High-Temperature-Endurable, Flexible Supercapacitors: Performance and Degradation Mechanism

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Current state-of-the-art supercapacitors all have a limited operational temperature, and thus, extension of the temperature range is in high demand. In this work, high-temperature-endurable, flexible supercapacitors were fabricated by a very simple method and by using commercially available, low-cost materials. The device could be operated efficiently at 120 °C, and even after 10000 cycles at an operation voltage of 2.5 V, approximately 75% of its capacitance was retained. Furthermore, its performance remained essentially unchanged even under high bending conditions. Cyclic voltammetry, electrochemical impedance spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy,

Introduction

Supercapacitors featuring high power density and a long cycle life have been intensively investigated during the last decade.^[1] However, high-temperature-endurable supercapacitors that could potentially meet the special requirements of the drilling, military, and space industries are still highly desirable. Unfortunately, studies with temperature reliability above 100 °C are very limited.^[2-9] Part of the major challenge is that for such high-temperature supercapacitors (HTSCs), every component, including the electrolyte, separator, packing case, and the active materials, should be thermally and electrochemically stable.

Probably, the most apparent issue to achieve such HTSCs is to have an electrolyte that is operational at a temperature and voltage that are as high as possible. As shown in Scheme 1, conventional aqueous electrolytes, though easy to fabricate, cannot sustain high temperatures owing to their low boiling points. The commonly used solvents in commercial supercapacitors, including acetonitrile (AN) and propylene carbonate (PC), can normally stand $< 100^{\circ}$ C for PC and <70°C for AN.[10-12] Phosphoric acid-doped solid-state electrolytes have been demonstrated to be able to stand temperatures higher than 200°C but with narrow operation voltages.^[2,3,6,13] Room-temperature ionic liquids (RTILs) have been considered as competitive candidates to address the issue of electrolytes for HTSCs, as they exhibit high thermal stability, a wide potential window, and low vapor pressure.[4,7-9,14-22] Another component of HTSCs is the separator, which allows the transport of ionic species and prevents electrical short circuits, and it also plays a major role in determining the operation temperature. Commercial separators such as cellulose and X-ray photoelectron spectroscopy revealed that there were three factors causing capacitance fading and an increase in the internal resistance. The first one was fusion of the separator during high-temperature electrochemical charging/discharging, which led to an increase in the internal resistance. The second factor was decomposition of the separator, which resulted in the accumulation of deposits on the surfaces of the positive and negative electrodes. The third factor was that possible physical separation of the active materials on the positive electrode from the current collector led to a drastic increase in internal resistance.

paper and polyethylene- and polypropylene-based porous films are not reliable for high-temperature applications, as they easily shrink at elevated temperatures, which leads to electrical shorts in the device.^[4,6,23] Glass fibers,^[8,10,12,17,20] porous alumina,^[15,16] polytetrafluoroethylene (PTFE) films,^[21] polyimide porous films,^[7] phosphoric acid doped polymers,^[2,3,6,13] clay-doped polymers,^[4,9] and SiO₂-doped polymer composites^[7,8,19] have all been studied as high-temperature separators.

Packing cases that are mainly used to seal the entire supercapacitor also play an essential role and impact the performance of supercapacitors at high temperatures. Conventional case materials such as aluminum-laminated films cannot sustain high temperatures, because polypropylene is attached inside the film.^[18] Stainless steel, which possesses high thermal stability, has been widely demonstrated as a case material of HTSCs with good performance.^[10-12,15,16,20,22] However, HTSCs using stainless-steel cases with operation

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	Supporting Information for this article can be found under: https://doi.org/10.1002/ente.201700368.

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Scheme 1. Components of conventional two-electrode SCs and the common materials used.

temperatures higher than 100 °C have rarely been reported, possibly because of the shuttle self-discharge effect determined by Fe^{2+} and Fe^{3+} ions^[24] that are derived from stainless steel at high operating temperatures and high voltages. A PTFE tape^[6] and a polyethylene terephthalate (PET) film sealed by silicon rubber^[3] were also reported in HTSCs with high operation temperatures, which is indicative of the great potential of polymers for HTSC applications. The aluminum case commonly used in commercial supercapacitors may also be applied to HTSCs, as the dense aluminum oxide on the surface of the aluminum case shows excellent thermal and electrochemical stability.

The active materials of the electrodes are also a key component of SCs that directly determine the electrochemical performance of devices. The main considerations of the active materials for the electrodes in HTSCs include cycle stability at high temperatures, effective specific surface area, and resistance. Activated carbon fabrics,^[10] carbon nanotubes,^[12] carbon nano-onions,^[16] reduced graphene oxide,^[3,4,9] carbide-derived carbons,^[21] and commercial activated carbon (AC)^[5,18,19] have all been investigated for HTSCs.

Although there are many reports on HTSCs, to the best of our knowledge, the performance of supercapacitors above 120°C with high cycling capability has only been rarely reported.^[3,4] More importantly, the degradation mechanism of HTSCs, crucial for designing better energy-storage devices, has not yet been fully addressed experimentally. Herein, we report the study of a HTSC that can operate efficiently at 120°C, and approximately 75% of its capacitance is retained after 10000 cycles at an operation voltage of 2.5 V. Moreover, the HTSC possesses outstanding flexibility, and its performance remains unchanged under bending curvatures of 0.05, 0.1, and 0.2 mm⁻¹ both at room temperature and at 120 °C. Furthermore, we systematically investigated the degradation mechanism of the HTSCs and found that the three main factors causing capacitance fading and an increase in the internal resistance were the fusion of the separator during high-temperature electrochemical charging/discharging, deposition of contaminants resulting from decomposition of the separator on the surfaces of the positive and negative electrodes, and possible physical separation of the active materials on the positive electrode from the current collector, thereby leading to a drastic increase in the internal resistance.

Results and Discussion

Optimization of electrolyte, separator, and case materials

Electrolyte

RTILs are promising candidates as electrolytes for HTSCs, as they exhibit excellent thermal stability and a wide electrochemical window.^[14] Two RTILs, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI) and 1ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄), were studied in the HTSCs, in which a glass-fiber separator, aluminum plate case, and commercial AC electrode were used. Figure S1a (Supporting Information) shows the constant-current (CC) charge-discharge measurement of the HTSCs by using EMIMBF₄ as the electrolyte at different temperatures; the figure shows that the discharge capacitance decreases drastically if the temperature is higher than 120°C. Figure S1b shows the CC curves corresponding to Figure S1a, and it shows that the voltage drop (IR drop) at initial discharge is very large at 120°C, probably as a result of corrosion of the glass-fiber separator by HF derived from the reaction of BF_4^- with residual H_2O in the RTIL during high-temperature charging/discharging. On the other hand, EMIMTFSI shows outstanding performance without apparent capacitance fading or an increase in resistance even at 150°C, as we will discuss below, and thus, it was used for further studies.

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Separator

Four types of separators were used to fabricate the HTSCs, including cellulose, PTFE, quartz fiber, and glass fiber. In this section, EMIMTFSI electrolyte, an aluminum plate case, and commercial AC were used. Figure S2a (Supporting Information) shows the CC test of the HTSCs with cellulose as the separator at different temperatures, and it is found that the cellulose separator cannot withstand temperatures higher than 120°C, at which the Coulombic efficiency rapidly decreases. Figure S2b shows the CC curves corresponding to Figure S2a, and it shows deviation from the ideal triangle shape at 120°C, which implies degradation of the SC. Such degradation is probably due to the relatively low thermal stability of cellulose, which may cause an electrical short circuit between the positive and negative electrodes. Figure S3 (Supporting Information) shows the CC test results of the HTSC with the PTFE separator at 120 °C, 2.5 V, and 1 A g⁻¹. An initial discharge specific capacitance of approximately 64 Fg^{-1} with a capacitance retention of approximately 87% after 5000 cycles is observable in Figure S3 a. One drawback of the PTFE separator is that the specific capacitance is low relative to that of the glass fiber separator ($\approx 107 \text{ Fg}^{-1}$ at $120 \,^{\circ}\text{C}$, 2.5 V, and 1 Ag^{-1} ; Figure 2a) if all of the other components in the HTSCs remain the same. Another drawback is that the IR drop is large (Figure S3b) and the internal resistance is high (Figure S3c) relative to that found with the glass-fiber separator (Figure 2b, c). The large internal resistance with the PTFE separator is confirmed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. Figure S4b (Supporting Information) shows the Nyquist plots of the HTSCs with the PTFE separator at room temperature and 120 $^\circ \text{C},$ and this result shows that the charge-transfer resistance is larger than that with the glassfiber separator (Figure 5 f). Figure S5a (Supporting Information) shows the variation in the specific capacitance with the cycle number by using the quartz-fiber separator at 120°C, 2.5 V, and 1 A g^{-1} , and it shows that the capacitance retention is approximately 80% after 5000 cycles and approximately 76% after 10000 cycles with an initial discharge specific capacitance of approximately 108 Fg⁻¹. The capacitance retention using the quartz-fiber separator is slightly larger than that using the glass-fiber separator, which is approximately 75% after 5000 cycles under the same conditions. However, the internal resistance with the quartz-fiber separator (Figure S5c) is also slightly larger than that with the glass-fiber separator (Figure 2c) if all of the other components in the HTSCs remain the same. On the basis of the above results, the glass-fiber separator was selected to study the HTSCs further.

Case materials

Three types of case materials were studied for the HTSCs, including a stainless-steel plate, an aluminum plate, and a polyimide film. In this section, EMIMTFSI, a glass-fiber separator, and commercial AC were used. Figure S6a (Support-

ing Information) shows the variation in the specific capacitance with the cycle number by using the stainless-steel plate case at different temperatures, and it indicates that the Coulombic efficiency decreases sharply at 130°C. Figure S6b (Supporting Information) shows the CC curves corresponding to Figure S6a at different temperatures. The shape of the CC curve at 130 °C is similar to that using the cellulose separator at 120 °C (Figure S2b, Supporting Information), which implies that electrical short circuits may be the reason for such a CC curve. Iron in the stainless-steel plate is likely to play a major role, resulting in electrical short circuits through the oxidation and reduction processes during the high-temperature charging/discharging measurements.^[24] Figure S6c (Supporting Information) shows that for the SC with the stainless-steel plate, the Coulombic efficiency decreases sharply at 120°C, at which point the CC curve (Figure S6d) also deviates from the triangle-type curve, which thereby implies breakdown of the SC. The other two types of case materials, that is, aluminum plate and polyimide film, both show outstanding high-temperature performance, as discussed below, and thus, they were used to study the HTSCs further. On the basis of the above results for the electrolyte, separator, and case materials, studies on the HTSCs were performed with EMIMTFSI as the electrolyte, glass fiber as the separator, aluminum plate/polyimide film as the case, and commercial AC as the active material.

High-temperature performance of the optimal HTSCs

The tolerated temperature and voltage of the HTSCs

The optimal HTSCs in this section consisted of EMIMTFSI as the electrolyte, a glass-fiber separator, an aluminum plate case, and commercial AC. As shown in Figure S7 (Supporting Information), HTSCs with different operation voltages were tested under various temperatures at 1 Ag^{-1} . Figure 1a-c shows the CC tests of the HTSCs with voltages of 3.5, 3.0, and 2.5 V. It is apparent that under a voltage of 3.5 V the highest endurable temperature of the HTSCs is 90°C, at which point a dramatic decrease in the specific capacitance begins to occur (Figure 1a), and this critical temperature increases to 120 °C for 3.0 V (Figure 1 b) and to 150°C for 2.5 V (Figure 1c). Moreover, the Coulombic efficiencies of the HTSCs with the improved temperature under 3.5 and 3.0 V (Figure 1a,b) tend to drop more drastically and markedly than under 2.5 V (Figure 1c). Figure 1d-f shows the CC curves corresponding to Figure 1 a-c, respectively. The curves deviate from the ideal triangle shape if the temperature is higher than 60° C for 3.5 V, higher than 100° C for 3.0 V, and there is no noticeable deviation for 2.5 V even at 150 °C; these values are also the highest endurable temperatures for each operation voltage. Figure 1g-i corresponds to the equivalent series resistance (ESR) values calculated from Figure 1 d-f, respectively. The ESR for all operation voltages decreases initially and then increases as the temperature increases. This indicates that the HTSCs possess a limiting operating temperature, above which the ESR increases rapidly.

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Figure 1. CC measurement of HTSCs at different temperatures for voltages of a) 3.5 V, b) 3.0 V, and c) 2.5 V. The highest temperature that supercapacitors can withstand is 90 °C for 3.5 V, 120 °C for 3.0 V, and 150 °C for 2.5 V. d–f) CC curves of the last cycle for each temperature in panels a–c, respectively. g–i) ESR calculated from the voltage drop at the beginning of discharge in panels d–f, respectively.

Furthermore, Figure 1 g–i displays that a higher operating voltage causes a larger ESR at the same temperature, and consequently, under high operation voltages, the HTSCs will degrade more quickly. In conclusion, the HTSCs can operate sufficiently at temperatures as high as $130 \,^{\circ}$ C within 2.5 V, because under such test conditions both the capacitance retention and Coulombic efficiency exhibit good performance (Figure 1 a–c), the CC curves show nearly ideal capacitive behavior (Figure 1 f), and the ESR is relatively low (Figure 1 g–i).

Performance at 120 °C, 2.5 V, and 1 Ag^{-1}

On the basis of the above CC test results, the performance of the optimal HTSCs directly operating at 120 °C, 2.5 V, and 1 Ag^{-1} was examined. Figure 2a illustrates that the HTSCs still possess a specific capacitance of approximately 80 Fg^{-1} after 5000 cycles (\approx 75% capacitance retention) with a Coulombic efficiency still >98%. Figure 2b displays the CC curves corresponding to different cycles in Figure 2a; this figure shows that the CC curves still possess the ideal triangle shape after 5000 cycles, which implies good capacitive properties. The ESR (Figure 2c) first increases and gradually reaches approximately 30Ω after 5000 cycles, and consequently, these HTSCs possess outstanding cycle stability without a drastic increase in the ESR. The rate capabilities of the HTSCs at 120°C and 2.5 V were also evaluated. Figure 2d shows the CC curves of the HTSCs at different current densities, and Figure 2e displays the dependence of the specific capacitance on the current density; both of these figures indicate excellent rate performance upon increasing the current density from 1 to 10 A g⁻¹. In conclusion, the HTSCs assembled with the EMIMTFSI electrolyte, a glass-fiber separator, an aluminum plate case, and commercial AC show outstanding performance at 120 °C and 2.5 V with an initial specific capacitance of approximately 107 F g⁻¹ and a capacitance retention of approximately 75% after 5000 cycles. The HTSCs also show good rate capability, and even under 10 Ag^{-1} , a discharge specific capacitance of approximately 106 Fg^{-1} is obtained.

Flexible HTSCs

The electrochemical performance and flexibility of the flexible HTSCs assembled by using the EMIMTFSI electrolyte, a glass-fiber separator, a polyimide-film case, and commercial AC were investigated. Figure 3a,b shows optical photographs of the flexible HTSCs and lighting of a light-emitting diode (LED) device at 120°C, respectively. Figure 3c shows the CC tests of the flexible HTSCs at 120°C, 2.5 V, and 5 Ag^{-1} without bending, which indicates that the capacitance retention after 10000 cycles is approximately 75% with an initial specific capacitance of approximately 101 Fg⁻¹ and a Coulombic efficiency of approximately 100% for almost all cycles. Figure 3d displays the CC curves of different cycles in Figure 3c, and it shows that the CC curves still possess the triangle shape after 10000 cycles, which implies ideal capacitive properties. Figure 3e shows the CV tests under a series of scan rates at room temperature and 120°C. Although the CV curves at room temperature slightly deviate from a perfect rectangular shape owing to the low ionic conductivity of EMIMTFSI and a high ESR,^[25] they exhibit a nearly rectangular-type curve at 120°C for all scan rates, which indicates ideal capacitive properties. Figure 3 f shows the EIS spectra at room temperature and $120^{\circ}C$ ($\approx 4.8 \Omega$ ESR at RT and $\approx 2.2 \Omega$ ESR at 120 °C), which indicates an improvement in the ionic conductivity and a reduction in the ESR as the temperature increases. The low-frequency part in Figure 3 f presents capacitive behavior, and the HTSCs at both room temperature and 120 °C show ideal capacitive properties, as indicated by the vertical curves.

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Figure 2. a) Cycle stability of HTSCs at 120 °C, 2.5 V, and 1 Ag⁻¹. b) CC curves corresponding to different cycles in panel a. c) R_{ESR} calculated from the voltage drop in panel b. d) CC curves at 120 °C with different current densities. e) Dependence of discharge specific capacitance on the current density at 120 °C and 2.5 V.

Bending tests were next performed for the flexible devices. Figure 4a, b shows the optical photographs of the flexible HTSCs in the bending state and lighting a LED device under curvature of 0.2 mm⁻¹. Figure 4c is the plot of the specific capacitance versus cycle number under different bending curvatures at room temperature and 120°C, and it shows that the specific capacitance remains unchanged under bending curvatures of 0.05, 0.1, and 0.2 mm⁻¹ at both room temperature and 120 °C. Figure 4d shows the CC curves corresponding to Figure 4c, and it also indicates little change in the shapes of the CC curves under different bending conditions. CV measurements of the flexible HTSCs (Figure S8, Supporting Information) also show little change for varied bending curvatures at both room temperature and 120°C, which is indicative of the minor effect of bending on the performance of the flexible HTSCs. In conclusion, the flexible HTSCs assembled with the EMIMTFSI electrolyte, a glassfiber separator, a polyimide-film case, and commercial AC show excellent performance at 120°C and 2.5 V with an initial specific capacitance of approximately 101 Fg⁻¹ and a capacitance retention of approximately 75% after 10000 cycles. Moreover, the HTSCs exhibit outstanding flexibility, and the specific capacitance, CC curves, and CV curves remain essentially unchanged under bending curvatures of 0.05, 0.1, and 0.2 mm^{-1} at both room temperature and 120°C.

Degradation mechanism of HTSCs

CV and EIS testing at different temperatures

The degradation mechanism of the HTSCs was investigated for devices assembled with the EMIMTFSI electrolyte, a glass-fiber separator, an aluminum plate case, and commercial AC. As shown in Figure S9 (Supporting Information), CV tests were performed at 25, 50, and 100 mVs⁻¹, and at each scan rate, the test was conducted for two cycles in a certain voltage range at a preset temperature. After the CV measurements, EIS was subsequently performed at the same

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Figure 3. Electrochemical performance of flexible HTSCs. Optical images of a) the supercapacitor and b) lighting a LED device at 120°C. c) Cycle stability of flexible HTSCs in flat shape at 120°C, 2.5 V, and 5 A g⁻¹. d) CC curves of different cycles for panel c. e) CV curves of flexible HTSCs under different scan rates at room temperature and 120°C. f) Nyquist plots of flexible HTSCs at room temperature and 120°C; inset is the enlargement.

temperature as that at which the CV tests were performed. In a typical procedure, one HTSC was generally tested at room temperature and at 40, 60, 80, 100, 120, 130, and 150 °C. Figure 5 a–c shows the CV curves under 3.5, 3.0, and 2.5 V at a scan rate of 25 mVs⁻¹ with different temperatures (other scan rates such as 50 and 100 mVs⁻¹ are shown in Figure S10, Supporting Information). Figure 5 a reveals that side reactions, which may include the oxidation and reduction of the electrolyte, glass-fiber separator, electrode, and case materials, become clear if the temperature exceeds 100°C for the 3.5 V voltage window, as indicated by the upward current upon charging to high voltages. Figure 5b shows that this temperature increases to 120°C for 3.0 V, and no marked upward current is observed for 2.5 V even at 150°C (Figure 5c). Therefore, it is concluded that more side reactions, as indicated by the upward current, will occur for higher operation voltages at high temperatures, and these side reactions may include the oxidation and reduction of the electrolyte, glass fiber, electrode materials, and even case materials.

Figure 5d-f shows the Nyquist plots of the HTSCs tested after the CV measurements. For a typical Nyquist plot, as shown in Figure 5 f at room temperature, the real axis intercept at high frequencies represents the solution resistance of the electrolyte (R_s) .^[10,12,26] The semicircle loop spanning along the real axis is related to the charge-transfer resistance $(R_{\rm ct})$,^[10,12] which is influenced by interfacial resistance between the current collector and the active material,^[27] interfacial resistance between activated carbon particles,^[28,29] the type and content of the conductive filler added to the activated carbon particles,^[30] and the separator. The region with a slope of 45° is generally attributed to Warburg impedance (W_{o}) .^[10,12] The vertical behavior in the low-frequency region represents the electrical double-layer capacitance (EDLC) of the supercapacitors.^[28] Here, the Nyquist plots of the HTSCs were described by equivalent circuits (ECs) in Figure S11 (Supporting Information), and the fitted data for the ECs are listed in Table S1. From Table S1 (Supporting Information), it is noticeable that R_{ct} continuously decreases and finally reaches zero as the temperature increases if the CV opera-

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Figure 4. Optical images of a) the flexible HTSCs in bending state and b) lighting a LED device under a curvature of 0.2 mm⁻¹. c) CC tests of flexible HTSCs under different bending curvatures at room temperature and 120 °C and d) the corresponding CC curves.



Figure 5. CV curves of HTSCs at different temperatures for voltages of a) 3.5 V, b) 3.0, and c) 2.5 V. d–f) Nyquist plots obtained after the CV tests. Panels a–c show that the supercapacitors can withstand 100°C for 3.5 V, 120°C for 3.0 V, and 150°C for 2.5 V without a significant upward current. Panels d–f show that R_{ct} continuously decreases and becomes zero upon increasing the temperature for 2.5 and 3.0 V, but it first decreases and then increases for the 3.5 V case.

tion voltage is 2.5 or 3.0 V, at which fewer side reactions occur, but $R_{\rm ct}$ first decreases and then increases for 3.5 V. It is reasonable that $R_{\rm ct}$ decreases upon increasing the temperature, because the transportation of ions becomes easier. However, the increase in $R_{\rm ct}$ for 3.5 V if the temperature exceeds 100 °C seems unreasonable. Actually, such an increase in $R_{\rm ct}$ is likely caused by side reactions during the CV tests at

high temperatures, and three factors were found to induce such an increase in R_{ct} , as discussed below.

Fusion of glass-fiber separator

To reveal possible reasons resulting in the increase in R_{ct} in Figure 5d, scanning electron microscopy (SEM) was conduct-

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Figure 6. a) Scheme of a HTSC with an aluminum-plate case; surface-1 to surface-6 represent the different interfaces that were characterized. b) SEM image of a pristine glass-fiber separator that has not undergone any electrochemical tests. c) SEM image of a glass-fiber separator that was tested at 120 °C and 2.5 V for an extended period of time. d) SEM image of a pristine electrode that has not undergone any electrochemical tests. e) SEM image of surface-3 that was electrochemically tested at 120 °C. f) SEM image of electrochemically tested surface-3 and g–j) corresponding mapping images. k) SEM image of electrochemically tested surface-1 and l–o) corresponding mapping images.

ed on several interfaces, which are designated in Figure 6a. Figure 6b,c compares the SEM images of a pristine glassfiber separator and a glass-fiber separator that has undergone CC tests at 120°C and 2.5 V for an extended period; it is apparent that the glass fibers seem to be fused together after electrochemical charging/discharging tests at 120°C. The fused separator will likely make ion transport more difficult, which will result in higher ESR.

To elaborate better the relationship between $R_{\rm ct}$ and the properties of the separator, the dependence of $R_{\rm ct}$ on the separator thickness was studied. Figure S12 (Supporting Information) shows the Nyquist plots of supercapacitors that possess different layers of the cellulose separator. This figure clearly indicates that $R_{\rm ct}$ becomes larger as the separator layer increases, which reveals that a thicker separator will result in a higher $R_{\rm ct}$ value. Therefore, we can conclude that the fusion of glass fibers will worsen the internal resistance.

Deposition of contaminations on the surfaces of the positive and negative electrodes

Careful examination of electrochemically tested (ECT) surface-3 (positive active electrode that faces the separator) reveals that many small particles are apparent on its surface (Figure 6e) relative to the number of small particles on the pristine electrode (Figure 6d). These small particles may block some of the pores in the AC; this is likely to make ion transport more difficult, which will reduce the specific capacitance of the SCs and increase the ESR. To determine the composition of these small particles on ECT surface-3, element mapping by energy-dispersive X-ray spectroscopy (EDS) was performed. The results (Figure 6 f-j) reveal that the deposited small particles on ECT surface-3 contain mainly Al and Na. Moreover, ECT surface-1 (negative electrode that faces the separator) is also covered by contaminants mainly containing Na and Si (Figure 6k-o). The constituents, derived from EDS and X-ray photoelectron spectroscopy (XPS), of these contaminants deposited on ECT surface-1 and ECT surface-3 are listed in Table S2 (Supporting Information), and the compositions of the pristine electrode and the pristine glass-fiber separator are also listed for comparison. The EDS and XPS data are consistent with the above element-mappings results. Moreover, Table S2 shows that the glass-fiber separator mainly contains O, Si, Na, Al, K, Zn, Ba, Ca, and Mg, which perfectly reveals that these deposited contaminants on ECT surface-1 and ECT surface-3 are from the glass-fiber separator. In conclusion, contaminants originating from decomposition of the glass-fiber separator will deposit on the surfaces of both electrodes during charging/discharging at high temperatures, and these contaminants may block some of the pores in the AC; this will make ion transport more difficult, which will lead to a lower capacitance and a higher $R_{\rm ct}$.

Separation of positive active material from current collector

Besides the fusion and deposition phenomena, spontaneous peeling of the active material in the positive electrode from the current collector after electrochemical tests in a harsh environment (usually at temperatures higher than 80 °C and a

voltage larger than 3.0 V) is also a critical factor contributing to the drastic degradation of HTSCs. Importantly, after electrochemical testing, a clear separation between the positive active electrode and its current collector (the carbon-coated Al foil) is observed. No such phenomenon is observed for the negative electrode. Figure S13a (Supporting Information) compares the optical images of a pristine electrode and a fresh carbon-coated current collector with an electrochemically tested and stripped positive electrode (ECT surface-4) and its current collector (ECT surface-5). This figure indicates that, after separation, most of the carbon coated on the current collector is stuck to the positive active electrode, leaving an aluminum foil with little carbon on its surface. Figure S13e,f (Supporting Information) shows the SEM images of ECT surface-4 and ECT surface-5, which also reveal that most of the coated carbon on the current collector is stuck to the positive active electrode side (ECT surface-4). In conclusion, the fusion of the glass fiber in the separator during charging/discharging at high temperatures, deposits resulting from decomposition of the separator on the surfaces of the positive and negative electrodes, and separation of the positive active material from the current collector all contribute to the degradation of the HTSCs, including capacitance fading and ESR increases.

Conclusions

To summarize, the temperature tolerance of different supercapacitors with various compositions of the electrolyte [1ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI)], separator [cellulose, polytetrafluoroethylene (PTFE), and quartz-fiber and glass-fiber separator], and case materials (stainless-steel plate, aluminum plate, and polyimide film) was investigated, and the optimal composition included the EMIMTFSI electrolyte, a glass-fiber separator, an aluminum plate/polyimide-film case, and commercial activated carbon (AC). On the basis of the above screening results, a flexible high-temperature supercapacitor (HTSC) assembled with the EMIMTFSI electrolyte, a glassfiber separator, a polyimide-film case, and commercial AC was fabricated, and it showed excellent performance at 120°C and 2.5 V with an initial specific capacitance of approximately 101 Fg^{-1} and a capacitance retention of approximately 75% after 10000 cycles. Moreover, the flexible HTSCs exhibited outstanding flexibility, and the specific capacitance, constant-current (CC) charge-discharge curves, and cyclic voltammetry (CV) curves remained unchanged under bending curvatures of 0.05, 0.1, and 0.2 mm⁻¹ at both room temperature and 120°C. Secondly, the degradation mechanism of the HTSCs was systematically investigated, and three factors were found to cause the degradation, mainly including fusion of the separator, deposition of contaminants resulting from decomposition of the glass-fiber separator on the surfaces of both electrodes, and separation of the positive active materials from the current collector. Considering all of the above results, it is expected that finding a more stable separator would greatly improve the cycle stability of HTSCs, and the use of a stronger binder for the carbon-coated current collector would also improve the temperature tolerance of the HTSCs. Moreover, the use of activated carbon possessing a higher specific capacitance would further improve the performance of the supercapacitors.

Experimental Section

Fabrication of HTSCs

Briefly, 85 wt % activated carbon YP50 (Kuraray Chemicals), 5 wt% carbon black (Super P, Timcal), and 10 wt% PTFE (Dupont) were homogeneously mixed in agate mortar. Then, the mixture was rolled into an approximately 80-100 µm thick sheet that was punched into 14 mm diameter electrodes. After drying at 120°C for 6 h under vacuum, the electrodes were weighted and hot pressed onto an aluminum current collector that contained conducting carbon coated on the surface, and they were then dried at 180°C for 6 h under high vacuum. The HTSCs were fabricated in a glove box filled with argon. The HTSCs consisted of two identical electrodes and a separator, all of which were sandwiched between two aluminum plate cases (or stainless-steel plate cases) sealed with rubber. For the flexible HTSCs, a polyimide-film case (thickness of 0.05 mm) sealed with silicone binder was used. EMIMTFSI and EMIMBF₄ (Lanzhou Greenchem ILs) were used as the electrolytes. Separators included a glass-fiber separator (Whatman, GF/A), a quartz-fiber separator (Whatman, QMA), a PTFE separator (MINGLIE MEM-BRANE), and a cellulose separator (NKK, TF4840).

Measurement of HTSCs

CC tests were performed on LAND and Arbin battery-testing systems. The CV and EIS tests were performed by using an Autolab (Metrohm). EIS was performed from 100 kHz to 10 mHz at an alternating voltage magnitude of 10 mV. For the CC tests, the gravimetric specific capacitance $C_{\rm s}$ [Fg⁻¹] was calculated according to Equation (1):

$$C_{\rm s} = \frac{4I}{m {\rm d}V/{\rm d}t} \tag{1}$$

in which *I* is the constant current [A], *m* is the total mass of the two electrodes [g], and dV/dt [V s⁻¹] is the slope obtained by fitting a straight line to the charge or discharge curve.

The ESR, R_{ESR} , was calculated according to Equation (2):

$$R_{\rm ESR} = \frac{V_{\rm drop}}{I} \tag{2}$$

in which V_{drop} is the voltage drop [V] at the beginning of discharge and I is the discharge current [A].

The Warburg constant σ was derived from Equation (3):

$$Z_{\rm w} = \frac{\sigma}{\omega^{1/2}} - j \cdot \frac{\sigma}{\omega^{1/2}} \tag{3}$$

in which $Z_w[\Omega]$ is the Warburg impedance, $\sigma [\Omega s^{-1/2}]$ is the Warburg constant, and $\omega [s^{-1}]$ is the angular frequency. By plotting the real and imaginary parts of Z_w versus $1/\omega^{-1/2}$ we could obtain

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two straight and parallel lines, the slopes of which were equal to σ . As the supercapacitors deviated slightly from the ideal ones, the slopes of the real and imaginary parts were slightly different. The Warburg constant (σ) was the average value of the real one (σ') and the imaginary one (σ'').

The capacitance, C[F], in the ECs was calculated from Equation (4):

$$C = -\frac{1}{2\pi f Z''} \tag{4}$$

in which f is the frequency [Hz] and Z'' is the imaginary part of the impedance.

The time constant, τ_0 [s], was calculated from Equation (5):

$$\tau_0 = \frac{1}{f_0} \tag{5}$$

in which f_0 is the frequency at which the phase angle is -45° .

Characterization

The electrodes that underwent electrochemical charging/discharging were first washed with acetone to remove any remaining EMIMTFSI. After the electrodes were totally dried, the surface composition and morphology were characterized by SEM and EDS (JEOL, JSM-7500F). The surface components were also confirmed by XPS with a monochromated AlK_{α} X-ray source (1486.71 eV photons).

Acknowledgements

The authors gratefully acknowledge financial support from the Ministry of Science and Technology of China (MoST, 2016YFA0200200) and the National Natural Science Foundation of China (NSFC, 51633002, 51472124, 5127309, and 21374050).

Conflict of interest

The authors declare no conflict of interest.

Keywords: charge transfer • energy storage • polymeric materials • stability • supercapacitors

 a) L. Zhang, F. Zhang, X. Yang, G. Long, Y. Wu, T. Zhang, K. Leng, Y. Huang, Y. Ma, A. Yu, Y. Chen, *Sci. Rep.* **2013**, *3*, 1408; b) L. Zhang, X. Yang, F. Zhang, G. Long, T. Zhang, K. Leng, Y. Zhang, Y. Huang, Y. Ma, M. Zhang, Y. Chen, *J. Am. Chem. Soc.* **2013**, *135*, 5921; c) Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen, Y. Chen, *J. Phys. Chem. C* **2009**, *113*, 13103; d) F. Zhang, Y. Lu, X. Yang, L. Zhang, T. Zhang, K. Leng, Y. Wu, Y. Huang, Y. Ma, Y. Chen, *Small* **2014**, *10*, 2285; e) Y. Lu, F. Zhang, T. Zhang, K. Leng, L. Zhang, X. Yang, Y. Ma, Y. Huang, M. Zhang, Y. Chen, *Carbon* **2013**, *63*, 508; f) F. Zhang, T. Zhang, X. Yang, L. Zhang, K. Leng, Y. Huang, Y. Chen, *Energy Environ. Sci.* **2013**, *6*, 1623.

- [2] R. S. Hastak, P. Sivaraman, D. D. Potphode, K. Shashidhara, A. B. Samui, *Electrochim. Acta* 2012, 59, 296.
- [3] S.-K. Kim, H. J. Kim, J.-C. Lee, P. V. Braun, H. S. Park, ACS Nano 2015, 9, 8569.
- [4] R. S. Borges, A. L. M. Reddy, M.-T. F. Rodrigues, H. Gullapalli, K. Balakrishnan, G. G. Silva, P. M. Ajayan, *Sci. Rep.* 2013, 3, 2572.
- [5] X. Liu, Z. Wen, D. Wu, H. Wang, J. Yang, Q. Wang, J. Mater. Chem. A 2014, 2, 11569.
- [6] T. Hibino, K. Kobayashi, M. Nagao, S. Kawasaki, Sci. Rep. 2015, 5, 7903.
- [7] B. Shen, R. Guo, J. Lang, L. Liu, L. Liu, X. Yan, J. Mater. Chem. A 2016, 4, 8316.
- [8] S. Fletcher, V. J. Black (Schlumberger Technology Corp.), US 9318271 B2, 2013.
- [9] R. S. Borges, K. Kalaga, M. T. F. Rodrigues, H. Gullapalli, L. M. R. Arava, K. Balakrishnan, G. G. Silva, P. M. Ajayan (Universidade Federal De Minas Gerais, William Marsh Rice University), US 2014/ 0315096 A1, 2014.
- [10] K. Hung, C. Masarapu, T. Ko, B. Wei, J. Power Sources 2009, 193, 944.
- [11] R. Kötz, M. Hahn, R. Gallay, J. Power Sources 2006, 154, 550.
- [12] C. Masarapu, H. F. Zeng, K. H. Hung, B. Q. Wei, ACS Nano 2009, 3, 2199.
- [13] R. S. Hastak, P. Sivaraman, D. D. Potphode, K. Shashidhara, A. B. Samui, J. Solid State Electrochem. 2012, 16, 3215.
- [14] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* 2009, *8*, 621.
- [15] W.-Y. Tsai, R. Lin, S. Murali, L. L. Zhang, J. K. McDonough, R. S. Ruoff, P.-L. Taberna, Y. Gogotsi, P. Simon, *Nano Energy* 2013, 2, 403.
- [16] R. Lin, P.-L. Taberna, S. Fantini, V. Presser, C. R. Pérez, F. Malbosc, N. L. Rupesinghe, K. B. K. Teo, Y. Gogotsi, P. Simon, J. Phys. Chem. Lett. 2011, 2, 2396.
- [17] A. Balducci, R. Dugas, P. L. Taberna, P. Simon, D. Plée, M. Mastragostino, S. Passerini, J. Power Sources 2007, 165, 922.
- [18] V. Ruiz, T. Huynh, S. R. Sivakkumar, A. G. Pandolfo, RSC Adv. 2012, 2, 5591.
- [19] L. Negre, B. Daffos, V. Turq, P. L. Taberna, P. Simon, *Electrochim. Acta* 2016, 206, 490.
- [20] C. Arbizzani, M. Biso, D. Cericola, M. Lazzari, F. Soavi, M. Mastragostino, J. Power Sources 2008, 185, 1575.
- [21] C. Largeot, P. L. Taberna, Y. Gogotsi, P. Simon, *Electrochem. Solid-State Lett.* 2011, 14, A174.
- [22] H. Wang, Z. Xu, A. Kohandehghan, Z. Li, K. Cui, X. Tan, T. J. Stephenson, C. K. King'Ondu, C. M. Holt, B. C. Olsen, *ACS Nano* 2013, 7, 5131.
- [23] W. J. Schell, Z. Zhang, presented at *Battery Conference on Applica*tions and Advances, California State University, 1999.
- [24] S. A. Kazaryan, G. G. Kharisov, S. V. Litvinenko, V. I. Kogan, J. Electrochem. Soc. 2007, 154, A751.
- [25] W. G. Pell, B. E. Conway, J. Power Sources 2001, 96, 57.
- [26] P. L. Taberna, P. Simon, J. F. Fauvarque, J. Electrochem. Soc. 2003, 150, A292.
- [27] a) C. Portet, P. L. Taberna, P. Simon, C. Laberty-Robert, *Electrochim. Acta* 2004, 49, 905; b) X. Liu, T. Osaka, J. Electrochem. Soc. 1996, 143, 3982.
- [28] Y. R. Nian, H. Teng, J. Electroanal. Chem. 2003, 540, 119.
- [29] T. Momma, X. Liu, T. Osaka, Y. Ushio, Y. Sawada, J. Power Sources 1996, 60, 249.
- [30] X. Liu, L. Juan, L. Zhan, L. Tang, Y. Wang, W. Qiao, X. Liang, L. Ling, J. Electroanal. Chem. 2010, 642, 75.

Manuscript received: June 14, 2017

- Revised manuscript received: June 23, 2017
- Accepted manuscript online: June 23, 2017

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In charge: Supercapacitors that can operate efficiently at 120 °C with high cycling capability are rarely studied. Also, capacitance fading and the increased internal resistance of supercapacitors operating at high temperatures have not yet been fully studied. Herein, a high-temperature-endurable and flexible supercapacitor operating at 120 °C with good cycle stability is fabricated and its degradation mechanism is systematically investigated.

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