



Effect of dimethyl carbonate (DMC) on the electrochemical and cycling properties of solid polymer electrolytes (PVP-MSA) and its application for proton batteries

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ABSTRACT

Proton-conducting polymer electrolyte systems (PVP-MSA), with polyvinylpyrrolidone as a host polymer and methanesulfonic acid as a proton donor, were prepared by a facile solution-cast technique. The effects of plasticizer, dimethyl carbonate, on the electrical and electrochemical properties of PVP-MSA complexes were plausibly investigated for the first time. The complexation behaviors of both plasticized and unplasticized polymer electrolyte systems were confirmed with the aid of Fourier transform infrared spectroscopy. The conductivity values were found to be enhanced due to the addition of DMC, and a maximum value of 3.27×10^{-5} S/cm was achieved. The ionic transport number values were found to be in the range of 0.96–0.99. The discharge analysis suggested that the proton battery constructed with the plasticized polymer electrolyte showed better performance compared to that constructed with the unplasticized polymer electrolyte, which in turn means it could be utilized as a promising candidate for primary proton batteries.

1. Introduction

In the past few decades, solid polymer electrolytes (SPEs) have played a crucial role in the development of modern electrochemical energy storage and conversion devices, such as batteries [1–3], fuel cells [4–6], dye-sensitized solar cells [7,8], supercapacitors [9,10], and sensors [11], because of their high mechanical stability and superior ionic conductivity [12,13]. In particular, proton-conducting SPEs have received attention in recent years because of their feasibility in low-energy-density devices [14]. SPEs have many advantages over liquid and gel electrolytes; for example, they are leakage free, easy to prepare, solvent free, and lightweight, and they corrode less [15,16]. However, the ionic conductivity of SPEs is only low as compared to that of liquid and gel electrolytes [17,18]. In order to enhance the ionic conductivity and maintain the other interior properties of SPEs, various approaches have been attempted, such as the blending of polymers, dispersion of inert fillers, and addition of plasticizers into the polymer host matrix [19,20]. Among these, plasticization is one of the most viable approaches to improve the ionic conductivity of SPEs [21,22]. The addition of a significant amount of plasticizer, such as ethylene carbonate

[23], propylene carbonate [24], polyethylene glycol [25], or dimethyl carbonate (DMC) [26,27], into the polymer matrix effectively improves the ionic conductivity by reducing the glass transition temperature of the polymer and enhancing the salt dissolution and ion migration. Moreover, the choice of the plasticizer depends on its molecular weight and dielectric constant [27].

In the past, various polymer hosts were employed for the preparation of SPEs, including polyvinyl alcohol (PVA) [28], poly acrylonitrile (PAN) [29], polyethylene oxide (PEO) [30], polyvinyl acetate (PVAc) [31], polymethyl methacrylate (PMMA) [32], and chitosan [33]. Recently, the synthetic polymer of polyvinylpyrrolidone (PVP) has been employed as a polymer host owing to its excellent physicochemical properties (e.g., eco-friendly nature, biodegradability, ease of preparation, and high mechanical, chemical, and thermal stability). The carbonyl group (C=O) and pyridine ring in PVP are readily available to form complexes with proton donors (inorganic salts/acids) [34]. Due to its excellent physicochemical properties, PVP based polymer electrolytes are studied extensively in the recent years [35,36]. For instance, Basha et al. have investigated the spectroscopic and electrochemical properties of PVP based electrolytes for magnesium battery applications

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[35]. PVP blended with polymer hosts such as PVDF and polysulfone based electrolytes have been utilized as a potential separator for high temperature proton exchange membrane fuel cells and vanadium redox flow batteries and reported elsewhere [37–39]. On the other hand, different kinds of ammonium salts, such as NH_4NO_3 [26], $\text{CH}_3\text{COONH}_4$ [40], NH_4SCN [41], and NH_4Br [42], are considered very good proton donors to the polymer matrix. Some inorganic acids, such as phosphoric acid (H_3PO_4) [43] and sulfuric acid (H_2SO_4) [44], were also employed as proton donors. Methanesulfonic acid (MSA), described as green acid [45], is an emerging ionic salt that possesses outstanding properties, such as high conductivity, high solubility, low corrosiveness, and low relative toxicity.

Herein, we report the effect of a plasticizer DMC on the physico-chemical and electrical properties of a PVP-MSA-based polymer electrolyte system for proton batteries. To the best of our knowledge, there are currently no systematic studies for proton batteries based on a PVP-MSA-DMC SPE system and we assure that the prepared electrolytes are better than other PVP based proton conducting electrolytes in terms of mechanical, conducting and electrochemical properties [38,46,47]. In addition, the systematic investigation is performed with an unplasticized (PVP-MSA) and plasticized (PVP-MSA-DMC) SPE system. The electrochemical properties of our prepared SPEs are characterized by electrochemical impedance spectra (EIS), linear sweep voltammetry (LSV), chronoamperometry, and dielectric analyses. In order to demonstrate the capability of our plasticized and unplasticized SPE system in a battery, it is employed in the fabrication of a $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O}/\text{SPEs}/\text{MnO}_2$ proton battery module, and the results are discussed in detail.

2. Experimental

2.1. Preparation of SPEs

The proton-conducting SPE systems were prepared by a facile solution-cast technique, as reported earlier [33,48]. The precursor materials of PVP_{K90} (M_w - 360,000), MSA (M_w - 96.11), DMC (M_w - 90.08), and dimethylformamide (DMF, M_w - 73.09) were used for the preparation process. In brief, the prepared SPE systems were grouped by system 1, which represented the unplasticized SPEs, and system 2, which represented the plasticized SPEs. The prepared SPE of system 1 and system 2 with the various compositions of PVP, MSA, and DMC are tabulated in Table 1. System 1 (unplasticized SPE) was prepared by dissolving a stoichiometric amount of PVP and MSA in DMF at 70 °C and then subjecting it to continuous stirring for 12 h. Thereafter, the obtained homogeneous solution was transferred into polypropylene petri dishes and vacuum dried at 70 °C for 12 h. In order to avoid moisture effects, the dried SPE films were stored in a desiccator. For system 2, the different mole percentage of DMC, as mentioned in Table 1, was added along with the PVP-MSA polymer complex, and then the above process was followed for the preparation of plasticized

Table 1
Various compositions of SPE system 1 and system 2.

System 1		System 2	
Sample code	Composition (mol%)	Sample code	Composition (mol%)
S1	95.75 PVP: 4.25 MSA	SP1	90.91 PVP: 4.22 MSA: 4.87 DMC
S2	91.56 PVP: 8.44 MSA	SP2	86.78 PVP: 8.38 MSA: 4.84 DMC
S3	83.23 PVP: 16.77 MSA	SP3	78.63 PVP: 16.58 MSA: 4.79 DMC
S4	79.18 PVP: 20.82 MSA	SP4	74.62 PVP: 20.62 MSA: 4.76 DMC
S5	75.19 PVP: 24.81 MSA	SP5	70.65 PVP: 24.61 MSA: 4.74 DMC

SPEs.

2.2. Fabrication of proton battery

Zinc metal powder, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, and activated carbon (AC) were taken in the weight ratio of 50:40:10. The powder sample was mixed together and ground well. The obtained product was made as a pellet with 12-mm-diameter to use as an anode. The cathode pellet was prepared with a mixture of manganese dioxide (MnO_2) and AC by the weight ratio of 80:20. All solid-state proton batteries were prepared using a pellet model with high conducting unplasticized and plasticized SPEs as a separator by the following cell structure:

Cell 1: $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{AC} \parallel \text{S4} \parallel \text{MnO}_2 + \text{AC}$

Cell 2: $\text{Zn} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{AC} \parallel \text{SP4} \parallel \text{MnO}_2 + \text{AC}$

2.3. Material characterization

Fourier transform infrared (FT-IR) spectroscopy measurement for the prepared SPEs was carried out using a JASCO – 4100 FT-IR spectrometer at room temperature with the wavenumber range of 550–4000 cm^{-1} . The signal resolution was 2 cm^{-1} . The conductivity analysis was recorded by using two probe methods with the aid of two stainless steel blocking electrodes (area – 1.4 cm^2). The ionic conductivity of the samples was determined by an IM6 Zahner-elektrik workstation in the frequency range between 100 MHz and 1 MHz. The ionic transport number, LSV, electrochemical impedance analysis, and battery discharge characteristics were studied using a Bio-Logic (model SP-300) electrochemical analyzer. For the ionic transport number measurement, a piece of SPE was sandwiched between two stainless steel strips. The variation of current with respect to time was monitored at a constant dc supply of 1 V. The LSV of the SPEs was recorded by sandwiching the polymer electrolyte between two stainless steel blocking electrodes at a scan rate of 5 mV s^{-1} .

3. Results and discussion

The proton-conducting SPE (PVP-MSA) systems were prepared without (S1, S2, S3, S4, and S5) and with (SP1, SP2, SP3, SP4, and SP5) a plasticizer (DMC), and their detailed composition percentages are tabulated in Table 1. The schematic representation of the plasticized SPE system interaction (PVP-MSA-DMC) is presented in Fig. 1.

3.1. Electrical properties

AC impedance spectroscopic analysis was carried out to study the conduction mechanism of the unplasticized and plasticized SPE systems. The Cole-Cole impedance spectra of system 1 and system 2 samples are shown in Fig. 2(a) and (b), respectively, at 303 K. The observed impedance plot shows two regions: a low-frequency spike region and a high-frequency semicircle region. The semicircle region is attributed to the grain boundary impedance in the charge transfer process, whereas the low-frequency inclined spike is related to the diffusion process [49,50]. The intercept of the semicircle or spike with the x-axis provides the bulk resistance (R_b) of the SPEs. The conductivity (σ) of the polymer electrolyte is determined using Eq. (1).

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where t and A are the thickness and area of the polymer electrolyte. Compared to the unplasticized SPE system, the plasticized SPE system has low bulk resistance, which in turn increases the conductivity of the system, as shown in Fig. 2. The addition of the plasticizer (DMC) into the polymer salt complexes (PVP-MSA) drastically enhances the protonic conductivity, which is explicitly indicated in Fig. 2. Among the prepared plasticized electrolytes, sample SP4 provides a highest ionic

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