Fiber asymmetric supercapacitor based on FeOOH/PPy on carbon fibers as anode electrode with high volumetric energy density for wearable applications

Gong, Xuefei; Li, Shaohui; Lee, Pooi See

2017

Gong, X., Li, S., & Lee, P. S. (2017). Fiber asymmetric supercapacitor based on FeOOH/PPy on carbon fibers as anode electrode with high volumetric energy density for wearable applications. *Nanoscale*, 9(30), 10794-10801. doi:10.1039/C7NR02896B

<https://hdl.handle.net/10356/138818>

<https://doi.org/10.1039/C7NR02896B>

© 2017 The Royal Society of Chemistry. All rights reserved. This paper was published in *Nanoscale* and is made available with permission of The Royal Society of Chemistry.

Downloaded on 26 Apr 2023 20:37:13 SGT

Nanoscale

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Gong, S. Li and P. S. Lee, *Nanoscale*, 2017, DOI: 10.1039/C7NR02896B.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Fiber asymmetric supercapacitor based on FeOOH/PPy on carbon fibers as anode electrode with high volumetric energy density for wearable applications

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Gong Xuefei,^a Li Shaohui^a and Lee Pooi See^{*a}

Fiber supercapacitors are promising energy storage devices for wearable applications. However, the fiber supercapacitors are currently limited by the mediocre capacitance performances due to the use of typical carbon materials as anode, sacrificing the volumetric energy density of the whole device. In addition, the inability to undergo washable cycles and poor self-discharge rate prevents the fiber-shaped supercapacitors to be a true energy textile and affects their practicability. Hence, the porous anode electrode FeOOH/PPy@CF has been firstly prepared with a high volumetric capacitance of 30.17 F cm⁻³, contributing to a high volumetric energy density of 2 mWh cm⁻³ (based on the whole encapsulated device) for a fiber asymmetric supercapacitor MnO₂@CF//FeOOH/PPy@CF in PVA/LiCl. Good flexibility could be exhibited when it was woven into a glove. Desired working voltage and capacity output could be easily obtained when connecting devices in series and parallel. The encapsulated device could work stably even after they were dipped multiple cycles in different solution and with intensive stirring water that assimilates washing cycles. The self-discharge rate can be mitigated when ionogel electrolyte ([EMIM][TFSI]/FS) was incorporated and further enhanced the energy density to 3.7 mWh/cm³. The outstanding properties of our assembled asymmetric fiber supercapacitor device is a good candidate for practical wearable energy storage devices.

Introduction

With rapid developments of wearable electronics, flexible energy conversion/storage devices have attracted more and more attention in recent years.¹⁻⁴ With the merits of small-size, lightweight, high flexibility and knittability or weavability, fiber supercapacitors (FSC) are considered as promising energy storage devices for wearable applications.^{1, 5-8} However, unsatisfactory energy density is one challenge for fiber-shaped supercapacitors even though they could deliver high power density and excellent cycling life.⁹

Recently, tremendous efforts have been devoted to improving energy density of fiber-shaped supercapacitors, including synthetic approach of nanostructured materials with high specific capacitance and employment of asymmetric design with extended voltage window. For example, Zhang's group¹⁰ incorporated pseudocapacitive materials of MoS₂ into the cathode electrode, thus contributing to obtain an enhanced energy density (1.4 mWh/cm³) of asymmetric fiber-shaped supercapacitors (MoS₂/rGO/MWCNT//rGO/MWCNT) with voltage window of 1.4 V. Similarly, a flexible fiber-shaped supercapacitor with PANI decorated carbon fibers as cathode

electrode and functionalized carbon fibers as anode electrode achieved energy density of 1.7 mWh/cm³ with wide voltage window of 1.8 V.¹¹ It should be noted that most of the fiber-shaped supercapacitors utilized carbon materials as anode electrode because of their high electrical conductivity and wide potential range. However, the limited specific capacitances of carbon based materials indicate the need of large volume to match the capacitance of cathode electrodes, thus sacrificing the volumetric capacitance and energy density of the whole device. Therefore, it is highly desirable to develop anode materials with high volumetric capacitance to match the excellent capacitive performance of cathode materials.

As a new class of negative electrode materials, iron-based materials hold great promise to replace carbon-based negative materials because of their large theoretical capacitance, wide voltage window in negative potential, rich abundance, low cost and environmental friendliness.¹²⁻¹⁸ Orthorhombic γ-FeOOH composes of layered structures with double chains of [FeO₆] octahedral unit. The interlayer is linked by hydrogen bonding with interlayer spaces of 12.52 Å, much larger than the size of solvated cations, which is beneficial to ion transport.¹⁹

Although fiber-shaped supercapacitors can be easily woven into textiles to realize easy knittability, washability is one essential step for wide utilization in practical wearable applications. However, the washability of fiber-shaped supercapacitors were rarely evaluated. Simply dipping fabric supercapacitors into water cannot totally simulate the real

^a School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Blk N4.1, 639798, Singapore. E-mail: pslee@ntu.edu.sg
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

wearables because sweat and rain drops are not neutral.²⁰ In addition, the real wearing environment is harsher and more intensive especially when they are subjected to washing by machine.

On the other hand, overemphasizing energy density while neglecting self-discharging rate cannot evaluate fiber-shaped supercapacitors appropriately. The self-discharge rate is the index of energy retention after charging of supercapacitors. Typically, the aqueous-based supercapacitors suffer from quick loss of stored energy. Unfortunately, most of the assembled fiber-shaped supercapacitors were fabricated with aqueous-based electrolyte (like PVA/H₂SO₄, PVA/KOH, PVA/LiCl)²¹ and their self-discharge performance were not accounted.

In this work, we report a simple electrodeposition method to synthesize porous FeOOH/PPy on carbon fibers (denoted as FeOOH/PPy@CF) as fiber anode electrode. To the best of our knowledge, this is the first report of nanowired γ-FeOOH/PPy being used as anode electrode materials. Coating conducting polymer (such as polypyrrole) on the surface of active materials is one favorable approach to improve electrical conductivity and further enhance capacitance.^{22, 23} In addition, conducting polymer could accommodate volumetric changes (swelling and shrinking) and prohibit structural collapse during charging and discharging processes, thus improving the cycling performance. With the highly porous structures and the protective layer of PPy, the as-prepared pseudocapacitive fiber anode electrode exhibited high volumetric capacitance, good rate capability and excellent cycling stability. Subsequently, an encapsulated fiber asymmetric supercapacitor (of total diameter of 1.3 mm, length of 2 cm) based on MnO₂ coated on carbon fiber (denoted as MnO₂@CF) as cathode electrode and FeOOH/PPy@CF as anode electrode in PVA/LiCl gel electrolyte package with Ecoflex was fabricated, which could deliver a high volumetric energy density of 2 mWh cm⁻³ (based on the whole device), comparable to those of a 4V-500 μAh thin-film lithium batteries²⁴ and higher than most reported fiber supercapacitor^{6, 24-27}. In addition, the as-assembled device displayed good flexibility when woven into a glove, easy scalability when connected in series and parallel and increasing length, and good stability at different moisture conditions even under intensive mechanical stirring. The employment of ionogel electrolyte further enhanced the energy density and mitigated self-discharge rate, thus contributing to lighting up a LED for several minutes, demonstrating a desirable energy storage device for practical wearable electronics.

Experimental

Materials

Carbon fibers (Toray®T1100G with tensile strength of 6.6 GPa) were cleaned with acetone, ethanol and deionized water for several times and dried at 60°C overnight for following experiments. All the chemicals used in our study were purchased from Sigma-Aldrich and of analytical grade without further purification.

Preparation of FeOOH/PPy and MnO₂ on carbon fibers as anode and cathode materials

DOI: 10.1039/C7NR02896B

The anode materials of FeOOH/PPy and cathode materials of MnO₂ nanowires on carbon fibers were synthesized through simple potentiostatically electrodepositions. Typically, the FeOOH was deposited on carbon fibers in a two-electrode system with a Pt foil as counter electrode. The deposition was performed at 0.7 V in 0.01 M ferrous ammonium sulfate ((Fe(NH₄)₂SO₄) and 0.04 M sodium acetate ((CH₃COO)Na) solution for different time. Prior to deposition, the solution was degassed with N₂ for 30 min. For the depositions of PPy on FeOOH and MnO₂ on carbon fibers, they were conducted in a standard three-electrode system with a Pt foil as counter electrode and Ag/AgCl as reference electrode. The electrolyte for deposition of PPy was 0.1 M pyrrole monomer and 0.5 M sodium chloride (NaCl) and the applied potential was 0.8 V. Similarly, cathode materials of MnO₂ were electrodeposited at 0.6 V in 0.1 M Manganese acetate tetrahydrate ((CH₃COO)₂Mn · 4H₂O) and 0.1 M sodium sulfate (Na₂SO₄) solution for 1 hour. The mass loading of active materials (FeOOH and MnO₂) were calculated from the total Faradic charge with the equation: The mass loading of active materials (FeOOH and MnO₂) was calculated from the total Faradic charge with the equation:

$$m = \frac{Q}{nF} \times M \quad (1)$$

Where Q is the total Faradic charge during electrodeposition processes, n is the charge transfer number, F is the Faradic constant and M is the relative molecular mass. For conducting polymer PPy, the mass loading was evaluated with minor revised formula:

$$m = \frac{Q}{(2+y)F} \times M \quad (2)$$

Where y is a stoichiometric factor evaluating the insertion degree of PPy. Here insertion degree of 0.2 was applied.²⁸ Through the above equations, the mass loading of FeOOH, PPy and MnO₂ on carbon fibers were 0.679 mg, 0.327 mg and 2.1 mg, respectively. The diameter of electrodes was 0.5 mm, seen from Figure S1.

Fabrication of solid-state fiber asymmetric supercapacitors

Aqueous gel electrolyte of PVA/LiCl was prepared through mixing LiCl (10.5 g) and PVA (6 g) in 50 mL deionized water under stirring at 80 °C until the solution became clear. Ionogel electrolyte of ([EMIM][TFSI]/FS) was synthesized by adding 167 mg fumed silica into 5 mL ionic liquid [EMIM][TFSI] and stirring for 2 days. The solid-state supercapacitors were assembled by immersing cathodes and anodes into gel electrolytes for 20 minutes and then twisted together, dried at 45 °C until gel solidification.

Encapsulation of full device with Ecoflex

The Ecoflex pre-polymer and the curing agent (Ecoflex 0050) were mixed with the weight ratio of 1:1. Subsequently, the assembled device was immersed in the uncured mixture for 5 minutes. After curing at room temperature for 1h, a thin film of Ecoflex could be obtained around the device (Figure S2).

The resultant diameter of the encapsulated fiber-shaped supercapacitor was 1.3 mm, as seen in Figure S2.

Materials characterization

The crystallographic information and chemical states and composition of electrode materials were investigated by X-ray diffraction (XRD, Bruker D8 Advance with the Cu K α radiation) and X-ray photoelectron spectroscopy (XPS, VG ESCALab 220i-XL with monochromatic Al K α radiation). The morphology and microstructures of electrode materials were characterized by field-emission scanning electron microscopy (FE-SEM 7600F) and transmission electron microscope (TEM, JEOL 2010).

Electrochemical measurements

All the electrochemical measurements were conducted using Autolab electrochemical workstation. Electrochemical impedance spectroscopy was measured at a frequency ranging from 0.1 Hz to 100 kHz with potential amplitude of 5 mV. The electrochemical performances of individual electrode were measured using three-electrode system with Pt foil as counter electrode and Ag/AgCl as reference electrode in 5 M LiCl. The capacitances were calculated derived from CV curves through integration current (i) and voltage (u). The volumetric capacitance was based on the volume of whole electrode.

$$C_{\text{electrode}} = \frac{1}{vU} \int_0^U i(u) du \quad (3)$$

$$C_{v\text{-electrode}} = \frac{C_{\text{electrode}}}{V_{\text{electrode}}} \quad (4)$$

For the full device, the electrochemical performances were tested with PVA/LiCl as gel electrolyte and charging-discharging profiles were used to calculate capacitances. The volumetric capacitances were based on the volume of whole device. The energy density and power density of the full device were obtained by the following formula.

$$C_{\text{device}} = \frac{It}{U} \quad (5)$$

$$C_{v\text{-device}} = \frac{C_{\text{device}}}{V_{\text{device}}} \quad (6)$$

$$E_{\text{device}} = \frac{1}{2} \frac{C_{\text{device}} U^2}{3600 V_{\text{device}}} \quad (7)$$

$$P_{\text{device}} = \frac{3600 E_{\text{device}}}{t} \quad (8)$$

Where v is the scan rate, U is the voltage window, I is discharging current, t is the discharging time, $V_{\text{electrode}}$ and V_{device} is the volume of single electrode and whole device, respectively. The individual electrode and full device was roughly considered as a cylinder and their volumes were calculated by using the equation:

$$V = \frac{\pi d^2 L}{4} \quad (9)$$

where d is diameter and L length of the fibers. The diameter of electrode and encapsulated device was around 0.5 mm (Figure S1) and 1.3 mm (Figure S2), respectively.

Results and discussion

Characterization of FeOOH/PPy@CF as anode materials

The simple two-step electrodeposition for the preparation of nanostructured FeOOH/PPy on carbon fibers is schematically shown in Figure 1a. FeOOH was first deposited onto the

Figure 1. Schematic diagram illustrating the synthesis procedure of FeOOH/PPy on carbon fibers. SEM of (b) pure carbon fibers, (c) FeOOH and (d) FeOOH/PPy on carbon fibers. (e) TEM of FeOOH/PPy.

substrate of carbon fibers. Subsequently, PPy was coated onto FeOOH/CF. The morphologies of pure CF, FeOOH@CF and FeOOH/PPy@CF were examined using scanning electron microscopy (SEM). As shown in Figure 1c, the prepared FeOOH exhibited one-dimensional nanowires and were vertically grown on carbon fibers, forming open porous structures and facilitating charge transport. Figure 1d reveals that the porous morphology remained after PPy coating on FeOOH. TEM was measured to further examine the FeOOH and PPy coating as seen in figure 1e. The diameter of the FeOOH nanowire is about 10 nm and the coating layer of PPy is about 3 nm.

The X-ray diffraction (XRD) patterns of pure CF, FeOOH@CF and FeOOH/PPy@CF are shown in Figure 2a. The typical diffraction peaks of (031), (051) and (002) could be indexed as orthorhombic FeOOH, in agreement with the JCPDS (No. 76-2301). The peak intensity of FeOOH/PPy was obviously weaker than that of FeOOH, which could be attributed to the semi-crystalline nature of PPy.^{22,29} The corresponding X-ray photoelectron spectroscopy (XPS) was measured to further analyze surface elements and valence states of as-prepared materials. As shown in Figure 2b, there are two distinct peaks located at 711.4 eV for Fe 2p_{3/2} and 725 eV for Fe 2p_{1/2} and one shake-up satellite at 719.5 eV in the Fe 2p core level spectrum, which are characteristics of Fe³⁺ in FeOOH.¹⁸ Figure 2c shows the O 1s spectrum of FeOOH/PPy@CF electrode, which could be fitted into two constituent peaks corresponding to Fe-O-Fe bond at 530.0 eV and Fe-O-H bond 531.2 eV.¹⁸ The N 1s spectrum was used to identify the neutral and positively charged nitrogen atoms in PPy, as seen in Figure 2d. The peaks

at 397.7 eV, 399.6 eV and 401.3 eV were corresponding to the deprotonated imine group (=N-), neutral pyrrolylium nitrogen (-NH-) and charged polaronic nitrogen (N⁺), respectively.^{30, 31}

Figure 2. (a) XRD patterns of pure carbon fibers, FeOOH and FeOOH/PPy on carbon fibers. XPS spectra of (b) Fe 2p, (c) O 1s and (d) N 1s of FeOOH/PPy@CF.

The electrochemical performances of prepared FeOOH@CF and FeOOH/PPy@CF for different electrodeposition time were measured by cyclic voltammetry methods. Figure S3a shows volumetric current of CV curves for FeOOH@CF enhanced significantly with deposition time from 1 h to 3 h at a scan rate of 50 mV/s, which was related to the increasing loading amount of active materials. However, the volumetric current of CV curve for 4 h deposition decreased due to poor utilization of active materials and increased resistance at higher thickness. The phenomenon could be also verified from the volumetric capacitances (based on the total electrode) of FeOOH@CF with different deposition time, as illustrated from Figure 3a. Hence, a longer electrodeposition time up to 3 hours could render higher porous active mass loading with improved volumetric capacitance and facilitated the ease of electrolyte diffusion in the porous FeOOH on carbon fiber. In other words, the optimized deposition time for FeOOH was 3 hours. Similarly, Figure 3b and S2b indicate the optimized electrodeposition time of PPy on FeOOH@CF

Figure 3. Volumetric capacitance of (a) FeOOH@CF and (b) FeOOH/PPy@CF with different deposition time at scan rates from 10-100 mV/s. (c) CV curves of anode electrode FeOOH/PPy@CF at different scan rates from 10-100 mV/s. (d) Cycling performances of FeOOH @CF and FeOOH/PPy@CF at scan rate of 50 mV/s.

was 180 s. Notably, the optimum volumetric capacitance of prepared FeOOH/PPy@CF electrode could be as high as 30.17 F cm⁻³ at scan rate of 10 mV/s, which is higher than many other reports, such as MnO₂/RGO/CF (12 F cm⁻³ @2 mA cm⁻²)²⁵, MoS₂-rGO/MWCNT fiber (6 F cm⁻³ @0.07 mA cm⁻²)²⁶, Activated carbon fiber (15 F cm⁻³ @10 mV s⁻¹)²⁷, PANI@CF (15 F cm⁻³ @10 mV s⁻¹)¹¹. The evident redox peaks from CV curves (Figure 3c) indicate typical pseudocapacitive properties of FeOOH and PPy, contributing to the high volumetric capacitance. The redox mechanism of γ-FeOOH involves in the reversible insertion/extraction of ions into/from the layered chains of [FeO₆] octahedral unit¹⁸, which can be described as the following equation:

As seen from Figure S3 (a) and (b), CV curves of FeOOH/PPy@CF displayed one evident pair of redox peaks (-0.1 V and -0.3 V) compared to that of FeOOH@CF, which can be ascribed from doping/undoping process of PPy during charging/discharging. EIS measurements (Figure S4) showed that equivalent series resistance was reduced after the coating PPy, thus indicating PPy could enhance the electronic conductivity of interior FeOOH. From Figure 3d, we can see the capacitance retention was 84% after 5000 cycles. It should be noted that the capacitance dropped at initial 1500 cycles while stabilized for the following 3500 cycles and there is a trend the stabilization can be continued, which suggests superior cycling stability. The improved cycling behavior could be attributed to conducting polymer PPy, which could prevent the dissolution of FeOOH and buffer the volume expansion/contraction of the interior FeOOH during charging/discharging process. Hence, the excellent electrochemical performance of FeOOH/PPy@CF present promising anode materials for fiber supercapacitor.

Electrochemical characterization of fiber asymmetric supercapacitor based on FeOOH/PPy@CF anode and MnO₂/CF cathode

In order to further investigate the superiority of FeOOH/PPy@CF as anode electrode, we designed a solid-state fiber asymmetric supercapacitor with MnO₂@CF as cathode electrode. As shown in Figure 4a, the fabricated device could be stably operated in different voltages, ranging from 0.8 V to 1.6 V. The CV curves at different scan rates (Figure 4b) showed approximately rectangular shape, indicating capacitive behavior. From Figure 4c, the volumetric capacitance (based on the whole volume of the device) could be as high as 5.5 F cm⁻³ at current density of 5 mA cm⁻³. Furthermore, 63.8% of the volumetric capacitance could be retained when the current density increased from 5 to 100 mA cm⁻³. The good rate capability could be ascribed to the porous structures of electrode materials which provided efficient ion channels. Figure 4d shows that 82% of the initial capacitance was retained after 5000 cycles, demonstrating good performance stability. As illustrated in the Nyquist plot of the device (Figure 4e), the intercept of high-frequency region with the real axis represents equivalent series resistance (ESR), which could be as low as 25 Ω. The small semi-circle region represents charge transfer resistance, estimated to be 5 Ω, indicating rapid charge transport. The nearly vertical line at low frequency region

Figure 4. (a) CV curves with different voltage windows at a scan rate of 20 mV/s, (b) CV curves at different scan rates, (c) volumetric capacitance at different current densities, (d) cycling performance at the scan rate of 100 mV/s, (e) Nyquist plots and (f) Ragone plots comparing with previous works of assembled device FeOOH/PPy@CF//MnO₂/CF.

indicates easy ion diffusion. All these analyses supported superior rate capability and cycling stability. Figure 4f shows Ragone plots of our assemble device compared with previous work. Significantly, the FeOOH/PPy@CF//MnO₂/CF device could deliver

a high volumetric energy density of 2 mWh cm⁻³ (based on the volume of the whole device), which was comparable to those of 4 V-500 μ Ah thin-film lithium batteries²⁴ and higher than most reported fiber supercapacitor, such as MnO₂/CF//MnO₂/CF (0.22 mWh cm⁻³)⁶, MnO₂/rGO/CF//Graphene Hydrogel/Cu (0.9 mWh cm⁻³)²⁵, MoS₂-rGO/MWCNT//rGO/MWCNT (1.4 mWh cm⁻³)²⁶, Activated CF//Activated CF (0.35 mWh cm⁻³)²⁷.

To test the flexibility for practical wearable application, a 4-cm length fiber asymmetric supercapacitor was woven into a glove, subjected to bending tests at different angles. The devices was firstly bended to 90°, and then 180°, subsequently, the device was recovered to 90° and back to 0°. As seen in Figure 5 b and c, CV curves at different bending states changed little and capacitance ratio maintained nearly one, indicating good flexibility for wearable application.

To meet the needs of operating voltage and energy output for practical application, two fiber asymmetric supercapacitors were assembled in serial and in parallel. As shown in Figure 6a, the operating voltage could extend from 1.6 to 3.2 V when two

devices are connected in series and the CV curve remained rectangular shape. When two devices are connected in parallel, the CV curve presents a larger integrated area, suggesting more charge stored compared to a single device. From Figure 6b, we can see two serially connected device could successfully be charged to 3.2 V with almost the same discharge time of a single device. For two devices connected in parallel, the discharge time was approximately two times of that for a single device. Furthermore, for the scalable application, fiber supercapacitors with different lengths were measured. As shown in Figure 6c, the dependence of the capacitance on the device length followed a linear relationship, suggesting the promising potential for the scale-up fabrication with desired energy output. Figure 6d shows the two assembled devices with series configuration was able to light a LED, further demonstrating our assembled devices for practical wearable applications.

Figure 5. (a) Digital images, (b) CV curves at a scan rate of 50 mV/s when subjected to various bending states and (c) capacitance ratio of a 4-cm assembled device woven into a glove at different bending states.

To demonstrate waterproof features of practical wearable

Figure 6. (a) CV curves at a scan rate of 100 mV/s and (b) charging-discharging curves at a current density of 100 mA cm⁻³ for two 2-cm length assembled devices with series and parallel configurations. (c) Experimental and calculated capacitance versus the length for a full cell assembled devices. (d) Two devices in

electronic textiles, we encapsulated the assembled device with Ecoflex. Figure 7a shows the CV curves of the encapsulated device after dipped in water, acid and alkaline. The minor difference suggests our encapsulated device could work at wet or moisture environment without being affected by sweat or rain drops. Figure 7b exhibits that the capacitance of encapsulated fiber supercapacitor could be retained nearly 100% after cycling 3 h continuously in water. Even when it was dipped in stirring water with 800 rpm for 8 h, the minor difference of CV curves indicates that capacitance could be maintained 100% (Figure 7c). All of these results suggest the high potential application of our encapsulated device for wearable and washable technology.

To further enhance energy density, ionic liquid gel (ionogel) electrolytes are attractive alternative in solid-state supercapacitors compared to aqueous gel electrolytes because they are combination of ionic liquids with solid components (like polymer and silica), thus preserving their individual properties of ionic liquid and solid components, such as their wider potential window, good thermal stability and non-volatility.²¹ Meanwhile, the solid component in the ionogel electrolytes can avoid the leakage issues, beneficial to the wide applications of solid-state supercapacitors. Here, the ionogel electrolyte [EMIM][TFSI]/FS was integrated with the electrodes $\text{MnO}_2\text{@CF}$ and FeOOH/PPy@CF to fabricate an solid-state asymmetric supercapacitor.

Figure S9 (a) shows the CV curves with different potential range. With the ionogel electrolytes of [EMIM][TFSI]/Fumed silica, the voltage window could be up to 3.5 V for our asymmetric supercapacitor $\text{MnO}_2\text{@CF//FeOOH/PPy@CF}$. When the voltage range was widened to 0–4 V, there was an irregular peak during the CV scanning, indicating the decomposition of the ionogel electrolytes. Figure S9 (b) displays that the CV curves exhibited redox peaks, thus indicating typical pseudocapacitive behavior. The pseudocapacitive behavior could also be verified

Figure 7. (a) A 4-cm encapsulated device dipped in DI water. (a) CV curves of an encapsulated device dipped in DI water, pH=1 and pH=13 solution at a scan rate of 50 mV/s. (b) Capacitance retention of the encapsulated device after cycling for 3h when dipped in water. CV curves of before and after the encapsulated device dipped in water (inset) at a scan rate of 50 mV/s. (c) CV curves of the encapsulated device before and after dipped in stirring water for 8 h at a scan rate of 50 mV/s. (d) Photograph of an encapsulated device was dipped in

from the charging-discharging curves in figure S9(c), implying insertion/extraction of cations [EMIM]. The capacitance could be up to 2.18 F/cm^3 at a scan rate of 50 mV/s for our asymmetric supercapacitor with ionogel electrolytes. Even at the high scan rate of 1000 mV/s, the capacitance could be up to 0.47 F/cm^3 . With the large potential window providing from the ionogel electrolyte of [EMIM][TFSI]/FS, the energy density could be up to 3.7 mWh/cm^3 and the corresponding power density could reach 190 mW/cm^3 , much higher than those of supercapacitors with aqueous-based electrolytes PVA/LiCl as shown in Figure 8(a). The CV curves of the supercapacitor with ionogel electrolyte has been provided under bending test (Figure S10(a)), which changed very minimal, indicating ionogel electrolyte supercapacitor has a good flexibility. The supercapacitor with ionogel electrolyte also exhibited good cycling performances. After 5000 cycles, the capacitance retained 88% of its initial capacitance (Figure S10(b)).

Charged supercapacitors are usually in a relatively high energy state. Thus, they tend to self-discharge to lower the energy state due to the thermodynamic force.³² The self-discharge behavior plays a significant role in practical applications. From Figure 8(b), we can see after being charged to maximum voltage for [EMIM][TFSI]/FS supercapacitors, 1 V could be remained on an open circuit even after 4 hours. While for PVA/LiCl supercapacitors, the voltage dropped quickly to 1 V in less than half an hour. Thus, ionogel electrolytes could also mitigate the fast self-discharge rate compared to aqueous-based electrolytes. Compared to conventional EDLC supercapacitors^{32–34}, our device exhibited poorer self-discharge performance due to the pseudocapacitive materials adopted, resulting from the electrons transfer during redox reactions to discharge supercapacitors.³⁵

To further investigate the self-discharge process, the plot was redrawn by setting $\ln V \propto t$ to fit the potential driving model ($V = V_{\text{initial}}e^{-t/RC}$) or $V \propto t^{1/2}$ to diffusion controlled model ($V = V_{\text{initial}} - mt^{1/2}$),³² where V is the potential difference between cathode and anode, V_{initial} is the initial voltage of self-discharge process, R is the resistance of supercapacitors, C is the capacitance of supercapacitors, m is the diffusion coefficient and t is the time of self-discharge process. As seen from the results of the fitting (figure 8(b) inset), at the initial 7 hours, the potential driving force controlled the voltage decay while after that point, diffusion controlled force governed the voltage drop, suggesting a dual-mechanism controlled model that leads to self-discharge process. In other words, it is the combination of potential field and concentration variation leading to ion migration that can be contributed to the

Figure 8. (a) Comparison of energy density and power density and (b) self-discharge behavior between ionogel-based electrolyte [EMIM][TFSI]/FS and aqueous-based electrolyte PVA/LiCl for $\text{MnO}_2\text{@CF//FeOOH/PPy@CF}$ supercapacitors. (Inset: model fitting of

self-discharge process.

Conclusions

In summary, porous structured FeOOH/PPy was simply electrodeposited on carbon fibers as anode electrode materials. With contributions from typical pseudocapacitive materials of FeOOH and PPy delivering large capacitance, PPy accommodating the volumetric changes during charging and discharging process and the porous structures facilitating ion transport, FeOOH/PPy anode materials could exhibit excellent electrochemical performances. A fiber asymmetric supercapacitor based on MnO₂@CF//FeOOH/PPy@CF in aqueous gel electrolyte PVA/LiCl was fabricated, delivering a high volumetric energy density of 2 mWh cm⁻³. In addition, the as-assembled device demonstrated a desirable energy storage device for wearable electronics, including good flexibility, easy scale-up and excellent water-proofed features. The energy density could be increased by applying ionogel [EMIM][TFSI]/FS, which was accompanied by retarded self-discharge rate, thus further indicating our prepared devices show great promises in practical wearable applications. Furthermore, a dual-mechanism controlled model that combines potential driving and diffusion controlled forces was firstly demonstrated to responsible for the self-discharge process of ionogel-based pseudocapacitors.

Acknowledgements

This work is supported by the NRF Investigatorship (NRFI) Award No. NRF-NRFI2016-05. Gong Xuefei acknowledges the scholarship awarded by Nanyang Technological University, Singapore.

References

1. W. Zeng, L. Shu, Q. Li, S. Chen, F. Wang and X. M. Tao, *Advanced materials*, 2014, **26**, 5310-5336.
2. X. Wang, X. Lu, B. Liu, D. Chen, Y. Tong and G. Shen, *Advanced materials*, 2014, **26**, 4763-4782.
3. X. Lu, M. Yu, G. Wang, Y. Tong and Y. Li, *Energy & Environmental Science*, 2014, **7**, 2160-2181.
4. K. Jost, G. Dion and Y. Gogotsi, *Journal of Materials Chemistry A*, 2014, **2**, 10776-10787.
5. V. T. Le, H. Kim, A. Ghosh, J. Kim, J. Chang, Q. A. Vu, D. T. Pham, J.-H. Lee, S.-W. Kim and Y. H. Lee, *ACS nano*, 2013, **7**, 5940-5947.
6. X. Xiao, T. Li, P. Yang, Y. Gao, H. Jin, W. Ni, W. Zhan, X. Zhang, Y. Cao and J. Zhong, *Acs Nano*, 2012, **6**, 9200-9206.
7. Y. Fu, X. Cai, H. Wu, Z. Lv, S. Hou, M. Peng, X. Yu and D. Zou, *Advanced materials*, 2012, **24**, 5713-5718.
8. J. Bae, M. K. Song, Y. J. Park, J. M. Kim, M. Liu and Z. L. Wang, *Angewandte Chemie International Edition*, 2011, **50**, 1683-1687.
9. Y. Li, K. Sheng, W. Yuan and G. Shi, *Chemical Communications*, 2013, **49**, 291-293.
10. G. Sun, X. Zhang, R. Lin, J. Yang, H. Zhang and P. Chen, *Angewandte Chemie International Edition*, 2015, **54**, 4651-4656.

11. H. Jin, L. Zhou, C. L. Mak, H. Huang, W. M. Tang and H. I. W. Chan, *Nano Energy*, 2015, **11**, 662-670.
12. J. Liu, M. Zheng, X. Shi, H. Zeng and H. Xia, *Advanced Functional Materials*, 2016, **26**, 919-930.
13. Y. Zeng, Y. Han, Y. Zhao, Y. Zeng, M. Yu, Y. Liu, H. Tang, Y. Tong and X. Lu, *Advanced Energy Materials*, 2015, **5**.
14. P. Yang, Y. Ding, Z. Lin, Z. Chen, Y. Li, P. Qiang, M. Ebrahimi, W. Mai, C. P. Wong and Z. L. Wang, *Nano letters*, 2014, **14**, 731-736.
15. Y. Sun, X. Hu, W. Luo, H. Xu, C. Hu and Y. Huang, *ACS applied materials & interfaces*, 2013, **5**, 10145-10150.
16. L.-F. Chen, Z.-Y. Yu, J.-J. Wang, Q.-X. Li, Z.-Q. Tan, Y.-W. Zhu and S.-H. Yu, *Nano Energy*, 2015, **11**, 119-128.
17. W.-H. Jin, G.-T. Cao and J.-Y. Sun, *Journal of Power Sources*, 2008, **175**, 686-691.
18. Y. C. Chen, Y. G. Lin, Y. K. Hsu, S. C. Yen, K. H. Chen and L. C. Chen, *Small*, 2014, **10**, 3803-3810.
19. J. Majzlan, L. Mazeina and A. Navrotsky, *Geochimica et Cosmochimica Acta*, 2007, **71**, 615-623.
20. Y. Yang, Q. Huang, L. Niu, D. Wang, C. Yan, Y. She and Z. Zheng, *Advanced Materials*, 2017.
21. C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang and J. Zhang, *Chemical Society Reviews*, 2015, **44**, 7484-7539.
22. Q. Qu, Y. Zhu, X. Gao and Y. Wu, *Advanced Energy Materials*, 2012, **2**, 950-955.
23. J. S. Lee, D. H. Shin, W. Kim and J. Jang, *Journal of Materials Chemistry A*, 2016, **4**, 6603-6609.
24. J. A. Lee, M. K. Shin, S. H. Kim, H. U. Cho, G. M. Spinks, G. G. Wallace, M. D. Lima, X. Lepró, M. E. Kozlov and R. H. Baughman, *Nature communications*, 2013, **4**.
25. Z. Zhang, F. Xiao and S. Wang, *Journal of Materials Chemistry A*, 2015, **3**, 11215-11223.
26. G. Sun, X. Zhang, R. Lin, J. Yang, H. Zhang and P. Chen, *Angewandte Chemie*, 2015, **127**, 4734-4739.
27. D. Yu, S. Zhai, W. Jiang, K. Goh, L. Wei, X. Chen, R. Jiang and Y. Chen, *Advanced materials*, 2015, **27**, 4895-4901.
28. H. Lin, L. Li, J. Ren, Z. Cai, L. Qiu, Z. Yang and H. Peng, *Scientific reports*, 2013, **3**, 1353.
29. X. Zhang, X. Zeng, M. Yang and Y. Qi, *ACS applied materials & interfaces*, 2014, **6**, 1125-1130.
30. Y. Wang, M. Rouabhi and Z. Zhang, *Journal of Materials Chemistry B*, 2013, **1**, 3789-3796.
31. N. Cioffi, L. Torsi, I. Losito, C. Di Franco, I. De Bari, L. Chiavarone, G. Scamarcio, V. Tsakova, L. Sabbatini and P. G. Zambonin, *Journal of Materials Chemistry*, 2001, **11**, 1434-1440.
32. Q. Zhang, J. Rong, D. Ma and B. Wei, *Energy & Environmental Science*, 2011, **4**, 2152-2159.
33. M. F. El-Kady and R. B. Kaner, *Nature communications*, 2013, **4**, 1475.
34. Q. Zhang, C. Cai, J. Qin and B. Wei, *Nano Energy*, 2014, **4**, 14-22.
35. L. Chen, H. Bai, Z. Huang and L. Li, *Energy & Environmental Science*, 2014, **7**, 1750-1759.