Electrochemical Interaction of Sn-Containing MAX Phase (Nb$_2$SnC) with Li-Ions

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Supporting Information

ABSTRACT: In this Letter, we report on the interaction of Nb$_2$SnC ternary transition metal carbide (MAX phase) with Li ions. Because of the presence of Sn layers, which can undergo alloying reaction with Li, this material may be promising for energy storage. Contrary to most electrodes, the performance of this material improves along with the cycle number; specifically, the capacity increases gradually from 87 to 150 mAh g$^{-1}$ at a current density of 500 mA g$^{-1}$ during 600 charge/discharge cycles. Postcycling study suggests that the alloying reaction makes the material break into smaller particles, increasing capacity. Because Nb$_2$SnC is just one of many MAX phases, this work lays the foundation for exploration of the MAX phases in lithium-ion or other batteries.

Developing energy conversion and storage device with excellent performance and high stability remains an important task.1 Rechargeable batteries with various ions (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$) have become the main means of electrical energy storage. Among those, lithium-ion batteries are the most popular and widely studied because of their high voltage and relatively long cycle life, but Li-ion capacitors and Li–S batteries also use Li-ions for energy storage. Tin is a prospective negative electrode material because of its attractive theoretical capacity from its alloying reaction with lithium (the theoretical capacity of Li$_4$Sn is 994 mAh g$^{-1}$), which exceeds the capacity of traditional graphite electrodes. However, excessive expansion of tin upon reaction with Li (~300% volume expansion) and poor cyclic stability limit the use of metallic tin as the anode material.2,3 Usually, carbon additions such as graphene are used to mitigate the volume expansion of Sn and obtained good electrochemical properties; for example, Wang et al. reported that 3D Sn–graphene shows a reversible capacity of 466 mAh g$^{-1}$ at 879 mA g$^{-1}$ with an outstanding cycling stability.3–6

Since 2011, ternary and 2D transition metal carbides and nitrides labeled MAX phases and their derivatives, MXenes, have attracted increasing attention for applications in the field of energy storage because of their layered structure and metallic conductivity.7–9 More than 155 kinds of MAX phases have been studied, of general chemical formula M$_n$AX$_n$$_{1-3}$, where M stands for transition metals (such as Ti, Nb, Mo, or V), A is the symbol of the A-group element (such as Al, Sn, or Si), X is carbon and/or nitrogen, and n is an integer from 1 to 3.9–13

Herein, we explore Li intercalation behavior of Nb$_2$SnC, which is one of the few known MAX phases with Sn as the “A” layer. The hypothesis that led to this study was that Nb$_2$SnC, having a layered structure similar to graphite, offers a metallic conductivity of Nb$_2$C layers combined with Sn layers in the Nb$_2$SnC layers, which have high theoretical capacity. Intercalation of Li into Si- and Al-containing MAX phases has been investigated in the past, showing promise7,14 but no MAX phase with Sn as A-element layers has been studied. This work focuses on exploring the behavior of the MAX phase containing Sn in a lithium electrolyte and studying its structural changes upon cycling, which may provide a basis for the exploration of other MAX phases in the energy storage field.

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The XRD pattern and SEM image of Nb$_2$SnC are shown in Figure 1. The XRD result shows the successful synthesis of Nb$_2$SnC (PDF # 04-005-0034), although NbC impurity was detected. NbC is a common carbide impurity that is difficult to eliminate during the synthesis of Nb-based MAX phases or by a post-treatment, but NbC does not exhibit any lithium capacity and its contribution to the total capacity can be ignored in this study. The bulk Nb$_2$SnC material seen in Figure 1b displays a typical layered structure with an average particle size of about 2 μm (±0.5 μm). The atomistic structure model of Nb$_2$SnC is shown in Figure 1c, which is similar to that of other 211 MAX phases, such as Ti$_2$AlC and Nb$_2$AlC. Figure 2a shows a TEM image of Nb$_2$SnC, which is typical for a MAX phase morphology. Furthermore, the selected area electron
diffraction pattern seen in Figure 2b confirms the hexagonal single-crystal structure of Nb$_2$SnC grains. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 2c–e) was used to examine the niobium, tin, and carbon element distributions in the particle and confirm that all of them are uniformly distributed and the observed particle is Nb$_2$SnC.

Figure 3a shows cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s$^{-1}$ in the voltage window from 0.01 to 3 V vs Li/Li$^+$ and compares the CVs of the first two cycles with those of the 501st and 502nd cycles. The existence of two irreversible peaks in the first cycle is attributed to the formation of a solid–electrolyte interface (SEI). It is worth noting that small peaks at around 0.5 and 0.6 V vs Li/Li$^+$ in the oxidation and reduction profiles, corresponding to alloying reaction of Sn, appeared after cycling. In order to make the peaks more pronounced, a half-cell Li-ion battery was assembled using pure Nb$_2$SnC powder as the working electrode (i.e., no conductive additives, no copper foil, no binder). Figure S1 shows the cyclic voltammogram of pure Nb$_2$SnC powder. In the lithiation/delithiation reactions, LiSn (0.64 V, 0.81 V), Li$_2$Sn$_3$ (0.49 V, 0.74 V), and Li$_{12}$Sn$_3$ (0.17 V, 0.52 V) confirmed the existence of alloying reaction of Sn. Another broad oxidation peak at about 1.2 V and a redox peak at 0.8 V may be the reaction between Li$^+$ and the MAX phase. Comparing the cyclic voltammograms of the 501st and 502nd cycles with the first two cycles, although no redox peak appeared or disappeared, the overall shape of the curve significantly changed as the original redox peaks became broader after 500 cycles. This indicates that the electrochemical capacity was significantly improved. Electrochemical impedance spectroscopy (EIS) at 3 V vs Li/Li$^+$ (Figure 3b) shows that the semicircles’ diameter decreased with the cycle number, which may come from the decrease of the charge transfer resistance, indicating self-improvement of the electrode and rapid electron transport during the electrochemical reactions, which may be one of the reasons for the increase in capacity. In the Nyquist plots of the 501st–503rd cycles, there is an additional semicircle corresponding to the SEI film, showing the SEI film’s presence on the surface of the material. The long cycle performance at a current density of 500 mA g$^{-1}$ and charge/discharge profiles at same current density at different cycles are presented in Figure 3c,d, respectively. Interestingly, the discharge capacity increased along with the cycle number, specifically from about 70 mAh g$^{-1}$ in the first cycle to about 156 mAh g$^{-1}$ after 1500 cycles.

Figure 4. Effect of cycling on electrochemical response of Nb$_2$SnC. (a) Rate performance of the MAX phase Nb$_2$SnC. (b) Cycling performance at a current density of 500 mA g$^{-1}$. (c) Rate performance after long cycling at 500 mA g$^{-1}$.

Figure 5. (a,b) SEM images and (c) TEM images of Nb$_2$SnC electrodes after 600 cycles. HRTEM images (d) before and (e,f) after 600 cycles.
The corresponding rate performance of the Nb$_2$SnC is shown in Figure 4. The discharge capacities reached 115, 110, 102, and 87 mAh g$^{-1}$ at current densities of 50, 100, 200, and 500 mA g$^{-1}$, respectively (Figure 4a). Importantly, the discharge capacity increased from 87 to 150 mAh g$^{-1}$ after 600 cycles at the current density of 500 mA g$^{-1}$, as shown in Figure 4b. Compared to the experiment shown in Figure 3c, results shown in Figure 4b were obtained after cycling at lower current densities, which activated the material and accelerated the reaction process. Moreover, after 600 cycles, the rate performance was further improved, as seen Figure 4c. At the same current densities of 50, 100, 200, and 500 mA g$^{-1}$, the capacity increased to 234, 224, 208, and 151 mAh g$^{-1}$, respectively, which are almost twice the original values.

Figure S2 shows the XPS spectra for the Sn 3d region of Nb$_2$SnC, before and after cycling. The valence of Sn in the original sample is close to 0 (493.3 eV, 484.8 eV), and traces of Sn$^{4+}$ were observed (495.5 eV, 487.3 eV).$^{30-32}$ Sn$^{4+}$ may come from oxidation of Sn powder during the solid-phase sintering process, but its content is negligible. However, after 600 cycles, there is no peak of Sn$^0$. This means that Sn was largely extracted from the MAX phase, at least from the surface layer analyzed by XPS.

Compared to the morphology of the pristine Nb$_2$SnC obtained from SEM (Figure 1a), the sample after 600 cycles has gaps between the layers, as shown in Figure 5a,b. By observing the difference in the cross-sectional SEM images before and after cycling (Figure S3), it can be concluded that the volume of the material increased significantly, even though there may be some SEI film on the surface. Moreover, from the TEM images in Figure 5c, there are many thin and even monolayer nanosheets. This phenomenon may be caused by the volume expansion of the alloying products during cycling, which makes some layers of the MAX phase appear to be exfoliated. Furthermore, as seen Figure 5d, there are some small particles, which could be the Sn (or tin oxide formed after exposure to air) that was extracted from the MAX phase.

In the high-resolution transmission electron microscope (HRTEM) images before and after cycling, shown in Figure 5e, the crystal planes of Nb$_2$SnC are identifiable by the 0.25 nm d-spacing, close to the d-spacing of the (102) planes. After 600 cycles, in addition to the Nb$_2$SnC (102) crystal plane, there are two other crystal structures with spacings of about 0.33 and 0.42 nm. The d-spacing of 0.33 nm is attributed to the (110) plane of SnO$_2$, probably coming from the repeated alloying reaction between Sn and Li, resulting in a small amount of Sn, which formed SnO$_2$ when exposed to air. The interlayer spacing of 0.42 nm is probably coming from the etched Nb$_2$SnC after removal of Sn. In addition, after hundreds of cycles, some smaller, nanometric, Nb$_2$SnC particles with larger spacing of about 0.61 nm appeared, as shown in Figure 5f. We suggest that this is due to the lithium ions entering the interlayers, which causes some of the MAX phase to break down into smaller particles. Because of the decrease of particle size and the gradual appearance of interlayer spacing, the specific surface area of Nb$_2$SnC increases. Therefore, logically, the contribution of EDLC/pseudocapacitance will increase gradually in the subsequent cycles.$^{37}$ This conclusion can also be drawn from the CV curves at different scan rates of the pristine electrode and after 600 cycles, as shown in Figure S5. By comparison, the redox peak was obvious initially, but after 600 cycles, the shape of the CV curves is closer to a rectangle and the redox peak is wider, closer to the capacitive mechanism, which may be one of the reasons for the capacity increase. Combined with the results of Figures 3–5, we speculate that the Li$^+$ ion alloyed with the edge of the Sn layer in Nb$_2$SnC, and the larger volume of Li,Sn broke the bond between Sn and Nb$_2$C layers. Due to the repeated expansion of the outer alloying products, Sn is extracted from the outer layer of MAX phase grains, which leads to a somewhat increased layer spacing. However, from the XRD patterns at different voltages and after 600 cycles (Figure S6), there is no obvious peak change that occurs in the discharge process, which could be because only Sn at the edge of the particle was in contact with lithium ions and participated in the alloying reaction, whereas Sn in the bulk was not involved in the redox process. However, after 600 cycles, there was little change in XRD results; the peaks widened significantly, which may be due to the smaller particle size.

Nb$_2$SnC is the first reported MAX phase with Sn as the “A” element, which shows attractive electrochemical performance in Li-ion electrolytes. At current densities of 50 and 500 mA g$^{-1}$, the capacity values reach 234 and 151 mAh g$^{-1}$ respectively, and there is a phenomenon of capacity increasing with cycling. The lithium ions react with Sn to form Li$_x$Sn, which can gradually exfoliate a few layers and single layers of Nb$_2$C, extract Sn from the structure, and break the large MAX phase particles into smaller and more electrochemically active particles, facilitating pseudocapacitive reaction and contributing to capacity improvement.$^{37}$ The volume expansion and cracking of the electrode are usually drawbacks in most Sn-based electrodes, but this work shows that it can be beneficial for highly conductive Nb$_2$SnC because it substantially increases its electrochemical performance. MAX phase Nb$_2$SnC as an anode in batteries combines the advantages of layered materials and alloying elements and has a longer cycle life than most nanomaterials with Sn nanoparticles. These results may provide inspiration for improving the stability of Sn and other alloying materials, as well as exploration of other MAX family members in electrochemical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01580.

Synthesis and characterization of Nb$_2$SnC; preparation of the electrode and electrochemical measurements; CV curves of pure Nb$_2$SnC powder at a scan rate of 0.1 mV s$^{-1}$; XPS spectra for the Sn 3d region of Nb$_2$SnC before and after 600 cycles; cross-sectional SEM images of Nb$_2$SnC electrodes before and after electrochemical cycling; TEM images of Nb$_2$SnC electrodes after 600 cycles; CV curves at different scan rates before and after cycling; XRD patterns at different voltages of the second cycle; XRD patterns before and after 600 cycles (PDF)

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Notes
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