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RAPID COMMUNICATION

Hierarchically structured nanocarbon electrodes for flexible solid lithium batteries

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Abstract
The ever increasing demand for storage of electrical energy in portable electronic devices and electric vehicles is driving technological improvements in rechargeable batteries. Lithium (Li) batteries have many advantages over other rechargeable battery technologies, including high specific energy and energy density, operation over a wide range of temperatures (−40 to 70 °C) and a low self-discharge rate, which translates into a long shelf-life (~10 years) [1]. However, upon release of the first generation of rechargeable Li batteries, explosions related to the shorting of the circuit through Li dendrites bridging the anode and cathode were observed. As a result, Li metal batteries today are generally relegated to non-rechargeable primary battery applications, because the dendritic growth of Li is associated with the charging and discharging process. However, there still remain significant advantages in realizing rechargeable secondary batteries based on Li metal anodes because they possess superior electrical conductivity, higher specific energy and lower heat generation due to lower internal resistance. One of the most practical solutions is to use a solid polymer electrolyte to act as a physical barrier against dendrite growth. This may enable the use of Li metal once again in rechargeable secondary batteries [2]. Here we report a flexible and solid Li battery using a polymer electrolyte with a

Abbreviations: CNT, carbon nanotube; CNH, carbon nanohorn; TEM, transmission electron microscope; STEM, scanning transmission electron microscope; SEI, solid electrolyte interface

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hierarchical and highly porous nanocarbon electrode comprising aligned multiwalled carbon nanotubes (CNTs) and carbon nanohorns (CNHs). Electrodes with high specific surface area are realized through the combination of CNHs with CNTs and provide a significant performance enhancement to the solid Li battery performance.

Introduction

Carbon, usually in the form of graphite, is a readily available and cost effective material commonly used as the negative electrode in Li-ion battery structures. The stability of the sp^2 covalent bonds and ability to weakly bind Li gives rise to large storage capacities at a high Li chemical potential. As far as carbon is concerned, graphite is particularly interesting owing to its high electronic (in-plane) conductivity resulting from the delocalized π-bonds. Li ions intercalate between the graphite layers, and theoretically, one Li atom requires six carbon atoms to intercalate, resulting in a theoretical capacity of 372 mAh/g of graphite. However, practical limits in performance have been reached for natural graphite electrodes.

Necessary characteristics for a material to be attractive as an anode material in lithium-based batteries are: high Li capacity, high chemical potential of the Li of the lithiated compound, fast Li insertion/extraction kinetics and small volume changes during Li insertion/extraction [3].

The development of nanostructured graphitic carbons, e.g. CNTs [4], permits some control over pore size and accessibility, opening the prospect of designing electrodes with higher reversible capacity as well as superior cycling stability. High electronic conductivity is important in bringing the electronic carriers from the current collector to the Li atom(ion) as rapidly as possible, as is a good diffusion rate of Li into the electrode, which permits a higher utilization of the electrode. These parameters may be enhanced by electrode design, for instance by orienting the CNTs vertically with a direct connection to the substrate, which would enable the extraction of quick bursts of energy (high power), by reducing the overall equivalent series resistance (ESR) of the cell.

While CNTs are a form of nanoscale tubular graphene sheet, CNHs are formed from graphene sheets in horn-like shapes with open ends [5]. They can be viewed as being formed from the crushing or origami-like contortion of a graphene sheet. CNHs can be prepared with high purity as a low-cost raw material in a process which is easily scalable to produce large volumes. The advantage of using CNHs in energy storage devices lies not only in their large surface area (1000–2000 m^2/g) but also in the easy permeation of gases and liquids [6,7] through their agglomerates.

In previous reports, aligned CNT forest electrodes were often fabricated in a multistep and usually complex manner, including peeling-off grown CNTs from the growth substrate and post sputtering of charge-collecting metal layers [8]. This is due to the complexity of growing CNT arrays onto flexible metallic substrates, which is common for battery fabrication and stable against corrosion. The cost of volume production of CNTs and the complexity of the fabrication processes have been the barriers for commercial adoption of these synthetic nanostructured carbon electrodes to date.

The electrolyte, the medium which transports charged ions between anode and cathode, typically consists of an organic solvent with a Li salt. Although a solid ion transporting medium would be ideal, polymer electrolytes to date have suffered from a poor room temperature ionic conductivity ($\sim 10^{-4}$ S/cm vs. $\sim 10^{-2}$ S/cm for liquid electrolytes) [9]. The Li-polymer battery, first released by Sony, achieved a compromise; it used a "gel" electrolyte composed of a polymer matrix swollen by a high proportion of a solvent for the lithium salt. The gel had a reported conductivity of 3×10^{-3} S/cm at 25 °C [10]. This structure benefits from acceptable ionic conductivity as well as structural stability.

Here we report a solid, yet flexible Li battery based on the hierarchical combination of CNTs and CNHs as the cathode and a solid poly(ethylene glycol) borate ester as the electrolyte. Vertically-aligned CNTs are synthesized directly on flexible charge collectors (e.g. aluminum foil) and used as scaffolds for CNHs. The use of these carbon electrodes with a hierarchy of nanostructures leads to a significant improvement in the battery performance. The combination of a polymer solid electrolyte with the nanostructured electrode provides further advantages of flexibility and safety in a solid lithium anode battery.

Materials and methods

A custom CVD method has been developed for the low temperature (520 °C) synthesis of packed vertically aligned CNT arrays. Multiwalled CNTs were grown directly on the charge collecting substrate, typically regular 10–15 μm thick aluminum (Al) foil. This provides an advantage to *ex-situ* chemical vapor deposition (CVD) growth and post processing (e.g. making mixtures of carbon with poly(vinylidine fluoride) etc.) [11]. Commercially available, 10–15 μm-thick Al foil was cut and cleaned using acetone and isopropanol, followed by a deionized (DI) water rinse and drying in nitrogen. A 10–15 nm-thick iron film sputtered onto the cleaned foils acted as the catalyst layer for the CNT growth. Multiwalled CNTs were grown using an Aixtron Nanoinstruments Plasma Enhanced Chemical Vapor Deposition system. Briefly, growth was carried out in a quartz vacuum chamber on a resistively heated graphite stage. Growth temperature was controlled by a thermocouple attached to the surface of the graphite stage. Following catalyst deposition, samples were placed on the graphite stage in the quartz chamber, which was then evacuated to 10^{-2} mbar. After that, samples were heated up to 480 °C with ammonia gas (NH_3, 200 sccm flow rate) and annealed at this temperature for 2 min. Catalytic nanoparticles were found on the foil after annealing, essential for low temperature growth. After annealing, the graphite stage temperature was ramped to 520 °C. NH_3 was turned off and acetylene (C_2H_2) was supplied (200 sccm flow rate) as the

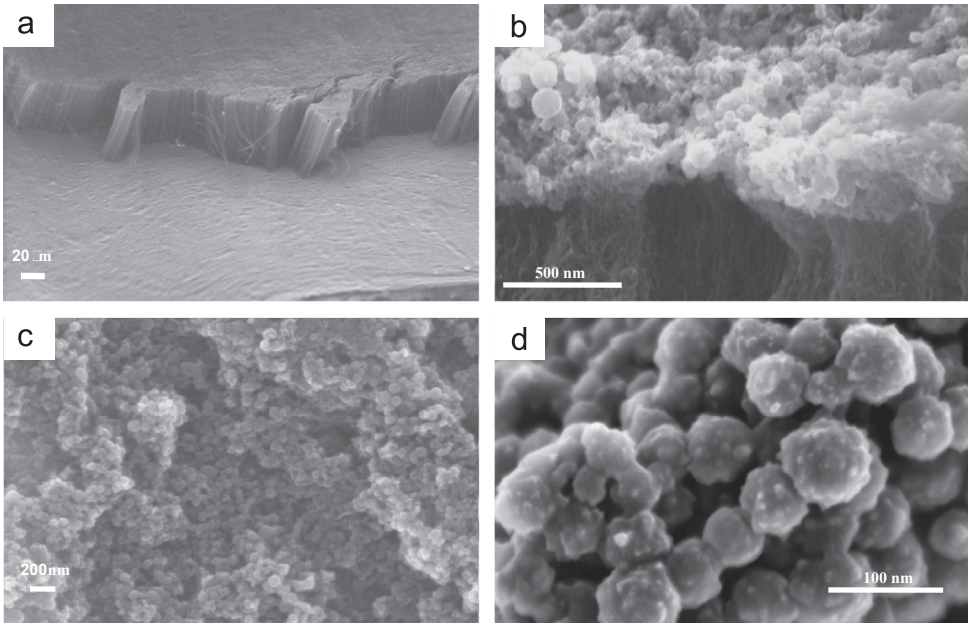

Figure 1 SEM images of carbon nanostructured materials. (a) Aligned multiwall CNT arrays grown on an Al foil charge collector, (b) CNHs deposited on the aligned CNTs (side view), (c) CNHs deposited on the aligned CNTs (top view) and (d) magnified view of CNHs.

carbon feedstock for the CNT growth. The chamber pressure was maintained at 10 mbar. After a growth period of 15 min, C_2H_2 flow and heating was removed and samples cooled to room temperature with nitrogen gas (200 sccm flow rate). 15 min of growth yielded 70 μm-long, vertically aligned, closely packed multiwalled CNTs, as shown in Fig. 1(a).

High surface area nanoporous CNHs were produced by arc discharge in liquid nitrogen between graphite anodes and cathodes [12], 3 and 12 mm in diameter respectively with an arc current of 100 A. At the end of the discharge process, CNHs were collected and subsequently dispersed in deionised (DI) water and drop-cast onto the aligned CNT arrays. The resulting hierarchically nanostructured CNH/CNT on Al foil was used as the cathode.

Fig. 1(b) and (c) show tilted side view and top view SEM images of the nanoporous CNH particles after they are drop-cast onto the CNT films, respectively. These images show that the CNHs (typical diameter 5–10 nm) form larger conglomerate particles with diameters ranging from 40 to 100 nm. The drop-casting method produces a thick layer of nanoparticles, which covers the top surface of the CNTs and extends approximately 50–100 nm deep into the CNT arrays. Fig. 1(d) shows a high magnification SEM image of the nanocarbon aggregate particles.

As made CNHs, form a free powder and as a result have poor adhesion to the metallic current collector. Typically, unless a binder [6] is used, there is no adhesion to each other or to the surface. With the presence of the CNT forest in the substrate, this adhesion improves, and the CNH powder is notably not so easy to remove. This binder-free structure has been noted a few times before [7,13]. Good surface binding of CNHs onto CNTs was observed by the naked eye. Hybrid CNT/CNH films suffered no visible variation in texture or conductivity after 200 bending cycles with a 7 mm bend radius.

The CNHs were imaged using a combined scanning and transmission mode electron microscope (STEM) (Hitachi S5 500STEM operating at 30 keV). This method of imaging is particularly informative as it allows the surface structure as well as the more detailed internal nanostructure to be imaged from the same sample in consecutive scans. Fig. 2(a) and (b) show surface STEM images of the CNH particles at increasing magnification. The horn structures into which the graphene sheets are contorted into are visible at the higher magnification.

The TEM image in Fig. 2(c) shows the overall horn structure. The particle edges/surface combine within its body to give an overall porous structure made up of a scaffolding of distorted graphene sheets. Agglomerates of CNHs can be seen within the samples. Horn openings are typically 3–5 nm in width and reduce to a graphene sheet curvature of 1–2 nm at the horn tips. HREM imaging was performed using a FEI Titan 60–300 kV. We chose to work at 60 kV acceleration voltage in order to minimize damage and to enhance scattering from the very thin CNH material and thus accentuate contrast in the image. Using the image corrector, the spherical aberration (Cs) was reduced to, typically, 500 nm. At such low acceleration voltages with Cs corrected, chromatic aberration is the main factor limiting image resolution. An in-line monochromator was used to disperse the beam at the front focal plane of the condenser system, creating rainbow illumination. At high imaging magnification (typically 600 k × or above) the area on the sample defined by the CCD camera corresponds to low enough energy dispersion ΔE for the resolution, in conjunction with an image corrector, to be about 0.16 nm and thus enable the imaging of the 0.21 nm fringes in graphene. The high resolution image in Fig. 2(d) shows that the CNHs are made of single layer graphene. The graphitic nature of the nanoparticles was supported by the strong G and D+G peaks in the Raman spectrum (not shown here).

Batteries were fabricated in an Ar glove box by sandwiching the polymer electrolyte in sheet form between Li metal foil anodes and CNT/CNH cathodes as shown schematically in Fig. 3. The polymer electrolyte used is a high molecular weight

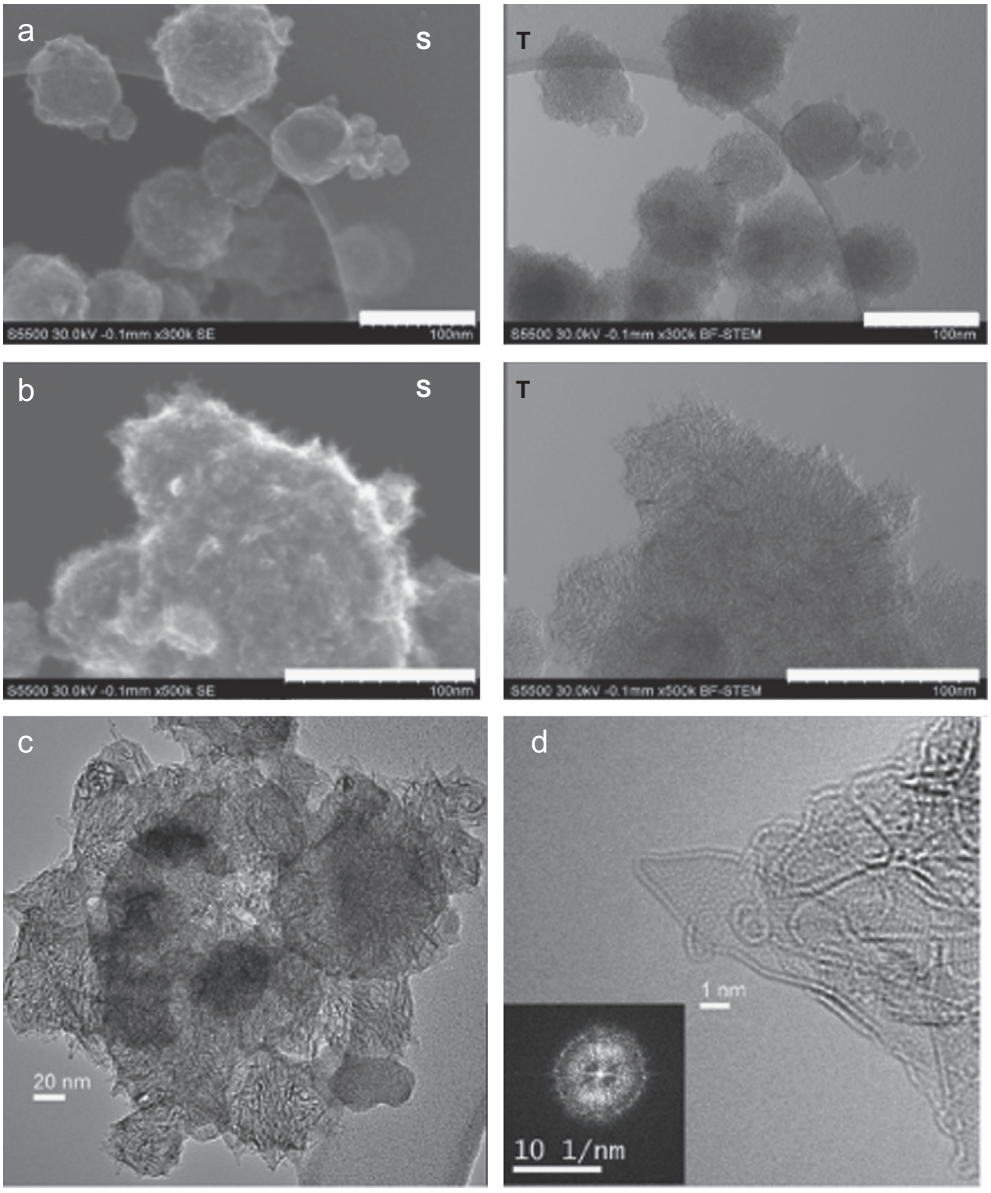

Figure 2 (a) Low and (b) high magnification STEM images of CNHs. (S for scanning mode and T for transmission mode). CNH particle conglomerates are in the 20–100 nm diameter range and are comprised of graphene sheets, forming a porous, agglomerated structure. Higher magnification shows the particle edge protrusions of graphene "horns". (c) Low magnification TEM image of a CNH particle where the CNH structures are clearly seen protruding from its surface. Horn openings are typically 3–5 nm in width and reduce to a graphene sheet curvature of 1–2 nm at the horn tips. (d) A high resolution image showing that the CNHs are made of single graphene layers. Even though an image corrected microscope (FEI Titan 60–300 cubed, operated at 60 kV) was used, the depth of image appears to be large enough to image the front and the back graphene sheets of the hollow CNHs. Therefore the images differ in some cases from those of flat and isolated single graphene. The inset shows the FFT of the acquired image where the 0.21 nm spots from the {110} planes are clearly visible.

poly(ethylene glycol) borate ester, the details of which are described in the literature [14,15]. The presence of Lewis acid centers in the borate esters interacts with the anion resulting in Li ion (Li^+) transport. The performance of such polymer electrolytes is comparable with some gel electrolytes at room temperature (high 10^{-3} S/cm). The use of such a polymer electrolyte also removes the need for a separator. The batteries were vacuum packed in a pouch cell and galvanostatically discharged and charged with a Maccor battery tester at room temperature.

Results and discussion

The discharge–charge cycling behavior of the batteries was measured between 4 V and 0 V at a constant specific current of 10 mA/g. The discharge–charge performance of two typical batteries made of aligned CNTs only and CNHs on aligned CNTs are compared in Fig. 4. It can be seen that the battery made with only CNTs in the electrode discharges with an irreversible capacity around 760 mAh/g (Fig. 4a), which is comparible with the previous value reported for batteries made of similarly

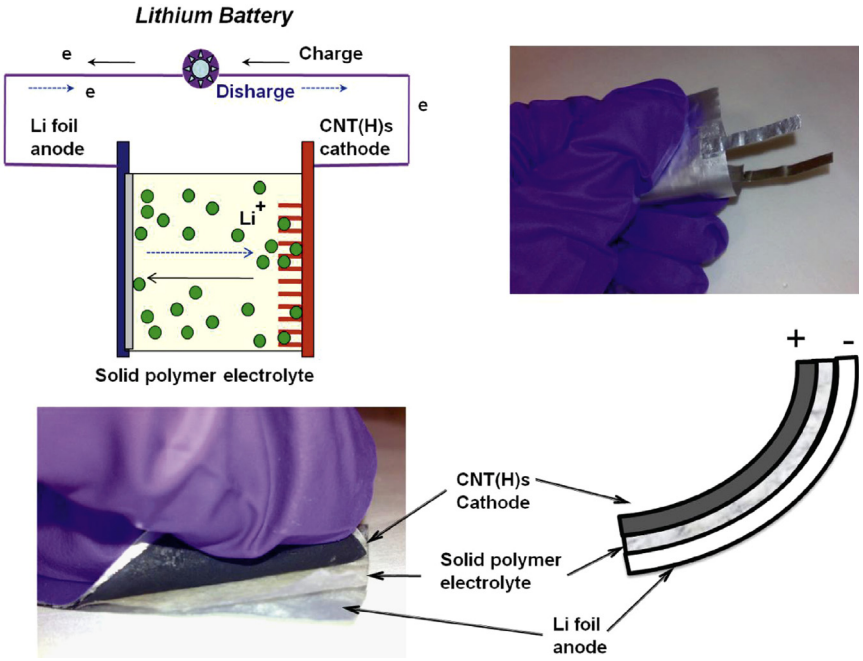

Figure 3 Structure and photographs of the solid state Li battery.

aligned CNTs in a liquid organic electrolyte[8]. The presence of two declining voltage plateaux during the first discharge in Fig. 4(a) is attributed to the formation of a solid electrolyte interface (SEI) layer. The formation of an SEI layer is an irreversible process and is also observed during the first discharging cycle of graphite and other carbonaceous electrodes. Once formed, this layer is stable and allows the reversible intercalation of lithium ions into the carbon electrode. Thus, the capacities of subsequent cycles stabilizes at around 190 mAh/g. In contrast, the battery made of CNHs on CNTs does not show this initial irreversible capacity. It seems the intercalation of Li ions into the hierarchically structured nanocarbon electrode is reversible from the first cycle as shown in Fig. 4(b), and stabilises at 352 mAh/g. This enhancement of the reversible capacity is ascribed to the better porosity (and hence higher Li penetration) as well as the higher surface area of the CNHs. The coulombic efficiency was calculated based on the charge-discharge curves (Fig.4). The average coulombic efficiency for battery made of CNT+CNHs was 97.1% while the average coulombic efficiency for the CNT only battery decreases with cycle number and is 92% on the 5th cycle. The energy efficiency of the batteries is also extracted to be about 60% and 25% respectively.

A comparison of the initial capacity change with cycle number is shown in Fig. 4(c). At 10 mA/g, the CNH/CNT electrode shows a better cycling behavior and capacity retention than the CNTs alone. Though it has higher stable reversible capacity, the open circuit voltage on initial discharge of the CNH/CNT battery (2.52 V) is lower than that from CNT alone (3.3 V). This may be due to the higher internal resistance which results from the thicker electrode as well as a contribution from the higher number of particle interfaces resulting from the CNH nanoparticles. On the other hand the CNHs allow for significantly more lithium ion intercalation into the electrode, the internal resistance decreases with the following cycles and the discharge voltage rises to 3 V (charge voltage of 4 V), similar to that of the CNT only device. The results show that the CNT/CNH hybrid electrode can reversibly intercalate lithium ions with a capacity of 352 mAh/g, which approaches the theoretical value (372 mAh/g) for graphite[16,17] and is twice that of the CNT only electrode. Nitrogen physisorption tests showed that the specific surface area (SSA) for CNTs alone was 272 m^2/g. For the CNHs used, which were oxidized at 400 °C to remove any residual amorphous carbon, a SSA of 1025 m^2/g was measured. The SSA of the CNH is comparable to that of activated carbon. Another clue to the improvement in capacity lies in the mercury porosimetry measurements, which show that CNHs have a very high porosity of 75%. During the battery charge/discharge operations, Li ions are intercalated and de-intercalated into/from the carbon host without any solvent co-interaction following the reaction to form Li_xC_6. This assumption is based on the Li ions being totally stored in the intercalation sites between the graphene layers to form LiC_6. Several authors have reported specific capacities higher than 372 mAh/g when using non-graphitized carbons such as meso-carbon micro beads (MCMB) [18] and CNTs [8]. It has also been reported that carbonaceous material prepared by heating polyparaphenylene at 700 °C had a capacity of 680 mAh/g [19]. Parameters such as electrode composition and electrolyte will affect the electrode capacity [20]. However, the in-excess-of-theoretical capacities reported above, as for the first irreversible capacity of a CNT-based battery, seem to be related to the contribution of cavities present in the carbon nanomaterials for Li penetration and to the possible occurrence of the covalent bonds between Li pairs which results in increasing the in-plane Li density (Li_xC_6, where $x>1$). Such excess capacity however is not maintained on cycling, as seen in Fig. 4 for the CNT-only battery. Yazami and Deschamps [21] have proposed a model involving the reversible epitaxial growth of Li multilayers on the carbon planes to explain the observed higher capacity and capacity approaching theoretical values. The surface of the CNH particles is irregular and is a form of distorted graphene "crumpled"

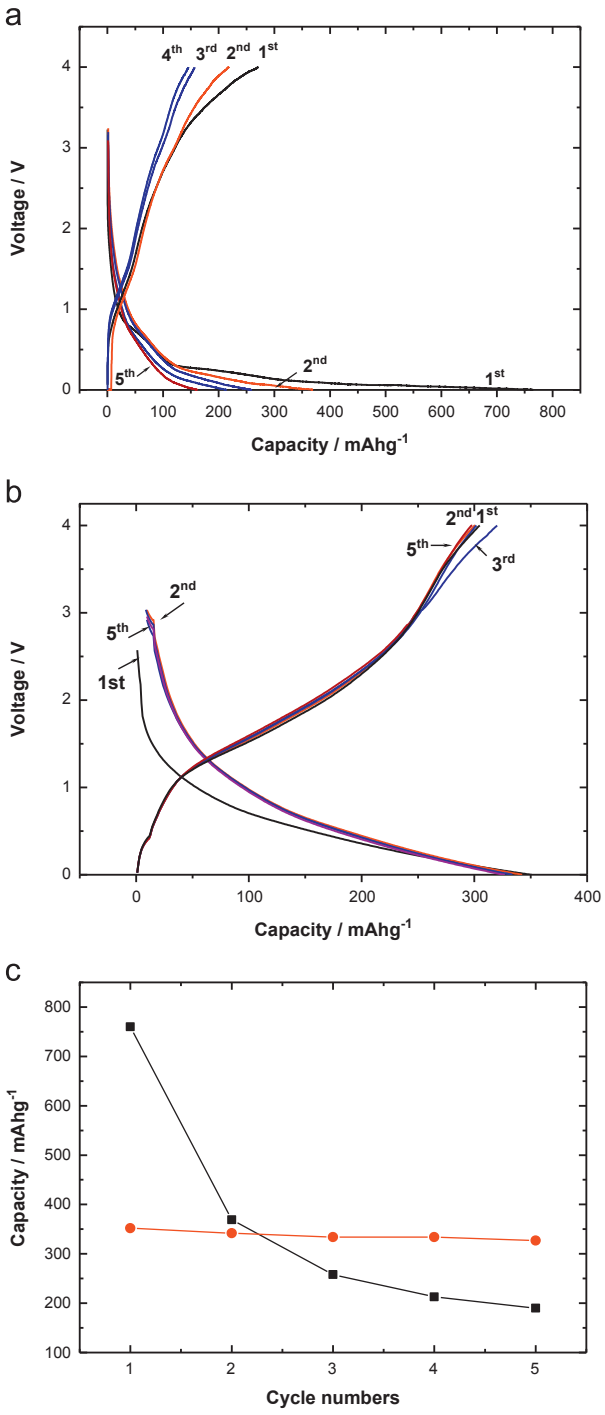

Figure 4 Discharge and charge curves of nanocarbon batteries. After the initial discharge, the batteries are charged to 4 V and the subsequent discharge cycle commences after a 5 min interval. (a) Aligned CNT cathodes. The open circuit voltage on first discharge is 3.3 V and is maintained around this value for subsequent discharge cycles. (b) Hierarchically structured cathodes with aligned CNTs decorated with CNHs. The open circuit voltage on first discharge is 2.5 V. On subsequent cycles, it rises to 3 V. (c) Initial capacity changes with cycle number for the battery with CNTs (square ■) and that with CNTs with CNHs (circle ●). The specific current for discharge and charge is 10 mA/g. The reversible charge retention capacity of the CNT-only cathode battery drops rapidly from 762 mA hg^{-1} to 190 mA hg^{-1} within the first 5 cycles. In the case of the hierarchically structured CNH/CNT cathode battery the reversible charge capacity remains virtually constant at 350 mA hg^{-1} within the first five cycles.

into a highly porous structure. Li ions can pass into, and through, the CNH particles via the nanoscale pores on the surfaces. The surface area enhancement within the CNH particles is achieved predominantly through pores approaching 2 nm in diameter (Barret–Joyner–Halenda (BJH) analysis, not shown). As an aside, the swelling of this carbon electrode should be limited, given the empty volume available between the CNTs [22] and within the pores of the CNH. This, taken

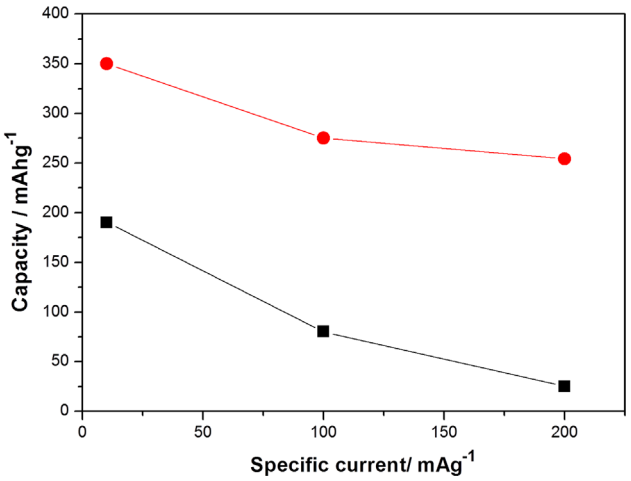

Figure 5 Specific capacity as a function of specific current at 10 mA/g, 100 mAg^{-1} and 200 mAg^{-1} for battery with CNTs (square ■) and with aligned CNTs combined with CNHs (circle ●).

together with the stable reversible capacity close to the maximum expected from graphite, makes it attractive from an applications perspective, especially in an all-solid flexible battery.

The rate capabilities are shown in Fig. 5. The capacity decreases as the current is increased due to the higher loss from Joule heating and the kinetic limitations of ion diffusion that come into play at higher current densities. It can be seen that the CNH/CNT decrease in capacity with increasing current is slightly lower than that of the CNTs alone. This is despite the thicker electrode of the hybrid device, and comes to show the benefits of the hybrid approach, that is, increase in the energy density as a result of the CNHs, whilst maintaining the power density brought by the CNTs.

Based on this marked advantage of CNHs compared to the CNT arrays, one would expect that batteries with electrodes made of CNHs deposited directly on Al foil would demonstrate similarly high performance in a battery. However, CNHs had poor adhesion to the Al foil. Therefore, there appears to be a distinct mechanical and charge transport advantage in combining CNHs with CNTs. First, the conducting CNT arrays, albeit with small SSA compared to CNHs, improve the electrical contact between the ion storage medium and the metal electrode. This is essential not only for efficient collection of Li ions at the front of the electrode structure but also for collection of charge from the metal when the external field is applied (charging) and removed (discharging). Resistance between the CNHs and the charge collection surface is minimized in the hierarchically nanostructured electrode through contact with, and conduction through the CNTs. The CNH particles do not simply sit at the top of the CNT array; but penetrate about 100 nm into it. Electrons can therefore be directly delivered into and removed from the volume of the CNH particles; an important aspect for achieving efficient charge collection. Finally, the CNT array improves the mechanical adherence of the CNH material to the flexible Al electrode and ensures the integrity of the device. In addition, the need for binders or conducting additives, which add extra contact resistance or weight, is eliminated within such hierarchically structured nanocarbon electrodes.

Conclusion

In summary, we have investigated a flexible battery structure comprising a solid polymer electrolyte and a Li foil together with different nanocarbon electrodes. When aligned CNTs are decorated with CNH nanoparticles, the cyclability of a Li battery improves significantly and the reversible capacity is twice that of one without the CNHs. The combination of a hierarchically structured nanocarbon electrode together with a polymer electrolyte and Li foil enables a new class of solid and potentially flexible rechargeable battery. They are suitable for volume manufacture and packaging, e.g. using roll-to-roll processing. Such batteries are attractive as power sources for future mobile electronic systems, such as those in development for intelligent/active clothing, where form factor is of high importance.

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References

[1] A. Colin, Solid State Ionics 134 (1-2) (2000) 159-167.
[2] L. Sannier, et al., Journal of Power Sources 144 (2005) 231-237.
[3] D. Linden, T.B. Reddy, Handbook of Batteries, 3rd Ed., McGraw-Hill, 2002 ISBN 0-07-135978-8.
[4] S. Iijima, Nature 354 (1991) 56-58.
[5] S. Iijima, et al., Chemical Physics Letters 309 (1999) 165-170.
[6] C.M. Yang, et al., Journal of the American Chemical Society 129 (2007) 20.
[7] A. Izadi-Najafabadi, et al., ACS Nano 5 (2011) 811-819.
[8] V.L. Pushparaj, et al., PNAS 104 (2007) 13574-13577.
[9] P.V. Wright, MRS Bulletin 597-602 (2002).
[10] K. Kezuka, T. Hatazawa, K. Nakajima, Journal of Power Sources 97-98 (2001) 755-757.
[11] J. Zhang, et al., Advanced Materials 20 (2008) 1450-1455.
[12] H. Wang, M. Chhowalla, N. Sano, S. Jia, G.A.J. Amaratunga, Nanotechnology 15 (2004) 546-550.
[13] P. Hiralal, et al., Journal of Materials Chemistry 21 (2011) 17810-17815.
[14] Y. Kato, et al., Solid State Ionics 150 (2002) 355-361.
[15] Y. Kato, et al., Journal of Materials Chemistry 13 (2003) 280-285.
[16] B. Aissa, et al., Electrochemistry Communications 11 (2009) 862-866.
[17] R. Yazami, K. Zaghib, M. Deschamps, Journal of Power Sources 52 (1994) 55-59.
[18] S. Hossain, Y.K. Kim, Y. Saleh, R. Loutfy, Journal of Power Sources 114 (2003) 264-276.
[19] K. Sayo, M. Noguchi, A. Demachi, N. Oki, M. Endo, Science 264 (1994) 556.
[20] K. Sekai, et al., Journal of Power Sources 43 (1993) 241-244.
[21] R. Yazami, M. Deschamps, Journal of Power Sources 54 (1995) 411-415.
[22] D. Futaba, et al., Nature Materials 5 (2006) 987-994.

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Dr. Pritesh Hiralal received the MPhys (Hons) degree in Physics from the University of Manchester, UK, in 2003. After spending time in business in Spain, and setting up Zendal Backup, he went on to complete a Ph.D. from the Department of Engineering at Cambridge University. He worked at the Nokia Research Centre on energy storage devices and is now a research associate as well as an adjunct lecturer at the University of Cambridge.

His current research interests include the understanding of the growth of nanomaterials and their utilisation in optical architectures for photovoltaics as well as energy storage devices including batteries and supercapacitors. He holds over 30 publications and numerous patents in the field.

Dr. Haolan Wang is a CTO in Shenzhen Bronze Technologies Ltd., China. He received his bachelor degree in material engineering from ShenYang University of Technology, and obtained his master degree in engineering from National University of Singapore (NUS) in 1994 and 2000, respectively. He finished his Ph.D in engineering from the University of Cambridge focusing on synthesizing nanostructured materials through liquid arc methods. In 2007, he continued his research works as a Post Dr. in the University of Cambridge on the fabrication of nano-composite materials and their application for energy storage under the Cambridge-Nokia Energy Harvesting and Storage project. In 2011, he joined Shenzhen Bronze technologies Ltd leading a project on novel nanomaterial synthesis and their application on energy storage funded by the Chinese government. Dr. Wang has published more than 30 papers and authored 8 patents on nanomaterial synthesis and applications. His current interest is the scale-up synthesis of nanomaterials and their applications in energy storage, gas sensor, water purification, conductive additives and drug delivery.

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He has authored many patents, peer-reviewed journal publications and chapters for four books on the topic of nanotechnology and electrochemical applications. His research interests include energy solutions, sensors, organic electronics etc. Dr. Wei has been senior member of Wolfson College at University of Cambridge since 2010 and is member of Royal Society of Chemistry (RSC), Cambridge Network and the International Society of Electrochemistry (ISE). He has been involved in R&D, technology transfer and high-tech business for more than 5 years.

Gehan Amaratunga FREng., FIET, CEng. obtained his B.Sc ('79) from Cardiff University and Ph.D ('83) from Cambridge, both in electrical/electronic engineering. He has held the 1966 Professorship in Engineering at the University of Cambridge since 1998. He currently heads the Electronics, Power and Energy Conversion Group, one of four major research groups within the Electrical Engineering Division of the Cambridge Engineering Faculty.

He has an active research programme on the synthesis and electronic applications of carbon nanotubes and other nanoscale materials. His group has many 'firsts' emanating from his research in carbon, including field emission from N doped thin film amorphous carbon and diamond, laboratory synthesis of carbon nanonions, tetrahedral amorphous carbon ('amorphous diamond')-Si heterojunctions, deterministic growth of single isolated carbon nanotubes in devices, high current nanotube field emitters and the polymer-nanotube composite solar cells. He currently sits on the steering committee of the Nokia-Cambridge University Strategic Collaboration on Nanoscience and Nanotechnology and is the head of the Nokia-CU Nanotechnology for Energy Programme.

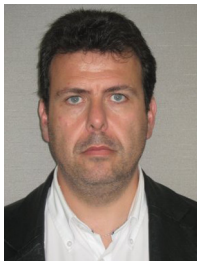
His group was amongst the first to demonstrate integration of logic level electronics for signal processing and high voltage power transistors in a single IC (chip). His current research is focussed on integrated power conversion circuits. He is a cofounder of CamSemi – which is commercialising a new generation of power and mixed-signal ICs for power management with venture capital investment. He is also a founder of Enecsys, a company formed with his research students to develop and market integrated electronics (microinverters) for grid connection of solar PV systems. Nanoinstruments, a company he founded with his colleagues to commercialise CNT synthesis equipment was acquired by Aixtron AG in 2007.

He has previously held faculty positions at the Universities of Liverpool (Chair in Electrical Engineering), Cambridge, and Southampton. He has held the UK Royal Academy of Engineering Overseas Research Award at Stanford University and been a Royal Society visitor at the School of Physics, University of Sydney. He has published over 450 journal and conference papers. Professor Amaratunga was elected a Fellow of the Royal Academy of Engineering in 2004. In 2007 he was awarded the Royal Academy of Engineering Silver Medal 'for outstanding personal contributions to British engineering'.

Mr. Markku Rouvala Holds Masters degrees in Electrical Engineering and Micro- and NanoTechnologies Enterprise from TKK Helsinki, Finland, and Cambridge University, UK. Markku joined Nokia in 1994 and has held several different positions in research and engineering R&D in telephony and mobile phone business units. He spent 2000–2003 in US, Maynard in Stratus Technologies developing high speed redundant multiprocessor servers and later joined back to Nokia for mobile phone research for development of high speed connectivity, EMC, modeling and nano-related energy research, and printed electronics. His career has involved electrical component and systems designs in computers and telephone/internet networking and mobile platform designs, and energy storage and harvesting with nanoenhanced technologies for future mobile platforms, multiprocessor computer designs, and electromechanical miniaturized structures for EMI design and connectivity. His current research interests include mobile device sensors and energy research, carbon Nanoelectronics specifically graphene-like materials, and electronics manufacturing.

H. Emrah Unalan received the BS degree in Metallurgical and Materials Engineering from Middle East Technical University, Turkey in 2002 and the MS and PhD degree in Materials Science and Engineering at Rutgers University, NJ in 2004 and 2006, respectively. From 2006 to 2008, he was a Research Associate in Electrical Engineering Division in Engineering Department at University of Cambridge, UK. In 2008, he joined Department of Metallurgical and Materials Engineering, Middle East Technical University, where he is currently an Associate Professor. His research interests include synthesis of nanotubes/nanowires and their utilization in flexible/transparent electronics and energy harvesting devices. He is a member of Materials Research Society (MRS), American Chemical Society (ACS) and a recipient of the MRS Graduate Student Silver Award in 2005 and Turkish Academy of Sciences Young Scientist Award in 2009.

Tapani Ryhänen is heading Nokia Research Center's Sensor and Material Technologies Laboratory in Cambridge, Espoo and Moscow, focusing on differentiating hardware and pervasive sensing solutions. He is responsible for Nokia's research collaboration with the University of Cambridge and the Skolkovo Institute of Science and Technology. He is a member of the Nokia CTO technology council and a board member of the Nokia Foundation. Before his current role he was leading Nokia's strategic research in the areas of future user interfaces, future device architectures and interfaces, mechanics and miniaturization. His previous work at Nokia also covers sensor technologies and applications, wellness and health applications, ambient intelligence, RF MEMS, microsystems, architectures and interfaces of sensor modules and mass storage solutions. He has authored publications and over fifty granted patents on superconducting thin-film devices, micromechanical sensors and actuators, biomagnetic measurements, nanotechnologies, and mobile phone technologies and applications. His is one of the creators of the Nokia Morph concept and an author and editor of a book "Nanotechnologies for Future Mobile Devices". He is a member in the Scientific Advisory Committee of the EU Graphene Flagship Project and advices the X PRIZE Foundation on its Nokia Sensing X Challenge for revolutioning digital healthcare.



Ioannis Alexandrou started his career by using analytical methods to prove that fullerene-like thin films can generically be formed by compacting fullerene fragments. His research interest is in the use of novel microscopy methods to investigate the origin of the properties of novel materials. He is currently a Senior Research Scientist at FEI Company concentrating on exploring advanced uses of electron optics in materials research.