



An examination of the cycling performance and failure mechanisms in mechanically alloyed composites containing antimony metal, iron oxide, and carbon black



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ABSTRACT

Composite anode materials prepared using high energy mechanical milling have exhibited stable cycling in several previous works. One such material, a composite of antimony metal, carbon black, and iron oxide, shows particular promise as a higher voltage alternative to graphite and silicon. This material can enable safe operation in applications requiring high charging rates while providing a lower voltage and higher capacity alternative to lithium titanate. However, the stringent requirements for commercializing new materials for lithium ion batteries can be a serious impediment for new materials reaching into this existing market. The key requirements investigated here are the capacity, 1st cycle coulombic efficiency, hysteresis, and cycle lifetime. It is found that the combination of these materials with high energy milling can enhance the cycle lifetime of the individual constituent components, while the other properties behave as a simple superposition of the constituent components. This behavior is due to the intimate composite structure formed by the high energy milling. The failure of the electrochemical cell is primarily caused by the impedance growth of the material, which seems to be caused by instability of the SEI layer that forms on this volume changing material.

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1. Introduction

Composite anode materials have received much attention in recent years due to the ability of these materials to stabilize the electrochemical cycling in a lithium ion battery when large volume changes exist during lithiation and delithiation [1]. It is hypothesized that the formation of the composite creates small domains of active material in an inert matrix, which can prevent electrochemical grinding [2]. This stability enables consideration of new active electrode materials, many with properties that provide useful alternatives to existing commercial anode materials such as graphite or lithium titanate [3]. Of these composites, one made from antimony metal and carbon black is of particular interest due to the high specific capacity and intermediate lithiation potential [4]. This composite solves the capacity fade problem due to the volume expansion of antimony alone [5]. These properties enable a disruption in the current trade-off between power performance

and capacity that exists between lithium titanate and either graphite or silicon. That is, antimony metal has a thermodynamic lithiation potential of around 0.9V which enables the large overpotentials that can drive the lithiation or delithiation reactions for rapid cycling without risk of lithium dendrite formation of the anode, but also has a high capacity of around 660 mAh g⁻¹ [6]. The use of a composite of antimony with a second phase that maintains a small particle size during cycling, such as carbon black, has been shown to enable stable cycling in a half cell for many cycles [4,7]. Similar composites have been made by several academic groups which add additional components, whether electrochemically active or inactive, or make simple replacements of the materials in this composite. These include antimony and carbon composites with copper [8], iron [9], bismuth [10], molybdenum [11], aluminum [12], and tin [13] added as a third component. In a similar manner, antimony and carbon composites have been made using graphite as the carbon source in place of carbon black [14]. In this work, a composite of antimony, carbon, and iron oxide is considered. This choice is advantageous for several reasons. The different chemistries and reaction mechanisms with lithium ion prevent true alloying of these materials, which keeps the materials

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separate during cycling and prevents the electrochemical grinding mechanism which can shorten the cycle lifetime. At the same time, the electrochemical activity of all three materials can be utilized since the voltage profiles are reasonably well matched, with the composite having a reaction mechanism that is the combination of the three materials independently. The high capacity and low cost of the iron oxide is also a welcome substitution for expensive antimony and low-capacity carbon. A proper mixture of these three components can therefore produce a cost-effective and performance-advantaged material when compared to several other existing compositions.

While the composite anode materials certainly are interesting and create excitement around the prospects of adding new capabilities or expanding the value of lithium ion batteries, much work remains to create a truly commercializable product. Specifically, a detailed examination of how these materials behave in electrochemical cells must be made and attention focused on identifying and understanding the shortcomings of this material which will serve as barriers to commercial adoption. In this paper, we will examine four properties of the material and determine the fundamental causes behind the observed performance: capacity, first cycle coulombic efficiency, hysteresis, and cycle lifetime. The capacity of the anode dictates the amount of material required to reach a desired energy, thus relating to the cost, weight, and volume of the battery. The first cycle coulombic efficiency has important implications for battery cost and energy density, considering that there is a finite quantity of cyclable lithium which is typically brought into the cell by the cathode. The hysteresis is important to the energy efficiency of the cell, the integration of the cell into a battery pack, and the coupling of the cell with external components such as an electric machine. The cycle lifetime of the cell is important for consumer satisfaction and total cost of ownership for the device or equipment. These parameters will be investigated to determine the fundamental causes of the shortcomings in this area, with the goal of providing additional focus to efforts which can bring these and other similar materials to market more rapidly.

2. Experimental Methods

The anode material used in this study is a composite consisting of antimony metal, carbon black, and iron oxide. The carbon black, obtained from Denka, had a surface area of $58\text{ m}^2\text{ g}^{-1}$ and an average particle diameter of around 36 nm. The iron oxide was pure hematite obtained from Aldrich with a particle size of less than $5\ \mu\text{m}$. In addition to this primary composition, the mechanism of performance was examined by replacing the iron oxide with lithium titanate, aluminum oxide, tin oxide, and antimony oxide, as well as omitting this material entirely. The ratio of the three components in this mixture was varied around an optimal composition, based on a balance of capacity and cycle lifetime, which was found to be approximately a 60:20:20 ratio of the three components by weight, with antimony comprising the largest quantity. These materials were thoroughly combined using an 8000 M Mixer/Mill from SPEX SamplePrep. It was found that the optimal product was obtained when using 4 pieces of 7/16 in tungsten carbide media which are loaded into a 55 mL tungsten carbide jar together with 10 g of sample in an argon atmosphere. The material is milled for 7 hrs using intervals of 100 mins separated by 15 mins of rest.

After mixing, the chemical composition was examined using XRD and it was found that the milling did not change the phase of any of the original components, with the exception of some possible trace oxidation of the antimony. Physical characterization of the material was performed using SEM and TEM. Electrochemical characterization of the resulting material was performed in a

2032 coin cell using the composite material as the cathode with a lithium foil anode. The active material was combined with a PVDF binder and carbon black a conductive additive in a 70:15:15 ratio. The active material was loaded on the copper current collector at around 2.5 mg cm^{-2} , unless otherwise specified, which is reasonable for high power applications for balancing rapid kinetics with cell materials cost. The cell was made using EC:DEC solvent in a 7:3 ratio with 30% FEC as an additive and 1.0 M LiPF₆ as an electrolyte salt. For testing the cycle lifetime, the cells were cycled five times at a rate of 0.2C for formation, then cycled at a 2C rate until the cells were less than 50% of their original capacity or 1000 cycles had been reached.

3. Results

To obtain a clear understanding of the composite system, we start by investigating the constituent materials separately, using processing conditions and electrochemical analysis techniques that are consistent with the evaluation of the composite material. For brevity, we choose to focus on a composite containing antimony, carbon black, and iron oxide, although similar results were obtained when other materials were substituted in for the iron oxide.

3.1. Antimony

Metallic antimony is the main active material in the composite material. The theoretical capacity of the antimony is 660 mAh g^{-1} and the thermodynamic reaction potential is around 0.9 V [5]. This material was milled for the same amount of time as the composite anode material prior to making the electrode, to ensure a fair comparison. However, it is worthwhile to note that although the milling process is the same, the microstructure of the product will be substantially different from the composite material, a fact which is largely responsible for the difference in the cycling stability. The theoretical capacity and voltage are close to those achieved in this work, as seen in Fig. 1. When this material is electrochemically cycled, it is observed that the capacity decreases rapidly, surviving for only 22 cycles before reaching 80% of the original capacity. This rapid decrease is likely due to electrochemical grinding of the active material due to the fusing of small particles into larger ones and the stresses and strains that form upon lithiation and delithiation causing crack formation, propagation, and finally disintegration of the active material [15]. The 1st cycle coulombic efficiency of the electrode made with pure antimony is 86%. However, it is important to note that the electrode was constructed with 15% carbon black as an additive along with the PVDF binder and which will reduce the coulombic efficiency of the electrode below that of the active material, which will be discussed in detail later.

3.2. Carbon black

Carbon black is used in the composite as a means of creating nanoscale domains of antimony metal and keeping these domains separate, thereby eliminating electrochemical grinding as a failure mechanism [4]. The chemistry and structure of carbon black are somewhat related to graphite, which is a widely used anode material for lithium ion batteries. The carbon black consists of turbostratic and amorphous carbon in which the graphene sheets are misaligned and do not exhibit long range stacking order. As a result, the carbon black has a very high surface area and is also electrochemically active. As shown in Fig. 1, the carbon black exhibits a very low coulombic efficiency, only 38%, likely due to the large surface area and corresponding large amount of SEI

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