CYCLIC VOLTAMMETRY ANALYSIS OF AN ELECTROCHEMICAL DOUBLE LAYER CAPACITOR

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ABSTRACT: *Present world is heading towards a serious energy crisis due to the mismatch between the supply and the demand which is increasing at an alarming rate. Main energy supply is from fossil fuels and the endangering state of fossil fuels is now well realized. This background has set the initiation of employing renewable energy sources for energy production. In par with that, requirement for energy storage has become an essential. Though batteries and conventional capacitors have been employed as energy storage devices, the present demand cannot be fulfilled only with them. Super capacitors have been recognized as a suitable solution and also as a bridge to link the gap between batteries and conventional capacitors. There are two types of super capacitors namely electrochemical double layer capacitors (EDLCs) and redox capacitors. This report presents about such EDLC fabricated using a polymer electrolyte and graphite electrodes. Polymer electrolyte is based on a polymer, a salt and an ionic liquid. For the preparation of electrodes, Sri Lankan natural graphite was used which might indirectly add a value to one of the natural resources in Sri Lanka. A thin electrolyte film was sandwiched in between two graphite electrodes deposited on aluminium substrate. The device is eco friendly and cost effective. Performance was evaluated using cyclic voltammetry technique which is a powerful analysis tool. One electrode was used as the working electrode while the other one used as the reference and counter electrodes.The potential window as well as the scan rate play a major role in determining the specific capacitance. Charge storage takes place purely via electrostatically. At higher scan rates, charge storage mechanism does not take place completely and hence, a reduction of capacitance is observed with increasing scan rate. The durability of the EDLC for long term operation is satisfactory.*

Keywords : Electrochemical double layer capacitors, Cyclic voltammetry, Specific capacitance

1. INTRODUCTION

According to the high demand for energy from various applications including entertainment, education, transport and health etc. in the modern technology-based world, supply from fossil fuels is not sufficient at all. Also, due to high usage, fossil fuels are predicted to be reaching the end soon. There are some issues with fossil fuels to match the universal concerns over green environment. It has hence becomes an utmost importance to switch towards renewable energy sources such as solar, wind and tidal [Bryan, 2016]. This has naturally spotlighted the need of energy storage devices to meet the energy challenge efficiently and effectively. Batteries and conventional capacitors have been playing a pivotal role as energy storage devices since long ago. But the present demand is so high that those two cannot cater that much. This has motivated to seek energy storage devices rich in power as well as energy. In this regard, super capacitors have been identified as a viable solution. As in normal electrochemical devices, super capacitors are having two electrodes separated by an electrolyte. There are two types of super capacitors depending on the type of the electrode materials namely electrochemical double layer capacitors (EDLCs) and redox capacitors. EDLCs use carbon materials as electrodes whereas redox capacitors are having transition metal oxides or conducting polymers [Kim, 2015, Snook, 2011]. Obviously, the charge storage mechanisms in the two categories are different. In EDLCs, charges are stored electrostatically. Non electrostatic or faradaic type charge storage connected with redox reactions exists in redox capacitors [Ramya, 2013]. Until last couple of years, all super capacitors were based on liquid electrolytes. But, due to the adverse effects of liquid electrolytes such as leakage, evaporation, spilling and design limitation, a considerable attention has been now focused on polymer electrolytes as an attractive class of electrolytes. Many of them are having ionic conductivities comparable to liquid electrolytes as well as mechanical integrities similar to solid electrolytes. The present study is based on fabrication of an EDLC using a polymer electrolyte and two graphite electrodes. There are several key features of the study. Polymer electrolyte is composed with a polymer, a salt and an ionic liquid (IL). It is a widely known fact that ILs are room temperature molten salts that can be incorporated as a salt as well as a solvent. The present polymer electrolyte does not include any solvent which are toxic in nature. The two electrodes are made up of Sri Lankan graphite. Hence, they are cheap and environmental friendly. The performance of the EDLC was evaluated using cyclic voltammetry techniques which is a powerful analyzing tool [Bard, 2001].

2. METHODOLOGY

2.1 Preparation of Electrodes

Graphite samples received from Bogala Graphite Lanka (Ltd) were used without prior treatment. Required amount of graphite was mixed with polyvinylidenefluoride (PVdF, Aldrich) and titanium dioxide (TiO_2 – Aldrich) in acetone. After sonication for some time in a sonicator (Athene Technology), it was stirred magnetically using a magnetic stirrer. The resultant homogeneous slurry was then coated on aluminium substrate having a cross section area of 1 cm^2. The electrodes were dried at room temperature under normal atmospheric conditions.

2.2 Preparation of Electrolyte

Polyvinyl chloride (PVC, Aldrich), magnesium trifluoromethanesulfonate ($Mg(CF_3SO_3)_2$ – MgTF, Aldrich) and 1-ethyl-3-methyl immidazolium trifluoromethanesulfonate (1E3MITF-Aldrich) were used as the starting materials. Firstly, PVC was dissolved in tetrahydrofuran and magnetically stirred with MgTF and 1E3MITF. After pouring on to a glass petry dish, solvent evaporation was allowed. It was possible to obtain a thin electrolyte film having no pin holes.

2.3 Fabrication and Analysis of EDLC

An electrolyte sample was sandwiched in between two graphite electrodes. Sealing was done to maintain proper contacts. The cross sectional area of the ELDC was 1 cm^2. Cyclic voltammetry test was carried out using a two electrode setup. One electrode was used as the working electrode while the other one as the reference and counter electrodes. Voltage – current measurements were collected varying the potential window and the scan rate. The single electrode specific capacitance (C_{sc}) was calculated using the equation, $C_{sc} = 2 \int IdV / m.S.\Delta V$ [Tey, 2016]

Here, $\int IdV$ is the area of the cyclic voltammogramme (CV), m is the mass of a single electrode, S is the scan rate, ΔV is the width of the potential window.

After determining the optimum values for the potential window and the scan rate that give rise to the highest single electrode specific capacitance, continuous cycling was done to monitor the ability of the EDLC to withstand for long term operation.

3. RESULTS AND DISCUSSION

3.1 Variation of Potential Window

Fig.1 shows the resulting CV obtained with varying the potential window.

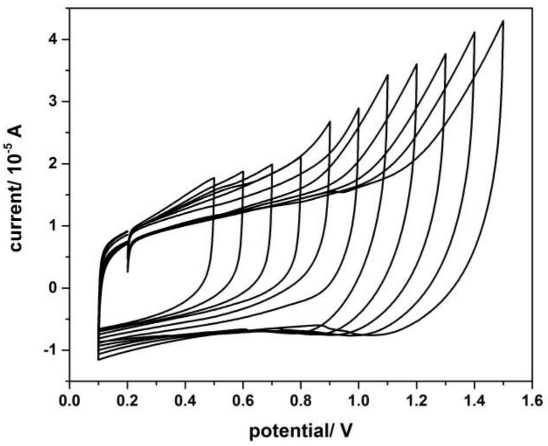

Fig. 1 Cyclic voltammograms obtained for different cycling potential windows at the scan rate of 10 mVs^{-1}

At narrow potential windows, the shape of the CV was a rectangular form which is a characteristic of EDLCs [Prasadini, 2018]. When the width was increasing, the anodic current increased gradually which might be due to an unwanted reaction. This might cause degradation of EDLC [Harankahawa, 2017]. But, rectangular shape is not distorted very much probably due to the wider potential stability window of the electrolyte [Pandey, 2010].The potential window of 0.1 V – 1.4 V was selected as the optimum for further investigations.

3.2 Variation of Scan Rate

Fig 2 illustrates the resulted CVs for different scan rates.

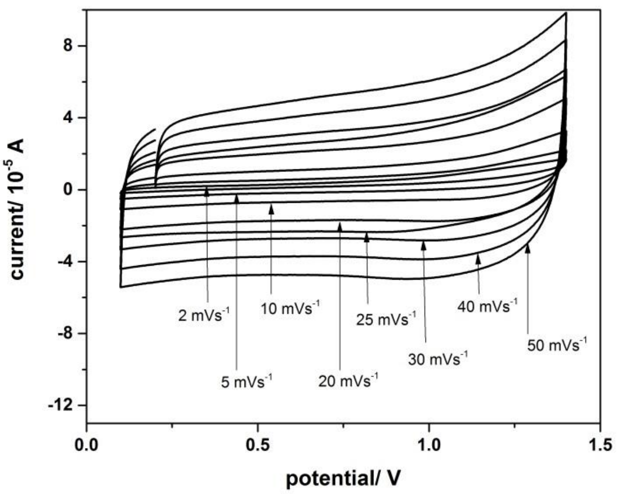

Fig. 2 Cyclic voltammograms obtained for different scan rates

As before, all CVs show rectangular shape. There are no peaks in CVs. Basically, peaks are appearing due to redox reactions incorporated with electron transfer. The absence of peaks well confirms the fact that charge storage takes place via electrostatically [Prabaharan, 2006]. With increasing scan rate, current in anodic side increased very much. This can give rise to a degradation in the electrolyte. Single electrode specific capacitance increased firstly while increasing scan rate but after a certain scan rate, it reduced. The initial increase might be due to inducing more charges to involve in charge storage process with increasing the value of potential perturbations. But, at very high scan rates, charges may not enter the inside pores instead they accumulate on the electrode surface [Fletcher, 2014]. So that, C_{sc} reduces.

3.3 Continuous Cycling Ability

Variation of C_{sc} with continuous cycling is shown in Fig. 3.

Initial C_{sc} is about 1.56 Fg^{-1}. During 600 cycles, the reduction of C_{sc} is about 22% which is quite satisfactory. At the beginning, there is a sudden drop of C_{sc}. It might be due to improper contacts within the EDLCs that weakens the charge storing process. Even after few cycles, the rate of decrease is not very fast. This is an indication for the stability among electrode/electrolyte components.

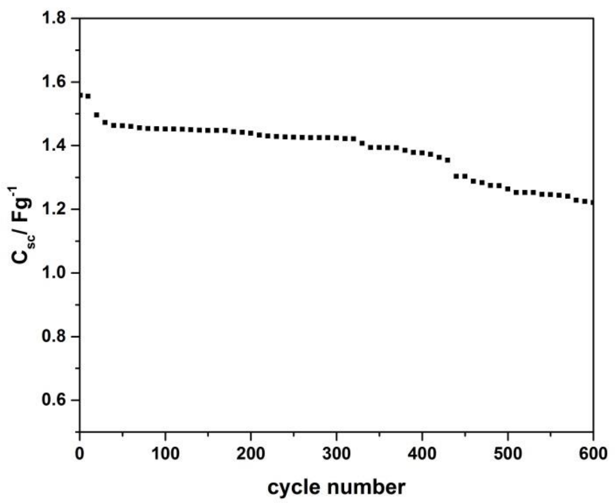

Fig. 3 Variation of single electrode specific capacitance, C_{sc} with cycle number at the scan rate of 10 mVs^{-1}

4. CONCLUSION

An EDLC was successfully fabricated using an ionic liquid-based polymer electrolyte and Sri Lankan natural graphite based electrodes. Potential window within which the EDLC was cycling as well as the scan rate of cycling play a major role in determining the specific capacitance. Wider potential windows as well as higher scan rates are not suitable as there are probabilities to occur unwanted reactions and also restrictions for the all charges to take part in the storage mechanism. EDLC is having the ability to withstand continuous cycling.

REFERENCES

Bard, A.J., Faulker, L.R. (2001) Electrochemical methods : Fundamentals and Applications, New York

Bryan A.M., Santino, L.M., Lu, Y., Acharya, S., D'Arcy J.M. (2016) Conducting polymers for pseudocapacitive energy storage, Chemistry of Materials, 28, 5989-5998.

Fletcher, S., Black, V.J., Kirkpatrick, I. (2014) A unique equivalent circuit for carbon based super capacitors, Journal of Solid State Electrochemistry, 18, 1377-1387

Harankawa N, Weerasinghe WADSS, Vidanapathirana KP, Perera KS (2017) Investigation of a Pseudo Capacitor with Polyacrylonitrile based Gel Polymer Electrolyte. Journal of Electrochemical Science and Technology, 8(2), 107-114

Kim, B.K., Sy, S., Yu, A., Zhang, J. (2015) Electrochemical super capacitors for energy storage and conversion, In Handbook of Clean Energy Systems, John Wiley and Sons Ltd.

Pandey, G.P., Hashmi, S.A., Kumar, Y. (2010) Performance studies of activated charcoal based electrical double layer capacitors with ionic liquid gel polymer electrolytes, Energy Fuels, 24, 6644-6652

Prabaharan S.R.S., Vimala, R., Zainal, Z. (2006) Nano structured mesoporous carbon as electrodes for super capacitors, Journal of Power Sources, 161, 730-736

Prasadini, K.W., Perera, K.S., Vidanapathirana, K.P. (2018) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate based gel polymer electrolyte for application in electrochemical double layer capacitors, Ionics, doi: 10.1007/s11581-018-2810-1
Snook, G.A.,Kao, P., Best, A.S. (2011) Conducting polymer based supercapcitor devices and electrodes, Journal of Power Sources, 196, 1-12.
Ramya, R., Sivasubramanian R., Sanganarayan, M.V. (2013) Conducting polymers based super capacitors-progress and prospects, Electrochimica Acta, 101, 109-129
Tey, J.P., Careem, M.A., Yarmo, M.A., Arof, A.K. (2016) Durian shell based activated carbon electrode for EDLCs, Ionics, 22/7, 1209-1217