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# Electrospun nanofibers: A prospective electro-active material for constructing high performance Li-ion batteries

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In the present review, we describe the development of a high energy density LIB fabricated with all 1D nanofibers as the anode and cathode, as well as a separator-cum-electrolyte prepared by an electrospinning technique without compromising the power capability and cycle life. Such a unique assembly certainly enables realizing the advantages of using 1D nanostructures in practical LIBs, irrespective of the anode or cathode in the presence of gelled polyvinylidene fluoride-*co*-hexafluoropropylene as the separator-cum-electrolyte. Outstanding cycling profiles with high power densities were noted for all the configurations evaluated. This excellent performance opens up new avenues for the development of high performance Li-ion power packs with a long cycle life and high energy and power densities to drive zero emission transportation applications in the near future, and opens up new research activities in this field as well.

## Introduction

Lithium-ion batteries (LIB) are considered as one of the most promising energy storage devices today because of their high volumetric and gravimetric energy density with light weight and good shape versatility.[1,2] Such advantages make LIBs as attractive candidates for miniature applications, such as laptops, cameras, and mobile phones, and they are currently employed to drive hybrid electric vehicles (HEV) and expected to power electric vehicles (EV) in the near future.[3–5] Although LIBs can deliver high energy density, achieving a high power capability remains an issue for the abovementioned applications. However, their poor power capability can be improved in three different ways: (i) nanostructuring the electro-active materials, (ii) surface modification with conductive coatings and (iii) utilizing both techniques together.[6–8] The usage of nanostructured materials certainly leads to a reduction of the volumetric capacity, but the severe reactivity towards the electrolyte solution has to be compromised.[6] Among the nanostructures investigated, the one-dimensional (1D) morphology has been found to be appealing, in terms of its shorter Li-diffusion pathways, high specific surface area and good contact with current collectors compared to the bulk.[6] A large variety of 1D morphologies like nanowires, nanotubes, nanorods, nanofibers, and nanowhiskers, have been proposed as prospective electro-active materials for either the anodes or cathodes with a core–shell or solid interior or hollow structured morphology.[6–10] Surface modification with carbon or with a composite with carbonaceous materials has also been reported to improve the battery performance.[11] Unfortunately, all the reported studies with the various 1D nanostructures are limited to half-cell configurations only, or they are otherwise tested with commercially available bulk materials in full-cell assemblies. Thus, the advantages of using 1D nanostructures in practical cells have not yet been fully realized. In order to recognize the performance of such 1D materials in full-cell assemblies, Ramakrishna and co-workers[12] recently reported the concept of fabricating LIBs using all 1D electro-active materials by electrospinning, *e.g.* polyvinylidene fluoride-*co*-hexafluoropropylene (PVdF-HFP) as the separator-cum-electrolyte, anatase $TiO_2$ as the anode and $LiMn_2O_4$ as the cathode, achieving excellent cyclability and energy density. Apart from the morphology, the preparation of the 1D material also plays a vital role in determining the electrochemical properties.[13,14] The electrospinning technique is one of the most efficient procedures

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to prepare 1D nanostructures with high performance materials for LIB applications. The high aspect ratio, reproducibility, and simplicity make this technique very attractive for making 1D architectures for multifarious applications.[15] Very recently, several start-up companies have started producing various nanostructures (such as membranes, metals, and metal oxides) by electrospinning, which clearly indicates the practical viability of this procedure.[14–18] Nevertheless, the proposed concept is not only limited to the aforesaid materials but can also be easily extended to the rest of the prospective electro-active materials tested for LIB applications in the bulk form. In this context, we would like to describe in detail the recent research activities on the utilization and demonstration of such practical LIBs composed of all 1D electrospun electro-active materials in our group.

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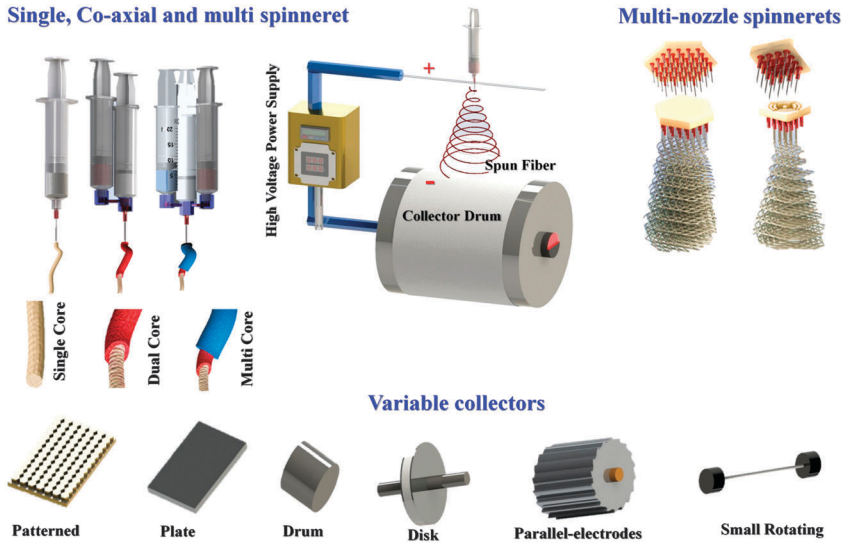


Fig. 1 Schematic representation of the electrospinning setup with variable needles, collecting substrates, and syringes.

## The principles of electrospinning

In a typical electrospinning process, three main components are predominantly utilized: a high voltage power supply, a capillary tube containing a needle or pipette with a small bore diameter, and conductive collecting substrates.[19,20] The high voltage electric field is applied between the collector and the polymer fluid stream (either in solution or in a melt) to induce free charge.[21–27] One electrode is placed into the spinning solution/melt and the other end is attached to the conductive collector. In general, the collector is simply grounded, as shown in Fig. 1. An applied electric field is subjected to the end of the capillary tube, which contains the solution fluid that is held by its surface tension. The charge carriers present in the organic solvents and polymers have a lower mobility compared to the aqueous media, and thus the charges are expected to move through the longer distance of

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the liquid.[28] When the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube (needle) elongates to form a conical shape called the Taylor cone. By further increasing the electric field, a critical value is ultimately attained when the repulsive electrostatic force overcomes surface tension, and then the charged jet of the fluid is ejected from the tip of the Taylor cone. The discharged polymer solution jet undergoes an instability and elongation process, which allows the jet to become continuous and thin. Moreover, the solvent evaporates, leaving behind a charged polymer nanofiber. In the case of the melt, the discharged jet solidifies as it travels through the air. The electrospun nanofibers possess unique characteristics, such as high surface-to-volume ratios, controllable fiber diameters and surface morphologies (dense, hollow, and porous), and fibrous structures.[29–32] These characteristic properties are obtained by changing the following parameters: (i) the system parameters such as the molecular weight, molecular weight distribution and architecture of the polymers (linear and branched), as well as the polymer solution properties (viscosity, conductivity, dielectric constant, and surface tension); (ii) the process parameters such as the electric potential, flow rate, polymer concentration, distance between the capillary and collection screen, and the ambient parameters (such as temperature, humidity and air velocity in the chamber) and motion of the collector as well as by altering the collector, multiple needles, and core–shell structures.[19,33,34] The influence of the abovementioned variable parameters during the spinning are schematically illustrated in Fig. 1.

## Nanofiber membranes

Polymer membranes/separators are one of the key parts of LIBs and should be electronically insulating, ionically conducting and flexible.[35–40] The important advantages of using polymer membranes in practical LIBs are mainly to overcome the leakage issue and provide shape versatility.[41,42] Several polymers, co-polymers and blend polymers have been explored as prospective separator-cum-electrolytes, but PVdF-HFP remains the unanimous choice for practical cells because of its salient features like high anodic stability (because of the presence of strong electron-withdrawing groups, *i.e.* –C–F) and high dielectric constant ($\varepsilon$ = 8.4, which assists the greater dissociation of lithium salts, and thus it provides a large number of charge carriers that facilitate the enhanced electrochemical performances).[39,43–45] Furthermore, the existence of crystalline VdF and amorphous HFP units are responsible for the excellent chemical and mechanical stability of the membranes, respectively.[43–46] However, the rest of the polymer membranes explored for LIB applications are omitted for practical applications, due to their own setbacks, for example poly(ethylene oxide), PEO, is one of the most comprehensively studied system and exhibits ionic conductivities of the order of $10^{-8}$–$10^{-3}$ S cm$^{-1}$ between 40 and 100 °C, which is mainly because of the high degree of crystallinity and low degree of salt dissociation in amorphous domain.[41] Polyacrylonitrile, PAN, is another important system and has shown excellent conductivity at ambient conditions ($10^{-3}$–$10^{-2}$ S cm$^{-1}$), but the syneresis of solvent molecules hinders the possibility of using them in practical cells.[39] Polymethylmethacrylate, PMMA, presents an ionic conductivity close to that of liquid systems ($10^{-3}$–$10^{-2}$ S cm$^{-1}$); nevertheless, its poor mechanical stability offsets its advantages. Although the homo-polymer PVdF alone is not suited for practical applications due to the poor swelling of liquids and long time to form a free standing film,[35,36,39,43–47] generally, electrospun membranes enable higher liquid uptake, provide lower interfacial resistance, a high Li-ion transport number and exhibit a liquid-like conductivity over conversional separators prepared by either solution casting or by a phase inversion process.[14,28,48] Taking the advantages of PVdF-HFP described above, nanofibers membranes were prepared by an electrospinning technique and their morphological and electrochemical properties are illustrated in Fig. 2. The non-linear increase in ionic conductivity suggests the electrospun PVdF-HFP membranes obey the Vogel–Fulcher–Tammann model and exhibit an ionic conductivity of $\sim$3.2 mS cm$^{-2}$ under ambient conditions.[49] The increase in conductivity with temperature is mainly attributed to the increase in the number of charge carriers (because of the higher activation energy).[50] The interfacial stability of the nanofibers membranes with a Li-metal electrode is an essential factor in demonstrating compatibility towards electrodes. Increases in the interfacial properties are found to be minimal after five days for electrospun membranes, and much lower compared to the same PVdF-HFP-based separator-cum-electrolytes prepared by conventional phase inversion or by the polymer dissolution process.[51,52] Based on the aforementioned advantages, we used electrospun PVdF-HFP nanofibers membranes as the separator-cum-electrolyte for the fabrication of high performance LIBs.

## Nanofiber electrodes

Present day LIBs predominantly comprise graphitic anodes with Li-containing transition metal oxide ($LiCoO_2$, $LiMn_2O_4$, and $LiFePO_4$) as a cathode because of its lower insertion potential ($<$0.1 V *vs.* Li), appreciable theoretical capacity ($\sim$372 mA h g$^{-1}$), low-cost and eco-friendliness.[1,2,53–55] Unfortunately, electrolyte decomposition in the first discharge, which leads to the formation of solid electrolyte interface, and SEI, and Li-plating at high current operation are the main issues from an HEV and EV point of view.[2] Therefore, high performance insertion anodes are anticipated to fulfill these requirements. Though conversion (displacement) and alloy-based anodes have shown higher capacities over insertion electrodes, both kinds of materials experience huge irreversible capacity loss (ICL) in the first cycle, a higher operating potential ($>$1 V *vs.* Li), large unit cell volume variations, and poor long-term cyclability, which renders them as "show-case" anodes.[56–60] Among the insertion anodes, anatase $TiO_2$ was found to be appealing in terms of its good cyclability, easy synthesis protocol and cost-effectiveness, although it had a high theoretical capacity ($\sim$335 mA h g$^{-1}$).[29,61–66] With the aim of demonstrating high performance LIBs, we first reported the electrochemical performance of anatase $TiO_2$ nanofibers prepared

 

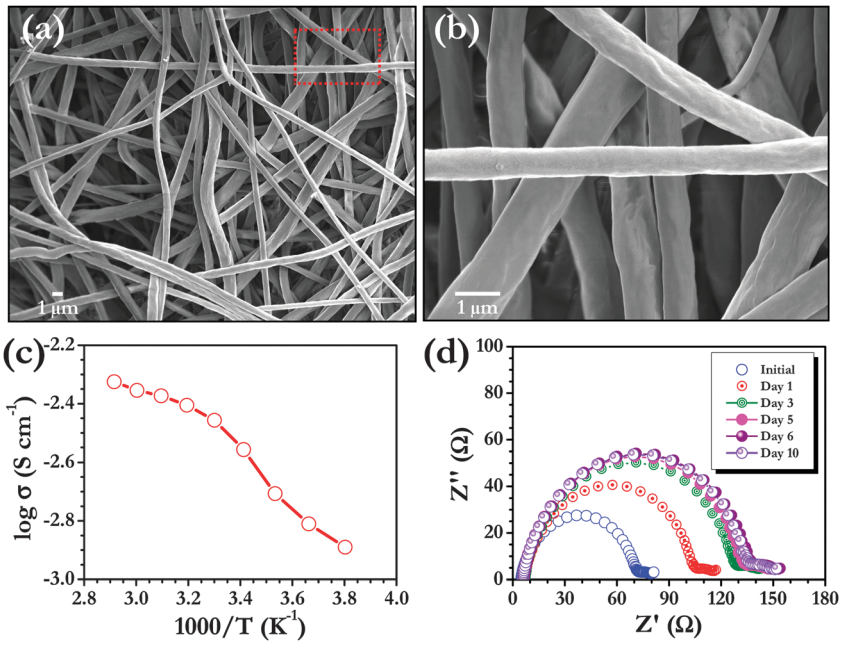


Fig. 2 (a and b) FE-SEM pictures of the electrospun PVdF-HFP membrane with different magnifications, (c) temperature dependence of the ionic conductivity recorded between two stainless steel blocking electrodes, and (d) complex impedance spectra studied between two metallic lithium non-blocking electrodes over time. Reproduced from ref. 12 with permission from The Royal Society of Chemistry.

by electrospinning in a half-cell assembly,[67] and then our group made substantial improvements[12,62] by adopting various procedures such as co-axial spinning,[29] using composites with multi-walled carbon nanotubes,[68] composites with graphene[63] and oxygen deficient ($TiO_{2-\delta}$) fibers.[31] Moreover, improvements made by other researchers,[69] such as using nitridated fibers,[70,71] multi-channel hollow fibers,[72] Ag and Au decorated $TiO_2$,[73–75] Nb-doped $TiO_2$,[76] N-doped mesoporous carbon decorated $TiO_2$ nanofibers,[77] for LIB applications are also worth mentioning. Before constructing all 1D LIBs, we conducted extensive studies on various anode and cathode configurations to evaluate the performance by keeping either the anode or cathode as bulk with homemade electrospun electrodes. For instance, a $LiFePO_4/TiO_2$ nanofibers cell was fabricated in the presence of a Whatman separator, and it delivered an excellent cyclability of 300 cycles with a capacity retention of ~88%. Although the $LiFePO_4/TiO_2$ system presented good electrochemical characteristics, its net operating potential was limited to ~1.4 V. Nevertheless, our main intention was to construct high energy density and high performance LIBs using electrospun electro-active materials. Thus, the electrospun $TiO_2$ nanofiber was coupled with a commercial high voltage (~4 V *vs.* Li, whereas $LiFePO_4$ is ~3.4 V *vs.* Li) $LiMn_2O_4$ cathode separated by a Whatman paper, and we evaluated the battery performance at a high current density of 150 mA $g^{-1}$.[62] The $LiMn_2O_4/TiO_2$ cell rendered ~81% of its initial reversible capacity after 100 cycles with an operating potential of ~2.2 V. Unfortunately, the $LiMn_2O_4/TiO_2$ cell experienced more capacity fade than the former system, which was mainly due to the sluggish Li-diffusion kinetics of the micron-sized $LiMn_2O_4$, and the poor compatibility in electrode/electrolyte interface as well.[49] To overcome the above issue, we successfully synthesized $LiMn_2O_4$ nanofibers with a hollow structured morphology by electrospinning. The $LiMn_2O_4$ hollow nanofibers delivered a reversible capacity of ~120 mA h $g^{-1}$, irrespective of the low (15 mA $g^{-1}$) and high (150 mA $g^{-1}$) current densities.[78] The half-cell rendered ~87% of its initial capacity after 1250 cycles (at high current rates) with a good elevated temperature performance as well. In addition, the improved cubic-tetragonal phase transformation was also noted for such electrospun $LiMn_2O_4$ nanofibers in a half-cell assembly (Fig. 3). Although few reports could be traced on the synthesis and electrochemical performance of electrospun $LiMn_2O_4$ cathodes, we observed that the capacity in our work had the best value in terms of its cyclability and rate capability.[79,80] This exceptional performance of electrospun $LiMn_2O_4$ logically led us to fabricate a full-cell assembly with all 1D electro-active materials. Therefore, we fabricated an assembly with all 1D LIB cells using $LiMn_2O_4$ as the cathode, the PVdF-HFP membrane as the separator-cum-electrolyte, and $TiO_2$ as the anode with an optimized mass loading based on the electrode performance in the half-cell assembly. For the mass balance between the electrodes, both electrodes were tested in the presence of the gelled electrospun PVdF-HFP separator-cum-electrolyte. Surprisingly, no obvious difference between the electrochemical properties was noted for the Whatman and electrospun membranes.[49,81] The full-cell, $LiMn_2O_4/TiO_2$ with a PVdF-HFP nanofiber membrane delivered an outstanding cyclability of 700 cycles with a capacity retention of ~90% at a current density of 300 mA $g^{-1}$.[12] This result clearly indicates the influence of the 1D morphology and it being favorable for electrochemical activity even under harsh testing conditions (*e.g.* a current density of 2.4 A $g^{-1}$).[62] Again, the energy density and operating potential remain the issue for all 1D $LiMn_2O_4/TiO_2$

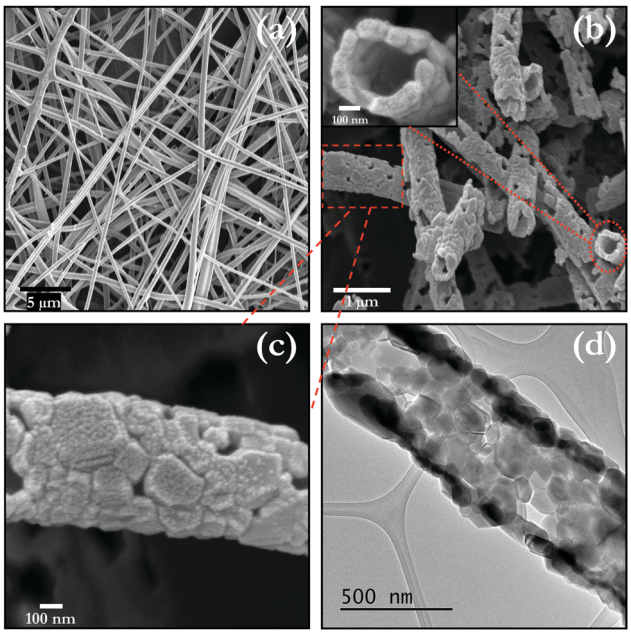


Fig. 3 (a) FE-SEM pictures of the as-spun $LiMn_2O_4$ nanofibers (green nanofibers), (b) FE-SEM picture of the electrospun $LiMn_2O_4$ hollow nanofibers sintered at 800 °C for 5 h. Inset: magnified view of the nanofibers, indicating their hollow structure, (c) magnified view of the single hollow nanofibers, (d) TEM image of the sintered electrospun $LiMn_2O_4$ hollow nanofibers. Reproduced from ref. 30 with permission from The Royal Society of Chemistry.

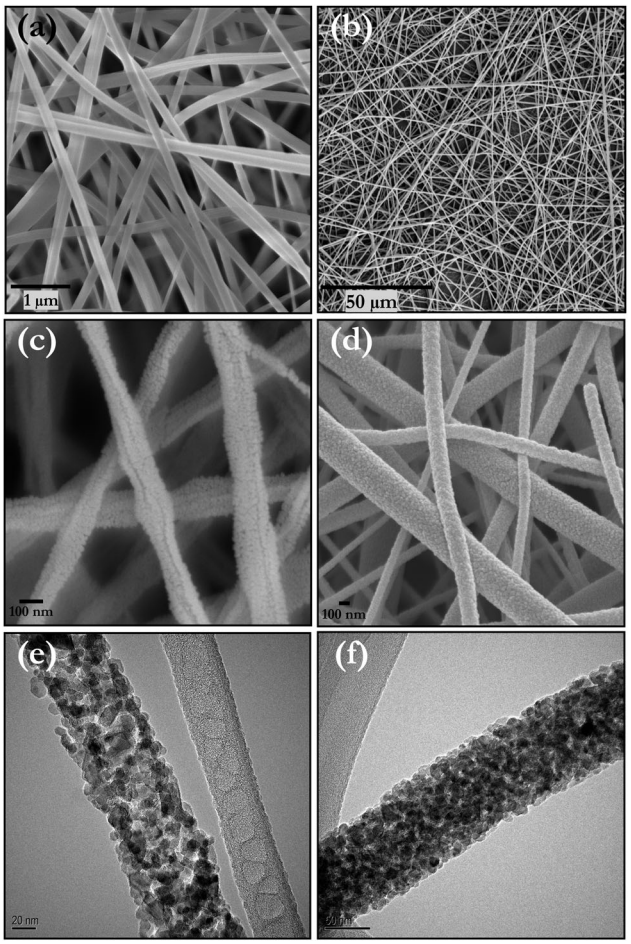


Fig. 4 FE-SEM pictures of (a) as-spun $LiNi_{0.5}Mn_{1.5}O_4$, (b) as-spun anatase $TiO_2$ nanofibers, FE-SEM images of calcined nanofibers of (c) $LiNi_{0.5}Mn_{1.5}O_4$, (d) anatase $TiO_2$, TEM pictures of calcined nanofibers (e) $LiNi_{0.5}Mn_{1.5}O_4$ and (f) anatase $TiO_2$. Reproduced from ref. 83 with permission from The Royal Society of Chemistry.

with PVdF-HFP membrane cells when considering HEV and EV, since the operating potential is limited to ~2.15 V. Therefore, we made an attempt to replace the $LiMn_2O_4$ by a high voltage $LiNi_{0.5}Mn_{1.5}O_4$ (~4.7 V *vs.* Li) using the same electrospinning approach (Fig. 4).[82] The homemade, electrospun $LiNi_{0.5}Mn_{1.5}O_4$ displayed much better electrochemical activity and stability than nanofibers in half-cell assemblies reported elsewhere.[83,84] As expected, in an all 1D configuration, the $LiNi_{0.5}Mn_{1.5}O_4/TiO_2$ cell operates at ~2.8 V with a reversible capacity of ~102 mA h $g^{-1}$. Interestingly the cycling profile of electrospun $LiNi_{0.5}Mn_{1.5}O_4$ cathodes is much better than that of its half-cell assembly (Fig. 5). Long-term cyclability is another important criterion and our evaluations clearly suggest the excellent durability of such cells in the all 1D architecture. Furthermore, the full-cell retained ~86% of its initial reversible capacity after 400 cycles, which is much better than the only available previous report by Brutti *et al.*[85] They used a ZnO-modified $LiNi_{0.5}Mn_{1.5}O_4$ cathode and nano-Li (2 wt%) powders incorporated anatase $TiO_2$ anode to achieve a capacity retention of ~75% after 50 cycles with less coulombic efficiency (~90%) and reversible capacity (~105 mA h $g^{-1}$) at a current density of 50 mA $g^{-1}$. On the other hand, an unmodified $LiNi_{0.5}Mn_{1.5}O_4/TiO_2$ cell displayed poor capacity profiles (reversible capacity of ~60 mA h $g^{-1}$) and presented ~70% reversible capacity after 50 cycles under similar testing conditions. This present in our work result clearly reveals and parallels the importance of the "nano-concept" to realize such electro-active materials in the unique 1D architecture made by electrospinning.

At this point, it is unfair to claim that the "nano-concept" is promising by just studying the same spinel phase cathodes ($LiMn_2O_4$ or $LiNi_{0.5}Mn_{1.5}O_4$) with anatase nanofibers. Thus, in order to support the 1D concept, we tested altering either the cathode or anode in the full-cell assembly. In this regard, to overcome the shortcomings observed in the anatase-based systems, such as the high operating potential (~1.7 V *vs.* Li) and ICL observed in the first cycle, which result in the suppression of the net energy density.[66] The former issue is associated with the reduction of the net operating potential, while the latter leads to a higher cathode active mass loading (in order to compensate the ICL in the first cycle), respectively. In addition, although $TiO_2$ shows a higher theoretical capacity (~335 mA h $g^{-1}$), its reversibility is limited to ~0.5 mole only.[64,66] Apart from the usage of high voltage cathodes, another approach to widen the energy density is the utilization of lower redox potential anodes.[49,66] On the other hand, spinel phase $LiCrTiO_4$ and $Li_4Ti_5O_{12}$ materials also exhibit a lower redox potential (~1.55 V *vs.* Li) than anatase $TiO_2$ (~1.7 V *vs.* Li), although the theoretical capacity is limited to ~157 and ~175 mA h $g^{-1}$, respectively.[86,87] Very recently,

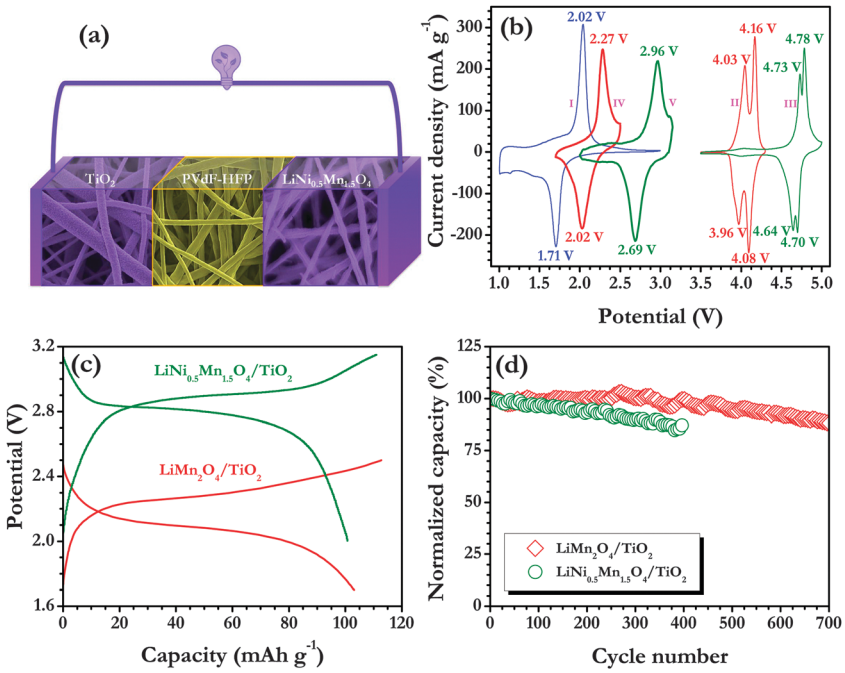


Fig. 5 (a) Schematic representation of a typical Li-ion battery comprising the all one-dimensional electrospun nanofibers ($LiMn_2O_4$/PVdF-HFP/$TiO_2$), (b) CV curves of all electrospun $LiMn_2O_4/TiO_2$(IV) or $LiNi_{0.5}Mn_{1.5}O_4/TiO_2$(V) full-cell assembly at a slow scan rate of 0.1 mV $s^{-1}$ (thin lines show the performance of Li/$TiO_2$(I), Li/$LiMn_2O_4$(II) and Li/$LiNi_{0.5}Mn_{1.5}O_4$(III) electrodes at a scan rate of 0.1 mV $s^{-1}$), (c) typical galvanostatic charge–discharge curves of $LiMn_2O_4/TiO_2$ (at a current density of 150 mA $g^{-1}$) and $LiNi_{0.5}Mn_{1.5}O_4/TiO_2$ (at a current density of 15 mA $g^{-1}$) full-cells, and (d) normalized capacity of $LiMn_2O_4/TiO_2$ (at a current density of 300 mA $g^{-1}$) and $LiNi_{0.5}Mn_{1.5}O_4/TiO_2$ (at a current density of 150 mA $g^{-1}$) full cells under ambient temperature conditions. Adopted and compiled from ref. 12 and 83 with permission from The Royal Society of Chemistry.

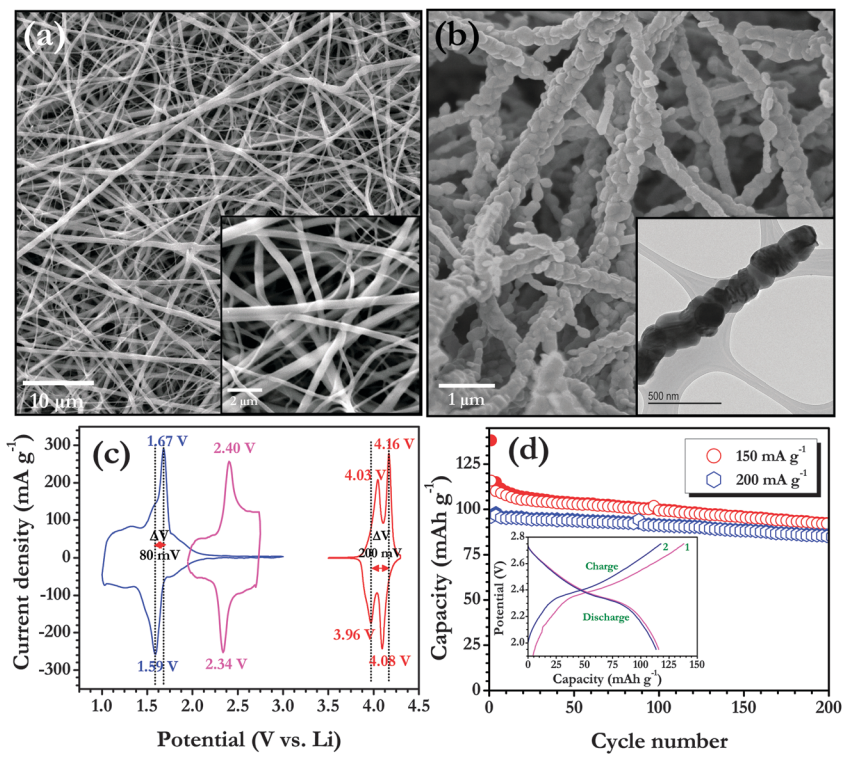


Fig. 6 (a) FE-SEM pictures of the as-spun $TiNb_2O_7$ nanofibers (green nanofibers), inset: magnified view, (b) FE-SEM picture of the electrospun $TiNb_2O_7$ nanofibers at 1000 °C for 4 h. Inset: TEM picture, (c) CV curves of the all electrospun $LiMn_2O_4/TiNb_2O_7$ full-cell assembly at a slow scan rate of 0.1 mV $s^{-1}$ (thin lines show the performance of both the $LiMn_2O_4$ cathode and $TiNb_2O_7$ anode in a half-cell assembly for comparison at a scan rate of 0.1 mV $s^{-1}$), and (d) cycling performance of the all electrospun $LiMn_2O_4/TiNb_2O_7$ full-cell at two different current densities, inset: typical charge–discharge curves recorded at a current density of 150 mA $g^{-1}$. Reprinted with permission from ref. 95. Copyright 2014 American Chemical Society.

Goodenough and co-workers[88,89] proposed a new anode framework material ($TiNb_2O_7$) with a higher theoretical capacity ($\sim$388 mA h $g^{-1}$ for 5 moles of Li), which has a similar operating potential to spinel $Li_4Ti_5O_{12}$ ($\sim$1.5 V *vs.* Li). The bulk $TiNb_2O_7$ anodes exhibit very high reversibility (>270 mA h $g^{-1}$),[90–93] but unusual coulombic efficiencies for such framework materials in a half-cell assembly. Under the optimized synthetic parameters, we successfully synthesized single phase $TiNb_2O_7$ nanofibers and subsequently evaluated their battery performance in a full-cell assembly.[94] In other words, the all 1D $LiMn_2O_7/TiO_2$ configuration anatase phase was replaced with $TiNb_2O_7$ nanofibers ($LiMn_2O_4/TiNb_2O_7$). The expected operating potential was at $\sim$2.4 V, which is $\sim$0.2 V higher than the former configuration, and hence a slightly higher net energy density was expected. Furthermore, excellent cyclability was noted for the all 1D $LiMn_2O_4/TiNb_2O_7$ configuration irrespective of the applied current densities (Fig. 6). Interestingly, the coulombic efficiency of the $LiMn_2O_4/TiNb_2O_7$ cell was very close to 100%, which is much higher than the $LiNi_{0.5}Mn_{1.5}O_4/TiNb_2O_7$ system reported by Goodenough and co-workers.[88,89] Hence, we strongly believe the presence of the 1D morphology certainly provides the enhanced coulombic efficiency with a long life-span, although it involves a slight reduction in volumetric capacity. Currently, we are making progress in increasing the energy density by using $LiNi_{0.5}Mn_{1.5}O_4$ cathodes and are simultaneously exploring new insertion anodes like $Li_3Nd_3W_2O_{12}$ ($\sim$0.3 V *vs.* Li) for constructing high energy density Li-ion power packs.[95] The above studies clearly suggests that the utilization of such a unique architecture provides a means to realize all 1D nanostructures in a full-cell assembly with a long cycle life and superior performance. Such kinds of LIB configurations could be extended to other nanostructures composed of different morphologies, such as nanowires, nanotubes, and nanorods, prepared by various synthetic approaches to aid our understanding of their advantages in practical cells.

## Conclusions

Overall, high voltage cathode ($LiNi_{0.5}Mn_{1.5}O_4$, $\sim$4.7 V *vs.* Li) and low voltage insertion anodes ($TiNb_2O_7$, $\sim$1.5 V *vs.* Li) with high capacity combinations were successfully fabricated and studied in an all 1D configuration. The desired energy density of the Li-ion cells can be tailored by choosing various anode and cathode combinations. It was very clear that the presence of 1D nanostructures prepared by electrospinning provides new avenues for the fabrication of high performance Li-ion cells. Generally, the usage of nanostructured materials dilutes the volumetric capacity of the system, although this is not completely true for all the systems. In fact, in the present case, all the test electrodes were prepared with 10 mg active mass loading (in a 200 $mm^2$ area), irrespective of the half-cell or full-cell assemblies. However, the reactivity towards the electrolyte solutions could not be avoided when using such nanomaterials. The unique 1D nanostructures are not only limited to the electrospinning technique, but also 1D materials prepared by other conventional techniques (such as hydrothermal method) can be explored to realize good performance in a full-cell assembly by a permutation combination to attain high performance Li-ion batteries towards HEVs and EVs.

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