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Fabrication of Asymmetric Supercapacitor Using Aqueous and Polymer Electrolytes for Energy Storage

By

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Abstract:

Supercapacitors represent an attractive alternative for portable electronics and automotive applications due to their high capacitance, specific power and extended life. In fact, the growing demand of portable systems and hybrid electric vehicles, memory protection in CMOS, logic circuit, VCRs, CD players, PCs, UPS in security alarm systems, remote sensing, smoke detectors, etc. require high power in short-term pulses. So, in the last 20 years, supercapacitors have been required for the development of large and small devices driven by electrical power. In this paper, asymmetric supercapacitors with high energy density were successfully fabricated using graphene as negative electrode and polyaniline as positive electrode. The weight of active material was 5.6 mg. The surface topography was characterized by scanning electron microscopy (SEM). The electrochemical properties of the composite were evaluated by cyclic voltammetry (CV), charge-discharge measurements and electrical impedance spectroscopy (EIS). The separator was a filter paper soaked in aqueous potassium hydroxide (6M).This enhances both the specific capacitance to 620.76 F/g at scan rate of 1 mV/s and the energy density to 86.22Wh/kg. Another low leakage supercapacitor was fabricated using polyvinyl alcohol (PVA) separator and 6 mole potassium hydroxide salt with specific capacitance of 220.35 F/g at scan rate of 1 mV/s.

Keywords:

Graphene oxide, graphene, Polyaniline, Asymmetric supercapacitors and Polymer electrolyte

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1.Introduction:

Supercapacitors, which are also termed as electrochemical capacitors or ultracapacitors, have been studied for application in digital communication devices, digital cameras, mobile phone, power supplies, and hybrid electric vehicles. Supercapacitors have higher power density and longer cycle life compared to secondary batteries and higher energy density compared to conventional electrochemical double-layer capacitors [1-3]. The performances of supercapacitors are primarily determined by the electrode materials [4]. Capacitance performance of supercapacitors depends on active electrode materials based on carbon materials, metal oxides, and conducting polymers, which are having their own advantages and disadvantages. Carbon-based materials can provide high power density and long cycle life, but its low specific capacitance limits its application for high energy density devices [5 ,6]. Among carbon-based materials, graphene is a new advanced carbon material with unique morphology that distinguishes it from other materials in the EDLC (Electric Double Layer Capacitor) market. A graphene sheet consists of many carbon atoms arranged into a large two-dimensional crystal lattice. Graphene is mechanically robust, exhibiting a quantum Hall effect at room temperature and undergoing ballistic conduction of charge carriers along the basal planes, resulting in good conductivity in the material [7]. Conducting polymers have been intensively studied as electrodes in supercapacitors due to their high electrical conductivity, electrochemical reversibility, larger pseudo-capacitance, and faster doping/dedoping rate during charge/discharge process, but they have low mechanical stability and cycle life [8]. Among the conducting polymers, polyaniline (PANI) has been regarded as one of the most promising conductive polymers due to its low cost, easy synthesis, controllable electrical conductivity, and good environmental stability [9].

Asymmetric hybrids combine Faradaic and non-Faradaic processes by coupling an EDLC electrode with a pseudocapacitor electrode. In particular, the coupling of an activated carbon negative electrode with a conducting polymer positive electrode has received a great deal of attention [7, 10]. The lack of an efficient, negatively charged, conducting polymer material has limited the success of conducting polymer pseudocapacitors. The implementation of a negatively charged, activated carbon electrode attempts to circumvent this problem. While conducting polymer electrodes generally have higher capacitances and lower resistances than activated carbon electrodes, they also have lower maximum voltages and less cycling stability. Asymmetric hybrid capacitors that couple these two electrodes mitigate the extent of this tradeoff to achieve higher energy and power densities than comparable EDLCs. Also, they have better cycling stability than comparable pseudocapacitors [7, 10]. Gel polymer electrolytes are one of the most promising candidates to replace liquid electrolytes in the energy storage devices including batteries and supercapacitors [9,10].

The gel polymer electrolytes possess many distinct advantages over their liquid electrolyte counterparts, such as less reactivity and leakage, improved safety, flexibility, and better manufacturing integrity. A gel polymer electrolyte is prepared by entrapping a liquid electrolyte (an ionic salt dissolved into a polar liquid) in a host polymer network. The ionic motion in such system is liquid like, where the polymeric network provides a mechanical integrity to the material. Gel polymer electrolytes possess many additional properties including high ionic conductivity, mechanical stability, wide enough electrochemical potential window, and generally good interfacial stability [11-14]. However, the poor thermal and electrochemical properties are generally observed for those gel electrolyte systems in which organic solvent based liquid electrolytes are employed. The volatile nature of organic solvents limits the thermal stability, whereas their relatively narrow electrochemical potential windows limit the electrochemical stability range of the gel polymer electrolytes [14].

This work is aimed to fabricate asymmetric supercapacitor based on graphene negative electrode and polyaniline positive electrode. Aqueous and polymer electrolytes were used. The supercapacitor performance was assessed using cyclic voltammetry (CV), electrical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements.The fabricated supercapacitors show high specific capacitance and high energy density.

2.EXPERIMENTAL WORK

2.1.Materials

Graphite powder was purchased from Fischer Scientific. Sulphuric acid (98 wt.%), nitric acid (70 wt.%), hydrazine hydrate (65 wt.%), potassium permanganate and sodium nitrite were purchased from Sigma-Aldrich Ltd. Barium chloride (99%) was purchased from ALEC. Potassium hydroxide, Silver chloride, Sodium hydroxide, Polyvinyl alcohol and hydrogen peroxide (30 wt.%) were obtained from local chemical companies. Aniline (99%) was purchased from CDH. Ammonium persulphate (98.5%) was purchased from WINLAB. Hydrochloric acid (37%) and camphor sulfonic acid were purchased from Mereck.

2.2.Graphene Electrode Preparation

Graphene oxide (GO) was prepared by modified Hummers method [15-20]. Typically, 4.0 g natural graphite powder and 2 g sodium nitrate were mixed with 92 mL sulfuric acid in a 2000 mL flask place in an ice bath. The obtained solution was stirred with slowly addition of 12 g potassium permanganate, the stirring was continued for

2 h. The mixture solution was transferred to a 35 ˚C water bath and stirred for 30 min. After that, 184 mL of deionized water was slowly added into the solution and the solution temperature monitored was about 98 °C. The mixture solution was maintained at this temperature for 30 min. Then, 560 mL deionized water and 40 mL of hydrogen peroxide were added sequentially to the mixture solution to terminate the reaction. The observed color of mixture was dark yellow. The resulting product was filtered and rinsed with 5% HCl solution to remove sulfate groups checked by barium chloride and repeated till no white precipitates exist. Distilled water was used to remove HCl for several times till no white color exists in the solution of silver chloride. The graphite oxide powder was obtained after drying in vacuum at 60°C overnight. The powder was then dispersed in distilled water to make concentration of 0.5 mg/mL, and exfoliated by ultrasonication for 1 h to get brown graphene oxide. GO was deposited on stainless steel substrate (type 304) with active area of 1 cm^2 and dried in an oven at 60°C for 12h. Graphene film was obtained by reduction of graphene oxide film on stainless substrate using hydrazine hydrate soaked in filter paper for 72h at room temperature.

2.3.Polyaniline Electrode Preparation

Aniline (0.2 M) was added to 0.2 M HCl then kept for 1 h at room temperature. Ammonium persulfate (APS) in 20 mL distilled water was then slowly added to the suspension under stirring. The molar ratio of aniline, hydrochloric acid and APS was 1:1:1. The reaction was conducted by the insitu polymerization method in ice bath for 1 h then left at rest to polymerize for 24 hours at room temperature. The prepared mixture was filtered, rinsed with distilled water. PANI was simultaneously dedoped by 25 mL 8 M sodium hydroxide at 95 ˚C for 20 h. The emeraldine salt was dried in air and then at 60ºC for 24h. PANI was doped with camphor sulfonic acid (CSA) and dissolved in chloroform. PANI was sprayed on the active area (1 cm×1 cm) of the stainless steel substrate using air compressor and a spray gun. PANI electrodes were dried in air and then at 60ºC for 12h.

2.4.Polymer Electrolyte Preparation

PVA–KOH polymer electrolyte was prepared by a solution-casting method [21]. First, 1 g PVA was dissolved in 5 ml deionized water with agitation 85 C for 1 h then 5 ml KOH (6M) was slowly added. After complete dissolution, the resulting solution was continuously stirred until having a homogeneous viscous appearance. Then, the mixture was poured to glass petri dish and left to dry at room temperature. Thus, a membrane of PVA-KOH polymer was obtained.

2.5.Fabrication of Supercapacitors

Supercapacitor was prepared by stacking PANI positive electrode, graphene negative electrode and a separator in between. Different separators were used. The first separator was a filter paper soaked in aqueous potassium hydroxide (6 M). The second separator was PVA–KOH polymer electrolyte. Fig. 1 shows the structure of fabricated supercapacitor.

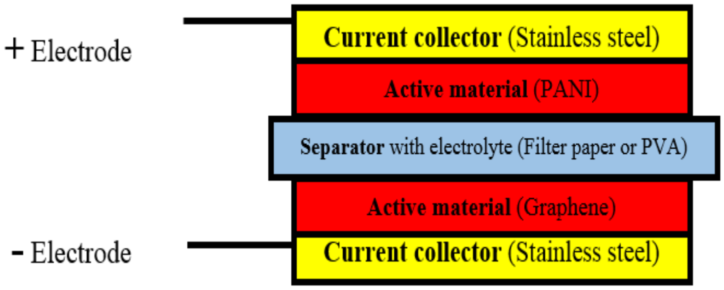

Figure (1): *Fabricated supercapacitor structure*

2.6.Electrochemical Measurements

The electrochemical performance for the fabricated supercapacitors was investigated in a two-electrode system by cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) was measured using Gamry (G750) instrument. The galvanostatic charge-discharge characteristic was measured with a Gamry Reference 3000. The cyclic voltammetry (CV) response of the electrodes was investigated at different scan rates varying from 1 mV/s to 100 mV/s. EIS measurements were measured without dc bias using sinusoidal signal of 5 mA over the frequency range from 0.05 Hz to 1MHz.

3.RESULTS AND DISCUSSION

Figure (2) shows CV of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide (6 M) using two probes connection at different scan rate from 1 mV/s to 100 mV/s with scanning potential window is from - 0.8 to 0.8V. The CV curve area is gradually enlarged with the increase of the scan rate. The calculated specific capacitance was 620.76 F/g at scan rate of 1 mV/s and the weight of active material was 5.6 mg. The fabricated supercapacitor has an increased energy density of 86.22 Wh/kg at potential difference of 1V.

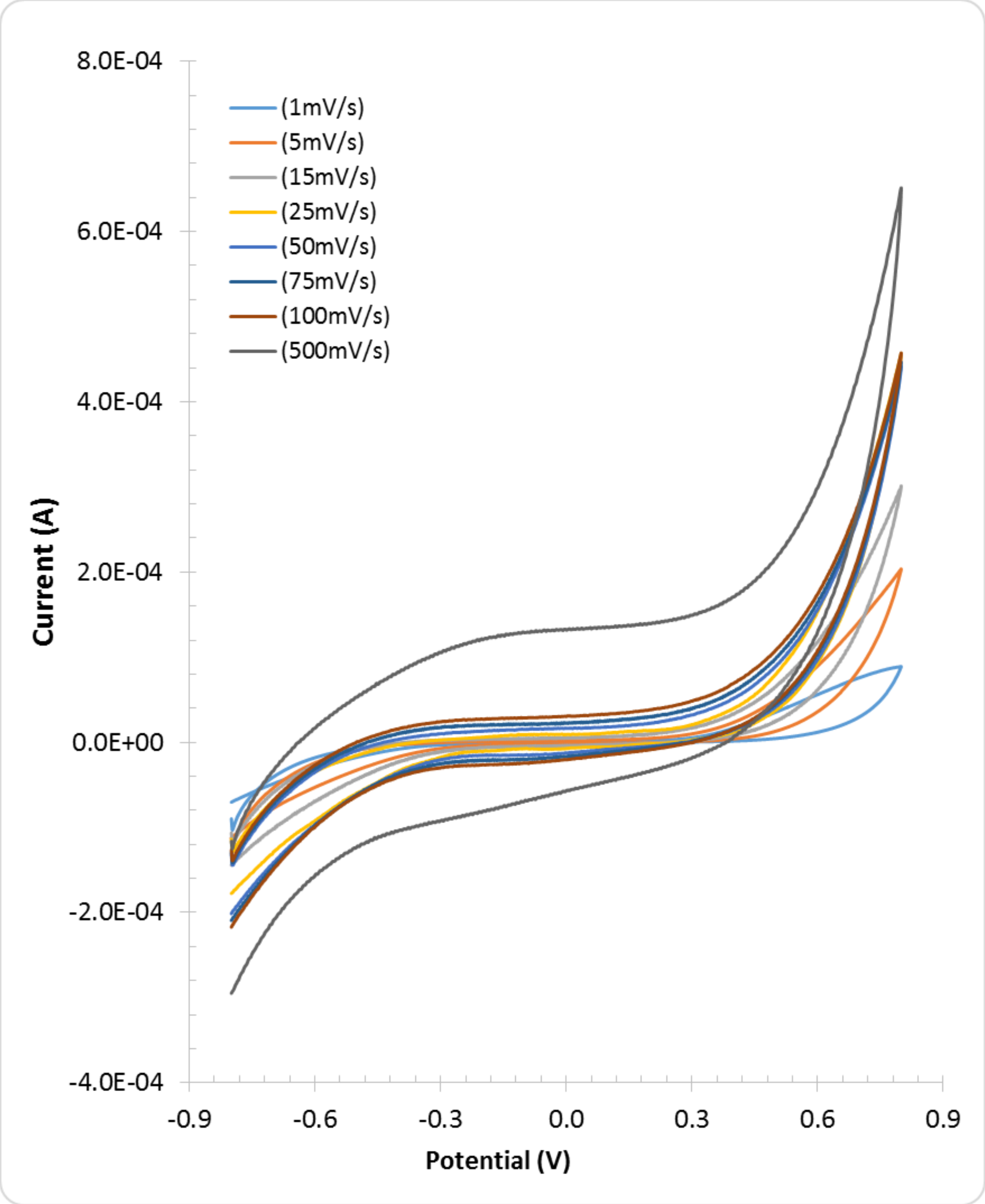

Figure (2): *CV of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide*

Figure (3) shows CV curves of asymmetric supercapacitor with separator of PVA-KOH polymer electrolyte using two probes connection at different scan rate from 5 mV/s to 100 mV/s with scanning potential window is from - 0.2 to 1V. The CV curve area is gradually enlarged with the increase of the scan rate [17]. The calculated specific capacitance was 220.35 F/g at scan rate of 5 mV/s and the weight of active material was 5.6 mg. The fabricated supercapacitor has an increased energy density of 30.60 Wh/kg at potential difference of 1V.

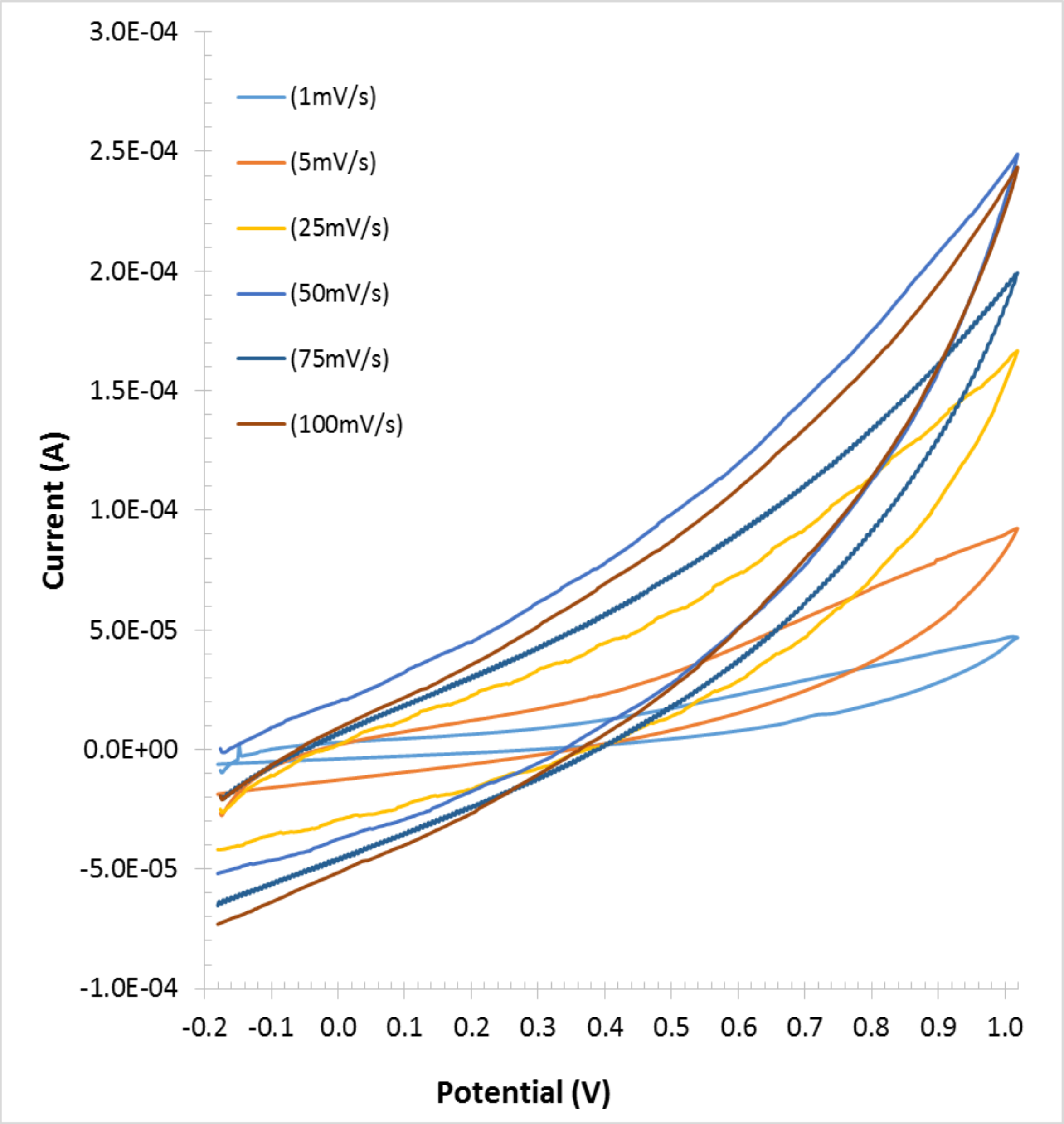

***Figure (3):** CV asymmetric supercapacitor with separator of PVA-KOH polymer electrolyte*

Figure (4) shows the Nyquist plot of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide (6 M) or PVA-KOH polymer electrolyte. Figure (4) shows the Nyquist plot of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide (6 M). The semicircle corresponds to charge transfer resistance (Rct). The value of charge transfer resistance is found to be 40.5 Ω. The intersection of the curve at the x-axis represents the internal or equivalent series resistance (ESR). ESR is the sum of the electrolyte resistance, the intrinsic resistance of the active electrode material and the contact resistance at the interface of the active material and the current collector. The value of equivalent series resistance is found to be 4.4 Ω.

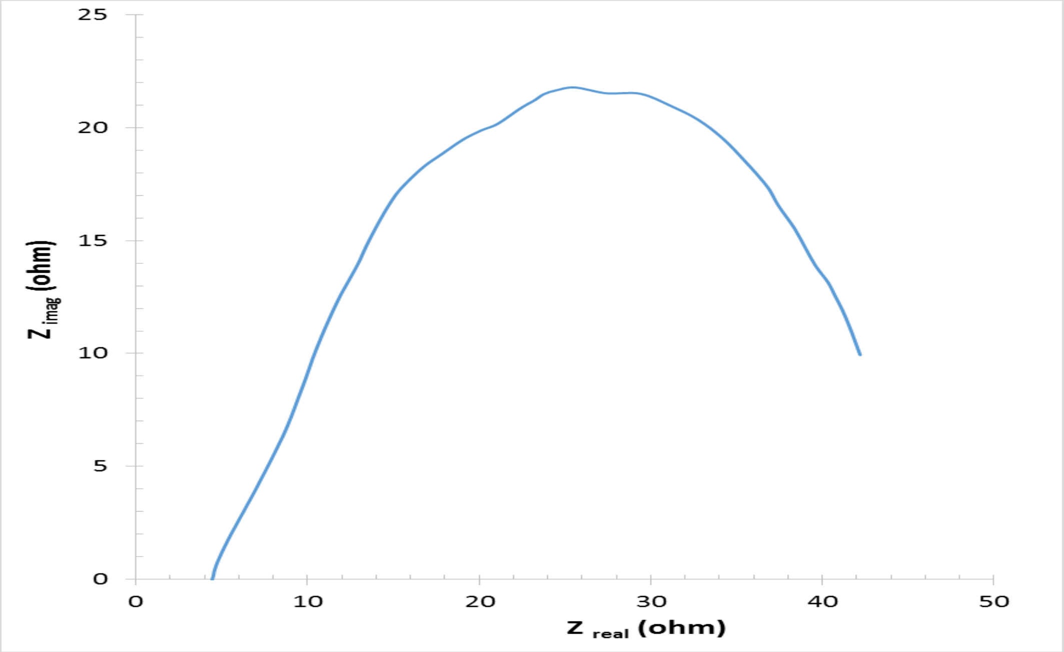

Figure (4): *Nyquist plot of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide*

Figure (5) shows the Nyquist plot of asymmetric supercapacitor with separator of PVA-KOH polymer electrolyte. The value of charge transfer resistance is found to be about 500 Ω. The value of equivalent series resistance is found to be 21.1 Ω. Using a separator of filter paper soaked in aqueous potassium hydroxide produced lower ESR and Rct which determine the rate of the charge and discharge and consequently the power capability of the supercapacitor. ESR value was greater than that of filter paper separator as aqueous electrolyte had high conductivity than polymer electrolyte.

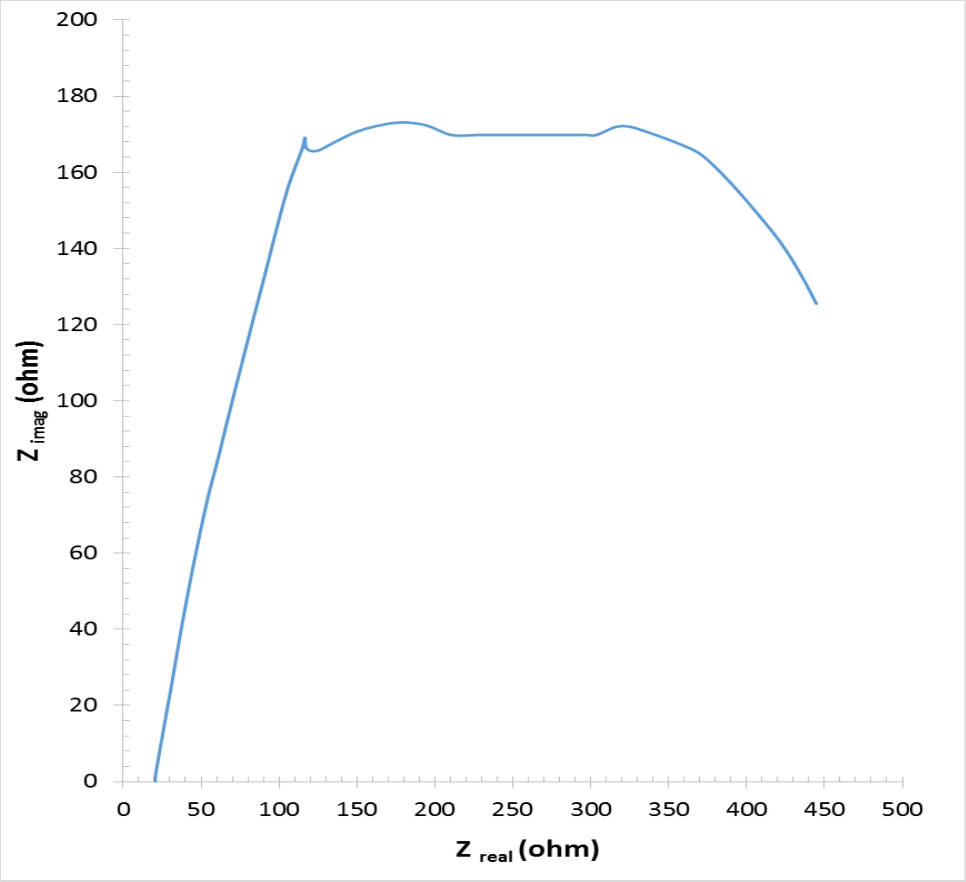

Figure (5):*Nyquist plot of asymmetric supercapacitor with separator of PVA-KOH polymer electrolyte*

Figure (6) shows the charge/discharge curves of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide and PVA-KOH polymer electrolyte. Both Supercapacitors were charged to 1 V at constant current of 3.5 mA. The charge–discharge duration was about 700 s for supercapacitor with PVA-KOH polymer and about 2000 s for supercapacitor with filter paper soaked in aqueous potassium hydroxide. For supercapacitor with filter paper soaked in aqueous potassium hydroxide, raise time (t_{rise}) is equal to 790 s and fall time (t_{fall}) is equal to 800 s. For supercapacitor with PVA-KOH supercapacitor raise time (t_{rise}) is equal to 276 s and fall time (t_{fall}) is equal to 282 s.

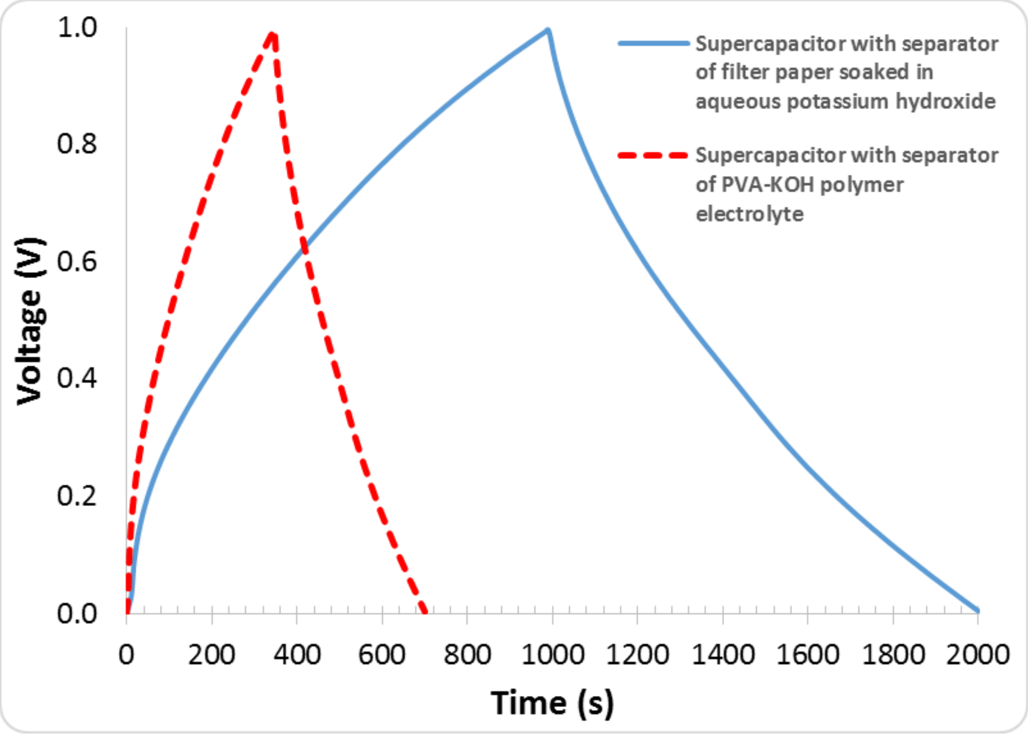

Figure (6): *Charge-discharge curves at constant current of 3.5 mA of asymmetric supercapacitor with separator of filter paper soaked in aqueous potassium hydroxide and PVA-KOH polymer electrolyte*

4.CONCLUSIONS

Asymmetric supercapacitors were fabricated using different separators of filter papers soaked in aqueous potassium hydroxide or PVA-KOH polymer electrolytes. The fabricated supercapacitors with aqueous electrolytes show higher values of specific capacitance and energy density compared to those with polymer electrolytes. Low leakage supercapacitors fabricated using PVA-KOH polymer electrolyte show specific capacitance of about 220.35 F/g. Both Supercapacitors had symmetric charge-discharge curves. Asymmetric supercapacitors using aqueous potassium hydroxide were preferred in power applications.

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