



Borotungstic acid – Polyacrylamide solid electrolytes for electrochemical capacitors with H₃PO₄ plasticizer

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ARTICLE INFO

Keywords:

Borotungstic acid
Polyacrylamide
Solid polymer electrolytes
Electrochemical capacitors
Phosphoric acid
Crystallization

ABSTRACT

Proton-conducting polymer electrolytes consisting of borotungstic acid (BWA) and polyacrylamide (PAM) were developed. The addition of BWA to PAM progressively improved the electrolyte conductivity. The as-fabricated BWA-PAM electrolyte exhibited a high ionic conductivity of *ca.* 27 mS cm⁻¹, but suffered from low shelf life due to poor water retention. With the modification of 10 wt% phosphoric acid (H₃PO₄), a longer shelf life and improved ionic conductivity of *ca.* 30 mS cm⁻¹ were achieved. A ternary electrolyte composition of 75BWA-PAM + 10% H₃PO₄ was identified to have a high conductivity and good shelf life. At BWA content greater than 75 wt%, the addition of H₃PO₄ led to an undesirable phase separation within the electrolyte. The ternary 75BWA-PAM + 10% H₃PO₄ electrolyte was used to assemble solid cells with CNT-graphite electrodes. The cells exhibited 11.2 mF cm⁻² at 50 mV s⁻¹ and high rate performance at 1 V s⁻¹. The cells also retained ≥90% of their initial capacitance and maintained *ca.* -85° phase angle after 10,000 charging-discharging cycles at 6 A g⁻¹.

1. Introduction

The development of polymer electrolytes has enabled development of solid-state, lightweight, and flexible energy storage devices such as electrochemical capacitors (ECs) [1–5]. These electrolytes have the advantage of a solid form factor that can prevent electrolyte leakage [6,7]. Proton-conducting polymer electrolytes are particularly promising because of their high ionic conductivity and compatibility with many pseudocapacitive materials [8,9]. The high ionic conductivity and environmental stability of proton-conducting solid electrolytes rely heavily on their water retention capability. Most of these electrolytes are polymer gel electrolytes with liquid acids (such as H₂SO₄ or H₃PO₄) blended into polymer hosts (such as polyethylene oxide, polyvinyl alcohol, or polyacrylamide) [9,10].

A very promising polymer host for solid polymer electrolyte applications is polyacrylamide (PAM). PAM has an amorphous structure and possesses higher water retention capability compared to other polymers. This feature enables its deployment in fuel cell electrolytes, absorbents for waste treatment, and moisture storage for soils [11–13]. However, most of the reported work utilizing PAM as an electrolyte requires the addition of either H₂SO₄ or H₃PO₄ to achieve desired levels of conductivity [14–18]. Wiczonek et al. demonstrated that PAM gel electrolytes with 40 vol% water doped with H₃PO₄ and H₂SO₄ exhibit room temperature conductivity of *ca.* 20 mS cm⁻¹ [18]. Rodriguez

et al. reported that adding 75 wt% H₃PO₄ into PAM solid electrolyte can achieve a room temperature conductivity of *ca.* 2.5 mS cm⁻¹ [16]. These proton-conducting PAM solid electrolytes have not yet been optimized as solid polymer electrolytes for high-rate ECs.

Solid proton-conducting electrolytes with heteropolyacids (HPAs) have been demonstrated to achieve high ionic conductivity because of their high proton concentration in both the liquid and solid state [19,20]. The most promising solid proton conductors are Keggin-type HPAs [21–24]. These hydrous acids are metal-oxide clusters of early transition metals formulated as H_z[XM₁₂O₄₀], where z is the charge of the anion, X is the heteroatom, and M is the addenda atom [25,26]. They exhibit high proton conductivity at room temperature compared to many inorganic acids due to the large number of crystallized water molecules in the HPA crystal hydrate which leads to a “quasi-liquid” state [9].

Borotungstic acid (BWA, H₅BW₁₂O₄₀) was demonstrated to exhibit a high conductivity among all Keggin-type HPAs [27]. BWA in a cross-linked PVA polymer electrolyte has been demonstrated to have ultra-high rate capability and a wide cell voltage window of 1.3 V with a high ionic conductivity of 13 mS cm⁻¹ under ambient conditions [28]. Despite the promising electrochemical performance, the cross-linked PVA electrolyte with BWA still suffered from dehydration [28]. Thus, it is necessary to leverage a highly hygroscopic polymer such as PAM combined with a suitable HPA to further improve these solid polymer

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electrolytes. HPAs have been previously studied in various polymer electrolytes such as polyvinyl alcohol (PVA), polyvinylidene fluoride (PVDF), Nafion®, and polyethylene oxide (PEO) [28–33] as summarized in Table 1. Nonetheless, a detailed study of HPAs in PAM for proton-conducting electrolytes and their application in EC devices has not been done to date [9].

The objective of this work is to investigate and optimize a BWA-PAM solid electrolyte system. The performance of binary BWA-PAM was first characterized in terms of the material compatibility and electrochemical performance. To enhance the electrolyte performance, phosphoric acid (H_3PO_4) acting as a plasticizer was added into the BWA-PAM electrolyte to form a ternary system to increase the ion hydration and proton conductivity [35]. In this paper, the interaction of the phosphoric acid plasticizer with the BWA-PAM electrolyte system will be reported and the performance of the ternary electrolyte in a solid EC device will be presented.

2. Experimental

2.1. Preparation of heteropolyacids

$H_5BW_{12}O_{40} \cdot xH_2O$ (BWA) was synthesized according to a modified Copaux's method [28]. In this method, $Na_2WO_4 \cdot 2H_2O$ (5 g) and H_3BO_3 (4 g) were mixed in hot water (25 mL) maintained at 60 °C. The solution was adjusted to a pH of 5.5 using 6 N HCl while continuously stirred and maintained at 60 °C for 2 h. The pH was then further lowered to 3.8 using 6 N HCl and the solution was further heated at 80 °C for 6 h. The solution was allowed to cool and set at ambient conditions overnight. Solid precipitates were filtered out with Whatman 2.5 μm filter paper and the filtrate solution was extracted with diethyl ether. The extracted solution was washed with DI H_2O and dried, yielding ca. 2 g of a white crystalline product [27,28].

2.2. Preparation of polymer electrolytes

The BWA-PAM electrolyte was prepared by mixing a 3 wt% PAM solution (Scientific Polymer, MW: 5–6,000,000 $g \cdot mol^{-1}$) with BWA powder to form precursor solutions at various BWA compositions (refer to Table 2). Maximum BWA content was limited to 85 wt% due to electrolyte degradation beyond this concentration (see Supplementary Information Fig. S1). The BWA-PAM mixtures formed homogenous precursor solutions which dried into a translucent film when cast under ambient conditions. The BWA-PAM + H_3PO_4 electrolytes were prepared by adding phosphoric acid (H_3PO_4 , Sigma Aldrich) to the aforementioned BWA-PAM electrolyte precursor solutions with the weight ratio controlled at ca. 10 wt% (refer to Table 3). All electrolyte films were measured with a Mitutoyo Model 293-831 digital micrometer and had an average thickness of ca. 0.15 mm.

2.3. Construction of solid cells

The metallic test cells were constructed with titanium foil (McMaster Carr, 0.05 mm thick) as the electrodes for the electrochemical characterization of the electrolyte, while CNT-graphite electrodes coated on a titanium foil current collector were used for the solid electric double layer capacitor (EDLC) devices [36]. The CNT-graphite electrodes was used to compare with those in previous reported HPA-based solid polymer electrolytes [26,27]. The preparation of the CNT-graphite electrodes was described in a previous report [27]. These electrodes had ca. 1.5–2 $mg \cdot cm^{-2}$ carbon loading (60 wt% CNT and 20 wt% graphite) with 20 wt% cross-linked PVA binder. The geometric area of the electrode was 1 cm^2 . The solid cells were assembled by casting the precursor solution onto each electrode followed by sandwiching the electrolyte together and protecting it with a polyester tape (ABI Tape, series 9180, 0.1 mm thick). The thickness of the test cell was measured with a Mitutoyo Model 293-831 digital micrometer. The

Table 1
Summary of HPA-based solid polymer electrolytes reported in the literature.

Polymer Electrolyte	HPA wt% in the composite ^a	Proton Conductivity ($mS \cdot cm^{-1}$)	Electrolyte production method	Cell design	Testing/storage environment	Reference
PWA-PVA	90 wt%	9	Solution casting on electrodes	Sandwiched with hot pressing	Room temperature	[30]
SIWA-PVA	90 wt%	11	Solution casting on electrodes	Sandwiched with hot pressing	Room temperature	[34]
SIWA-PWA-PVA	45 wt% PWA; 45 wt% SIWA	13	Solution casting on electrodes	Sandwiched with hot pressing	Room temperature	[30]
BWA-XLPVA	90 wt%	13	Solution casting on electrodes	Sandwiched with hot pressing	Room temperature	[28]
PWA-PVDF	20 wt%	23	Free-standing film	Sandwiched	Room temperature	[32]
PWA-Nafion® 117	–	16	Free-standing film	Sandwiched	Soaked in 1 M H_2SO_4 at 100 °C	[31]
SIWA-Nafion® 117	–	95	Free-standing film	Sandwiched	Soaked in 1 M H_2SO_4 at 100 °C	[31]
SIWA-PEO	3 wt%	0.531	Solution casting on electrodes	Sandwiched with hot pressing	Room temperature	[33]

^a Calculated based on dried HPA/polymer film.

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