A Three-Dimensional Carbon Nano-Network for High Performance Lithium Ion Batteries

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Abstract: Three-dimensional (3D) network structure has been envisioned as a superior architecture for lithium ion battery (LIB) electrodes, which enhances both ion and electron transport to significantly improve battery performance. Herein, a 3D carbon nano-network is fabricated through chemical vapor deposition of carbon on a scalably manufactured 3D porous anodic alumina (PAA) template. As a demonstration on the applicability of 3D carbon nano-network for LIB electrodes, the low conductivity active material, TiO_2 , is then uniformly coated on the 3D carbon nano-network using atomic layer deposition. High power performance is demonstrated in the 3D C/ TiO_2 electrodes, where the parallel tubes and gaps in the 3D carbon nano-network facilitates fast Li ion transport. A large areal capacity of $\sim 0.37 \text{ mAh cm}^{-2}$ is achieved due to the large TiO_2 mass loading in the $60 \text{ }\mu\text{m}$ -thick 3D C/ TiO_2 electrodes. At a test rate of C/5, the 3D C/ TiO_2 electrode with 18 nm -thick TiO_2 delivers a high gravimetric capacity of $\sim 240 \text{ mAh g}^{-1}$, calculated with the mass of the whole electrode. A long cycle life of over 1000 cycles with a capacity retention of 91% is demonstrated at 1C. The effects of the electrical conductivity of carbon nano-network, ion diffusion, and the electrolyte permeability on the rate performance of these 3D C/ TiO_2 electrodes are systematically studied.

Keywords: Three-dimensional nano-network, carbon, Li-ion battery, anode

1. Introduction

The rapid development of portable electronics and electric vehicles has led to a great demand for high energy density, high power, and long cycle-life lithium-ion batteries (LIBs). Since energy is released or stored in LIBs by the flow of Li ions and electrons between the anode and cathode electrodes [1-3], the efficient transport of Li ions and electrons is the key to the energy and power density of LIBs. Three-dimensional (3D) micro/nanostructured networks present great benefits for high performance LIBs, such as a large surface area for

fast Li ion insertion/extraction, interconnecting paths for fast electron conduction, and high porosity for fast electrolyte diffusion and volume change alleviation [4-6]. An ultra-high rate of over 1000C LIB was demonstrated using porous Ni framework with pore size of $\sim 2 \mu\text{m}$ as conductive network loaded with lithiated MnO_2 [7]. Similarly high areal capacity and excellent rate performance have been achieved in batteries with active materials such as LiCoO_2 [8], Fe_3O_4 [9], TiO_2 [10], and silicon [11] on 3D metal networks. However, metallic conducting networks are usually too heavy as inactive materials, which significantly reduce the gravimetric capacity of these 3D LIB electrodes. On the other hand, low mass density conducting carbon nanostructures, such as carbon nanotubes, activated carbon fiber papers, and graphene has been widely explored to overcome the density barrier [12-14]. Electrodes consists of random mixture of active materials and conducting carbon nanostructures, such as carbon fiber papers and graphene papers, usually suffers from non-uniform distribution of active material or conductive medium [15, 16], which does not form a continuous conducting network or a uniform electrolyte diffusion channel. One-dimensional carbon nanotube or nanofiber array might offer straight channels for fast electrolyte diffusion into the electrodes. However, the thickness and the performance of such electrodes are usually limited by the agglomeration of nanotubes/nanofibers [17, 18]. Porous carbon structure with well-controlled and uniform pore size is thus desirable for stable and high performance electrodes. Carbon aerogels consisted of meso-pores with a size of $<10 \text{ nm}$ offer very high surface areas for LIB and supercapacitors [19-21]. However, the diffusion of the electrolyte and transport of ions are greatly impeded due to the small pores in carbon aerogels, especially when the electrodes are thicker than $10 \mu\text{m}$ [22], which greatly harms the rate capability of the electrodes [23-25]. For example, mesoporous carbon/ Co_3O_4 composite maintained only 32% of its capacity when the test current was increased by 10 times from 200 mA g^{-1} to 2000 mA g^{-1} [25]. As such, porous carbon with large pore sizes ($> 1 \mu\text{m}$) was developed to improve the rate capability of electrodes [26, 27]. A LiFePO_4 /carbon composite electrode with $1 \mu\text{m}$ to $5 \mu\text{m}$ pores retained

89% of its capacity when the test rate was increased by 10 times from C/10 to 1C [28, 29]. Accompanying with the improved power performance of these electrodes, the volumetric capacity and energy density are greatly reduced due to the large size of the pores and the thin active materials, which leaves most space in the porous electrodes empty.

A low mass-density conducting network with pore size in the range of hundreds of nanometers is in great need, which could potentially enhance both ion and electron transport without sacrificing energy density. Some efforts have been made to develop 3D conducting networks with pore size in the range of several hundred nanometers. Porous carbon with pore size of ~ 300 nm encapsulated with sulfur retained 52% of its capacity when test rate was increased by 10 times from C/5 to 2C [30]. Nanoparticles entrapped in carbon inverse opal with 220 nm diameter pores maintained 50% of the capacity when the test current increased 10 times from $1 \text{ A}\cdot\text{g}^{-1}$ to $10 \text{ A}\cdot\text{g}^{-1}$ [31]. All these previous efforts demonstrate the importance of the 3D conducting network with appropriate pore size in the LIB electrodes.

In this work, we develop a novel 3D carbon nano-network as highly efficient current collector for the high-power and long-cycle-life LIB electrodes. The 3D carbon nano-network, synthesized by chemical vapor deposition (CVD) of carbon on 3D porous anodic alumina (PAA) templates [32], consists of parallel trunk carbon tubes connected together by numerous branch carbon tubes to form an interconnected network (See Section 1 of the Supporting information for the 3D configuration and fabrication process). The diameters of both the trunk tubes and the branch tubes are in the range of hundreds of nanometers, which are ideal as 3D porous current collector for the LIB electrodes as articulated earlier. The thickness of these carbon tube walls is controllable from a few nanometers to tens of nanometers depending on the carbon CVD time. As a demonstration, the low conductivity active material, TiO_2 , is then uniformly coated on the 3D carbon nano-network using the atomic layer deposition (ALD) process. Electrochemical performance of such 3D C/ TiO_2 nano-network electrodes were

tested, which demonstrates large areal capacity, high gravimetric capacity, long cycle life and high rate capability. The effects of the electrical conductivity of carbon nano-network, ion diffusion in the active material, and the electrolyte permeability on the rate performance of these 3D C/TiO₂ electrodes are systematically studied, which gives insights on high performance LIB electrodes with 3D architecture.

2. Experimental Section

2.1. Sample Preparation

A 3D carbon nano-network was fabricated by chemical vapor deposition (CVD) of carbon on the 3D porous anodic alumina (PAA) templates. The fabrication of 3D PAA templates using low purity 1000 series (99% purity, McMaster 9060K16) Al foils was described in an earlier paper [33]. The 3D PAA template was first sputtered with a 100 nm thick Au layer for electrical conductance and then electrodeposited with Co at -1.2V vs. Ag/AgCl for 1 min as the catalyst for the later carbon CVD process [34]. To uniformly deposit carbon on the 3D PAA template, the CVD process takes place at 700 °C and at the ambient pressure with a gas flow rate of 262 sccm Ar, 90 sccm H₂, and 60 sccm C₂H₄ at 700 ° [35]. After CVD, the PAA template was removed by wet etching of Al₂O₃ in 1M NaOH solution for 5 hours, which leaves the free standing 3D carbon nano-network ready after supercritical drying to be used for the deposition of active materials to form 3D nanostructured electrodes. The thickness of the CVD carbon layer scales linearly with the CVD deposition time (Figure S3a in Section 3 of the Supporting information). 3 nm thick carbon coating is obtained after 3.5 hours of CVD.

Atomic layer deposition (ALD) is used to uniformly deposit LIB active material, TiO₂, on the 3D carbon nano-network in the kinetic mode with ultra-high purity (UHP) grade N₂ as the carrier gas [36]. Base pressure of the reactor was kept below 1 Torr. To facilitate the uniform ALD TiO₂ process, an Al₂O₃ (alumina) seed layer of 2 nm was pre-deposited by 50 cycles of sequential dosing of trimethylaluminum (TMA) for 150 ms and water for 750 ms at

150 °C (Section 4 of the Supporting information). An ALD TiO₂ layer was then coated with different thickness of 7 nm to 27 nm by sequential dosing of 200 ms Titanium tetrachloride (TiCl₄) and 750 ms water at 150 °C from 150 cycles to 600 cycles.

2.2. Structural and Electrical Characterization

The field emission scanning electron microscope (FE-SEM, JEOL JSM-7401F) was used to study the morphology of the 3D carbon nano-networks and the 3D C/TiO₂ electrodes. Cross-sectional images of the 3D nano-networks were taken by tearing the samples apart with tweezers to expose fresh cross sections and mounting them on a tilted SEM stage. Transmission electron microscopy (TEM, Philips CM-10) and high resolution transmission electron microscopy (HR-TEM, FEI Tecnai F30) were used for structural characterization. Selected area electron diffraction (SAED) pattern was operated under 300keV electron beam with camera length of 1.2m. Electrical conductivities of the 3D nano-networks were tested with the four point probe method (Kulicke & Soffa model 3007). The electrodes after electrochemical cycling test were carefully taken out of the coin-cell battery in the glovebox and soaked and washed in DMC for 5 times to remove the electrolyte before characterization.

2.3. Electrochemical Characterizations

The as-prepared 3D carbon nano-network and 3D C/TiO₂ nanostructured anodes were tested by assembling half-cell in the CR2032 coin-type cell with an electrolyte containing 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio, Aldrich) and with Li foil (Alfa Aesar) as counter-electrode. The CR2032 coin-type cells were assembled in an argon-filled glove box system (Vacuum Atmosphere Nexus model) and tested with a computer controlled potentiostats/galvanostats system (MTI, 5V1mA). The discharge-charge experiments were performed galvanostatically within the voltage window of 1.0 - 2.6 V (vs. Li/Li⁺).

3. Results and Discussion

Figure 1a shows the optical image of a 20 cm² free-standing 3D carbon nano-network. The sizes of these samples are scalable depending on the size of starting Al foils for PAA template fabrications. The sample has a thickness of 60 μm, which is determined by the thickness of the 3D PAA template (see Section 5 of the Supporting information for cross-sectional images of 3D PAA template and 3D carbon nano-network). **Figure 1b** shows the cross-sectional scanning electron microscope (SEM) image of a 3D carbon nano-network after 3.5 hour CVD carbon coating. The 3D carbon network consists of parallel trunk tubes (colored to red on left side), which are connected together by branch tubes (colored to green on left side) to form a freestanding film. No agglomeration of the carbon tubes were observed due to the support of the branch tubes between the neighboring carbon tubes, similar to the 3D Ni nanowire network published before [33]. The interconnection of carbon tubes inside the sample was also readily observable by the transmission electron microscope (TEM) characterization, as shown in **Figure 1c** and **1d**. The tube diameter is ~ 250 nm. Such tube diameter can be tuned at a range of 40-400nm by the fabrication process of PAA templates [32]. The thickness of the carbon layers is uniformly 3 nm, after 3.5-hour CVD. The carbon layer thickness is scalable with CVD time (see Section 3 of the Supporting information for the relationship between carbon thickness and CVD time). The high-resolution TEM (HRTEM) image in **Figure 1e** shows partially crystalline structure of the carbon layer. The selected area electron diffraction (SAED) pattern in the **inset figure** is consistent with the HRTEM image, showing both amorphous diffraction rings and crystalline diffraction points.

Electrical conductivity of electrodes plays an important role in the rate capabilities of LIBs. A study on phospho-olivines shows that the rate capability was significantly increased (about 57% capacity retention from C/10 to 10C) when the electrode conductivity increase from 10⁻⁷ S·m⁻¹ to 10⁻¹ S·m⁻¹ through doping [37]. As the conducting network for LIB electrodes, the 3D carbon nano-network is expected to have high electrical conductivity so

that low conductivity active materials can be loaded. The in-plane (vertical to the main carbon tube direction) electrical conductivity of the 3D carbon nano-network film with 3 nm thick of carbon layer was tested to be $\sim 110 \text{ S}\cdot\text{m}^{-1}$ using the four-probe method (See Section 3 of the Supporting information). By adjusting the thickness of carbon coating *via* changing the CVD time, the electrical conductivity of the 3D carbon nano-network films can be readily tuned. The thickness of the carbon layer after 10 hours of CVD is increased to 8 nm and the electrical conductivity is increased to $159 \text{ S}\cdot\text{m}^{-1}$. Usually the ionic conductivity of the electrolyte, (1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio, Aldrich)), which is $\sim 10^{-1} \text{ S}\cdot\text{m}^{-1}$ is the bottleneck of LIB power performance [38, 39]. The electrical conductivity of our as-obtained 3D carbon nano-network is much greater than the ionic conductivity of the electrolytes, which renders great opportunity to enhance the electrical conductivity of low conductivity active materials to meet the requirement of electron transport for high power performance in LIB electrodes [40]. To evaluate the performance of a 3D carbon nano-network as the 3D conductive network in an electrochemical cell, we conducted proof-of-concept studies using TiO_2 as the electrochemically active material, since TiO_2 has been considered as an attractive material for use in LIB anodes due to its low cost, safety, and environmental benignity [41-43]. The electrical conductivity of amorphous TiO_2 is very low, $\sim 10^{-12} \text{ S}\cdot\text{m}^{-1}$, which significantly limits its electrochemical performance [44]. Many efforts have been made to increase the electrical conductivity of TiO_2 -based anodes by carbon coating, mixing with single-wall carbon nanotubes, mixing with graphene, *etc.* [45-48]. In this work, by incorporating the 3D conducting carbon nano-network with TiO_2 , the 3D C/ TiO_2 electrodes have conductivities in the range of $78.1\text{-}93.5 \text{ S}\cdot\text{m}^{-1}$ (Section 3 of Supporting information).

TiO_2 layers with different thicknesses were uniformly deposited on the 3D carbon nano-networks using the atomic layer deposition (ALD) process [49]. To facilitate the

uniform ALD TiO₂ process, an Al₂O₃ (alumina) seed layer of 2 nm was pre-deposited (See Section 4 of the Supporting information for the thickness information of the Al₂O₃ layers). Earlier research by the authors has shown that this seed layer won't react with Li ions or affect the electrochemical performance of the electrode [49, 50]. **Figure 1f** shows a HR-TEM image of the layered structure with the 7 nm TiO₂ coating after 150 cycles of ALD coating. The thickness and the mass loading of TiO₂ layer is scalable with ALD cycle number. Three different thicknesses of TiO₂ layer were used in this work, 7 nm, 18 nm and 27 nm with ALD coating cycle numbers of 150, 300 and 600, respectively (See Section 6 of Supporting information for the images and mass loading). The SAED pattern in **inset Figure** indicates the amorphous nature of TiO₂ coating, which is due to low ALD deposition temperature (150 °C) [51, 52].

Figure 2a shows that the 60-μm thick 3D carbon nano-network film delivers an areal capacity of ~ 0.03 mAh cm⁻² without any TiO₂ coating at C/5. With the ALD TiO₂ coating, the areal capacities of the electrode were significantly increased to ~ 0.15 mAh cm⁻² for the 7 nm thick TiO₂ sample and to ~ 0.37 mAh cm⁻² for the 27 nm thick TiO₂ sample at C/5 (Here, C/n is referred as the charging/discharging rate to complete one charging/discharging cycle with full capacity C in n hours.). With the electrode thickness of 60 μm, the volumetric capacity is 61.67 mAh cm⁻³. High areal capacity and volumetric capacity render high energy density for the whole batteries by reducing the amount of accessory components. In the previous works, an areal capacity of 0.45 mAh cm⁻² was reported for anodized 9 μm long TiO₂ nanotube arrays at C/10 [53], and a value of 0.15 mAh cm⁻² for anodized 8.2 μm long TiO₂ nanotube arrays at C/2 [54]. Although these nanotube arrays show comparably high areal capacities, their gravimetric capacities and rate capabilities are very poor due to the lack of electrical conducting medium. For example, the gravimetric capacity for the 9 μm long TiO₂ nanotubes is only 170 mAh g⁻¹ at C/10 and 90 mAh g⁻¹ at 2C [53]. Some efforts have

been made to increase the rate capability by incorporating 3D conducting networks into TiO₂ electrodes. A 3D electrode of TiO₂ on Al nanorods reaches 0.01 mAh cm⁻² at C/5 [10] and a 32 μm thick 3D Ni nanowire network coated with ALD TiO₂ delivered an areal capacity of 0.13 mAh cm⁻² at C/4 [33]. Due to the high weight percentage of the metal conducting networks, the gravimetric capacity of such 3D electrodes with metallic conducting networks cannot keep up with the high areal capacities. In comparison, our novel lightweight 3D carbon nano-network can potentially realize high areal capacity, high gravimetric capacity, and high rate capability simultaneously.

There are different ways to calculate the gravimetric capacities of electrodes depending on whether the mass of only the active material or the whole electrode is used. **Figure 2b** shows that the gravimetric capacities of 7 nm and 18 nm thick TiO₂ coatings have a similar value of ~ 260 mAh g⁻¹ at C/5 when calculated by subtracting the areal capacity of the 3D carbon nano-network from that of the tested electrodes and divided by the mass loading of TiO₂. This value is higher than earlier works on pure TiO₂ nanotubes (223 mAh g⁻¹ at 1C) [55], and comparable to porous TiO₂ nanowire arrays (265 mAh g⁻¹ at C/5), likely benefitting from the conducting network [56]. However, the reversible gravimetric capacity becomes smaller, ~ 195 mAh g⁻¹ when the TiO₂ layer thickness increases to 27 nm in 3D C/TiO₂.

When the contribution of the 3D carbon network to the capacity and mass are both counted in, Figure 2b shows whole electrode gravimetric capacities of ~ 228 mAh g⁻¹ for the 7 nm TiO₂ electrode and ~ 235 mAh g⁻¹ for the 18 nm TiO₂ electrode. By using light-weight carbon instead of a metallic conducting network, the gravimetric capacity of the whole electrode is increased dramatically compared to earlier works on nanostructured TiO₂ electrodes. In an earlier work using Ni as conducting network with similar fabrication and testing process, the overall gravimetric energy density of the electrodes was only ~ 37 mAh g⁻¹

¹ where inactive Ni counts ~81 wt % while the active material TiO₂ counts only ~15 wt% [33]. The gravimetric capacities based on whole electrodes are only 87 – 175 mAh g⁻¹ in other nanostructured TiO₂ electrodes such as nanocrystallites, nanoparticle, nanowires, and nanotubes with 50% - 70% weight percentage of TiO₂ where carbon black and polymer binders are often added [57-62].

Figure 2c shows the galvanostatic discharging/charging curves of the 3D C/TiO₂ electrodes with 3 nm thick carbon and 7 nm thick TiO₂ tested at C/5. Due to the amorphous nature of the ALD-deposited TiO₂ [33], the electrode shows large irreversible discharging capacity at the first cycle with a broad plateau within 1.1 V- 1.7 V, which is different from crystalline TiO₂, which has a typical voltage plateau at 1.7 V [56]. Large irreversible capacities in the first cycles are due to the formation of solid-electrolyte interface and incomplete Li-ion extraction [63-65]. We also notice that the capacity in the first cycle is larger than the theoretical capacity of TiO₂, 330 mAh·g⁻¹, likely due to the storage of Li ions in the grain boundary and interfaces of the nanostructured TiO₂ [66].

A significant advantage of the 3D C/TiO₂ electrodes is the long cycle life without the need of conducting additives and polymer binders. **Figure 3a** shows the prolonged electrochemical test of the 3D C/TiO₂ electrodes with different TiO₂ thicknesses at a test rate of 1C. The 3D C/TiO₂ electrode with 7 nm thick ALD TiO₂ shows very stable performance and lasts more than 1000 cycles with a capacity retention of 91% (Due to the large capacity loss in the first cycle, it is not reasonable to use the first-cycle capacity as the initial capacity. Here, the initial capacity is the third-cycle capacity, where the capacity stabilizes. The capacity retention is then calculated by dividing the initial capacity with the 1000th cycle capacity). However, as the thickness of the TiO₂ increases, the cycle life of the electrodes decreases. The capacity degrades to below 86 % after 700 cycles for the 18 nm TiO₂ electrode and to below 87 % after 400 cycles for the 27 nm TiO₂ electrode. Samples of 3D TiO₂ nano-

network without any conducting network was also fabricated for comparison by depositing TiO_2 on 3D PAA template using ALD process and then removing the 3D PAA template with NaOH solution. Without a 3D carbon nano-network, the 3D TiO_2 electrode with 7 nm TiO_2 layer delivers a small initial gravimetric capacity $\sim 100 \text{ mAh g}^{-1}$ at 1C which degrades quickly to less than 50 mAh g^{-1} after 180 cycles. The fast degradation was also observed in earlier studies on nanostructured TiO_2 electrodes, which are plotted in the same figure for comparison [57, 67]. This comparison clearly proves that the 3D carbon network helps prolong the cycle life of the 3D C/ TiO_2 electrodes.

An *ex-situ* TEM study of the electrodes was conducted to observe the change of the electrodes during the prolonged electrochemical test. The 3D C/ TiO_2 electrode with 7 nm TiO_2 coating was carefully taken out of the coin cell after 150 cycles of electrochemical test and characterized with TEM. **Figure 3b** shows that the tubular structures are retained in the electrodes after 150 cycles, confirming the structural stability of the 3D C/ TiO_2 electrode. The TiO_2 layer is still attached to both inside and outside of the carbon tubes. The total wall thickness increases to 33 nm with the TiO_2 layer thickness increases to 12 nm after lithiation (the middle layer that consists of carbon and ALD Al_2O_3 seed layer is increased to 9 nm in Section 7 of the Supporting information). **Figure 3c** shows the TEM images of the 3D C/ TiO_2 electrode with 27 nm TiO_2 after 500 cycles. The tubular carbon structure still remained, but some of the tubes lost the TiO_2 layer and the corresponding wall thickness reduced to ~ 14 nm. Although the volume change of TiO_2 is only 3%, the repeating insertion/extraction of Li ions can cause the detachment of TiO_2 layer from the carbon network [68, 69]. The TiO_2 falling-off from the carbon tubes leads to the capacity reduction.

Figure 4a shows the measured rate capabilities of 3D C/ TiO_2 electrodes with different TiO_2 thicknesses on a 3 nm carbon nano-network. Here, 1C yields 235 mA g^{-1} for 7 nm, 200 mA g^{-1} for 18nm and 140 mA g^{-1} for 27 nm thick TiO_2 . During the first 30 cycles, the test

current was controlled to increase the charging/discharging rate after every 5 cycles. When the test rates are slow ($\leq C/2.5$), the 3D C/TiO₂ electrodes with 7 nm and 18 nm TiO₂ show very similar capacities, while the 28 nm TiO₂ electrode shows lower capacities. At low test rates, the thickness of the TiO₂ layers is so thin that the Li ions are able to diffuse through the active materials without impacting the rate capability. However, a decrease of capacity is observed in thick TiO₂ electrode when the time needed for Li ion to diffuse through the solid TiO₂ is comparable to the charging/discharging time constant. At higher rates, all three of the samples show considerable capacity loss. The thicker the TiO₂ layers, the larger the capacity loss. For example, the 7 nm TiO₂ sample only delivers a gravimetric capacity of $\sim 117.5 \text{ mAh g}^{-1}$ at a test rate of 10C, which is only 38% of its capacity at C/10.

There are three different mechanisms that cause the capacity degradation at high rates:

- 1) Longer diffusion length and diffusion time of the Li ions in the thicker TiO₂ layer reduce the rate capability.
- 2) Current collection ability of the 3D carbon network might be too low to match with the generation due to fast Li ion reaction.
- 3) Starting with the same pore size in the PAA templates, a thicker TiO₂ layer reduces the pore size in the electrode that greatly affects the permeability of Li ions, which consumes more Li ions and ultimately causes faster Li ion depletion.

In **Figure 4b**, the rate capabilities of TiO₂ nanostructures with and without conducting networks are compared to illustrate the effect of electrical conductivity [47, 67, 70]. Both the nanostructured TiO₂ electrodes without any conducting network and the nanostructured TiO₂ electrodes made by mixing carbon black or graphene in conventional ways show lower capacities than our 3D C/TiO₂ network. the electrical conductivity of the 3D carbon network with 3 nm carbon layer is $\sim 110 \text{ S m}^{-1}$. When the carbon layer thickness is increased from 3 nm to 8 nm, the electrical conductivity increases to 159 S m^{-1} . The improvement of rate capability of 3D C/TiO₂ nano-network electrodes due to the increase of

the electrical conductivity of electrodes is clearly shown by comparing the LIB electrode performance of 3nm and 8nm thick carbon. A further enhancement on rate capability due to electrical conductivity of electrodes is evidenced by comparing the rate capability of 3D C//TiO₂ and Ni/TiO₂ network electrodes. Our earlier work showed that 3D Ni/TiO₂ nanowire network has an electrical conductivity of $\sim 10^6 \text{ S m}^{-1}$ [33]. However, considering that the metal conducting network would reduce the gravimetric capacity of the electrodes due to the high weight percentage of inactive metallic materials, it is desirable to increase the electrical conductivity of the 3D carbon nano-network.

At high rates, large capacity loss is observed even with the highly conductive 3D Ni network, which is likely due to the low permeation rate and depletion of Li ions in such 3D electrodes. **Figure 4c** compares normalized rate capability of TiO₂ film electrodes, the 3D Ni/TiO₂ nanowire network electrode, and the 3D C/TiO₂ nano-network electrode with similar TiO₂ thicknesses. Their capacities at different test rates are normalized to their capacity at C/10. Here the TiO₂ film electrode is fabricated by directly depositing TiO₂ layer on Cu foil current collector using ALD process. In thin film electrodes, the electrons are directly transported to the current collector when generated and the electrolyte has direct access to TiO₂ active material without any permeation resistance or depletion problem. At low rates (<1C), the 3D Ni/TiO₂ and the TiO₂ film electrodes exhibit similar capacity loss, which indicates that the permeation of Li ions in the 3D architecture is sufficient and does not harm the rate capability. However, a much larger capacity loss is observed in 3D C/TiO₂ electrode with a lower electrical conductivity, which indicates that electron transport plays an important role in the rate capability of these electrodes at low rates. When the test rate is much higher than 1C, the capacities of both 3D Ni/TiO₂ and 3D C/TiO₂ drop dramatically, while that of the TiO₂ film only drops slightly, which indicates that the permeation resistance and depletion of

Li ions could play an important role in the capacity loss at high test rates in such 3D electrodes.

4. Conclusions

In summary, we have successfully fabricated a 3D carbon nano-network by CVD of carbon on scalably manufactured 3D porous anodized alumina templates. The manufacturing of the 3D carbon nano-network is also scalable in terms of sample size, the thickness of carbon layer, and the diameters of carbon nanotubes. The highly conductive 3D carbon nano-network can be used to significantly enhance the performance of LIB electrodes made of low conductivity active materials. As a proof-of-concept demonstration, 3D C/TiO₂ nano-network electrodes are fabricated by uniformly coating TiO₂ on the 3D carbon nano-network using the atomic layer deposition process. A large areal capacity of $\sim 0.37 \text{ mAh cm}^{-2}$ is achieved in 60- μm thick 3D C/TiO₂ electrode due to the large mass loading of active material TiO₂. At a test rate of C/5, the electrode with 18 nm-thick TiO₂ uniformly coated on the 3D carbon nano-network delivers a high gravimetric capacity of $\sim 240 \text{ mAh g}^{-1}$ using the mass of the whole electrode in the calculation. High areal capacity and large gravimetric capacity based on the whole electrode render high energy density of the whole battery. A long cycle life of over 1000 cycles is demonstrated at 1C with a capacity retention of 91%. The effects of the electrical conductivity of carbon nano-network, ion diffusion in the active material, and the electrolyte permeability, on the rate performance of these 3D C/TiO₂ electrodes are systematically studied, which gives insights on high performance LIB electrodes with 3D architecture.

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Figure Captions

Figure 1. **a)** Optical image of a free-standing 3D carbon nano-network. **b)** cross-sectional SEM image and **c)** TEM image of the 3D carbon nano-network after 3.5 hours of carbon CVD. **d) & e)** HR-TEM image of the 3D carbon nano-network from the marked area in **c)** and **d)**, respectively. Inset in **e)**: electron diffraction pattern of the 3D carbon nano-network. **f)** HR-TEM image of the 3D carbon nano-network with ALD TiO_2 coating. Inset: electron diffraction pattern of the 3D C/ TiO_2 nano-network.

Figure 2. **a)** Areal capacities of the 3D C/ TiO_2 electrodes with different thicknesses of TiO_2 on 3 nm-thick carbon nano-network. **b)** Gravimetric capacities of the 3D C/ TiO_2 electrodes with different thicknesses of TiO_2 on 3 nm-thick carbon nano-network. The open symbol plots are calculated using only the weight of TiO_2 and the solid symbol plots are calculated using whole electrode weight. **c)** Galvanostatic discharging/charging curves of the 3D C/ TiO_2 electrode with 7 nm TiO_2 coating on 3 nm-thick 3D carbon nano-network. Test rate is C/10 for the first two cycles and then C/5 for the rest of the curves.

Figure 3. **a)** Stability of the 3D C/ TiO_2 electrodes with different thicknesses of ALD TiO_2 on 3 nm-thick carbon nano-network at a test rate of 1C, in comparison with TiO_2 nanowires[57], TiO_2 nanoparticles[67], and 3D TiO_2 without carbon nano-network. **b)** TEM image of the C/ TiO_2 structure with 7.5 nm-thick TiO_2 on 3 nm-thick carbon nano-network after 150 charging/discharging cycles. **c)** TEM image of the C/ TiO_2 structure with 27 nm-thick TiO_2 on 3 nm-thick carbon nano-network after 500 charging/discharging cycles.

Figure 4. **a)** Rate capability of 3D C/ TiO_2 electrodes with different thicknesses of ALD TiO_2 coatings on 3 nm-thick carbon nano-network. **b)** Rate capabilities of TiO_2 electrodes with different conducting networks. **c)** Normalized rate capabilities of TiO_2 electrodes with different conducting networks.

Figure 1

Figure 2

Figure 3

Figure 4