



# Effect of poly (vinylidene fluoride)/poly (vinyl acetate) blend composition as cathode binder on electrochemical performances of aqueous Li-ion battery



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## ABSTRACT

In this study, the effect of poly (vinylidene fluoride)/poly (vinyl acetate) (PVDF/PVAc) ratio in the cathode binder of the  $\text{LiMn}_2\text{O}_4$  (LMO) electrode on the electrochemical performance of a rechargeable hybrid aqueous battery (ReHAB) is investigated. The miscibility of two polymers is confirmed by Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC) measurements. The binary blends with different PVDF/PVAc ratios (100/0, 75/25, 50/50, 25/75 and 0/100) are used as binder for the LMO cathode preparation. It is found that incorporation of PVAc in the blend decreases the crystallinity of PVDF and increases the cathode hydrophilicity, leading to better wetting by the aqueous electrolyte. The morphology and electrochemical properties of the cathode are also studied. Electrochemical cyclic voltammogram, discharge capacity, capacity retention, electrochemical impedance and rate capability are investigated. It is concluded that the blend with a PVDF/PVAc ratio of 25/75 has the best cycle performance (80% capacity retention after 100 cycles at the rate of 1 °C), with 0.2 °C discharge capacity (110 mAh  $\text{gr}^{-1}$ ) and the best rate capability.

## 1. Introduction

Lithium-ion batteries (LiBs) are a family of rechargeable batteries that are being used for portable computers, mobiles hybrid electronic vehicles and smart grids [1–7]. Although, the wide electrochemical stability window of organic electrolytes allows LiBs to operate at high voltage, these electrolytes however, are highly flammable and therefore, safer alternatives are needed if LiBs are to be used on large commercial scales. Accordingly, several researchers have studied the aqueous-based electrolytes for LiBs, and investigated the stability of the electrode materials in the aqueous solution electrolyte [3–7].

Rechargeable hybrid aqueous electrolyte battery (ReHAB) is a type of aqueous LiBs that has been introduced first by Yan et al. in 2012 [7]. In this battery, spinel-structured lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$  abbreviated as LMO) and zinc metal (Zn) are used as cathode and anode electrodes, respectively, in aqueous electrolyte containing two electrochemically active ions ( $\text{Li}^+$  and  $\text{Zn}^{2+}$ ). As reported, ReHAB could operate at electrochemical window of about 2 V and show good cycling performance and high energy density [7].

In the cathode composition of all LiBs including ReHAB, a conductive additive like carbon black (CB) and a polymeric binder are also

used for electrical conductivity and component cohesion, respectively [8]. Although, the polymeric binder is used in few weight percent in a composite electrode, it plays a critical role in mechanical property and electrochemical performance of LiB [9,10]. The binder provides integrity within the LiB cathode components (LMO and CB) and promotes their adhesion to the current collector [11].

Poly(vinylidene fluoride) (PVDF) is the most widely used binder in commercial LiB as it exhibits excellent electrochemical stability [2]. In spite of strong binding strength of PVDF, this polymer suffers from low flexibility that results the cycle life deterioration of the battery due to breaking of the bond between active material particles [1,12,13]. In addition, PVDF can be easily swollen, and dissolved (or gelled) in liquid electrolyte leading to bursting of electrode components that results in capacity fading [2]. As an electrode binder in aqueous LiBs and especially in ReHAB, PVDF cannot play therefore, appropriate binding function, as it is a hydrophobic polymer that does not get soak by aqueous electrolyte easily. Thus, application of a hydrophilic polymer that improves the wetness of electrode while keeping the advantages of PVDF is vital in order to obtain a competitive performance for ReHAB as compared with conventional LiBs. Poly(vinyl acetate) (PVAc) is a partially hydrophilic polymer that is commercially used as adhesive and

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binder [14]. This polymer is expected to have a better wetness in comparison with PVDF, while still sufficient resistance against dissolution in aqueous electrolytes.

PVAc has already been employed in LiB as electrode binder by previous authors [15–17]. Prosinini et al. used this polymer as binder in LiB and found a good electrochemical performance as compared with the cathode using PVDF binder [18,19]. The cathode with PVAc as binder shows however, lower capacity and lower rate capability than cathode with PVDF. Fortunately, PVDF and PVAc are thermodynamically compatible [20] and it seems therefore, that the blend of PVDF/PVAc with an optimum composition can satisfy various necessary aspects of a polymeric binder in aqueous LiBs including ReHAB. To the best knowledge of the authors of this article, there is no report available suggesting the utilization of PVDF/PVAc blend as binder in these batteries.

In this work, the effects of PVDF and PVAc binders and the blends of these two polymers with three different compositions were studied on the electrochemical properties of ReHAB. The cathode morphology was investigated with scanning electron microscopy (SEM) and its wettability was studied by contact angle measurement. The cathode electrochemical performances including cycling voltammogram, discharge capacity, capacity retention, electrochemical impedance spectra and rate capability were investigated. The optimum blend was characterized further by Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC).

## 2. Experimental

### 2.1. Materials

Two commercially available polymers were used as binders: PVDF (CAS Number 24937-79-9, melting point: 155–160°, Alfa Aesar, USA) and PVAc (CAS Number 9003-20-7,  $M_w = 100,000$  g/mol, Sigma-Aldrich, USA). Their chemical structures are shown in Fig. 1. The other materials used were as follow: *n*-methyl-2-pyrrolidinone (NMP) (Merck, Germany), LMO (CAS Number 12057-17-9, spinel, powder, < 0.5  $\mu\text{m}$  particle size (BET), purity > 99%, Sigma Aldrich, USA), Super P™ carbon (Cabot corporation, USA),  $\text{Li}_2\text{SO}_4$  and  $\text{ZnSO}_4$  with 99.9% purity (both Merck grades), (PE/C) (polyethylene film with 49% wt. carbon, China), AGM (absorbed Glass Mat, NSG corporation, Japan).

### 2.2. Cathode and electrolyte preparation

The binder solutions were prepared by dissolving the specified amounts of PVDF and/or PVAc in NMP. Composite cathodes were prepared by mixing LMO, carbon, and binder (with the ratio of 80:10:10), in NMP by magnetic stirrer for 30 min. Further drops of NMP were added to slurry (about 1 ml) to achieve adequate viscosity and homogeneity. Then, the slurry was casted, with 300  $\mu\text{m}$  thickness, on a PE/C conductive film as current collector by a Dr. Blade® casting knife.

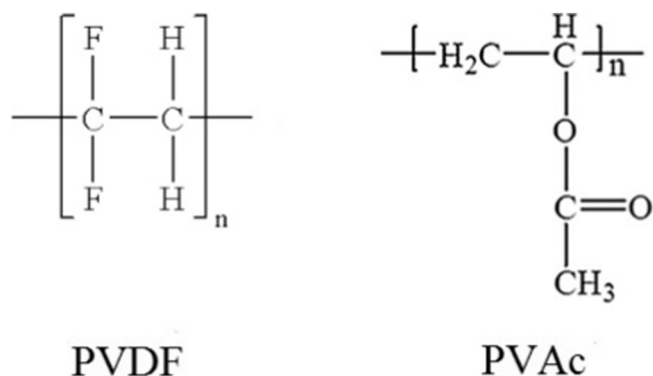


Fig. 1. Chemical structures of PVDF and PVAc.

The cathode film was heated under vacuum in the oven at 65 °C for 2 h to remove solvent. Disks of 12 mm in diameter were cut by electrode cutter and soaked in the aqueous electrolyte solution under vacuum for 30 min. The electrolyte was prepared by dissolving 2 M  $\text{Li}_2\text{SO}_4$  and 1 M  $\text{ZnSO}_4$  in deionized water and adjusting the solution to pH = 4 by a few drops of 1 M  $\text{H}_2\text{SO}_4$  solution. A 12 mm-diameter zinc foil was used as anode. AGM wet with the electrolyte was used as separator.

### 2.3. Electrode characterization

Five-electrode Swagelok-type cells (Canada) were used for galvanostatic charge-discharge cycling at room temperature by means of a battery tester ((Kimia-stat 128, Kimia Pardaz Samaneh Co., I.R. Iran) at various C-rates calculated based on the practical specific capacity of  $\text{LiMn}_2\text{O}_4$  spinal (1C = 130 mAh) [21].

Cycling voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in  $\text{LiMn}_2\text{O}_4/\text{Zn}$  coin cell on a Metrohm Autolab instrument (The Netherlands). The CV test was carried out with a scanning rate of  $1 \text{ mV s}^{-1}$  in the voltage range of 1.2–2.4 V.

The ionic conductivity values of the prepared binders and the charge transfer resistances of the resulted cathodes (made from LMO, carbon black and binder) were analyzed by EIS using the open-circuit voltage (OCV) measurement over the frequency range of  $10^{-2}$  to  $10^5$  Hz.

The morphology of the electrodes was analyzed with SEM (Zeiss Co., Ultra Plus, Germany) equipped with an energy-dispersive X-ray spectrometer (EDX) (Zeiss Co., Ultra Plus, Germany) and Field Emission Scanning Electron Microscope (FESEM), (Zeiss Co., Sigma, Germany).

The wettability of electrodes with electrolyte was estimated by examination of contact angle. The pictures were taken by SONY camera (Japan) and angles were determined by ImageJ™ software.

DSC measurements were carried out under nitrogen atmosphere with (Mettler Toledo, Model DSC1, Switzerland) and each sample was scanned at a heating rate of 10 °C/min.

FT-IR spectroscopy studies were carried out using (JASCO, FTIR-6300, Japan) spectrophotometer in the range 400–4000  $\text{cm}^{-1}$ .

## 3. Result and discussion

### 3.1. Cathode morphology

Fig. 2 shows the SEM/FESEM images of cathode electrodes using five different binder systems. It is implied that all binders with different PVDF/PVAc ratios results in similar morphologies as observed in SEM (Fig. 2(a) and (b)) or FESEM (Fig. 2(c), (d) and (e)) micrographs. This may indicate the miscibility of these polymers and their similar mixing property with the other components. The cathode components are well bound with PVDF, PVAc or their blends while keeping enough porosity for easy replacement of lithium ion between cathode and electrolyte during the battery charge/discharge processes. The agglomerated particles in the size of 5 to 20  $\mu\text{m}$  are LMO and C particles adhered by the binders that are well distributed on the current collector.

The cathode components were analyzed by EDX (Fig. 3) for random points in SEM images in Fig. 2((a) and (b)). The presence of main elements including Mn (in LMO), F (in the cathode with PVDF as binder) and the higher ratios of O and C due to presence of acetate groups (in the cathode with PVAc as binder), in these randomly selected points together with similarity in morphologies, may indicate the acceptable distribution of LMO and binders in the cathodes.

### 3.2. Cathode wettability

The cathode wettability was studied by water/electrode contact angle measurement. This technique is conventional for investigating the hydrophilicity of materials [22,23]. The water contact angles of electrodes with different binders are shown in Table 1. The angle between

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