An all-in-one supercapacitor working at sub-zero temperatures

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Among energy storage devices, electrochemical capacitors (ECs) possessing ultrahigh power density and long-term stability have attracted numerous research interests and thus enriched our arsenal when coping with specific issues [1–10]. While a large number of aqueous ECs could run well at room temperature, demand for their survival and operation under thermal extremes is rising. For example, military-grade electrochemical energy storage (EES) devices are expected to operate from –40 to 60°C and equipment for cold climates or high altitudes can experience temperatures as low as –60°C [11]. However, as temperature goes lower to sub-zero region, aqueous electrolytes suffering from the formation of ice and consequent precipitation of electrolytic salt usually show rapid decrease of ionic conductivity, which in turn hampers aqueous ECs from delivering desirable performances. Thus, developing anti-freezing aqueous electrolyte capable of working at extremely low temperatures is of great importance, and fortunately there are many lessons we can learn from the nature. For example, in the Arctic Circle, the deep ocean water under glaciers exists in the liquid state because of its high salinity. Also, functional chemicals such as antifreeze proteins endow some living species with the ability of surviving in polar circles. Actually, on the basis of Raoult's law, the freezing point of a non-volatile solution could be calculated according to the equation:

$$T_f = T_f^* - K_f \cdot b(B), \quad (1)$$

where T_f^* is the freezing point of solvent (K), K_f is the freezing point constant (K kg mol^{-1}), and $b(B)$ refers to the molality of solute (mol kg^{-1}). Since T_f^* and K_f are constants determined by the solvent, the freezing point of a specific solution decreases with increasing concentra-

tion of solute. For instance, the concentrated aqueous solutions have been reported for supercapacitors working at temperatures below 0°C due to their lower freezing points [12–14].

For aqueous electrolytes, another approach to resist low temperatures is replacing pure water with binary solvents, a strategy widely applied in cryoprotectants. For example, as a well-known anti-freezing agent, ethylene glycol (EG) could form strong H-bonds with water molecules and prevent the formation of crystal ices. Thus, electrolytes using water/EG mixture as solvent have been proved to be reliable for ECs at temperatures as low as –30°C [15,16]. Recently, the anti-freezing binary solvent system has also been successfully employed in fabricating conductive organohydrogels with polyvinyl alcohol (PVA), which exhibit stable flexibility and strain-sensitivity at temperature of –40°C and thus pave the way for their application in flexible devices [17].

Herein, we propose an all-in-one supercapacitor comprising multiwall carbon nanotubes (MWCNTs) electrodes and PVA-KOH organohydrogel electrolyte. In the organohydrogel electrolyte, EG and water interact with hydrophilic hydroxyl groups in PVA and induce the gelation through a simple cooling-thaw process, while KOH acting as ion carrier is well-dispersed within the cross-linking network. And then by infusing the above electrolyte into the 3D MWCNTs network, electrode-electrolyte interfaces stable at sub-zero temperatures are obtained. As a consequence, the all-in-one supercapacitor shows ideal capacitive behavior at temperatures as low as –36°C and excellent cycling performance with no capacitance decay after 10,000 cycles at –18°C. This work will shed light on further fabrication of anti-freezing energy storage and conversion devices.

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Fig. 1 schematically illustrates the procedure used herein to fabricate the all-in-one supercapacitor (details are available in the Supplementary information). Firstly, the MWCNTs were modified with surface functional groups *via* a common acid-treating method. Taking advantage of the interaction between the surfactant (cetyltrimethyl ammonium bromide, CTAB) and functional groups, the surface-modified MWCNTs were re-dispersed in deionized (DI) water, forming a stable colloidal solution. Then, the MWCNTs films were prepared by vacuum filtration of the dispersion onto a cellulose membrane along with washing by excessive DI water to remove the surfactant. The films were dried overnight to evaporate the water and infused by gel electrolyte to produce flexible electrodes. Generally, a flexible supercapacitor is comprised of a gel electrolyte sandwiched by two electrodes. Meanwhile, in most cases, the gel electrolyte only contacts the surface of electrodes or partially infills the porous electrodes, resulting in insufficient formation of electrode-electrolyte interfaces (Fig. S1). Under those conditions, additional liquid electrolytes are needed to provide extra pathways for ions and activate the system to reach its full potential. As a result, such a system often suffers from poor cycling stability due to the inevitable loss of solvent in long-term operation. In this work, with a bottom-up infilling method and a consequent cooling-thaw process, the porous MWCNTs films were fully infilled with PVA-KOH organohydrogel electrolyte, maximizing the formation of electrode-electrolyte interfaces and making them ideal for flexible supercapacitors. Shortly, the electrolyte with dissolved KOH was cast into dried MWCNTs films in which cellulose membranes acted as gas-permeable substrates. A water-impermeable cover was then placed over the organosol, forcing the solvents in the electrolyte to evaporate

downwards and taping into the capillary forces to continuously refill the pores [18]. On the other hand, in the binary solvent system, the strong hydrophilic hydroxyl groups on the PVA chains endow them with good affinities to EG and water molecules, thereby inducing facile gelation through H-bonding (Fig. 2a) [19]. Consequently, the gel electrolyte shows a freezing point lower than -40°C and maintains good ionic conductivities at sub-zero temperatures (Fig. 2b and Fig. S2). Besides, the cooling process facilitates the crosslinking and renders the PVA film certain degree of stretchability (Fig. 2c). After being dried, the gel-infused MWCNTs films can be detached and inherit the flexibility of PVA films (Fig. 3a). *Via* layer-by-layer stacking, two MWCNTs films were separated by a PVA film and pressed to form a symmetric supercapacitor. A field emission scanning electron microscope (FESEM) was applied to examine the morphologies of the as-fabricated supercapacitor. As shown in Fig. 3b–d, the front side of MWCNTs electrode contacting with the gas-permeable substrate shows rough surfaces with bare MWCNTs, rendering it good connection with current collectors. The sandwich-like structure could be clearly seen from the cross-sectional SEM image (Fig. 3e). Besides, the energy-dispersive X-ray spectroscopy (EDS) mapping analyses of the cross section reveal well spatial distribution of O, K and C (Fig. 3f).

To better evaluate the gel distribution within porous electrodes, thicker MWCNTs films were also prepared and separated by a PVA film in a reversed configuration, i.e., the front side with bare MWCNTs contacts with the PVA film directly. As shown in Fig. S3a, b, in the gel-infused MWCNTs films, the rugged surface with some vertically standing MWCNTs is well-maintained, favoring fast electron transportation between electrode materials and current collectors. There is an interface due to

Figure 1 Schematic illustrating the preparation procedure of MWCNTs films and the corresponding gel-infused MWCNTs electrodes. Millipore filter refers to the porous cellulose membrane, and organosol refers to viscous PVA-KOH electrolyte dissolved in EG/H₂O binary solvent.

Figure 2 (a) Schematic illustration, (b) DSC curves and (c) optical images of the PVA-KOH organohydrogel.

Figure 3 (a) Optic images of MWCNTs films and gel-infused MWCNTs electrodes. SEM images of the all-in-one supercapacitor from top view (b–d) and cross-sectional view (e). (f) EDS mapping images of the all-in-one supercapacitor, showing the distribution of C, K and O.

the extra amount of electrolyte, and both the enlarged SEM image and the EDS mapping results demonstrate the uniform distribution of gel electrolyte in the MWCNTs network (Fig. S3c, d).

After being assembled in a coin cell, electrochemical behaviors of the all-in-one MWCNTs electrode were evaluated. Fig. S4 shows its CV curves over the tem-

perature range of room temperature (RT, 25°C) to −36°C. Clearly, at all temperatures, CV curves present rectangular shapes which maintain well with increasing scan rates from 2 to 20 mV s^{−1}, revealing its good capacitive behavior [20]. Also, such a good capacitive behavior does not degrade with decreasing temperatures. As shown in Fig. 4a, in several cooling cycles, rectangular CV curves

Figure 4 Electrochemical performances of the all-in-one supercapacitor. (a) CV curves and (b) the corresponding capacitance retentions over several cooling cycles. (c) GCD curves at various temperatures. (d) CV curves of flexible EC in flatting and bending states. The inset shows optic images of the flexible device. (e) Capacitances at various current densities and different temperatures. (f) Cycling performance at -18°C , inset: optical images of the supercapacitor before and after 10,000 cycles.

show no obvious distortion except for the shrinkage of integral areas when temperature goes lower. According to the following equation:

$$C_a = \frac{1}{\nu V} \int_0^{0.5} I_a dV, \quad (2)$$

where ν is the potential scan rate (mV s^{-1}), V is the potential (V) and I_a is the current density (A cm^{-2}). The EC exhibits capacitance retentions of 86.5% and 75.2% as temperature decreases from RT to -18°C and -36°C , re-

spectively. Also, the capacitance of EC experiencing several cooling cycles could return to its initial state along with temperature recovery, demonstrating its resistance to harsh conditions as well as adaptability to temperature variations (Fig. 4b). Besides, as displayed in Fig. 4c, its symmetric galvanostatic charge-discharge (GCD) curves are well-maintained as temperature decreases, indicating its superior ability of working at extreme temperatures. In details, according to the equation:

$$C_a = \frac{I_a t}{V}, \quad (3)$$

where t is the discharge time (s), such an all-in-one device shows capacitances of 1.41, 1.14, and 0.99 mF cm⁻² at RT, -18 and -36°C, respectively (0.05 mA cm⁻²).

The all-in-one supercapacitor was also embedded between two indium-tin oxide coated polyethylene terephthalate (ITO-PET) films to form a flexible device and its stable potential window was measured to be 0–0.8 V (Fig. S5). Its CV curves are almost the same at flatting and bending states, demonstrating its workability (Fig. 4d). Fig. S6 displays its GCD performances. Not surprisingly, its capacitance decreases with increasing current densities, resulting from the larger i - R drops and kinetically hampered ion transfers. As shown in Fig. 4e, the capacitances are 32.9, 24.0 and 23.7 F g⁻¹ at 25, -18 and -36°C, respectively (at 32 mA g⁻¹). According to the Ragone plots (Fig. S7), its specific energy decreases from 10.5 to 7.6 W h kg⁻¹ when the temperature goes lower from RT to -36°C, corresponding to 72.4% retention (32 mA g⁻¹). On the basis of above results, when its capacitance decays as temperature goes lower, it could always store and release energy following ideal capacitive reactions which might be endowed by its stable configuration. If that is the case, either the decreasing response current in CV curves or the increasing i - R drop in GCD curves should be attributed to the increasing resistance of electrolyte rather than structural damages. More direct evidences interpreting changes of ion transportation in cooling processes could be obtained from the electrochemical impedance spectroscopy (EIS) results (Fig. S8). Generally, the internal resistance of a device (notated as R_Ω), i.e., the point intersecting with real axis at high frequency, includes ionic resistance of electrolyte (R_A), intrinsic resistance of electrode materials (R_B) and contact resistance (R_C) [21]. In the all-in-one EC, as temperature decreases, the change of $R_B + R_C$ is negligible due to the high conductivities of MWCNTs and current collectors. Therefore, the increasement of R_Ω could be mainly ascribed to the sluggish ion transfer in the gel electrolyte under low temperatures, which in turn results in capacitance decline. On the other hand, the polarization resistance (R_p , i.e., the diameter of semicircle) and diffusion resistance (R_D , i.e., the length of the 45° line in the middle frequency region) are often used to evaluate the penetrating ability of electrolyte into porous electrode and the migrating rate of ions from electrolyte inside pores to the surface of electrode, respectively [22]. From this perspective, the disappearance of semicircle reveals that the porous 3D MWCNTs network is fully infused with gel

electrolyte, forming stable electrode-electrolyte interfaces favoring fast ion exchanges. Besides, at all temperatures, its Nyquist plots show no obvious difference in middle and low frequency regions, which further demonstrates its stable structure being able to resist cooling shocks.

In consideration of practical applications, to achieve a long lifespan is the prerequisite for any kind of energy storage device. For supercapacitors, there are typically two causes responsible for capacitance fading in long-term operation. One is that the electrode materials might suffer from physical or chemical damages, which are common phenomena in pseudocapacitors or hybrid capacitors because most of those materials store and release energy through chemical reactions [23,24]. In this case, many factors such as the aggregation or amorphization of electrode materials could lead to irreversible capacitance loss. The other is that from the view of devices, a specific supercapacitor might experience structural failures in long-term cycling, e.g., electrode materials shedding off from current collectors or disconnecting with electrolyte. As displayed in Fig. 4f, the all-in-one EC presents stable cycling performance with no capacitance decay after 10,000 cycles at -18°C (0.04 mA cm⁻²). Since MWCNTs could be assumed to be stable in operation, its superior cycling performances reveal that the all-in-one configuration is reliable at both RT and sub-zero temperatures (Fig. S9).

In summary, we demonstrated an all-in-one supercapacitor based on MWCNTs and PVA-KOH-EG-H₂O gel electrolyte. The resultant device exhibited superior performances including high capacitance retention in long-term operation and anti-freezing capability of working at sub-zero temperatures. Actually, the all-in-one structure satisfies several requirements for advanced supercapacitors. First, the configuration with MWCNTs network buried in the gel electrolyte is stable with no agglomeration or collapse, which is to some extent like the reinforced concrete used in architecture. From this perspective, the infused gel electrolyte and the MWCNTs network function synergistically, i.e., the former renders the system certain degrees of integrity and flexibility while the later further improves its mechanical strength. Also, such an all-in-one design eliminates the usage of binders and thus evades the risk of capacitance decay induced by binder failure. On the other hand, the stable electrode-electrolyte interfaces not only allow fast charge exchanges throughout the system, but also guarantee its maintenance-free operation in a long time period. The anti-freezing feature endowed by the gel electrolyte allows it to tolerate harsh environments, and thus provides more

opportunities of being utilized in a wide range of regions or specific fields. While using MWCNTs as electrode materials does not demonstrate its full potential because of the low capacitance, the strategy proposed herein to fabricate all-in-one supercapacitors is applicable for practical applications and further work adopting this tactic to assembly devices with higher specific capacitances without sacrificing their performances is highly encouraged.

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Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and the supporting electrochemical results are available in the online version of the paper.

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一种可在0°C以下工作的一体式超级电容器

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摘要 具有低温工作性能是超级电容器应对特殊工作环境(高海拔/高纬度)的重要保障, 也有利于其在更多领域中的应用. 本文首先制备了一种可在低温下保持柔韧性和离子传导性能的碱性凝胶电解质, 并利用其制备了一种一体式超级电容器, 其可在零点温度以下(−36°C)仍具有稳定的工作能力.