A High Areal Capacity Flexible Lithium-Ion Battery with a Strain-Compliant Design

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Early demonstrations of wearable devices have driven interest in flexible lithium-ion batteries. Previous demonstrations of flexible lithium-ion batteries trade off between low areal capacity, poor mechanical flexibility and/or high thickness of inactive components. Here, a reinforced electrode design is used to support the active layers of the battery and a freestanding carbon nanotube (CNT) layer is used as the current collector. The supported architecture helps to increase the areal capacity (mAh cm\(^{-2}\)) of the battery and improve the tensile strength and mechanical flexibility of the electrodes. Batteries based on lithium cobalt oxide and lithium titanate oxide shows excellent electrochemical and mechanical performance. The battery has an areal capacity of \(\approx 1\ \text{mAh cm}^{-2}\) and a capacity retention of around 94\% after cycling the battery for 450 cycles at a C/2 rate. The reinforced electrode has a tensile strength of \(5.5-7.0\ \text{MPa}\) and shows excellent capacity retention after repeatedly flexing to a bending radius ranging from 45 to 10 mm. The relationships between mechanical flexing, electrochemical performance, and mechanical integrity of the battery are studied using electrochemical cycling, electron microscopy, and electrochemical impedance spectroscopy (EIS).

1. Introduction

Flexible batteries and flexible devices have a common goal but different design challenges. Flexible electronics with a wide variety of functionalities such as displays,[3] skin-like pressure sensors,[2] health sensors,[3,4] light-emitting diodes,[5] solar cells[6] and flexible circuits[7] have been demonstrated. Flexible electronics are typically fabricated by using solution processed organic semiconductors[8] and conductors or by patterning traditional inorganic components in ultrathin form (<100 nm).[9] This enables the electronic device to be flexible to a bending radius of less than 1 cm without reaching its fracture limit (≈1\% strain).[10,11] Electronics fabricated on soft polymeric substrate can conform over curvilinear surfaces and form the building blocks for wearable electronics. Powering these devices while maintaining the flexibility and form-factor of the device is a challenge. Towards this goal there have been numerous attempts to develop thin, flexible and stretchable supercapacitors,[12–17] energy harvesters,[18–22] and batteries.[14,23–52] Due to their high energy and power density, flexible rechargeable batteries are an essential part of a power module.[53] Commercially available batteries are typically rigid due to their packaging and thick electrode stack. Flexible batteries require that all of the key components (current collector, active layer, separator, packaging) be bendable. Such devices are currently fabricated by using a thin conductive layer supported on a non-conductive substrate as a current collector, on which a thin active layer (20–60 µm) is printed. The areal capacities of flexible lithium-ion batteries have been comparatively low (0.05–0.20 mAh cm\(^{-2}\) vs 1–2 mAh cm\(^{-2}\) for traditional systems) as the active layers are printed thin to reduce the electrode degradation during flexing and the inactive layers associated with supporting the current collectors increase the thickness of the battery.[26,35,41,44,54]

Here we demonstrate a flexible rechargeable lithium-ion battery with an areal capacity of \(\approx 1\ \text{mAh cm}^{-2}\). We use lithium cobalt oxide (LCO) and lithium titanate oxide (LTO) as the positive (cathode) and negative (anode) electrodes, to form a battery with a nominal potential of \(\approx 2.5\ V\)[55–57]. The flexible battery with CNT as the current collector had negligible drop in capacity after electrochemically cycling the battery for 450 cycles at C/2 rate. The areal capacity (mAh cm\(^{-2}\)) of the battery was increased by printing active layers as thick as 150 µm while improving their mechanical property by embedding the active layers inside a fibrous support. The fibrous membrane binds the active layers while carrying the stress associated with flexing. The reinforced electrodes have a tensile strength of \(5.5-7.0\ \text{MPa}\), an order of magnitude higher than conventional non-flexible electrodes, making the electrode resistant to cracking and mechanical fatigue. The battery maintained capacity during electrochemical cycles under flex conditions and after undergoing repeated flexing cycles. EIS was used to analyze the structural changes...
within the reinforced electrodes after repeatedly flexing the battery. The EIS data suggests that bending the reinforced electrodes leads to a slight increase in the porosity of the electrodes causing no apparent capacity fade.

2. Results and Discussion

2.1. Flexible Current Collector

Current collector electronic conductivity is important to efficient charge transfer in a battery.\(^{[58]}\) Commercial lithium-ion batteries rely on thin metallic foils of aluminum and copper to serve as current collectors for the positive and negative electrodes, respectively. Such foils (typically \(\approx 15–20\) µm) are stiff, and subject to fatigue failures and therefore cannot be used in flexible batteries.\(^{[59]}\) In recent reports, nickel-coated fabrics have been used as current collectors in flexible lithium-ion and alkaline batteries.\(^{[35,40]}\) Nickel was deposited on the fabrics using electroless deposition techniques to produce a conformal coating on the fabric. The low sheet resistance (\(\approx 0.35\) Ω/□) and high flexibility of nickel-coated fabrics makes them an excellent candidate for current collectors in flexible batteries. But thicknesses of 100–300 µm lead to a significant increase in the mass of the inactive components in the battery. Previously we used commercially available conductive inks such as silver (\(\approx 0.015\) Ω/□) and carbon (\(\approx 50\) Ω/□) to serve as current collectors for MnO\(_2\) and zinc electrodes.\(^{[31,38,39]}\) Due to the oxidation and dissolution of silver at potentials above 3 V,\(^{[30]}\) silver current collectors cannot be used in rechargeable lithium-ion batteries, and the low conductivity of carbon leads to a significant Ohmic potential drop during charging and discharging. Hu et al. demonstrated the use of CNT coated on paper to serve as current collectors for lithium-ion batteries.\(^{[14,28]}\) The CNT layer had a sheet resistance of \(\approx 5–10\) Ω/□ and the batteries did not show any significant Ohmic potential drop during cycling. Recently, a similar approach was used to embed CNT ink inside of laboratory Kimwipes to serve as current collectors for foldable and origami lithium-ion batteries.\(^{[44,54]}\) Both approaches have relied on the use of a non-conductive substrate to support the CNT layer, which was followed by printing the active ink on top of the CNT layer. It would be beneficial to remove the non-conductive substrate after printing the active layer to reduce the overall thickness of the battery. In this work, we used an airbrush to spray aqueous CNT ink on top of a stainless steel (SS) foil to form a thin CNT layer, which can then be transferred on top of a self-standing anodic/cathodic electrode (Figure 1). Spray printing has been used previously to deposit CNT inks on substrates to serve as current collectors for batteries\(^{[46]}\) or electrodes for supercapacitors.\(^{[60]}\) Spray printing is a versatile technique and can be easily modified to print inks with wide range of viscosities over large areas. In this work, the inactive support layer is removed during the transfer process, which helps to reduce the thickness of inactive layers within the battery. The aqueous CNT ink was prepared by mixing 2 mg mL\(^{-1}\) of CNT with 20 mg mL\(^{-1}\) of sodium dodecylbenzenesulfonate (SDBS) surfactant.\(^{[61]}\) The final thickness and loading of the CNT layer was \(\approx 3\) µm and \(\approx 0.125\) mg cm\(^{-2}\), respectively. The CNT layer prepared with this method shows sheet resistance of \(\approx 10\) Ω/□.

2.2. Dip Coated Electrode and CNT Transfer

The electrochemically active layer in a battery is a mixture of active metal oxide, carbon (to improve the conductivity) and binder (to hold the mix together).\(^{[62]}\) The active layer is brittle and can crack during flexing.\(^{[26]}\) Considerably less attention has been put towards improving the mechanical integrity of the active layer. Previous approaches have relied on using a flexible current collector as a support for the active layer, and have limited the electrode thickness to 20–60 µm to reduce the flex induced strain and cracking.\(^{[26,38,41,44,54,63]}\) The low thickness of the active layer reduces the areal capacity and the battery requires a larger footprint to achieve the required capacity. Recent reports have proposed folding the battery multiple times to increase its areal capacity (mAh cm\(^{-2}\)). But even after 4 folds (16 times thicker), the capacity of the battery increased only to 1.5 mAh cm\(^{-2}\).\(^{[44,54]}\) Additionally, folding the batteries multiple times would make the battery pack thicker, less flexible and potentially unsuitable for some applications. It would be preferable to increase the areal capacity of the battery by increasing the thickness of the active layer without degrading its mechanical integrity. In our previous work, we reported on flexible primary alkaline batteries with an areal capacity of \(\approx 6\) mAh/cm\(^2\) using a mesh design.\(^{[31]}\) A similar concept was used to make stretchable alkaline batteries by embedding the active ink within fibers of a silver coated stretchable fabric.\(^{[34]}\) Here, we use similar principles and embedded the active layers of a lithium ion battery inside a porous membrane composed of non-woven fibers. The membrane acts as a substrate and absorbs stresses generated during flexing. We embedded the active material into the membrane by dipping it into an ink bath (Figure 2). The ink is absorbed into the membrane by capillary action. The excess ink (ink not embedded inside the fabric) was removed with a doctor blade. After being coated, the membrane with was heated in an oven at 80 °C for two hours to dry it. The membrane with the LCO or LTO mix had a thickness of \(\approx 150\) µm. The loading of the LTO and LCO electrode was 13.2 and 11.6 mg cm\(^{-2}\), respectively. Figure 2 shows optical images of the membranes after embedding them with the LCO and LTO mix. The supported electrodes were quite flexible and can be flexed repeatedly without any cracking or delamination of the active layer.
Before the CNT transfer process, the SS with CNT was cut into smaller squares (2.4 × 2.4 cm²). Due to the poor adhesion between the CNT and SS, the CNT layer floats in water in ≈1 min (Figure 3). The LCO or LTO electrode was pressed on top of the CNT layer and the LTO/CNT or LCO/CNT electrode was taken out of the water bath. The CNT layer adheres to the LCO and LTO electrode by Van der Waals interactions. Due to the low thickness of the CNT layer (≈3 µm), the CNT forms a conformal coating on top of the LTO/LCO electrode. The LCO/CNT and LTO/CNT electrodes are washed in fresh water 2–3 times to remove traces of surfactants. Figure 3 shows an optical image of the LTO and LCO electrode with the CNT current collector before sealing them in a pouch.

Figure 4A shows a scanning electron microscopy (SEM) image of the fibrous non-woven membrane with a thickness of ≈120 µm. The membrane is made of chemically inert polyimide fiber with diameter of ≈10 µm and is used as a separator in Ni-Cd batteries. Due to its open framework structure it serves as an excellent flexible support for the active layer. Figure 4B shows a SEM image of the membrane embedded with LCO mix with CNT current collector on top of the electrode. Due to the low thickness of the CNT layer (≈3 µm), the LCO electrode is visible through the CNT layer. The SEM shows an excellent conformal coating of CNTs on top of the LCO electrode. The LCO particles have sizes ranging between 5–10 µm (Figure S1A, Supporting Information). Figure 4C shows top-view of the LTO mix embedded within the membrane. The LTO particles have an average size of ≈0.5 µm (Figure S1B, Supporting Information). Figure 4D shows a cross sectional micrograph of the membrane embedded with the LTO mix to give an electrode with thickness of ≈150 µm with CNT layer on top of the electrode to serve as the current collector. The SEM shows that the active mix occupies all the open spaces in the membrane.

2.3. Mechanical Testing

An electrode for flexible batteries should have high strength and retain its mechanical integrity after undergoing repeated flexing. We study the mechanical stability of the reinforced electrodes by repeatedly flexing them (Figure 5A), and observe the region of the electrode under stress using SEM. Figure 5B,C shows the optical and SEM images of LCO and LTO electrodes, respectively, before and after flexing them 300 times to a bending radius of 1 mm. SEM images of electrodes after flexing show no cracking or delamination, demonstrating superior mechanical property of the reinforced electrodes. Unsupported LCO and LTO electrodes (electrodes printed on thin metallic foils) delaminated and cracked within few flexing cycles.

Breaking stress (maximum force applied to the electrode before it ruptures) is a useful
with 40–20% porosity was breaking stress of the reinforced electrode using an Instron. The speed of 0.197 mm s\(^{-1}\) for the unloaded membrane was higher than values reported for unsupported electrodes.\(^{[64,65]}\) The breaking stress of electrodes ranging from 0 to 50%.\(^{[64]}\) The breaking stress of electrodes limits the rate capability of the full cell. After studying the electrochemical performances of the LCO/CNT and LTO/CNT electrodes in half-cell configuration, full cells were made by sealing the electrodes inside an aluminum-laminated pouch (Figure 8A). The aluminum barrier layer reduces moisture permeation through the pouch. Nickel and aluminum tabs were used to make electric contact to the CNT current collectors. The total thickness of the battery was around 600 µm (including 250 µm for the battery pouch).

2.4. Half Cell and Full Cell Testing

The LTO/CNT and LCO/CNT electrodes were tested using a half-cell configuration with lithium metal as the counter electrode in a coin cell. Before carrying out the half-cell and full-cell tests, the cells were cycled for 2 cycles at C/20 rate (referred as formation-cycle). The columbic efficiency for the first cycle was around 70–80% due to formation of solid-electrolyte-interphase layer and consumption of lithium due to side reactions with impurities in the electrodes.\(^{[66–68]}\) The columbic efficiency increased to around 97–99% for the 2nd cycle. The columbic efficiency after the initial formation cycle was always above 99%. Figure 7A,D show the charge and discharge curve for the LTO/CNT and LCO/CNT electrodes vs lithium metal, respectively. The LTO/CNT electrode was cycled between 1 and 2 V at C/4 rate vs Li/Li\(^+\) and showed a plateau at \(\approx 1.55\) V vs Li/Li\(^+\). The LCO/CNT electrode was cycled between 3 and 4.2 V at C/4 rate vs Li/Li\(^+\). These charge/discharge curves match the results previously obtained for LTO and LCO electrodes using standard current collectors.\(^{[55,57]}\) The charge/discharge curve showed no polarization effects, indicating sufficient conductivity of the CNT current collectors. The LTO/CNT electrode demonstrated an initial specific capacity of \(\approx 132\) mAh g\(^{-1}\), which decreased to \(\approx 131\) mAh g\(^{-1}\) after 80 charge/discharge cycles at C/4 rate, a capacity drop of less than 1% over this period (Figure 7B). The LCO/CNT electrode demonstrated initial specific capacity of \(\approx 134\) mAh g\(^{-1}\), which decreased to 124 mAh g\(^{-1}\) after 80 charge/discharge cycles at C/4 rate, showing a capacity retention of 92.5% (Figure 7E). The columbic efficiencies of both the cells were above 99%. The rate capabilities of both the LTO/CNT and LCO/CNT electrodes were studied by cycling the electrode at different C-rate (10 cycles each at C/8, C/4, C/2, C and C/8 rate). The LTO/CNT showed an initial specific capacity of \(\approx 132\) mAh g\(^{-1}\) at C/8 rate, which decreased to around \(\approx 120\) mAh g\(^{-1}\) at 1C rate, demonstrating a capacity retention of 91% at 1C rate (Figure 7C). The LCO/CNT electrode had relatively poor rate capability showing an initial capacity of \(\approx 134\) mAh g\(^{-1}\), which decreased to \(\approx 110\) mAh g\(^{-1}\) and \(\approx 59\) mAh g\(^{-1}\) at C/2 and 1C rate, respectively (Figure 7F). Hence the LCO/CNT electrode limits the rate capability of the full cell. After studying the electrochemical performances of the LCO/CNT and LTO/CNT electrodes in half-cell configuration, full cells were made by sealing the electrodes inside an aluminum-laminated pouch (Figure 8A). The aluminum barrier layer reduces moisture permeation through the pouch. Nickel and aluminum tabs were used to make electric contact to the CNT current collectors. The total thickness of the battery was around 600 µm (including 250 µm for the battery pouch). Figure 8B shows the charge/discharge capacity for the LTO-LCO full cell cycled over 450 cycles. The active area of the battery was 2.5 × 2.5 cm\(^2\). The batteries demonstrated excellent capacity retention after 450 charge/discharge cycles. The initial areal capacity of the battery at C/2 rate was \(\approx 0.94\) mAh cm\(^{-2}\) and it decreased to \(\approx 0.88\) mAh cm\(^{-2}\) after 450 cycles, showing a capacity retention of \(\approx 93\%\) during this period. The excellent electrochemical stability of full cell demonstrates the stability.
of the freestanding CNT based current collectors. The capacity retention and areal capacity (mAh cm\(^{-2}\)) of the battery was significantly better than previous reports on flexible lithium-ion battery with similar chemistry and is beneficial while powering devices with small footprint.[28,36,44,54] Figure 8C shows the rate capability of the battery. The battery was operated between C/4 to 1C rate for 150 cycles. The battery was able to retain above 75% of capacity at 1C rate. Figure 8D shows charge–discharge curve of the full cell at various C-rates (C/4, C/2 and 1C). The specific capacity of the battery drop to 104 (89%) and 90 (77%) mAh g\(^{-1}\) at C/2 and 1C rates, respectively.

The drop in capacity at high C-rates can be related to the low conductivity of the CNT, which leads to an Ohmic potential drop during charging and discharging. The Ohmic potential drop can be reduced by increasing the thickness of the CNT layer or by depositing a thin layer of metal on top of the CNT layer.

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**Figure 5.** A) Mechanical flexing of the LCO/LTO electrodes over a tube with a radius of 1 mm. SEM images and optical images of B) LCO and C) LTO electrodes after flexing them 300 times to a bending radius of 1 mm, respectively. The dotted square shows the region of the electrode under stress during the flexing cycle.

**Figure 6.** Stress-strain curves of A) the membrane, B) the LCO, and C) the LTO electrode with the membrane support.
2.5. Performance Under Flexing

A battery while powering a flexing device would be in a state of flex and undergo mechanical fatigue during its lifetime. A flexible battery in such an application should retain its capacity at different bending radius and have high resistance to fatigue. Currently, flexible batteries are tested by flexing them 20–100 times and the capacity of the battery before and after
flexing are compared.\cite{28,35,38,52,69} In earlier reports, the batteries were flexed only once and the effects of mechanical fatigue on the batteries were not considered.\cite{26,45} Herein, we study the effect of both flexing and mechanical fatigue on the battery while it was cycled at C/2 rate for 95 cycles. The battery was mechanically flexed 100 times to a bending radii of 45, 30, 20 and 10 mm on the 19, 38, 57 and 76th electrochemical cycle. After the battery was flexed 100 times to a certain bending radius, the battery was kept at that bending radius until the next set of flexing cycles. Figure 9A shows the areal capacity of the battery flexed to different bending radius. Overall, the capacity of the battery did not drop significantly after flexing. In standard electrochemical cells, flexing can lead to delamination or cracking/swelling of the active layers. Delamination of the active layers increase the contact resistance between the current collector and the active layer, leading to an Ohmic potential drop during the start of charge/discharge cycles. Cracking/swelling in the active layers can cause a loss in capacity due to loss of electrical contact between the particles and an increase in impedance within the active layers. Delamination/cracking of the active layers will cause a shift in charge/discharge profiles of the battery. Figure 9B shows the charge/discharge curves of the battery before and after the flexing 100 times to different bending radius. The comparisons of charge/discharge curves indicate that there is no polarization or loss in capacity relating to delamination or cracking of the active layers. The areal capacity of the battery before the first flexing cycle (18th cycle) was 0.936 mAh cm$^{-2}$.

**Figure 9.** A) Areal capacity (mAh cm$^{-2}$) of the full cell (LTO/LCO) under different state of flex ($R = \infty$ mm to $R = 10$ mm). The battery was flexed 100 times to a bend radii of 45, 30, 20 and 10 mm on the 19, 37, 57 and 76th electrochemical cycles, respectively. B) Comparison of the Galvanostatic charge/discharge curves of the full cell, before and after flexing the battery 100 times to a bending radius of 45, 30, 20 and 10 mm on the 19, 37, 57 and 76th electrochemical cycles, respectively.
and it decreased to 0.880 mAh cm\(^{-2}\) (80\(^{th}\) cycle) after flexing the battery 400 times to bending radius ranging from 45 to 10 mm, a capacity drop of less than 6% during this period.

We further analyze the effect of mechanical flexing on the structural changes within the reinforced electrodes using electrochemical impedance spectroscopy (EIS). EIS is a non-destructive technique and is used extensively to study the effect of cycle life, state of charge, electrode composition, and electrode design on the charge transfer/kinetic processes in a battery.\(^{[70-73]}\) The EIS measurements were carried out at 50% depth of discharge at frequencies ranging from 10\(^{6}\)–0.1 Hz with voltage fluctuation of 5 mV from the open circuit voltage (OCV). The battery was allowed to equilibrate at OCV for a minimum of 2–3 h before carrying out the EIS scans. EIS measurements were carried out on the cell undergoing flexing cycles on the 1, 19, 38, 57, 76 and 95\(^{th}\) electrochemical cycle. On the 19, 38, 57 and 76\(^{th}\) electrochemical cycle, the battery was flexed 100 times to a bending radius of 45, 30, 20 and 10 mm, respectively. EIS measurements were done before and after flexing the cycles (Figure 10A). For comparison, EIS measurements were also carried out on a flat battery on the 1, 19, 38, 57, 76 and 95\(^{th}\) electrochemical cycle (Figure 10B). The EIS response had two semicircle loops, one from high frequency to mid-frequency and the second from mid-frequency to low frequency and a small linear tail towards the end of the curve is due to solid state diffusion of lithium ions within the electrode and is represented by the Warburg diffusion element (W).

The comparison of EIS scans for the flat cell and the cell undergoing multiple flexing cycle show that the resistance of the electrolyte (R\(_{\text{elec}}\)) and the resistance of charge transfer (R\(_{\text{ct}}\)) is almost constant with cycle number and flexing cycles (Table S1 and S2, Supporting Information). The slight increase in R\(_{\text{ct}}\) with cycle number is due to ageing of the electrodes. For the flat cell, the first semicircle loop increases initially and remains contact after certain number of cycles. The initial increase in R\(_{\text{ct}}\) is due to formation of a passivation layer on top of the active particles. The resistance is constant once a stable passivation layer is formed. For cell undergoing mechanical flexing cycles, the first semicircle loop increases after the battery undergoes mechanical flexing cycle on the 19, 38, 57 and 75\(^{th}\) electrochemical cycle, which relates to an increase in the contact resistance (R\(_{\text{A}}\)) within the electrode. As mentioned earlier R\(_{\text{A}}\) includes, R\(_{\text{cc}}\), R\(_{\text{pas}}\) and R\(_{\text{c}}\). A delamination or cracking of the passivation layer will lead to a decrease in the columbic efficiency of the battery after flexing. From Figure 9A we observe that there is no drop in columbic efficiency after flexing. Hence, the increase in R\(_{\text{A}}\) is due to formation of a passivation layer on top of the active layers, which includes the current collector/active layer interface (R\(_{\text{pas}}\)),\(^{[76]}\) active material/passivation layer interface (R\(_{\text{elec}}\))\(^{[75]}\) and particle-to-particle interface (R\(_{\text{cc}}\)).\(^{[64]}\) Since these processes have similar time constants and it is difficult to extract individual resistances. We denote total resistance for processes taking place from high frequency to mid frequency as R\(_{\text{A}}\) (R\(_{\text{A}}\) = R\(_{\text{cc}}\) + R\(_{\text{pas}}\) + R\(_{\text{c}}\)) and the double layer capacitance as CA. The second depressed semicircle loop from mid to low frequency is related to the charge transfer processes between the active particle and the electrolyte (R\(_{\text{ct}}\) C\(_{\text{dl}}\)) and the straight line towards the end of the curve is due to solid state diffusion of lithium ions within the electrode and is represented by the Warburg diffusion element (W).

![Figure 10](image_url)

**Figure 10.** A) EIS scans on the full cell at 50% DOD on the 1, 19, 38, 57, 76 and 95\(^{th}\) electrochemical cycle. The cell was flexed 100 times to a bending radius of 45, 30, 20 and 10 mm on the 19, 38, 57 and 76\(^{th}\) electrochemical cycle, respectively. EIS scan were carried out before and after flexing the electrode. B) EIS scans on the full cell (LTO/LCO) at 50% depth of discharge (DOD) on the 1, 19, 38, 57, 76 and 95\(^{th}\) electrochemical cycle with the cell in the flat state (R = \(\infty\) mm). C) Equivalent circuit to represent the full cell.
in $R_A$ cannot be related to structural changes in the passivation layer ($R_{\text{pass}}$). From the author’s experience, delamination of the current collector from the active layer leads to a significant increase in the Ohmic potential drop during the start of charge and discharge cycle. The comparison of the charge/discharge curves of the battery before and after flexing (Figure 9B) shows no Ohmic potential drop. Hence, the increase in $R_A$ cannot be related to delamination of the current collector ($R_{\text{cc}}$). Zheng et al. showed that the radius of the first semicircle loop increases with the porosity of the electrode. Electrodes calendared to lower porosity have low contact resistance ($R_A$). The increase in $R_A$ observed in our cells after flexing can be related to an increase in the porosity of the electrode ($R_A$). The electrochemical data suggests that the increase in porosity is not sufficient high to cause a drop in capacity. A slight increase in porosity can be beneficial to improve the transport of electrolyte through the electrode. A detailed analysis of the increase in porosity of the electrode with flex extent and microscopy study of the electrode after flexing is beyond the scope of this paper and these issues will be addressed in future publications. For current cell design, the electrochemical and EIS data suggest that flexing leads to a slight increase in the porosity of the electrode. But the increase in porosity is not sufficiently high to lead to a drop in capacity of the battery.

Figure 11A–C shows optical images of the flexible lithium-ion battery connected to a voltmeter A) when flat, B) after flexing once, and C) after flexing for 50 cycles to a bending radius of 4 mm, respectively. D) Demonstration of the flexible lithium-ion battery connected in series with a 200 $\Omega$ resistor and a green light-emitting diode (LED). The battery powered the green-LED continuously even after flexing 50 times to a bend radius of 4 mm (E).

### 3. Conclusion

We have demonstrated a technique to fabricate flexible rechargeable lithium-ion batteries with high areal capacity by printing thick active layers supported in a porous membrane. The tensile strength of the electrode was an order of magnitude higher than standard electrodes. A freestanding CNT based current collector minimized the thickness of inactive components within the battery. The lithium cobalt oxide and lithium titanate oxide based batteries with CNT as current collector have excellent capacity retention and were cycled for more than 450 cycles with a nominal capacity of $\approx$1 mAh cm$^{-2}$ and they were able to maintain their capacity after repeated flexing to a bending radius of 10 mm. The areal capacity (mAh cm$^{-2}$) of the battery with membrane support was 3–4 times higher than other reports on flexible lithium-ion batteries with LTO and LCO as the active materials. Batteries with high areal capacity and flexibility are important for powering future generation of flexible and mobile electronics devices. The technique demonstrated here can be easily used with other batteries chemistry with higher energy density and operating voltages.
4. Experimental Section

**CNT Ink:** Aqueous CNT ink was prepared by mixing 2 mg mL\(^{-1}\) of SWNT (Carbon Solutions Inc.) in D.I. water with 20 mg mL\(^{-1}\) of sodium dodecylbenzenesulfonate (SDBS, Sigma Aldrich) as surfactant to disperse the SWNT in water. The ink was sonicated using a Branson 450 digital sonifier for 20 min at amplitude of 40% and at 30 W. The CNT ink was spray coated on a stainless steel (SS) foil using commercial available backdrop (Badger Model 150). 4 mL of 0.2 wt% CNT solutions was sprayed over 4.5 \times 2.2 inch\(^2\) with an air pressure of 25 PSI to give a CNT layer with thickness of 3 \(\mu\)m and weight of 0.125 mg cm\(^{-2}\). During spraying, the SS substrate was heated at 140 °C.

**LTO/LCO Electrode Fabrication:** Lithium cobalt oxide (LCO, MTI Corp.) and lithium titanate oxide (LTO, MTI Corp.) slurries were prepared by mixing 77.5 wt% active material with 12.5 wt% carbon black (Super P, TIMCAL) and 10 wt% polyvinylidene fluoride (PVDF, Kureha Corp.) binder in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) as the solvent. The slurries were homogenized by stirring overnight using a vortex mixer. The inks were embedded inside a nonwoven fibrous membrane (Freudenberg, Germany) by dipping the membrane inside an ink bath for 1 min. The electrodes were dried by heating on an oven at 80 °C for testing LTO/CNT and LCO/CNT electrode (2.5 cm\(^3\)) in a glove box at 140 °C under vacuum for 12 h to remove traces of solvent from the electrode.

**Fabrication and Electrochemical Testing of Half and Full Cell:** Half cells for testing LTO/CNT and LCO/CNT electrodes were prepared by making coin cells with lithium metal electrodes as the counter electrode. The lithium metal and the LTO/CNT or LCO/CNT electrode were punched in round shapes with diameters of 0.5 inch. The coin cell parts were purchased from MTI Corp. The full cells were prepared by stacking LTO/CNT or LCO/CNT electrode on both sides of the coin cell. The coin cells were cut into smaller squares (2.4 \times 2.4 cm\(^2\)) and then dipped in a water bath. Due to the poor adhesion of the CNT on SS, the CNT layer delaminates from the SS in \(\approx 1\) min. The SS with a spray coated CNT layer was cut into small squares (2.4 \times 2.4 cm\(^2\)) and then dipped in a water bath. During spraying, the SS substrate was heated at 140 °C during spraying. The SS substrate was heated at 140 °C during spraying. The SS substrate was heated at 140 °C during spraying. The SS substrate was heated at 140 °C during spraying.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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