Spray Printing of Self-Assembled Porous Structures for High Power Battery Electrodes

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Abstract

A novel, generic methodology to manufacture hierarchically porous electrode structures directly onto current collectors has been developed based on layer-by-layer spray printing, here exemplified using $\text{TiO}_2(\text{B})$ nanotubes for lithium-ion batteries. By exploiting and optimizing the bi-solvent drying behavior of the spray printed ink to trigger self-assembly of the active $\text{TiO}_2(\text{B})$ into a coral-like structure, controlled through-thickness pore channels were created, which were shown to promote lithium-ion mobility throughout the electrode. Using these optimized structures, the electrode thickness-dependent performance of $\text{TiO}_2(\text{B})$ electrodes at high charge/discharge rates was compared with conventionally slurry cast electrodes and revealed the superiority of the self-assembled electrodes, especially at the highest discharge powers. We also show this self-assembly effect in other active materials and over large areas, suggesting the potential for wide use of this approach for electrodes where fast dynamic response is prioritized.

Keywords

Spray printing, self-assembly, porous channel structure, titanium dioxide (B) nanotube, lithium -ion battery.

Driven by the demand for increasingly thin, portable and powerful electronic devices such as laptop computers and mobile phones over the last several decades, Li-ion batteries have come to dominate these applications for energy storage due to their high energy density (100-260 Wh/kg), high cell voltage (3.8 V), low self-discharge and no memory effect.¹⁻³ However, their power capability (fast charge/discharge) and some safety aspects (toxic, flammable electrolyte) must be improved to meet further demands of electric vehicles and grid-scale storage systems. To overcome these limitations and then to take a step towards the next generation of energy storage devices, scientific endeavor has increasingly focused on concurrently developing higher performing electrode structures alongside new materials, driven by the strengthening understanding that battery performance is strongly dependent not only on the intrinsic electrochemical behavior of active materials but also on the structural or geometric arrangement of these materials within electrodes (and within the full cell or stack), particularly the electrode pore fraction, morphology, tortuosity and any spatial distribution, dispersion and/or alignment.⁴⁻⁶

TiO₂-based materials including anatase TiO₂, TiO₂-Bronze (TiO₂(B)) and Li₄Ti₅O₁₂ have been studied extensively for Li-ion battery electrodes owing to their small volume expansion (< 5 %) during repeated lithiation/delithiation processes, high lithiation potential in the range of 1.5 to 1.9 V (vs. Li/Li⁺) and excellent thermal/chemical stability in harsh conditions, leading to comparatively safe and high power performance in a Li-ion battery configuration.⁷⁻⁹ Amongst the various forms of TiO₂, TiO₂(B) is a promising anode material that can readily substitute for conventional graphite-based anodes because of its comparable theoretical capacity (~ 335 mAh/g). In addition, it has excellent rate capability

that is attributed to its open framework structure and pseudocapacitive faradaic energy storage mechanism.¹⁰⁻¹²

From an electrode structure point of view, porous electrode designs facilitate Li-ion containing electrolyte penetration and access to active sites “deep” in the electrode and thus sustain rate capacity as the charge/discharge rate increases.¹³⁻¹⁷ Furthermore, pores may accommodate active material swelling during repetitive lithiation/delithiation processes, helping to reduce stored strain energy and thus to sustain a stable charge/discharge capacity over many cycles. Recognizing and considering the importance of porosity and a high accessible active surface area, there have been many investigations of how to fabricate porous or hollow morphologies of $\text{TiO}_2(\text{B})$ including hydrothermal, solvothermal and sacrificial template methods.¹⁸⁻²⁰ In almost all cases, the arising well-defined porous and hollow $\text{TiO}_2(\text{B})$ structures have been processed into electrodes *via* a standard composite slurry route with conductivity enhancers and polymeric binders in an aqueous or non-aqueous suspension. The resulting slurry or paste is cast onto a current collector by a doctor blade technique. The slurry composition, rheology and wetting behavior are critical in controlling the final electrode structure, and for example, excessive binder will obscure and fill porous and hollow materials. Within these constraints and inherent capabilities of slurry casting, only a narrow range of final pore shape, tortuosity and fraction are possible, which may not lie in the range that fully realizes the capability of the $\text{TiO}_2(\text{B})$ or other porous active materials. Therefore, processing approaches that retain the inherent high performance of $\text{TiO}_2(\text{B})$ (and other high performance materials) while providing sufficient electrode structural integrity and scalability are of continuing interest.

In this paper, self-assembling porous electrode structures based on $\text{TiO}_2(\text{B})$ nanotube (NT) materials were fabricated directly onto current collectors using a spray printing process. By careful optimization of the fugitive bi-solvent liquid carrier used in the sprayed suspension, the fast *in-situ* drying of each thin layer of deposited suspension droplets can be manipulated to drive the scalable self-assembly of the $\text{TiO}_2(\text{B})$ NT bundles into a coral-like network. The optimization of the resulting through-thickness porous channels for electrochemical performance was investigated for practical electrode thicknesses in the range of 10 to 80 μm , with a 80 μm thick self-assembled, porous electrode ($\sim 146 \text{ mAh/g}$) showing a 70 % improvement in rate capability at 30 C when compared with an otherwise identical electrode prepared by slurry casting ($\sim 85 \text{ mAh/g}$). The layer-by-layer self-assembly in spray printing is shown to provide extra flexibility and performance over equivalent slurry casting and is a promising process to boost electrode performance in practical Li-ion battery devices.

Results and discussion

Fig. 1a presents a schematic of the idealized configuration of $\text{TiO}_2(\text{B})$ NTs, where single NT structures are entangled and aggregated into pseudo-spherical secondary particles, but with sufficient open porosity that Li-ions can readily penetrate into the aggregates. Fig. 1b shows a scanning electron microscope (SEM) image of the actual $\text{TiO}_2(\text{B})$ NT bundles synthesized by a hydrothermal process (see experimental details). The agglomerated secondary particles of 3-5 μm diameter had a “ball of wool” type entangled NT morphology, as highlighted in the magnified inset image. $\text{TiO}_2(\text{B})$ NTs were investigated further by transmission electron microscopy (TEM) in Fig. 1c that shows a low magnification TEM image that resolves individual $\text{TiO}_2(\text{B})$ NTs, while the high-resolution TEM (HRTEM) image in the left lower inset shows the NT individual morphology. The outer diameter of the $\text{TiO}_2(\text{B})$ NTs was ~ 10 nm, and the tube walls comprised several layers of ~ 2 nm in thickness. The selected area electron diffraction (SAED) in the right upper inset shows concentric ring patterns corresponding to (110) and (020) planes of $\text{TiO}_2(\text{B})$.^{21,22} Fig. 1d shows representative X-ray diffraction (XRD) and Raman spectra for the as-synthesized $\text{TiO}_2(\text{B})$ NTs. In the Raman spectrum, three strong peaks were detected at $\sim 190\text{ cm}^{-1}$, 280 cm^{-1} and 450 cm^{-1} , indicating $\text{TiO}_2(\text{B})$ phase.^{23,24} In the XRD patterns, there were major peaks at approximately $2\theta = 24^\circ$, 28° and 49° , which were indexed as (110), (002) and (020) planes of monoclinic $\text{TiO}_2(\text{B})$ (JCPDS Card No. 74-1940), respectively.^{25,26} A small peak at approximately $2\theta = 38^\circ$ indicated a minor fraction of anatase TiO_2 .^{27,28}

The layer-by-layer spray process used to form self-assembling porous electrode structures is shown schematically in Fig. 2a. The process is accomplished in two steps: (i) preparation of a liquid suspension with appropriate

rheology and stability for spraying, and then (ii) repeating, reciprocating spraying of the suspension over a heated current collector to form, layer-by-layer, the electrodes incrementally. As described in the experimental section, the suspension or “ink” for spraying comprises TiO₂(B) bundles, conductivity enhancer (Super P) and polymeric binder (carboxymethyl cellulose, CMC), suspended and dispersed in the fugitive liquid carrier. Compared with slurry casting, the inks are comparatively dilute (5×10^{-3} g/mL) to facilitate pumping and atomization. Given this higher liquid fraction, it is important that the spray printing process is operated under conditions that efficiently evaporate the liquid at the substrate, and there is no liquid build-up on the forming electrode structure that would re-suspend the various materials, and instead the electrode forms layer-by-layer from the superimposition of only highly transitory liquid droplets.

To investigate the effect of suspension formulation on the electrode layer drying behavior, a series of electrodes were manufactured using suspensions based on a bi-solvent mixture of deionized (DI) water and isopropyl alcohol (IPA) at ratios of 100:0, 70:30, 50:50, 30:70 and 0:100. DI water was required to dissolve the CMC while IPA assisted the dispersion of the TiO₂(B) NTs and the Super P, and the suspensions were readily mixed under sonication. Fig. S1a-e in ESI† shows SEM images of a portion of the spray printed electrodes for each of the five DI:IPA ratios, manufactured under otherwise identical conditions. For suspensions formulated with only DI or IPA (Fig. S1a and S1e, respectively), the particulates on the current collector were inhomogeneously deposited and the mass of material deposited was comparatively low, suggesting a lack of suspension stability prior to or during spray printing, with the solid component of the suspension unable to be transported consistently and reliably. For mixtures of

DI and IPA, the deposition efficiency increased markedly, and it was noticeable by eye that suspensions were more stable (no settling or separation of solids during spraying). At a 50:50 DI:IPA volume ratio, Fig. S1c shows the best deposition efficiency and a micro-porous structure, which further experiments showed to be robustly reproducible, as now described.

Fig. 2b shows a SEM image of the surface morphology of a $\sim 10\ \mu\text{m}$ thick spray printed electrode using a 50:50 bi-solvent suspension in which the same porous structure in Fig. S1c of ESI† was reproduced. The pores had a diameter of $10 \pm 3\ \mu\text{m}$ while the solid network comprising an intimate mixture of the $\text{TiO}_2(\text{B})$ NTs, Super P and CMC binder formed “walls” of thickness of $8 \pm 3\ \mu\text{m}$ between the pores, with an overall microstructure reminiscent of a coral-like morphology. Fig. 2c shows a cross-section of the same electrode with pores extending from the electrode surface “deep” into the electrode, and in some cases to the current collector. Overall there was a hierarchy of larger pores at micron-scale through the electrode thickness and finer sub-micron pores within the interconnected $\text{TiO}_2(\text{B})$ -NT-based solid framework (see Fig. S2 in ESI†).

Fig. 3 shows a series of SEM images of spray printed $\text{TiO}_2(\text{B})$ -NT-based electrodes using the optimum 50:50 DI:IPA ratio with controlled thicknesses of 10, 20, 40 and 80 μm , achieved by progressively increasing the concentration of the solid component in the suspension (see the experimental section). Fig. 3a-d shows the sprayed electrode surface morphology as the electrode thickness increased from 10 to 80 μm . There was a progressive increase in pore diameter and decrease in pore fraction, as shown in the summary data in Table 1, which arose as adjacent, smaller pores were combined and merged into larger pores as layer-by-layer deposition proceeded, as previously reported for other porous

channel structures.^{29,30} Tilted SEM images in Fig. 3e-h revealed the coral-like morphology of the spray printed electrode structure, and the electrode cross-sections in Fig. 3i-l confirmed the penetration of hollow channels deep into even the thickest electrodes.

The mechanism for the formation of through-thickness pore channels, which operated robustly even at different solid concentrations and electrode thicknesses, was dependent upon the DI:IPA ratio in the suspension. Although the dynamics of the self-assembled formation of the coral-like structure were not studied, for example using high speed imaging, we nonetheless suggest the following mechanism that is consistent with experimental observations, and is also depicted schematically in Fig. S3 in ESI†. (I) On deposition of sprayed droplets of the suspension onto the heated current collector, IPA is readily evaporated due to its comparatively low boiling point (~ 80 °C). (II) As the IPA evaporates, TiO₂(B) and Super P that are preferentially dispersed in the IPA (since it was not possible to produce a stable suspension with water only as shown in Fig. S1 in ESI†) increasingly prefer to agglomerate with one another rather than to remain suspended in the remaining, unpreferred water; these agglomerates start to form what will become the coral-like structure. (III) As the water finally starts to evaporate, the CMC preferentially dissolved in the water permeates into and is precipitated onto the agglomerates of TiO₂(B) and Super P, and the pores between the assembly of agglomerates become defined and increasingly robust as the layer is eventually fully dried. On the next pass of the spray head over the current collector, suspension droplets again deposit across the pre-formed structure, with TiO₂(B) and Super P preferring to add to the pre-defined structures as the IPA again firstly evaporates. This cycle of deposition and preferential evaporation

firstly of IPA and then water repeats, sustaining the pore structure, even up to 80 μm electrode thickness. Note that here, a relatively low CMC weight fraction of only 2.7 % was used, much lower than typically used in electrode slurries,^{31,32}. The photograph in Fig. S4 of ESI† shows the robust and flexible properties of the as-spray printed electrode as it is severely flexed, even with the relatively low binder fraction and without the need for a post-calendering; there was no noticeable damage or cracking even after twisting and bending vigorously.

Fig. 4 presents cyclic voltammetry (CV) profiles for a $\sim 10\ \mu\text{m}$ self-assembled $\text{TiO}_2(\text{B})$ NT electrode. Three pairs of cathodic/anodic peaks were detected at approximately 1.48 V/1.54 V, 1.55 V/1.65 V and 1.75 V/2.00 V, which is typical of $\text{TiO}_2(\text{B})$.^{33,34} The two redox peak pairs between 1.48 V and 1.65 V (denoted as S peak) were associated with pseudocapacitive reaction of Li-ions with $\text{TiO}_2(\text{B})$, whereas the redox pair of 1.75 V and 2.00 V (A peak) was attributed to the Li-ion intercalation in anatase TiO_2 phase. The inset in Fig. 4 presents the galvanostatic charge/discharge profiles at a constant current density of 33.5 mA/g (0.1 C). The $\text{TiO}_2(\text{B})$ electrode was spontaneously discharged from open-circuit voltage to a cut-off voltage of 1.0 V and subsequently charged up to a cut-off voltage of 3.0 V. In the 1st discharge, a voltage plateau at approximately 1.75 V was attributed to lithiation of anatase TiO_2 , while the sloped region from 1.75 to 1.5 V corresponded to $\text{TiO}_2(\text{B})$ lithiation that contributed the majority of the overall capacity, especially at high rates.^{35,36} In the 1st cycle, the $\text{TiO}_2(\text{B})$ electrode had discharge and charge capacities of ~ 260 and 230 mAh/g, respectively, which was ascribed to a relatively high contribution of an underlying irreversible reaction between the electrode and electrolyte. The electrode delivered a discharge

capacity of ~ 204 mAh/g at the 50th cycle, indicating 92 % capacity retention (versus the 2nd discharge capacity of ~ 222 mAh/g).

To investigate the potential benefits of the porous electrode structure on reversible Li-ion storage performance, electrodes were also prepared by conventional slurry casting. The morphology of the slurry cast electrodes was markedly different, as shown in Fig. S5 in ESI†, lacking tortuous inter-connected porosity or pore channel structure. Fig. 5 shows the discharge profiles for self-assembled and conventional electrodes for thicknesses of (a) 10 μm , (b) 20 μm , (c) 40 μm and (d) 80 μm respectively at various rate conditions of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 30 C. For a 10 μm electrode in Fig. 5a, the self-assembled and conventional electrodes showed almost identical rate performance, with only a slightly higher capacity of 170 mAh/g for the self-assembled electrode compared with 160 mAh/g for a conventional electrode at 30 C. Any benefit of the through-thickness pores in the self-assembled electrode was marginal for these thin electrodes. However, with increasing electrode thickness in Fig. 5b-c, the difference in the deliverable capacity of the self-assembled and conventional electrodes at high rate conditions (≥ 5 C) became significant. For example, at 80 μm , the self-assembled electrodes had a discharge capacity of ~ 140 mAh g⁻¹ at 30 C, while the conventional electrodes delivered only 80 mAh g⁻¹. Critically, the through-thickness pore channels showed benefit in volumetric capacity at high rate conditions. Fig. S6 in ESI† presents the volumetric discharge capacities of 80 μm self-assembled and conventional electrodes with increasing C-rate, where volumetric capacities were estimated by normalizing the gravimetric capacities by the electrode mass per unit area and thickness (see Table S1 in ESI†). At relatively low rates (≤ 5 C), the conventional electrode had a higher volumetric capacity

because they were comparatively dense and ion mobility in the inter-connected porosity remained relatively easy. The volumetric capacity gap between the self-assembled and conventional electrodes narrowed with increasing C-rate. Eventually, the self-assembled electrode had a superior volumetric performance at 20 and 30 C because the benefits of the directional pores and relative ease of ion transfer to all parts of electrode outweighed the lower density.

Fig. 6 exhibits the capacity retention at different C-rate conditions for the self-assembled and conventional electrodes. Here, capacity retention is defined as the ratio of the discharge capacities obtained at different rate conditions of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 30 C to the discharge capacity at 0.1 C. It is inevitable that capacity retention for both types of electrode structures declined with increasing C-rate. However, in Fig. 6a for the self-assembled electrodes, this decrease in capacity retention was virtually unaffected by the electrode thickness so that even at 30 C all the self-assembled electrodes had a capacity retention higher than 65 %. In contrast, Fig. 6b for the conventional electrode shows that capacity fade was accelerated as the electrode thickness increased to 80 μm , with a retention of only 40 % at 30 C. The through-thickness pore architecture in the sprayed electrode leads to better Li-ion mobility and availability for energy storage reactions, even deep in the electrode at high C-rates, consistent with various modeling studies.^{37,38}

To quantify the effect of the pore structure on the electrode reaction kinetics, the Li-ion diffusion coefficient was estimated from CV data at increasing scan rates of 0.05, 0.1, 0.2, 0.5 and 1.0 mV/s for the 80 μm thick self-assembled and conventional electrodes. As seen in Fig. 7a-b, as the scan rate gradually increased from 0.05 to 1.00 mV/s, the contribution of the S peak to the overall current density increased, implying that the pseudocapacitive process in the $\text{TiO}_2(\text{B})$ was

the predominant Li-ion storage mechanism at high rates, as previously described for Fig. 4.^{39,40} Fig. 7c-d shows plots of the anodic S peak current density as a function of the square root of the scan rate for the self-assembled and conventional electrodes. The peak current density showed a good fit to a linear relation, and the Li-ion diffusion coefficient was derived using the Randles-Sevcik equation:^{41,42}

$$I_p = (2.69 \times 10^5) n^{3/2} A C_0 D_{Li}^{1/2} v^{1/2} \quad (1)$$

where I_p is the peak current [A], n is the number of electrons transferred, A is the electrode area [cm²], C_0 is the bulk concentration of the Li-ions in the electrode [mol/cm³], D_{Li} is the Li-ion diffusion coefficient [cm²/s] and v is the scan rate [V/s]. From Equation 1 and using the slope of I_p -versus- $v^{1/2}$, the self-assembled and conventional electrodes were estimated to have diffusion coefficients of $\sim 1.3 \times 10^{-10}$ and 5.0×10^{-11} cm²/s, respectively, supporting the hypothesis that the through-thickness porous channel structures promoted efficient access of Li-ions to active sites throughout the electrode structure.

The galvanostatic discharge plots for the 80 μ m thick self-assembled and conventional electrodes at a constant charge/discharge rate of 1 C are displayed in Fig. 8. As the charge/discharge cycles are reversibly repeated up to the 200th cycle, the self-assembled and conventional electrodes sustained 83 % and 75 % of the initial capacity (the discharge capacity at the 2nd cycle), respectively. The excellent capacity retention of both electrodes was associated with the well-known small volume expansion of TiO₂-based materials.^{43,44} However, the self-assembled electrodes had a discharge capacity of ~ 163 mAh g⁻¹ at the 200th

cycle, whereas the conventional electrode capacity had reduced to $\sim 137 \text{ mAh g}^{-1}$. The morphology of the pores in an electrode after 200 cycles is shown in Fig. S7 in ESI†. The through-thickness porous channels were well-preserved with cycling, supporting both the high capacity and its stability. Excluding the first few cycles where side and other minor reactions dominate, the self-assembled and conventional electrodes had a coulombic efficiency of approximately 98 %, as seen in Fig. 8.

In the field of electrode manufacturing, a number of advantages can be expected from the layer-by-layer spray printing methodology in light of the greater controllability of electrode arrangements and the scalability of the approach. Self-assembly of the through-thickness porous electrode structures using a bi-solvent and layer-by-layer approach has been demonstrated to be effective in achieving a better compromise in the inevitable trade-off between power and energy density in a Li-ion battery anode. Fig. 9a schematically shows the merits of the through-thickness porous structures for high-power Li-ion battery electrodes. First, the through-thickness micron-scale pore channels facilitate the diffusion and mobility of Li-ions in the electrolyte throughout the whole electrode. The meso-scale NT structures promote the transfer of Li-ions from the electrolyte to the active surface of the electrode materials, leading to the fast charge/discharge kinetics even at accelerating rate conditions. For example in Fig. 9b, capacity retention defined by the ratio of the deliverable discharge capacity of 10, 20, 40 and 80 μm thick electrodes to the discharge capacity of a 10 μm thick electrode at 30 C for both the self-assembled and conventional electrode structures emphasizes the efficiency of the through-thickness porous channel structure. The directional pore electrodes had a capacity retention of almost 90 %,

even at 80 μm thickness, whereas the conventional electrode retention faded to 60 %. This type of “bottom-up” process for manufacturing directional pores in electrodes onto large area current collectors without expensive and sophisticated lithography equipment has been rarely achieved previously.

Conclusions

Self-assembly of through-thickness pores in electrodes based on hydrothermally synthesized $\text{TiO}_2(\text{B})$ nanotubes, spray printed directly onto current collectors, was successfully demonstrated. To trigger the formation of through-thickness pore and a coral-like structure in the active material, the drying behavior of the bi-solvent fugitive carrier used in the ink suspension was optimized, which then allowed through-thickness pore structures to be maintained even in 80 μm thick electrodes. The self-assembled electrodes showed a superior thickness-dependent rate capability with increasing charge/discharge rate when compared with otherwise identical electrodes made by a conventional slurry cast route. The through-thickness pore channels promoted Li-ion mobility, boosting electrode charge/discharge kinetics most notably at the highest charge/discharge rate of 30 C where both gravimetric and volumetric capacity significantly outperformed conventional equivalents. Although the through-thickness pore channel benefits were investigated in detail here only for $\text{TiO}_2(\text{B})$, we have also shown the same coral-like active structure and through-thickness pore channels in other bi-solvent spray printed active inks (e.g. graphene in Fig. S8 in ESI[†]), suggesting that the layer-by-layer self-assembly approach can be implemented for other electrode materials, particularly where electrode dynamic response, e.g. fast-charge automotive application, is of primary importance.

Experimental section

Synthesis of TiO₂(B) NTs

Fabrication of TiO₂(B) NTs began with dispersing 6 g of anatase TiO₂ in aqueous NaOH solution (15 M). The suspension was then transferred into a Teflon-coated autoclave and heated at 150 °C for 72 h. The obtained white precipitate was washed with DI water, followed by acid treatment in aqueous HCl solution. The materials were rinsed with DI water several times and then freeze-dried under vacuum condition. The final products were obtained by heat treatment process at 400 °C for 3 h.^{25,26}

Spray printing process

Prior to the spray process, TiO₂(B) NTs, Super P and CMC in a controlled mass ratio of 75.7:21.6:2.7 were dispersed into a mixture of DI water and IPA and then sonicated for 30 min using ultrasonication. A current collector was placed on a hot plate that was set to a certain temperature higher than the boiling point of the liquid solvent (> 100 °C) that resulted in the rapid *in situ* drying of each thin deposited electrode layer. The suspension was then sprayed at an atomizing air pressure of 0.3 bar. The spray nozzle moved in a pre-programmed pattern in the *X* and *Y* plane and a fixed spray distance *Z* for multiple cycles, which produces uniform layers of electrode structure over areas of 200 mm × 200 mm (in the current apparatus but larger areas are easily achievable) and permitted the electrode thickness to be precisely controlled, from several hundreds of nanometers to a few millimeters, simply by modifying the spray ink concentration and/or by controlling the spray scan cycle. Pore sizes and electrode thicknesses were measured from SEM images (Fig. 3), while the pore density was estimated

by counting the number of the resulting pores in a certain area ($100 \times 100 \mu\text{m}^2$) by hand.

Electrochemical tests

Coin cells (CR2032) were assembled in an Ar-filled glovebox ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$), and pure Li chips (99.9% trace metals basis, MTI Corporation) were used as counter/reference electrodes. The working and counter electrodes were electrically separated by a polyethylene separator (Cellgard 2400). The electrolyte solution was 1 M LiPF_6 dissolved in a 1:1 mixture (by volume) of ethylene carbonate and dimethyl carbonate (Merck). Galvanostatic charge/discharge tests were carried out in the voltage window of 1.0 and 3.0 V (vs. Li/Li^+) at various rate conditions of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 30 C at room temperature using an Arbin battery cyclers (Arbin BT-G-25). The charge/discharge capacities were obtained on the basis of the mass of the active material ($\text{TiO}_2(\text{B})$ NTs).

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Electronic supplementary information (ESI) available: Morphology change of the sprayed electrodes according to a change in the volume ratio of DI water to IPA, magnified SEM images for the pore region, scheme for the through-thickness pore formation, slurry cast electrodes, electrode after cycling and graphene-based through-thickness porous structure.

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Fig. 1 (a) Graphical illustration of the synthesized $\text{TiO}_2(\text{B})$ NT configuration. (b) SEM image of as-synthesized $\text{TiO}_2(\text{B})$ NT secondary agglomerates. The magnified image in the upper inset shows the synthesized $\text{TiO}_2(\text{B})$ NTs. (c) TEM image of the synthesized $\text{TiO}_2(\text{B})$ NT bundles. The detailed structures of the synthesized $\text{TiO}_2(\text{B})$ NT were investigated by SAED (the right upper inset) and HRTEM (the left lower inset). (d) Raman and XRD spectrum for the synthesized $\text{TiO}_2(\text{B})$ NTs.

Fig. 2 (a) Schematic diagram of the spray printing of self-assembled electrode layers on a current collector. The magnified cartoon shows an idealized morphology of the $\text{TiO}_2(\text{B})$ -NT-based electrode with deep pores predominantly in the through-thickness direction. (b) SEM image of the surface of the hierarchical and coral-like $\text{TiO}_2(\text{B})$ -NT-based electrode structures formed by spray printing. (c) Cross-sectional view of the spray printed electrode structure, with through-thickness pores highlighted in yellow dotted lines.

Fig. 3 Plan, surface SEM images of spray printed $\text{TiO}_2(\text{B})$ -NT-based electrodes with thicknesses of (a) 10 μm , (b) 20 μm , (c) 40 μm and (d) 80 μm , respectively; (e-h) tilted view; and (i-l) cross-sectional images.

Table 1 Summary of the self-assembled electrode porosity and mass loading with controlled thickness.

Thickness (μm)	Pore size (μm)	Pore density (mm^{-2})	Mass loading (mg/cm^2)
10	10 ± 4	1933 ± 60	0.53 ± 0.02
20	16 ± 5	1533 ± 50	0.98 ± 0.03
40	26 ± 4	508 ± 40	2.01 ± 0.02
80	40 ± 6	175 ± 40	3.99 ± 0.04

Fig. 4 CV profiles of the self-assembled through-thickness porous $\text{TiO}_2(\text{B})$ -NT-based electrodes for the first three cycles at a scan rate of 0.05 mV/s. The inset indicates charge/discharge profiles in a potential range of 1.0 to 3.0 V (vs. Li/Li^+) at a constant current density of 33.5 mA/g.

Fig. 5 Discharge capacity plots of the self-assembled and conventional electrodes with thickness of (a) 10 μm , (b) 20 μm , (c) 40 μm and (d) 80 μm at various C-rates in the potential range of 1.0 to 3.0 V (vs. Li/Li^+).

Fig. 6 Capacity retention profiles of the (a) self-assembled and (b) conventional electrodes with varying electrode thickness from 10 to 80 μm at various C-rate conditions. The yellow bands indicate the region of thickness-dependent capacity decay with increasing C-rates for the self-assembled and conventional electrodes.

Fig. 7 CV profiles of the (a) self-assembled and (b) conventional electrodes at various scan rate conditions from 0.05 to 1 mV/s. Relationship between the current density of the anodic S peak and the square root of the scan rate for the (c) self-assembled and (d) conventional electrodes.

Fig. 8 Galvanostatic charge/discharge plots for the self-assembled and conventional electrodes in the voltage window of 1.0 to 3.0 V (vs. Li/Li⁺) at 1 C, and the corresponding coulombic efficiency.

Fig. 9 (a) Schematic diagram of the ideal concept for Li-ion mobility in the self-assembled through-thickness pore structure of TiO₂(B)-NT-based electrodes. (b) The thickness-dependent capacity retention plots at 30 C for the self-assembled and conventional electrodes.

Graphical table of contents

Self-assembled porous structures were manufactured directly onto current collectors based on layer-by-layer spray printing of $\text{TiO}_2(\text{B})$ nanotubes. The through-thickness porous channels in the electrode structures enabled the liquid Li-ion electrolyte to be efficiently penetrated into the resulting coral-like electrode, leading to an improvement in the thickness-dependent power capability of the battery electrodes.

Spray printing, self-assembly, porous channel structure, titanium dioxide (B) nanotube, lithium -ion battery

Spray Printing of Self-Assembled Porous Structures for High Power Battery Electrodes

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