Nanotechnology institutions

Apparao M. Rao*

Energy and our future: a perspective from the Clemson Nanomaterials Center

DOI 10.1515/ntrev-2015-0046
Received August 31, 2015; accepted September 1, 2015; previously published online September 29, 2015

Abstract: Our increasing energy demands have spurred a rigorous search for renewable energy sources to reduce our dependence on fossil fuels. However, efficient use of renewable energy is possible only with advances in both energy generation and storage. Today's batteries and capacitors, which are the main energy storage devices, cannot meet the world's demand for combined power and energy densities. To enhance the viability of such energy storing devices, the Clemson Nanomaterials Center (CNC) has developed a mix of scalable processes for carbon nanotube-based hybrid electrodes that show promise as a cost-effective alternative to standard activated carbon-based electrodes. Working together with industrial partners, CNC has fabricated supercapacitors with energy and power densities in the range of ~11–35 Wh/kg and ~1.2–9 W/kg, respectively. Although this research development is transformative, further studies to optimize the separator and electrolyte technologies are needed to maximize both the energy and power density in a single device.

Keywords: carbon nanotubes; Clemson Nanomaterials Center; energy storage; supercapacitors.

1 Introduction

In recent times, bioenergy (agricultural and livestock residues), solar energy (photovoltaics and concentrating solar power), geothermal energy (heat extraction from the Earth's interior), hydropower (run-of-river and dams), ocean energy (ocean currents), and wind energy (on- and offshore systems) [1] have received much attention and are all promising candidates for clean energy production. However, the integration of new renewable energy resources into present and future energy storage systems is a complex and long-term challenge that necessitates multidisciplinary and synergistic efforts. In this regard, a team of scientists and engineers at the Clemson Nanomaterials Center (CNC) (Figure 1) have developed scalable processes for high-performance electrodes for use in energy storage devices.

Figure 2 shows the general performance metrics for commercially available formats of charge/energy storage devices. This plot, also known as the Ragone plot, depicts electrical capacitors (on the top left-hand side), which exhibit a high power density due to electrostatic charge storage, and batteries and fuel cells (on the bottom right-hand side), which exhibit a large energy density due to the chemical/ionic basis of their reactions. The drawback of electrical capacitors is their inability to store large amounts of energy, while the batteries are incapable of fast charge/discharge cycles due to the slow nature of the ion diffusion processes. This gap between capacitors and battery performance has been a major roadblock in electrochemical energy storage [2, 3]. The electrochemical capacitors (or supercapacitors) have been proposed to bridge the gap between these disparate devices by incorporating elements of both technologies. But in order to push such technologies toward practical use, we need to (i) explore new directions using compatible materials that can store and appropriately discharge the energy from traditional renewable energy sources and (ii) provide scalable nanomanufacturing technologies for large-scale production of such devices.

While several elements such as copper, bronze, and iron have been the predominant resources for technology development (tool making) in their eras, carbon is undoubtedly proving to be the copper and iron of the 21st century. This is largely due to carbon's unique ability to form covalently connected bulk and nanostructured materials with varying *sp* hybridized bonding states.

While graphite and diamond represent the sp^2 and sp^3 hybridized bulk forms of carbon, carbon nanotubes and fullerenes represent nanostructured forms of carbon with

***Corresponding author: Apparao M. Rao,** Department of Physics and Astronomy, Clemson University, 202 C Kinard Lab of Physics, Clemson, SC 29634, USA, e-mail: arao@g.clemson.edu; Clemson Nanomaterials Center, 202 C Kinard Lab of Physics, Clemson University, Clemson, SC 29634, USA; and Center for Optical Materials Science and Engineering Technologies, Clemson University, Clemson, SC 29634, USA

Figure 1: Team members of the Clemson Nanomaterials Center at Clemson University.

intermediate hybridization sp^x, where $2<x<3$. Graphene, which is the most recent and widely studied form of nanostructured carbon, is a single sheet of carbon atoms that is isolated from the graphite bulk material. In other words, any of the shaded two-dimensional (2D) sheets that compose graphite, when isolated from the bulk, acquire a new form, known as graphene (Figure 3).

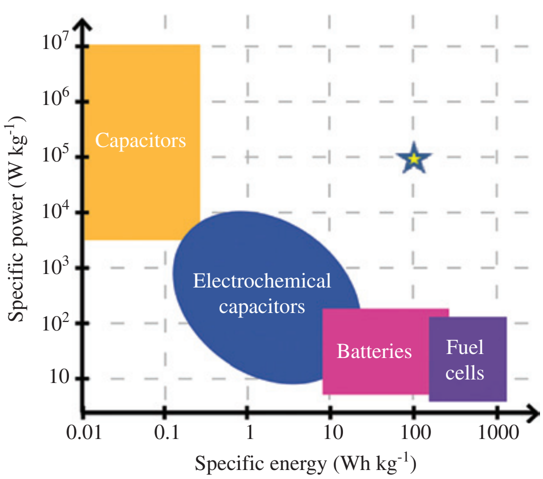

Figure 2: A Ragone plot showing specific power vs. specific energy for common electrical energy storage devices. Supercapacitors are expected to bridge the gap between batteries and capacitors and impact nearly every area of electrical energy usage. Supercapacitors with energy and power densities of the order of 100 Wh/kg and 100 kW/kg (indicated by ★), respectively, are needed for providing bursts of electric energy that for instance can help electric cars to accelerate at comparable or better rates than traditional petrol-only engine vehicles, while achieving a significantly reduced fuel consumption and mitigating global warming.

The advent of the carbon allotropes depicted in Figure 2 behooves us to develop designer electrodes based on new carbon allotropes that could significantly boost the performance of storage devices. The Central to today's battery and supercapacitor performance is the activated carbon, which is a form of carbon processed from graphite to acquire small, low-volume pores that increase the surface area available for adsorption or chemical reactions. A gram of activated carbon can have a surface area in excess of 500 m^2, with 1500 m^2 being readily achievable [5–7]. As such, activated carbon powder of a large surface area is the preferred material for making superior electrodes for use in energy devices. A highly porous electrode that embodies very high surface area leads to increased capacitance due to the extremely small distance that separates the opposite charges, as defined by the electric double layer (EDLC). However, the large porosity reduces the conductivity of the activated carbon electrode, and hence, conductive additives/binders are required to fabricate robust conducting electrodes. While the supercapacitors available today perform well, it is generally agreed that there is considerable scope for improvement (e.g. fabrication of binder-free electrodes to alleviate delamination of the active carbon from the underlying metal foils upon repeated charge-discharge cycling, scalable

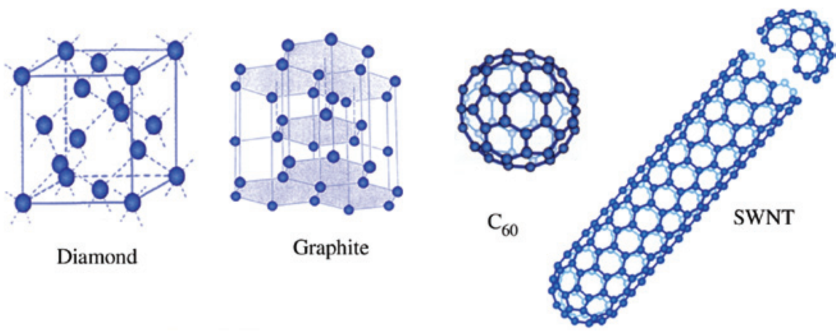

Figure 3: Schematic representations of allotropes of carbon [4]. Allotropes are different arrangements of the same element, which in this case is the humble carbon atom represented by the blue dots. The diameter of a single-walled carbon nanotube (SWNT) is ~1 nm, and its typical aspect ratio (length/diameter) is ~500.

fabrication processes, and improved performance at high frequencies). Thus, it is likely that carbon will continue to play a principal role in supercapacitor technology, mainly through further optimization of porosity, surface treatments to promote wettability, and reduced interparticle contact resistance. Specifically, the new carbon allotropes are posited to lead to a dramatic improvement over conventional activated carbon for energy storage devices.

2 CNC's contributions

In the last decade, there has been a considerable growth in the widespread use of carbon nanomaterials across a range of industries. But the most common bottleneck to any further development is the scalability of their production. Although multiwalled carbon nanotubes (MWNTs) can be synthesized in large quantities, present processes for the growth of vertically aligned MWNT forests – particularly of interest to the electronics market – are limited to a small range of substrate materials. This limitation is largely due to the fact that the low-cost substrates (such as kitchen-grade aluminum foil, 12 μm in thickness and 2 cm in width, Reynolds brand) melt around 660°C, while MWNT forests are grown at temperatures above 750°C in a conventional thermal chemical vapor deposition (CVD) process. Thus, issues related to substrate selection and their instability at relatively high MWNT growth temperatures have rendered the fabrication of MWNT-coated aluminum electrodes complex and inefficient. Additionally, the need to eliminate additives/binders in the preparation of MWNT-coated electrodes has made an already challenging situation even more challenging. To address these challenges, CNC has developed low-cost roll-to-roll processes that negate these issues by adapting a standard CVD system as depicted in Figure 4. A syringe

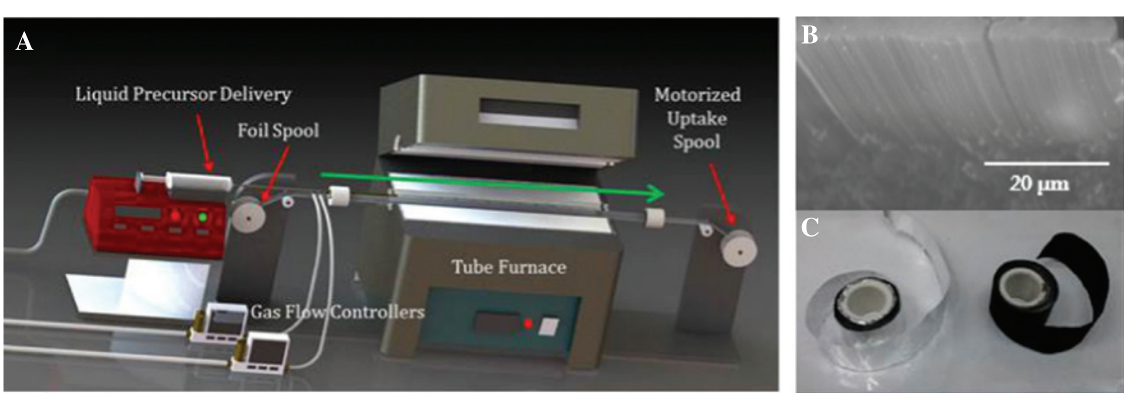

Figure 4: (A) A schematic of a roll-to-roll process for directly growing MWNT forests (B) on kitchen-grade aluminum ribbons using a thermal CVD process. The aluminum ribbon (C) is fed into the hot zone in the direction indicated by the green arrow, while a syringe pump simultaneously injects a ferrocene-xylene mixture, which acts as the precursor for the growth of MWNTs [9]. Aided by the flow of Ar, C_2H_2, and H_2 gases, the CNC team has managed to decrease the growth temperature of MWNT forests to 600°C, which is below the melting temperature of aluminum. (B) Scanning electron microscope (SEM) image of an as-grown MWNT forest on aluminum ribbon. (C) Images of spools containing the starting aluminum ribbon (left) and the MWNT-coated aluminum ribbon (right). Adapted from Ref. [10].

pump continuously feeds the ferrocene-xylene precursor into the hot zone that is maintained at ~600°C, well below the melting point of aluminum. As the aluminum ribbon is drawn continuously across the CVD reactor, Fe decomposed ferrocene (Aldrich) catalysts (diameter ~30 nm) from decomposed ferrocene deposit on the aluminum ribbon and seed the growth of MWNT forests via thermal decomposition of xylene (Aldrich) and acetylene (Airgas). The argon and hydrogen flow rates were optimized to grow 50 μm tall forests, on the aluminum ribbon at a rate of ~0.5 cm/min, which is compared to the best draw rates reported for roll-to-roll growth of MWNT forests on metal ribbons [8].

CNC has also developed two alternate scalable processes for fabricating binder-free carbon electrodes that use commercially available MWNTs. One of these processes entails direct spray coating of MWNTs onto flexible aluminum foils, akin to painting a car or a wall in your home (Figure 5). As we [11] and others [12] have shown previously, MWNTs can be doped with nitrogen, and highly stable dispersions of nitrogen-doped MWNTs can be readily prepared in bulk quantities. By spraying MWNT solutions onto flexible electrodes, porous aluminum foils in this case, high-energy density supercapacitor electrodes can be prepared without the need of any binder (Figure 5). This process is highly scalable (draw rates of m/min), and the resulting supercapacitors have a 10-times higher power density compared to the state-of-the-art supercapacitors on the market. Another advantage of the roll-to-roll spray-coating process is a significantly lower cost – the final price of the spray coated MWNT electrodes could be reduced by almost 17%, which includes material and production cost.

A third scalable process that is based on a simple vacuum filtration method for preparing buckypapers of MWNTs is also planned. Buckypapers exhibit major advantages over other MWNT/graphene composites in that they (i) retain many of the properties of the 1D MWNTs, (ii) are very flexible and easy to handle, and (iii) exhibit reproducible, stable, and controlled electrical properties unlike devices based on percolated carbon networks. To scalably produce buckypapers, 0.1 wt.% sodium dodecyl sulfate (SDS) (from Amreso, Solon OH) solution will be added to each mg of MWNTs (purchased from Cheap Tubes, Inc., Cambridgeport, VT) used in the setup shown in Figure 6 and ultrasonicated (20 W) for 30 min. Next, the resulting suspension will pass through a filtration system using a roll-to-roll polymer filter with 1-μm pore diameter. Finally, the filter paper holding the buckypaper will be air-dried, allowing the buckypaper to naturally peel off. The filter paper is then recycled. In preliminary experiments, we have prepared buckypapers using the recipe described above, which under voltammetric cycling in sulfuric acid showed a combination of EDLC and Faradaic energy storage arising from the defects and impurities present in the electrode [14].

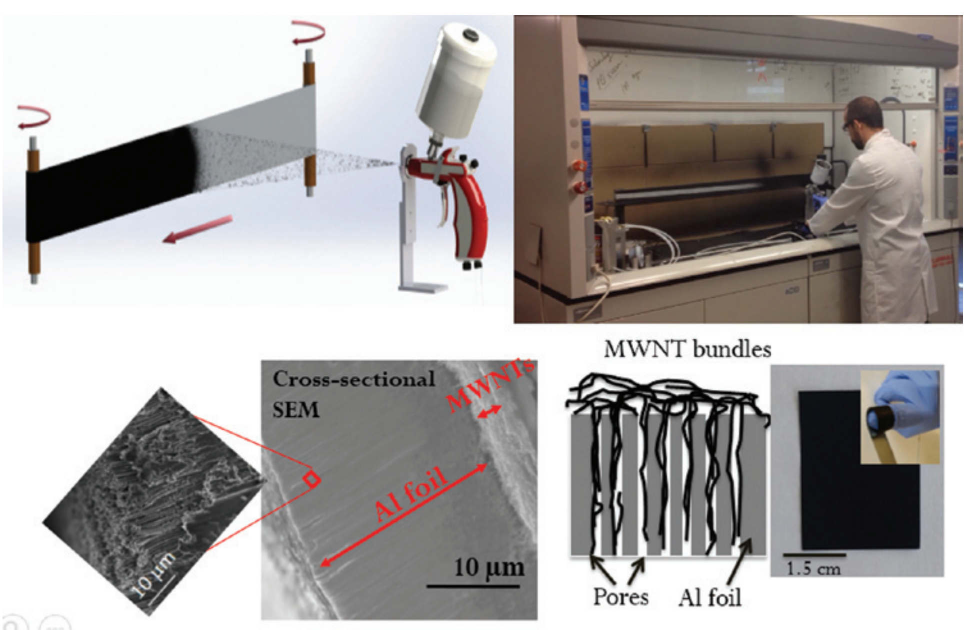

Figure 5: Top row: A schematic (left) and a lab demonstration (right) of the facile roll-to-roll spray coating process for producing MWNT-based electrodes. Bottom row: The cross-sectional SEM images of an industrial-grade aluminum ribbon, which show micron-wide pores that span across its thickness. These pores enable the sprayed MWNTs to anchor strongly to the ribbon and form a coating of randomly oriented MWNTs. Adapted from Ref. [13].

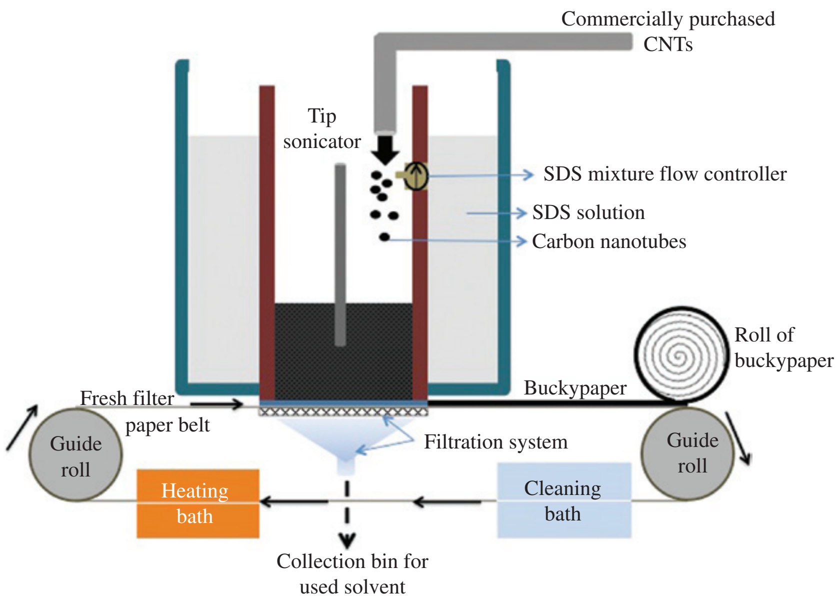

Figure 6: Scalable production of MWNT buckypaper. As-purchased MWNTs are tip sonicated in the presence of SDS to form stable homogenous suspensions, which is subsequently passed through the filtration system to form a buckpaper.

The CNC team together with Cornell Dubilier, Inc., (a leading capacitor manufacturer in Liberty, SC, USA) and Sai Global Technologies (manufacturer of tailored nanomaterials in San Antonio, TX, USA), has prepared jelly roll and coin cell-type supercapacitors and tested their performance via cyclic voltammetry, electrochemical impedance spectroscopy, and charge-discharge cycle stability tests. Figure 7 summarizes the performances of supercapacitors prepared using electrodes from the three scalable methods described above, with excellent cycle stability over at least 10,000 cycles. When compared to the commercially available supercapacitors that use activated carbon electrodes (e.g. Maxwell supercapacitors), clearly the spray coated electrodes or those comprised of helically coiled MWNTs with polymers (e.g. lignin, polyaniline) exhibit far superior performance in terms of energy and power densities (cf. Figure 7). Composites of carbon nanomaterials and redox polymers have synergistic properties beneficial to supercapacitors, such as high capacitance and stability, and eliminate the use of binder, substrate or additional inactive weight.

3 Sustainability

Energy storage technologies can potentially offset the inherent intermittency problem of renewable energy

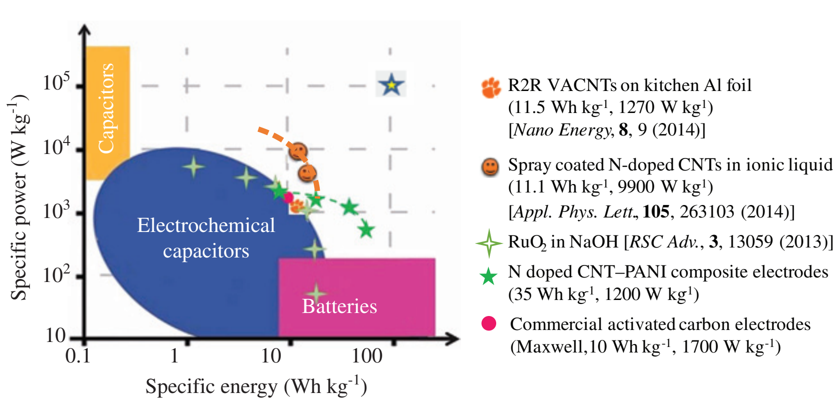

Figure 7: Performance of supercapacitors that use MWNT-based electrodes developed by CNC.

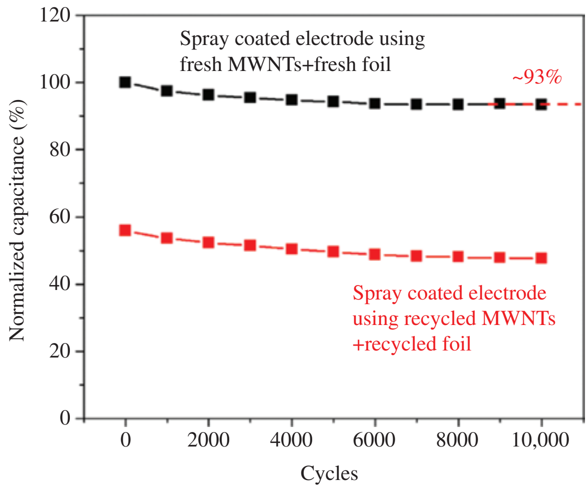

Figure 8: Cycle stability of spray coated aluminum electrodes coated with as-purchased (black squares) and recycled (red squares) MWNTs.

sources by storing the generated intermittent energy and then making it accessible upon demand. Thus, energy storage devices, such as supercapacitors, are key components for creating sustainable energy systems with the added advantages of superior cyclability and power density over batteries. At the end of the lifetime of electrodes prepared at CNC, the MWNTs from the used electrode can be recycled to make another new electrode. As depicted in Figure 8, the performance of the recycled electrode is ~60% of that exhibited by the original electrode. This is a great advantage in terms of sustainability as the average life span of most devices are becoming shorter than that of the material, which makes the device, owing to customer demand for new features. Moreover, polymers such as lignin when integrated with the buckypaper electrode result in an overall superior performance of the supercapacitor, thus, circumventing the need for expensive ruthenium oxide that holds the record for the highest capacitance values in commercial supercapacitors.

4 Conclusions and future perspective

The above-described advances in scalable nanomanufacturing for fabricating new supercapacitor electrodes are soon expected to bridge the energy density gap for some commercial applications. The industrial collaboration with Cornell Dubilier and Sai Global Technologies is a vital component of this research and is the process of translating lab-based technology to the market place. A rising penetration of renewable energy generation and storage technologies is needed to cumulatively displace greenhouse gases.

Acknowledgments: CNC is thankful to the National Science Foundation for granting an award to undertake the above-described projects, which would have lasting impact on the global energy landscape.
Funding: Division of Civil, Mechanical and Manufacturing Innovation, (Grant/Award Number: SNM Award No. #1246800).

References

[1] Special report of the intergovernmental panel on climate change, Cambridge University Press, ISBN 978-1-107-60710-1, 2012.
[2] Rolison DR, Nazar LF. Electrochemical energy storage to power the 21st century. *MRS Bull*. 2011, 36, 486–493.
[3] Simon P, Gogotsi Y. Materials for electrochemical capacitors. *Nat. Mater*. 2008, 7, 845–854.
[4] Rao AM. The rise of carbon nanoscience in South Carolina. *J. S. C. Acad. Sci*. 2015, 13, 5.
[5] Bansal RC, Goyal M. Activated carbon adsorption, Taylor & Francis: Boca Raton, ISBN 978-0824753443, 2005.
[6] Marsh H, Rodríguez-Reinoso F. Activated carbon, Elsevier, San Diego, CA, ISBN 978-0080444635, 2006.
[7] Yang RT. Adsorbents: fundamentals and applications, Wiley-Interscience, Hoboken NJ, ISBN 0471297410, 2003.
[8] Guzman de Villoria R, Hart AJ, Wardle BL. Continuous high-yield production of vertically aligned carbon nanotubes on 2D and 3D substrates. *ACS Nano* 2011, 5, 4850–4857.
[9] Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, Dickey EC, Chen J. Continuous production of aligned carbon nanotubes: a step closer to commercial realization. *Chem. Phys. Lett*. 1999, 303, 467–474.
[10] Arcila-Velez MR, Zhu J, Childress A, Karakaya M, Podila R, Rao AM, Roberts ME. Roll-to-roll synthesis of vertically aligned carbon nanotubes for electrical double layer capacitors. *Nano Energy* 2014, 8, 9–16.
[11] Sadanadan B, Savage T, Gaillard J, Bhattacharya S, Tritt T, Cassell A, Pan Z, Wang ZL, Rao AM. Synthesis and thermoelectric power of nitrogen doped carbon nanotubes. Special issue of the *J. Nanosci. Nanotechnol*. 2003, 3, 99.
[12] Ayala P, Arenal R, Rümmeli MH, Rubio A, Pichler T. Doping carbon nanotubes with Nitrogen and their potential applications. *Carbon* 2010, 3, 575–586.
[13] Karakaya M, Zhu J, Raghavendra AJ, Podila R, Parler SG Jr, Kaplan JP, Rao AM. Roll-to-roll production of spray coated N-doped carbon nanotube electrodes for supercapacitors. *Appl. Phys. Lett*. 2014, 105, 263103.
[14] Emmett R, Karakaya M, Podila R, Arcila-Velez MR, Zhu J, Rao AM, Roberts M. Can Faradaic processes in residual iron catalyst help overcome intrinsic EDLC limits of carbon nanotubes? *J. Phys. Chem. C* 2014, 118, 26498–26503.