

# Rationally engineered amorphous $\text{TiO}_x/\text{Si}/\text{TiO}_x$ nanomembrane as an anode material for high energy lithium ion battery

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## ABSTRACT

Energy density is the main performance indicator of lithium ion batteries (LIBs) that has driven the entire technology forward over the past decades. However, the current LIBs cannot meet the ever-increasing energy storage demand. Herein, a stable lithium-ion full battery with high energy density of  $525 \text{ Wh kg}^{-1}$  has been demonstrated, using a newly designed 3D amorphous  $\text{TiO}_x/\text{Si}/\text{TiO}_x$  nanomembranes (NMs) as the anode. The  $\text{Li}^+$  penetrable and electron conductive  $\text{TiO}_x$  coating on the Si surface effectively improves the  $e^-/\text{Li}^+$  transportability and enhances the structural stability of the  $\text{TiO}_x/\text{Si}/\text{TiO}_x$  NMs. The nanoscaled multi-winding membranes provide shortened pathway for rapid  $e^-/\text{Li}^+$  transport, and empty channels allowing for free volume expansion of the Si without mechanical breaking. As a result, the customized  $\text{TiO}_x/\text{Si}/\text{TiO}_x$  NMs display improved lithium storage performance with high initial coulombic efficiency (ICE), long cycle life and excellent rate capability. When pairing this special anode with a commercial  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  (NCM) cathode, the  $\text{TiO}_x/\text{Si}/\text{TiO}_x$ -NCM full-battery delivers good cycling stability, excellent power capability and, most remarkably, an unprecedented improvement in the gravimetric energy density. Therefore, it is believed that this unique  $\text{TiO}_x/\text{Si}/\text{TiO}_x$  nanomaterials may hold promise for the next-generation LIBs with high energy density.

## 1. Introduction

Lithium ion batteries (LIBs) with high energy density and superior energy conversion efficiency have been extensively employed in portable electronics and mobile communication devices [1–5]. However, it is generally believed that even when fully developed, LIBs cannot deliver enough energy storage capacity for key applications, for example in electric vehicles [6], because of their limited energy densities of around  $200 \text{ Wh kg}^{-1}$ . Therefore “beyond Li-ion” technologies, such as lithium-air (Li- $\text{O}_2$ ) and lithium-sulfur (Li-S) batteries with high theoretical energy densities, have received intense interest at present and the goal is to develop stable batteries with an energy density over  $500 \text{ Wh kg}^{-1}$  in the coming years [6].

Nevertheless, LIBs have been studied extensively and commercialized already since 1991 [7]. Many of the long-standing challenges related to LIBs have been successfully addressed in recent years, providing important prerequisites to develop ultra-stable LIBs with super-high energy densities over  $250 \text{ Wh kg}^{-1}$ . To achieve this goal, it is

firstly required to use the electrode materials with high specific capacities. Silicon is an excellent choice for the anode owing to its exceptionally high specific capacity ( $3579 \text{ mAh g}^{-1}$  for  $\text{Li}_{15}\text{Si}_4$  at room temperature), high abundance in the earth crust, high safety and low reaction potential with  $\text{Li}^+$  ( $< 0.4 \text{ V versus Li/Li}^+$ ) [8–13]. To date, the main challenges for any practical implementation of Si anodes are the enormous volume variation during lithiation/delithiation processes ( $> 300\%$ ) and unstable solid electrolyte interphase (SEI) layers, resulting in electrode pulverization, low cycling efficiency and rapid capacity decay [14].

Extensive efforts have been devoted to solving the aforementioned problems. One typical approach to overcome these problems is the design and synthesis of nanostructured silicon materials (e.g., nanoporous [15], nanoparticles [16], nanowires [17], and nanotubes [18]) that can accommodate large volume change and maintain their structural integration over many cycles. Among them, two-dimensional (2D) nanomembranes are appealing nano-architectures for stable lithium storage because of their facilitated accessibility by  $\text{Li}^+$  and

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small volume expansion inherited from the ultrathin structure [19–23]. In addition, if the 2D nanomembranes are naturally rolled up into 3D tubular structures, their mechanical tolerance against stress as well as the loading density can be significantly enhanced compared to that of the thin film designs [24]. Moreover, the utilization of amorphous silicon has been demonstrated to be quite effective to further improve the performances of silicon anodes [8,25,26] because the amorphous Si has a smaller predicted volume expansion and charge transfer resistance over crystalline Si, which can effectively eliminate the anisotropic expansions that usually exist in crystalline Si [27].

The lithium storage performance has also been effectively improved through functional surface coating, via which the SEI layer can be stabilized and the volume change is buffered. Thin film deposition is a highly efficient method to employ functional surface coating with high controllability (regarding thickness, composition, stacking sequence etc.). For example, atomic layer deposition (ALD) has been widely used to coat the active materials with oxide layers [28,29] to stabilize the SEI layer and improve cycling stability. However, these oxide coatings usually exhibit poor electronic and ionic conductivities that deteriorate the LIB performance. Therefore, designing conductivity-enhanced coatings is highly desired to improve the cycling stability and coulombic efficiency without sacrificing the rate capability.

Here, based on the above considerations, we successfully demonstrate a stable lithium-ion full battery with excellent power capability and high energy density of 525 Wh kg<sup>-1</sup> (based on the electrodes mass), using a newly designed 3D amorphous TiO<sub>x</sub>/Si/TiO<sub>x</sub> nanomembrane (NM) material as the anode. The TiO<sub>x</sub>/Si/TiO<sub>x</sub> anode was prepared via the physical vapor deposition combined with the strain-released rolled-up technology [30] (Fig. 1). The amorphous Si and the e<sup>-</sup>/Li<sup>+</sup> conductive TiO<sub>x</sub> coatings are prepared *in-situ* by an e-beam evaporator [31,32]. The sandwich design improves the cycling stability and rate capability of the electrode. The ultrathin nanomembrane and amorphous nature facilitates superfast Li<sup>+</sup> diffusion and alleviates volume variation. The TiO<sub>x</sub>/Si/TiO<sub>x</sub> NM anode has been paired with commercially available LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (NCM) cathode, forming a Li-ion full battery, which can deliver high energy density and fully satisfy the high energy density requirement for next generation LIBs.

## 2. Experimental section

### 2.1. Synthesis of TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs

An AR-P 3510 photoresist was firstly spin-coated as a sacrificial layer onto an Al foil coated Si substrate at 3500 rpm for 30 s (polymethyl methacrylate, PMMA can also work as the sacrificial layer in this work), and then baked at 90 °C for 5 min. Subsequently, the TiO<sub>x</sub> layer (5 nm) was deposited onto the sacrificial layer with a rate of 0.4 Å s<sup>-1</sup> by electron beam evaporation (BOC Edwards FL400) under an oxygen background (the chamber pressure was controlled to be 1.4 × 10<sup>-4</sup> mbar). Then the Si layer (30 nm) was deposited on top of the TiO<sub>x</sub>

layer with a rate of 10 Å s<sup>-1</sup> under the chamber pressure of 1–3 × 10<sup>-6</sup> mbar. Finally, another layer of TiO<sub>x</sub> (5 nm) was deposited onto the Si, forming a TiO<sub>x</sub>/Si/TiO<sub>x</sub> sandwich structure. Pure Ti pellets (Kurt J. Lesker) and Si pellets (Kurt J. Lesker) were used as the source materials for TiO<sub>x</sub> and Si depositions, respectively. The thicknesses of the three layers were controlled by a quartz crystal microbalance. After the deposition, the Al foil was unwrapped from the Si substrate and immersed into acetone to remove the sacrificial layer. Then the trilayer nanomembranes were peeled off from the Al foil and self-rolled up into 3D microtubes. Next, the TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs were washed by isopropanol repeatedly until the photoresist was thoroughly rinsed away. Finally, the samples were dried in a critical point dryer (Tousimis, Autosamdri-931). In the control sample, bare Si NMs were also prepared without the deposition of TiO<sub>x</sub> layers. The bare TiO<sub>x</sub> was prepared without the deposition of Si layer.

### 2.2. Material characterizations

Raman spectroscopy measurement was carried out at room temperature, and the signals were recorded by an Invia Raman Microscope (Invia Microscope, Renishaw) using a 442 nm excitation laser. The morphology of all the products was observed using a scanning electron microscope (SEM, Zeiss DSM982, Gemini) equipped with a field-emission gun at 3 kV acceleration voltage. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDS) were performed on a FEI ChemiSTEM 80–200 microscope operating at 200 kV. The surface electronic state of Ti was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5600) using monochromatic Al Kα X-rays (350 W) and a pass energy of 29 eV.

### 2.3. Electrochemical measurements

The anode (cathode) was fabricated by mixing TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs (NCM) with conductive carbon black (Timcal) and Na-alginate binder (Aldrich) in an 80: 10: 10 weight ratio. The resultant TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs and NCM slurries were then coated on a Cu and Al foil (Goodfellow), respectively and dried in a vacuum oven at 100 °C for 12 h. The active material loading of TiO<sub>x</sub>/Si/TiO<sub>x</sub> electrode is around 0.4 mg cm<sup>-2</sup>. For comparison, the TiO<sub>x</sub>/Si/TiO<sub>x</sub> electrodes with higher active material loading of 1.17 and 2 mg cm<sup>-2</sup> were prepared and tested. The TiO<sub>x</sub>/Si/TiO<sub>x</sub>-Li and NCM-Li half batteries were assembled using TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs or NCM as the working electrode, Li foil as the counter and reference electrode, 1 M solution of LiPF<sub>6</sub> in EC/DEC/DMC (1:1:1 w/w/w) containing 2.0 wt% VC as electrolyte and glass fibers (GF, Whatman) as separators. The TiO<sub>x</sub>/Si/TiO<sub>x</sub>-NCM full battery was assembled by using TiO<sub>x</sub>/Si/TiO<sub>x</sub> and NCM as the anode and cathode, respectively. Before assembly, the TiO<sub>x</sub>/Si/TiO<sub>x</sub> anode was prelithiated by contacting it directly with the Li foil for 30 min in a Swagelok-type device to compensate its initial irreversible capacity. The cells were assembled in an argon-filled glove-box. Cyclic voltammetry (CV) measurements were carried out using a Zahner IM6 electrochemical workstation at sweep rates ranging from 0.1 to 2 mV s<sup>-1</sup>. Electrochemical impedance spectra (EIS) were measured with an electrochemical workstation (Autolab PGSTAT 302 N) in the 100 kHz to 10 mHz frequency range. Galvanostatic discharge/charge cycling was studied in a potential range of 0.01–1.5 V, 2.8–4.2 V and 2.8–4.2 V for TiO<sub>x</sub>/Si/TiO<sub>x</sub>-Li, NCM-Li and TiO<sub>x</sub>/Si/TiO<sub>x</sub>-NCM, respectively, with a multichannel battery testing system (Arbin BT 2000).

## 3. Results and discussion

The typical fabrication procedure of TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs is schematically illustrated in Fig. 1a. The sacrificial layer is firstly spin-coated

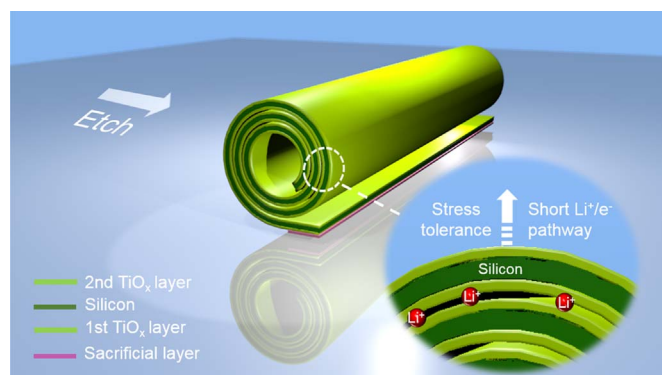


Fig. 1. Schematic illustration of the fabrication process of 3D TiO<sub>x</sub>/Si/TiO<sub>x</sub> NMs.

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