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Multilayered Nanoarchitecture of Graphene Nanosheets and Polypyrrole Nanowires for High Performance Supercapacitor Electrodes

Sanjib Biswas and Lawrence T. Drzal*

Department of Chemical Engineer and Materials Science, Composite Materials and Structures Center, Michigan State University, East Lansing, Michigan 48824-1226

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A novel nanoarchitecture is developed by combining the nanostructured conductive polymer polypyrrole with highly electrically conductive graphene nanosheets in a multilayered configuration to achieve high specific capacitance and low electronic resistance for supercapacitor electrode applications. The fibrous network of polypyrrole nanowires with high electrolyte ionic accessibility was interspersed with electrically conductive monolayers of highly aligned large sized graphene nanosheets as a series of current collectors within the macroscopic configuration for enhanced electronic charge transport inside the electrode. A fabrication method relying on capillary force driven self-assembly coupled with the strong van der Waals attraction between highly aromatic graphene basal plane and π conjugated conductive polymer chains was employed to create a 100% binder free multilayered composite structure of these two distinct nanoscale elements to construct the electrode. This multilayer composite electrode exhibits a high specific capacitance of ~165 F/g with a nearly ideal rectangular cyclic voltammogram at increasing voltage scanning rates and high electrochemical cyclic stability.

Introduction

The highly aromatic two-dimensional macromolecule graphene, with exceptionally low intrinsic electrical resistivity, is a potential candidate as a novel electrode material for electrochemical energy storage applications.[1−3] Exfoliated graphene nanosheets with stacks of a few single layers of graphene can be simply and inexpensively prepared from acid intercalation and thermal exfoliation of natural graphite without requiring extensive chemical oxidation to graphite oxide and subsequent reduction back to graphene.[4,5] The average thickness of these nanosheets ranges from 3 to 5 nm with a lateral dimension close to 15 μm.[4,5] A homogeneous and orderly distribution of these highly aromatic large sized nanosheets in combination with other nanomaterial can be nanostructured into a bulk macroscopic configuration which can exploit the unique properties as well as maximize device performance.

In an electrical double layer capacitor, the electrochemical charge storage ability of aromatic graphene basal plane arises from the electronic and the ionic charge separations at the electrode−electrolyte interfaces.[6−8] On the other hand, the faradic charge transfer mechanism across the electrode−electrolyte interface significantly boosts the charge storage capacity of redox or pseudocapacitors when graphene is combined with conductive polymers.[6,9−14] The use of a conductive polymer like polypyrrole is particularly promising owing to its high energy storage capacity, good electrical conductivity, ease of low cost synthesis, and environmental stability.[9−12] However, the realization of high specific capacitance is only possible with effective electrolyte transport to the active sites for enhanced faradic charge transfer reactions. A nanostructured fibrous network of polypyrrole is, therefore, expected to demonstrate rapid ionic transport within the bulk matrix.[10,15−17] However, even with increased ionic transport to the active sites, the rate capability of conductive polymers is limited by the change in the structural conformation with repeated ion exchange and consequent diminution of electrical properties

(1) Allen, M. J.; Tung, V. c.; Kaner, R. B. *Chem. Rev*. **2010**, *110*, 132–145.
(2) Rao, C. N. R.; Sood, A. K.; Subrahmanyam, K. S.; Govindaraj, A. *Angew. Chem., Int, Ed.* **2009**, *48*, 7752–7777.
(3) Geim, A. K. *Science* **2009**, *324*, 1530–1534.
(4) Fukushima. H. Graphite Nanoreinforcements in Polymer Nanocomposites. Ph.D. Dissertation, Michigan State University, East Lansing, MI, 2003.
(5) Biswas, S.; Drzal, L. T. *Nano Lett*. **2009**, *9*, 167–172.
(6) Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*; Springer: 1999.
(7) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science* **2006**, *313*, 1760–1763.
(8) Lota, G.; Centeno, T. A.; Frackowiak, E.; Stoeckli, F. *Electrochim. Acta* **2008**, *53*, 2210–2216.
(9) Wang, H. L.; Hao, Q. L.; Yang, X. J.; Lu, L. D.; Wang, X. *Electrochem. Commun*. **2009**, *11*, 1158–1161.
(10) Wu, Q. F.; He, K. X.; Mi, H. Y.; Zhang, X. G. *Mater. Chem. Phys*. **2007**, *101*, 367–371.
(11) Zhou, C.; Kumar, S. *Chem. Mater*. **2005**, *17*, 1995–2002.
(12) An, K. H.; Jeon, K. K.; Jeong, K. H.; Lim, S. C.; Bae, D. J.; Lee, Y. H. *J. Electrochem. Soc*. **2002**, *149*, A1058–A106.
(13) Gupta, V.; Miuraa, N. *Electrochem. Solid State Lett*. **2005**, *8*, A630–632.
(14) Najafabadi, A. I.; Tan, D. T. H.; Madden, J. D. *Synth. Met*. **2005**, *152*, 129–132.
(15) Arico, A. S.; Bruce, P.; Scrosati, B.; Terascon, J. M.; Schalkwikj, W. V. *Nat. Mater*. **2005**, *4*, 366–367.
(16) Manthiram, A.; Murugan, A. V.; Sarkar, A.; Muraliganth, T. *Energy Environ. Sci*. **2008**, *1*, 621–638.
(17) Centi., G.; Perathoner., S. *Eur. J. Inorg. Chem*. **2009**, *26*, 3851–3878.

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with increasing electrochemical cycles.[18] Introduction of carbon nanomaterials such as carbon nanotubes or graphene is highly favorable to create an electrically conducting network to improve the electrochemical cyclic stability of the electrode. The conventional techniques such as the electropolymerization or chemical polymerization uniformly encapsulate the carbon nanomaterials with a thick polymer coating, and individual nanosheets can no longer form an interconnected network inside the bulk electrode matrix which is highly desirable to reduce the electronic resistance to improve the electrochemical stability and also to achieve rapid charge−discharge characteristics at high discharge current densities.[12,14,19,20] This research shows that it is possible to integrate the polymerized nanostructure polypyrrole with graphene nanosheets in a directed self-assembly approach governed by the large van der Waal's force of attraction between the graphene basal plane and the π conjugated polymer in a layered composite structure. Taking advantage of capillary force driven self-assembly of layers of polypyrrole nanowires and graphene nanosheets, this approach can create a multilayered nanoarchitecture with a homogeneous and orderly distribution of graphene nanosheets for an enhanced performance supercapacitor electrode.

Experimental Procedure

Pyrrole monomer, cetyltrimethylammonium bromide (CTAB), ammonium persulfate (APS), and sodium chloride was purchased from Sigma Aldrich and were used without any further purification.

Graphene nanosheets were prepared by following the method described earlier.[4] Polypyrrole nanowire was prepared by following the method by Wu et al.[10] In this chemical polymerization process, 0.91 g of the surfactant CTAB is mixed with 0.3 mL of pyrrole monomer in 125 mL of 0.2 M aqueous HCl solution. The mixture was then stirred at 0−5 °C for 2 h. Then, the oxidizing agent ammonium per sulfate (APS), dissolved in 10 mL of 0.2 M HCl solution, was added dropwise to the CTAB and pyrrole mixture. The mixture turned light green to dark green in a few minutes. The mixture was allowed to stir at 0−5 °C for 24 h. The black precipitate was filtered and washed with copious amounts of water to remove any excess acid or surfactant.

Monolayer films of graphene nanosheets were prepared by following the technique described earlier.[5] To prepare the nanowire film, 0.1 g of nanowire was dispersed in water by sonicating the mixture for a few minutes. Then, chloroform was added as the second immiscible phase, and the mixture was again sonicated to cause the nanowire to adsorb at the liquid−liquid interface. The interface was then shaken to produce emulsified droplets, which float to the air−water surface where the chloroform evaporates, leaving a dry thin film of nanowires at the air−water interface. This film was then transferred by pulling the substrate through the interface.

For electrochemical measurements, a 1 M NaCl aqueous solution was used as electrolyte. The multilayer structure of graphene nanosheets and polypyrrole nanowire was assembled on a stainless steel current collector which was separated by a Whatman filter paper. The two electrode assembly was compressed between transparent nylon plates at the top and bottom and was immersed in the electrolyte for electrochemical measurements.

Instrument. All the electrochemical measurements were carried out in a "versaSTATMC" multichannel potentiostat/galvanostat instrument from Princeton Applied Research, Ametek. The frequency response characteristics were analyzed using versastudio software from Princeton Applied Research. Electrochemical impedance spectra (EIS) was measured at a frequency range from 10 000 to 0.01 Hz with 0 V mean voltage and amplitude 10 mV. Field emission scanning electron microscopy (FESEM) images were taken by a JEOL JSM-7500F scanning electron microscope. The electrical conductivity was measured by a four point probe set up from a Keithley 2400 source meter.

Results and Discussion

Fabrication of multilayered nanoarchitecture with large and small sized nanosheets of graphene nanosheets from the liquid−liquid interfacial approach have been earlier demonstrated to develop a supercapacitor electrode with enhanced capacitance and improved rate capabilities.[29] In this approach, the use of monolayers of highly electrically conductive large sized graphene nanosheets serves as a series of current collectors within the multilayer configuration to achieve rapid charge−discharge characteristics with minimum equivalent series resistance.[29] In a similar approach, here, we integrate the large sized graphene nanosheets with polypyrrole nanowires to investigate the effect of reduced electronic resistance and increased ionic accessibility from the presence of a fibrous network of nanowires on the electrochemical energy storage, rate capability, and cyclic stability of this new composite supercapacitor electrode.

A surfactant assisted soft template approach was employed to prepare polypyrrole nanowire with an average diameter from 40 to 60 nm.[10,21] The specific surface area of the fibrous nanowire, obtained from nitrogen adsorption technique at liquid nitrogen temperature, was 91 m^2/g. The total pore volume obtained from single point adsorption at ~0.98 relative pressure was 0.376 cm^3/g. Self-assembly of hydrophobic organic nanowires at the liquid−liquid interface was demonstrated earlier.[22] The hydrophobicity of polypyrrole nanowire was confirmed by the contact angle (~ 69°) formed by a water droplet on a dry film. With this reasonable hydrophobicity, these nanowires can be adsorbed at a liquid−liquid interface and can be subsequently transported to the air−water interface to form a thin film, floating on the water surface. The film can then be easily transferred on a desired substrate by pulling the substrate through the air−water interface.

To investigate the morphology and dispersion of polypyrrole nanowires on the graphene nanosheets, a thin film of nanowires was first transferred to a substrate coated with a monolayer film of graphene nanosheets.[5] The nanowires

(18) Otero, T. F.; Padilla, J. *J. Electroanal. Chem.* **2004**, *561*, 167–171.
(19) Oh, J.; Kozlov, M. E.; Kim, B. G.; Kim, H. K.; Baughman, R. H.; Hwang, Y. H. *Synth. Met.* **2008**, *158*, 638–643.
(20) Zhou, C.; Kumar, S.; Doyle, C. D.; Tour, J. M. *Chem. Mater.* **2005**, *17*, 1997–2002.
(21) Zhang, X.; Zhang, J.; Song, W.; Liu, Z. *J. Phys. Chem. B* **2006**, *110*, 1158–1165.
(22) Zhang, C.; Zhang, X.; Zhanga, X.; Ou, X.; Zhang, W.; Jie, J.; Chang, J. C.; Lee, C. S.; Lee, S. T. *Adv. Mater.* **2009**, *21*, 4172–4175.

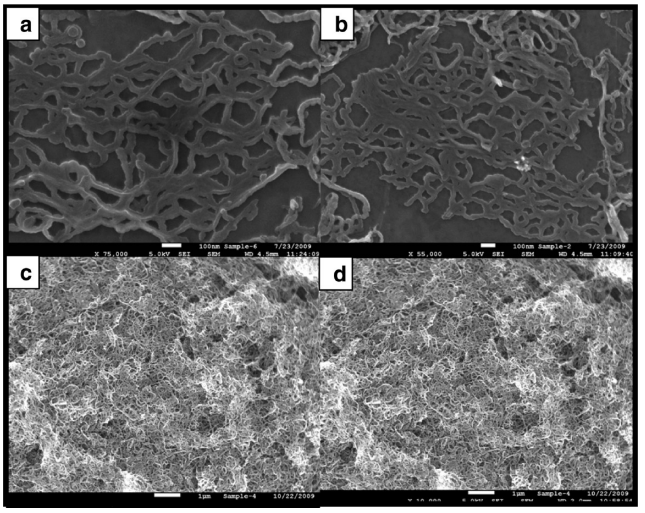

Figure 1. Morphology of polypyrrole nanowire: A highly dispersed network polypyrrole nanowire with an average diameter of 40−60 nm is attached to the large basal plane of graphene nanosheets in (a and b). With multilayer deposition, the highly fibrous morphology of these nanowires is shown in (c and d).

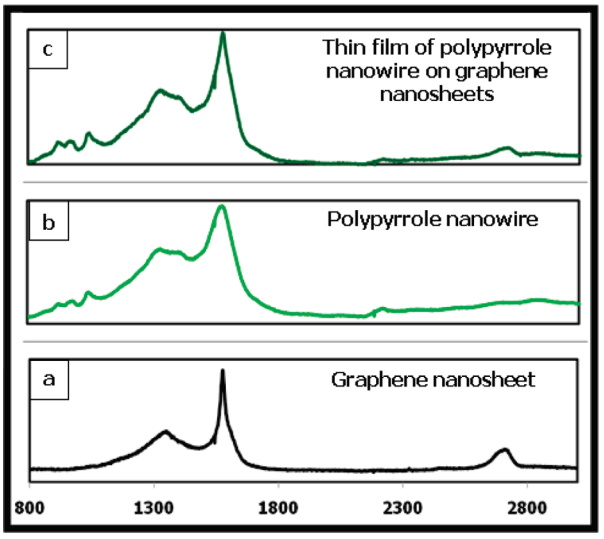

Figure 2. Raman spectra analysis: (a) Graphene nanosheets with sharp G band, D band, and 2D peaks at 1575, 1344, and 2700 cm^{-1}. (b) Polypyrrole nanowire with peaks near 927, 977, 1046, 1330, and 1572 cm^{-1} (c) Thin film of polypyrrole nanowire deposited on graphene nanosheets with peaks near 927, 977, 1046, 1338, 1575, and 2700 cm^{-1}.

are wet by a thin film of water and are in close contact with the graphene nanosheets. With continuous evaporation of water, the strong capillary force causes the interlayer separation between the nanowires to decrease and the layers to collapse on each other. After complete liquid evaporation, the strong van der Waal's force of attraction between the highly aromatic graphene basal plane and the π conjugated polymer film assembles these two nanostructures on top of another. The adhesion of the nanowires to the graphene nanosheets was found to be sufficiently strong to resist removal under flowing water. FESEM micrographs in Figure 1a,b clearly show the highly dispersed network of polypyrrole nanowires deposited on the graphene nanosheet.

The interaction between the nanowires on the aromatic graphene basal plane was investigated by Raman spectra analysis. For graphene the nanosheets in Figure 2a, the high intensity of the G band peak at 1575 cm^{-1} as compared to the low intensity "disordered and defect" D band peak at 1344 cm^{-1} demonstrates the aromatic purity of the graphene basal plane. As shown in Figure 2b, for the control polypyrrole nanowire sample, the appearance of peaks near 1572 and 1330 cm^{-1} arises from the π conjugated structure and ring stretching mode of the polymer backbone, respectively.[23−26] The broad peak obtained near 1046 cm^{-1} corresponds to the C−H in-plane deformation and two small peaks near 927 and 977 cm^{-1} are associated with the quinoid polaronic and bipolaronic structure, respectively.[23−26] With the deposition of thin film of polypyrrole nanowire on the graphene nanosheet, the Raman spectra as shown in Figure 2c is essentially composed of both pure polypyrrole and graphene nanosheets. For this composite thin film, reappearance of bands near 927, 977, and 1046 cm^{-1} are identical to the pure polypyrrole sample. However, as compared to the pure polypyrrole sample, the increase in the ratio of the sharp G band peak at 1575 cm^{-1} as compared to the defect band near 1338 cm^{-1} reflects the interaction between the π conjugated nanowire and aromatic graphene basal plane without compromising the chemical identity of either of these two nanomaterials.

The electrical conductivity of the polypyrrole nanofibrous film was 65 S/m measured with a standard four point probe method. The graphene nanosheet film on the other hand exhibited more than 2 orders of magnitude higher electrical conductivity of the order of 1.25×10^4 S/m.[29] In order to exploit this high electrical conductivity of graphene nanosheets, polypyrrole nanowires were interspersed between graphene nanosheets in a multilayer configuration to form a supercapacitor electrode.

As illustrated in Figure 3a, the fabrication of the multilayer film electrode requires the formation and deposition of a bilayer film of large sized graphene nanosheets on the stainless steel plate to minimize the interfacial contact resistance between the active electrode material and the current collector surface.[29] Multiple layers of polypyrrole nanowires were then deposited on top of this monolayer film of graphene nanosheets to create a fibrous network of nanowire as shown in Figures 1c,d and 3b. Subsequently, another monolayer of large sized graphene nanosheets was placed to uniformly cover the fibrous network of polypyrrole nanowires (Figure 3c).

The FESEM images in Figure 4 show that the nanosheets are highly dispersed and form an edge shared interconnected network to create a highly electrically conductive conduit inside the bulk electrode. These nanosheets are not only connected with each other near their edges

(23) Wu, T. M; Chang, H. L.; Lin, Y. W. *Compos. Sci. Technol.* **2009**, *69*, 639–644.
(24) Fan, J.; Wan, M.; Zhu, D.; Chang, B.; Pan, Z.; Xie, S. *J. Appl. Polym. Sci.* **1999**, *74*, 2605–2610.
(25) Wanekaya, A. K.; Lei, Y.; Bekyarova, E.; Chen, W.; Haddon, R.; Mulchandani, A.; Myung, N. V. *Electroanalysis* **2006**, *18*, 1047–1054.
(26) Han, G.; Yuan, J.; Shi, G.; Wei, F. *Thin Solid Films* **2005**, *474*, 64–69.

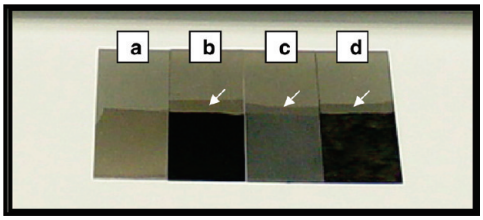

Figure 3. Development of multilayer structure of graphene nanosheets and polypyrrole nanowire: In (a), the stainless steel substrate was coated with a bilayer film of graphene nanosheets; in (b), a multilayer of polypyrrole nanowire was deposited on the bilayer graphene nanosheets film; in (c), a monolayer of graphene nanosheets was deposited covering the PPy nanowire and also extended to the top section to attach to the current collector surface; in (d), one layer of PPy nanowire was deposited on the monolayer graphene film; the process was repeated to create the multilayer structure.

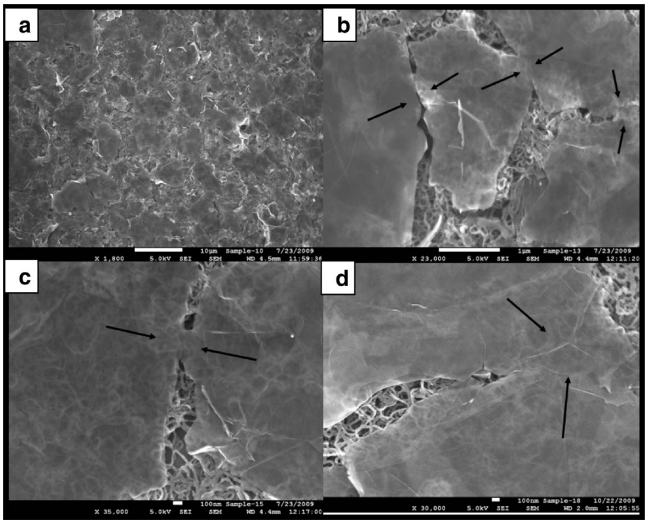

Figure 4. Morphology of graphene nanosheets deposited on polypyrrole nanowire: A low magnification image in (a) demonstrates the uniform monolayer coverage of graphene nanosheets deposited on the fibrous network of polypyrrole nanowire. High magnification images from (b−d) clearly exhibit the dispersed interconnected network of graphene nanosheets near their edges (indicated by the arrows).

(shown by the arrows in Figure 4b−d) but also interact with the polypyrrole nanowire through strong van der Waal's force of attraction with the highly aromatic graphene basal plane. As shown in Figure 3b−d (shown by the arrows), in the top section, the large sized nanosheets are firmly attached to the current collector surface to serve as a series of current collectors within this multilayer configuration. Multilayered deposition of these two nanostructured materials was repeated to produce a 100% binder free electrode for supercapacitor applications.

The electrochemical property of this multilayered film was characterized using a two electrode cell immersed in 1 M aqueous NaCl solution. To assess the effect of addition of graphene nanosheets on the capacitative response and the electrical properties of the film, a control sample was prepared by the same technique from multilayer deposition of the polypyrrole nanowires directly on the metal current collector. In Electrochemical double layer capacitor (EDLC) performance, an oblique and narrow shaped cyclic voltammogram results from large internal and

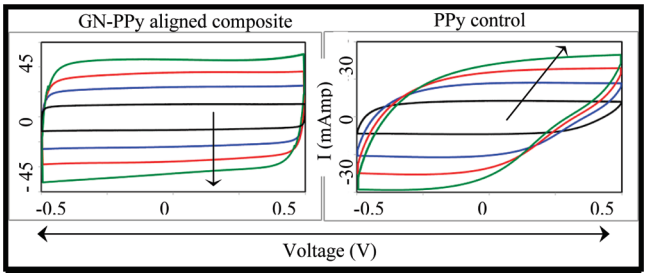

Figure 5. Electrochemical characterization. Cyclic voltammetric characteristics of multilayer composite of polypyrrole (PPy)/graphene nanosheets and control polypyrrole sample are compared at an increasing voltage scanning rate of 25, 50, 75, and 100 mV/s.

interfacial contact resistance of the active electrode materials inside the bulk electrode.[6] Figure 5 compares the cyclic voltammetry characteristics of the layered composite of polypyrrole nanowires and graphene nanosheets with the control polypyrrole nanowire sample. A nearly ideal rectangular shaped cyclic voltammogram (CV) for the aligned composite at increasing voltage scanning rate from 10 to 100 mV/s clearly demonstrates excellent ionic and electronic transport within the bulk multilayered configuration of polypyrrole nanowires and graphene nanosheets. Under similar measurement conditions, the fibrous network of the control polypyrrole sample failed to maintain the capacitative response with increasing voltage scanning rate. While the electrolyte ionic accessibility inside the bulk electrode is highly favorable from the fibrous network of the polypyrrole, it appears that the presence of a series of aligned graphene nanosheets within the bulk matrix facilitates enhanced electronic transport with high capacitative response even with increasing voltage scanning rate.

The enhanced electronic transport with the incorporation of aligned graphene nanosheets is also evident from the impedance analysis. The equivalent circuit of different elements from the impedance spectra is presented in Figure 6a. This equivalent circuit includes bulk solution resistance Rs, the contact interface resistance Rc, the double layer capacitance C_d, and a pseudocapacitative element C_p from the redox process involving the conductive polymer.[27,28] The bulk solution resistance Rs and the contact interface resistance Rc is obtained from the Nyquist plot, where the high frequency semicircle intercepts the real axis at Rs and (Rs + Rc) respectively.[27,28] As shown in Figure 6c,d, the bulk solution resistance Rs differs by only 20−30 mΩ for these two electrodes. However, the contact interface resistance Rc for the aligned composite is more than 1 order of magnitude smaller than the control polypyrrole sample. This clearly demonstrates the reduced interfacial contact resistance between the active electrode materials inside the bulk electrode and minimum interfacial contact resistance of two-dimensional large sized graphene nanosheets with the current collector surface. Moreover, the above analysis points to the strength of the underlying van der Waal's force of interaction

(27) Wang, K. P.; Teng, H. *J. Electrochem. Soc.* **2007**, *154*, A993–A998.
(28) Huang, C. W.; Teng, H. *J. Electrochem. Soc.* **2008**, *155*, A739–A744.
(29) Biswas, S.; Drzal, L. T. *ACS Appl. Mater. Interfaces* **2010**, *2*(8), 2293–2300.

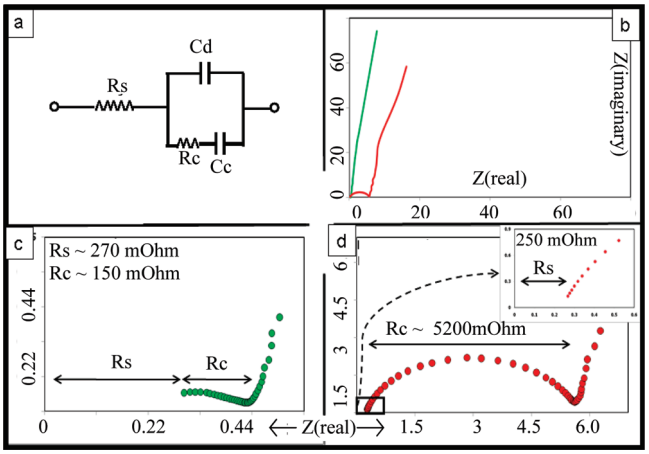

Figure 6. Complex plane impedance analysis: (a) represents the equivalent circuit diagram of different elements from the impedance spectra analysis; (b) compares the complex plane impedance characteristics from high to low frequency for the multilayer composite of polypyrrole/graphene nanosheets (green) and control polypyrrole sample (red); (c and d) compare the high frequency responses with corresponding measurement of solution resistance Rs and contact interface resistance Rc.

between the polpyrrole nanowire and large aromatic graphene basal plane for facile interlayer charge transport within the composite multilayer configuration. Instead of encapsulating the graphene nanosheets with a thick polymer coating by chemical or electro-polymerization, in this new approach, a series of edge shared highly aligned monolayer films was incorporated inside this multilayer electrode configuration not only to reduce the electronic resistance between the active electrode materials but also to enhance the charge transport from the interior of the bulk electrode to the current collector surface through the strongly attached graphene nanosheets at the top section of the electrode. The higher rate capability of the aligned composite is evident from a knee frequency close to 50 Hz, as shown in Figure 6c.

The increase in the charge transport also had a stabilizing effect on the capacity retention of polypyrrole nanowires under continuous electrochemical cycling. As shown in Figure 7, at the end of one thousand cycles, the aligned composite electrode maintains a symmetric charge−discharge shape with more than 92% capacitance retention at 1 A/g cyclic discharge current density. However, it was found that with increasing voltage drop (IR drop) the control specimen of polypyrrole nanowire failed to maintain the capacitative response in less than 250 electrochemical cycles at 1 A/g discharge current density.

The volumetric swelling and contraction of the polymer chain from continuous injection and rejection of solvated ions and electronic charges during the cyclic electrochemical oxidation and reduction process significantly modifies the charge distribution and conformation of π conjugated polymer chains.[18] It is possible that the increasing IR drop for the control polypyrrole electrode is due to this deteriorating electrical performance with increasing electrochemical cycling. The high electrochemical stability

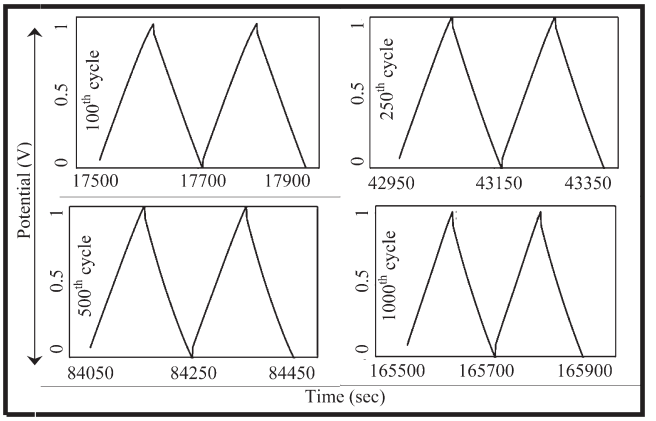

Figure 7. Cyclic stability. At 1 A/g constant current density, the multilayer composite of polypyrrole and graphene nanosheets continues to maintain highly symmetric charge−discharge characteristics from 100th to 1000th electrochemical cycles with a potential drop of only 30 mV.

obtained with the incorporation of graphene nanosheets again verifies the strong interlayer interaction between the aromatic graphene nanosheets and the π conjugated polymer chains for enhanced charge transport within the multilayered nanostructure during an electrochemical cyclic stability test. The specific capacitance obtained from the discharge slope of constant current galvanostatic technique was 165 F/g at the end of 1000 cycles at 1 A/g discharge current density.

Conclusion

Previous research employed a chemical or electropolymerization approach to uniformly cover graphene nanosheets or carbon nanotubes with a thick polymer coating for fabrication of composite electrodes for supercapacitor applications. In this new approach, aligned monolayers of graphene nanosheets are interspersed within the fibrous network of polypyrrole to function as a series of current collectors inside the multilayer bulk electrode configuration. This nanostructured electrode exhibits high ionic and electronic transport due to the combined presence of the fibrous network of polypyrrole and electrically conductive graphene nanosheets. Impedance analysis clearly shows the low equivalent series resistance obtained from the interlayer charge transport between the large graphene basal plane and the π conjugated polymer chain. The facile electronic charge transport due to the presence of graphene nanosheets also had a stabilizing affect on the electrochemical cyclic stability of this composite electrode. This multilayer film electrode displays symmetric charge−discharge characteristics and a nearly ideal rectangular cyclic voltammogram with increasing voltage scanning rate from 10 to 100 mV/s. While maintaining a high frequency capacitative response with a knee frequency close to 50 Hz, this nanostrctured composite electrode exhibits 165 F/g specific capacitance at 1A/g discharge current density even after 1000 electrochemical cycles.