Rechargeable Flexible Paper Battery using PAV, PSSPDEDOT Polymer

Thakir H. Abed¹, Meethaq. M. Abed², Burak Y. Kadem³, Ahmad T. Jaiad⁴
¹Ministry of Education, Directorate of Education-Babylon city, Babil, Iraq
²Polymer engineering, Al-Furat Al-Awsat Technical University, Technical Institute of Kerbala, 56001, Karbala, Iraq
³College of Renewable Energies and Environmental Science, Al-Karkh University for Science, Baghdad, Iraq
⁴Ministry of Electricity, Babil, Iraq

*Email: mee1sa2012@gmail.com

Abstract. The main idea of this research is to design a rechargeable paper battery from local cheap and available materials. The practical part is represented by adding Polyvinyl alcohol (PVA) to conductive polymer (PSS PEDOT) with adding different mineral salts for then study the quantum of electrical conductivity and heat influence on electrical conductivity and acidity factors of the Electrolyte solution. The next step was to produce a rechargeable, flexible battery manufactured from regular cellulose paper, sulfone, and ionic solution. The measurements were made using modern laboratory devices to study the electrical properties, conductivity, resistance (Hall Effect), and voltage quantum of the ionic solution. Through the results we obtained, we noticed an increase in the conductivity of the ionic solution when adding mineral salts. The voltage quantum of one battery ranged between 0.3-0.3 volts, also several batteries were connected in series, and the result was 1.8 volts. Manufactured paper batteries can be recharged with a direct current source and recover their efficiency marked up 98-99%.

Keywords: paper battery, metal salts, polymer PVA, PEDOT: PSS.

1. Introduction
Polymeric materials are considered one of the most used materials at present. Polymeric materials are cheap, easy to manufacture, with specifications that often reach very good. It is known that most of the polymeric materials are insulating materials and that these materials have been used in the electrical and electronic industries for a long time as an auxiliary material, but the good properties of these materials led to their inclusion in the list of candidate materials for study to be used as a basic material in the electrical and electronic industries. These materials have very good electrical insulation specifications, as well as some polymeric materials have good thermal insulation characteristics as well as good mechanical and optical properties and properties. Therefore, the process of changing the electrical properties of the polymeric insulating materials is one of the important matters with good positive returns in the electrical and electronic industries [1]. On the other hand, some metals have been replaced by polymers in many uses because these polymers possess good conductivity properties, including their use in batteries. Like the case that the polymeric materials can change their electrical properties using several techniques, four of which are popular techniques, which are [2].
• Ion implantation technique.
• Creating defects by using the nuclear radiation technique.
• Creating defects by using alloys of different materials technique.
• Creating defects by adding impurity materials technique.

Each technology has advantages and disadvantages that differ from other technologies. The ion implantation technique is one of the limited feasibility techniques due to the inability of this technique to provide defects (charge carriers) with an appropriate density that significantly changes the electrical properties. The technique of changing the electrical properties is by using nuclear radiation, the polymeric materials showed that their effect is limited to changing the behavior of charge carriers with a slight increase in the conductivity value of the polymeric materials (this increase in conductivity is less than the amount required to convert the material from an insulating material to a conductive) [3]. The technique of changing the electrical properties is by using polymeric alloys, this technique often leads to the emergence of new stages in the electrical properties of these phases, which lead to a reduction in the efficiency of the performance of these materials, as well as that the change that occurs in the conductivity of these materials is often within a range Alteration unable to convert material from dielectric to conductive [4]. As for the conversion of the polymeric material by deformation from an insulating material to a conductive material, this method is one of the methods that have great chances of success because The ability of polymeric materials to contain deformation materials (due to the possibility of converting these materials into liquid materials).

The likelihood of impurity binding with polymeric chains is great due to the availability of a large number of binding sites with these gigantic compounds. The availability of many elements that can be homogeneous with polymeric materials in the liquid state. The normal battery mechanisms work.Electricity in general is the process of movement of charges through a conductive path such as metal wire, which is commonly called an electrical circuit. The battery has three main parts. Two electrodes are the cathode (-), the anode (+), and the electrolyte solution. The cathode and the anode are the two terminals in a standard battery that are usually connected in the external electrical circuit. The chemical reaction process present in the electrolyte solution leads to the building of negative charges on the anode (electrons), which produces an electric potential difference between the cathode and the anode (this voltage difference is unstable at the beginning until the process of collecting negative charges at the anode continues) [5]. Where the process of collecting the electrons at the anode in order to get rid of the potential difference generated by them. This process is done as follows, the electrons perform a repulsive process with each other to salvage to a place where the electrons are less abundant, which is the cathode, but the electrolyte solution prevents this from happening directly from the anode to the cathode. When the circuit is closed, the electrons can move to the cathode. This process is usually limited in batteries due to the electrochemical reaction present that will change the chemistry of the anode and cathode and thus stop supplying the electrons over time. Therefore, rechargeable batteries are represented by reversing this process by connecting the battery with an external source such as a solar cell [6].

2. Experimental Part

2.1 Samples Preparation

In this research, various mineral salts were used i.e, lithium chloride (LiCl2), copper chloride (CuCl2), nickel chloride (NiCl2), zinc chloride (ZnCl2), cadmium chloride (CdCl2), and tin chloride (SnCl2), separately, 1 mg of these salts dissolved in Methanol, the solution was placed in the vibrator using ultrasound waves (Ultrasonic bath) for about half an hour to obtain a homogeneous solution and good solubility. On the other hand, polyethylene dioxythiophene polystyrene sulfonate (PEDOT: PSS) was used, which is one of the most popular conductive polymers that are available either. In the form of dry pills or the form of a liquid dissolved in water. Ratios of salts solutions mixed with 1 milligram of (PEDOT: PSS) then the mixture was placed in the vibrator using ultrasound for about half an hour to ensure complete homogeneity between the two materials. Then 5 mg of polyvinyl alcohol was
dissolved in distilled water, after that the mixture placed again in a vibrator using ultrasound. The work was done according to certain percentages of mixing the solutions to obtain a homogeneous ionic solution in proportions as follows (5%, 10%, 15%, 20%, and 25%), the ratio of (PEDOT: PSS) solution with salts to the ratio of polyvinyl alcohol solution. To ensure the stability of the solutions for a sufficient period, the solutions were stored in suitable small containers tightly sealed, where the solutions recorded fairly good stability after being shaken with ultrasound for 20 minutes to ensure the homogeneity of the final solution. The stability of the solutions was laboratory after keeping the samples for 4 consecutive days, and the stability of the solutions was very good.

![The solutions used after shaking with ultrasound](image)

The electrolyte solution was prepared in the form of a compound of (PEDOT: PSS) with PVA with the used salts, a normal cellulose paper is coated with this prepared material in various proportions to obtain a semi-dry and flexible electrolyte solution with the flexibility of the paper. Various samples were prepared to be suitable for the type of measurements made during this research as figure. 1.

### Results and Discussion

3.1. **The effect of temperature on the conductivity and the (PH)**: factor of the prepared liquids, the electrical conductivity of the prepared liquids was calculated using (DDS307W-micro processer conductivity meter of British origin), the acidity (PH) ratio of the prepared liquids was calculated using a (PH meter) from the British fisher scientific company with the change of temperature. This device contains two electrodes, one to measure the temperature of the liquid and the second to measure the percentage of acidity in the liquid. The conductive polymer used in this research was vaccinated with several different salts separately. The effect of mineral salts on the conductivity of the ionic solution at various temperatures was studied, as in Figure 2.

![The effect of temperature on the electrical conductivity of ionic polymeric solutions using various salts](image)
It can be recognized from the figure that the electrical conductivity using tin chloride recorded the highest readings with the conductivity of (22mS), followed by lithium chloride with the conductivity of (9mS) compared to the electrical conductivity of the polymeric solution without salts with the conductivity of (1 mS). This increase was also evident with the increase in temperatures. The figure shows the gradual increase in the electrical conductivity of the electrolytic polymeric solutions with increasing temperature. Where we deduce from this relationship the possibility of using these solutions in regions with high temperatures such as Iraq and the Arab Gulf states. The effect of the acidity and base ratio of these solutions was also studied with the change of temperature, as it was found that when the temperature increased, the PH factor decreased and the electrical conductivity of the ionic liquid increased because the increase in the concentration of salts inside the solution would increase the number of reduced electrons and break the bonds between the molecules of the substance, and increase the temperature working On the increase in the movement of free charges inside the liquid. Figure .3 shows the effect of temperature on the PH factor of solutions. Where acids are defined as chemical substances that contain an empty electron field capable of acquiring a pair of electrons, while bases are considered to have electronic orbits in which the electrons are free [7]. It is noticeable that all prepared electrolytic solutions are within the acid range, where their value is less than 7, and these values are preferred in preparing batteries in general, as in Figure (2)

Figure .3: The effect of temperature on the PH factor of ionic polymeric solutions using various salts

4. Hall Measurements
Some electrical properties of the prepared membrane were calculated on a standard sheet of liquids prepared using a Hall effect measurement device from Ecopia. Where the paper used was in the form of a square with dimensions (1.5 x 1.5) cm to be suitable for measurement within the special base of the device shown in Figure (5). The sample contains four electrodes prepared from the silver paste. The electrical properties of the compositions prepared using a Hall phenomenon were calculated. Table (1) shows the values of the electrical conductivity, resistivity, and surface resistance of the models, while Table (2) shows the values of the Hall coefficient, Bulk concentration of the carriers, and the concentration of the carriers on the sheet concentration, a small paper was coated by placing some drops of the solution on it and letting the paper dry to form a membrane, then making measurements of Hall for the membrane.
Table .1: some electrical properties extracted using Hall’s phenomenon

|          | Sheet Resistivity (Ohm/seq) | Resistivity (Ohm.cm) | Conductivity(1/Ohm.cm) |
|----------|-----------------------------|----------------------|------------------------|
| Pure     | 5.33E+08                    | 1.60E+05             | 6.25E-06               |
| CuCl2    | 3.40E+09                    | 7.20E+05             | 1.39E-06               |
| ZnCl2    | 7.30E+09                    | 2.19E+06             | 4.57E-06               |
| SnCl2    | 6.91E+09                    | 2.07E+06             | 4.82E-06               |
| NiCl2    | 6.91E+09                    | 2.08E+06             | 4.81E-06               |
| LiCl     | 2.63E+08                    | 7.90E+04             | 1.27E-05               |
| CdCl2    | 6.50E+09                    | 1.95E+06             | 5.13E-06               |

Table .2: Concentration of carriers on the sheet, inside the material and the Hall parameter for the studied materials

| Bulk concentration (cm3) x10^{11} | sheet concentration (cm2) x10^{6} | Hall coefficient (cm3/C) |
|-----------------------------------|-----------------------------------|--------------------------|
| Pure                              | -135                              | -4060                    | -4.62E+05                |
| CuCl2                             | -0.278                            | -8.35                    | -2.44E+08                |
| ZnCl2                             | -0.277                            | -8.32                    | -2.52E+08                |
| SnCl2                             | -0.132                            | -3.97                    | -4.72E+08                |
| NiCl2                             | -3.71                             | -111                     | -1.69E+07                |
| LiCl                              | 5.38                              | 161                      | 1.16E+07                 |
| CdCl2                             | -0.278                            | -8.35                    | -2.25E+08                |

The results of Hall phenomenon measurements show the extent to which the composites are affected by the quality of salts added to polymers, as we note the value of the electrical conductivity of the polymer solution without salts (pure), the lowest values of which were recorded compared to polymeric solutions with salts.

The highest value of electrical conductivity recorded was -11.27x10^{-5}\Omega^{-1}\cdot cm^{-1} when adding lithium chloride (LiCl) to the polymeric solution compared to the polymeric solution without salts (pure) 6.25x10^{-4}\Omega^{-1}\cdot cm^{-1}. A remarkable decrease was also observed in the values of resistivity and surface resistance of the membranes coated on the paper for the same solution, as shown in Table (1). On the other hand, there was a noticeable change in the quality of the majority charge present in the membranes coated on paper, and this difference came according to the different types of salts used. Where we notice that some values contain the negative sign present in the values of the carrier concentration, whether surface or total or Hall coefficient, while there are positive values for others. When a voltage is applied to a semiconductor, the charge carriers try to travel in one straight direction, but the collision with the particles of the material continues, and thus it continuously deviates from its path, but if the applied voltage is high, it will force it to walk in a straight path. When a magnetic field is shed in another direction, the electrons will be forced to change course. Consequently, the electric field will force the electrons to gather to the bottom of the material and the gaps to collect at the top of the material, and the voltage difference between the two ends of the material will generate a voltage known as the Hall voltage. From Table (2) it can be seen that the majority of charge carriers are gaps in nickel chloride and lithium chloride, while the rest of the salts have negative values, which means that electrons are the majority charge carriers. For example, lithium chloride has an ionic bond between the metal (lithium) and the non-metal (chlorine) and when they separate, the positively
charged lithium-ion is formed, which is responsible for transporting charges in the compound, and since the electron affinity of the element of lithium is very small, the possibility of its separation from the chloride is easy Compared to the rest of the salts, in which the electron affinity is higher than the lithium salt-forming minerals.

5. Optical Microscope

The pre-prepared liquids were poured into a plastic container (Petre dish) and the drying process was carried out for 48 hours at room temperature to obtain a thick membrane suitable for the process of measuring surface properties and knowing the homogeneity of the composite materials used. Images were taken of the prepared samples surface using an optical microscope (Hot selling 8LED 1000xUSB digital microscope) from KALINU TECHNOLOGY CO., LTD, China, which works through a computer program to capture images with a magnification of up to 1000 times. The surface of the dry ion solution membrane was scanned using a light microscope as shown in Figure 4. The observed change between the electrolytic polymeric solutions can be seen using various salts. Membrane images give a clear reflection of the nature of the films and the homogeneity between the membrane-forming materials of conductive and insulating polymers and salts. Homogeneity is important in various applications, including the application of the battery, as this homogeneity in the surface indicates a good mixture of materials and thus no unwanted agglomerations. Also, this homogeneity facilitates the process of moving the charge easily between components in a better way than if it were in the form of clusters.

![Membrane images](image)

Figure 4: Optical microscopy images of membranes prepared from polymeric solutions

6. Battery Measurements

The voltages generated for the prepared samples calculated using a time-dependent system, which records the voltages that vary with time, as the model is linked to the Avometer device from (Uni-T), which is linked through a special program with the computer.

6.1. Electrolytic solution measurements (voltage with time)

measuring the voltage change with time for electrolytic solutions prepared using a graphite electrode with a titanium electrode at room temperature and as shown in Figure 4.
Figure 5: Voltage change with time of the electrolyte solution

Figure 5 shows that the values of the generated voltages change with the change of the added salts. The highest values of voltages were recorded when using tin chloride salts, about 0.5 volts, but this value began to gradually decrease until it reached the stability limit of about 0.4 volts. These values are consistent with the results of the electrical conductivity of SnCl2 solution, which recorded the lowest PH values and the highest conductivity values. Whereas, the use of lithium chloride recorded relatively stable voltages at 0.32 volts. As for the voltages of the rest of the salts used, they ranged at values less than 0.2 volts.

6.2. Paper Battery Measurements (Voltage with Time)
A battery was manufactured using the electrolyte solution, as was previously explained, and this battery was foldable without any effect on the recorded voltage values. Figure 6 shows the shape of the paper battery before and after folding it.

Figure 6: The paper battery before and after folding
Figure. 7: The change in voltage over time of the paper battery

At the beginning of the battery manufacture, its voltage was unstable due to the chemical reaction taking place between its components, then after about half an hour, its voltage began to stabilize. After that, a measurement of the voltage change over time at room temperature was performed. The results showed a clear change in the values of the voltages generated using different solutions with relatively regular voltages with time, more regular than the voltages generated by the electrolyte solution, and more stable and preserving their charge, as shown in Figure. 7. The highest recorded voltages were approximately 0.37 volts for the electrolyte solution, using lithium, tin, and zinc chlorides separately. After that, the battery was left without charging, and the process of losing its charge was monitored over time for a continuous week, and the results were as shown in table (3).

| Time | Pure | CuCl₂ | NiCl₂ | CdCl₂ | ZnCl₂ | LiCl | SnCl₂ |
|------|------|-------|-------|-------|-------|------|-------|
| 1day | 0.231| 0.256 | 0.337 | 0.271 | 0.371 | 0.371| 0.373 |
| 2day | 0.221| 0.231 | 0.273 | 0.251 | 0.343 | 0.363| 0.361 |
| 3day | 0.214| 0.221 | 0.247 | 0.232 | 0.312 | 0.333| 0.345 |
| 4day | 0.201| 0.210 | 0.212 | 0.205 | 0.287 | 0.297| 0.303 |
| 5day | 0.184| 0.185 | 0.186 | 0.176 | 0.265 | 0.281| 0.292 |
| 6day | 0.157| 0.157 | 0.167 | 0.142 | 0.236 | 0.264| 0.267 |
| 7day | 0.104| 0.132 | 0.143 | 0.110 | 0.212 | 0.249| 0.246 |

The results showed that the battery loses a small portion of its charge during one day due to the continuation of the chemical reaction between the components of the battery, in addition to the temperature factor of the surrounding battery, the loss of a characteristic inherent in any type of
battery where it loses part of its charge during time. Charging under normal conditions, it was recharged to a DC source with a voltage of 9 volts, and the test results showed that the battery was received from the source and the charger can be recharged with an increase in its voltage, as shown in Table .4.

Table .4: illustrates the process of recharging the battery.

| Pure    | CuCl₂ | NiCl₂ | CdCl₂ | ZnCl₂ | LiCl  | SnCl₂ |
|---------|-------|-------|-------|-------|-------|-------|
| Before charging | 0.104 | 0.132 | 0.143 | 0.110 | 0.212 | 0.249 | 0.246 |
| After charging  | 0.226 | 0.242 | 0.315 | 0.264 | 0.353 | 0.362 | 0.361 |

6.3. Connect a group of cells to increase the voltage:
A number of cells were connected in series as in Figure. 8 and the resulting voltages were calculated, where the voltages were the product of the collection of cell voltages in the case of series connection. It was also noticed that the effect of polarity in these cells on linking the series was clear. Figure 8.a shows linking four types of thin paper cells with each other in succession, where the output voltage is 1.819 volts. While Figure 8.b shows the same cells when combined and isolated with a sheet of paper between every two cells to avoid leakage between cells as the product of these cells was approximately the same voltage of 1.503 volts. Figure 7.c shows the mechanism of increasing a second cell to connect the series (five cells in a series) and how the voltage increases with the increase in the number of cells, but to avoid the final cell becoming somewhat thick, using a small number of cells is preferred in this case.

Figure 8: four cells linked in series, b) four cells linked and linked in a row, and c) five cells linked in a series

6.4 Ion dry solution
A quantity of liquid polymeric ionic solution was placed in a clean glass container and left to dry relatively, not completely, so we obtained a dry ionic solution (in the form of a membrane). A battery was made using this membrane, this solution helped the battery to give it an adequate amount of moisture and flexibility because it is a polymeric material and it helped the battery maintain some moisture that helps to maintain the battery’s work and maintain its charge. Table (5) shows the results of the voltages generated from these cells manufactured using the polymeric solution as an electrolytic gelatinous solution before and after shipment after one week. As the results showed that the voltage values increase significantly after charging, as it is known that when charging a battery, the electrode connected to the negative pole of the charger will show a negative charge as a result of the
accumulation of electrons on it. Between them, due to the repulsion of these electrons with the accumulated electrons on the electrode.

Table .5: shows the voltage results for paper batteries using gelatinous solution before and after charging the battery

|                | Pure  | CuCl₂ | NiCl₂ | CdCl₂ | ZnCl₂ | LiCl  | SnCl₂ |
|----------------|-------|-------|-------|-------|-------|-------|-------|
| Before charging| 0.29  | 0.3   | 0.37  | 0.3   | 0.5   | 0.37  | 0.37  |
| After charging | 0.4   | 0.41  | 0.44  | 0.31  | 0.55  | 0.58  | 0.65  |

7. Conclusions
The possibility of obtaining a flexible rechargeable battery and its production from available, low-cost, and non-toxic materials, it can be used in portable electrical devices, especially mobile phone chargers, laptops, as well as operating remote tracking devices. That's where conventional batteries were often used. Polyvinyl alcohol (PVA) and (PEDOT: PSS) are non-toxic materials and do not affect the health of users. The use of polymeric compounds as an electrolyte solution enriched with salts gave good results in generating voltages suitable for daily use. Therefore, it is possible to develop this experiment by using other polymeric materials and to study the extent to which the paper battery performance improves.

References
[1] Nicholson, J., 2017. The chemistry of polymers. Royal Society of Chemistry.
[2] Nuri Al-Jamal, Solid State Physics, 2000 edition.
[3] N.S. Hudak, Chloroaluminate-Doped Conducting Polymers as Positive Electrodes in Rechargeable Aluminium Batteries, J. Phys. Chem. C. 118 (2013) 5203-5215. Q.F. Li, N.J. Bjerrum, Aluminium as anode for energy storage and conversion: A review, J. Power sources. 110 (2002) 7-8.
[4] Utracki, L.A. and Weiss, R.A. eds., 1989. Multiphase polymers: blends and ionomers. American Chemical Society.
[5] Sharrow, J.F., Solomon, K.W., Peterkin, F.E., Bernardes, J.S. and Hankla, B.J., US Secretary of Navy, 2006. Battery mechanism. U.S. Patent 7,108,940.
[6] Goodenough, J.B. and Park, K.S., 2013. The Li-ion rechargeable battery: a perspective. Journal of the American Chemical Society, 135(4), pp.1167-1176.
[7] Lewis, Gilbert (1923). Valence and the Structure of Atoms and Molecules.