

Development of Sodium Ion Conducting Polymer Electrolyte for Solid State Battery Application

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Abstract

A new sodium ion conducting polymer electrolyte based on polyethylene oxide (PEO) with polyvinyl pyrrolidone (PVP) systems were prepared by solution cast technique. Experimental measurements such as electrical conductivity in the temperature range 313 to 375K and transport number were used to characterize these electrolytes. The electrolyte which contains 9 wt % of NaClO_2 has the highest conductivity about $2.09 \times 10^{-3} \text{ S/cm}$. The ionic transference number (t_{ion}) for the PEO-PVP polymer electrolyte synthesized with different concentration of NaClO_2 was determined by Wagner's dc polarization technique. The transference number for the polymer electrolytes prepared with 5, 6, 7, 8 and 9 wt % of NaClO_2 were 0.940, 0.990, 0.824, 0.987 and 0.961 respectively. The conductivity Vs temperature plot shows the linear variation. The highest conductivity was found to be at 9 wt % of NaClO_2 electrolyte.

Using those electrolyte; electrochemical cells have been fabricated with the configuration Na / Electrolyte / C; Na / Electrolyte / Na + C and Na / Electrolyte / Na + C + Electrolyte powder and their discharge characteristics were studied. The values of open circuit voltage for different cells were found to be 0.230, 1.9 and 2.5V respectively. The values of short circuit current for different cells were found to be 210, 1800 and 1500 μA respectively. The other cell parameters were also measured for all the system at room temperature such as current density, energy density etc. by using load of $1\text{k}\Omega$.

Keywords

Polymer electrolyte, Solid state battery, characteristics.

I. INTRODUCTION

The solid state cells are very much popular because of their diversified applications in various fields, e.g. batteries, fuel cells, electrochemical devices etc.[1-3]. The polymer electrolyte (Solution) serve as

electronic insulator between the anode and cathode but it must be a good ionic conductor. Polyethylene oxide (PEO) is used as the polymer matrix because it is chemically inert, able to dissolve in number of inorganic salts and it provides moderate ionic conductivity [4-5].

A solid state cell is used for measuring the activity of a component of a mixture using solid ionic conductor, which is in contact on one side with a reference phase and on the other side with a phase sensitive to the gas component to be determined. A solid state cell in which a mixture of both compounds which continuously changes in its composition vertically to the interface, is formed as a transition zone at least between said solid ionic conductor and said gas sensitive phase. There are two main types of batteries 1) Primary batteries, 2) Secondary batteries

Primary batteries are ready to produce current as soon as they are assembled. They transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means. Disposable batteries are called as primary cells and they are used once and discarded.

Secondary batteries can be recharged, that is, they can have their chemical reactions reversed by supplying electrical energy to the cell, restoring their original composition.

These batteries must be charged before use; they are usually assembled with active materials in the discharged state. Rechargeable batteries or secondary cells can be recharged by applying electrical current, which reverses the chemical reactions that occur during its use.

A wide range of electrically conducting polymer electrolyte systems is now available. The conductivity of polymer electrolyte is at least 100 or 1000 times less than in liquid or the better ceramic electrolytes at a given room temperature. Though it is necessary that the highest conductivity is preferable

but conductivity of polymer electrolyte has been shown to be sufficient for applications in thin film electrochemical cells. In recent development polymer electrolyte batteries are used in portable entertainment, computing and telecommunication equipment.

Many sodium ion conducting polymer electrolytes based on polyethylene oxide (PEO) complex with NaClO_3 , AgNO_3 and NaYF_4 etc. have been reported [6-11]. Some polyvinyl pyrrolidone (PVP) complexes with NaClO_3 salt have been prepared as polymer electrolyte [12-14]. Also some sodium ion conductivity polymer electrolytes based on polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP) complex with NaClO_3 salt have been reported [15].

Keeping this view, in the present paper, authors reported a new sodium ion conducting polymer electrolyte based on PEO/PVP-sodium salt NaClO_2 for the solid state cell. We have prepared three cells having different anode and cathode materials.

II. PREPARATION OF POLYMER ELECTROLYTE

Polymers polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP) were taken separately at different weight % ratio with NaClO_2 salt as PEO: PVP: NaClO_2 . The wt% of PEO is changed as 1 to 5 at the cost of NaClO_2 keeping PVP constant at 90 wt%. Each mixture was dissolved in methanol for making polymer-salt solution. To obtain the perfect solution of this mixture, the solution was stirred well for 24 hours and then poured on the polypropylene dishes. The solution was slowly evaporated at room temperature. Thus, thin film of polymer electrolyte was prepared by solution cast technique. Further these films were crushed into powder form. This powder was pressed on the Hydraulic press having pressure 6 ton/cm^2 at room temperature in circular shapes.

Thickness of all the samples was measured by using Digimatic Micrometer (Mitutoyo Make, Japan) with least count $1 \mu\text{m}$. Thicknesses of pellets vary in the range of 0.651 to 1.164 mm.

A) Transference Number Measurement

The transference number gives quantitative information of the extent of ionic and electronic contribution to the total conductivity. The ionic/electronic transference number (t_{ion}/t_e) was measured using dc polarization technique suggest by Wagner and Wagner [7]. A conducting polymer electrolyte is sandwiched between blocking and non-blocking electrodes. A constant dc potential (0.5V) is applied across sample. The current in the

circuit is measured as a function of time. A typical 'current versus time' plot is obtained from which the electronic and ionic contribution is determined.

B) DC Conductivity

The dc conductivity of the samples is measured by two-probe method, in which resistance of the sample was measured at different temperature. Sample under test was sandwiched between two electrodes of the sample holder. A constant dc voltage was applied to the sample and corresponding current was noted. Knowing the dimensions of the electrodes and sample thickness the conductivity is calculated using the formula $\sigma = t/RA$.

Where, A is the cross-sectional area, R is the resistance of the sample, t is the thickness and σ is the conductivity of the sample. The measurement of conductivity was done in the temperature range 313 to 375 K. The silver electrodes were used to paint on the either side of the sample before measurement. The temperature of the furnace was measured by digital thermometer.

C) Fabrication of Polymer Electrolyte Cell

By using the solution cast technique we obtained thin films having different ratios of PEO, PVP and NaClO_2 . These films are dried so that we get fine powder for preparation of sample in the form of circular pellets.

The optimization of conductivity with NaClO_2 concentration is done at temperature (323K). The sample which has the highest conductivity is used as a polymer electrolyte for cell fabrication. Using this polymer electrolyte, we fabricated three cells having configurations Na / Electrolyte / C; Na / Electrolyte / Na + C and Na / Electrolyte / Na + C + Electrolyte powder. The discharge characteristics of cell under constant load $1 \text{ k}\Omega$ are studied. Copper plates were used as a current collector on both sides of the cell. The composite cathode material was prepared in the ratios 1, 1:1 and 1:1:1 for the cell as graphite, graphite + sodium and graphite + sodium + electrolyte powder. The cell parameters such as open circuit voltage, short circuit current, current density, power density, discharge time, discharge capacity etc. are measured at room temperature (303K).

III. RESULTS AND DISCUSSION

$$t_{\text{ion}} = \sigma_{\text{ion}}/\sigma_T = I_{\text{ion}}/I_T$$

$$t_e = \sigma_e/\sigma_T = I_e/I_T$$

Where, $\sigma_{\text{ion}}/\sigma_e$ and I_{ion}/I_e are the conductivity and current contribution due to ions/ electrons respectively.

The current versus time plot of the PEO-PVP- NaClO_2 polymer electrolytes with different NaClO_2 wt% are shown in fig. 1.

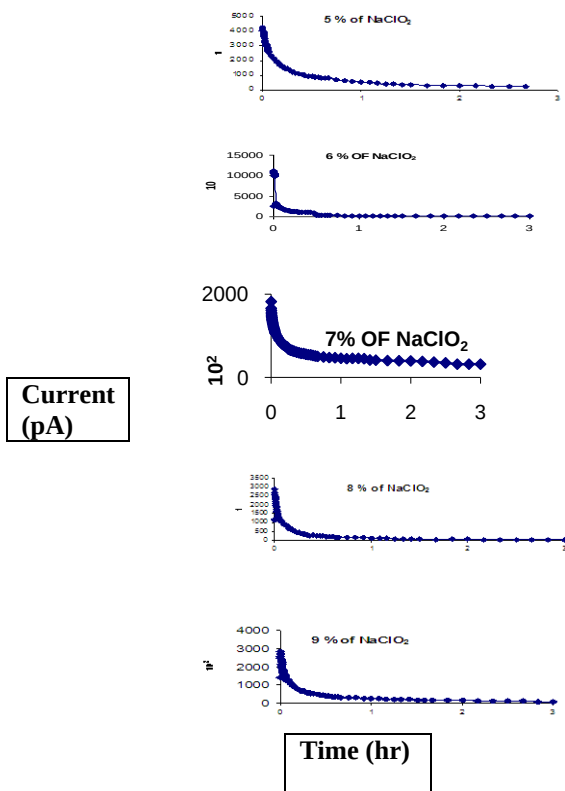


Fig.1 Current vs Time plots for Different NaClO_2 Concentration

The high current is observed at initial time period and it starts decreasing with time and then the total current becomes nearly constant at some non zero value. All the samples show the same trend. The final residual current is mainly due to electrons/ holes. The ionic transference number is calculated separately from the polarization current versus time plots. The calculated ionic transference numbers for different NaClO_2 wt % are found to be nearly unity, suggests the ionic transport mechanism.

The variation of transference number with concentration of NaClO_2 is shown in fig. 2.

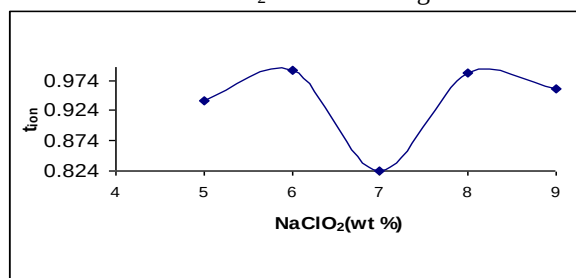


Fig.2: Variation of ionic transference number with NaClO_2 wt%.

From fig.2, it appears that with increase in concentration of NaClO_2 transference number increases then it decreases and again increases and then again it will decrease. The ionic transference number is found to be higher for 6 wt% NaClO_2 sample and smaller for 7 wt. % sample.

DC conductivity of the samples of different NaClO_2 wt% was measured in the temperature range 313 to 375K by measuring the resistance of the samples. It is observed that the value of resistance depends on temperature.

The variation of dc conductivity with concentration of NaClO_2 (wt %) for polymer electrolyte at 323K is shown in fig. 3.

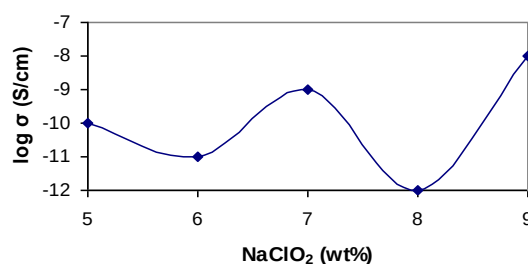


Fig.3: Variation of conductivity with NaClO_2 wt% at 323 K.

From fig.3, it is seen that as concentration of NaClO_2 increases, conductivity decreases then it increases and again decreases and when the concentration of NaClO_2 is 9 wt% the conductivity increases rapidly and reaches to 2.09×10^{-8} S/cm.

The temperature dependence of conductivity for different NaClO_2 wt % is shown in fig. 4. The conductivity increases with increase in temperature linearly. As temperature increases, mobility of the ions increases, which results the rise in conductivity. From the plots, the activation energies for conduction were calculated.

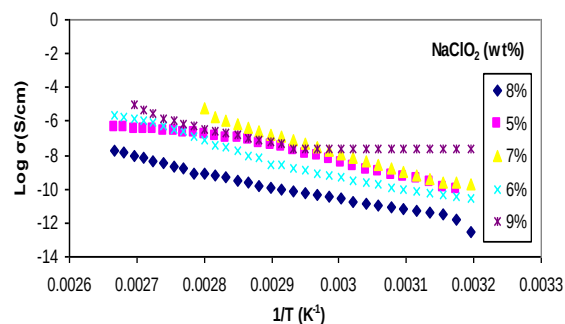


Fig.4: Temperature dependence of conductivity for different NaClO_2 wt %.

The behavior of $\log \sigma$ Vs $1/T$ suggests the polaron ionic hopping conduction; which may be due to Na^+ ions only. The PEO can acts like base material but the conductivity is entirely due to sodium ions.

Variation of activation energy with NaClO_2 wt% is shown in fig. 5.

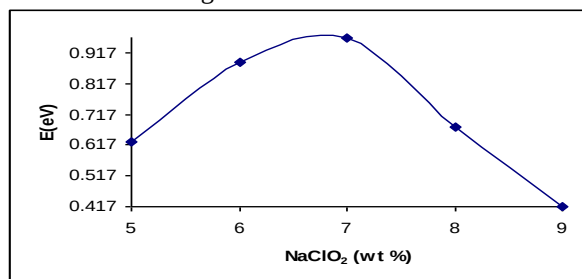


Fig.5: Variation of activation energy versus NaClO_2 wt%.

It is observed that value of activation energy increases with NaClO_2 wt % and again decreases for higher concentration of NaClO_2 . The activation energy is maximum for 7 wt % of NaClO_2 electrolyte.

IV. SOLID STATE CELL (BATTERIES)

From fig. 3, it is observed that the sample which contains 9 wt % of NaClO_2 has the highest conductivity. So, this sample is used as a (polymer) electrolyte for the preparation of cells with configuration Na / Electrolyte/ C, Na / Electrolyte / Na + C, Na / Electrolyte / Na + C + Electrolyte powder.

The calculated values of cell parameters are presented in table 1.

Table 1: Values of cell parameters for different cell configuration.

Cell parameter at 30°C for load of 1kΩ	Cell configuration		
	1 Na/Electrolyte/C	2 Na/Electrolyte/Na+C	3 Na/Electrolyte/Na+C+Electrolyte powder
Area of the cell (cm^2)	0.8007	0.8007	0.8007
OCV (V)	0.230	1.9	2.5
SCC (μA)	210	1800	1500
Current Density ($\mu\text{A}/\text{cm}^2$)	262	2248	1873
Discharge time (h)	780	311	123
Discharge capacity ($\mu\text{A}/\text{h}$)	0.26	5.787	12.195
Powder density (w/kg)	0.268	22.352	29.069
Energy density (wh/kg)	209	6951	3575

The discharge characteristics of cells are studied under constant load of 1kΩ. The discharge curve for all three cell configuration is presented in fig. 6, 7 and 8 for Na / Electrolyte / C; Na / Electrolyte / Na + C and Na / Electrolyte / Na + C + Electrolyte powder respectively.

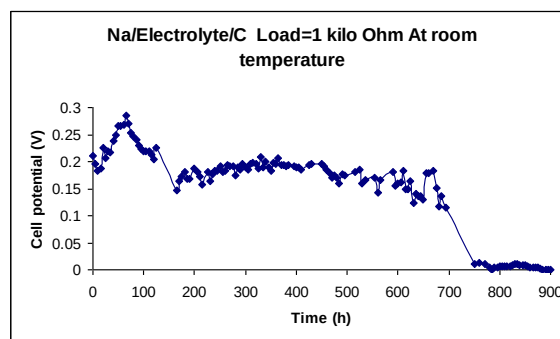


Fig.6: Discharge characteristic curve for cell configuration Na/Electrolyte/C.

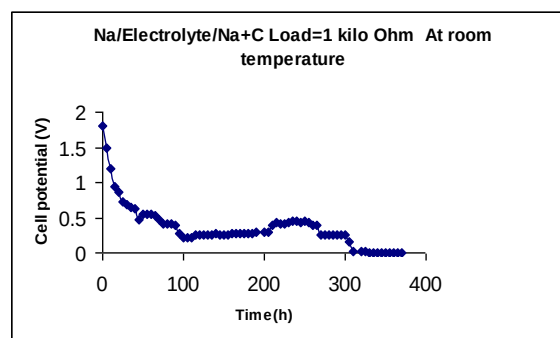


Fig.7: Discharge characteristic curve for cell configuration Na/Electrolyte/ Na + C.

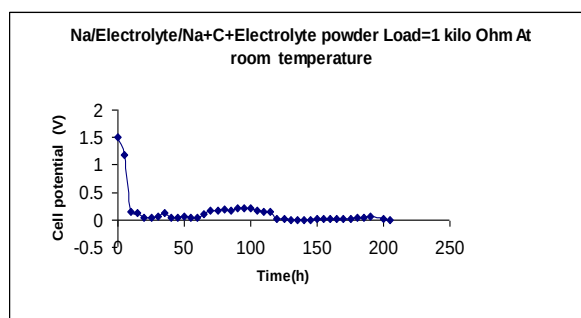


Fig. 8: Discharge characteristic curve for cell configuration Na /Electrolyte/ Na + C +Electrolyte powder.

From fig. 6, it is observed that initially, cell potential is lower, it decreases and then increases up to 0.3V and then decreases up to 0.117 V and then remain constant for longer duration. After 780 hrs, it

becomes zero that is cell discharges completely. Whereas, for cell configurations Na / electrolyte / Na + C and Na / electrolyte / Na + C electrolyte powder; the cell potential is found to be higher than earlier configuration. It is about 1.5 to 2 V. It decreases with time and remains constant.

For second cell configuration, Na / Electrolyte / Na + C (1:1) open circuit voltage is found to be 1.9V with a short circuit current 1.8 mA. This voltage decreases up to 0.3V for 1k Ω load in a 100 hrs and then remains constant for sufficient longer duration.

Similarly for third cell in which the counter electrode is Na + C + Electrolyte powder (1:1:1) the open circuit voltage is found to be 2.5V, with short circuit current 1.5mA and discharges with shorter time.

It is observed that the OCV increases with the addition of graphite (C) and Electrolyte powder but the discharge time becomes lesser and lesser.

The cell fabricated with configuration of Na / PEO:PVP:NaClO₃ / C + I₂ + Electrolyte have open circuit voltage (OCV) and short circuit current (SCC) in the range of 2.96 to 2.54V and 168 to 432 μ A respectively^[15].

In the present cell, the values of OCV and SCC are found to be in the range of 0.230 to 2.5V and 210 to 1500 μ A respectively. Though the value of OCV is smaller than that cell but value of SCC is larger. Also, it is found that discharge time for that cell is smaller than our prepared cell.

V. CONCLUSION

A sodium ion conducting polymer electrolyte based on PEO with PVP was prepared by solution cast technique. Polymers PEO and PVP were taken separately at three different ratios with NaClO₂ salt.

Transference number for different NaClO₂ wt % and PEO-PVP polymer electrolyte was found to be greater than 0.5, which suggest the presence of ionic conduction.

Temperature dependence of dc electrical conductivity showed the linear variation with temperature. The conductivity is found to be of the order of 6.39 x 10⁻¹² to 2.09 x 10⁻⁸ S/cm at room temperature and it increases with increase in temperature. The log σ Vs 1/T curve follows Arrhenius behavior. The activation energy is calculated from log σ Vs 1/T plot and is found to be of the order of 0.4 to 0.9 eV. The electrical conductivity and activation energy are found to be NaClO₂ composition dependent. The conductivity is found to be highest for 9 wt% NaClO₂ composition. The same sample (i.e. 9wt %) NaClO₂: PEO: PVP was used as electrolyte for three different cell configurations.

Amongst these three cells, the cell having counter electrode material as (Na + C + Electrolyte powder) generating higher potential than others. Also the short circuit current is found to be more for this cell. The other cell parameters such as current density, discharge time, discharge capacity, power density and energy density are found to be reasonable.

An endeavour is made to lit the LED on the fabricated cell. It was observed that for sufficient duration the LED was enlightened.

It is concluded that the cell configuration in which counter electrode is (Na + C + Electrolyte powder) has better performance. Hence, it can be used for small power consumption devices like wrist watches or electronic clocks or devices where CMOS ICS are used.

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