for 20 h. The material demonstrated a non-negligible stable capacity of ~ 100 mAh g⁻¹, as shown in Figure S3a, with the electrochemical profile in Figure S3b showing no definitive reaction peaks.

Electrochemical impedance spectroscopy (EIS) was carried out on cycled half-cells of both

FeSn₂-C and FeSn₂-TiC to demonstrate the performance effects of the TiC reinforcing matrix relative to carbon black. The measurement was done with a Solartron SI1260 with a signal amplitude of 10 mV relative to the measured cell voltage and a frequency range of 10 kHz to 0.01 Hz. EIS measurements were taken after 0, 1, and 10 charge/discharge cycles with the active material as the working electrode and lithium foil as the counter/reference electrode. The Nyquist plots shown in Figure S4 can be broken into three regions: a high-frequency semi-circle associated with the SEI-layer resistance, a middle-frequency semi-circle associated with the charge-transfer resistance between the electrolyte and the electrodes, and the linear low frequency region of the Warburg impedance associated with the diffusion of Li⁺ ions in the bulk electrode. At 0 cycles in Figure S4a the electrodes have not yet undergone conditioning and as such have large impedance associated with the SEI-layer and charge-transfer. In the Warburg region, though, the FeSn₂-TiC composite demonstrates a steep slope, meaning greater diffusivity of lithium in the bulk composite. After a single cycle, Figure S4b shows that the surface layer and charge-transfer resistances of both samples have been drastically reduced relative to the uncycled condition, with FeSn₂-TiC showing slightly lower surface resistance. In addition, FeSn₂-TiC again shows greater bulk lithium diffusivity than FeSn₂-C in the low frequency region. In Figure S4c after 10 cycles, FeSn₂-C shows increasing SEI-layer resistance roughly equal to the value observed for FeSn₂-TiC. However, FeSn₂-TiC now shows a second semi-circle arising from a charge-transfer resistance that is not present in the FeSn₂-C material. Once again, the bulk diffusivity of FeSn₂-TiC is higher than that of FeSn₂-C.

Overall the EIS analysis shows that both materials have similar SEI-layer resistance that increases with cycling after an initial conditioning cycle. The implementation of a TiC reinforced composite yields greater bulk lithium diffusion than a carbon black composite, though the higher

content of TiC must also be considered. In addition, after 10 cycles, the TiC containing composite shows a charge-transfer resistance that is not present, or much lower, in the carbon black composite.

Figure S1. XRD pattern of as synthesized electrode powders of the baseline materials: (a) Sn-TiC and (b) FeSn₂-C.

Figure S2. Nitrogen adsorption/desorption isotherm measurements of FeSn₂-TiC used in the determination of the BET surface area.

Figure S3. The electrochemical performance of TiC synthesized by HEMM showing: (a) the material cycle life and stable capacity value and (b) the voltage versus capacity profile over the first three cycles.

Figure S4. Electrochemical impedance spectroscopy of FeSn₂-C and FeSn₂-TiC shown in the form of Nyquist plots after (a) 0 cycles, (b) 1 cycle, and (c) 10 cycles.