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ELECTROCHEMICAL STUDIES ON PLASTICIZED PROTON CONDUCTING POLYMER ELECTROLYTE BASED ON POLY (VINYL PYROLIDONE)-AMMONIUM SULFAMATE

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ABSTRACT

Unplasticized polymer electrolytes comprising poly (vinyl pyrolidone) (PVP)-ammonium sulfamate (AS) (99:01, 97:03, 95:05, 93:07, 91:09, 88:12, 85:15 and 80:20) were prepared by solution casting method. The ionic conductivity of PVP-AS polymer electrolytes was studied over the temperature range of 303K-343K and the frequency range of 42Hz-1MHz by means of ac impedance spectroscopy. Higher ionic conductivity of 2.18 x 10^{-8}S/cm at 303K was observed for 85 mol% PVP-15 mol% AS. This electrolyte was plasticized with PEG and DMF with different concentration. The ionic conductivity was enhanced by three orders of magnitude for 10 mol % of PEG_{400} (1.64 x 10^{-5}S/cm) and 51% of DMF (8.2 x 10^{-5}S/cm) plasticized polymer electrolytes. PVP-AS-PEG based plasticized polymer electrolyte was not a free standing film and it was not suitable for primary proton battery application. DMF plasticized polymer electrolyte was used to fabricate the proton battery and discharge characteristics has also been studied.

Key words: PVP, Ammonium sulfamate, Proton battery, Polymer electrolytes.

INTRODUCTION

Plasticized proton conducting polymer electrolytes are studied widely because of their important applications in electrochemical device fabrication particularly in primary proton batteries[1,2]. Solid polymer electrolytes (SPE) are prepared by dissolving suitable ion donating salts/acids into high molecular weight polymers, which act as host. Some of the host polymers are poly (ethylene oxide) (PEO), poly (vinyl) alcohol (PVA), poly (vinyl) pyrrolidone (PVP) etc and many host polymers are partially crystalline in nature, which is an

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unfavorable property for achieving high ionic conductivity. Among these host polymers PVP is amorphous, biocompatible, water soluble and the presence of rigid pyrrolidone group in PVP, which is capable of forming complex with many organic/ inorganic substances[3,4]. The pyrrolidone group is a strong electron withdrawing group that makes PVP different from other polymer electrolytes[5]. For primary proton battery fabrication, there are lacks of good proton conductive polymer electrolytes working at ambient temperatures and hence search for the new systems based on ammonium ion as conducting species have been hotly perused in the past few years. The influence of ammonium sulfamate on the conductivity of polymer complexes as a proton conducting polymer electrolyte is not yet studied in the literature**.** Plasticization is one of the most adopted approaches used to suppress the crystallinity of polymer electrolytes. Low molecular weight polymers or organic solvents are normally used as plasticizer. For example, low molecular weight polyethylene glycol (PEG_{200}, PEG_{400}, PEG_{600}), dimethylforamide (DMF), ethylene carbonate (EC), propylene carbonate (PC) etc are reported as good plasticizers.In the present work, $PEG_{400\ \mathrm{and}}$ DMF are used as plasticizing agent. Plasticized electrolytes are characterized by ac impedance spectroscopy studies to optimize its suitability in proton batteries.

EXPERIMENTAL

Thin films of unplasticized polymer electrolytes comprising of PVP-K_{90} (SDFCL-99%) (111.1417 g/mol) and ammonium sulfamate ($NH_2SO_3NH_4$) (114.12 g/mol) have been prepared with different molar ratios (99:01) (97:03) (95:05) (93:07) (91:09) (88:12) (85:15) and (80:20) by solution casting technique using distilled water as solvent. The plasticized polymer electrolytes are prepared by using the unplasticized polymer electrolyte sample, which shows high conductivity have been plasticized with PEG ($_{400}$) (Merck) and DMF (Merck) with different molar ratio of ((85:15):10), ((85:15):19), ((85:15):31) ((85:15):41) and ((85:15):51) and ((85:15):10), ((85:15):20) ((85:15):30) ((85:15):40) ((85:15):51), respectively by same solution casting technique using distilled water as solvent. AC impedance spectroscopic studies of the polymer electrolytes have been carried out in the temperature range of 303K-343K over the frequency range of 42 Hz-MHz using a computer controlled HIOKI 3532 LCR meter. The construction of battery and electrolyte preparation are discussed elsewhere[1-6]. The proton battery is discharged using biologic electrochemical work station by Galvanostatic mode at constant current of 10 μA and 50 μA.

RESULTS AND DISCUSSION

Concentration dependence of conductivity

The ionic conductivity of the polymer electrolyte depends on the number of charge (n), charge of the mobile carrier (q) and mobility of the carrier (μ) as described by the relation, σ = nqμ. The ionic conductivity as a function of salt (AS) concentration of unplasticized polymer electrolytes (PVP-AS) is shown in Fig. 1a.

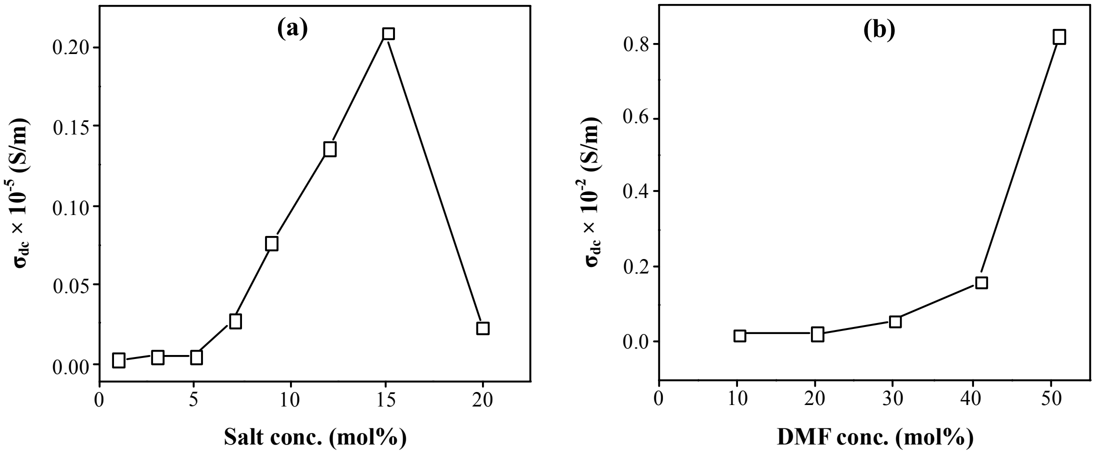

Fig. 1a & b: Variation of dc conductivity as a function of salt concentration (AS) and DMF concentration at 303 K

It shows that the ionic conductivity of PVP-AS polymer electrolytes follows increasing trend up to 15 mol% AS and beyond, which it decreases. The increase in ionic conductivity with increasing salt concentration may be due to the increase in the number of free ions in the polymer electrolytes. The decrease in the ionic conductivity at higher salt concentration can be due to the formation of aggregates in the polymer electrolytes. The ionic conductivity of polymer electrolytes is extracted from the conductance spectra (not shown). The maximum conductivity is found to be 2.08516 × 10^{-6} S/m corresponding to 15 mol% of AS concentration. The unplasticized polymer electrolyte is added with different concentration of PEG_{400} and DMF. The maximum ionic conductivity of PEG_{400} based plasticized polymer electrolyte is reached to 1.64 × 10^{-3} S/m for 10 mol% PEG. No free standing with poor mechanical stability films are seen even for PEG plasticized polymer electrolyte. So, it is not suitable for further studies. The increase of ionic conductivity is found upto 51 mol% DMF (Fig. 1b) in polymer electrolyte and the conductivity of plasticized polymer electrolyte is found as 8.2 × 10^{-3} S/m. The increase of dc conductivity with increase of plasticizer concentration is due to the plasticizing effect that leads to increase of flexibility of the polymer matrix and raises the ionic mobility in the polymer matrix.

Characterization of primary proton battery

The primary proton battery is constructed by using PVP-AS-DMF polymer electrolyte.

The cell is obtained from the configuration of (Zn + $ZnSO_4.7H_2O$ + C + PVdF)/PVP-AS-DMF/(MnO_2 + C + PVdF).

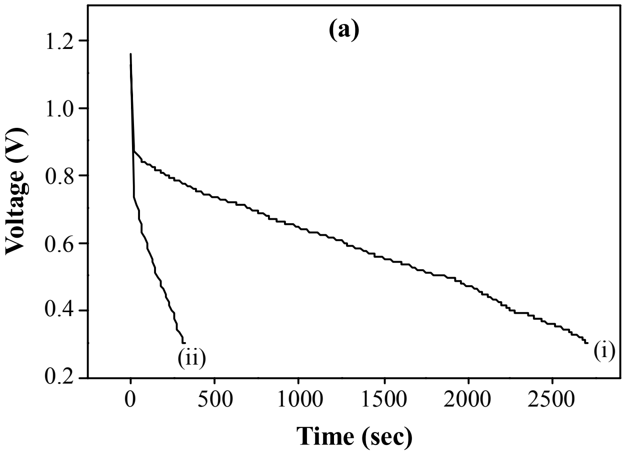

Fig. 2(a): Discharge characteristics curve for PVP-AS-DMF at (i) 10 µA and (ii) 50 µA at room temperature

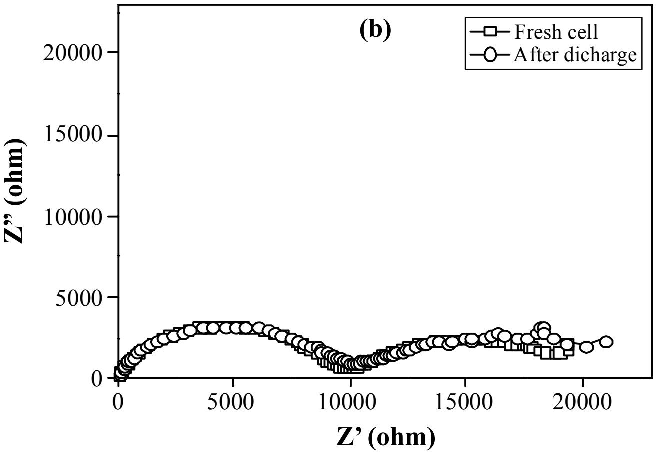

Fig. 2(b): Impedance plot for fresh and after discharge at 10 µA

The OCV of this cell is 1.18 V. The cell is discharged through constant current of 10 µA and 50 µA at room temperature. Fig. 2a shows the cell potential variation as a function of time for 10 µA and 50 µA current. It is found that during discharge, the load voltage of the cell initially decreases sharply and then decreases gradually. The sharp decrease in the cell voltage may be due to the activation polarization[7]. When discharge with low current (10 µA), the time of stable performance of cell is longer than compared with discharge with high current (50 μA) for a cut of potential of 0.3 V. The above statement implies that the cell performance fairly well when discharged through a low current than high current. Electrochemical impedance plot for before and after discharge of the cell at 10 μA at room temperature is shown in Fig. 2b. The cole-cole plot shows that the electrochemical impedance of before and after discharge is nearly same and two semicircles are observed for both cases.

CONCLUSION

The conductivity is maximum for the plasticized polymer electrolyte. Conductivity is calculated of the order of 10^{-3} S/m. DMF plasticized electrolyte shows more stable nature than PEG plasticized electrolyte. The open circuit voltage of 1.18 V and the discharge profile at two different constant current of the cell using PVP-AS-DMF as solid electrolyte are noted. The cell impedance of fresh and after discharge is also measured.

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