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# Enhanced performance of supercapacitor based on boric acid doped PVA-H<sub>2</sub>SO<sub>4</sub> gel polymer electrolyte system

B. Karaman <sup>a</sup>, A. Bozkurt <sup>b,\*</sup>

<sup>a</sup> Department of Bio&Nano Technology Engineering, Istanbul University, Avcilar, İstanbul, Turkey

<sup>b</sup> Department of Biophysics, Institute for Research and Medical Consultations (IRMC), Imam Abdulrahman Bin Faisal University, PO Box:1982 Dammam, 31441 Saudi Arabia

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## ABSTRACT

Proton Conducting gel polymer electrolytes (GPEs) are taking much attention compared to liquid electrolytes for supercapacitor applications because of their physical properties, electrochemical stability and operation over broader temperature window. Among different GPEs PVA/acid blend electrolytes such as PVA/H<sub>2</sub>SO<sub>4</sub>, has drawn great attention in recent years. In this study, PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPE was introduced for electric-double layer capacitor (EDLCs) application, in which electrospun free-standing carbon nanofibers are used as electrodes. Introduced PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPE serves as both separator and the electrolyte in the supercapacitor. Symmetric Swagelok cells including GPEs were assembled via using two electrode arrangements and the electrochemical properties were searched. Electrochemical performance studies demonstrated that PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPE had a maximum specific capacitance (Cs) of 134 F g<sup>-1</sup> and showed great capacitance retention (%100) after 1000 charge/discharge cycles. Furthermore, PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub>GPE yielded an energy density of 67 Wh kg<sup>-1</sup> with a corresponding power density of 1000 W kg<sup>-1</sup> at a current density of 1 A g<sup>-1</sup>.

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## Introduction

Electrochemical capacitors (EC) are also referred as ultracapacitors, are very popular in the electric vehicles, portable system industry and safe energy storage systems due to their high power supply in short term [1,2]. Electrochemical capacitors are similar to batteries in design and store charges depending on both of these systems i.e. (i) pseudo capacitance, which includes active electrode material (ii) electric-double layer capacitor (EDLC) which bears electrochemically

inactive material so that there is no a net ion exchange between electrode and electrolyte. This is how energy stored in this system [3–5].

Although EDLCs have limited energy density, compared to the batteries, they have many advantages like high power density, good cycling stability, and safety which are mostly determined by the electrolytes that is used in EDLCs [4–7]. Consequently, increasing the energy density of these kind of capacitors is in a center of interest in these days [8].

Recently, gel polymer electrolytes have attracted a great attention as an alternative to liquid electrolytes for

\* Corresponding author.

E-mail address: [abozkurt@uod.edu.sa](mailto:abozkurt@uod.edu.sa) (A. Bozkurt).

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applications to super capacitors because they have many additional advantages like low volatility, electrochemical stability and suitability for applications over wide temperature domains. During applications, low electronic conductivity, high ionic conductivity at room temperature and good mechanical properties are important issues that should be provided by a polymer electrolyte [9]. One of the important types of liquid electrolytes is gel polymer electrolytes (GPE) which are suitable for different applications because of their electrochemical properties [10]. GPEs are synthesized by two steps; firstly, salt is solved in a polar or ionic solvent and then immobilized in a polymer matrix which has both the diffusive property of the liquid and cohesive property of solid [11]. As much as good electrochemical performance high safety is also important for a super capacitor and GPEs are safer than liquid electrolytes. GPEs also have high ionic conductivity which is difficult to have in solid electrolytes [12]. The advantages of the GPEs, compared to liquid electrolytes, are proper electrode/electrolyte contact and reducing the possible risk of leakage [10]. Besides, non-volatility is the main advantage of the GPEs. Temperature and the weight ratio of the ionic liquid are terms that affect the ionic conductivity of the GPEs. As they increase, ionic conductivity also increases [13].

In the supercapacitor applications, some hydrogel electrolyte studies have been conducted mostly by using poly (acrylamide) (PAAM), polyvinyl alcohol (PVA), PVA-KOH (Potassium hydroxide) and PVA/PAAM. Hydrogels were classified as amorphous, semi-crystalline, hydrogen-bonded etc., depending on the physical nature of the networks. Among them PVA has drawn more attention since it is non-toxic, cheap and chemically stable. Previously, it was reported that PVA hydrogels have good mechanical property as well as structural unity which may crosslink or make complexes depending on additives [14,15]. The host matrix PVA bears –OH groups which are bonded to the methane carbon of the backbone carbon chain, leading the formation of polymer electrolytes [16,17].

Acid/polymer based electrolytes, especially PVA/H<sub>2</sub>SO<sub>4</sub>, have been applied for EDLC with active carbon (AC), graphene, and carbon nanofibers (CNFs) electrodes to have a flexible structure [5]. For example, Wu et al. worked on graphene-based in-plane micro-supercapacitors which can be charged-discharged up to 1.000 Vs<sup>-1</sup>. This supercapacitor included PVA/H<sub>2</sub>SO<sub>4</sub> as electrolyte and yielded area capacitance of 80.7 μFcm<sup>-2</sup> [18]. In Fan and Wu's study, PVA-H<sub>2</sub>SO<sub>4</sub>-VOSO<sub>4</sub> and PVA-H<sub>2</sub>SO<sub>4</sub>-Na<sub>2</sub>MoO<sub>4</sub> GEPs were prepared with two redox additives of VOSO<sub>4</sub> and Na<sub>2</sub>MoO<sub>4</sub>. They had the specific capacitance and energy density of 543.4 F g<sup>-1</sup> and 17.9 Wh kg<sup>-1</sup>, respectively [19]. Ramesh and his group synthesized PVA based proton conducting polymer electrolytes and they had a capacitance of 21.89 F g<sup>-1</sup> [20]. Choudhury et al. studied on PVA/PAA based blend hydrogel PEs in acidic, alkaline and neutral medium. In acidic medium, they observed a capacitance of 110 F g<sup>-1</sup> with BP carbon as electrode and the ionic conductivity of 10<sup>-3</sup> S cm<sup>-1</sup> [21].

PVA/Borate complexes have drawn great attention because of their distinguished chemical and physical properties [22]. PVA/Borate gel system can be prepared by incorporating PVA and boric acid in aqueous system [22–24]. H<sub>3</sub>BO<sub>3</sub> has several advantages such as, non-combustibility and chemical durability etc. Carbon based materials such as, CNTs (carbon

nanotubes) and CNFs (carbon nanofibers) have been effectively studied to use as electrodes in the application of EDLCs due to their high chemical stability and non-toxicity. To increase the specific surface area of the electrodes based upon the material that is used, different methods have been studied. Thus, a significant improvement of energy and power has observed in EDLCs [25].

In this study, PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPE was introduced for high-performance supercapacitor applications. Several combinations of PVA-H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>BO<sub>3</sub> were studied and H<sub>3</sub>BO<sub>3</sub> doping ratio was the ¼ th of PVA repeating unit, was found to be optimum composition in the matrix. Electrochemical performances of the PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPEs were examined in a symmetric supercapacitors cell configuration using electrospun carbon nanofibers as the electrodes. Conductivity, galvanostatic charge-discharge, and cyclic voltammetry tests were performed to investigate the electrochemical properties of the PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPEs. The results showed that PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> GPEs are promising electrolyte candidate for next-generation supercapacitor applications.

## Experimental

### Materials

Poly (Vinyl Alcohol) (PVA) (M<sub>w</sub>: 89.000–98.000, 99+ % hydrolyzed) was supplied from Sigma-Aldrich, H<sub>3</sub>BO<sub>3</sub> was purchased from (Alfa Aesar, 99+ %), H<sub>2</sub>SO<sub>4</sub> was provided from Merck (95–97%), Glass Microfiber Filter (GF/D Whatman) was used as the separator and carbon nanofibers were used as electrodes.

### Preparation of GPE

PVA-H<sub>2</sub>SO<sub>4</sub> based polymer electrolyte was produced according to following procedure; Firstly, 1 g of commercial PVA was dissolved in distilled water at 90 °C and stirred until getting transparent solution. This was followed by addition of the diluted H<sub>2</sub>SO<sub>4</sub> (1 g of H<sub>2</sub>SO<sub>4</sub> in a distilled water) to the solution to obtain PVA-H<sub>2</sub>SO<sub>4</sub>.

PVA-H<sub>2</sub>SO<sub>4</sub>-H<sub>3</sub>BO<sub>3</sub> based polymer electrolyte was produced by dissolving H<sub>3</sub>BO<sub>3</sub> in hot distilled water and then inserted into the PVA-H<sub>2</sub>SO<sub>4</sub> solution. The mole fraction was arranged to ¼ of the PVA repeating unit. After the stirring 2 h at RT, gel polymer electrolytes were obtained (Fig. 1). The final electrolytes for ultracapacitor testing included 20% of water in weight. Several blending combinations of PVA/H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>BO<sub>3</sub> were studied to observe the optimized combination in terms conductivity as well as electrolyte stability. As the amount of boric acid increased in the matrix, excess sulfuric acid was excluded due to cross linking, especially at lower solvent content. This resulted in the reduction of proton conductivity. Therefore, the mole fraction of H<sub>3</sub>BO<sub>3</sub> was chosen as ¼ of PVA repeating unit. Within this optimized limits, the polymer electrolytes showed better conductivities as well as stability.

### Preparation of PCNFs

Poly carbon nanofibers (PCNFs) were prepared according to previous literature [25]. In general, PAN and PMMA was

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