

RESEARCH ARTICLE

Investigation of a gel polymer electrolyte based on polyacrylonitrile and magnesium chloride for a redox capacitor

C.M. Bandaranayake¹, Y.M.C.D. Jayathilake¹, K.S. Perera^{1,*}, K.P. Vidanapathirana¹ and L.R.A.K. Bandara²

¹Department of Electronics, Wayamba University of Sri Lanka, Kuliyaipitiya, Sri Lanka

²Department of Physics, University of Peradeniya, Peradeniya, Sri Lanka

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Abstract: To supplement the ever increasing power demand in the present day world, supercapacitors have emerged as one of the suitable power storage devices. Redox capacitors have received a considerable attention due to factors such as high cycle ability, satisfactory specific capacitance and good stability. There are many reports on redox capacitors based on liquid electrolytes but these have several drawbacks. In this study, a magnesium chloride (MgCl₂) based gel polymer electrolyte was prepared and characterized for its suitability to be used in a redox capacitor. The composition, 0.1 polyacrylonitrile (PAN):0.4 ethylene carbonate (EC):0.4 propylene carbonate (PC):0.125 MgCl₂ (weight ratios) exhibits the highest room temperature conductivity of 4.08×10^{-4} S cm⁻¹. Conductivity variation of this sample with the temperature shows Arrhenius behavior. The ionic transference number is 0.84. This shows that the GPE is an ionic conductor. Redox capacitors were fabricated with two polypyrrole (PPy) electrodes. They were characterized using Cyclic Voltammetry technique, Impedance Spectroscopy and Galvanostatic Charge Discharge test. Cycling at the scan rate of 10 mV/s within the potential window of -1.4 V to +1.4 V showed a specific capacitance of 120.35 F/g. Impedance data showed the electrochemical behavior of the device having resistive and capacitive behavior. Galvanostatic charge discharge test results exhibit average power density and energy density of 341 W/kg and 5 Wh/kg respectively.

Keywords: Redox capacitor, gel polymer electrolyte, polyacrylonitrile, magnesium chloride.

INTRODUCTION

At present, there is a rising demand for portable power with the rapid growth of various applications including hybrid and electric

vehicles, space crafts, memory backups, toys and many other devices. To meet this high demand, efficient and low cost batteries and supercapacitors are being developed all over the world as energy storage devices (Palacin *et al.*, 2009; Abruna *et al.*, 2008). Batteries can store energy but their power is low compared to supercapacitors. It is possible to define supercapacitors as power sources bridging the gap between batteries and conventional capacitors. Due to shorter time needed for full charging, high columbic efficiency and longer life than batteries, supercapacitors are widely employed in many applications today (Simon and Gogotsi, 2008; Yan *et al.*, 2014). There are two types of supercapacitors namely redox capacitors and electrochemical double layer capacitors (EDLCs). Redox capacitors use electrodes made by conducting polymers or transition metal oxides (Ramya *et al.*, 2013). They derive the capacitance from the storage of charge in the electrode material in response to a redox reaction. EDLCs use carbon based electrodes. The capacitance arrives from pure electrostatic attraction between ions in the electrolyte and the charged surface of an electrode (Zhong *et al.*, 2015). In view of a larger number of charge discharge cycles, satisfactory specific capacitance and good stability, redox capacitors have become prominent. In addition, the easy and less complex methods of fabrication as well as good flexibility of conducting polymers have given the redox capacitors a global attention. Most reports on redox capacitors are based on liquid electrolytes (Fonseca *et al.*, 2006; Uppugalla *et al.*, 2014).

*Corresponding Author's Email: kumudu31966@gmail.com

Due to adverse effects arising from liquid electrolytes such as leakage, evaporation and dye desorption, nowadays attention has been focused on fabrication of redox capacitors with gel polymer electrolytes (GPEs) which exhibit liquid-like ionic conductivities while having mechanical properties similar to solid electrolytes (Tripathi *et al.*, 2013; Hashmi *et al.*, 2005).

In this study, redox capacitors were fabricated using a GPE based on polyacrylonitrile (PAN) with magnesium chloride ($MgCl_2$) and polypyrrole (PPy) electrodes and were characterized using Cyclic Voltammetry, Electro-chemical Impedance Spectroscopy (EIS) and Galvanostatic Charge Discharge (GCD) cycling. The composition of the GPE was fine tuned first to obtain a high conducting, free standing thin film and its nature of conductivity was also investigated.

EXPERIMENTAL

Preparation of Gel Polymer Electrolyte samples

PAN (Aldrich, 99%), ethylene carbonate (EC) (Aldrich, 98%), propylene carbonate (PC) (Aldrich, 99%) and $MgCl_2$ (Aldrich, 98%) were used without further purification. First, the required amount of $MgCl_2$ was dissolved in EC and PC using magnetic stirring. When $MgCl_2$ was completely dissolved, required amount of PAN was added to the mixture and stirring was continued until a homogenous mixture was formed. Then, it was heated at 120 °C for 45 minutes inside a glass tube furnace. Resultant highly viscous mixture was pressed in between two well-cleaned glass plates.

Several samples were prepared with different PAN and $MgCl_2$ concentrations to find the composition that has the highest room temperature conductivity. EC and PC weight ratio was fixed as 1 : 1 throughout the study.

AC Conductivity measurements

A circular shape sample with 14 mm diameter was cut from each GPE film. It was sandwiched between two stainless steel (SS) electrodes and assembled in a spring loaded brass sample holder. AC impedance measurements were taken from 2.5 MHz to 0.01 Hz frequency range using a computer controlled Metrohm Autolab M101

frequency response analyzer. Conductivity of GPE, σ was calculated using the Eq.(1).

$$\sigma = (1/R_b)(t/A) \quad (1)$$

where t is the thickness and A is surface area of the GPE pellet. R_b was calculated using the resultant impedance plot and Non Linear Least Square fitting programme.

To study the conductivity behavior with temperature, impedance data were collected from 28 °C to 50 °C for the sample having the highest room temperature conductivity.

DC polarization Test

DC polarization test using blocking electrodes was performed to identify the contribution from ions and electrons to the conductivity. The GPE pellet was sandwiched in between two stainless steel (SS) electrodes and the current through the GPE pellet was measured as a function of time by applying 1.0 V DC bias potential. t_i was calculated according to the Eq.(2).

$$t_i = 1 - i_e / i_T \quad (2)$$

where t_i is the ionic transference number, i_e and i_T are stabilized current and initial total current respectively.

Preparation of redox capacitors

Pyrrole which was purchased from Aldrich and stored in the dark in a refrigerator was electrochemically polymerized in the presence of dodecylbenzenesulfonate (DBS - Aldrich) on fluorine tin oxide (FTO) glass plates by electrochemical polymerization using a computer controlled potentiostat (Metrohm Autolab101). The three electrode electrochemical cell used for electrochemical polymerization consisted of a working electrode (FTO), a Ag/AgCl reference electrode and a Pt counter electrode. Polypyrrole (PPy) films of the thickness of about 1.0 μm were prepared by applying a current density of 1 $mA\ cm^{-2}$. A GPE film was sandwiched in between two PPy electrodes each of area 1 cm^2 to fabricate the redox capacitors.

Characterization of redox capacitors

For the cyclic voltammetry tests, a three electrode electrochemical cell was used where one electrode of the redox capacitor was used as the working electrode and the other one as the

reference and counter electrodes. Cycling was done by varying the potential window using a computer controlled potentiostat (Metrohm Autolab M101) at the scan rate of 10 mV/s. Specific capacity was calculated using the Eq.(3) (Wang *et al.*, 2013).

$$C_s = 2(\int IdV) / m\Delta vS \quad (3)$$

In the Eq. (3), $\int IdV$ is the integrated area of the cyclic voltammogram, m is the mass of a single electrode, Δv is the potential window and S is the scan rate.

The redox capacitors were tested using EIS. Impedance measurements were taken using the Metrohm Autolab impedance analyzer over the frequency range 0.01 Hz - 0.4 MHz at room temperature.

For GCD test, the potential response vs time was recorded at a constant current of 100 μ A. Charging and discharging of the redox capacitor was done at the potential limits 1.4 V and 0 V. Following equation (Eq.(4)) was used to calculate the discharge capacity (Wang *et al.*, 2013).

$$C_d = 2I / m(dV / dt) \quad (4)$$

where I is the constant discharge current, m is the single electrode mass, dt is the discharge time and dV is the potential drop upon discharging excluding IR drop.

Specific energy density (E_s) and specific power density (P_s) were calculated using the following equations (Eq.5 and Eq.6) (Wang *et al.*, 2013).

$$E_s = CV^2/2 \quad (5)$$

$$P_s = E/t \quad (6)$$

Here C is the specific capacitance, V is the charging potential and t is the discharging time.

RESULTS AND DISCUSSION

Determination of the optimum composition

Variation of the room temperature conductivity with $MgCl_2$ concentration is shown in Figure 1. It is seen that the room temperature conductivity increases with increasing $MgCl_2$ concentration and attains the maximum conductivity of $4.08 \times 10^{-4} \text{ S cm}^{-1}$. Further increase of $MgCl_2$ decreases the conductivity. It is known that conductivity of an ionic conductor is governed by several factors mainly by the concentration as well as mobility of charge carriers.

The initial increase of conductivity with salt concentration is evidently due to the increasing of charge carrier concentration. The subsequent decrease of conductivity after reaching the maximum value is very likely due to formation of ion pairs in the GPE which do not facilitate conductivity (Kumar and Munichandraiah, 2001).

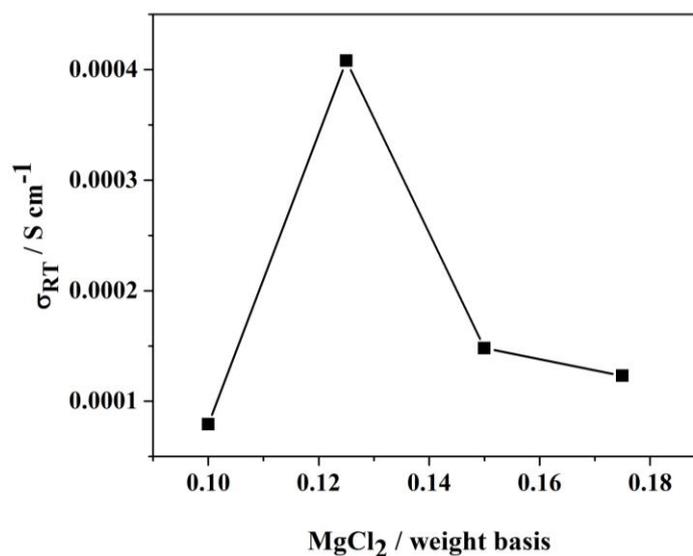


Figure 1: Room temperature ionic conductivity variation of the gel polymer electrolyte with $MgCl_2$ concentration

In order to change the composition of GPE further to obtain the highest conductivity, the polymer concentration was also varied. Conductivity variation with PAN concentration is shown in Figure 2. Room temperature conductivity increases with PAN concentration and reaches a maximum at 0.1 (by weight), followed by a decreasing trend thereafter. When increasing the PAN concentration, assistance for ion motion from polymer network may increase. This might be the reason for initial conductivity increase. As PAN concentration increases further, viscosity of the system also increases so that there will be a resistance for the ion mobility (Sharma and Sekhon, 2006). Due to this, the conductivity may be reduced.

From these two studies, it could be concluded that the composition, 0.1 PAN:0.4 EC

: 0.4 PC : 0.125 MgCl₂ (weight basis) shows the highest room temperature ionic conductivity of $4.08 \times 10^{-4} \text{ S cm}^{-1}$. This composition resulted a thin and a flexible film free of bubbles and pinholes.

Conductivity variation of the highest conductive gel polymer electrolyte sample with temperature is shown in Figure 3. It has a linear behavior suggesting that conductivity variation with temperature follows the Arrhenius behaviour given by the following equation.

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad (8)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy for conduction, k is the Boltzmann constant and T is the temperature.

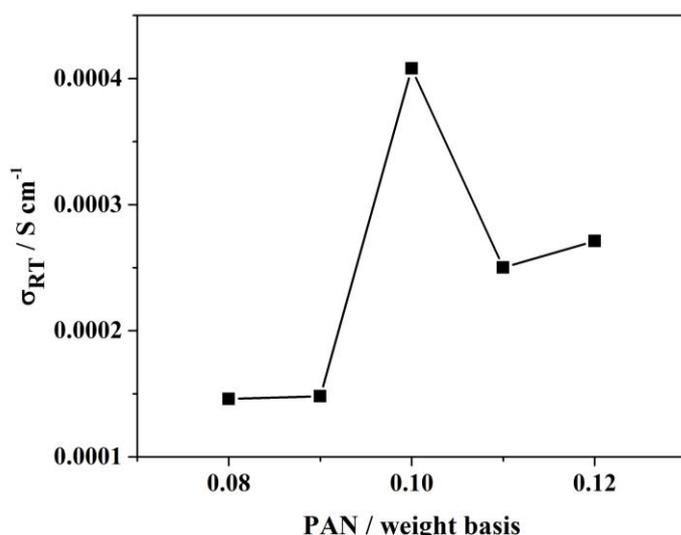


Figure 2: Room temperature ionic conductivity variation of the gel polymer electrolyte with PAN concentration.

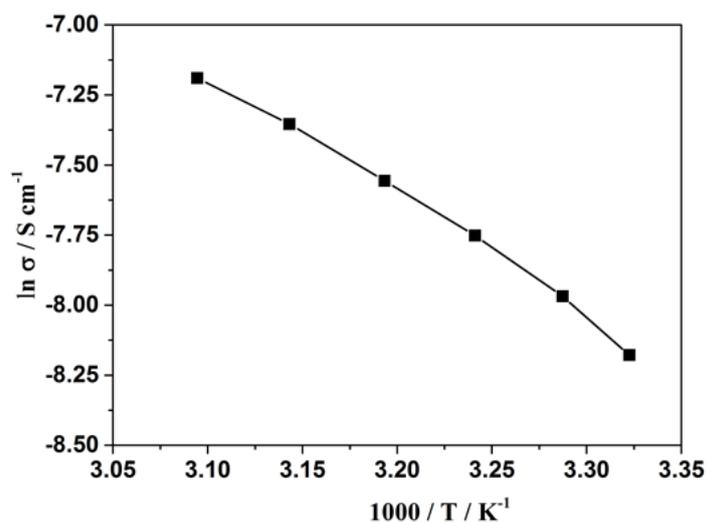


Figure 3: Temperature dependence of the conductivity of the composition, 0.1 PAN:0.4 EC : 0.4 PC : 0.125 MgCl₂ (weight basis)

Calculation of ionic transference number

The ionic transference number (t_i) was estimated by DC polarization test using two stainless steel (SS) electrodes. Figure 4 shows the current variation through the GPE with time. Ionic transference number was calculated using Eq.(2) and it was 0.84. This is an indication for the predominantly ionic nature of the conductivity (Osman *et al.*, 2012).

Characterization of redox capacitors

Figure 5 shows is the resulting cyclic voltammograms obtained for different potential windows when cycled at the scan rate of 10 mV/s. Mirror image current response of voltammograms on voltage reversal exhibits the good reversibility of the redox capacitor (Wu *et al.*, 2010).

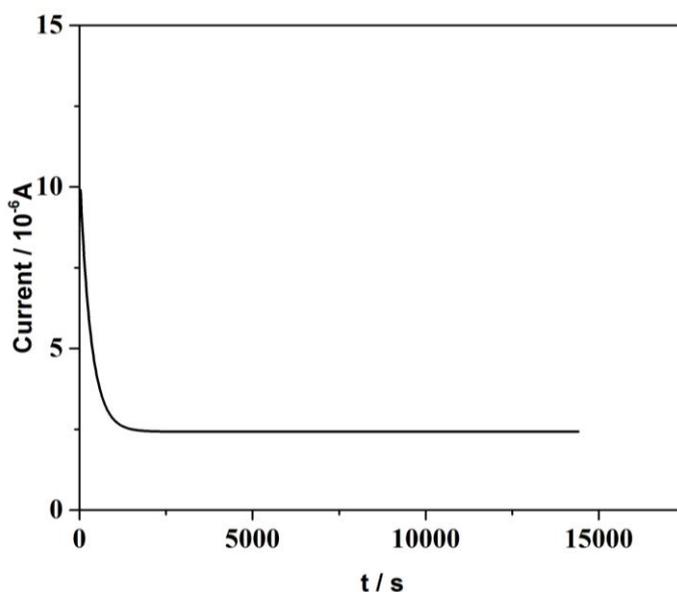


Figure 4: Variation of current through the symmetric cell with two SS electrodes under 1.0 V DC bias potential.

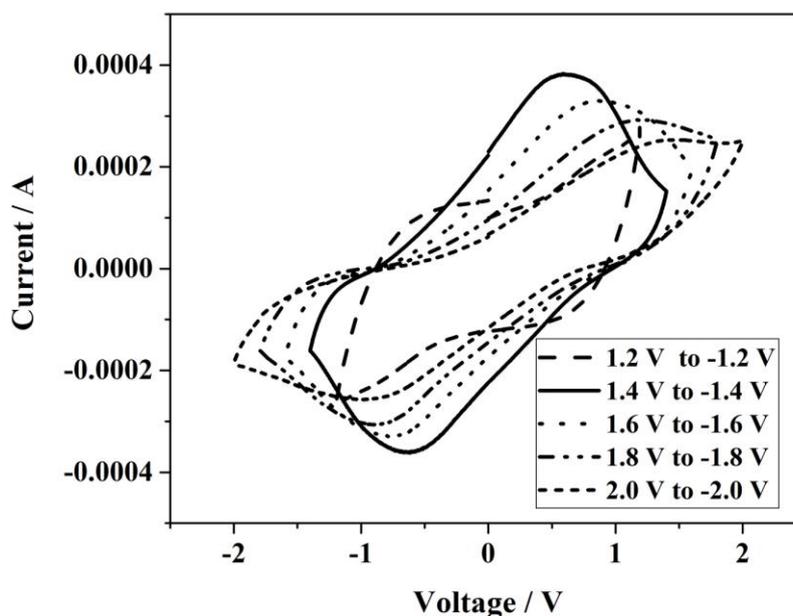


Figure 5: Cyclic Voltammograms obtained by varying the potential window of cycling of the redox capacitor (scan rate : 10 mV/s)

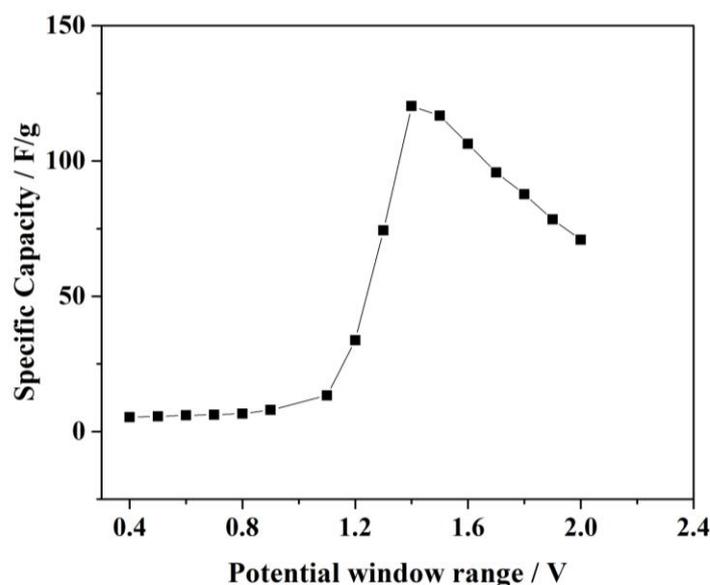


Figure 6: Variation of specific capacity with potential window of cycling.

Specific capacitance (C_s) was calculated for each window and it is shown in Figure 6. With the increase of the potential window, C_s increases first and then, decreases after a maximum value of 120.35 F/g. The potential window that results the highest specific capacity is in the range -1.4 V to 1.4 V. In redox capacitors, capacitance is derived from redox reactions which are very fast and faradaic. When increasing the potential window, the probability for the occurrence of the complete redox reaction is high, so that, C_s can increase. However, further enhancement of the potential window will not support for redox reactions and therefore, C_s reduces.

The average value of C_s was 120 F/g which is quite satisfactory compared to some reported values for redox capacitors based on GPEs (Gupta and Tripathi, 2013; Hashmi *et al.*, 2005). Figure 7 shows the Nyquist plot resulted from impedance data. In general, a Nyquist plot of a conventional capacitor consists of a vertical line parallel to the imaginary impedance axis. For normal situations, that does not appear due to some other factors. Hence, it consists of numerous features at different frequency regions

as can be observed in Figure 7. For the case of redox capacitors, at high frequency a semi circle appears representing the resistance of the bulk electrolyte. Second semicircle appears at intermediate frequency region due to the charge transfer resistance. With lowering frequency, the capacitive behaviors become dominant. A tilted line can be seen due to the capacitance related to Warburg diffusion and it will be followed by another line having a steep rising behavior. It shows the capacitive behavior. The line having the steep rising behavior is not perfectly parallel to imaginary axis of impedance as for a typical capacitive behavior. It may be due to the surface roughness as well as non uniform active layer thickness (Prabhakaran *et al.*, 2006). Figure 8 shows the results of galvanostatic charge discharge test. The linear shape suggests the capacitive behavior (Wang *et al.*, 2013).

The energy density of the redox capacitor was 5 Wh/kg and the power density was 341.64 W/kg. The discharge capacity was about 50 F/g. This low value may be due to some iR drop due to possible interfacial contacts between the electrode and electrolyte.

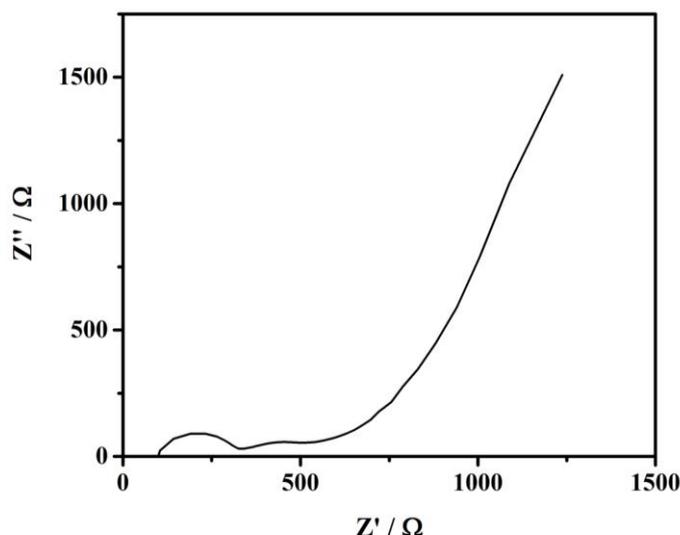


Figure 7: Nyquist plot obtained for the redox capacitor.

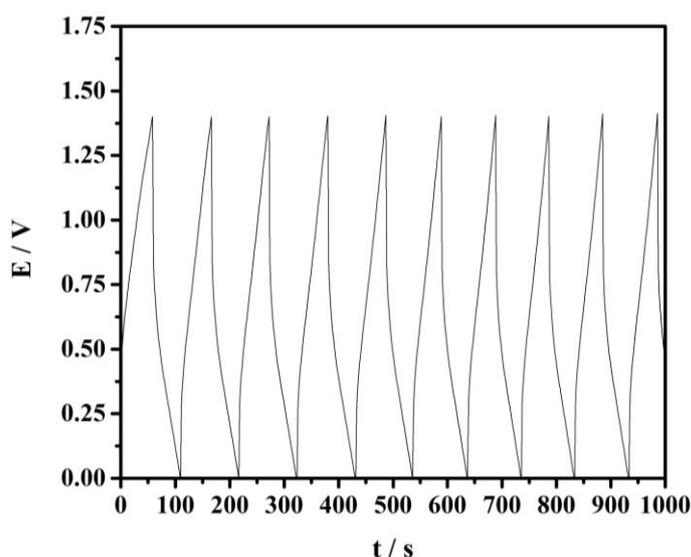


Figure 8: GCD curves obtained for the redox capacitor (charging and discharging current: 100 μ A)

CONCLUSIONS

GPE prepared with 0.1 PAN : 0.4 EC : 0.4 PC : 0.125 MgCl_2 yields a bubble free thin free-standing electrolyte film having a conductivity of $4.08 \times 10^{-4} \text{ S cm}^{-1}$. DC polarization test confirmed that the nature of the conductivity is predominantly ionic. When employed in a redox capacitor based on PPy electrodes, it showed an average specific capacity of 120 F/g for the scan rate 10 mV/s within the potential window -1.4 V to 1.4 V. From the Electrochemical Impedance Spectroscopy, Warburg type diffusion as well as capacitive behavior was observed. The average

energy and power densities were 5 Wh/kg and 341.64 W/kg respectively.

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