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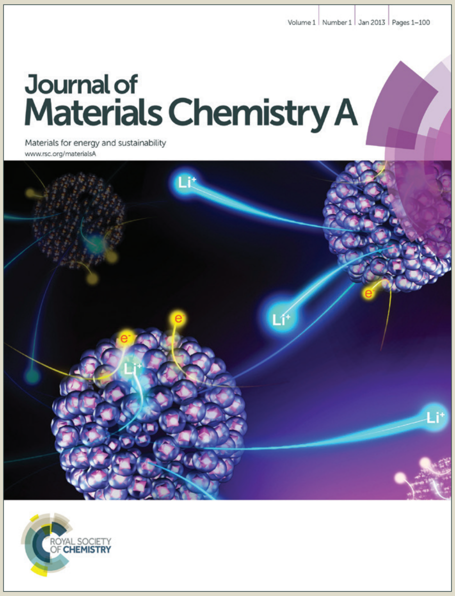

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Enhancing 5V capacitorperformance by adding single walled carbon nanotube into ionic liquid electrolyte

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Nanofluid electrolyte of single walled carbon nanotubes and ionic liquids can enhance the energy density, power density and cycling stability of nanotube electrodes with surface area of 600 m^2/g at 5V,by decreasing internal resistance from the bulk phase of ILs to the electrolyte/electrode interface.

Introduction

The supercapacitor (SC) is an important energy storage system, owing to its high power density, excellent cycling stability and intrinsic safety.[1] Increasing the energy density of electrode in appreciate electrolyte is the first priority in current stage for various potential applications.[2-14] In detail, energy density of novel carbon electrodes such as carbon nanotubes (CNTs) or graphene can be increased from 50-60 Wh/kg (in organic electrolyte) at 3 V to 90-110 Wh/kg (in ionic liquids (ILs) electrolyte) at 4 V.[3-9] Theoretically, elevating voltage window of SCs to 5 V will further increase the energy density. But most 5 V ILs available, depending on its chemical structural stability, have higher viscosity and lower ionic conductivity, compared to 3-4 V ILs including PIP_{13}-FSI, PYR_{14}-FSI, and $EMIBF_4$ etc.[15-17] These features are unfavorable to the transport of ions and electrons from the bulk phase of electrolyte to the electrode/electrolyte interface. On the other hand, nanofluids adding metal nanoparticles, graphite or metal oxide nanowires are effective to enhance the Brownian motion and convectional flow, and consequently, exhibit much higher mass and heat transport property as compared to host solution.[18-22] Recently, nanofluids have been applied into 4 V IL SC, which allowed the increase of the performance of SCs operated at 4 V. [23] However, there is no report on nanofluid used in 5 V SC, in which electrochemical environment is more complex and tougher.

Herein, we expanded the nanofluid electrolyte into the 5 V SC system. The effect of the weight ratio of SWNTs on the ionic conductivity of ILs was studied. We evidence that nanofluid electrolyte, used for 5 V SCs, can enhance the capacitance, energy density and broaden the power density range of a model CNT buckypaper electrode. Cycling stability of 5 V SCs is greatly improved due to the decrease of bulk phase resistance of ILs. The improvement of the performance of 5 V SC will provide insight on the understanding the complex electrochemical process and is favorable to further development of high voltage SC.

Results and discussion

Experimentally, SWNTs, prepared by chemical vapor deposition method,[24] had a diameter of 1.2-2 nm and length of 3-10 µm and purity of 98%. The IL is N-butyl-N-methyl pyrrolidiniumbis-(trifluoromethylsulfonyl) amide (BMPL NTf2) with a voltage window high up to 6.8 V. Experimental and calculative methods can be found in the supporting information materials. The comparison in the present work was irrelevant to the pore structure, the surface property and surface area of the model electrode,[25-28] and the effect of ILs with the electrode, since these were all the same and the change was made in the bulk phase of electrolyte.

SWNTs formed a uniform suspension in ILs (Figure S1) and remained stable for several months, due to the strong interaction of SWNTs and ILs[29-31], and the relatively large viscosity of ILs. After washing off ILs of the nanofluid, the SWNTs left formed a network with high porosity (Figure 1a), where SWNTs mainly existed as individual tube or very small bundles (Figure 1b). Since SWNTs have a very large aspect ratio, they all form a porous network after washing off ILs, independently of the pristine weight ratio (0.1-0.5 wt%) in ILs. The addition of 0.5 wt% SWNTs increases the viscosity at 25 °C by 30 %, but the viscosity of nanofluid becomes closer to that of pure ILs with the elevated temperature till to 80 °C (Figure 1c). The viscosity of nanofluid adding 0.2 wt% SWNTs has a reasonable middle value between those of pure ILs and nanolfluid with 0.5 wt% (Figure 1d). Since most SCs work safely below 60 °C[33], the SWNTs added don't influence the diffusion of ions of ILs (to electrode surface) seriously. The addition of SWNTs in BMPL NTf2 results in the sharp increase of ionic conductivity of nanofluid electrolyte (Figure 1d). Maximal value is 4.3 mS/cm as adding 0.2 wt% SWNTs, about 35 % higher than that of pure ILs. Further addition of SWNTs with the weight ratio of 0.3-0.5 wt% increases

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x the viscosity of nanofluid and decreases the mobility of ions (Figure 1d). Therefore, the ionic conductivity of ILs decreases gradually and backs to the value of pure ILs again as the addition of SWNTs increases. The contribution of SWNTs may originate from its conductive network or solely breaking the ion pairs of ILs.[15] To distinguish the two effects, we also added Al_2O_3 and Ag nanoparticles with the same weight ratio into ILs. They don't change the conductivity of ILs (Figure 1d), suggesting the low weight ratio of additives is unable to break the ion pairs of ILs. Thus, the increased ionic conductivity of nanofluid electrolyte is due to the network of SWNTs.

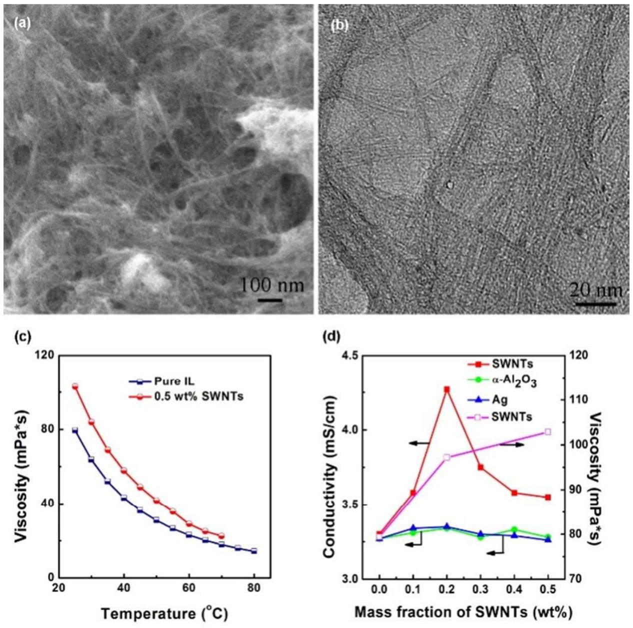

Figure 1. Characterization of SWNTs-IL nanofluids. (a) SEM image of the porous SWNTs network after removal of IL, from the nanofluid added by 0.5 wt% SWNTs. (b) TEM image of SWNTs in nanofluids containing 0.5 wt% SWNTs . (c) Viscosity values of pure IL and nanofluids with 0.5 wt% SWNTs at different temperatures. (d) Comparison of ionic conductivities of nanofluids adding SWNTs, alumina nanoparticles (30 nm) and Ag nanoparticles (30 nm), and Viscosity of SWNTs-IL nanofluids with different weight ratios at 25 °C. Open symbol: viscosity, filled symbol: conductivity. (Figure 1d has been revised)

The capacitance of SC cell was studied by scanning their cyclic voltammogram (CV) at different scan rates (Figure 2a, 2b and Figure S2). The CV curves of SCs using different electrolytes are similar, except the enlarged area enclosed below the curve as using nanofluid electrolyte at 100 and 200 mV/s scan rates (Figure 2a and 2b). The shape of CV curve at low scan rates suggests that there's some but insignificant redox reactions in SCs (Figure S2). In high scan rates, CV curves deviate from the identical symmetric trapezoid shape, because the process has become ion diffusion limited (Figure 2a and 2b). Meanwhile, galvanostatic charge/discharge curve was measured (Figure S3a). The IR drop, associated with the SC internal resistance, in the nanofluid containing 0.2 wt% SWNTs is about 0.9 V, lower than that (1.5 V) of pure IL SCs. Similar, the calculation based on galvanostatic charge/discharge method indicates the nanofluid-based SCs have higher capacitance than the pure IL ones. Specifically, the use of nanofluid electrolyte increases the capacitance by 75 % under high scan rate, where the charge process becomes ion/electron diffusion limited in such thick electrodes (Figure 2c). Similar, the energy density is doubled or much higher at a power density of 0.8 kW/kg as using nanofluid with 0.5 wt% SWNTs, compared to the pure ILs (Figure 2d). In addition, the ion diffusion in the thick buckypaper is very difficult, which makes SCs using electrolyte of pure ILs unable to work in the power density range exceeding 0.8 kW/kg. In sharp contrast, the power density range is extended up to 1.5-2 kW/kg in the use of nanofluid electrolyte, as well as maintaining energy densities of 35-40 Wh/kg at an increased power density of 1.3 kW/kg (Figure 2d). Note that, such thick electrode only has an energy density of 15-25 Wh/kg at 4V in similar power density.[23] Note that, 5 V SCs using the thick electrode of double walled and multiwalled CNTs exhibit an energy density (>100 Wh/kg), which is far larger than that (35 Wh/kg) at 4V and comparable to the best results of 4 V SC using electrode of graphene and SWNTs. Considering that the surface area of this electrode (600 m^2/g) is smaller than that of SWNTs (1100-1300 m^2/g) and graphene (single layer, 2000-3000 m^2/g), it can be expected that much better results can be achieved if using much better electrodes.

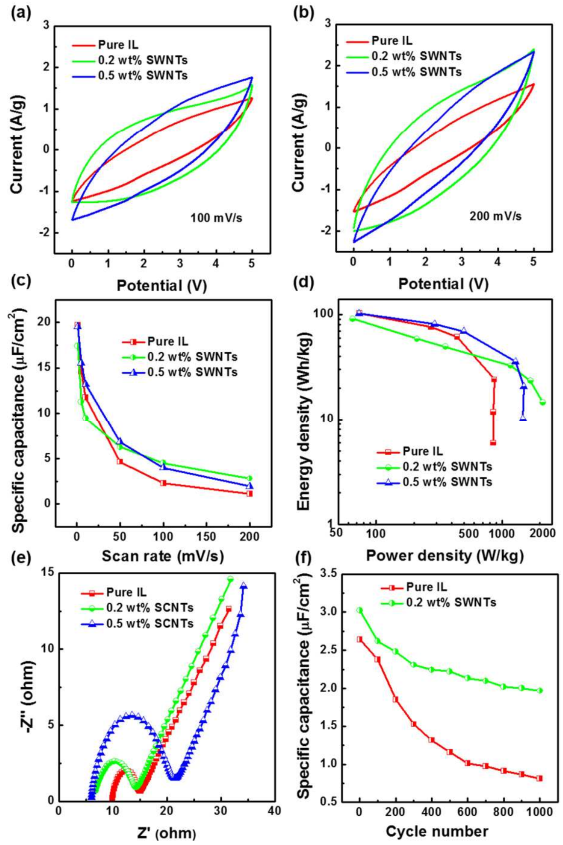

Figure 2. Capacitance performance of SCs using pure IL and different SWNTs-IL nanofluids as electrolyte. CV curves of SCs at the high scan rate of (a) 100 mV/s and (b) 200 mV/s. (c) Specific capacitance of SCs with different electrolytes under different scan rates (The data of Figure 2a, 2b and 2c under high scan rates was

obtained after the test under small scan rates in sequence). (d) Energy densities of SCs at different power densities (The data was calculated from Figure 2c). (e) Electrochemical impedance spectroscopy (EIS) of different SCs. (The data was tested before CV scan). (f) Cycling stability of different SCs under 5 V at the scan rate of 100 mV/s (The data was obtained directly under high scan rate, not via the small scan rate as in Figure 2c).

On the other hand, as to the effect of weight ratio of SWNTs, the contribution of SWNTs directly to the capacitance is very small, considering the small amount of SWNTs in electrolyte, compared to that of nanotube electrode. In theory, the capacitance of electrode in nanofluid with 0.1-0.5 wt% SWNTs should be very close under low scan rate and the capacitance using nanofluid with 0.2-0.3 wt % should have a middle value between that using pure IL electrolyte and that using nanofluid with 0.5 wt%. However, the data deviates from this trend to some degree (Figure 2c, 2d and Figure S3), probably because of the fabrication of SCs using nanofluid with different weight ratio of SWNTs or the SWNT sample uniformity. However, nanofluids adding 0.2 wt% SWNTs with higher ionic conductivity definitely give higher capacitance or higher energy density than those adding 0.5 wt% in high scan rate or high power density range (Figure 2c and 2d). Similar trends are observed if comparing the data of using nanofluid adding 0.1 wt% SWNTs and 0.3 wt% SWNTs (Figure S3). The investigation above suggests that the capacitance performance of ILs can be significantly improved by using nanofluid electrolyte.

EIS results were obtained (Figure 2e) and the capacitance behavior in the SCs was analyzed by simulation using ZSimpWin software (Figure S4). The effect of nanofluids can be further understood when the capacitance processes are divided into the parts occurred in bulk phase of electrolyte and at the electrolyte/electrode interface. Key parameters including R_Ω, C_d, R_{ct} and Z_w are assigned to the electrical resistance of bulk phase of electrolyte, the electrochemical double layer capacitance effect of electrodes, transfer resistance of electric charge, and Warburg resistance, respectively. The value of R_Ω and Z_w are decreased by 40 % and 10 %, respectively, as using nanofluids containing 0.2 wt% SWNTs, compared to that of pure ILs (Table S1). The addition of more SWNTs, e.g. 0.5 wt%, results in further decrease of R_Ω, but increases the R_{Ct} and Z_w a little bit. Therefore, nanofluid containing 0.2 wt% SWNTs, which has maximum ionic conductivity and moderate viscosity, gives the most excellent capacitance performance. Apparently, although the electrolyte doesn't contribute to the capacitance or energy density directly, it improves the performance of SC by decreasing the resistance. Since the capacitance performance of electrode doesn't change monotonously with the increased weight ratio of SWNTs, it suggests that the ionic conductivity and viscosity of nanofluid both influence the performance of electrodes. However, the ionic conductivity plays the dominant role in influencing the capacitance performance of 5 V SCs under the high scan rate up to 200 mV/s. There are similar changing trends of capacitance, energy density, power density of electrode with the ionic conductivity of nanofluids as varying the weight ratio of SWNTs. The effect of nanofluids on cycling stability of SCs was tested at 5 V and the scan rate of 100 mV/s for 1000 cycles (Figure 2f). Retention of relative capacitances using nanofluid containing 0.2 wt% SWNTs is sustainably much higher than that using pure ILs electrolyte as expected. These confirm that the nanofluid increases the cycling stability significantly, which effect can last for long time.

Raman characterization was made to understand why the capacitance decreased with operation times even using nanofluid electrolyte (Figure 3a). The intensity ratio (I_D/I_G) of D band (about 1340 cm^{-1}) and G band (about 1590 cm^{-1}) of CNTs is used to reveal the defect degree of CNTs. I_D/I_G values are 0.175 and 0.161 for dry CNT electrode and CNT electrode immersed in ILs before capacitance test, respectively. However, after 1000 cycles test, the value increases from 0.161 to 0.170 as using pure ILs electrolyte, and from 0.163 to 0.168 as using nanofluid electrolyte with 0.2 wt% SWNTs, respectively. First, the both increase of I_D/I_G value after 1000 cycles test is in agreement with the fact of capacitance decrease. Second, lower I_D/I_G value of electrode as using nanofluid electrolyte, compared to pure ILs electrolyte, evidences that nanofluid electrolyte is capable of lowering the decomposition rate of ILs. Third, pure ILs becomes somewhat yellow after 1000 cycles test, but ILs in nanofluid electrolyte containing 0.2 wt% SWNTs doesn't (Figure 3b). Apparently, high internal resistance of pure ILs results in the production of huge Jouler heat in charge and discharge process, which will decompose the ILs. The result implies that the conductive SWNTs network in nanofluid plays an important role in transferring heat from the electrolyte/electrode interface to the bulk phase of electrolyte. These features will be much useful for the thermal management of large sized capacitor[34], although the temperature increases insignificantly in small sized SC with alumina shell, which is a good thermal conductor. Further investigation in optimizing the electrode type, ILs type with high voltage and much high stability, and the thickness of electrodes, as well as the improvement of the purities of them (to exclude their negative effect[35]) is underway.

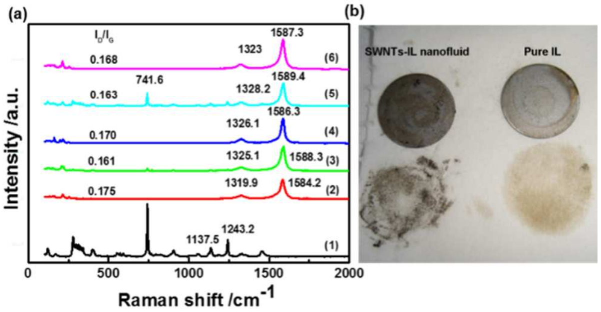

Figure 3. (a) Raman spectra of ILs and CNT electrode (LabRAM HR800, Horiba JobinYvon, France, 633 nm laser): (1) Pure BMPL NTf2 electrolyte, (2) CNT electrode, (3) CNT electrode in pure ILs electrolyte, before capacitance test. (4) CNT electrode in pure ILs electrolyte, after 1000 cycles test under 5 V at the scan rate of 100 mV/s. (5) CNT electrode in nanofluid electrolyte with 0.2 wt% SWNTs, before capacitance test. (6) CNT electrode in nanofluid electrolyte with 0.2 wt% SWNTs, after 1000 cycles test under 5 V at the scan rate of 100 mV/s. (b) Photos of SWNTs-IL nanofluid electrolyte with 0.2 wt% SWNTs and pure IL electrolyte after 1000cycles test under 5 V at the scan rate of 100 mV/s.

Conclusions

In conclusion, the addition of SWNTs in ILs of BMPL NTf2 forms a stable nanofluid electrolyte with increased ionic conductivity and, consequently, decreases the internal resistance of a 5 V SC to exhibit the higher capacitance, higher energy density and wider power density range, compared to the SCs using pure ILs electrolyte. Raman characterization evidences that the nanofluid stabilizes the electrolyte in charge and discharge with high current density and consequently, gives a much improved cycling stability of SCs.

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