Electrochemical Performance of MnO_2 for Energy Storage Supercapacitors in Solid-State Design

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Abstract- In this work, solid-state supercapacitors with ionic liquid gel polymer electrolyte and MnO_2 electrodes were fabricated and characterized. The MnO_2 electrode was prepared by ultra-short pulsed electrochemical deposition over flexible graphite substrates. The ionic liquid gel polymer electrolyte was prepared by immobilizing ionic liquid $BMIBF_4$ with PVdF-HFP. The electrochemical performance of the solid-state supercapacitor was evaluated by three electrochemical characterization techniques including cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS). CV measurements were conducted at two different voltage ranges showing typical capacitive character evidenced from the nearly rectangular shape. Charge-discharge analysis showed specific energy and specific power values of 1.27 Wh kg^{-1} and 0.292 kW kg^{-1}, respectively. EIS analysis confirmed the capacitive character of the device and produced an areal capacitance density of 39.68 mF cm^{-2} (equivalent to a specific capacitance of 36.68 F g^{-1}). The presence of MnO_2 in the electrodes was confirmed by Raman spectroscopy with two major peaks observed at 550 cm^{-1} and 630 cm^{-1}.

Keywords Supercapacitors; Pseudocapacitors; Manganese Oxide; Energy Storage; Solid-State Design; Pulsed Electrochemical Deposition

1. Introduction

Due to their sustainability and cost effectiveness, renewable and efficient energy systems including energy storage technologies are being actively researched [1-8]. Supercapacitors are electrochemical energy storage devices that are designed to bridge the gap between batteries and conventional capacitors. Supercapacitors have attracted significant attention due to their high power density, excellent reversibility, and high cycle life. Furthermore, they can be used in a wide variety of applications including portable electronics, memory back-up systems, hybrid electric vehicles, and military missile systems [9]. Depending on the electrode material, supercapacitors are generally classified into electrical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs are designed with carbon materials such as graphene and carbon nanotubes. Pseudocapacitors are designed with conducting polymers such as polypyrrole, polyaniline, and polythiophene, and transition metal oxides such as RuO_2, Fe_3O_4, and MnO_2 [10, 11]. RuO_2 has shown the highest electrochemical performance among all transition metal oxides. However, the very high cost and low porosity of RuO_2 limited the viability of this material [12, 13]. MnO_2 is a good replacement of RuO_2 due to its low cost, high energy density, natural abundance, and environmental friendliness [10, 11, 14-19]. Furthermore, MnO_2 has a high theoretical specific capacitance of 1370 F g^{-1} [13, 14, 16, 18-20]. However, this value was rarely achieved in practice due to the low electrical conductivity of MnO_2 [9, 16, 18, 20]. Different synthesis techniques have been reported and used to prepare MnO_2 including co-precipitation, thermal decomposition, hydrothermal synthesis, sol-gel processes, physical vapor deposition, dip coating, electrophoresis, deposition from

colloidal suspension, and sputtering electrochemical oxidation [10, 11, 19]. However, in this work, the pulsed electro-deposition techniques was used to deposit MnO_2 on flexible graphite substrate from an aqueous electrolyte consisting of manganese sulfate ($MnSO_4$), lithium perchlorate ($LiClO_4$), and sodium dodecyl sulfate (SDS). The pulsed electro-deposition technique is highly feasible, environmentally friendly, and the growth of the film can be easily controlled by setting the appropriate experimental parameters. MnO_2 is a pseudocapacitive material that stores electrical energy via redox reactions at the surface and in the bulk of the electrode [19, 20]. However, as indicated earlier in this paper, the low electrical conductivity of MnO_2 is a major drawback. Therefore, various approaches have been adopted in the literature to enhance upon the electrochemical performance of MnO_2. For example, researchers have reported the use of nanostructured MnO_2 having large surface area such as nanosheets, nanorods, and nanotubes. Another approach is the integration of MnO_2 with other constituents such as carbon nanotubes, graphene, and conducting polymers [18, 19].

The energy density of a supercapacitor is given by the equation $E = ½\ CV^2$ Therefore, the capacitance and the operating voltage of a supercapacitor are the major factors that contribute directly to the energy density. A supercapacitor consists of two electrodes and an electrolyte ionically conducting both electrodes. The electrolyte of a supercapacitor is a very important factor that affects the electrochemical performance and the energy density of a supercapacitor. Most of the MnO_2 electrode based supercapacitors reported so far are based on the conventional liquid electrolytes including aqueous and organic electrolytes. However, aqueous electrolytes have limited potential windows and organic electrolytes are hazardous in nature [21]. Overall, the use of conventional aqueous and organic electrolytes in supercapacitor devices can create many practical limitations such as electrolyte leakage problems, bulky design, and corrosion problems [24]. Ionic liquids, which are room temperature molten salts, could be a replacement to conventional aqueous and organic electrolytes due to their unique properties of excellent chemical and thermal stability, non-volatility, low vapor pressure, and wider electrochemical potential window [21-24]. The solid-state design of supercapacitors is created by utilizing ionic liquid gel polymer electrolyte in electrochemical cell assembly instead of conventional aqueous and organic electrolytes. The solid-state design of supercapacitors has been previously reported and realized due to its importance in creating flexible, compact, reliable, and environmentally friendly electrochemical energy storage devices. For example, a hybrid supercapacitor with PEDOT and graphene electrodes was created with flat stackable solid-state platform and it was further integrated with a solar cell module to store solar electricity [21]. Symmetrical graphene electrodes and ionic liquid gel polymer electrolyte were used to create solid-state supercapacitors achieving an optimum capacitance of 80 mF cm^{-2} [22]. PEDOT was also used to design solid-state supercapacitors that created lightweight, low-cost, and high-performance devices showing considerable potential for energy storage applications [23, 24]. The unique features of solid-state supercapacitors including safety, flexibility, reduced thickness, lightweight, and environmental friendliness make them promising for flexible and wearable electronics [21-25].

Since most of the MnO_2 electrode based supercapacitors were studied in conventional aqueous and organic electrolytes, the aim of the present investigation is to report on the electrochemical performance and behavior of MnO_2 supercapacitors with ionic liquid gel polymer electrolyte $BMIBF_4$ in solid-state design. The performance characteristics of the MnO_2 solid-state supercapacitors were evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy (EIS). Raman spectroscopy was used to confirm the presence of MnO_2 in the electrode samples that were prepared by pulsed electrochemical deposition. This paper is basically divided into four major sections: the introduction, the experiment, results, and conclusions. The introduction of the paper overviews the theory behind electrochemical energy storage, solid-state design, and electrochemical properties of MnO_2 as supercapacitor electrode material. The experimental section overviews electrode synthesis, preparation of gel polymer electrolyte, fabrication of supercapacitor cells, and electrochemical characterization of the proposed solid-state supercapacitor. The results section discusses the electrochemical performance of the solid-state supercapacitor including CV, CD, EIS, and Raman spectroscopy. And finally, the conclusions section highlights the outcomes of the present work.

2. Experiment

2.1 Synthesis of MnO_2 Film and Characterization

The pulsed electrochemical growth of the MnO_2 film was carried out in a three-electrode electrochemical cell over a flexible graphite substrate which was used as a working electrode. The precursor electrolyte was prepared by dissolution of 0.07 M sodium dodecyl sulfate (SDS), 0.2 M manganese oxide ($MnSO_4.5H_2O$), and 0.1 M lithium perchlorate ($LiClO_4$), respectively in an aqueous medium. A platinum sheet was used as a counter electrode and the electrochemical potentials were measured against a saturated Ag/AgCl reference electrode. The electrochemical growth was carried out by applying sequential unipolar anodic current pulses of current density ~4 mA cm^{-2} for 10 ms on and 100 ms off. Followed by the growth, the electrodes were rinsed in deionized water and naturally dried prior to supercapacitor cell assembly. The presence of MnO_2 on the prepared electrode was investigated by the DXR Raman microscope.

2.2 Preparation of Gel Polymer Electrolyte

The ionic liquid gel polymer electrolyte was prepared by mixing 1butyl-3-methylimidazolium tetrafluoroborate (BMIBF4) to a solution of P(VdF-HFP) polymer in acetone in the 80:20 weight ratio. The mixture was magnetically stirred for at least 10 hours. The viscous solution of ionic liquid gel polymer electrolyte was used to fabricate solid-state supercapacitor cells.

2.3 Fabrication of supercapacitor cells

The ionic liquid gel polymer electrolyte was spread gently on top of each electrode covering an active surface area of 1.0 cm^2. Both electrodes were then placed on top of each other and pressed lightly to form the complete cell. This supercapacitor cell in solid-state design was then left overnight to dry naturally prior to any further evaluation. Such a cell design is compact, simple, highly reliable, and environmentally friendly.

2.4 Electrochemical characterization of solid-state supercapacitor

The Solartron 1287 Electrochemical Interface and Solartron Impedance Analyzer (Model: 1260) were used to perform cyclic voltammetry (CV), galvanostatic charge-discharge (CD), and electrochemical impedance spectroscopy measurements. The areal capacitance density of supercapacitor cells was evaluated using the equation,

$$C = (ia + ic)/2s \quad (1)$$

, where *ia* and *ic* are the anodic current and cathodic current respectively, and s is the scan rate. The specific capacitance was calculated from the CD curves using the equation,

$$C_d = i.\Delta t/\Delta V \quad (2)$$

,where i is the constant discharge current density, Δt is the discharge time, and ΔV is the voltage drop upon discharging (excluding the IR drop). The energy and power densities were evaluated from CD using the equations $E = ½ C_d V^2$ and $P = V^2/4m.ESR$, respectively, where m is the mass of the electrode and ESR is the equivalent series resistance. The impedance measurements were carried out using the Solartron impedance analyzer (Model: 1260) in the frequency range from 10 mHz to 100 kHz at a signal level of 10 mV. The value of overall capacitance of the supercapacitor cells was evaluated using the expression.

$$C = 1/(2\pi fz) \quad (3)$$

, where z is the imaginary part of the impedance.

3. Results and Discussion

3.1 Cyclic Voltammetry Analysis of Solid-State Supercapacitor

The electrochemical performance characteristics of the solid-state supercapacitor with pure MnO_2 electrodes were evaluated in terms of CV for two voltage ranges: (-0.5 to 0.5) V and (-1.0 to 1.0) V under different scan rates as shown in Figure 1. The maximum areal capacitance densities were found to be 10.28 mF cm^{-2} and 18.16 mF cm^{-2} under a voltage range of (-0.5 to 0.5) V and (-1.0 to 1.0) V, respectively at a scan rate of 10 mV s^{-1}. The CV curve of the pure MnO_2 based solid-state supercapacitor show nearly rectangular behavior, which testifies the pseudocapacitive and redox properties of the MnO_2 electrode that was prepared by pulsed electrochemical deposition of $MnSO_4$ in aqueous medium.

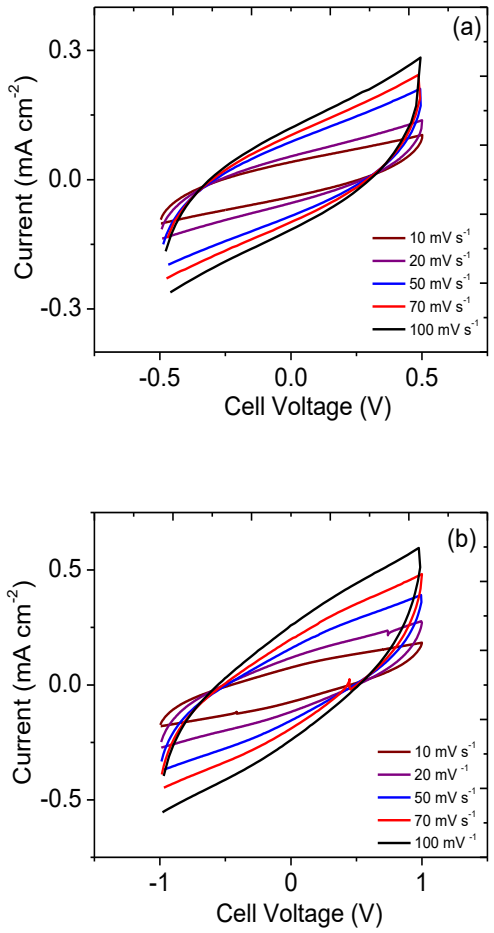

Figure 1. CV Curves of the MnO_2 based solid-state supercapacitor under a voltage range of (a) (-0.5 to 0.5) V and (b) (-1.0 to 1.0) V. CV curves were used to report areal capacitance densities.

The areal capacitance density values of the MnO_2 based solid-state supercapacitor were plotted as a function of the scan rate in Figure 2, for both voltage ranges. The areal capacitance values show degradation up to 50 mV s^{-1}, and then become relatively stable from 50 mV s^{-1} to 100 mV^{-1}.

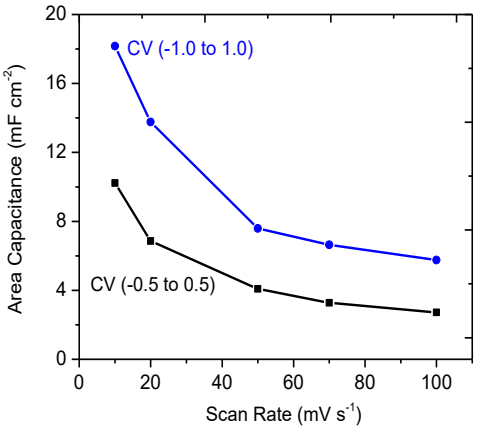

Figure 2. Areal capacitance densities of the MnO_2 solid-state supercapacitor plotted as a function of the scan rate

3.2 Charge-Discharge Analysis of Solid-State Supercapacitor

The charge-discharge characteristics of the MnO_2 solid-state supercapacitor were measured at different constant current densities and plotted as shown in Figure 3 (a). The supercapacitor exhibits relatively linear discharge characteristics with a minimum ESR of 210 Ω cm^2 arising from the internal resistance of the device. It is generally important to have a small Ohmic drop because this means less internal resistance and therefore better and more efficient energy storage capabilities. The discharge capacitance densities of the MnO_2 solid-state supercapacitor were plotted as a function of the current density, as shown in Figure 3 (b). There is a significant degradation of the discharge capacitance observed from 0.1 to 0.25 mA cm^{-2}. However, only a slight fading was observed from 0.25 to 0.5 mA cm^{-2}. The specific energy and specific power values evaluated at different constant current densities of the MnO_2 solid-state supercapacitor are listed in Table 1. The specific energy and specific power values obtained from CD analysis were used to construct the Ragone plot shown in Figure 4, where the x-axis of the Ragone plot represents the power density and the y-axis represents the energy density.

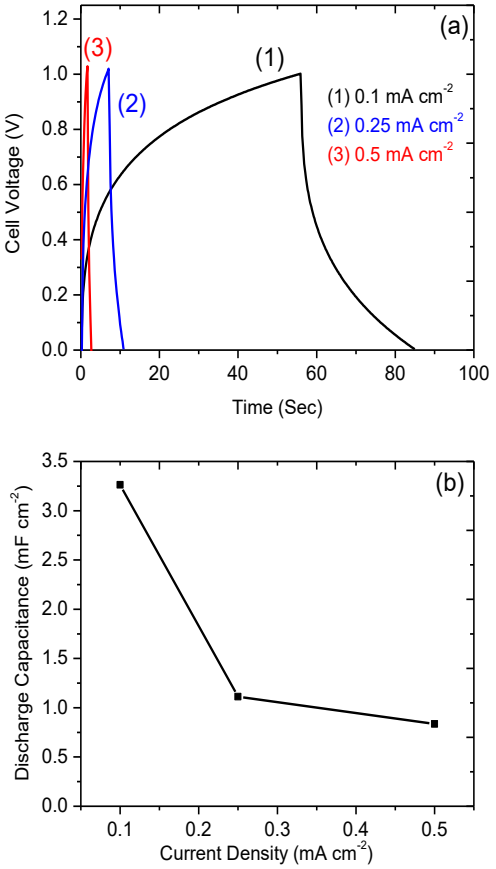

Figure 3. CD curves of the MnO_2 solid-state supercapacitor evaluated at different constant current densities, and (b) Discharge capacitance plotted as a function of current density. CD Curves were used to calculate ESR, energy, and power densities.

Table 1. Specific energy and specific power values of the MnO_2 solid-state supercapacitor

Current Density (mA cm^{-2})	ESR (Ω cm^2)	Energy Density E (Wh kg^{-1})	Power Density P (kW kg^{-1})
0.1	292	1.27	0.252
0.25	210	0.36	0.292
0.5	262	0.085	0.0823

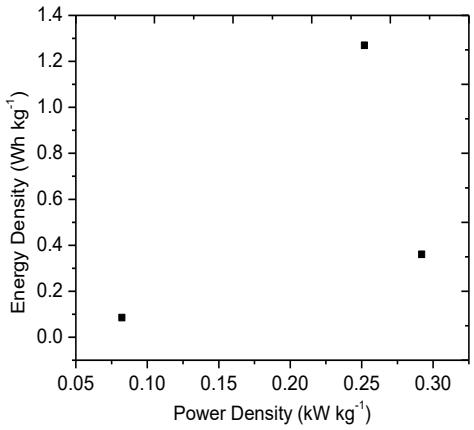

Figure 4. Ragone plot showing specific energy versus specific power of the MnO_2 solid-state supercapacitor as an electrochemical energy storage device

3.3 Electrochemical Impedance Spectroscopy Analysis of Solid-State Supercapacitor

Electrochemical impedance spectroscopy (EIS) is useful to evaluate the resistive and capacitive properties of a supercapacitor. A Nyquist plot is usually generated for that purpose with two axes: x-axis (real part of the complex impedance) and the y-axis (imaginary part of the complex impedance). The x-axis is used to evaluate the resistive properties and the y-axis is used to evaluate the capacitive properties of the supercapacitor. The impedance response of an ideal supercapacitor is represented by a straight line parallel to the imaginary (y-axis) of the Nyquist plot. In the present work, the impedance measurement was carried out in the frequency range of (10 mHz – 100 kHz), at room temperature. Figure 5 shows the Nyquist plot of the MnO_2 based solid-state supercapacitor, and the capacitive properties are confirmed by the steep rising behavior in the low frequency region. Furthermore, no clear semicircular features were observed in the present case, which means that the system is kinetically fast. Various electrochemical information can be extracted from the Nyquist plot in accordance with the frequency region. The resistive properties of the supercapacitor device are extracted from the high-frequency region. The ion diffusion properties are extracted from the medium frequency region. And the capacitive properties of the supercapacitor are extracted from the low-frequency region. The bulk resistance (R_b) of the solid-state supercapacitor was evaluated by taking the x-axis intercept in the high-frequency region, and it was found to be 74.24 Ω cm^2. The extrapolation for the low frequency data gives another x-axis intercept that is equal to R_b + W, where W is the Warburg impedance. Table 2 shows the electrochemical parameters evaluated from impedance analysis. The Nyquist plot of the solid-state supercapacitor is fitted by an equivalent circuit as shown in the inset of Figure 5, where R_b is the bulk resistance, W is the Warburg impedance, C_{dl} is the double layer capacitance, and C_F is the faradic capacitance.

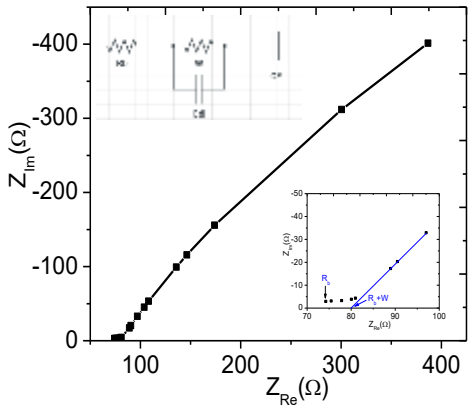

Figure 5. Nyquist plot of the MnO_2 solid-state supercapacitor recorded at room temperature in the frequency range of 10 mHz – 100 kHz. This plot is used to evaluate resistive and capacitive properties of the device.

Table 2. Electrochemical parameters of the MnO_2 solid-state supercapacitor evaluated from impedance analysis

	R_b (Ω cm^2)	W (Ω cm^2)	C (mF cm^{-2})	C (F g^{-1})
Supercapacitor Cell	74.24	5.61	39.68	39.68

3.4 Raman Spectroscopy

The pure MnO_2 electrode that was prepared by pulsed electrochemical deposition of SDS, $MnSO_4.5H_2O$, and $LiClO_4$ in aqueous medium was analyzed by the DXR Raman microscope to confirm the presence of MnO_2 in the sample electrode. Figure 6 shows the Raman spectrum of the MnO_2 electrode. Two main peaks were observed at 550 cm^{-1} and 630 cm^{-1} which is in close agreement with the MnO_2 peaks reported elsewhere [26, 27]. The band at 550 cm^{-1} could be attributed to the Mn-O stretching vibration, and the band located at 630 cm^{-1} could be attributed to the symmetric stretching vibration of Mn-O of the MnO_6 groups.

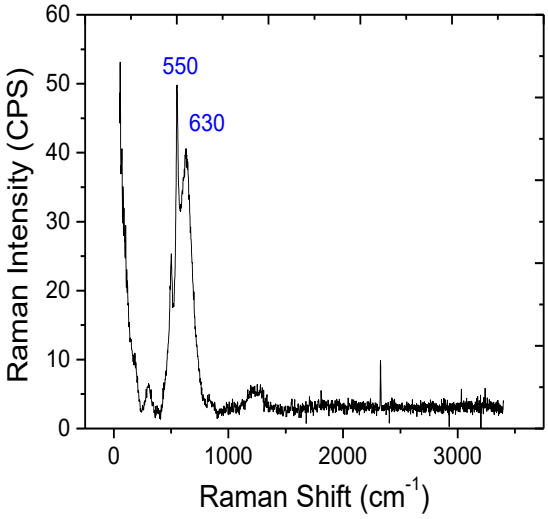

Figure 6. Raman spectrum of the MnO_2 electrode prepared by pulsed electrochemical deposition. The spectrum was used to observe MnO_2 peaks to confirm its presence.

4. Conclusion

Solid-State supercapacitor with MnO_2 electrodes and ionic liquid gel polymer electrolyte ($BMIBF_4$) was fabricated and characterized. The solid-state supercapacitor produced an areal capacitance density of 39.68 mF cm^{-2} (equivalent to a specific capacitance of 39.68 F g^{-1}) obtained from impedance spectroscopy analysis. The maximum specific energy and specific power were found to be 1.27 Wh kg^{-1} and 0.292 kW kg^{-1}, respectively. The presence of MnO_2 was further confirmed by Raman spectroscopy and two peaks were identified at 550 cm^{-1} 630 cm^{-1}. The potential of MnO_2 supercapacitors in solid-state design was demonstrated and further enhancements can be achieved by designing nanocomposites of MnO_2 and other materials such as conducting polymers to enhance the electrochemical energy storage performance.

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