



Experimental Studies on Poly(3-Hexylthiophene) Electrode Based Supercapacitors: A Comparison of Electrolytic Species

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Abstract

Poly(3-hexylthiophene) electrode based pseudocapacitors lithium and sodium salt incorporated lithium and sodium ion conducting gel polymer electrolytes, and an acidic electrolyte were constructed and characterized. For comparison, three electrolytes were used to fabricate pseudocapacitor comprised of poly(vinylidene fluoride)-co-hexafluoropropene (PVdF-HFP)-sodium thiocyanate (NaSCN), gel electrolyte poly vinyl alcohol (PVA) – sulphuric acid (H₂SO₄) and liquid electrolyte of lithium salt 1 Molar lithium perchlorate (1.0M LiClO₄) in ethylene carbonate(EC)+ propylene carbonate (PC). The comparative performance characteristics of the supercapacitor cells based on impedance analysis were presented. The role of ions and the acidic environment was important in the dramatic improvement of the supercapacitor cells' performance. The optimum capacitance value of 32 mF cm⁻² was achieved for the EC+PC+LiClO₄ electrolyte based cells.

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Introduction

Li-ion batteries are presently a mature technology, however, the disadvantages include, high cost, availability of lithium salts, safety, reliability. Magnesium-ion batteries are attractive and getting global attention due to the promises of low cost and abundance of magnesium on the earth crust.

With respect to their safety, gel polymer electrolytes based batteries have substantial merits over the liquid electrolyte. However, some specific properties of GPEs make them attractive from their application point of view in batteries. These include liquid like electrical properties, solid like mechanical properties and the homogeneous distribution of electrolytes.

Taking into account that the overall energy demand of a modern electric car is about 200 Wh kg⁻¹, and that the weight of the power source should be as low as possible, it is Electrochemical Capacitors (ECs), often called supercapacitors, ultracapacitors or power caches, have attracted research interest worldwide because of their potential applications as energy/power storage devices in many fields (transportation, military, aerospace etc.) [1-5].

The supercapacitors describe a diverse class of energy-storage devices that incorporate a variety of active materials (high surface-area carbons, transition metal oxides, nitrides, conducting polymers, composites of carbon materials with conducting polymers and metal oxides and composites of conducting polymers and metal oxides) for electrodes, electrolytes (conventional aqueous and non-aqueous electrolytes, polymer electrolytes and ionic liquids), and device configurations (symmetric, asymmetric and hybrid) [1-19].

The diversity and design flexibility are important advantages that make clear why electrochemical capacitors (ECs) cover such a

broad region on the power vs. energy density plane i.e. Ragone plot, and bridge the critical performance gap between the high power densities offered by conventional capacitors and the high energy densities of battery system. From both a fundamental and a practical perspective, ECs are closely related to batteries, and in fact the distinction between these two classes of energy-storage devices has been diminished with the recent advancements in “high-rate” batteries, and with the discovery that many battery materials exhibit capacitor-like electrochemical responses (*i.e.*, “pseudocapacitance”) when prepared in nanoscale and disordered forms. As a general rule, however, electrochemical capacitors can be differentiated from high-rate batteries by their operational characteristics: (i) charge–discharge response times that are on the order of seconds; (ii) sloping and symmetric charge–discharge profiles; and (iii) exceptionally high cycle life (typically many tens to hundreds of thousands of cycles).

On the basis of the energy storage mechanisms, types of the electrodes used and their configuration, supercapacitors can be classified into three categories. One is the electrical double layer capacitor (EDLC), where the capacitance comes from the pure electrostatic charges accumulated at the electrode/electrolyte interface; therefore it is strongly dependent on the surface area of the electrode materials (mainly various forms of carbon) that is accessible to the electrolyte ions. The other category is the pseudocapacitor, in which fast and reversible faradic processes take place due to electro-active species. These two mechanisms can function simultaneously depending on the nature of the electrode materials. Another type namely hybrid supercapacitors in recently introduced in which asymmetric configuration of the device are important. Capacitors, which employ the electroactive materials such as conducting polymers (e.g. polythiophene, polypyrrole etc.) or insertion type compounds (noble metal oxides e.g. NiO, RuO₂ etc.)

as active electrodes, are known as redox supercapacitors. The fast faradic oxidation-reduction (redox) reactions, in which the charges are partially blocked where some charges diffuse into the electrode material and intercalate is the basis for pseudocapacitance. The term pseudocapacitors or redox supercapacitors is commonly used to explain the pseudocapacitance behavior of such capacitors [1-14].

Although, the pseudocapacitor has electrochemical reaction similar to the batteries (the faradic mechanism), the distinction between a battery and an electrochemical pseudocapacitor is not explicit. A battery relies on electrochemical reactions that involve active materials in the electrode, where the charges are not blocked, diffuse into the electrode materials and intercalate. In this case, active means that the materials participate in the reaction and a transfer of electrons between the active material and ionic species from electrolyte occurs across the interface.

An electric double-layer capacitors (EDLCs) are known for relatively high energy density and much higher power density as compared to conventional batteries or fuel cells. The EDLCs employ large surface area carbon or other similar materials as blocking electrodes, which do not participate in any electrochemical reaction including charge transfer at the electrode-electrolyte interface. Charges are stored electrostatically in polarized double layers between an ionically conducting electrolyte and an electron conducting polarizable electrode under the application of electric potential. This would create a charge separation between the solvated ions and the electrode material that resembles the charge storage mechanism similar to conventional capacitor. The polarized charges at both the positive and negative electrodes resemble two capacitors connected in series. Helmholtz has first identified the existence of a 'double layer' in the electrochemical cell in 1879. And it is named after him as Helmholtz layer.

In general, positive and negative charges are arrayed at counter position with an extremely short distance, such as atomic distance (~10 Å), between both the contact interface of two different phases where, the two phases are the solid carbon electrode and the electrolyte. The excess charge on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the solution. This structure behaves essentially as a capacitor as it possesses the double layer. The amount of charge is a function of the electrode potential [15-19].

In the present paper, a part of the work related to the fabrication and characterization of the redox supercapacitor based on poly-3-hexyl thiophene electrodes and different liquid| polymer| gel electrolytes have been presented.

Experimental

The polythiophene-based solid state redox supercapacitors have been constructed using three different electrolytes. Gel polymer electrolyte poly(vinylidene fluoride)-co-hexafluoropropene (PVdF-HFP)-sodium thiocyanate (NaSCN), gel electrolyte poly vinyl alcohol (PVA) – sulphuric acid (H₂SO₄) and liquid electrolyte of lithium salt 1 Molar lithium perchlorate (1.0M LiClO₄) in ethylene carbonate(EC)+ propylene carbonate (PC). The capacitors have been characterized using a.c impedance.

Materials

Films of polymer electrolytes PVA-H₂SO₄ (60:40w/w) blend, PVdF-HFP(1M sol. of NaSCN in EC-PC sol.(1:1w/w) ratio) and EC+PC-(LiClO₄) were prepared using a solution cast technique. The materials as received were used.

The polythiophene was electrochemically deposited on indium tin oxide coated conducting glass. Electrosynthesis were carried

out in one compartment, three electrode cell containing 0.1M 3-hexyl thiophene and 0.02M tetra(n-butyl)ammonium hexafluorophosphate Bu₄NPF₆ in standard solution of 50ml nitrobenzene. The electrodepositions were made on ITO using 2 different methods (1) with a constant current of 3mA for 10min, (2) with a constant voltage of 2.7mV. The deposition are was limited to about 3 cm². Deposition is done using CH instrument (USA).

The preparation of electrolyte and electrode for the fabrication of the electrochemical supercapacitor cell has been carried out in this work.

Electrochemical measurements

If a potential is applied across the, a current is caused to flow through the cell, with a value determined by the mechanism of reaction taking place. The reaction is the formation of new chemical species as a result of movement of ions through the electrolyte. The ionic movement are caused by the applied potential difference, and constitute a flow of electric current.

The capacitor cells were constructed using PVA-H₂SO₄ blend, PVdF-HFP+NaSCN and liquid electrolyte EC+PC-LiClO₄ electrolyte sandwiched between two symmetrical polythiophene electrodes deposited on ITO glass. The apparent surface area of the electrodes were kept to about 3cm². The capacitance performance was characterised using impedance measurement and cyclic voltammetry measurements. The impedance measurement were carried out with a high frequency of 1MHz, low frequency of 0.01MHz and amplitude of 10mV. The overall capacitances C of the cells were calculated using the formula:

$$C = -I / (\omega Z'') \quad (1)$$

where $\omega = (2\pi f)$ is the angular frequency and Z'' is the imaginary part of the total complex impedance. The single electrode specific capacitance values were evaluated by multiplying the overall capacitance by a factor of two and dividing by the mass of a single active electrode.

Electrochemical cell

It is a one compartment 3-electrode cell containing working electrode: (indium tin oxide) ITO counter electrode: platinum, Reference electrode: saturated calomel electrode (SCE)

CONSTANT CURRENT

Cell-A P3HT|PVA-H₂SO₄|P3HT
Cell-B P3HT|PVdF-HFP+NaSCN|P3HT
Cell-C P3HT|EC-PC-LiClO₄|P3HT

CONSTANT VOLTAGE

Cell-D P3HT|PVA-H₂SO₄|P3HT
Cell-E P3HT|PVdF-HFP+NaSCN|P3HT
Cell-F P3HT|EC-PC-LiClO₄|P3HT

Results and Discussion

The impedance analysis of the electrochemical supercapacitor cell has been carried out in this part.

Impedance analysis

The redox-capacitor cells show capacitive behavior at the lower frequency range. It may be noted that the steeply rising behavior of Z'' almost parallel to y-axis (Fig-1) indicate the capacitive behavior.

This shows that P3HT films are electrode materials for supercapacitors fabrications. The results indicate that the polymer

electrolytes can be used for the fabrication of solid state form of supercapacitors. These solid state capacitors give good capacitance values, although the gel polymer electrolysis shows equivalent performance with liquid electrolyte. The impedance analysis of the electrochemical supercapacitor cell has been carried out.

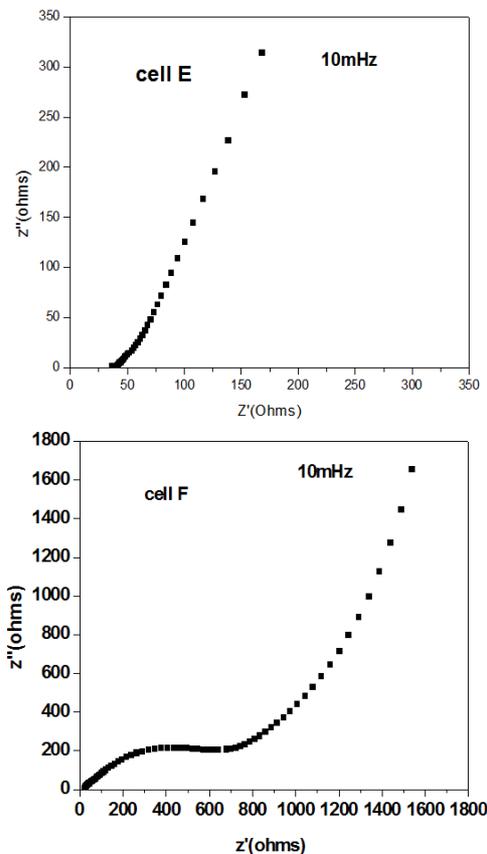
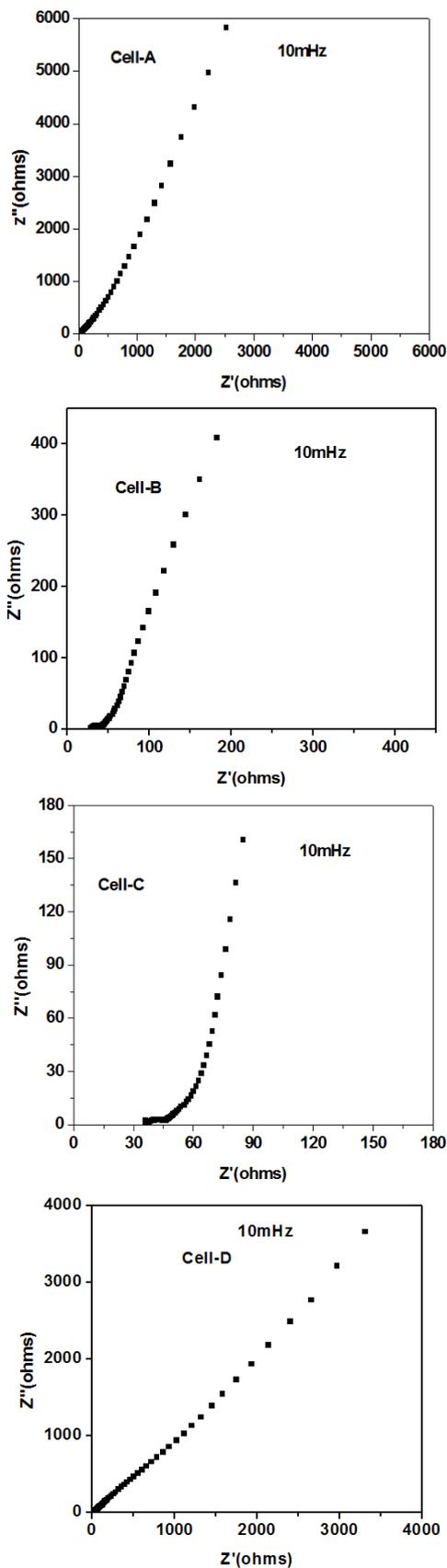


Figure 1: Complex impedance plots of cells (Cell-A to Cell-F) with different electrolytes on Poly(3-hexylthiophene) P₃HT electrodes, recorded at room temperature in the frequency range from 100 kHz to 10 mHz.

All the redox-capacitor cells show capacitive behavior at the lower frequency range. It may be noted that the steeply rising behavior of Z'' almost parallel to y-axis (Fig-1) indicate the capacitive behavior. This shows that P₃HT films are electrode materials for supercapacitors fabrications. The values of specific capacitance have been calculated for all the cells A-F using equation (1) and listed in the following table.

Table 1: The values of specific capacitance

Cells	Capacitor combination	Deposition method	Z''(Ohms)	Capacitance (mF/cm ²)
A	P3HT PVA-H ₂ SO ₄ P3HT	Constant Current	5799	0.91
B	P3HT PVdF-HFP+NaSCN) P3HT	Constant Current	399	12.99
C	P3HT EC-PC-LiClO ₄ P3HT	Constant Current	159	32.97
D	P3HT PVA-H ₂ SO ₄ P3HT	Constant Voltage	3598	0.015
E	P3HT PVdF-HFP+NaSCN) P3HT	Constant Voltage	309	15.95
F	P3HT EC-PC-LiClO ₄ P3HT	Constant Voltage	1595	2.98

The results indicate that the polymer electrolytes can be used for the fabrication of solid state form of supercapacitors. These solid state capacitors give good capacitance values, although the gel polymer electrolysis shows equivalent performance with liquid electrolyte.

Conclusions

1. The conducting Poly-3-methyl thiophene (P3HT) films have been prepared using electrochemical methods for their applications in supercapacitor fabrication.

2. Different electrolyte EC-PC-LiClO₄, PVdF-HFP-EC-PC-NaSCN, PVA-H₂SO₄ films have been prepared using solution cast method and used to fabricate supercapacitors.
3. Supercapacitors have been characterized using Impedance analysis and cyclic voltammetry.
4. Best capacitors have been obtained using gel electrolyte with specific capacitor value of ~33 mF/cm².
5. Gel electrolyte also offers good capacitor with capacitance value of ~13 mF/cm².

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References

1. M. F. Yu, O. Lourie, M J Dyer, K. Moloni, F K. Thomas, R. S. Ruoff RS. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science* 2000, 287, 637–40.
2. J. Zhou, G. Lubineau, Improving electrical conductivity in polycarbonate nanocomposites using highly conductive PEDOT/PSS coated MWCNTs. *ACS Appl Mater Interfaces*, 2013, 5, 6189–200.
3. G. Lubineau, A. Rahaman, A review of strategies for improving the degradation properties of laminated continuous-fiber/epoxy composites with carbon-based nano-reinforcements. *Carbon* 2012, 50, 2377–95.
4. P. Xu, T. Gu, Z. Cao, B. Wei, J. Yu, F. Li, et al. Carbon nanotube fibre based stretchable wire-shaped supercapacitors. *Adv Energy Mater* 2013, 4 1300759.
5. H Sun, Z Xu, C Gao, Multifunctional, ultra-flyweight, synergistically assembled carbon aerogels. *Adv Mater* 2013, 25, 2554–60.
6. Ata S, Kobashi K, Yumura M, Hata K. Mechanically durable and highly conductive elastomeric composites from long single-walled carbon nanotubes mimicking the chain structure of polymers. *Nano Lett* 2012;12:2710–6.
7. Wu X, Wen T, Guo H, Yang S, Wang X, Xu A. Biomass-derived sponge-like carbonaceous hydrogels and aerogels for supercapacitors. *ACS Nano* 2013;7:3589–97.
8. Chen W, Rakhi RB, Hu L, Xie X, Cui Y, Alshareef HN. High performance nanostructured supercapacitors on a sponge. *Nano Lett* 2011;11:5165–72.
9. Wu ZY, Li C, Liang HW, Chen JF, Yu SH. Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose. *Angew Chem* 2013;125:2997–3001.
10. Tovmash AV, Polevov VN, Mamagulashvili VG, Chernyaeva GA, Shepelev AD. Fabrication of sorption-filtering nonwoven material from ultrafine polyvinyl alcohol carbonized fibres by electrospinning. *Fibre Chem* 2005;37:187–191.
11. Sveningsson M, Morjan RE, Nerushev OA, Sato Y, Ba'ckstro'm J, Campbell EB, et al. Raman spectroscopy and field emission properties of CVD-grown carbon-nanotube films. *Appl Phys A Mater Sci Process* 2001;73:409–18.
12. Morishita T, Soneda Y, Tsumura T, Inagaki M. Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors. *Carbon* 2006;44:2360–7.
13. Qian H, Greenhalgh ES, Shaffer MSP, Bismarck A. Carbon nanotube-based hierarchical composites: a review. *J Mater Chem* 2010;20:4751.
14. Qian H, Bismarck A, Greenhalgh ES, Kalinka G, Shaffer MSP. Hierarchical composites reinforced with carbon nanotube grafted fibers: the potential assessed at the single fiber level. *Chem Mater* 2008;20:1862–9.
15. Bin Xua, b, Feng Wua, , Shi Chena, Gaoping Caob, Zhiming Zhoua, A simple method for preparing porous carbon by PVDC pyrolysis, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* Volume 316, Issues 1–3, 5 March 2008, Pages 85–88.
16. Zussman E, Yarin AL, Bazilevsky AV, Avrahami R, Feldman M. Electrospun polyaniline/poly(methyl methacrylate)-derived turbostratic carbon micro-/nanotubes. *Adv Mater* 2006;18:348–53.
17. U K Fatema, A J Uddin, K Uemura, Y Gotoh, Fabrication of carbon fibers from electrospun poly(vinyl alcohol) nanofibers. *Text Res J* 2010, 81, 659–72.
18. W. Huang, H. Zhang, Hierarchical porous carbon obtained from animal bone and evaluation in electric double-layer capacitors, *Carbon* 49 (2011) 838.
19. Q. Wang, Q. Cao, X. Wang, B. Jing, H. Kuang, L. Zhou, A high-capacity carbon prepared from renewable chicken feather biopolymer for supercapacitors, *Journal of Power Sources* 225 (2013) 101.

