

Practical Li-Ion Battery Assembly with One-Dimensional Active Materials

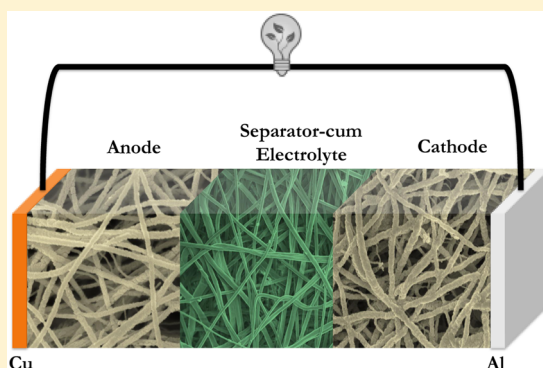
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ABSTRACT: Research activities on the development of one-dimensional (1D) nanostructures and their successful implementation in the fabrication of high-performance practical Li-ion batteries (LIBs) are described. Although numerous 1D-structured materials have been explored for use in LIBs as anodes, cathodes, and separator-cum-electrolytes, only a very limited number of studies report the practical assembly of LIBs using these components. As a result, the salient features of using 1D materials in charge-storage devices have not been realized from an application perspective. Exceptional battery performance is reported when all-1D-based electro-active materials are used to fabricate LIBs. Using all-1D nanostructures not only provides high power capability, energy density, and durability, it also opens up new avenues for developing high-performance next-generation Li-ion power packs.



One-dimensional (1D) nanostructures are promising electro-active materials (anode, cathode, and separator-cum-electrolyte) for energy-storage applications, especially Li-ion batteries (LIBs). Utilizing 1D nanostructures offers several unique features, such as (i) a high surface area-to-volume ratio, which increases the electrochemical activity via improved Li-ion flux across the electrode/electrode interface; (ii) shorter Li-diffusion pathways, which lead to complete participation of the active material during electrochemical reaction compared with bulk materials, especially at high current rates; (iii) improved electron transport; (iv) kinetic tailoring of the crystallographic orientation to facilitate the transport properties; (v) better accommodation of the volume variation associated with Li-insertion/extraction; and (vi) improvement in fatal issues like pulverization and cracking of the electrode materials (particularly alloying type) upon alloying/dealloying by adopting hollow 1D structures with or without surface modification.^{1–5} On the other hand, there are certain drawbacks to using such materials, like the significant acceleration of unwanted side reactions with electrolyte solutions and dilution of the volumetric energy density due to the lower tap density of 1D materials compared with bulk materials; additionally, the scalability of these materials from an industrial perspective cannot be ignored.^{2,6–8} To date, many 1D-structured electrodes, like rods (NRs), wires (NWs), fibers (NFs), tubes (NTs) with solid and hollow interiors, and multishell structures, have been reported for use as both anodes and cathodes.⁹ In most cases, dramatic improvements in the electrochemical properties were reported when using these nanostructures in a half-cell configuration.¹⁰ Unfortunately, analyzing the half-cell perform-

ance of 1D materials is only a preliminary study, and it is unlikely that the same performance will be replicated in practical configurations, e.g., a full-cell configuration, for all cases.^{3,11–13} As a result, most of the interesting features/advantages of using 1D-nanostructured materials are not realized in practical configurations/applications. Nonetheless, continuous exploration of the half-cell performance of various 1D structures is in full-swing, as evident from the increasing number of original and review articles being published.¹⁴

Analyzing the half-cell performance of 1D materials is only a preliminary study, and it is unlikely that the same performance will be replicated in practical configurations.

Interestingly, apart from the active materials (anode, cathode, and separator-cum-electrolyte) used in LIBs, the current collectors (i.e., Al for the cathode and Cu for the anode) are also important components that facilitate the electron transport in both electrodes. Efforts to improve the battery performance have also focused on the current collectors; in particular, both Cu and Al substrates have been tailored to 3D structures that

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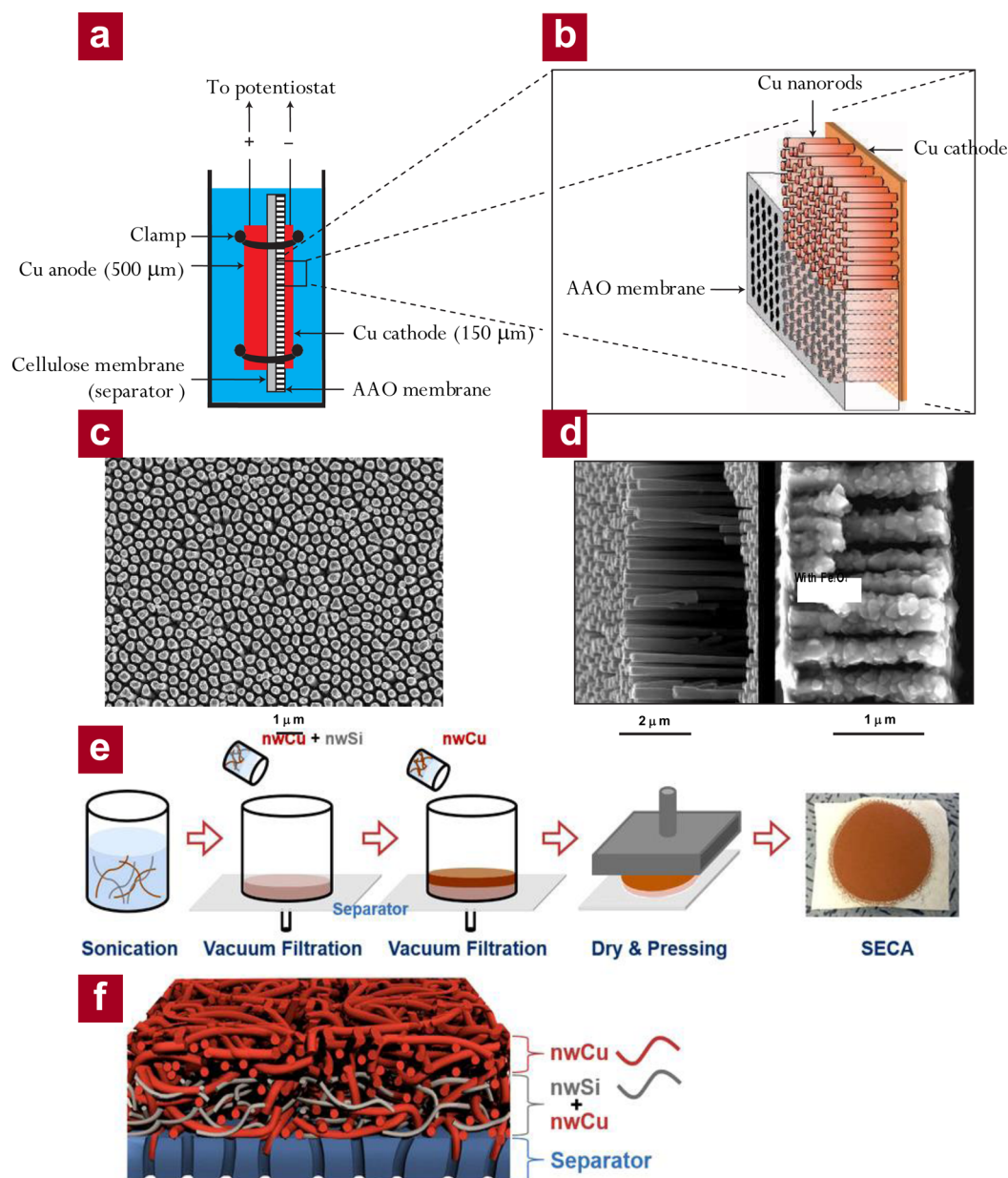


Figure 1. Electrochemical cell and the nanostructured current collector. (a) Diagram of the electrochemical cell used for template synthesis of nanostructured Cu current collector. (b) Diagram of the nanostructured current collector expected to be obtained at the end of the electrolysis, before and after removal of the anodic aluminum oxide (AAO) membrane. (c) Top view of the Cu current collector obtained after electrolysis and membrane removal. (d) Cross-sectional views of Cu-nanostructured current collector before (left) and after (right) Fe_3O_4 deposits. Reproduced with permission from ref 15. Copyright 2006, Nature Publishing Group. (e) Fabrication process of separator-electrode-current collector assembly (SECA). (f) Schematic cross-sectional view illustrating intertangled nanowires in SECA. Reproduced with permission from ref 21. Copyright 2015, Nature Publishing Group.

are composed of vertically grown 1D NRs. Active materials have then been electrodeposited over a 1D current collector to realize the high power capability of active materials. Fe_3O_4 ^{15–17} and Sn ¹⁸ deposited Cu nanoarchitectures are perfect examples of such an anode. This technique not only provides high power capability, it also maintains high reversibility as well.¹⁹ Elimination of the binder and associated solvent evaporation in this procedure is also worth mentioning. An Al nanoarchitecture has also been used for TiO_2 deposition.²⁰ Such modification of the current collectors is certainly useful for the development of Li-ion microbatteries. Very recently, considering the merits of 1D nanostructures discussed above, a binder-free alloy-type Si-NW anode was reported along with a Cu-NW

conductive additive and current collector.²¹ All-ethanol-based suspensions have been used according to the schematic presented in Figure 1. This kind of binder-free electrode architecture is certainly useful for constructing shape-versatile miniature LIB power packs that require tailored energy and power capabilities. Apart from their Li-insertion properties, carbon nanotubes (CNTs, which include single, double, and multiwall)²² have been unconventionally used as a substrate for both anodic and cathodic sides, with the aim of fabricating binder-free electrodes for constructing shape-versatile (i.e., flexible) power packs.^{23–25} The usage of CNTs has been described in many reviews and original articles, and, hence, it is not discussed in the present work.²⁴ Nevertheless, active

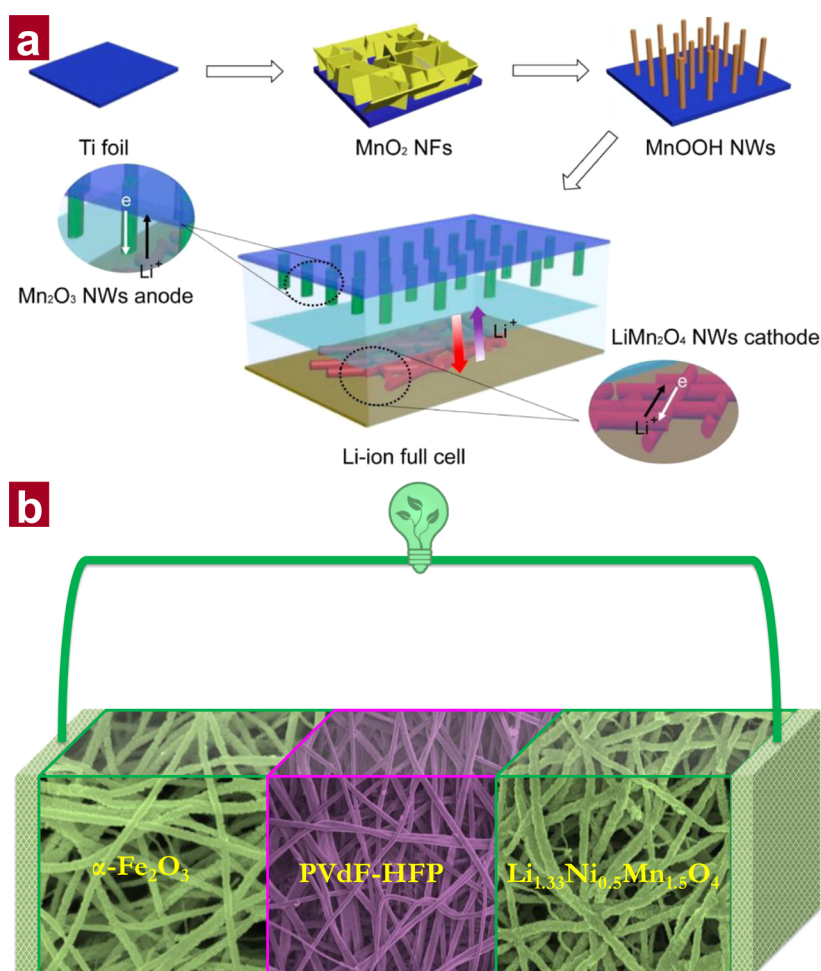


Figure 2. (a) Schematic of the synthesis and fabrication of the Mn₂O₃/LiMn₂O₄ LIB full-cell. Reproduced with permission from ref 30. Copyright 2014, American Chemical Society. (b) FE-SEM pictures of an all-1D-based LIB prepared by electrospinning; here, the cathode (LiNi_{0.5}Mn_{1.5}O₄) has been electrochemically prelithiated (Li_{1.33}Ni_{0.5}Mn_{1.5}O₄) to mitigate the ICL. Reproduced with permission from ref 40. Copyright 2016, Elsevier.

materials grown over carbon cloth, graphene sheets, and conducting polymers have very recently been proposed as promising substrates for fabricating flexible and wearable Li-ion power packs.^{19,26,27} The usage of carbon cloths is not only limited to LIB applications, they are also useful for supercapacitor electrodes as well.

Lu et al.²⁸ reported the fabrication of 1D-material-based Li-ion power packs using vertically aligned CNTs (VA-CNTs) as the anode and V₂O₅-coated VA-CNTs as the cathode in the presence of ionic liquid (1 M LiTFSI in *N*-ethyl-*N,N*-dimethyl-2-methoxyethylammonium bis(trifluoromethylsulfonyl) imide). This interesting configuration was capable of delivering a maximum energy density of ~297 Wh kg⁻¹, though its cyclability was not reported. Later, Kong et al.²⁹ attempted to encapsulate V₂O₅ with graphitic carbon (V₂O₅-G) in a 1D form via chemical vapor deposition. This assembly can be viewed as a hollow graphitic nanotube filled with V₂O₅, which can be used as a binder-free positive electrode. In a similar fashion, SnO_x-filled hollow graphitic nanotubes (SnO_x-G) were prepared and prelithiated before being employed as the anode in a flexible Li-ion power pack. A porous polypropylene separator was used in the presence of a conventional 1 M LiPF₆:ethylene carbonate (EC):diethyl carbonate (DEC) electrolyte solution. There is no detailed information available for the V₂O₅-G/SnO_x-G configuration, though it displayed a maximum energy density

of ~360 Wh kg⁻¹. This unique assembly also displayed exceptional robustness, as clearly evident from bending and folding studies; for example, the open circuit potential only dropped by 0.04% after 200 bending trials. Wang et al.³⁰ claimed the fabrication of an all-NW-based Li-ion cell composed of a conversion-type-Mn₂O₃ anode and a LiMn₂O₄ cathode (Figure 2). However, the usage of commercial Celgard 2400 membrane is questionable for their claim as an all-NW-based Li-ion cell. Both the anode and cathode were prepared by a conventional hydrothermal approach on a Ti substrate. Mn₂O₃ is a conversion-type material and, hence, it was tested in a half-cell assembly over three cycles to ensure the elimination of irreversible capacity loss (ICL) before being paired with LiMn₂O₄ in the presence of LiPF₆ (1 M) in EC/DEC/dimethyl carbonate (1:1:1 w/w). The full-cell LiMn₂O₄/Mn₂O₃ showed a decent cycling profile with a maximum reversible capacity of ~104 mAh g⁻¹. NFs are similar to NWs and are one of the most investigated 1D morphologies for charge storage. Generally, NFs are prepared by electrospinning, and the resultant product morphology can be tailored by adjusting the various parameters.⁴ Interestingly, several startup companies have already commercialized NF products for multifarious applications.³¹ Along these lines, Aravindan et al.³² reported the first fabrication of all-1D-NF-based “rocking-chair” cells using anatase TiO₂, spinel LiMn₂O₄, and polyvinylidene fluoride-co-

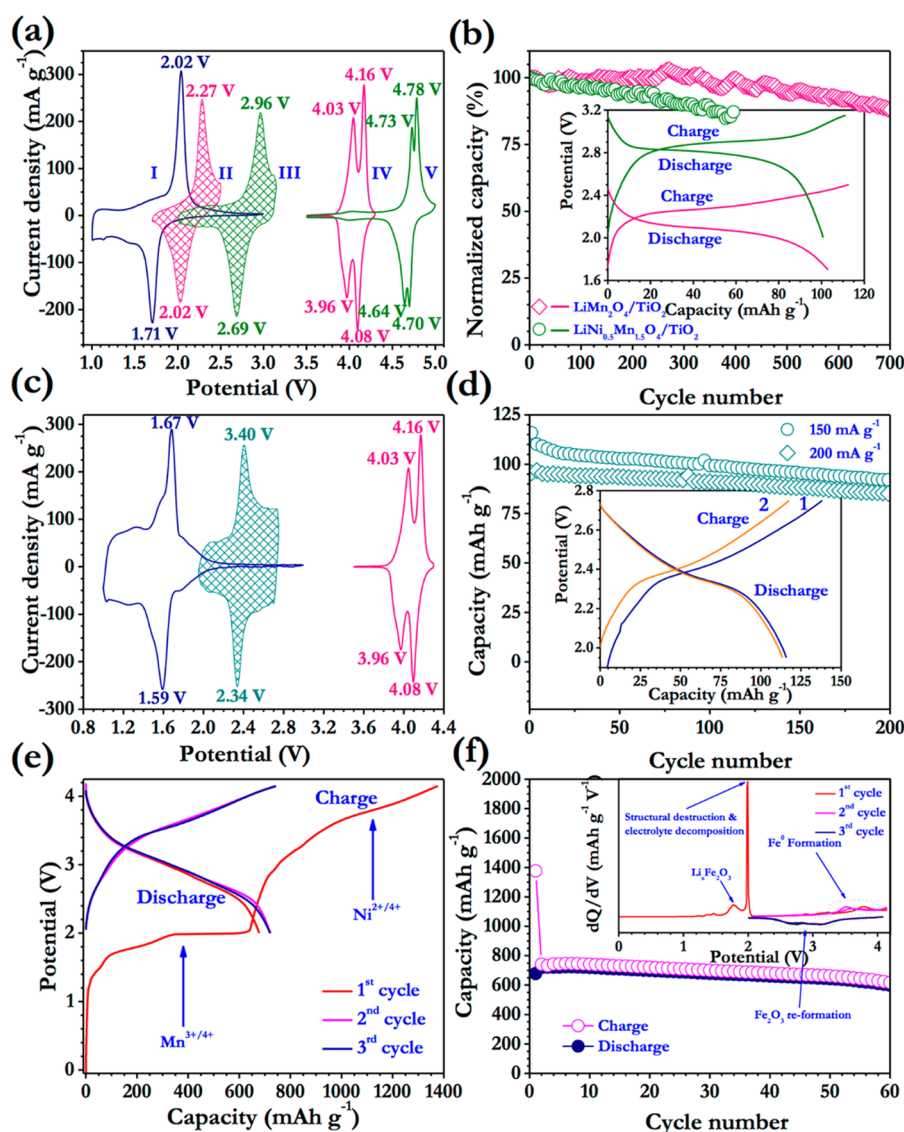


Figure 3. (a) Cyclic voltammetry (CV) curves of an all-electrospun $\text{LiMn}_2\text{O}_4/\text{TiO}_2$ (IV) or $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{TiO}_2$ (V) full-cell assembly recorded at a slow scan rate of 0.1 mV s^{-1} (un shaded curves show the performance of Li/TiO_2 (I), $\text{Li}/\text{LiMn}_2\text{O}_4$ (II) and $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (III) electrodes at a scan rate of 0.1 mV s^{-1}). (b) Normalized capacity of $\text{LiMn}_2\text{O}_4/\text{TiO}_2$ (at a current density of 300 mA g^{-1}) (Reproduced with permission from ref 32. Copyright 2013, The Royal Society of Chemistry) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{TiO}_2$ (at a current density of 150 mA g^{-1}) full-cells at ambient temperature (Reproduced with permission from ref 33. Copyright 2014, The Royal Society of Chemistry); inset: typical galvanostatic charge–discharge curves of $\text{LiMn}_2\text{O}_4/\text{TiO}_2$ (at a current density of 150 mA g^{-1}) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{TiO}_2$ (at a current density of 15 mA g^{-1}) full-cells. (c) CV curves of an all-electrospun $\text{LiMn}_2\text{O}_4/\text{TiNb}_2\text{O}_7$ full-cell assembly at a slow scan rate of 0.1 mV s^{-1} (the unshaded curves 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}). (d) Cycling performance of an all-electrospun $\text{LiMn}_2\text{O}_4/\text{TiNb}_2\text{O}_7$ full-cell at two different current densities; inset: typical charge–discharge curves recorded at a current density of 150 mA g^{-1} . Reproduced with permission from ref 36. Copyright 2014, American Chemical Society. (e) Typical charge–discharge curves for a $\text{Li}_{1.33}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4/1 \text{ M LiPF}_6$ gelled $\text{PVdF-HFP}/\alpha\text{-Fe}_2\text{O}_3$ cell between 2 and 4.15 V at a current density of 100 mA g^{-1} . (f) Cycling profiles, in which the capacity is based on the anode loading; inset: differential capacity profiles for the first three cycles. Reproduced with permission from ref 40. Copyright 2016, Elsevier.

hexafluoropropylene (PVdF-HFP) as the anode, cathode, and separator-cum-electrolyte, respectively (Figure 3a,b). Prior to cell assembly, a PVdF-HFP NF membrane was gelled with conventional carbonate electrolyte solutions (i.e., 1 M LiPF_6 in EC:DEC). The authors also used planar stainless-steel-mesh (planar weave) current collectors for both the anode and cathode. Therefore, we believe that this is the perfect kind of all-1D-based LIB compared to the work of Wang et al.³⁰ owing to the usage of 1D NF membrane rather than commercial Cegard. The $\text{LiMn}_2\text{O}_4/\text{gelled PVdF-HFP}/\text{TiO}_2$ cell delivered an exceptional performance, with $\sim 90\%$ of the initial reversible

capacity retained after 700 cycles and a working potential of $\sim 2.2 \text{ V}$; the reversible capacity of $\sim 100 \text{ mAh g}^{-1}$ (based on the cathode loading) at a current density of 100 mA g^{-1} is also noteworthy. To date, this is one of the best results reported for this configuration, which is mainly attributed to the fascinating characteristics of the 1D electro-active materials used, including the gelled PVdF-HFP and planar substrates. The same group of authors subsequently attempted to increase the energy density of LIBs to some extent by replacing the native-spinel LiMn_2O_4 cathode with a high-voltage Ni-substituted ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) cathode (Figure 3a,b).³³ As expected, the full-cell Li-

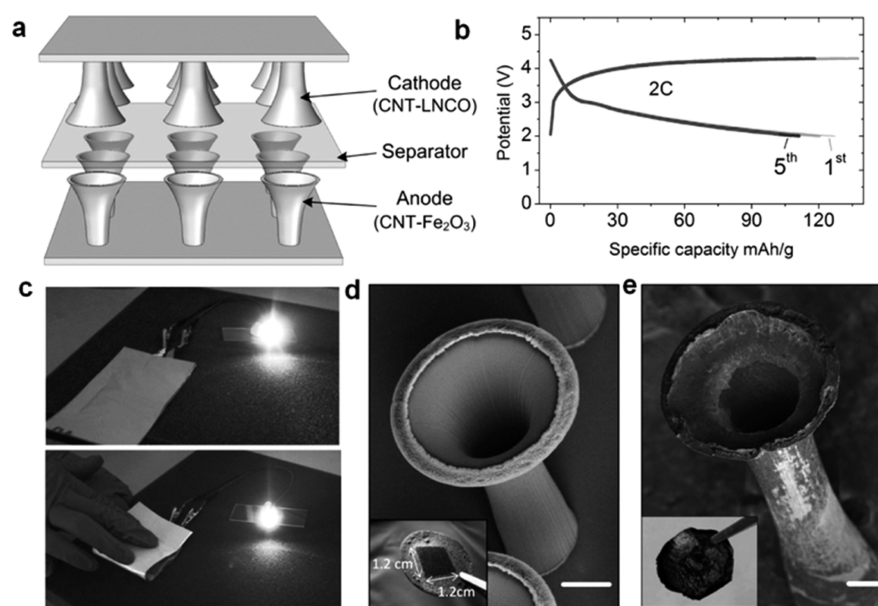


Figure 4. Full flexible cell fabrication and characterizations. (a) Schematic representation of the full cell with a CNT-cone anode and cathode. (b) Charge/discharge curves of full cell: iron oxide–CNT cones and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (LNCO)–CNT cones at 2C (first and fifth cycles indicated). (c) Flexible CNT-cone battery connected to a 3 V white-light LED. (d) SEM image of CNT cone, taken at 35° tilt angle, before testing in a full cell. The inset shows $1.2\text{ cm} \times 1.2\text{ cm}$ area coverage of transferred CNT cones on PCP film. Scale bar: $20\text{ }\mu\text{m}$. (e) SEM image of CNT cone, taken at 40° tilt angle, and picture of the electrode (inset) after 1000 charge/discharge cycles and repeated bending of the electrode. Scale bar: $10\text{ }\mu\text{m}$. Reproduced from ref 42. Copyright 2016, John Wiley and Sons.

$\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /gelled PVdF-HFP/ TiO_2 displayed a working potential of $\sim 2.8\text{ V}$ and delivered exceptional battery performance, with $\sim 86\%$ retention of the initial capacity after 400 cycles, which is similar to its parent material (LiMn_2O_4). This is also one of the best results reported for such high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes in a “rocking-chair” configuration.^{33–35} Interestingly, the same kind of behavior, i.e., electrochemical activity, was also reported when using the high-capacity anode TiNb_2O_7 with native spinel (LiMn_2O_4 /gelled PVdF-HFP/ TiNb_2O_7) (Figure 3c,d).³⁶ These three “rocking-chair” configurations clearly vindicate the use of perfect all-1D-architected materials for fabricating practical Li-ion configurations, with both cell-assembly advantages and excellent battery performance provided.³⁵

Fabricating all-1D-NFs in a “rocking-chair” configuration is a very straightforward procedure, in which optimization of the mass balance and cutoff potential is sufficient to attain the maximum energy density. However, utilizing high-capacity anodes, like conversion/displacement- and alloy-type materials that experience fatal issues such as huge ICL in the first cycle and poor cyclability, requires a large amount of cathode loading.^{37–39} As a result, the volumetric energy density is dramatically diluted.³⁴ Therefore, such an assembly requires an additional pretreatment step to eliminate the ICL observed in such anodes.³⁸ Aravindan et al.⁴⁰ explored this concept for fabricating an all-1D-NF-based LIB with a high-capacity anode material; specifically, a conversion-type anode ($\alpha\text{-Fe}_2\text{O}_3$) was used in this unique assembly instead of a topotactic-insertion-type anode (Figure 3e,f). Using an electrochemically overlithiated cathode ($\text{Li}_{1+x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$) has also been proposed as a way to eliminate the ICL; this is an unusual process in that the cathode is pretreated instead of the anode.⁴¹ Eventually, the full-cell, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /gelled PVdF-HFP/ $\alpha\text{-Fe}_2\text{O}_3$ displayed excellent battery performance upon cycling.^{38,41} Similarly, an ultraflexible LIB was also reported using a conversion-type

Fe_2O_3 anode in which the flexible substrate was prepared using a composite of poly(vinylidene difluoride), double wall CNTs, and phenyl-C61-butyric acid methyl ester (PCP) (Figure 4).⁴² As usual, the CNT cones were prepared by chemical vapor deposition and transferred into the PCP substrate. The cones were then decorated with Fe_2O_3 nanocrystals/commercial $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and eventually employed as the anode/cathode. The Fe_2O_3 -decorated CNT cones displayed enhanced electrochemical activity compared to conventionally coated electrodes (Figure 4); however, not much information was presented on the cell assembly and ICL elimination ($\sim 48\%$ is clearly seen from the half-cell measurements). Rolling and bending of said configuration upon cycling is clearly evident, and it delivered a capacity of $\sim 120\text{ mAh g}^{-1}$ with a working potential of $\sim 3.1\text{ V}$. As expected, the full-cell was not stable upon harsh current testing, but *ex situ* studies confirmed the structural integrity of the metal-oxide-decorated CNT cones. This clearly suggests that using all-1D-nanostructured electro-active materials in LIBs provides a dramatic improvement in battery performance, irrespective of the reaction mechanism.

The successful demonstration of all-1D-nanofiber (anode, cathode, and separator-cum-electrolyte)-based Li-ion power packs with excellent performance provides new avenues for further exploring and realizing the advantages of using nanostructures. Such 1D LIBs have been constructed with various kinds of materials; in particular, exceptional battery performance has been reported irrespective of the anode’s reaction mechanism (i.e., insertion and conversion). Unfortunately, scaling up the synthesis procedure (electrospinning) is a big challenge in the commercialization of these active materials, compared with conventional processes like solid-state and sol-gel synthesis. Nevertheless, many start-up companies have recently commercialized materials prepared by electrospinning, which is a positive sign for exploration of this synthesis technique.³¹ Other morphologies like NWs, NTs, and NRs

must also be further explored in all-1D configurations to realize the advantages of using such unique morphologies. However, 1D separator-cum-electrolytes can only be prepared by electrospinning. Using 1D-architected current collectors and conductive additives would be interesting approaches, but they have yet to be evaluated in practical configurations. Nevertheless, 1D-structured plain-weave stainless steel mesh has been studied as a current collector for both positive and negative electrodes, with interesting results. There are big questions regarding the scalability, cost and flexibility when using such stainless-steel-mesh substrates, but they are perfectly suited for laboratory-level studies. Similarly, the development of metal-oxide-filled 1D carbon nanostructures represents one of the great attempts at fabricating flexible Li-ion power packs. This approach could easily be translated to conventional cathodes, with a corresponding dramatic increase in the energy density of the system. Such increase in the energy density of the system certainly increasing the potential safety of the system is worth mentioning. However, great challenges remain in preparing unique architectures like V_2O_5 -G/SnO_x-G, and Li-Ni_{0.8}Co_{0.2}O₂-CNT/Fe₂O₃-CNT. It is well known that using such carbonaceous materials dilutes the net energy density of the cell, i.e., suppression of the volumetric energy density. Additionally, the extensive utilization of nanostructures in a single assembly triggers inevitable side reactions owing to the high specific surface area and its unique properties. This in turn provides the decomposition of the electrolyte solution that occurs prior to the anticipated potential in both oxidative and reductive conditions. As a result, the formation of thick solid electrolyte interphase is inevitable, which certainly leads to the unwanted side reaction and increase the cell impedance. These unwanted reactions eventually ruin the cell performance. These challenges should be kept in mind while attempting to develop such interesting battery assemblies using 1D active materials. Apart from the commercialization perspective, plenty of useful information could be obtained from such unique assembly, which is necessary for better understanding of the fundamental chemistry behind it.

The extensive utilization of nanostructures in a single assembly triggers inevitable side reactions owing to the high specific surface area and unique properties.

Overall, using 1D architectures provides a dramatic improvement in battery performance compared with bulk materials, irrespective of the various active materials and configurations. Future research activity must focus on the following aspects: preparation of 1D nanostructures using active materials with relatively lower specific surface areas to minimize the unwanted side reactions; utilizing the minimum amount of carbonaceous support required to enhance the power capability without compromising the volumetric sacrifices; and the development of scalable, cost-effective, and eco-friendly preparation procedures.

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Notes

The authors declare no competing financial interest.

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