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Stretchable and Self-Healable PVA-Nickel-Borax Electrodes for Supercapacitor Applications

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Abstract In this study, a self-healing and stretchable PVA-nickel-borax (PNB) material for supercapacitor applications is presented. The PNB solid-flexible samples were fabricated by chemical composition method and characterised with different techniques to investigate their supercapacitor potential. In order to characterise structural properties of PNB samples, SEM, XRD and Raman techniques were utilised. For the capacitive properties, however, CV analysis was performed. The result of the CV analysis and the calculations showed that a charge and discharge capacitances as high as 88.95 F/g (49.42 Wh/kg energy density and 18.75 kW/kg a power density) and 33.75 F/g (35.58 Wh/kg energy density and 13.50 power density kW/kg), respectively, can be obtained for nickel based PVA-Borax polymers. In addition to their high capacitance, PNB capacitors were also shown to be flexible and self-healable in this study. Therefore, it is believed that this study will be an important reference for future flexible and self-healable supercapacitors.

Keywords Polyvinyl Alcohol; Stretchable; Nickel; Supercapacitor; Selfhealable

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1. Introduction

Stretchable, flexible and self-healable electronic materials have recently received extensive attention due to potential applications in wearable electronics such as electronic skin, flexible electrical display, electronic textiles, biosensor and capacitive touch screen [1-5]. When being stretched, twisted or bent, the electronic devices are damaged and discarded. However, self-healable materials can decrease the breakdown and prevent the propagation of the crack by their self-repairing feature. In this way, the lifetime of the electronic materials may increase [6]. On the other hand, with the development of portable and wearable electronic devices, energy requirements of electronic products should be fulfilled [7]. Therefore, it is important to design the stretchable and self-healable energy storage devices for realizing the above mentioned applications.

Among the energy storage devices, supercapacitors held a great promise in the last decade [8]. Lithium-ion batteries are the most popular energy storage technology in the electronic market owing to their highenergy density [9]. But, they have shortcomings such as, fast degradation, slow life, ageing effect and explosion. When compared to lithium-ion batteries, the supercapacitors have higher power density, high chargedischarge speed, long life and remarkable cycling stability [9,10]. Moreover, the supercapacitors with flexible and stretchable properties have attracted considerable interest in recent years due to the fact that they withstand several mechanical deformations, such as twisting, compressive stress, folding, bending and stretching. In addition, the supercapacitors with self-healable performance are key to prevent the breakage occurring in the wearable electronic device [11].

Polymers have extensively been preferred to fabricate the supercapacitors with self-healable properties [12]. Polyvinyl alcohol (PVA) is one of the most widely used polymers with this purpose because it is biocompatible, chemically stable, water-soluble and high hydrophilic as well as non-toxic [12,13]. Similar to PVA, non-polymer borax is a mineral that is easily soluble in water, harmless to human health and environment,

and is inexpensive [26]. Borax is a widely used material in industry especially for PVA and similar structures to form flexible-solid form [26, 27]. Also the self-healable property of PVA/borax mixture may be important for materials to be used in energy storage systems of the future [27].

In electrochemical supercapacitor applications, the metal-oxide structures such as CuO, NiO, RuO₂, Cu₂O, Fe₂O₄, CoO, MnO have capacitive performances ranging from 100 to 1000 F/g [30-37]. Among these metal-oxides, NiO provides an advantage for electrochemical capacitors by contributing to the capacitance with redox and faradic reactions by different oxidation states [38]. In this study, in order to evaluate this advantage, the electrode materials were created for use in electrochemical capacitors by doping NiO to the PVA/borax structure. The structural and morphological properties were characterized via XRD, SEM, Raman measurements, and the energy storage mechanism was investigated in detail via cyclic voltammetry (CV) measurements of the self-healable and stretchable PNB electrodes.

2. Experimental

As illustrated in Fig. 1, the preparation procedure of Nickel(II) sulphate (NiSO₄) doped PVA-Borax gel consists of three steps; individual solution preparation, mixing all solutions and curing. PVA/NiSO₄/Borax flexible samples were synthesized with 97% pure polyvinyl alcohol (PVA), 98% pure NiSO₄, high purity commercial borax and millipore distilled water as shown in Fig. 1.



Fig. 1 Each of the components is dissolved individually into water, before being mixed together thoroughly, followed by curing.

The borax doping to the $PVA_{(aq)}$ solution generally solidifies the $PVA_{(aq)}$ by bonding the diol-borate in the borax with the PVA chains [27]. On the other hand, when the SO_4^{-2} (from NiSO₄) is doped to the PVA/borax structure, it exhibits a diol-borate-like behavior, causing the PVA/borax solution to solidify even more. For this reason, many experimental studies have been carried out to achieve ideal solidification rates with observations. To obtain homogeneous PVA/NiSO₄/borax samples three solutions were prepared according to the following recipe:

Solution – 1: Dissolving 2 gr of PVA into 10 gr of distilled water at 50 °C.

Solution – 2: Dissolving 0.1 gr of Borax into 5 gr of distilled water at room temperature.

Solution – 3: Dissolving 0.5 gr of $NiSO_4$ into 5 gr of distilled water at room temperature.

All these three solutions were prepared on a magnetic stirrer separately until all the materials dissolved completely in the water. Then the prepared solutions were mixed on a magnetic stirrer at 50 $^{\circ}$ C and the mixture was left at room temperature for 72 hours for a homogeneous gel formation.

In order to structurally characterize the synthesized samples, Raman measurements were performed with the WITech alpha 300R Micro Raman Microscopy system. Raman spectra in this study were acquired by using 532 nm laser excitation.

The energy storage properties of PNB material were investigated with the Gamry brand model 1010-E galvanostat/potentiostat system. The 2-electrode method was applied to measure electrode properties with CV measurements. The CV measurements were carried out at a constant scan speed of 200, 400, 800, 1200 and 1600 mV s⁻¹. The cellulosic paper membrane was used as the separator and 6 mol $KOH_{(aq)}$ was used as electrolyte. The cycle life study capacitance measurements were performed under 400 mV s⁻¹ constant scanning speed in a range of 0-2 V for 400 cycles. Then, the capacitance values of the samples were calculated as in the reference [17].

3. Results and Discussion

3.1. Material Synthesis and Structural Characterization

In the first stage of analyses, the homogeneity and solidification conditions of PNB samples were observed experimentally. In many experiments performed during material synthesis, excessive solidification, excessive gel formation or inhomogeneous structures were observed depending on the amounts of PVA, Borax and NiSO₄. Based on these observations, the synthesis amounts with homogeneous and self-healable properties were determined and shown in Fig. 2.



Fig. 2 (a) Self-healing process of Ni-doped PVA/Borax structure in disjointed state in about 8 minutes, (b) Determination of homogeneous and ideal solidification rates of PNB samples determined by experimental studies, (c) Testing the stretchable properties of PNB materials, which can stretch an average 2 times.

Fig. 2(a) shows the self-healable feature of the PNB samples. The self-healable process starts in the direction of the arrow, also the initial distance between the two samples was ~2 mm. The PNB material could completely repair itself in about 8 minutes by means of the touch made from the bottom part. The 8 minutes refer to the fast-repairing effect of PNB materials against deformation and rupturing of electrode materials, especially in moving energy storage systems. On the other hand, Fig. 2(b) shows the ideal doping rates for self-healable PNB synthesis. Remarkably, the sulphate (SO-4) ions, which can cause a similar effect with borax doped PVA, can produce a favorable effect on the solidification process [14,15]. For the synthesis of self-healable material, it is significant to adjust the amounts of PVA, Borax, NiSO4 correctly. While the amount of PVA decreases, excessive solidification occurs due to the addition of borax and NiSO4, and as a result, H₂O and solid PNB samples are obtained. On the

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other hand, when PVA content is high and borax with $NiSO_4$ are kept at low levels, the material remains in liquid-gel form without adequate solidification. For this reason, self-healable material can be obtained homogeneously by synthesizing at the rates specified in the experimental part. In addition to self-healable features, synthesized samples also exhibit stretchable features as shown in Fig. 2(c). As can be seen in Fig. 2(c), the sample is stretched to a certain distance and when the tensile force is removed, the sample returns to its nearly original shape.



Fig. 3 (a)XRD shows a largely amorphous structure, with a broad peak at ~18deg, with crystallisation peaks that originate from various Ni compounds, which are also observed and confirmed in Raman spectroscopy (b).

Fig. 3(a) shows the XRD analysis of the PNB samples. Amorphous structure XRD pattern is seen in the ranges of $15-25^{\circ}$ and $35-45^{\circ}$ corresponds to PVA/NaOH structure [16]. Other crystallization peaks that are observed outside these angles may belong to NiC_x, Ni₂O₃, NiB, NiS, NiS_{1.03}, Ni(OH)₂ and NiS(OH) structures. From the analyzes, it was determined that SO_4^{-2} ions behave like BO_4^{-2} in the standard PVA-Borax structure, especially with NiSO₄ doping, and do not form an additional impurity phase. The probability of Ni⁺ ions leaving the NiSO₄ structure to bond with C, B, OH or SOH was determined. This was particularly helpful identifying the possible redox reactions. Raman analysis was performed in

order to examine the formed phases in more detail. Fig. 3(b) shows the Raman analysis of the PNB sample. According to literature, it was determined that the peaks corresponded to PVA/Borax, Ni(OH)₂ and NiO structures [17-19]. While the peaks observed in the range of 500-2700 cm⁻¹ consist of NiO and Ni(OH)₂ structures, the peaks between 2912 and 3418 cm⁻¹ may belong to PVA/Borax or PVA/SO₄ structures. Under normal conditions, SO₄ can bind PVA chains by performing a borax-like function [14]. Considering that the peak observed at 3418 cm⁻¹ should be sharper based on our previous studies, it can be argued that the vibration obtained from this peak is caused by SO_4^{-2} [17].

Another important point is the $NiSO_4$ reduction observation in the results obtained XRD and Raman analysis. In the material mixture, especially SO_4 -2 structures, bonding with the PVA chains can cause the NiO and Ni(OH)₂ formations in the structure. This situation shows that the mixture of PVA, NiSO₄, and borax can be called as PVA/Ni/Borax (PNB) structure.



Fig. 4 SEM photos of PNB samples with broad and single-particle structure. (a) 500x magnification with 10 μm scale, (b) 5000x magnification with 1 μm scale.

Fig. 4 shows SEM images of PNB samples. SEM analyzes were performed with dried samples which were dried under room temperature (\sim 298 K) conditions. The drying process was carried out especially considering the possibility of burning that may occur during image

acquisition. As a result of the 500x and 5000x magnification images, it was seen that the PNB samples ordinarily had a broad and single-particle structure. In SEM photos some small particles were also observed. These particles may have emerged from the cutting process during the preparation of the material for SEM.



3.2. Electrochemical Tests

Fig. 5 (a) CV analyzes at different swep rates of PNB samples showing redox activities at different voltage levels, (b) Redox peak shift starting at \sim 1.5 volts and continuing up to \sim 2V depending on the scan rate, (c) Distances of peak values from 0V in order to observe the probability that the peak shifts are due to molecular structure change, (d) dI/dV analysis for more precise determination of redox peak values of PNB samples.

Fig. 5 shows the CV analyzes of the PNB sample. Fig. 5(a) shows CV patterns for a range of scanning speeds and Fig. 5(b) shows the zoomed

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view of Fig. 5(a). From the figures the capacitive plateaus and redox reaction peaks are fairly obvious. Additionally, the redox peak shifts are observed with increasing CV scanning speeds. For instance, a redox peak is observed at ~1.6 V with 200 mV/s scan speed, and it shifts to ~1.7 V with 1600 mV/s scan speed. Given that these peaks may correspond to oxidation or hydroxylation reactions, the observed peak shift indicates intercalation difficulties of O- or OH- ions in the material. [21]. Fig. 5(c) shows whether the increased CV scanning rate causes a possible molecular structure change in the material. Under normal conditions, peak shifts are expected in a CV graph due to the increasing scanning speed, and these shifts occur at certain modest rates. In other words, if a redox peak occurs at 0.2 V and this peak shifts to 0.4 V with increasing scanning speed, it may indicate that some anomalies have developed in the material. In the PNB samples, this situation showed a maximum 0.04 V changes in the range of 200-1600 mV/s. The redox peak, which starts with 0.17 V (200 mV/s) in the positive voltage region, shows a shift of only 0.04 V in the process up to 1600 mV/s, specifying that there is no structural change for the PNB samples. In parallel, no abnormal changes were observed in the other redox peaks of the PNB samples. Fig. 5(d) shows the dI/dV calculation graph to observe the exact voltage values of the redox reactions occurring in the PNB capacitors. In general, the intercalation-deintercalation voltage ranges in the positive voltage region are close to each other, but there are differences between the 2 redox peaks observed especially at the -0.5 V level. This indicated that the PNB could be in anodic structure and more amenable to use in positive zone energy storage systems.

It has been demonstrated by our previous studies on this material that the redox peaks occurring at ± 0.25 V levels originate from the PVA/Borax structure [17]. As a result of literature studies, it was determined that the redox peaks formed over ± 1 V ranges belong to Ni(OH)₂ and NiO structures [22,23]. In particular, the observation of redox peaks originating from the Ni(OH)₂ structure may indicate that Nickel or Nickel-oxide ions are connected to the PVA-Borax chains. In other words,

instead of Nickel ions trapped between PVA/Borax chains, there may be Nickel structures that take on a task within the structure. Notably, the redox peak observed at ~1.3 level was determined to be due to Ni(OH)₂ or NiO, while the second redox peak occurring at ~1.7 V levels was thought to originate from NiO structures.



Fig. 6 Energy storage properties of capacitors builded with PNB electrodes. a) Charge-discharge capacity changes show the capacity loss in the first 50 cycles and the increasing after up to the 100th cycle, b) CV analysis shows redox peak shifts during 400 cycles that indicating easier ionic diffusion, c) Charge cycle-life analyse shows stable cycle performance after 10 cycles and d) Discharge cycle-life analyse shows the increasing discharge capacitance after an average of 5 cycles and stabilization of the capacitance after about 50 cycles.

Fig. 6 shows the symmetric capacitor performances of the PNB samples. In Fig. 6(a), when charge-discharge performances are analyzed, 17.79 F/g charge capacitance and 7.15 F/g discharge capacitance are calculated. The obtained energy differences in the first charge-discharge may support the PNB anodic properties. However, when the chargedischarge cycle-life performances are taken into account, it has been observed that the difference in charge-discharge capacitance values of the material decreases. In order to examine this situation in more detail, CV analyzes were examined for 400 cycles. According to CV analysis, it was determined that there were leftward shifts (to 0 V) in the redox peaks during 400 cycles. This indicates that redox reactions are at lower voltages, and ions can diffuse faster for molecules [21]. Particularly, the rapid diffusion and acceleration of ion intercalation-deintercalation into the structure show the compatible structure of PNB materials with energy storage systems. The fact that ion intercalation and deintercalation are difficult in the first cycle and then become more coherent suggests that this may be due to the increase in bond lengths and larger diffusion volume in the PVA/Borax chain structures. This reveals another beneficial feature brought by the self-healable feature.

Fig. 6(c) and (d) show the capacity performance of 400 cycles. Although the charge capacitance values were stable during 400 cycles, the discharge capacitance showed a stable state after an average of 50 cycles. Moreover, at the end of 50 cycles, the charge and discharge capacitance values were stabilized, but after 150 cycles the discharge capacitance was obtained as ~0.4 F/g, which is more than the charge capacitance. This situation showed that the material passed from the anodic structure to the cathodic state. This can also be seen in Fig. 7 which shows the analyses of dI/dV of the 400 cycles CV results.

An evaluation was also carried out for the analysis results in Fig. 6(c) and (d). This evaluation only shows the capacitance values that can be obtained according to the amount of doped NiSO₄ (right axis). According

to Nickel-based capacitance calculations, 17.79 F/g charge capacitance value is calculated as 88.95 F/g, and 7.15 F/g discharge capacitance value reaches to 33.75 F/g. These different values in the calculations are due to the total electrode weight of the PNB material and the only amount of NiSO₄ as active material weight. While it is observed, that similar calculations are made for the electrode performance of energy storage systems; only the Ni-based capacitance value was desired to be observed [24, 25].



Fig. 7 dI/dV analysis show the double cathodic redox reactions (in between 0.75 and 1.25 V) depending on the number of cycles.

The dI/dV analysis can help to explain why the discharge capacitance of the PNB samples increased and gave more energy after 150 cycles. Especially after the first cycle, only one cathodic reaction (negative current region) occurred in the structure. Then this reaction turned into a double cathodic reaction during the increasing charge-discharge cycles. This has clarified the theory that the formation of double cathodic peaks at ~1.2 V is caused by Ni(OH)₂ and NiO, which we previously revealed in Fig. 5. While it is thought that the expansion of the PVA/Borax chain structure is

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caused by the structural shift of the peak voltages, this situation might affect the Ni(OH)₂ structure of the second peak formation. For these reasons, the source of the second redox peak formation may be Ni(OH)₂. Double cathodic redox reaction, which occurred due to increment of charge-discharge cycles, showed its effect as an increase in discharge capacitance. Moreover, in the 400th cycle, these two redox peaks started to reach almost equal voltage values.

In the scope of the study, the energy (E) and power (P) densities were also calculated depending on charge and discharge capacitance values by (1) and (2) equations [28].



where, C is the capacitance (F), ΔV is the potential window, and t is the time. When the energy and power density amounts are calculated from the capacitance values; according to the PNB-based weighted capacitance results, an energy density of 9.88 Wh/kg and a power density of 7.12 kW/kg are obtained. In case of discharge, 3.97 Wh/kg energy density and 2.86 kW/g power density are provided. On the other hand, these values are according to Ni-based weighted charge capacitance values; It corresponds to an energy density of 49.42 Wh/kg and a power density of 18.75 kW/kg. In case of discharge, an energy density of 35.58 Wh/kg and a power density of 13.50 kW/kg are obtained. These values can be compared with literature studies. It was observed that for honeycomb nanostructure Ni(OH)₂ supercapacitor Dong et al. obtained the energy of approximately ~ 50 Wh/kg [29]. In the study of Huang et al. NiO hollow nanoparticles showed 40.2 Wh/kg energy density value [28]. Compared to these Ni-based studies, it is seen that the energy and power density values obtained for PNB capacitors in this study match the literature. In addition, the self-healable and stretchable properties have been added to Ni-based materials with our study.

When a general evaluation is made in the last part of the study, it has been determined that self-healable PNB materials can store a high amount of energy as a supercapacitor. Also, it can provide noteworthy performance during the long charge-discharge cycles. In addition, the material's ability to exhibit anodic properties and then cathodic properties has increased the importance of the material for energy storage systems. Moreover, the results suggest that an alternative solution should be produced to the question of whether the material can provide higher performance. The SEM results can explain the low capacitance values as the material is generally single grained, resulting in low surface area. In other words, the formation of a porous structure increases the surface area of the PNB materials and contributes positively to the capacitance value. In addition, redox or capacitive currents can be further improved to achieve higher capacitances by means of different electrodes and asymmetric capacitors.

4. Conclusions

In this article, it has been shown that a stretchable supercapacitor that allows self-healing can be made by using the PVA-nickel-borax gel structure. The XRD analysis showed different-type Ni-structure formations in the PVA/borax system. The SEM photos showed that the PNB samples have single particle formation, causing reduced active surface area according to other high performance supercapacitor porous materials. The symmetric capacitor was formed with PNB samples and a two-electrode method was employed to determine the capacitance within the range of 0-2 V. The electrochemical CV measurements at 200, 400, 800, 1200 and 1600 mV/s constant scan rates showed that the faster charge-discharge process can perform with the PNB electrodes in 0-2 V range. The redox reaction was determined by CV measurements, and these reactions were caused via NiO₂ and Ni(OH)₂ molecules. Also, it was determined that the redox peak shifts occurs to lower voltages, during 400 cycles. These shifts

show the faster ionic diffusion properties of PNB samples, and PNB can adapt to ion intercalation-deintercalation with their self-healable structure. The capacitance values were calculated firstly by considering whole electrode material weight and secondly according to Nickel doping percentage. These capacitance values were calculated to be 17.79 F/g charge capacitance and 7.15 F/g discharge capacitance for the whole PNB electrode, and 88.95 F/g charge and 33.75 F/g discharge capacitance for Ni doping percentage. As a result of the analysis, it was revealed that with using this material, 49.42 Wh/kg energy density and 18.75 kW/kg a power density can be obtained for charge and 35.58 Wh/kg energy density and 13.50 power density kW/kg can be obtained for discharge. In this context, it is thought that this study will be a very useful reference from supercapacitors to the production of wearable batteries.

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Author Contribution

The authors confirm contribution to the paper as follows: study conception and design: K. Cicek; data collection: S. Demirel; analysis and interpretation of results: S. Demirel, R. Topkaya, and K. Cicek; draft manuscript preparation: R. Topkaya, K. Cicek. All authors reviewed the results and approved the final version of the manuscript.

Conflict of Interest Disclosure

The authors declare that they have no conflict of interest.

Research Data Policy and Data Availability Statements

The whole research data is available on request.

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a)







Voltage (V)

Cycle Number

