MULTIFUNCTIONAL COMPOSITE MATERIALS USING LITHIUM ION FUNCTIONALIZATION

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Keywords: carbon fibres, sensing, actuation, energy harvesting, piezo-electrochemical

ABSTRACT

In this paper we show how one can functionalise carbon fibres by using them as an electrochemical electrode. The electrochemical process is the same as in a lithium-ion battery cell so that the carbon fibres act as an active electrode in future structural battery concepts. The functionalization of carbon fibres using lithium ion intercalation reveals three novel and interesting possibilities enabling carbon fibres composites to obtain several other multi-functionalities. These are strain sensing, actuation and energy harvesting.

We have found that by intercalating lithium ions into the nano-/micro-structure of carbon fibres a piezo-electrochemical effect is revealed. This is observed as a change in the potential of the carbon fibre electrode when applying a mechanical load. The response is direct and easily measurable being in the order of several mV. This can be utilised as a strain sensor since there is a relation between the potential change and the strain in the carbon fibre.

Secondly, we have measured substantial axial expansion of carbon fibres when intercalated with lithium ions. The strain measured is as high as 1\%. Since the stiffness of carbon fibres is very high, this corresponds to very large forces. This can be used for actuation or morphing.

Thirdly, the newly found piezo-electrochemical effect can be used to harvest energy by converting mechanical work to electrical energy. Applying a tensile force to carbon fibre bundles used as Li-intercalating electrodes results in a response of the electrode potential of a few mV which allows, at low charge rates, discharge at higher electrode potential than at charge. More electrical energy is thereby released from the cell at discharge than provided at charge, harvesting energy from the mechanical work of the applied force.

1. INTRODUCTION

Reduced system mass for improvements in system performance has become a priority for a wide range of applications that includes load-bearing components in a system which requires electrical energy. Use of lightweight materials has been identified as the key for successful electrification of future road transport. Structure and energy storage are usually subsystems with the highest mass contributions but energy storage devices are structurally parasitic. One creative path towards realisation of this is to develop composite materials which perform several functions at the same time – multifunctional materials. Combining functions in a single material entity will enable substantial weight savings on the systems level. To meet this challenge research aiming at developing so-called structural batteries, which are hybrid and multifunctional material assemblies, is being pursued [1]. In such a multifunctional composite material carbon fibres are used as the primary load-carrying material due to their excellent strength and stiffness properties, but also as the active negative battery electrode providing the battery function.

During the initial work towards structural batteries a number of interesting phenomena were
encountered which opens up for several additional and completely new research questions for structural batteries involving the special properties obtained from carbon fibres when intercalated with lithium [2].

Rechargeable batteries are the primary electrical energy-storage medium for today’s mobile and wearable electrical devices. Li-ion batteries are attractive for their high specific energy, high operating voltage and very slow self-discharge. Intermediate modulus polyacrylonitrile-based (PAN) carbon fibres electrodes exhibit promising specific electrochemical storage (Li-intercalating) capacities as battery electrodes [3-5]. Using carbon fibre electrodes, instead of today’s mesocarbon microbeads (MCMB) powder form graphite, allows the electrode to also carry mechanical loads [6-8]. In fact, carbon fibres retain their high stiffness and strength even after large amounts of Li have been intercalated [6,8]. Recent research has highlighted a piezo-electrochemical effect in Li-intercalated carbon fibres (CFs) used as electrodes in Li-ion cells [2]. When a tensile strain was applied a response of the Li-intercalated CF electrode potential was measured. It has also been found that carbon fibres expand then lithium ions are intercalated into the graphitic micro-structure [7]. These effect could potentially lead to the use of carbon fibres and carbon fibre composites as actuators, sensors and/or energy harvesters potentially with an integrated energy storage (battery) function.

2. MATERIALS AND METHODS

This study was conducted on PAN-based CF bundles of Torayca T800HB 6K 40B P1 BB 223tex and unsized Toho Tenax IMS65 24K 830tex. These grades have high tensile strength and elastic modulus, and good electrochemical specific capacities to intercalate Li which can be up to 300-350 mAh/g at low current densities when the diffusion of Li in the electrolyte and carbon fibre bundle is not rate limiting [4,5]. The test specimens for the various experiments are shown in Figure 1. The IMS65 bundle was split to ease the diffusion of Li in the bundle. End tabs made from glass/epoxy laminates were attached to each side of each bundle to enable mechanical testing.

![Figure 1: a) The test specimen consisting of a carbon fibre bundle is used as electrode and composite end tabs allow applying an axial mechanical force to the bundle. b) Photo of set-up for expansion experiment. c) Photo of experimental set-up for energy harvesting.](image)

The specimens were manufactured from dry CF bundles according to methods described in [6,9]. The Li-ion cell used, as shown in Figure 1a, was manufactured in a glovebox under inert argon atmosphere with less than 1 ppm oxygen and water at ambient temperature. The cell consisted of a single carbon fibre working electrode (specimen), a glass microfibre separator (Whatman GF/A, 260 μm thick, 90 % porosity) impregnated with 1200 μL of 1.0 M LiPF6 in EC:DEC (1:1 w/w, LP40 Merck) electrolyte and a Li metal counter electrode. Copper and nickel foils were used as current collector tabs. The layup was packed in a vacuum sealed bag (Skultuna Flexible, PET/Al/PE, 12 μm / 9 μm / 75 μm thick). The cell current collectors were connected to a Solartron 1286 Electrochemical Interface potentiostat controlled with the CorrWare software.

Swelling experiments were performed using a microtester, a 300N tensile stage from Deben UK, and were performed inside the glovebox [7]. The set-up is shown in Figure 1b. In the energy harvesting
experiments the mechanical tests were performed in an Instron 5567 equipped with a 5 kN load cell using pneumatic grips to maintain a constant force to the specimen end tabs during long-lasting tests [9]. Figure 1c shows a finished cell in the grips of the mechanical tester and connected to the potentiostat.

3. THE PIEZOELECTROCHEMICAL EFFECT

The carbon fibre bundle test specimen as shown in Figure 1b was subjected to 5 electrochemical cycles at about 1C-rate and 50 h of cell relaxation. The tensile strain was varied while measuring the Open Circuit Potential (OCP). Figure 2 shows this piezoelectrochemical effect which is exhibited by a response of the measured OCP to the tensile force acting on an IMS65 CF specimen. The tensile extension was first increased and then decreased of the same, low (8e-5 s-1) and high (1e-3 s-1) strain rate, consecutively. When the force increases, the OCP increases. The microstructure of the CF seems to reflect a lower state of charge when stretched longitudinally leading to a higher electrode potential. The tensile strain is linear elastic and the OCP response is also linearly reversible whatever the strain rate, and faster than the sample time used for data acquisition (100 ms).

![Piezoelectric effect](image)

Figure 2: Piezoelectric effect. Measured OCP response to the external tensile force applied on an IMS65 CF electrode after full lithiation at about 1C-rate.

The strain sensitivity $k$ (in V) can be estimated from

$$\Delta E = k \times \Delta \varepsilon \quad (1)$$

where $\Delta E$ the change of the measured OCP induced by the variation of the tensile strain $\Delta \varepsilon$ in the CFs. When the tensile strain is increased 0.60%, the OCP goes up about 4.5 mV, so that $k$ is 0.75 V and 0.74 V for IMS65 and T800, respectively. For sensing purposes $k$ can be seen as gauge factor.

In a more recent study [9] this was tested again but at different states of charge (SOC), i.e., lithium content in the fibre. The response varied with SOC to reach a maximum of about 5.4 mV and 3.6 mV for the T800 and IMS65 specimens, respectively, both found at approximately 50% SOC. At higher and lower SOC the response was smaller. At the highest potential (0 % SOC), it was still possible to measure a fairly high OCP response (~4 mV for T800 and ~3 mV for IMS65) which is attributed to Li that remains intercalated (trapped) in the delithiated fibres at the defined 0 % SOC [7].

A consequence of this piezoelectrochemical effect is that charged carbon fibres creates a change of the electrochemical potential in the order of several mV’s when an external load is applied. A carbon fibre could thus also be used to sense the load by measuring the electrochemical potential changes in the material. Our measurements indicate that the response is fast, but this needs to be further studied. With the sensing capability we have a functionalised material, which could be used in applications where the level and spatial distribution of loads in structures are of interest to monitor, e.g. aircraft wing spars. This would facilitate low-cost sensing of both small and large structures.
4. PIEZO-ELECTROCHEMICAL ACTUATION

Research [10] has shown that structural changes occur in lithium intercalated graphite. As Li is intercalated into graphite, the interlayer spacing increases by about 10%, with a simultaneous expansion of about 1% of the basal planes. In the microstructure of CFs, the graphene layers tend to be oriented parallel to the longitudinal axis of the fibre [11].

The longitudinal expansion of CFs can be measured in-situ, using CF specimens as a structural electrode in a pouch cell. The stiffness of the carbon fibre bundle is unaffected by the lithium intercalation and the amount of intercalated lithium (state-of-charge) [6,7]. Carbon fibre bundles in pouch cells, as shown in Figure 1b, where subjected to a constant tensile deformation in the micro-tester. The carbon fibres were then intercalated and deintercalated with Li-ions causing the fibres to expand and contract due to the swelling. The longitudinal expansion strain is then measured indirectly via the force variation on the carbon fibre bundle [6]. The expansion [%] is calculated as the variation of the tensile load divided by the tensile stiffness of the CF specimen, measured in a tensile test. The measurements were made using different charge rates, using a new cell with a single CF specimen electrode. These charge rates (C-rates) correspond to different states-of-charge, i.e. different Li-ion content in the fibre bundle. The longitudinal expansion of the CF was measured for both CF grades at about 6C, 3C, 1C, 0.4C and 0.1C-rates separately during 5 to 10 electrochemical cycles. In this context 6C means fast charge resulting in a low ion content where 0.1C corresponds to a low charge rate resulting in a very high ion content. These charge rates converts to capacities of the carbon fibre electrode between approx.. 55 to 350 mAh/g from 6C to 0.1C charge rates, respectively.

Figure 3 shows the variations of the tensile load carried by the IMS65 CF specimens subjected to a constant extension during electrochemical cycling at the different rates. Similar results were found for T800 CFs. The green curve (with square markers) is for the bag relaxation only (no fibres loaded), and is used as a reference to distinguish the variations of the load carried by the CF specimen and the residual load relaxation in the bag. For each cycling rate, the relaxation of the load carried by the bag is obvious during the first 3h after which the electrochemical cycling is started. The force drops during lithiations, remains unchanged during potential relaxations and increases during delithiations. Since the CF stiffness can be considered as unchanged [6], these curves indicate a longitudinal expansion of the CFs during Li insertion which is partially recovered with a longitudinal contraction after extraction of the same.

![Figure 3: Tensile load carried by IMS65 CF specimens subjected to a constant extension during electrochemical cycling at different rates.](image)

For each rate the drop of load during the first lithiation is not fully recovered by the load increase during the first delithiation. There is a first-cycle irreversible expansion which remains in the CFs. For the next cycles the expansion is reversible as well as the measured capacity.
Figure 4 shows the longitudinal expansion of IMS65 and T800 CFs with the specific capacities measured after 5 cycles at different cycling rates. The tendencies of the measurements are similar for both CF grades. The reversible expansion during lithiation increases almost linearly with the measured capacity. The irreversible expansion of the delithiated fibres remains almost unchanged after the first cycle and is also higher for higher measured capacities during electrochemical cycling. Thus, the main impact of the measured capacity is seen on the total expansion of the lithiated fibres. At the fastest cycling rate (about 6C), the measured capacity is about 56mAh/g and the expansion of the lithiated fibres is the smallest measured, about 0.15% for both CF grades. On the contrary, at the lowest rate (about 0.1C) the measured capacity is close to the saturated value of lithium storage in pure graphite (372mAh/g). The CFs are considered as fully lithiated, the expansion is the highest, about 1.03% for IMS65 fibres and 1.05% for T800 fibres.

![Figure 4: Longitudinal expansion of IMS65 and T800 CFs for different capacities measured after 5 electrochemical cycles.](image)

The electrical work, in this case transferred from the cell (since the CFs are connected to a Li electrode), $W_{elec}$ (in J/kg) is given by

$$W_{elec} = I \times \int E\, dt/m$$

where $I$ is the constant current applied (in A), $\int E\, dt$ is the definite integral of the measured cell potential (in V) over the charging time (in s), and where $E$ depends on the choice of counter electrode. The specific strain energy $U_{mech}$ (in J/kg) stored in the CF specimen (mechanical work available) is

$$U_{mech} = \Delta F^2/(2Km)$$

where $K$ is the tensile stiffness of the CF specimen (in N/m), $\Delta F$ is the change measured in the tensile force (in N), and $m$ is the mass of CF electrode (in kg). Specific strain energies of 294 J/kg (523 kJ/m$^3$) and 401 J/kg (726 kJ/m$^3$) were measured during the fifth lithiation with IMS65 and T800 CFs, respectively, for a 1C charge rate. Already these values are three times higher than for lead zirconate titanate (PZT) piezoelectric ceramics (~100 kJ/m$^3$) and achieved at much lower driving voltage [12]. Yet, at lower charge rates (0.1C) the extension is 2-3 times higher and will result in 5-10 times higher actuation energies. Since carbon fibres are extremely stiff, very large forces can be created at low electrical potential.

A carbon fibre with a Young’s modulus of 300 GPa that can swell 0.5% when intercalated with lithium would have a gravimetric energy density of more than 2000 J/kg, i.e. 100 times higher than for PZT! Such an actuator would however be slow compared to PZT but would on the other hand create very large forces per unit weight, and at much lower voltage. This actuation can also be coupled to internal electrical energy storage in the same device reducing or even eliminating the need for external energy supply. New approaches to create morphing structures (structures that change shape), e.g.
5. PIEZO-ELECTROCHEMICAL ENERGY HARVESTING

Applying a mechanical force to Li-intercalated carbon fibres results in a response of the open circuit potential (OCP), i.e., of the carbon fibre electrode potential when disconnected from any circuit as discussed above.

A battery generally delivers less electrical energy during discharge than provided during charge because of a higher cell potential at charge than at discharge (electrochemical hysteresis), as shown in Figure 5a. This is due to the total cell overpotential, an induced voltage difference caused by the electrochemical processes and originating from the charge transfer processes, resistances and transport limitations in the battery cell. However, if the OCP response to a mechanical force carried by the carbon fibre electrode (piezo-electrochemical effect discussed above) overtakes the induced overpotential, more electrical energy will be delivered from the cell than provided, as schematically shown in Figure 5b. This can be achieved by lowering of the charge rate (low C-rate) making the electrochemical losses decrease, i.e. the overpotential decreases.

The carbon fibre have a higher electrode potential than the Li metal and are in essence used as positive electrodes in our setup. That leads to a higher cell potential during delithiation (cell charge) than lithiation (cell discharge) of the carbon fibre electrode, opposite to the behaviour of a normal Li-ion battery cell where the carbon material acts as the negative electrode. However, the electrode potential of the counter electrode is not important for demonstration of the concept.

The procedure for harvesting energy is to carry out a 4-step harvesting cycle according to the following route [9],

1. In step 1 the applied strain is increased at OCP, which results in an increase of the OCP from an initial potential $E_0$ to $E_1$;
2. In step 2 the cell is discharged at a constant current density while maintaining the applied strain;
3. In step 3 the discharge is stopped and the applied strain is decreased, which results in a decrease of
the OCP to $E_1 < E_0$, since the fibres have been lithiated during step 2;
4. In step 4 the cell is charged at the same current density and duration as for the discharge. Thus, the final cell potential is then back to $E_0$ since the applied strain and state of charge are the same as before step 1.

The specific electrical energy harvested per cycle $W_{elec}$ is the difference between the electrical work delivered during lithiation (cell discharge) and the electrical work provided during delithiation (cell charge) of the carbon fibre electrode (the area of the encircled charge/discharge cycles shown in Figure 5b marked with “Harvested energy”):

$$W_{elec} = I \times \int_0^T E_{li} \, dt/m - I \times \int_0^T E_{deli} \, dt/m$$

where $E_{li}$ and $E_{deli}$ are the cell potentials during lithiation and delithiation, respectively, $I$ is the absolute value of the applied current, $T$ is the duration of the galvanostatic steps and $m$ is the mass of carbon fibre electrode. The harvester specific power is the useful energy per cycle divided by the cycle time. The specific energy per cycle and the specific power were measured for different current densities at electrode potentials of about 0.80 V, 0.43 V, 0.21 V and 0.07 V vs. Li/Li$^+$ (about 6 %, 24 %, 54 % and 81 % SOCs). The overpotential still induces a voltage drop between OCP and lithiation so that $\Delta E_{li} < 0$ and a voltage increase between OCP and delithiation $\Delta E_{deli} > 0$.

Lithiation of the carbon fibre electrode was consistently performed at higher potential than delithiation which clearly demonstrates the concept of piezo-electrochemical energy harvesting. Depending on the SOC, the current density below which it was possible to perform a harvesting cycle was 1.2-2.5 mA/g and the specific power reaches a maximum at 0.8-1.2 mA/g. The specific power is expectedly lower at the lowest current densities because the measured capacities are smaller during those galvanostatic steps. At higher charge rates the specific power is also expectedly smaller because the overpotential increases. A maximum of 0.85 µW/g was measured at an electrode potential of 0.43 V vs. Li/Li$^+$ (about 20% SOC) for a current density of 1.2 mA/g. At higher and lower SOC the specific power was lower.

Considering a density of 7.5 g/cm$^3$, the typical specific power of MEMS PZT piezoelectric energy harvesters are in the order of 100 µW/g. However, the frequencies are typically 100-1,000 Hz which leads to a specific energy per cycle in the order of 0.1-1 µJ/g per cycle. The specific energy per cycle of the present harvester is much higher, 100-350 µJ/g per cycle at a frequency of 2.5 mHz (for 400 s cycle time), and it could be even higher for higher cycle times. The energy should therefore be harvested from mechanical motions of very low frequencies. There are, however, several paths to significantly increase the frequency and power.

6. CONCLUSIONS AND FUTURE WORK

This work shows completely new paths for sensing, actuation and energy harvesting using Li intercalation in carbon fibres which appears to be general this type of material. It could open up for a new field of research possibly involving other ion intercalating materials and electrochemical processes.

There are several paths to significantly increase the frequency and power of both the actuation and energy harvesting functions. We have used carbon fibre bundles herein but the overpotentials can be decreased and the rate of lithiation increased significantly when using single fibres. By using e.g. spread fibre bundles one can increase the current density (charge rates) and thereby both increase the actuation rate and energy harvesting power. Both these functionalities are dependent on the rate of ion transport in the electrolyte and the rate of diffusion in the carbon fibre, so any means to increase these will increase the performance.

Since this approach is based on the concept for Li-ion battery technology the same device can also be used for storing energy by just adding an appropriate counter electrode, forming a true Li-ion battery cell. One vision of this work is to construct a material combination that can sense loads, actuate (and morph) and harvest mechanical energy and store it in the same device.
ACKNOWLEDGEMENTS

We thank the Swedish Research Council, projects 621-2012-3764 and 621-2014-4577, the Swedish Energy Agency, project 37712-1 and the strategic innovation programme LIGHTer (provided by Vinnova, the Swedish Energy Agency and Formas) for financial support. The Swedish research group Kombatt is acknowledged for its synergism throughout this work.

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