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Research Article

Impact of effective mass of active material in the electrode for the performance of symmetrical, all solid-state double layer supercapacitors

K.S. Perera*, K.P. Vidanapathirana

Department of Electronics, Wayamba University of Sri Lanka, Kuliyapitiya, Sri Lanka.

Abstract

Supercapacitors have been identified as one of the key energy storage devices with their excellent ability to bridge the gap between batteries and conventional capacitors in terms of power and energy. A great amount of research activities is being carried out to improve their performance to serve for worldwide day-to-day applications such as power backups, automobiles and power generators. This study is about determining the suitable active mass loading of reduced graphene oxide (RGO) based electrodes in solid state supercapacitors using cyclic voltammetry technique. The potential window of (0.01-1.2) V showed the highest single electrode specific capacitance (C_{sc}) for the mass loading of 2 mg cm^{-2}. As per the selected scan rates for the test, 10 mV s^{-1} exhibited the optimum C_{sc} again for the same mass loading. Continuous cycling was done for 1000 cycles. Supercapacitor with the same mass loading had a higher C_{sc} continuously throughout the 1000 cycles and also, its rate of reduction of C_{sc} was lower.

Keywords: Double layer supercapacitors, Reduced graphene oxide, specific capacitance

* Corresponding author: kumudu@wyb.ac.lk

1. INTRODUCTION

Power crisis has become one of the dreadful challenges face by every country in the world. Due to endangered state and realization of adverse effects of fossil fuels, which have been playing a key role in fulfilling power demands, researchers have diverted their attention on exploring other alternatives to manage the thirst for power. In this regard, renewable energy sources such as solar, wind and tidal have been identified as attractive candidates and a massive number of research activities are being devoted towards their development and scaling up[1]. However, the dependence of renewables on location and time has highlighted the importance of coupling energy storage devices with renewable energy sources to cater stable, continuous supply. Currently, supercapacitors have received prominent attention in areas such as power backups, automobiles, and power generators[2,3], where quick access to off-grid power is required. This has laid a strong background for fabricating a diverse range of supercapacitors having various types of electrodes and electrolytes.

When the electrodes are based on carbon materials, supercapacitors are called as double layer capacitors whereas with transition metal oxides and conducting polymer-based electrodes, they are categorized as redox capacitors. In addition, there is another classification of super capacitors as symmetric, asymmetric and hybrid. Symmetrical capacitors are fabricated with two identical electrodes. Asymmetric supercapacitors have electrodes of two different materials. Hybrid supercapacitor is a new concept based on composite electrodes. A great deal of research studies is going on to develop novel types of supercapacitors while attempting to improve the performance in terms of parameters like power and energy densities, lifetime etc.

A large number of studies have been reported about different electrode materials for supercapacitors[4]. Composite electrodes based on activated carbon have been successfully employed for supercapacitors by Jang et al[5]. With functionalized activated carbon nano particles-based electrodes, they have obtained a single electrode specific capacitance (C_{sc}) of 154 F g^{-1}. Tey et al. have tested durian shell based activated carbon electrodes in double layer capacitors with an aqueous electrolyte and have noted a C_{sc} of 93.1 F g^{-1} [6]. Some have attempted to develop electrolyte properties to enhance the performance of the respective capacitor. Maher et al. have incorporated a redox additive to the electrolyte and have observed a notable capacitance enhancement[7]. Ionic liquids have been investigated in place of salts in electrolytes and those systems have been tested for supercapacitors[8].

In this project, it was aimed at determining impact of effective mass of the reduced graphene oxide (RGO) electrodes on the performance of the all solid state double layer supercapacitors using cyclic voltammetry technique. RGO is a derivative of graphite showing high pore volume which are essential for high charge storage. Hence, it has been highly investigated for electrodes in supercapacitors. Due to the adverse effects of liquid electrolytes that hinders safety, design flexibilities and miniaturization of devices, a solid polymer electrolyte (SPE) was used for the present study to fabricate the double layer supercapacitors. A natural rubber based SPE with a Zinc salt was prepared and used in this regard. As per the literature survey, novelty of the reported work is high as many research activities have been carried out with the priority of optimizing surface area and pore size of active materials in the electrodes.

2. EXPERIMENTAL

2.1 Preparation of reduced graphene oxide (RGO) electrodes

RGO received from Sakura Mines (PVT) Ltd, Sri Lanka was used as received. It was mixed with activated carbon (AC) (Aldrich) as the electronic conductor and polyvinylidenefluoride (PVdF) (Aldrich) as the binder in the composition, 80:10:10 (by weight %). N methyl pyrolidene (NMP) (Aldrich) was used as the solvent. After stirring magnetically for few hours at room temperature, final solution was deposited on well cleaned fluorine doped tin oxide (FTO) glass plates according to doctor blade method. Area of an electrode was 1 x 1 cm^2. Electrodes were heated at 110 °C for 3 hours. Four electrodes were prepared, each having the active mass loading of 1, 2, 3 and 4 mg cm^{-2}.

2.2 Preparation of solid polymer electrolyte (SPE)

Methyl grafted modified natural rubber (Associated Specialty Rubbers (PVT) Ltd, Kegalle, Sri Lanka) was minced into smaller pieces and allowed to dissolve in tetrahydrofuran (THF) (Aldrich) overnight. Magnetic stirring was done for another 24 hours. Required amount of zinc trifuloromethanesulfonate ($Zn(CF_3SO_3)_2$ – ZnTF) (Aldrich) was dissolved in THF using magnetic stirring. Both mixtures were combined and magnetic stirring was continued for another 24 hours. Final solution was poured onto a well cleaned glass petri dish and allowed overnight for solvent evaporation at room temperature. It was possible to obtain a bubble free, thin electrolyte film to be used for the double layer capacitor.

2.3 Fabrication and characterization of double layer capacitor

An electrolyte film having the identical shape and size of electrodes was sandwiched in between two electrodes and properly sealed. For cyclic voltammetry test, one electrode was used as the working electrode while the other as the counter and reference electrodes. Firstly, cycling potential window was changed and current variation with voltage was measured using a Metrohm M101 Autolab potentiostat. After determining the potential window which gives the highest C_{sc}, cycling scan rate was changed starting from 10 mV s^{-1}. Continuous cycling was done within the selected potential window and at the selected scan rate for 1000 cycles. All the tests were carried out for the four double layer capacitors having electrodes with different mass loadings.

3. RESULTS AND DISCUSSION

Single electrode specific capacitance, C_{sc} was calculated using the equation,

$$C_{sc} = 2(\int IdV) / mS\Delta V \quad (1)$$

where $\int IdV$ is the area of cyclic voltammogramme (AV), m is the mass of an electrode (g), S is the scan rate (mV s^{-1}) and ΔV is the potential window (V).

3.1 Variation of cycling potential window

Fig. 1 shows the variation of C_{sc} with potential window for each type of double layer super capacitor.

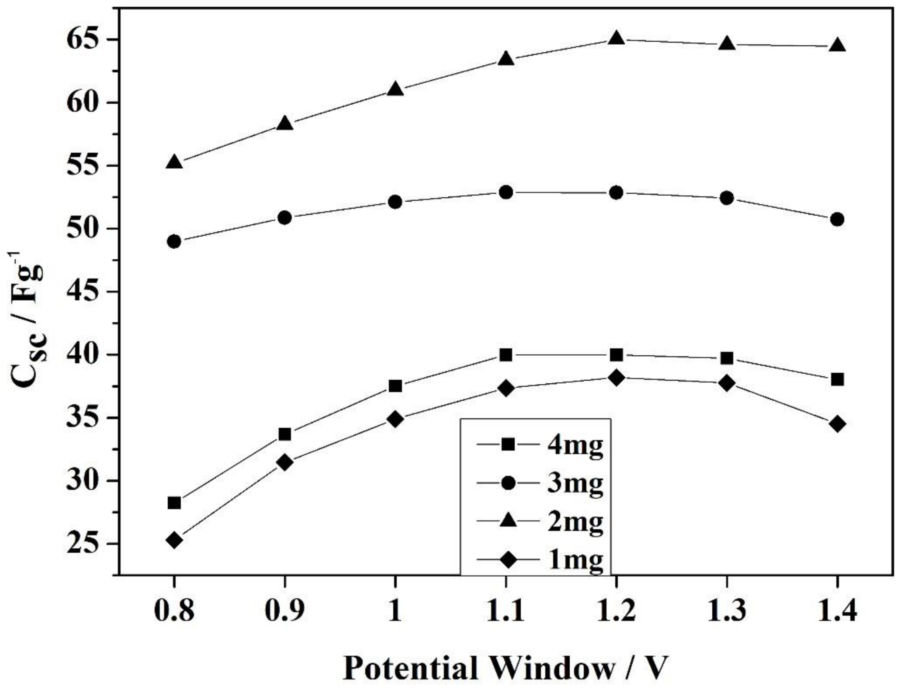

Fig. 1 Variation of C_{sc} with the cycling potential window (starting potential is 0.01 V)

For all supercapacitors with different mass loadings, C_{sc} is low within narrow potential windows. And it increases with widening potential window. A similar observation has been reported for RGO-polypyrrole composited electrode based supercapacitors[9]. This may be due to insufficient potential range to occur full charge storage process. After the potential window of (0.01-1.20) V, C_{sc} tends to become stable or reduces and as such, it was selected as the suitable window for further investigations. Even C_{sc} becomes stable, further studies need to be done to verify that any unwanted reactions do not take place with widened potential windows. Reduction of C_{sc} may be due to involvement of ions to other reactions without assisting proper storage process. When ions engage with other reactions, this can lead to shorten the life time of the super capacitors as well.

It is clearly seen that highest C_{sc} is available with the electrodes of mass loading is 2 mg cm^{-2}. As per the curves, the trend of C_{sc} has a pattern for mass loadings as follows.

2 mg cm^{-2} > 3 mg cm^{-2} > 4 mg cm^{-2}> 1 mg cm^{-2}

Variation of four curves shows the existence of an effect of the active mass loading on C_{sc}. It is a well-known fact that sufficient surface area is essential for better charge storage which leads to high C_{sc} [10,11]. With a low mass loading of 1 mg cm^{-2}, the amount of active material may not be sufficient to cater high charge storage. As a result, C_{sc} may be smaller. But, with increasing mass loading above 2 mg cm^{-2}, there may be excess amount of active material available which will disturb the charge storage process giving rise to decrement of C_{sc}.

Fig. 2 illustrates the variation of C_{sc} with the scan rate.

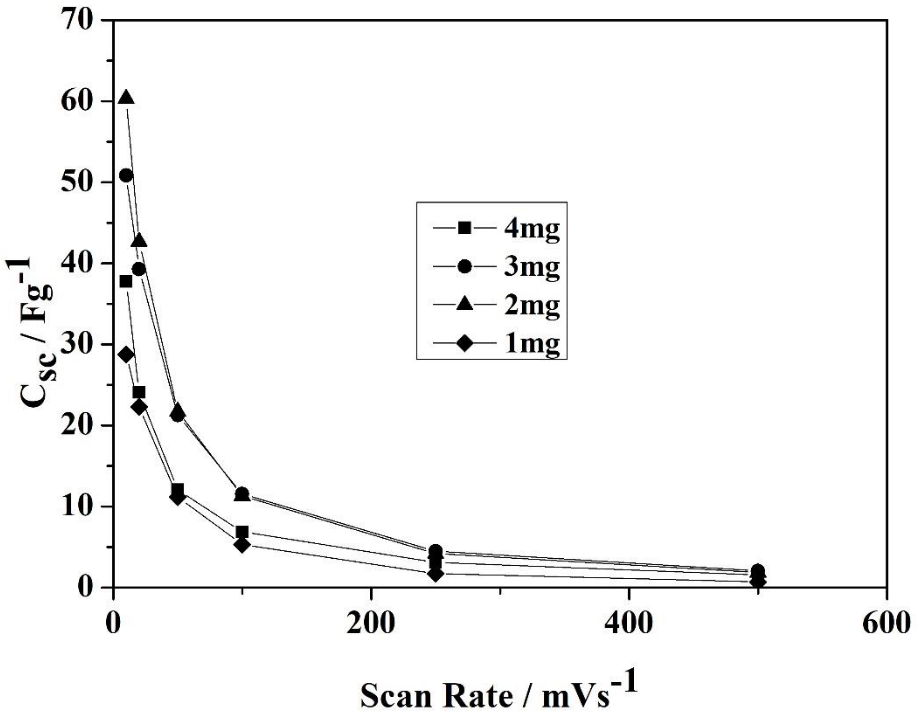

Fig. 2 Dependence of C_{sc} on the cycling scan rate within the potential window of (0.01-1.20) V

As observed by many researchers, C_{sc} decreases with increasing scan rate for each supercapacitor [8,12]. One possible reason is with increasing scan rate, ion accessibility to pores and hence the charge storage can become limited. This leads to reduction of C_{sc}. However, even at higher scan rates, C_{sc} becomes constant which indicates the fast ion switching behavior at the solid polymer electrolyte and electrode interface [13]. This observation on the other hand confirms the suitability of the electrolyte to serve in the supercapacitors. Again as in the previous test, mass loading of 2 mg cm^{-2} exhibits the highest C_{sc} among the mass loadings. Since there is a possibility to occur adverse reactions at very low scan rates except required charge storage, lower values than 10 mV s^{-1} were not considered and the value of 10 mV s^{-1} was chosen for continuous cycling. Fig. 3 shows the variation of C_{sc} with the cycle number for all four different super capacitors.

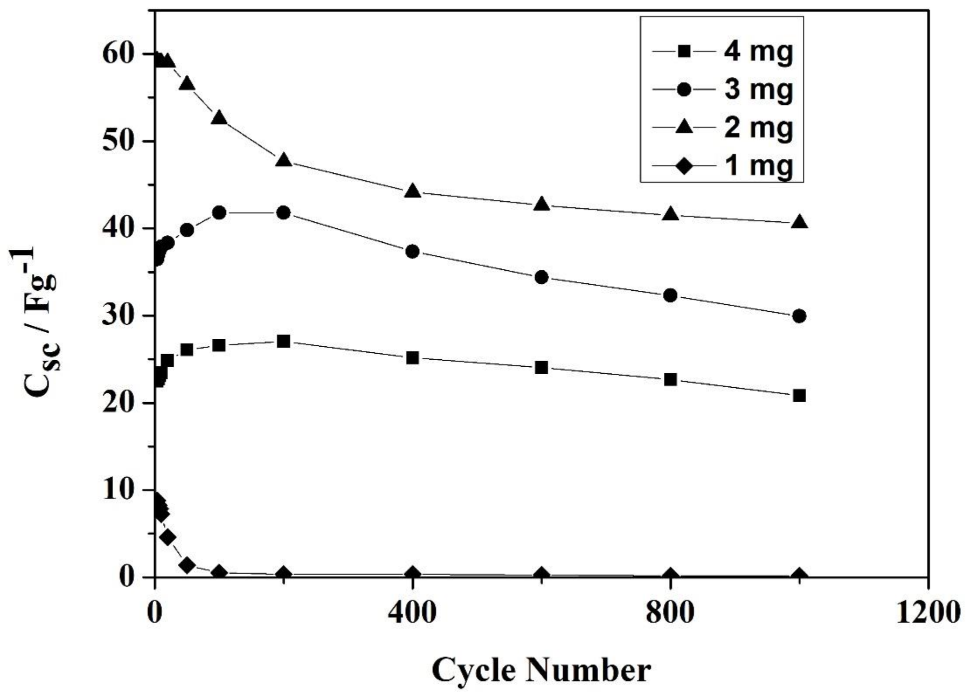

Fig. 3 Variation of C_{sc} within the potential window of (0.01-1.20) V and at scan rate of 10 mV s^{-1} with the cycle number.

With mass loadings of 1 and 2 mg cm^{-2}, C_{sc} decreases with continuous cycling as reported by many studies [8,14]. Initial fading might be due to consumption of charges for irreversible reactions or blockade of a few small size pores while inserting and de-inserting of electrolyte ions during first cycles or adsorption of electrolyte ions on the RGO surface[15]. Due to low amount of active material (mass loading of 1 mg cm^{-2}), C_{sc} has reached a very low value (near zero) during continuous cycling. However, mass loadings of 3 and 4 mg cm^{-2}, show an increment of C_{sc} first and then a reduction. This might be due to immature state that exists with high amount of active material leading to increase of C_{sc} during few cycles initially. When it reaches maturity, C_{sc} decreases accordingly. Supercapacitor with mass loading of 2 mg cm^{-2} has the highest C_{sc} and also rate of reduction is comparatively lower than others. Obtained results verify that mass loading of 2 mg cm^{-2} of RGO is preferred for fabricating supercapacitors with good performance.

4. CONCLUSION

Supercapacitors were fabricated successfully using four different active masses of 1, 2, 3 and 4 mg cm^{-2} of RGO, PVdF and AC as electrodes and a solid polymer electrolyte with NR, ZnTF. Cyclic voltammetry test done varying the potential window revealed that the window, (0.01-1.2) V gives the optimum C_{sc}. Cycling scan rate of 10 mV s^{-1} was chosen for continuous cycling test which was done for 1000 cycles. With the C_{sc} values throughout the test and its rate of reduction, it can be concluded that 2 mg cm^{-2} of RGO is a suitable mass loading to get satisfactory performance from the supercapacitors. Further investigations are progressing to confirm this further.

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