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Short communication

The role of anthraquinone sulfonate dopants in promoting performance of polypyrrole composites as pseudo-capacitive electrode materials

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We report the role of anthraquinone sulfonate dopants in promoting performance of electrosynthesized polypyrrole (PPy) composites for use in electrochemical supercapacitors. The incorporation of anthraquinone sulfonate species into the polymer matrix can significantly improve the surface area of PPy composites that are composed of submicron-/nano-sized particles, as evidenced from scanning electron microscopy (SEM) results. Cyclic voltammetry and galvanostatic charge–discharge measurements in 1 M KCl solution reveal that these dopants result in an improved specific capacitance, a wide working potential range and enhanced long-cycle stability as compared to ClO_4^- dopant. Among the samples investigated, the resulting PPy/AQS (9,10-anthraquinone-2-sulfonic acid sodium salt) composite exhibits the highest specific capacitance of 608 F g^{-1} at a scan rate of 5 mV s^{-1} within a potential range between −0.9 and 0.5 V (vs. saturated calomel electrode, SCE).

1. Introduction

Electrochemical capacitors are attractive energy storage devices that fill the gap between batteries and traditional dielectric capacitors; they can be classified into two types depending on the charge storage mechanism and the electrode material used, known as electrochemical double-layer capacitors (EDLCs) and redox supercapacitors. Recently, redox supercapacitors that store energy using the pseudo-capacitive behavior of redox-active species have been the subject of intense study [1,2], because they feature higher energy densities as compared to EDLCs [1,2]. Conducting polymers [3–9] and metal oxides [10,11] are widely used as electrode materials for redox supercapacitors. Many studies [3–9] in this field have been focused on investigating conducting polymers due to their low cost, high conductivity, excellent electrochemical reversibility, and good processability.

Polypyrrole (PPy) represents an important conducting polymer successfully used in the redox supercapacitors with high charge storage capabilities [5–9]. However, PPy and other conducting polymers suffer from an inherent drawback of the limited stability upon repeated cycling. This is caused by nucleophilic attack (a reaction that involves the transfer of free electrons from a nucleophilie to its reaction partner) of other species in the electrolyte on the polymer matrix and gradual degradation in the mechanical strength during the charge–discharge process [12]. To improve the cycleability of the conducting polymer, attempts have been made using aryl sulfonates [7–10] as large-molecule dopants that are incorporated into the polymer matrix during the oxidative polymerization. It has been demonstrated that Nafion [9,10], as one typical aryl sulfonate, can release the mechanical stress and suppress the nucleophilic attack by cross-linking with the PPy chains.

Consisting of sulfonate groups similar to Nafion, the family of anthraquinone sulfonate compounds is considered to present another promising option to promote the cycleability of PPy, once these species were used as PPy dopants. More importantly, as pseudo-capacitive materials themselves, anthraquinone groups show fast redox chemistry in aqueous solutions. Previous studies [13–15] have shown that the introduction of quinone groups onto the carbon surface helps to achieve enhanced specific capacitance. Furthermore, the immobilized anthraquinone compounds are expected to widen working potential window of PPy because the redox potential of anthraquinone is negative to the potential [13,14] at which the bulk PPy is in its undoping status and loses its capacitive behavior. These advantageous features thus stimulate our interest to incorporate anthraquinone sulfonate species into the PPy matrix and understand their contributions to the capacitive performance.

In the preset study, we reported the synthesis of PPy doped with different types of anthraquinone sulfonate compounds via constant-potential anodic electropolymerization, and the role of these dopants on performance of PPy composites as pseudo-capacitive electrode materials. Four sulfonate compounds having

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Fig. 1. Chemical structures of four anthraquinone sulfonates investigated.

the similar anthraquinone group but different molecule units were taken into consideration. Their impacts on capacitive performance of the resulting polymer were discussed in terms of specific capacitance, operating potential and long-cycle stability. Such performance characteristics were obtained by taking voltammetric and galvanostatic charge–discharge measurements.

2. Experimental

The starting working electrode was a highly-doped Si wafer (n-type, 0.008–0.02 Ω cm, 510–540 μm thick) with a sputtered TiW (200 Å) + Au (2000 Å) layer on both sides of the substrate. The wafer was cut to make each sample have an effective working area of 0.64 cm^2 when it was embedded in a Teflon holder for experiments. The Teflon holder allowed one side to be immersed in the solution and the other side to function as an ohmic contact linking with an external power. The PPy composites were electrochemically deposited onto the Au surface using a three-electrode, single-chamber electrochemical cell that was controlled by a CHI 660C potentiostat (ShangHai CH Instrument Company, China). A saturated calomel electrode (SCE) electrode and a Pt mesh electrode were inserted into the cell as reference electrode and counter electrode, respectively. All the potential values reported in this study were against SCE.

The pyrrole monomer was purified by distillation prior to use. The electropolymerization of the pyrrole monomer onto the working electrode was conducted following the similar procedures as described elsewhere [16,17]. Briefly, a constant potential of 0.8 V was applied for the anodic electropolymerization in a non-stirred N_2-saturated solution that contained 0.1 M pyrrole monomer and 5 mM ionic compound. The ionic compound supplied counter-ions (dopants) for the resulting PPy composites. Four types of anthraquinone sulfonates (Fig. 1) including AQS (9,10-anthraquinone-2-sulfonic acid sodium salt), AQDS (9,10-anthraquinone-2,6-disulfonic acid sodium salt), ARS (3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid sodium salt, Alizarin Red's), AGS (3,3′-[(9,10-dihydro-9,10-dioxo-1,4-anthracenediyl)diimino]bis(6-methylbenzenesulfonic acid) disodium salt, Alizarin Green's) were selected as the dopants, forming PPy composites denoted as PPy/AQS, PPy/AQDS, PPy/ARS and PPy/AGS, respectively. For comparison, a PPy/ClO_4^- composite was also synthesized with 5 mM $NaClO_4$ solution. The weight of electrodeposited PPy composites was controlled by adjusting the amount of charge applied according to the Faraday's law.

The surface morphology of the resulting composites was examined using a JEOL JSM-6390 scanning electron microscope (SEM). Cyclic voltammetry (CV) and galvanostatic charge–discharge tests were performed in 1 M KCl solution. The CV curves were recorded within the potential window of −0.9 to 0.5 V at a scan rate of 5 mV s^{-1} and the charge–discharge curves were recorded within the potential window of −0.8 to 0.5 V at a current load of 0.28 mA cm^{-2}.

3. Results and discussion

The identity of dopants plays a significant role in the morphology of the conducting polymer. For being used as pseudo-capacitive electrode materials, the resulting PPy composites with small par-

Fig. 2. SEM images of (a) PPy/ClO_4^-, (b) PPy/AGS, (c) PPy/ARS, (d) PPy/AQDS and (e) PPy/AQS composites synthesized with at 0.8 V with a charge density of 170 mC cm^{-2}. (f) The magnified image of the nano-sized structure of PPy/AQS.

ticle size and high porosity are desirable, because these features enable more surface active sites for redox reactions and thus help to achieve higher specific capacitance. Fig. 2 shows the SEM images of the electro-synthesized PPy/ClO_4^-, PPy/AGS, PPy/ARS, PPy/AQDS and PPy/AQS composites. The PPy/ClO_4^- composite has a cluster-like morphology and consists of smooth, unequal clusters with size more than 5 μm (Fig. 2a). On the other hand, use of anthraquinone sulfonate dopants leads to a significant decrease in particle size (Figs. 2b–f). These observations should be ascribed to the fact that the presence of quinone and sulfonate groups makes the surface hydrophilic [7,8] and hence prevents the particles to agglomerate. As it can be seen, each anthraquinone sulfonate-doped PPy sample exhibits a rough and granular morphology. The PPy/AQS composite is composed of particles with the smallest size among four samples. The high-magnification picture (Fig. 2f) clearly shows that it has a nano-sized structure and the particles have a size range between 50 and 100 nm.

Cyclic voltammograms of PPy film provide important information about its pseudo-capacitive performance as a function of the type of dopants. Fig. 3 shows voltammograms of PPy/AQS, PPy/AQDS, PPy/ARS and PPy/AGS in 1 M KCl solution. For comparison, voltammogram of PPy film using ClO_4^- as the counter-ion was also recorded in each figure. In the potential range of −0.2 to 0.5 V, the PPy/ClO_4^- electrode features a typical pseudo-capacitive profile, which is originated from the repeating intercalation and ejection of ions in the aqueous solution into and out of the PPy polymer during the redox processes [18,19]. The incorporation of different anthraquinone sulfonate species in the PPy matrix significantly improves the specific capacitance, as indicated by important differences in cyclic voltammograms. The first distinct difference is that four anthraquinone sulfonate-doped PPy composite electrodes exhibit higher output current than the PPy/ClO_4^- electrode within the similar potential range (e.g., from −0.2 to 0.5 V), demonstrating the enhanced specific capacitance. This result should be attributed to the improved surface area of these electrodes, as illustrated in the SEM images (Fig. 2). The second visible difference is that additional redox peaks are observed at poten-

Fig. 3. Cyclic voltammograms of (a) PPy/AQS, (b) PPy/AQDS, (c) PPy/ARS, (d) PPy/AGS and PPy/ClO_4^- (this is contained in every figure for comparison purposes) composite electrodes in 1 M KCl solution. Cyclic voltammogram of a bare Au electrode in 5 mM AQS, AQDS, ARS or AGS aqueous solution was also recorded in the corresponding figure. All the cyclic voltammograms were recorded at a scan rate of 5 mV s^{-1} within a potential range between −0.9 and 0.5 V.

tials negative to the redox potential of PPy. These additional redox peaks are associated with oxidation–reduction processes of hydroanthraquinone/anthraquinone groups [13,14] present in the PPy matrix, since their positions are consistent with those observed from CV tests using bare Au electrode in an aqueous solution containing 5 mM anthraquinone sulfonate compounds. These observations confirm the successful incorporation of anthraquinone sulfonates into the PPy matrix. It can be seen that such doping processes are capable of widening the potential range over fast redox reactions, indicating that anthraquinone sulfonate-doped PPy composites can be used as promising capacitor electrode materials.

The specific capacitance (C) of PPy doped with different types of counter-ions was calculated from the CV plot in Fig. 3 using equation C =(+)/(2 × × Δv), where , , , Δv are indicative of the sum of anodic voltammetric charge, the sum of cathodic voltammetric charge, the mass of polymer and the potential window of CV test, respectively. The PPy/AQS and PPy/AQDS electrode possess a value of 608 and 506 F g^{-1}, respectively, increased by 2.5 and 2.0 times as compared to PPy/ClO_4^- (243 F g^{-1}). These high specific capacitances are comparable to the maximum value in other reports [5,6] concerning the capacitive performance of pure PPy materials. Likewise, the PPy/ARS and PPy/AGS electrode also exhibit higher specific capacitance than PPy/ClO_4^-, with a value of 359 and 355 F g^{-1}, respectively. However, the amount of the increased specific capacitance for PPy/ARS and PPy/AGS is significantly smaller than that corresponding to PPy/AQS and PPy/AQDS. This can be explained by the less facile and reversible redox behavior of ARS and AGS species (Figs. 3c and d), and by the less roughness of the polymer surface (Fig. 2).

Galvanostatic charge–discharge curves of different PPy materials were recorded (Fig. 4a) at a current load of 0.28 mA cm^{-2} within the potential window from −0.8 to 0.5 V. Each curve features a mirror-like profile during one charge–discharge cycle, indicating theses polymers have good charge–discharge reversibility as capacitive materials. It should be noted that the galvanostatic discharge curves for the PPy composites are not linear and they are characterized by varying slopes during discharge particularly for the PPy/AQS and PPy/AQDS samples. The difference in slope is related with potential range-dependant pseudo-capacitance behavior which is also evidenced from CV curves (Fig. 3). For example, the PPy/AQS composite exhibits a quasi-linear pattern of discharge curves in the potential range from −0.4 to 0.5 V, caused by the repeating intercalation and ejection of cations and anions from aqueous solution. The discharge curves of PPy/AQS in the potential range from −0.8 to −0.4 V are also quasi-linear but with a different slope. This result should be attributed to the fast electrochemical redox reaction of the immobilized anthraquinone groups. The lower slope of the discharge curve is indicative of a higher specific capacitance according to C =(× t)/(×), where is the charge–discharge current, t is the discharge time, is the potential widow. The specific capacitance calculated for each PPy composite within the total potential range decreases in the order of PPy/AQS (617 F g^{-1}) > PPy/AQDS (520 F g^{-1}) > PPy/ARS (351 F g^{-1}) > PPy/AGS (341 F g^{-1}) > PPy/ClO_4^- (242 F g^{-1}). It is found that the galvanostatic and CV measurements provide very close values of C for the composite electrodes.

As an efficient pseudo-capacitive material, its stability subjected to long-time charge–discharge cycles is an important consideration. The charge–discharge cycling tests were performed for 1000 cycles. The specific capacitance was calculated and plotted as a

Fig. 4. (a) Galvanostatic charge–discharge curves of different PPy composite electrodes at a current load of 0.28 mA cm^{-2} within a potential range between −0.8 and 0.5 V in 1 M KCl solution. (b) Specific capacitance of different PPy composite electrodes calculated based on galvanostatic charge–discharge tests as a function of cycle number.

function of cycling number, as presented in Fig. 4b. Notice that the specific capacitance of PPy/AQS, PPy/AQDS, PPy/ARS, PPy/AGS and PPy/ClO_4^- after 1000 cycles retains 87%, 84%, 88%, 81% and 51% of its initial value, respectively. It is clear that the incorporation of anthraquinone sulfonate groups allows a slow decrease in the specific capacitance. This increasing stability of PPy composites should be explained by the following reasons: (i) the large-molecule anthraquinone sulfonate ions are considered to be "fixed" as bulky dopants [8,20], thus they are more difficult to be expelled from the polymer as compared to ClO_4^- and (ii) the presence of both anthraquinone and sulfonate groups in the PPy matrix promotes cross-linking of the polymer chain, leading to the formation of submicron-/nano-sized PPy structure in which the mechanic stress caused during repeated cycling can be released.

4. Conclusions

We have demonstrated that the anthraquinone sulfonate dopants can significantly improve performance of PPy composites as pseudo-capacitive electrode materials. In comparison with PPy/ClO_4^-, four anthraquinone sulfonate-doped conducting polymers including PPy/AQS, PPy/AQDS, PPy/ARS, and PPy/AGS possessed higher surface area, higher specific capacitance, wider working potential window and better long-cycle stability, as evidenced from SEM, CV and galvanostatic charge–discharge measurements. These benefits were attributed to the facts that the anthraquinone and sulfonate dopants can generate more hydrophilic surfaces with the submicron-/nano-sized structure, and that the immobilized anthraquinone groups themselves show fast redox electrochemistry. This study offers a promising strategy to the preparation of electro-active conducting polymers for supercapacitor applications.

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References

[1] K. Naoi, M. Morita, Electrochem. Soc. Interface 17 (2008) 44–48.
[2] P. Simon, Y. Gogotsi, Nat. Mater. 7 (2008) 845–854.
[3] H. Li, J. Wang, Q. Chu, Z. Wang, F. Zhang, S. Wang, J. Power Sources 190 (2009) 578–586.
[4] R. Liu, S.I. Cho, S.B. Lee, Nanotechnology 19 (2008) 215710–215717.
[5] L.Z. Fan, J. Maier, Electrochem. Commun. 8 (2006) 937–940.
[6] R.K. Sharma, A.C. Rastogi, S.B. Desu, Electrochem. Commun. 10 (2008) 268–272.
[7] M.D. Ingram, H. Staesche, K.S. Ryder, Solid State Ionics 169 (2004) 51–57.
[8] M.D. Ingram, H. Staesche, K.S. Ryder, J. Power Sources 129 (2004) 107–112.
[9] B.C. Kim, J.M. Ko, G.G. Wallace, J. Power Sources 177 (2008) 665–668.
[10] R.Y. Song, J.H. Park, S.R. Sivakkumar, S.H. Kim, J.M. Ko, D.Y. Park, S.M. Jo, D.Y. Kim, J. Power Sources 166 (2007) 297–301.
[11] R.K. Sharma, A.C. Rastogi, S.B. Desu, Electrochim. Acta 53 (2008) 7690–7695.
[12] J.M. Ko, K.S. Ryu, S. Kim, K.M. Kim, J. Appl. Electrochem. 39 (2009) 1331–1337.
[13] Z. Algharaibeh, X. Liu, P.G. Pickup, J. Power Sources 187 (2009) 640–643.
[14] K. Kalinathan, D.P. DesRoches, X. Liu, P.G. Pickup, J. Power Sources 181 (2008) 182–185.
[15] M. Seredych, D. Hulicova-Jurcakova, G.Q. Lu, T.J. Bandosz, Carbon 46 (2008) 1475–1488.
[16] C. Feng, P.C.H. Chan, I.-M. Hsing, Electrochem. Commun. 9 (2007) 89–93.
[17] C. Feng, L. Ma, F. Li, H. Mai, X. Lang, S. Fan, Biosens. Bioelectron. 25 (2010) 1516–1520.
[18] C. Peng, S. Zhang, D. Jewell, G.Z. Chen, Prog. Nat. Sci. 18 (2008) 777–788.
[19] M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A.H. Windle, Chem. Mater. 14 (2002) 1610–1613.
[20] C. Zhong, K. Doblhofer, Electrochim. Acta 35 (1990) 1971–1976.