Multifunctional Performance of Sodiated Carbon Fibers

Ross Harnden,∗ Kevin Peuvot,† Dan Zenkert,‡ and Göran Lindbergh§

‡Lightweight Structures, Department of Aeronautical & Vehicle Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden
§Applied Electrochemistry, Department of Chemical Engineering, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

An investigation is conducted into the potential for sodiated PAN-based carbon fibers (CFs) to be used in multifunctional actuation, sensing, and energy harvesting. Axial CF expansion/contraction is measured during sodiation/desodiation using operando strain measurements. The reversible expansion/contraction is found to be 0.1% — which is lower than that of lithiated CFs. The axial sodiation expansion occurs in two well-defined stages, corresponding to the sloping and plateau regions of the galvanostatic cycling curve. The results indicate that the sloping region most likely corresponds to sodium insertion between graphitic sheets, while the plateau region corresponds to sodium insertion in micropores. A voltage-strain coupling is found for the CFs, with a maximum coupling factor of 0.15 ± 0.01 V/unit strain, which could be used for strain sensing in multifunctional structures. This voltage-strain coupling is too small to be exploited for harvesting mechanical energy. The measured axial expansion is further used to estimate the capacity loss due to solid electrolyte interphase (SEI) formation, as well as capacity loss due to sodium trapped in the CF microstructure. The outcomes of this research suggest that sodiated CFs show some potential for use as actuators and sensors in future multifunctional structures, but that lithiated CFs show more promise.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0971813jes]

Manuscript submitted July 19, 2018; revised manuscript received September 11, 2018. Published October 11, 2018. This was Paper 1986 presented at the Seattle, Washington Meeting of the Society, May 13–17, 2018.

Multifunctional structures have been the focus of a great deal of research in recent years. The motivation behind such structures is to increase efficiency and functionality, often with the goal of reducing weight and/or volume in structures. By combining two or more functions into the same material it is possible to minimize redundancy between subsystems, and decrease the overall weight and/or volume of a structure. This often equates to lower energy use and hence lower CO2 emissions in many applications, particularly in the aerospace and automotive industries. These applications could range in scale from large structural parts, such as morphing aircraft wings, to very small, such as in microelectromechanical systems (MEMS). One potential route to realizing multifunctional structures is by exploiting electrochemical phenomena in carbon fibers (CFs), to create energy storage, actuation, strain sensing, and energy harvesting materials that can simultaneously bear structural loads.

CFs are good candidates for use in multifunctional structures as they are already employed in many structures for their good strength/weight ratio, and are most beneficial in weight-critical applications such as in the aerospace and automotive industries. As well as being excellent load bearers it has recently been shown that polyacrylonitrile (PAN)-based CFs can offer further functionalities such as energy storage, actuation, strain sensing, and energy harvesting.1–4 These functionalities open the door to a range of multifunctional concepts based on PAN-based CFs. Although a lot of research has recently focused on developing multifunctional energy storage,1,5 less emphasis has been placed on other functionalities.

Electrochemical actuation, strain sensing, and energy harvesting have previously been demonstrated using lithium (Li)-intercalated PAN-based CFs.5,6 Given the recent increase in interest for sodium (Na)-based battery technologies,6 this study focusses on whether the same functionalities exist for sodiated CFs, and whether they might in fact offer advantages — such as a larger actuation strain or a larger voltage-strain coupling — over Li-based multifunctional CFs. Within the Na-ion battery (NIB) field, hard carbons — carbons that cannot be graphitized — have emerged as the most viable cathode material.7 These hard carbons have a microstructure that consists of randomly oriented, curved graphene layers, similar to the often-cited “house of cards” model proposed in Dahn et al.8 Intermediate modulus PAN-based CFs (carbonized between 1100 °C and 1600 °C)9 have a microstructure that is very similar to that of hard carbons that have been carbonized at similar temperatures,10 suggesting that Na insertion mechanisms should be similar. Work conducted by Thomas and Billard11 showed that PAN-based CFs can indeed be sodiated/desodiated with a maximum capacity around 209 mAh/g, which is considerably less than the 354 mAh/g achieved for lithiation/delithiation at a similar charge rate.2 PAN-based CFs were shown to expand axially by as much as 1% when intercalated with Li at low charge rates, as well as offering an actuation energy density of around 2400 kJ m−3 in comparison with around 100 kJ m−3 for commonly used piezo-ceramics.12 By modeling this expansion it has been shown how such CF actuators could be used to generate bending and twisting actuation motions, as well as expansion and contraction, through the variation of the ply lay-up in a multifunctional composite laminate.13 In graphite intercalation compounds, mechanical deformations are the result of expansion of the interlayer spacing between graphitic sheets by the insertion of ions.14 Since Na-ions have a radius that is approximately 40% larger than that of Li-ions,15 it is hypothesized that expansion of PAN-based CFs when sodiated may be larger than when lithiated. Work conducted by Luo et al.16 showed that the interlayer d-spacing of graphitic sheets increases by as much as 17% in soft carbons when sodiated, in comparison to a maximum of around 13% for graphite when lithiated.16 This suggests that using sodiation to expand CFs for applications in structural actuators may result in greater expansions than when using lithiation.

Electrochemical strain sensing works by exploiting a coupling between mechanical strain and voltage. This has been observed previously in ion-intercalated materials through a phenomenon known as the piezo-electrochemical transducer (PECT) effect.16,17 It was shown that lithiated PAN-based CFs exhibit a linearly proportional change in cell potential in response to mechanical strain, with a coupling factor of up to 1.5 V/unit strain.3 Furthermore, this voltage-strain coupling has been demonstrated to enable energy harvesting.3,4,18,19,20 By mechanically straining an electrode after a charge cycle and thereby increasing the cell potential, it is possible to discharge the cell at a higher potential than that which it was originally charged at, provided that the voltage-strain coupling is large enough to overcome the internal cell losses. In this way it is possible to harvest some of the mechanical energy used to strain the electrode, and convert it to electrical energy. This was demonstrated for PAN-based CFs by Jacques et al. using lithiated fibers.4
The work presented in this paper quantifies the amount of global axial expansion caused by Na insertion into the PAN-based CF microstructure using operando measurements, in an effort to assess the viability of the use of sodiated CFs as structural actuators. In doing this it is possible to add to the discussion about which part of the galvanostatic cycling curve corresponds to which Na insertion mechanism. This work also quantifies the voltage-strain coupling in PAN-based CFs at various states of charge in order to assess the viability of the use of sodiated CFs as structural strain sensors as well as energy harvesters. The change in the CFs’ mechanical properties caused by sodiation/desodiation are also given. Lastly, using the measured axial expansion, estimations are given for how much Na is irreversibly trapped in the microstructure after the first sodiation/desodiation cycle, as well as how much Na is consumed in the formation of the solid electrolyte interphase (SEI) layer. The ultimate aim of this work is to investigate whether it is worth pursuing multifunctional actuation, sensing, and energy harvesting based on Na insertion, rather than Li insertion, in PAN-based CFs.

Experimental

Carbon fiber sample preparation.—All CF samples were manufactured using intermediate modulus Toray T800HB CFs which were split into bundles of approximately 1500 fibers from an original 6000 fiber tow. This was done in order to decrease mass transport losses when cycling. The density of the CFs used is taken to be 1800 kg/m³,¹¹ and the linear mass distribution for the actuation samples was measured to be 6.66×10⁻⁵ g/mm.

In order to be able to grip the samples in a tensile tester it was necessary to adhere end-tabs to the CF tows. These end-tabs were made from DeltaPreg W105P/DT806W glass fiber prepreg and were adhered to the CF tows using DeltaPreg AX003 epoxy adhesive. A section of 260 μm thick glass microfiber filter paper (Whatman GF/A) was also adhered between the two tabs to act as a separator layer and the resulting samples were heat cured under vacuum at 120 °C for 1 hour. The samples were then immersed in an acetone bath solvent in order to remove contamination as well as to partially remove the sizing from the CFs in order to achieve stable electrochemical cycling. The sizing was found to negatively affect the cycling stability in preliminary tests. These samples were then dried overnight in a vacuum oven at 70 °C, before being placed in an argon-filled glove box ready for cell manufacture. See Figure 1 for schematic of the CF samples used.

Electrochemical cells.—Standard laboratory half-cells in pouch cell format were used for all cycling. In this setup the CFs acted as the working electrode, a Na metal foil (manufactured using Sigma Aldrich 99.9% purity cubes) acted as the counter electrode, and the glass microfiber filter paper acted as a separator. The pouch cell bags were laminated constructions of PET/Al/PET from Skultuna Flexible with layer thicknesses of 12 μm/9 μm/75 μm respectively. Aluminium current collectors were attached to both the Na foil and CFs. Prior to sealing the pouches, the separator was impregnated with 200 μL of electrolyte made up with 0.6M NaPF₆ (Alfa Aesar > 99% purity) in diglyme (diethylene glycol dimethyl ether, Sigma Aldrich, 99.5% purity). Diglyme solvent was chosen as an electrolyte solvent as it was found to offer superior cycling stability and significantly lower overpotentials versus Na metal in comparison to carbonate-based solvents.²²⁻²⁴ It has also been shown that Na can intercalate into graphite via a co-intercalation phenomenon using diglyme,²⁵ which is not possible with carbonate-based solvents.²⁶ The pouch cells were manufactured inside a glove box under inert atmosphere with less than 2 ppm O₂ and H₂O at ambient temperature.

Electrochemical cycling.—Electrochemical measurements were performed using a BioLogic VSP potentiostat, controlled using BioLogic EC-Lab software. Cycling was carried out between 2.5 V and 0.01 V vs. Na/Na⁺, with the latter voltage considered as the fibers being fully sodiated, and the former as the fibers being fully desodiated. A maximum capacity of 170 mAh/g for the CFs was established by cycling fibers at low charge rates (between 3−7 mA/g) — allowing a charge rate of C/3 (fully sodiated in 3 hours) to be assigned, corresponding to 34 mA/g. At the end of each sodiation cycle a short constant voltage step was added, in which the voltage was held at 0.01 V and a current up to 10% of the applied galvanostatic sodiation current was allowed to flow. This step was added to maximize the amount of Na capacity in the CFs. Due to the use of a Na metal counter electrode (problems with which are described in Tchitchekova et al.),²³ as well as the use of epoxy tabbing in the cell, cycling performance was observed to degrade after 4 cycles. For this reason, all expansion and voltage-strain coupling measurements were carried out during the first 4 cycles. In future this issue could be overcome by finding a tabbing material and adhesive that interact less with the electrochemical system, as well as an alternative counter electrode such as Na₃V₂(PO₄)₃ (NVP) or Na₃V₂(PO₄)₂F₃ (NVPF).²⁴ Due to the reported instability of the potential of Na metal counter electrodes,²¹ and a suspicion that Na metal may in fact be plating on the CFs during the lengthy plateau voltage close to 0 V, a test was carried out to establish the plating potential for the CFs against Na metal. A cell was cycled at approximately C/5 without a voltage cutoff to terminate the cycle. The characteristic v-shaped potential rise and then plateau indicative of plating was found to occur around −0.015 V, and therefore capacity achieved above this potential was considered to be due to Na insertion rather than Na metal plating.

Axial expansion measurement.—Axial expansion/contraction of the CFs during Na insertion/extraction was carried out using the same operando measurement method described in Jacques et al.² The axial direction is considered to run along the lengthwise direction of the CFs as shown in Figure 1, as opposed to the radial direction. For each test, a pouch cell containing a CF sample was mounted in a Deben UK micro-tensile tester, while connected to the potentiostat (see Figure 2). The sample was then loaded in tension by applying an axial strain,
which was then held constant under the entire duration of the following electrochemical cycling. During each electrochemical cycle, a force drop was measured during sodiation, followed by a rise in force during desodiation. Assuming that the axial stiffness of the CFs remained constant during the sodiation/desodiation cycle — which was verified using ex-situ tensile measurements (see Table I) — these force changes could be attributed entirely to axial expansion/contraction of the CFs. The axial expansion/contraction could then be resolved from the force data using the specimens’ stiffness, which was measured separately by means of a tensile test. All specimen stiffnesses were calculated using a least-squares fit of the linear section of the resulting force-displacement curve.

Since the pouch cell bag exhibited viscoelastic behavior, the samples were left under tension for 6 hours prior to electrochemical cycling to allow the stress-relaxation to become linear. This viscoelastic behavior was quantified in a separate test, whereby a pouch cell bag was strained and left to relax over several days. This result was then used to subtract the stress-relaxation from the final expansion results in order to obtain the force changes due only to CF axial expansion/contraction. The total force change was then taken as the difference between the force at full desodiation and force at full sodiation. These force changes were subsequently converted to axial strains using the specimen stiffness and gauge length.

The specific actuation energy \( U \) was calculated using Equation 1 taken from Jacques et al.\(^2\):

\[
U = \frac{\Delta F^2}{2 \cdot K \cdot V}
\]

where \( \Delta F \) is the total measured force change (in N), \( K \) is the tensile stiffness of the CF specimen (in N/m), and \( V \) is the volume of the CF electrode (in m\(^3\)). The active volume of the CF electrode was calculated to be \( 8.14 \times 10^{-10} \) m\(^3\).

A sampling rate of 0.2 Hz was used for all mechanical aspects of the axial expansion measurements, resulting in approximately 4000 strain data points for each sodiation/desodiation cycle. All electrochemical data was recorded at a sampling rate of 1 Hz.

**Voltage-strain coupling measurements** — Measurements of the voltage-strain coupling were carried out using the same method as described in Jacques et al.\(^3\) In summary, CFs were strained using the same micro-tensile tester as was used for the expansion measurements, while the voltage response was monitored using the Biologic VSP potentiostat. The cell was cycled through 2 full sodiation/desodiation cycles in order to establish corresponding cell potentials for 0%, 25%, 50%, and 100% states of charge, and on the third cycle the current was stopped at these potentials in order to measure the voltage-strain coupling. After stopping the current the cell was left to rest for 5 minutes before strain was applied in order to let the potential stabilize. A cyclic axial strain of 0.36% was applied, based on a gauge length of 22 mm, at a strain rate of 0.1 mm/min, and a rest time between cycles of 15 seconds. 5 cycles were measured for each state of charge and the mean value of the response was taken. Measurements were carried out and compared on both the sodiation and desodiation cycles.

**Results and Discussions**

**Stiffness and failure strength** — Sodiated CF samples were cycled through 2 full sodiation/desodiation cycles, and then the tensile properties were tested after a further sodiation cycle. Desodiated CF samples were cycled through 3 full sodiation/desodiation cycles, so that both sets of fibers had been through the same number of sodiation cycles. The tensile properties for uncycled, sodiated and desodiated fibers are given in Table I, with the ultimate tensile strain calculated based on a gauge length of 22 mm, and an average stiffness of 573.50 N/mm. It was found that the stiffness of the CFs remained constant regardless of the state of sodiation of the fibers, within the margin of error of the test method. The ultimate tensile strain on the other hand, was observed to decrease by 27% for sodiated fibers in comparison with uncycled fibers. This drop in ultimate tensile strain is slightly greater than that observed for lithiated CFs, which experience a drop of approximately 20%.\(^2\) It is likely that this drop in ultimate tensile strength is due to Na deforming graphitic crystals within the CFs’ microstructure. The loss in ultimate tensile strain in sodiated CFs was found to be partially reversible, with desodiated fibers having an ultimate tensile strain approximately 7% lower than uncycled fibers. This irreversible loss in failure strain is an indication that some Na may become trapped in the CF microstructure after the first sodiation cycle, leaving a permanent microstructural deformation. This trapped Na would contribute to the first cycle capacity loss, together with the formation of the SEI layer as suggested by Lotfabad et al.\(^2\).

**Actuation** — Figure 3 shows the direct axial force data for 3 complete sodiation/desodiation cycles. The force drop/rise corresponding to axial expansion/contraction of the CF can be seen to correspond to the sodiation/desodiation of the electrode, indicated by the electrode potential. The stress-relaxation behavior of the viscoelastic pouch cell bag was measured in a separate test, and is denoted by the dashed line in Figure 3. By subtracting the stress-relaxation behavior from the axial force data from the electrode, it was possible to obtain the force changes due only to electrode expansion/contraction. The axial strains could then be resolved from the force data using the CF specimen stiffnesses and gauge length.

Figure 4a shows the axial expansion of the CFs during sodiation, while Figure 4b shows the axial contraction of the CFs during desodiation. Data for the same fibers when lithiated, taken from Jacques et al.\(^2\), is shown in Figure 4a for comparison. First cycle capacities tended to be around 120 mAh/g, with subsequent cycles dropping to a capacity of around 90 mAh/g, as can be seen in Figure 4a. It can be seen that the maximum expansion on the first sodiation cycle is approximately 0.15% strain, dropping to a reversible expansion strain of up to 0.09% for cycles 2–4. This reversible expansion strain is a factor of 4 less than that of lithiated CFs at an equivalent charge rate, albeit with approximately 3 times less capacity.\(^2\) Normalising for capacity,
this gives sodiated PAN-based CFs a maximum axial expansion approximately 25% less than that of the same CFs when lithiated. The first cycle irreversible expansion of 0.06% (shown in Figure 5a) is thought to be caused by Na trapped in the CF microstructure.28

Due to the CFs’ low density they perform well in terms of specific actuation energy, obtaining a reversible energy output of 150.16 kJ/m3 (83.42 J/kg) — calculated according to the method described in Jacques et al.3 — which is similar to commonly used piezo-ceramics which exhibit actuation energies around 100 kJ/m3. Despite this, it is clear that the same CFs perform better when lithiated, with strains around 4 times larger, giving specific actuation energies around 2400 kJ/m3 (1300 J/kg) for a similar charge rate.2

A very clear staging is observed in the axial strain, with two stages observed for each sodiation and desodiation as can be seen in Figures 4a and 4b, and also illustrated for sodiation in Figure 5b. The stages in the strain curves correspond to the stages in the galvanostatic cycling curves, with the first stage corresponding to the sloping region, and the second stage corresponding to the plateau region as can be seen in Figure 5a. Both stages are approximately linear, allowing schematics of the stages to be drawn.

Figure 5b shows an approximation of the reversible expansion curve based on linearized curves for a typical sodiation during cycles 2–4. There are two main expansion gradients during the course of the sodiation, m1 and m2, corresponding to the two main stages in the galvanostatic cycling curve commonly referred to as the sloping and plateau regions.12 Gradients were calculated using a least-squares fit, and the transitions between the stages are defined by the point at which the linear gradients intersect. Each gradient then represents an axial expansion per unit capacity. The gradient m1 in the sloping region is approximately 3.5 times greater than m2 in the plateau region, showing that the expansion per unit capacity is significantly greater in the sloping region. It is known that interlayer spacing of graphene sheets can increase by as much as 17% when sodiated,17 and it was shown by Komaba et al.,29 using ex-situ XRD analysis, that the interlayer d-spacing increased linearly during the sloping region of the galvanostatic cycling curve — suggesting ion insertion between graphic sheets. It was shown in the same study that the rate of d-spacing expansion appeared to slow down with respect to capacity during the plateau region. This corresponds very well to the global axial expansion observed here. It is therefore likely that the sloping region corresponds predominantly to insertion of Na between graphic sheets, while the plateau region corresponds predominantly to insertion of Na in micropores. It is however acknowledged that this point is currently a topic of ongoing debate in the NIB literature, a comprehensive review of which can be found in Sauret et al.30

The magnitudes of the gradients m1 and m2 were the same for the sloping and plateau regions of the desodiation curves shown in Figure 4b—suggesting that the sodiation mechanisms are reversed during desodiation.

It is possible to estimate how much capacity and strain result from each stage of the galvanostatic cycling curve by using the definition described above to establish the point of transition between the stages. These results are shown in Figures 6a and 6b for the capacity and axial strain respectively. The reversible capacities for the two regions of the expansion curve are approximately the same, with 50% of the capacity coming from the sloping region and 50% coming from the plateau region for both sodiation and desodiation, as can be seen in Figure 6a. This pattern changes slightly for the first sodiation, with the inclusion of region 1, also illustrated in Figure 5c—which is thought to be the region in which the majority of the SEI layer is formed, as is discussed later in Losses due to SEI formation and Trapped Na section. The capacity contribution from region 1 and the sloping region account for approximately 58% of the total first sodiation capacity.

The reversible axial expansions attributable to the slope and plateau regions are not evenly divided. On average the plateau region contributed only 25% of the axial strain for both sodiation, and desodiation, while the sloping region contributed 75%, as can be seen in Figure 6b. For actuation applications where higher strain rates are required it would therefore be advisable to use only the sloping region of the galvanostatic cycling curve, i.e. sodiate/desodiate between 2.5 V and 0.1 V. For the charge rate used here this would result in a 20% increase in specific actuation power. For battery purposes it would be advisable to design electrodes that increase the plateau region as this is where the least expansion occurs, and would likely result in less cell degradation.

Sensing and energy harvesting.—The voltage-strain coupling in the CFs was measured to establish the viability for structural strain sensing and energy harvesting. The coupling was measured at several different cell potentials during both the sodiation and desodiation cycles, corresponding to approximately 0%, 25%, 50%, 75%, and 100% states of charge. A coupling factor between the voltage and strain is defined in Equation 2 and is a metric that indicates the magnitude of the voltage change per unit strain. A higher coupling factor is desirable for strain sensing and energy harvesting applications. The coupling factor is defined as:

\[ k = \frac{\Delta E}{\Delta \varepsilon} \]  

where \( E \) is the cell potential, and \( \varepsilon \) is the axial tensile strain in the CFs.
Figure 5. a) Axial expansion and electrode potential during sodiation cycles 1–2 b) Linearized schematic of axial sodiation expansion representing cycles 2–4 c) Linearized schematic of first cycle axial sodiation expansion and evaluation of capacity loss due to SEI.

Figure 6. a) Distribution of capacity attributable to different regions of the galvanostatic cycling curve. b) Distribution of axial strain magnitude attributable to different regions of the galvanostatic cycling curve.
are the gradients in the galvanostatic cycling curves for the sloping regions and the plateau regions. This suggests that after region 1, the Na insertion mechanisms are the same between cycle 1 and cycles 2–4. This would indicate that the majority of the SEI layer formation occurs early in the first sodiation.

Using the difference between gradients $m_1$ and $m_2$, it is possible to estimate the amount of capacity lost to SEI formation. By extrapolating the axial expansion curve with gradient $m_1$ back to intersect the capacity axis (as shown in Figure 5c), the difference between the extrapolated intercept and the real intercept should give the capacity lost to SEI formation. For the cells cycled in this paper, capacity loss due to SEI formation corresponded to $\sim 10$ mAh/g, from a total first cycle loss of $\sim 30$ mAh/g. Assuming that the total first cycle capacity loss is due to capacity lost to SEI formation as well as Na trapped in the microstructure — evidence of which is indicated by the drop in ultimate failure strain after desodiation, as well as the irreversible expansion — the capacity loss due to trapped Na is $\sim 20$ mAh/g. Brunauer-Emmet-Teller (BET) surface area measurements were previously carried out by Hagberg et al.\(^\text{11}\) on the same batch of CFs used here, giving a specific surface area of 0.52 m$^2$/g. This is relatively low in comparison to most other hard carbons, and so it is likely that SEI formation would account for a proportionally larger amount of the first cycle loss in other hard carbons.\(^\text{12}\)

**Conclusions**

The aim of this work was to explore sodiated CFs as an alternative to lithiated CFs for multifunctional actuation, sensing, and energy harvesting based on PAN-based CFs. Sodiated CFs may function as structural actuators provided that the actuation strain required is small (in the range of 0.1%). The specific actuation energy was found to be 150.16 kJ/m$^3$. In comparison, lithiated CFs have an actuation strain approximately 4 times larger, giving a specific actuation energy around 2400 kJ/m$^3$ at a similar charge rate.

The fact that the expansion rate is 3.5 times larger during the sloping region of the galvanostatic cycling curve suggests that this region is where Na ions are inserted in between the graphitic sheets of the CF microstructure, while the low expansion rate during the plateau region of the curve would suggest that this is where Na is inserted into micropores. Although the sloping and plateau regions contribute an equal share of the overall reversible capacity, around 75% of the axial expansion occurs during the sloping region. This has implications for the future design of Na-based actuators and batteries.

Sodiated PAN-based CFs may function as structural sensors with a maximum voltage-strain coupling factor of 0.15 $\pm$ 0.01 V/unit strain observed for a state of charge of around 45%. This is a factor of 10 less than that of lithiated CFs at a similar state of charge. The voltage-strain coupling was found to be too small to overcome the internal cell losses and therefore could not be used effectively for energy harvesting.

A comparison of the gradients of the capacity vs. axial expansion curves allows the amount of Na consumed in the formation of the SEI layer to be estimated to $\sim 10$ mAh/g. An irreversible drop in ultimate tensile strain as well as an irreversible axial expansion after the first cycle indicates that Na becomes trapped in the CF microstructure. Assuming that the first cycle capacity loss is due to a combination of SEI formation and trapped Na, the capacity loss due to trapped Na was calculated to be $\sim 20$ mAh/g.

Overall, this work has shown that there is potential for sodiated PAN-based CFs to be used in future multifunctional structures for actuation and sensing, although lithiated PAN-based CFs appear to show more potential, with larger axial expansions, stronger voltage-strain couplings, and the potential to harvest mechanical energy.

**Acknowledgments**

This work was supported by the Swedish Energy Agency (project 37712-1), the Swedish Research Council (projects 2017-03898 and 621-2014-4577), Formas (projects 2016-20058 and 2016-01520), and the strategic innovation program LIGHTer (funding provided by...
Vinnova, the Swedish Energy Agency and Formas). The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

ORCID
Ross Harnden https://orcid.org/0000-0001-6760-5192
Kevin Peuvot https://orcid.org/0000-0003-4466-7555
Dan Zenkert https://orcid.org/0000-0002-9744-4550
Göran Lindbergh https://orcid.org/0000-0001-9203-9313

References
1. L. E. Asp and E. S. Greenhalgh, Structural power composites, Compos. Sci. Technol., 101, 41 (2014).
2. E. Jacques, M. H. Kjell, D. Zenkert, G. Lindbergh, and M. Behm, Expansion of carbon fibers induced by lithium intercalation for structural electrode applications, Carbon, 59, 246 (2013).
3. E. Jacques, M. Kjell, D. Zenkert, and G. Lindbergh, Piezo-electrochemical effect in lithium-intercalated carbon fibers, Electrochem. commun., 35, 65 (2013).
4. E. Jacques, G. Lindbergh, D. Zenkert, S. Leijonmarck, and M. Kjell, Piezo-electrochemical Energy Harvesting with Lithium-Intercalating Carbon Fibers, ACS Appl. Mater. Interfaces, 7(25), 13898 (2015).
5. A. Javaid, K. K. C. Ho, A. Bismarck, M. S. P. Shaffer, J. H. G. Steinke, and E. S. Greenhalgh, Multifunctional structural supercapacitors for electrical energy storage applications, J. Compos. Mater., 48(12), 1409 (2014).
6. K. Kubota and S. Komaba, Review — Practical Issues and Future Perspective for Na-Ion Batteries, J. Electrochem. Soc., 162(4), A2538 (2015).
7. E. Irisarri, A. Ponrouch, and M. R. Palacin, Review — Hard Carbon Negative Electrode Materials for Sodium-Ion Batteries, J. Electrochem. Soc., 162(4), A2476 (2015).
8. B. Zhang, C. Matei, Ghimbeu, C. Laberty, C. Vix-Guterl, and J. B. Cannarella, On the coupling between stress and voltage in lithium-ion pouch cells, In Proc. SPIE, volume 9115, 2014.
9. T. Zheng, Y. Liu, E. Fuller, S. Tseng, U. von Sacken, and J. R. Dahn, Lithium insertion in structural batteries due to electrode expansions, Compos. Struct., 179, 580 (2017).
10. C. Massey, G. McKittrick, W. Barvosa-Carter, and P. Liu, Reversible work by electrochemical intercalation of graphitic materials, Proc. SPIE, 5759, 322 (2005).
11. M. D. Slater, D. Kim, E. Lee, and C. S. Johnson, Sodium-Ion Batteries, Adv. Funct. Mater., 23(4), 947 (2013).
12. W. Luo, Z. Jian, Z. Xing, W. Wang, C. Bommier, M. M. Lerner, and X. Ji, Electrochemically Expandable Soft Carbon as Anodes for Na-Ion Batteries, ACS Cent. Sci., 1, 516 (2015).
13. E. Vogel, H. S. Abdel-Aty-Zohdy, and R. L. Ewing, Dynamic PECT Effect for Nanotransducers and Hybrid Devices, In 49th IEEE Int. Midwest Symp. Circuits Syst., volume 2, pages 235–239, San Juan, Puerto Rico, 2006.
14. J. Cannarella, C. Z. Leng, and C. B. Arnold, On the coupling between stress and voltage in lithium-ion pouch cells, In Proc. SPIE, volume 9115, 2014.
15. J. Cannarella and C. B. Arnold, Toward Low-Frequency Mechanical Energy Harvesting Using Energy-Dense Piezoelectrochemical Materials, Adv. Mater., 27(45), 7440 (2015).
16. Torsay Carbon Fibres America Inc. T800H Data Sheet, Technical report, Santa Ana, CA.
17. Z. W. Seh, J. Sun, Y. Sun, and Y. Cui, A highly reversible room-temperature sodium metal anode, ACS Cent. Sci., 1(8), 449 (2015).
18. D. S. Tchitchekova, D. Monti, P. Johansson, F. Bardé, A. Randon-Vitanova, M. R. Palacin, and A. Ponrouch, On the Reliability of Half-Cell Tests for Monovalent (Li+), Na+ and Divalent (Mg2+, Ca2+) Cation Based Batteries, J. Electrochem. Soc., 164(7), A1384 (2017).
19. K. Westman, R. Dagas, P. Jankowski, W. G. Wieczorek, G. Gachot, M. Morcette, E. Irisarri, A. Ponrouch, M. R. Palacin, J. Tarascon, and P. Johansson, Diglyme based electrolytes for sodium-ion batteries Diglyme based electrolytes for sodium-ion batteries, ACS Appl. Energy Mater., 1(6), 2671 (2018).
20. B. Jach and P. Adelhelm, Use of graphite as a highly reversible electrode with superior cycle life for sodium-ion batteries by making use of co-intercalation phenomena, Angew. Chemie - Int. Ed., 53(38), 10169 (2014).
21. D. A. Stevens and J. R. Dahn, The Mechanisms of Lithium and Sodium Insertion in Carbon Materials, J. Electrochem. Soc., 148(8), A803 (2001).
22. E. Jacques, M. H. Kjell, D. Zenkert, G. Lindbergh, M. Behm, and M. Willgert, Impact of electrochemical cycling on the tensile properties of carbon fibers for structural lithium-ion composite batteries, Compos. Sci. Technol., 72(7), 792 (2012).
23. E. Irisarri, P. Kalsiwaat, A. Kohandelghani, D. Karpuzov, and D. Militin, Origin of non-SEI related coulombic efficiency loss in carbons tested against Na and Li, J. Mater. Chem. A, 2(46), 19685 (2014).
24. S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, and K. Fujiwara, Electrochemical Na insertion and solid electrolyte interphase for hard-carbon electrodes and application to Na-ion batteries, Adv. Funct. Mater., 21(20), 3859 (2011).
25. D. Sauler, B. Orayech, B. Xiao, D. Carriazo, X. Li, and T. Rojo, From Charge Storage Mechanism to Performance: A Roadmap toward High Specific Energy Sodium-Ion Batteries through Carbon Anode Optimization, Adv. Energy Mater., 8(17), 1 (2018).
26. M. H. Kjell, E. Jacques, D. Zenkert, M. Behm, and G. Lindbergh, PAN-Based Carbon Fiber Negative Electrodes for Structural Lithium-Ion Batteries, J. Electrochem. Soc., 158(12), A1455 (2011).
27. K. Kubota and S. Komaba, Review — Practical Issues and Future Perspective for Na-Ion Batteries, J. Electrochem. Soc., 162(4), A2476 (2015).
28. J. Hagberg, S. Leijonmarck, and G. Lindbergh, High Precision Coulometry of Commercial PAN-Based Carbon Fibers as Electrodes in Structural Batteries, J. Electrochem. Soc., 163(8), A1790 (2016).
29. P. Thomas and D. Billand, Sodium electrochemical insertion mechanisms in various carbon fibers, Electrochem. Acta, 46(22), 3359 (2001).
30. Y. Koyama, T. E. Chin, U. Rhyner, R. K. Holman, S. R. Hall, and Y. M. Chiang, Harnessing the actuation potential of solid-state intercalation compounds, Adv. Funct. Mater., 16(4), 492 (2006).
31. F. Dionisi, R. Harnden, and D. Zenkert, A model to analyze deformations and stresses in structural batteries due to electrode expansions, Compos. Struct., 179, 580 (2017).