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Piezo-electrochemical effect in lithium-intercalated carbon fibres

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Abstract

In this paper we have conducted experiments to investigate the coupling between electrochemical and mechanical properties of lithium (Li)-intercalating carbon fibres (CFs). The results show promising potential for new functionalities of CFs for electrochemical actuation, sensing and energy harvesting. Li-intercalation at 1C-rate in CFs subjected to a constant tensile extension induced a reversible longitudinal expansion of approximately 0.30 % which can be used as mechanical actuation. Varying the tensile extension of lithiated CFs resulted in a piezoelectric response of the open-circuit potential, in the range of several mV, enabling strain sensing. If the electrical potential is kept constant during a tensile extension a piezo-electrochemical current response is found with a ~50 % mechanical to electrical energy conversion efficiency, enabling energy harvesting.

Keywords: Carbon fibres; Lithium intercalation; Electrochemical actuation; Piezoelectric effect; Piezo-electrochemical effect

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1. Introduction

A novel solution to mass reduction is possible for many applications such as hybrid vehicles which require mechanical components and energy storage devices, by combining the two functions in a lightweight material using carbon fibres (CFs) as structural electrodes. Indeed, the CF has high specific tensile properties and a carbonaceous microstructure which enables reversible lithium (Li)-intercalation reactions.

Previous research [1,2] has shown that the electrochemical energy storage capacities of polyacrylonitrile (PAN)-based CF tows depend on the electrochemical cycling rate (C-rate), but can be as good as ordinary graphite-based commercial electrode materials. Other research [3,4] has shown that Li-intercalation induces a drop of the ultimate tensile strength and a longitudinal expansion of the CFs. However, the effect of an external tensile force on the electrochemical performance of the CFs, which is of high interest for the multifunctional modelling of structural electrodes, is still unknown [5].

Specimens are manufactured from two grades of PAN-based CF tows. The electrochemical behaviour of specimens subjected to a constant tensile extension and simultaneously lithiated at 1C-rate is first tested. The lithiated specimens are then subjected to a varying tensile extension while measuring either the cell open-circuit potential (OCP) or a possible current response at a constant potential. For each test, the measured electrochemical properties are correlated with the tensile force acting on the CF specimens.

2. Material and methods

2.1 CF tensile specimens

Two grades of intermediate modulus PAN-based CFs, IMS65 24K 830tex unsized (Toho Tenax) and T800HB 6K 40B P1 BB 223tex sized (Torayca) were used. Their electrochemical capacities, measured after 10 electrochemical cycles at 1C-rate, are 177 mAh/g and 136 mAh/g respectively [2]. Specimens made of CF tows were manufactured with 22 mm gauge length and end tabs which fit in a 300 N microtester, as described in [3,4]. The CF mass estimates of the IMS65 and T800H specimens were

about 2.2 ± 0.1 mg (2890 ± 130 filaments) and 3.0 ± 0.1 mg (3770 ± 180 filaments), respectively.

2.2 Electrochemical cells

The CF specimens were used as electrodes in laboratory Li-ion half-cells manufactured in a glovebox under inert argon atmosphere with less than 1 ppm $[O_2]$ and $[H_2O]$ at ambient temperature. Each cell was made of a single CF specimen and a Li metal foil electrode with copper and nickel foils as current collectors, and a glass microfibre separator (Whatman GF/A) impregnated with 150 μ L 1.0 M $LiPF_6$ in EC:DEC (1:1 w/w, LP40 Merck) electrolyte. The cell assembly was heat sealed inside a vacuum bag (Skultuna Flexible, PET / Al / PE, 12 μ m / 9 μ m / 75 μ m thick). For details, see [4,5].

2.3 Experimental setup

The cell current collectors were connected to a Solartron 1286 Electrochemical Interface and the laminate bag was clamped onto the end tabs of the CF specimen inside the jaws of the microtester [4,5]. The bag and the CF specimen were therefore loaded in parallel. The external tensile force acting on the CF specimen was estimated from the specimen tensile stiffness (measured in a subsequent tensile test) times the tensile extension applied. Prior to testing, a constant tensile extension (~ 0.50 % of strain in the CF) was applied to allow the load relaxation in the bag for about 3h.

3. Results and discussion

3.1 Electrochemical actuation

In the first series of tests the behaviour of a CFs subjected simultaneously to a constant tensile extension and a galvanostatic electrochemical cycling at about 1C-rate was investigated. Figure 1 shows the electrode potential during the fifth electrochemical cycle and the variations of the tensile force carried by a CF specimen which reflect a reversible longitudinal expansion of 0.20 % and 0.28 % for IMS65 and T800H, respectively, as measured in [4]. The main result here is that the expansion of the CFs due to intercalated Li corresponds to an elastic tensile strain that allows mechanical actuation, which consists of converting electrical work into mechanical work.

Fig. 1. Electrochemical actuation. Changes in the tensile force carried by an IMS65 CF electrode which reflect a tensile strain growth induced by intercalated Li at 1C-rate.

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

$$W_{\text{elec,Galvanostatic}} = I \times \int E \, dt / m \quad (1)$$

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

$$U_{\text{mech}} = \Delta F^2 / (2 \times K \times m) \quad (2)$$

where K is the tensile stiffness of the CF specimen (in N/m), ΔF 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/m³) and 401 J/kg (726 kJ/m³) were measured during the fifth lithiation with IMS65 and T800H CFs, respectively. The values are three times higher than for lead zirconate titanate (PZT) piezoelectric ceramics (~100 kJ/m³) and achieved at much lower driving voltage [6]. Yet, at lower charge rates (0.1C) the extension is 2-3 times higher [4] and would thus results in 5-10 times higher actuation

energies. The energy conversion efficiencies ($U_{\text{mech}} / W_{\text{elec}}$) are in the order of 0.20-0.26% and quite low. However, since carbon fibres are extremely stiff, very large forces can be created at low electrical potential.

3.2 Piezoelectric response of the OCP to the tensile force

In the second type of test the effect of a varying tensile strain on the OCP was investigated. CFs were subjected to 5 electrochemical cycles at about 1C-rate and 50 h of cell relaxation. The tensile strain was varied while measuring the OCP. Figure 2 shows this piezoelectric 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 ($8\text{e-}5 \text{ s}^{-1}$) and high ($1\text{e-}3 \text{ s}^{-1}$) 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).

Fig. 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

$$\Delta E = k \times \Delta \epsilon \quad (3)$$

where ΔE the change of the measured OCP induced by the variation of the tensile strain $\Delta \epsilon$ 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 T800H, respectively. For sensing purposes k can be seen as gauge factor.

3.3 Piezo-electrochemical current response to the tensile force at a constant potential

In the third test series the cell potential was kept constant while applying a varying tensile strain on charged CFs lithiated at about 1C-rate. The tensile strain was first increased and then decreased to its initial value, at the same low strain rate as used in section 3.2. Figure 3 shows this piezo-electrochemical current response induced by the tensile force acting on a lithiated IMS65 CF specimen. When the force is increased and stabilized at a higher value, a negative current is generated reflecting a lithiation for about ~ 1 h, charging the carbon fibre. The reason is that the OCP increases as in section 3.2 due to the increase of the force, and a change in the degree of lithiation is induced to bring the CFs to a new equilibrium. The reverse reaction (potentiostatic delithiation) occurs when the tensile force is decreased. The response appeared to be reversible whatever the strain rate, and is triggered faster than the sample time used for data acquisition (100 ms).

The mechanical work W_{mech} delivered to the CFs results not only in a change of the specific strain energy, but also in an electrochemical work $W_{\text{elec,Potentiostatic}}$ (also affecting the specific strain energy, as shown in 3.1) which are calculated from

$$W_{\text{mech}} = K \times \Delta L^2 / (2 \times m) \quad (4)$$

$$W_{\text{elec,Potentiostatic}} = E \times \int I \, dt / m \quad (5)$$

where K is the tensile stiffness of the CF specimen (in N/m), ΔL is the change in the tensile extension applied (in m), E is the constant potential of the cell (in V), $\int I \, dt$ is the definite integral of the measured current (in A) over the Li-intercalation reaction duration (in s), and m is the mass of CF electrode (in kg). When the tensile strain is increased $\sim 0.60\%$, the mechanical to electrochemical energy conversion $W_{\text{elec,Potentiostatic}} / W_{\text{mech}}$ is about 58 % and 47%, and $W_{\text{elec,Potentiostatic}}$ is 1176 J/kg and 853 J/kg for IMS65

and T800H CFs, respectively. This corresponds to an increase of intercalated Li of 1.56 mAh/g and 1.34 mAh/g, respectively.

Fig. 3. Piezo-electrochemical effect. Measured current response at constant potential to the external tensile force applied on an IMS65 CF electrode after full lithiation at about 1C-rate.

3.4 Overview of the results

Figure 4 presents an overview of the results. For each of the three test series, an arrow indicates the response to a pulse indicated with another arrow. In the actuation test, the strain increases as a response to the increased degree of lithiation of the CFs. In the piezoelectric test, the OCP reflects the electrochemical potential and goes up when the strain is increased. Lastly in the piezo-electrochemical effect, a current is induced to bring the CFs to a new equilibrium when the strain is increased at a constant potential. Further work is needed to measure the relationship between the strain sensitivity of the OCP and the current response with the initial amount of intercalated Li in the CFs. The conversion between mechanical, electrical and electromechanical energy also needs to be clarified.

Fig. 4. Overview of the multifunctional behaviour of Li-intercalated CFs. Pulses and responses in the electrochemical actuation (circle marker), piezoelectric effect (plus sign marker) and piezo-electrochemical effect (asterisk marker).

4. Conclusion

New functionalities of Li-intercalated CFs are presented in this work. Li-intercalation reactions induce a reversible longitudinal expansion of the CFs providing mechanical work which could be used for actuation. A piezoelectric effect is measured as a linearly reversible response of the OCP to a tensile force acting on lithiated CFs which can be used for sensing purposes. Finally, a current response is generated from the mechanical work of tensile force acting on lithiated CFs at a constant potential, providing a piezo-electrochemical effect which could be used to convert mechanical energy to electro-chemical energy.

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