Evolution of Reduced Graphene Oxide–SnS$_2$ Hybrid Nanoparticle Electrodes in Li-Ion Batteries

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ABSTRACT: Hybrid nanomaterials where active battery nanoparticles are synthesized directly onto conductive additives such as graphene hold the promise of improving the cyclability and energy density of conversion and alloying type Li-ion battery electrodes. Here we investigate the evolution of hybrid reduced graphene oxide–tin sulfide (rGO-SnS$_2$) electrodes during battery cycling. These hybrid nanoparticles are synthesized by a one-step solvothermal microwave reaction which allows for simultaneous synthesis of the SnS$_2$ nanocrystals and reduction of GO. Despite the hybrid architecture of these electrodes, electrochemical impedance spectroscopy shows that the impedance doubles in about 25 cycles and subsequently gradually increases, which may be caused by an irreversible surface passivation of rGO by sulfur enriched conversion products. This surface passivation is further confirmed by post-mortem Raman spectroscopy of the electrodes, which no longer detects rGO peaks after 100 cycles. Moreover, galvanostatic intermittent titration analysis during the 1st and 100th cycles shows a drop in Li-ion diffusion coefficient of over an order of magnitude. Despite reports of excellent cycling performance of hybrid nanomaterials, our work indicates that in certain electrode systems, it is still critical to further address passivation and charge transport issues between the active phase and the conductive additive in order to retain high energy density and cycling performance.

INTRODUCTION

Li-ion batteries (LIBs) have become a ubiquitous energy storage solution with applications ranging from consumer electronics to electric vehicles. To fulfill the increasingly demanding requirements of these applications, there is growing need for batteries with higher capacity, rate capability, and greater cycling stability. Currently, graphite is used as the anode material.4,12,27,28

The layered dichalcogenide structure of SnS$_2$ is composed of tin atoms that are sandwiched between hexagonally close-packed sulfur atoms. Similar to insertion electrodes, SnS$_2$ can intercalate Li ions between its layered structure, but eventually undergoes a conversion reaction followed by an alloying reaction with Li$^+$ ions.10,11 In general, pure SnS$_2$ electrodes are cyclable only at low rates (e.g., 0.1C), and their capacity fades to more than half of their initial capacity in just a few cycles,12,13 followed by a further continuous capacity fade.11,14 At higher rates (e.g., 1C and above), the pure SnS$_2$ electrodes exhibit severe capacity fade because of irreversibility in the above two reactions and large volume expansions. In addition, these electrodes exhibit high polarization and low conductivity across electrodes over battery cycling, and these issues severely limit the application of pure SnS$_2$ electrodes as anodes especially with low carbon content (less than ~10 wt %). Table S1 in the Supporting Information summarizes the performance of some of the pure SnS$_2$ electrodes reported in the literature.

This capacity loss is often partially mitigated by using nontraditional conductive additives such as graphene, reduced graphene oxide (rGO),14–16 carbon nanotubes,17 and graphitic carbon-coatings.18 The high surface area, flexibility, and mechanical resilience of graphene, as well as its morphological compatibility with two-dimensional nanostructures such as SnS$_2$ platelets have been shown to have beneficial effects on capacity and cycling stability.9,14–16,19–28 Such advantages, in combination with nanostructuring of SnS$_2$, offer short Li-ion diffusion paths and reduces crack formation of the electrode material.4,12,27,28

A particularly interesting approach to improve the interface between both materials is to synthesize SnS$_2$ nanoparticles
directly on the surface of conductive additives such as rGO or carbon nanotubes (CNTs) to form “hybrids” rather than physical mixing of the components to form “composites”.29 This can lead to enhanced charge transfer across electrodes due to the efficient charge transfer between the inorganic active particles and the carbon conductive additive30 and has been found to result in improved capacity retention in LIBs.11,15,21

In this paper, we investigate the evolution of rGO-SnS2 electrodes with particular attention to the electrical accessibility of active particles over battery cycling. The SnS2 nanoparticles are synthesized directly on the rGO surface using a solvothermal microwave reaction. This microwave process allows a simultaneous reduction of GO to rGO. Here we provide novel insights related to the evolution of rGO-SnS2 electrodes over many cycles using electrochemical impedance spectroscopy (EIS), galvanostatic intermittent titration (GITT), differential capacity analysis (dQ/dV), and post-mortem studies after extended cycling using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman analyses. These measurements indicate also these hybrids can show a strong passivation of the rGO surface, which is detrimental to battery cycling performance.

■ EXPERIMENTAL SECTION

Preparation of rGO-SnS2 Hybrids. In a typical synthesis, 15 mg of GO was synthesized using the Tour method31 and subsequently sonicated in 7.5 mL of dimethylformamide (DMF) for 1 h. Na2S·9H2O and SnCl2·5H2O were mixed in the molar ratio 2:1 as adapted from previous reports32 and added to the GO dispersion. The mixture was loaded into an Anton Parr microwave hydrothermal reactor and heated to 160 °C for 1 h. Na2S subsequently sonicated in 7.5 mL of dimethylformamide (DMF) for 1 h. The reaction product was washed in acetone and automatically controlled by the reactor to maintain the desired temperature. The reaction product was washed in acetone and deionized water via vacuum filtration and dried on a hot plate at 60 °C for 12 h.

The resulting rGO-SnS2 powder was then mixed with polyvinylidene fluoride (PVDF) in a weight ratio of 93:7. The composite slurry was coated onto Cu current collectors and dried at 120 °C for 24 h. CR2032 type cells were assembled in an Ar glovebox, and pure Li metal was used as both reference and counter electrode. Glass fiber papers were used to separate the electrodes, and 1 M LiPF6 in diethyl carbonate and diethyl methyl carbonate in volume ratio 1:1 was used as the electrolyte.

Instrumentation. Characterization of the morphology of rGO-SnS2 was performed by scanning electron microscopy, energy dispersive X-ray analysis (EDX, Hitachi S5500), and transmission electron microscopy (FEI Philips Tecnai). X-ray diffraction was measured by a Bruker D8 Advance instrument. Raman spectra was obtained using a Ezraman-N instrument. Electrochemical measurements were carried out using a Biologic-VMP3 instrument. Thermogravimetric analysis was carried out using a PerkinElmer TGA 4000 system.

■ RESULTS AND DISCUSSION

In this work, we developed a microwave-enhanced solvothermal synthesis, where hexagonally shaped SnS2 nanoplatelets were synthesized directly on GO sheets as depicted in Figure 1. Important benefits of the microwave reaction are both a fast synthesis and simultaneous reduction of the GO sheets,33 resulting in the formation of rGO-SnS2 hybrid nanostructures.

Figure 2 shows the morphology of our rGO-SnS2 hybrid nanostructures using SEM and TEM. The SnS2 platelets are typically ~100 nm wide and are randomly distributed on rGO sheets of size ~5 μm (Figure 2a). EDX analysis of a few SnS2 platelets indicates an atomic ratio of 2:1 of sulfur and tin atoms, respectively (Figure 2b). Furthermore, the SEM analysis suggests that the SnS2 nanoplatelets tend to nucleate on the rGO sheets rather than in the bulk solution during the reaction, thus ensuring SnS2 platelets are well-connected to rGO, which should make the active phase (SnS2) electrically more accessible during battery cycling. Additionally, the presence of SnS2 particles prevents the restacking of rGO which in turn acts as a mechanical support for the SnS2 particles.20 The lattice spacing of 0.6 nm measured by TEM analysis (Figure 2c) matches the (001) plane of layered hexagonal SnS2, an example of which is shown in Figure 2d.

The XRD spectra in Figure 3a confirms the crystalline nature of the SnS2 platelets (JCPDS 00-023-0677). The peak at ~15.1° corresponds to the (001) plane and a lattice parameter for c of ~5.9 Å, suggesting a well-stacked layered structure along the c axis. Based on the Scherrer equation, the thickness of the SnS2 platelets was calculated to be around ~25 nm according to the (001) peak. The Raman spectra (Figure 3b) shows the characteristic D and G peaks for graphite oxide at 1350 and 1590 cm−1, respectively, and a peak at 311 cm−1 which corresponds to the A1g mode of SnS2.34 The intensity ratio of the D to G peaks in graphite oxide is indicative of the degree of reduction. In this case, ID/IG was greater for rGO-SnS2 (1.08) compared to untreated GO (0.92) as shown in the inset of Figure 3b, confirming reduction of GO to rGO during the synthesis due to microwave heating.33

Next, we investigated the electrochemical performance and phase transformation of rGO-SnS2 electrodes using galvanostatic charge–discharge, cyclic voltammetry, EIS, GITT, and dQ/dV analyses. The rGO-SnS2 cells were cycled at room temperature between 3 and 0 V vs Li/Li+, and in some cases after a few initial cycles the charging potential was limited to ~2.6 V or less (see additional discussion below).

In SnS2 electrodes, the first cycle capacity is typically the sum of a large irreversible capacity (theoretical ~587 mAh g−1) originating from conversion reactions and a reversible capacity (~645 mAh g−1) from alloying reactions.35,36 Figure 4a shows the initial capacity of our electrodes reaches ~1600 mAh/g at 0.1 A/g in the first cycle.7 The cells were cycled continuously.
with increasing rates and delivered a capacity ~400 mAh/g at 1.2 A/g and sustained a capacity of over ~600 mAh/g when the rate was reverted to 0.1 A/g. In the first cycle in Figure 4a, the plateau at ~1.4 V vs Li+/Li corresponds to the conversion reaction (SnS$_2$ + 4Li$^+$ + 4e$^-$ → Sn + 2Li$_2$S), where Li ions first intercalate between SnS$_2$ layers and react with sulfur to produce Li$_2$S and Sn. The lower plateau at around 0.3 V vs Li+/Li corresponds to alloying reactions (Sn + xLi$^+$ + xe$^-$ ↔ Li$_x$Sn), where metallic Sn from the above conversion reaction reacts with Li$^+$ ions to form Li$_x$Sn alloy (0 ≤ x ≤ 4.4). Figure 4b shows the cycling of a rGO-SnS$_2$ electrode at 0.1 A/g, where a large drop in capacity can be noticed after only 25 cycles. This capacity fade is even faster at higher rates, especially above 1 A/g (see Figure 4b).

To investigate the rapid phase transition of SnS$_2$ and the capacity fade associated with these processes, we performed differential capacity analysis $dQ/dV$ (Figure 4c). In the $dQ$/d$V$ plot, the peaks can identify the effects of degradation mechanisms and changes in the battery chemistries as a result of repeated lithiation and delithiation of rGO-SnS$_2$ electrodes in charge–discharge cycles. In the first discharge (cathodic sweep), the small peaks from 1.9 to 1.6 V are due to the stepwise insertion of Li$^+$ into SnS$_2$ particles leading up to conversion reactions. At 1.4 V, the prominent peak is due to the conversion reaction that produces Li$_2$S and Sn metal. At potentials below 0.7 V, metallic tin (extruded as a result of Li$^+$ insertion) begins to react with Li$^+$ and gives rise to a shoulder at 0.3 V due to the formation of Li$_x$Sn alloys. This potential regime (from ~1.2 V and below) also involves the decomposition of electrolyte (SEI) which partly accounts for the capacity loss from the first cycle to the second. After cycling (up to 1.2 A/g as in Figure 4a), the $dQ$/d$V$ profiles of the electrode look different. The conversion reaction peak at 1.3 V (Li$_2$S, Sn) disappears, but the broad shoulder at 0.3 V due to the alloy formation is still present. This reveals that the conversion reaction is in fact limited and becomes almost nonreversible in a few cycles, which corroborates why more than half the capacity is lost in just a few cycles. On the other hand, the alloying reaction (Li$_x$Sn) is more reversible as the broad peak in the charge process (anodic sweep) around ~0.5 V is due to the dealloying reaction, which accounts for the reversible capacity in the rest of the battery life. Similarly, in the cyclic voltammetry (CV) profiles (Figure 4d), the shoulders at ~1.3, 0.3 V and 0.2, 0.5 V vs Li/Li$^+$ are indicative of the above
two reactions, while the broad shoulder at $\sim 1.3$ V (associated with the conversion reaction) eventually disappears, in line with the galvanostatic charge–discharge cycles and $dQ/dV$ profiles. Figure 4e shows a GITT analysis of the electrodes in order to evaluate the Li content as a function of charge–discharge potentials (V), which suggests that in the first cycle, $\sim 11$ mol equivalent of Li is inserted per formula unit of rGO-SnS$_2$. This is in slight excess of the actual number of moles of Li$^+$ ions that should be involved according to both of the above reactions, which can be due to the presence of rGO sheets inserting additional Li$^+$ ions. The proportion of rGO in the hybrid material is estimated to be $\sim 5\%$ based on the ratios between the reagents in the synthesis and thermogravimetric analysis (TGA) results (Figure S1).

The calculated chemical diffusion coefficient of Li$^+$ ($D$) from GITT measurements shows a large variation as a function of the charge–discharge potentials (V) of the cells in the first cycle (see the Supporting Information for more details on the $D$ calculation). As shown in Figure 4f, $D$ decreases from $\sim 10^{-9}$ cm$^2$ s$^{-1}$ to $10^{-14}$ cm$^2$ s$^{-1}$ at potentials where Li$^+$ intercalates into SnS$_2$ layers leading to conversion reactions (at $\sim 1.4$ V) and alloying reactions (at 0.3 V). First, the drop in $D$ values at $\sim 1.3$ V is due to the conversion reaction of SnS$_2$. Because this basically involves a redox process, the solid-state Li diffusion in
Li-rich converted regions is severely disrupted. Second, as the Li insertion continues in SnS$_2$, the occupation of Li vacancies is quickly diminished, which hinders Li ion mobility further. This however seems to recover to some extent in the rest of the charge–discharge states after the phase conversion (i.e., SnS$_2$ into Li$_x$S and Sn). At around 0.3 V, the Li$_x$Sn alloying reaction takes place, and this phase transformation is reflected again in the drop of $D$ values corresponding to Li ion diffusion in Li$_x$Sn phases ($0 \leq x \leq 4.4$), in agreement with dQ/dV analysis (Figure 4c) and CV data (Figure 4d). These fluctuations in $D$ values reveal a slow Li diffusion during the phase transformation of SnS$_2$ as these electrodes turn into amorphous or poorly crystalline Li rich and alloy phases forming a gel-like matrix already in the first discharge. During charging, $D$ values also fluctuate and drop considerably after ~1.5 V where the decomposition of lithiated phases and oxidation of metallic Sn should be taking place, most likely due to the accumulation of Li polysulfides. This seems to limit the charging potential of these electrodes to ~2.6 V or less after the initial cycles. We found that the Li diffusion in the cycled electrodes further decreases by a factor of 10 or more (from $D \sim 10^{-9}$ cm$^2$/s to $D \sim 10^{-10}$–$10^{-11}$ cm$^2$/s) after 100 cycles, as shown in Figure 5a. As expected, at this stage of cycling there is not much variation in $D$ as a function of the charge–discharge potentials because the electrode has become amorphous; this is confirmed by XRD analysis (see the following discussion).

Despite the hybrid nature of the rGO-SnS$_2$ electrodes, the above-mentioned measurements indicate a clear loss in performance after less than 100 cycles. The capacity drop can be due to many factors, including pulverisation, the dissolution of polysulfides in the battery electrolyte which can degrade the electrodes, and the formation of insulating phases on conductive additives which can decrease electron conductivity across electrodes. To better understand the capacity fade over cycling, we performed EIS on these electrodes, revealing that the electrode’s initial resistance ($\sim$25 $\Omega$) doubles in about ~25 cycles ($\sim$50 $\Omega$) and increases up to ~4 times ($\sim$90 $\Omega$) after 50 cycles (Figure 5b). This may be caused by a passivation layer forming between the active particles and the rGO additive by sulfur enriched conversion products.

To further understand the evolution of the hybrid rGO-SnS$_2$ nanoparticles in electrodes during extended charge–discharge cycles (although the capacity had faded significantly), batteries were run for 50, 200, and 500 cycles at ~1 A/g and were subsequently opened and analyzed in delithiated state by SEM, Raman, and XRD analyses. Although the presence of PVDF binder in the electrode material and the formation of a gel-like matrix after such vigorous cycling makes high-resolution imaging by SEM difficult, the formation of large agglomerates in the battery electrode is still observable in post-mortem SEM measurements (see Figure S2). Figure 6a shows the XRD patterns indicating that the electrode composition is mostly amorphous in all cases and that no SnS$_2$ was detected in completely delithiated electrodes, as indicated by GITT and dQ/dV analyses. Many of the XRD peaks can be assigned to metallic Sn (JCPDS 04-0673) according to the alloying–dealloying reaction (Li$_x$Sn); this is also evident in the CV and dQ/dV where the peak at ~0.5 V on charge indicates Li$_x$Sn dealloying which releases metallic Sn. Similarly, Raman spectra show no peaks associated with SnS$_2$ phases. Interestingly, the presence of rGO was only just detectable at 50 cycles and was no longer detectable after 200 cycles (Figure 6b). Faint signals for the presence of rGO were still detectable in some cases when the battery was cycled at a slow rate (100 cycles at 0.1 A/g; see the Supporting Information). Similar observation where the prominent D and G peaks of CNTs were significantly reduced upon increasing the amount of sulfur onto the CNT surface in Li–S battery electrodes was recently report by Chen.
et al.\textsuperscript{41} The above measurements suggest that from the early cycles, converted products such as polysulﬁde phases might adsorb onto the rGO and compromise the interface between SnS\textsubscript{2} and rGO. Eventually, as the batteries are cycled further, the progressive accumulation and the increased binding of polysulﬁdes might completely passivate the rGO sheets irreversibly, which then compromise the battery lifetime.

\section*{CONCLUSION}
This paper presents a solvothermal microwave reaction where SnS\textsubscript{2} nanoparticles are synthesized directly on rGO conductive supports. In the first cycle, GITT analysis conﬁrms that the phase conversion of SnS\textsubscript{2} taking place via conversion and dealloying becomes the dominant electrode reaction accounting for the sustained capacity as shown by dQ/dV analysis. However, despite the hybrid nature of our electrodes, we observe a fast decrease in capacity as shown by the initial cycles, the Li and Sn alloying transport between the conductive additive and the active phase. This decreases the effective charge transfer between the conductive additive and the active phase during battery cycling.

\section*{ASSOCIATED CONTENT}
\section*{Supporting Information}
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b02878.

Materials used for synthesis and Li-ion battery fabrication, GITT measurement and Li-ion diffusion calculation, TGA measurement of rGO-SnS\textsubscript{2} hybrid material, post-mortem SEM characterization of batteries cycled 50 and 100 times, post-mortem XRD and Raman analysis of electrodes cycled to 100 times, and review of literature on pure SnS\textsubscript{2} electrodes (PDF)

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