HWCVD MoO$_3$ nanoparticles and a-Si for next generation Li-ion anodes

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ABSTRACT

We have employed hot wire chemical vapor deposition (HWCVD) for the generation of MoO$_3$ nanostructures at high density. Furthermore, the morphology of the nanoparticles is easily tailored by altering the HWCVD synthesis conditions. The MoO$_3$ nanoparticles have been demonstrated as high-capacity Li-ion battery anodes for next-generation electric vehicles. Specifically, the MoO$_3$ anodes have been shown to have approximately three times the Li-ion capacity of commercially employed graphite anodes in thick electrodes suitable for vehicular applications. However because the materials are high volume expansion materials ($\geq$100%), conformal Al$_2$O$_3$ coatings deposited with atomic layer deposition (ALD) were required before high rate capability was demonstrated. Recently, NREL is exploring high capacity Si anode materials that have a volume expansion of ~400%. It is assumed that new ALD coatings will need to be developed in order to stabilize Si as an anode material. Silicon is a superior choice for an anode material to the metal oxide structures due to both a higher capacity and a significantly lower hysteresis in the voltage vs. Li/Li$^+$ for the charge/discharge profiles.

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1. Introduction

The majority of the world energy consumption is derived from fossil fuels. The conversion reactions required for retrieving energy from carbon resources result in the production of green house gases and subsequent global warming effects. Furthermore, the United States consumption of petroleum vastly exceeds its production, with the majority of the petroleum being consumed in the transportation sector. Alternative forms of transportation, that rely on renewable energy resources, with an emphasis on hybrid electric, plug-in hybrid electric and fully electric vehicles are consequently being explored [1]. Li-ion batteries are currently employed in most portable electronics [2]. However, before Li-ion batteries are suitable for vehicular applications significant improvements in both energy density and rate capability must be achieved [3]. We previously reported that HWCVD-generated nanoparticles (~10 nm in diameter) exhibited a high reversible capacity and good rate capability when tested as a porous thin film electrode ~2 μm thick without any conductive additive or binder. Specifically, a capacity of ~630 mAh/g was observed at C/2 (one charge/discharge in 2 h), and it was possible to deliver 500 mAh/g at 2C (one charge/discharge in 30 min) [4]. However, thin films are not appropriate for vehicular applications, as the weight of the current collector will then limit the energy density of the battery.

More recently the MoO$_3$ electrodes were fashioned into thick electrodes containing 70% nano-MoO$_3$, active material, 20% poly (vinylidenefluoride) (PVDF), binder, and 10% acetylene black (AB), conductive additive. In this case nearly the theoretical capacity of ~1000 mAh/g was reported, but in order to achieve stable cycling, it was necessary to reduce the rate to C/10 (one charge/discharge in 10 h) [5]. Then by using atomic layer deposition (ALD) to coat the full electrode with ~8 Å of Al$_2$O$_3$, it was possible to achieve better rate capability than that previously observed for the thin film electrode. It was speculated that the ALD coating enabled better adhesion of the high volume expansion MoO$_3$ ($\geq$100%) to the current collector [6]. In general volume expansion can lead to fracturing and a loss in mechanical integrity that can lead to dissolution and/or loss in electronic conductivity.

Resurgence in interest in Si as a high capacity Li-ion anode was initiated by the 2008 report of Chan et al. where Si nanowires were shown to have a reversible capacity of ~3500 mAh/g at C/5 (one charge/discharge in 5 h) for 20 cycles [7]. The same group later reported a nanocore shell design based on c-Si nanowires surrounded by a-Si shells with a reversible capacity of ~1000 mAh/g at C/5 for 100 cycles. The a-Si was also shown to react with lithium at a slightly higher potential than c-Si [8]. The higher potential relative to Li/Li$^+$ for the a-Si material could mitigate lithium plating which is a major safety concern [3]. A sputter deposited 275 nm thick a-Si film was reported to have an initial capacity of 3134 mAh/g at C/40 (one charge/discharge in 40 h) and then cycle at C/5 rate with gradual fading and a capacity of ~1500 mAh/g [9]. Thus, durable high-rate cycling has not been achieved even with the utilization of thin film a-Si
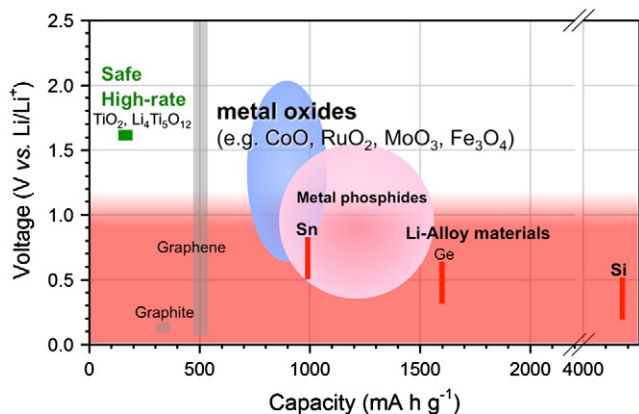
Fig. 1. Pictorial representation of possible anode materials for Li-ion batteries.

technologies where the effects of volume expansion are not as extreme. Here we discuss the potential for using HWCVD generated materials, both MoO_3 and a-Si, coupled with ALD coatings that are applied to the full electrode in order to fabricate next-generation anodes that may be suitable for vehicular Li-ion technologies.

2. Experimental details

MoO_3 was synthesized by hotwire chemical vapor deposition as previously described [10]. The average particle size was ~10 nm and could be controlled by both temperature and pressure during synthesis [11]. However, a post-treatment bake to ensure the particles were stoichiometric MoO_3 caused the particles to agglomerate slightly, and an average particle size of ~40 nm was then observed. The HWCVD techniques to grow a-Si have also been reported previously in detail [11–13]. In order to obtain a-Si powders, amorphous silicon films several microns in thickness were grown on aluminum foil. The foil was subsequently dissolved in dilute HCl, and flakes of a-Si were obtained.

For MoO_3, composite electrodes were fabricated with active material (AM), acetylene black (Alfa Aesar) conductive additive, and poly-vinylidene difluoride (Alfa Aesar) binder. The anode composition was 70:10:20 (AM:AB:PVDF). AM and AB powders were mixed using a mortar and pestle and then added to PVDF dissolved in *n*-methyl pyrrolidinone (Alfa Aesar). The slurry was then mechanically spread onto a current collector (copper) using a notch bar. Electrodes were dried in air for 1 h at 80 °C, calendared to 75% of initial thickness (20 μm), and then vacuum dried at 125 °C overnight. Four atomic layers of Al_2O_3 were grown directly onto the prefabricated MoO_3 electrode using the ALD technique found in Ref. [6]. The anodes then underwent

additional heating overnight in an argon glove box at 250 °C as previously described [5]. Electrodes were punched with ~½″ diameter and tested in a 2032 coin cell architecture with a thick, porous silica separator and 1 M $LiPF_6$ 1:1 EC:DMC electrolyte. For preliminary a-Si results thin films were deposited on a stainless steel electrode.

3. Results and discussion

In order to achieve Li-ion batteries with higher energy densities, it is necessary to develop new electrode materials with higher capacities. Fig. 1 depicts possible anode materials plotted with their potential vs. Li/Li$^+$ against their specific capacity in mAh/g. Graphite is currently the anode of choice for portable electronics [14] with a capacity of ~370 mAh/g. However, for application in hybrid electric, plug-in hybrid electric and possibly fully electric vehicles, it is desirable to improve both the capacity and also design an anode that operates at a slightly higher potential to avoid Li-plating. Lithium plating can lead to the possibility of a short circuit and subsequent fire due to the flammable organic electrolyte, which is a major safety concern [3]. The metal oxide materials have a significantly higher capacity than graphite of ~1000 mAh/g but suffer from a volume expansion that is >100% consequently making durable cycling difficult, especially at high rate. Silicon has a very high theoretical capacity of ~4000 mAh/g (higher than that of Li-metal) but suffers from an even higher volume expansion of ~400%.

Recently we have shown that it is possible to improve the rate capability for composite 20 μm thick MoO_3 electrodes, containing AB and PVDF, by applying a thin ALD coating of on the composite electrode [6]. To demonstrate proof of concept, a simple and well-known ALD process for Al_2O_3 ALD utilizing inexpensive trimethylaluminium (TMA) and H_2O as the precursors was employed: [15,16]

$$(A) \quad AlOH^* + Al(CH_3)_3 \rightarrow AlO-Al(CH_3)_2^* + CH_4 \tag{1}$$

$$(B) \quad AlCH_3^* + H_2O \rightarrow Al-OH^* + CH_4 \tag{2}$$

These self-limiting surface reactions constitute one cycle of Al_2O_3 ALD. The film thickness deposited during one ALD cycle on high surface area samples is ~2 Å. For the MoO_3 electrodes it was found that four cycles of this ALD process provided optimal results. Thus the coating was ~8 Å thick. Fig. 2 shows the rate capability of the ALD coated MoO_3 composite electrode. Note that a capacity of ~600 mAh/g is delivered at 5C (one charge/discharge in 12 min). Both the capacity and rate capability represent a significant improvement over graphite. Furthermore, this ALD-coated thick electrode has better rate capability than the thin film (~2 μm) of MoO_3, where a capacity of ~500 mAh/g was delivered at 2C (one charge/discharge in 30 min) [4]. This
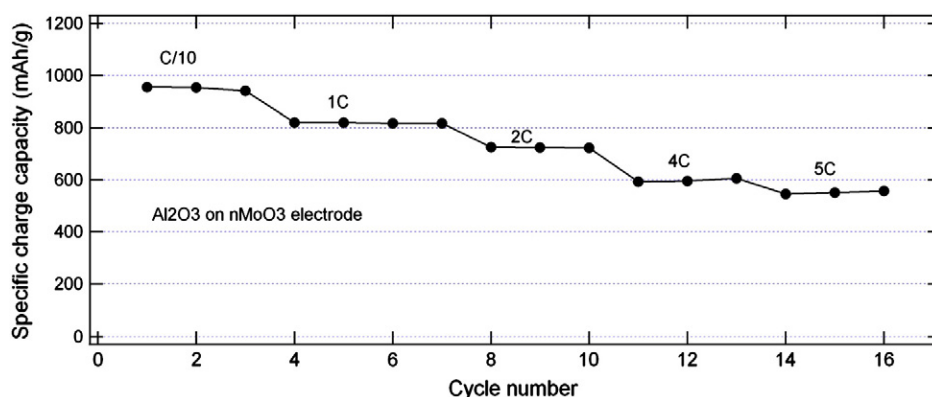

Fig. 2. Rate capability of an ALD-Al_2O_3 coated (~8 Å) composite MoO_3 electrode that is ~15 μm thick.

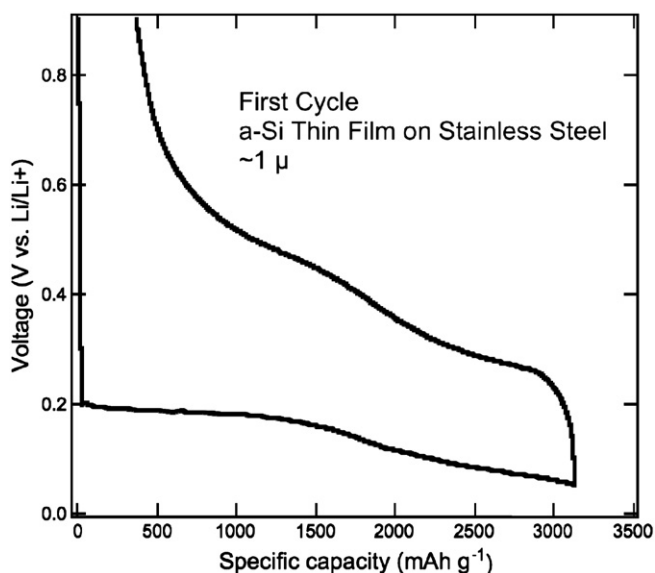**Fig. 3.** Voltage profile for the first discharge /charge of a thin ~1 μm thick a-Si film deposited on stainless steel.

suggests that ALD coatings will be very important for the development of next generation Li-ion battery materials [17,18].

Due to its very high theoretical capacity, we have recently turned our focus towards the development of a-Si anodes for vehicular Li-ion applications. In addition to its high theoretical capacity, a-Si is more desirable than the metal oxide structures due to a much smaller hysteresis in the charge/discharge profiles. Fig. 3 displays a voltage composition profile of a thin a-Si film (~1 μm) that was deposited on a stainless steel electrode. The initial capacity of a little more than 3000 mAh/g is a reasonable value for a-Si [9]. Note, that the voltage difference vs. Li/Li^+ for Li insertion and subsequent extraction is on the order of ~0.3 V vs. Li/Li^+. Unfortunately the oxides suffer from a voltage hysteresis that is generally ~1.5 V vs. Li/Li^+ due to the fact that a conversion reaction to the metal species and Li_2O is observed at low voltage [19]. We are currently trying to develop thick a-Si electrodes that will also contain a conductive additive and binder. To date, we have employed HWCVD to deposit thick films (≥ 7 μm) on aluminum foil and have then subsequently dissolved the aluminum foil in dilute HCL to obtain flakes of a-Si [20]. Fig. 4 displays a picture of a vial containing the a-Si flakes that were isolated by this process. In the future we will both fabricate thick composite electrodes (containing conductive additive and binder) and develop superior ALD coatings that will withstand the ~400% volume expansion of the silicon active material.

4. Conclusions

HWCVD is being investigated for the development of high capacity anode materials that may be suitable for employment in next generation electric vehicles. We have demonstrated that HWCVD nano-MoO_3 particles have a significantly higher capacity than the state-of-the-art graphite electrode, and that the rate capability in a thick composite electrode may be significantly improved by applying an ~8 Å thick coating of Al_2O_3 with ALD. We are currently employing previously pioneered HWCVD techniques to obtain a-Si powders. These powders will also be fashioned into thick electrodes, and the development of new ALD coatings to withstand the ~400% volume expansion of silicon upon Li-ion insertion will be explored.

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Fig. 4. Picture of a vial containing HWCVD-generated a-Si flakes.