

ZrO₂ nanofiller incorporated PVC/PVdF blend-based composite polymer electrolytes (CPE) complexed with LiBOB

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Abstract

A novel lithium bis(oxalato)borate (LiBOB)-based zirconium dioxide dispersed poly(vinylidene fluoride) (PVdF)/poly(vinylchloride) (PVC) blend composite polymer electrolytes (CPE) has been prepared by conventional solution casting technique by varying the filler concentrations. The prepared membranes were all subjected to SEM, XRD and ac impedance studies. The conductivity results show that the enhanced conductivity 1.53×10^{-3} S/cm at 343 K is obtained only for 2.5 wt% filler containing membrane. The XRD results also confirm that increase in the degree of crystallinity with the further increase in the filler content beyond 2.5 wt%. The phase morphological studies also confirm the enhancement in conductivity. The calculated activation energy is also in support of increase in amorphousity of the membrane. Synthesis of LiBOB salt has also been described.

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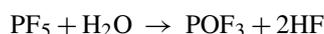
Keywords: LiBOB; Nanocomposite; Activation energy; Polymer blend

1. Introduction

In the recent years R&D works based on the development of new salts for lithium ion batteries are of popular interest. Electrolyte is a key factor which limits the performance of the batteries. Presently, LiPF₆ is the most commonly used electrolyte salt in the commercial Li-ion battery systems. This salt may decompose spontaneously to LiF and PF₅. In solvents, the anion of this salt (PF₆)⁻ undergoes equilibrium



where the strong Lewis acid (PF₅) tends to react with organic solvents and thus move the above equilibrium toward products. Furthermore, labile P–F bonds are highly susceptible to hydrolysis by even trace amounts of moisture in the electrolyte solvent [1]. At the same time the Li⁺ insertion and reinsertion in the LiF layer is found to be very difficult.



Hence, HF is unavoidably present in all LiPF₆ solutions. The presence of HF, in solutions seems to induce, the dissolution of cations of the transition metal of the cathode materials, which causes structural changes that lead to capacity fading [2].

LiClO₄ salt exhibits excellent conductivity, but is explosive during the charge–discharge cycling. Though LiBF₄ shows better conductivity, it too seems to suffer the HF contamination problem and is inferior in solid electrolyte interphase (SEI) formation. LiAsF₆ is highly poisonous due to the presence of Arsenic. All the three salts—LiCF₃SO₃, LiN(CF₃SO₂)₂ (LiTFSI) and LiC(CF₃SO₂)₃ make severe corrosion on aluminium current collector. Moreover, the later two salts were difficult to synthesize and also expensive [3]. LiN(CF₃CF₂SO₂)₂ (LiBETI) was also investigated, it was unable to produce the polymeric species on the cathodic side, which leads to the thermal runaway of the battery [4]. Though LiBF₃(CF₃CF₂) (LiFAB) has been reported as a better alternative, it cannot be used above 4 V [5].

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Lithium bis(oxalato)borate (LiBOB) and Lithium fluoroalkylphosphate (LiFAP) have been proposed as a potential replacement for LiPF₆ [3,6–10]. It meets the basic requirements for a salt to be used in lithium-ion cells, exhibiting (i) ability to form a stable SEI; (ii) good stability in a wide potential window; (iii) acceptable solubility in alkyl carbonate organic solvents like EC, DMC, DEC, etc.; (iv) high conductivity in various non-aqueous solvent systems; (v) good cycling behavior. Furthermore, it gives better thermal stability than LiPF₆ in organic solvents [8]. Crystalline LiBOB is also much more stable than crystalline LiPF₆. LiFAP similarly fulfills the basic requirements for the electrolyte salt, at the same time the use of this salt is doubtful because of its prohibitive cost.

LiBOB salt is complexed with the PVdF/PVC polymer blend in the presence plasticizers EC and DEC as well as the filler like ZrO₂ nanoparticle. By the addition of PVC into PVdF the mechanical and electrochemical stability increases as well as the film formation time gets reduced. The nanogel polymer electrolytes are perceived as a potential replacement in the future for Lithium-ion batteries, because of their appealing properties like good conductivity, electrochemical stability, thermal stability and good compatibility towards the anode as well as cathode materials [12,13].

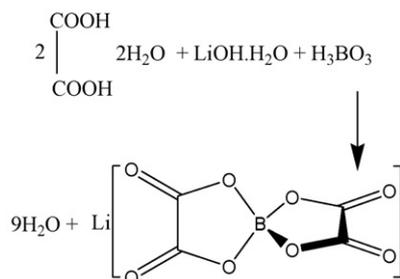
2. Experimental

2.1. Materials

Poly vinylidene fluoride (PVdF) (MW = 5.34 × 10⁵) poly vinylchloride (PVC) (MW = 5 × 10⁵), ethylene carbonate (EC), lithium hydroxide mono hydrate (LiOH·H₂O) and zirconium dioxide ZrO₂ (20–30 nm with the surface area of 35–45 m²/g) were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) oxalic acid dihydrate (C₂O₄H₂·2H₂O) and boric acid (H₃BO₃) were purchased from E. Merck India, and the plasticizer diethyl carbonate (DEC) was purchased from SRL, India and used without further purification.

2.2. Synthesis of LiBOB

In the present study, we have prepared LiBOB salt as well known solid-state reaction method. The method is as described follows [10,11,14].



LiBOB salt is recrystallized using the boiling tetrahydrofuran/diethyl ether (1:1 molar ratio) mixture and cooled –25 °C. After the cooling, the sample was placed in the vacuum oven at

Table 1
Composition of composite polymer electrolytes

Sample	Polymers		Plasticizers (1:1)		LiBOB	ZrO ₂
	PVdF	PVC	EC	DEC		
S1	25	5	32.50	32.50	5	00.0
S2	25	5	31.25	31.25	5	02.5
S3	25	5	30.00	30.00	5	05.0
S4	25	5	28.75	28.75	5	07.5
S5	25	5	27.50	27.50	5	10.0

The combinations are in their weight percentages.

60 °C for about 48 h, to give the white solid like powder. This LiBOB powder is used in our present study [11].

2.3. Preparation of composite polymer electrolytes (CPE)

Appropriate amounts of PVdF, PVC, EC, DEC and LiBOB were dissolved in THF (see Table 1). All the materials were mixed together and followed by the addition of ZrO₂ nanoparticles. Solution obtained was stirred continuously until the mixture becomes homogeneous viscous liquid appearance. The solutions of different compositions were cast on to a glass plates and allowed to evaporate slowly at room temperature. This provides freestanding, mechanically stable and flexible thin films thickness of 80–140 μm. Then CPE are kept under vacuum for complete removal of THF, if any.

2.4. Instrumentation

Ionic conductivities of LiBOB-based membranes were measured by ac impedance spectroscopy carried out in the 5 MHz–1 Hz frequency range by using Solartron 1260 Impedance/Gain Phase analyzer coupled with a Solartron Electrochemical interface with two stainless steel (SS) blocking electrodes (SS/CPE/SS). X-ray diffraction measurements were carried out using the PANalytical with the angle 10–80°. Morphological analyses were carried out by using Hitachi Model S-3000H Scanning Electron Microscope.

3. Results and discussion

3.1. Ionic conductivity

Electrochemical impedance spectroscopy is a relatively new and powerful method to characterize many of the electrical properties of materials and their interfaces with the electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic—ionic and even insulators (dielectrics). Ionic conductivity of PVdF/PVC blend electrolytes was measured as a function of the amount of PVdF in the polymer blend (Table 1). Variations in ionic conductivity was also analyzed for LiBOB-laden membranes with different proportions of the ZrO₂ filler with respect to the plasticizer content (EC/DEC), keeping the PVdF/PVC blend ratio constant. In Fig. 1(a) is given a typi-

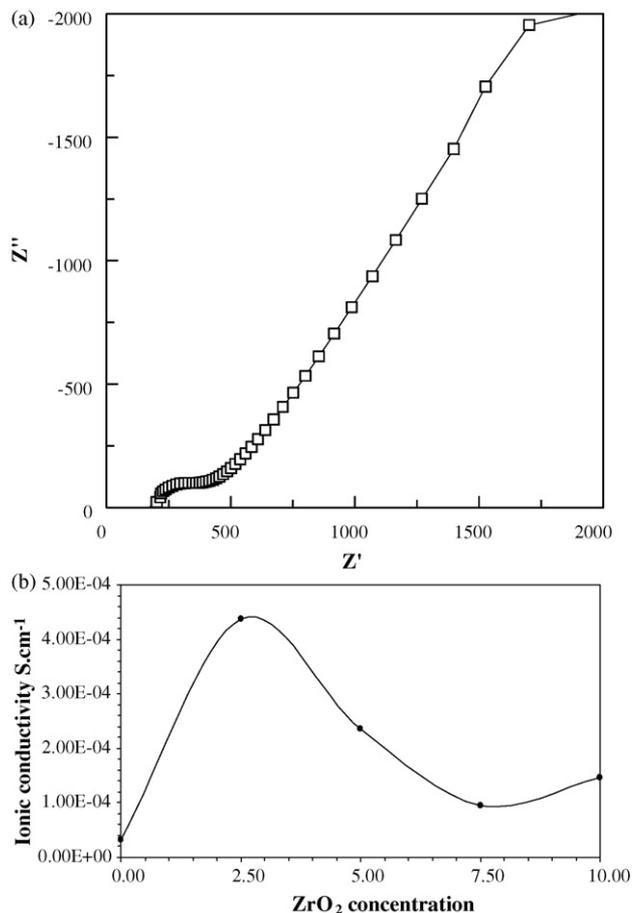


Fig. 1. (a) A typical impedance spectrum recorded with the CPE using 1 cm^2 stainless steel blocking electrodes and (b) variation of ionic conductivity with filler content.

cal impedance spectrum recorded with the CPE using 1 cm^2 stainless steel blocking electrodes.

The variation in ionic conductivity as a function of the filler content is given in Fig. 1(b). The conductivity of the filler free membrane showed $3.27 \times 10^{-5} S \cdot cm^{-1}$. In the case of filler free membranes containing PVC and PVdF, the PVC phase acts as a mechanical support and the plasticizer rich-phase acts (appeared as pores in the SEM images) as a tunnel for ionic transport. Since, the PVC phase is a solid like medium; it is difficult for ions to penetrate this phase. Then the transport of ions must occur via indirect motion along a convoluted path restricted to the plasticizer phase, which is responsible for lower conductivity than the filler containing membranes (CPE) [16] (Fig. 1 (b)). The maximum conductivity of $4.38 \times 10^{-4} S \cdot cm^{-1}$ was obtained at a filler content of 2.5 wt%. Further increase in the filler content (beyond 2.5 wt%), the conductivity tends to decrease upto 7.5 wt%. It may due to the aggregation of the nanoparticles, which is strongly interact with the polymer chains and immobilize it. Beyond 7.5 wt%, a slight improvement of conductivity is observed [15]. This report is contrary to the observations of Nan et al. [13], who investigated a PEO + EC/PC + $LiClO_4$ + SiO_2 composite polymer electrolyte. They showed that the maximum conductivity was exhibited by a CPE with 15 wt% SiO_2 (conductivity of $2 \times 10^{-4} S \cdot cm^{-1}$ at ambient temperature, activation

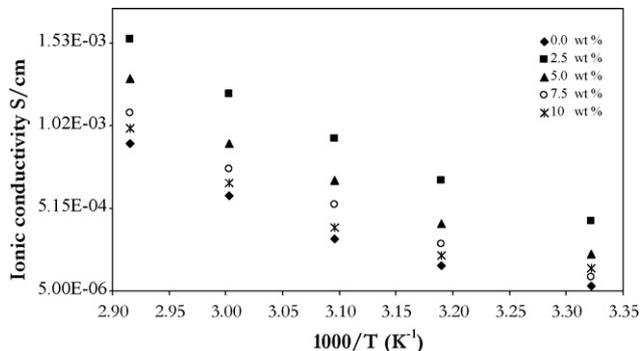
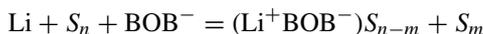
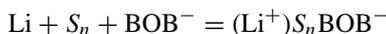


Fig. 2. Temperature dependence of ionic conductivity of the composite polymer electrolyte.

energy around 0.5 eV) [13]. Although the nature of the filler material has an important influence on the conductivity behavior, other factors may also come into play. For example, the bulky BOB anion may be expected to act as a plasticizer, lowering the amount of filler material required to obtain reasonable conductivity values. Moreover, the strong polarizing effect of the bulkier BOB can also influence charge transport. Fig. 2 shows the conductivity versus temperature inverse plots of composite gel polymer electrolyte. The curvature shown in this plot indicates the ionic conduction in the polymer electrolyte system obeys the VTF (Vogel–Tamman–Fulcher) relation, which describes the transport properties in a viscous polymer matrix [17]. It also supports that ions are moves through the solvent rich phase, which is the conducting medium and involves the salt and ceramic nanoparticles.

Gel polymer electrolyte containing different ratios of ZrO_2 is given in Table 1. Highest conductivity was obtained the electrolyte containing 2.5 wt% filler, which exhibits the maximum conductivity around $1.53 \times 10^{-3} S \cdot cm^{-1}$ at 343 K. Temperature increases the conductivity also increases, as the temperature increases, the polymer can expand easily and produce the free volume. The resulting conductivity is represented by the overall mobility of ions and the polymer chains, is determined by the free volume around the polymer chain. Therefore, as temperature increases, the free volume increases this lead to an increase in ion mobility and segmental mobility that will assist ion transport and virtually compensate for the retarding effect of the ion clouds. The BOB anion is a bulkier anion which also having two types of ion pairs and solvated ion pairs in the electrolyte solution. These may be represented by the equilibria



where S represents the solvating species. Redissociation of such ion pairs can occur due to long range coulombic forces giving rise to free ions, which contribute to conductance. At higher concentrations, short range ion solvent interactions take over and therefore, even though the number of ions dissolved in the electrolyte medium is higher, the effective number of charged species available for charge transport gets reduced [16]. Since

the optimization of LiBOB has been optimized and fixed for 5 wt%.

The enhancement of ionic conductivity by adding filler mainly due to decrease in the crystalline phase of the polymer electrolyte (addition of nanoparticles prevent the polymer chain reorganisation, resulted in increased amorphosity). Therefore, the ionic conductivity of the polymer electrolyte can be improved by an increase in the career number of lithium ions. Generally ionic conductivity in polymer electrolytes, ions moves in a dynamic environment created by polymer chain motion in the amorphous region above glass transition temperature (T_g). The segmental modes, involving the motion of groups of atoms on the polymer chains, are usually relatively slow, limiting the hopping rate and results maximum conductivity [18].

3.2. Activation energy for Li^+ ion transport

Fig. 2 depicts the dependence of ionic conductivity on temperature in the range 27–70 °C for the polymer electrolyte. The activation energy for ion transport, E_a , can be obtained by using the Vogel–Tamman–Fulcher model

$$\sigma = \sigma_0 T^{-1/2} \exp\left(\frac{-E_a}{T - T_0}\right) \quad (1)$$

where σ is the conductivity of polymer electrolyte, σ_0 the pre-exponential index, T_0 glass transition temperature and T is the testing temperature, respectively. Fig. 3 shows the relationship between the amount of ZrO_2 nanoparticles in the polymer film and the activation energy for ions transport. It suggests that the activation energy for ions transport is maxima for filler free electrolytes and increases from 2.5 to 7.5 wt% and it again decreases for 10 wt% decreases.

At low filler concentrations (2.5 wt%), they are uniformly dispersed through out the volume leads to conductivity enhancement. When increasing the filler concentrations (2.5–7.5 wt%), the blocking effect leads to immobilize the polymer chains leads to drop in conductivity. As the further increase in filler content, the filler grains are get close enough to each other so that the high conducting regions in the vicinity of the grain surfaces start to get interconnected. Then the migration of ionic species now can travel along and between these interconnected and high conduct-

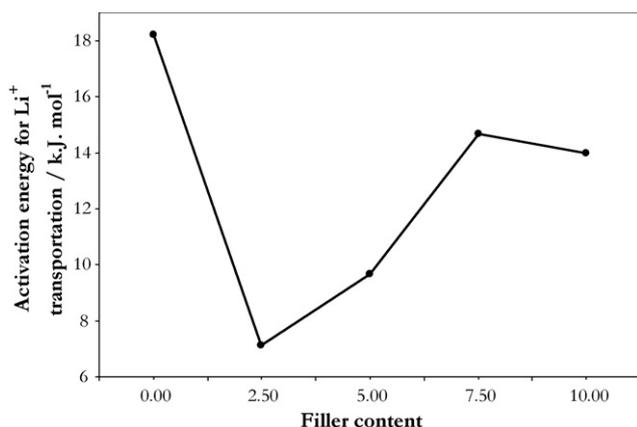


Fig. 3. Activation energy at different filler concentrations.

ing pathways give rise to the increase in conductivity beyond 7.5 wt%, which also reflect in activation energy calculations [15].

3.3. X-ray diffraction studies

X-ray diffraction measurements were conducted to examine the nature of the crystallinity of the polymer film with respect to the host polymer. X-ray diffraction patterns of composite polymer electrolytes are given in Fig. 4 to prove the dominant crystal phases with increasing the ZrO_2 content. At low content (i.e. 2.5 wt%), the films show some weak intensity characteristics peaks of PVdF α phase crystals at $2\theta = 18.12, 19.83$ and 38.77° , which are corresponding to spherulites grown dominantly. The existence of PVdF γ phase crystal is also possibly by the peak $2\theta = \sim 19^\circ$, corresponding to a mixture of (1 1 0) plane of α phase and (0 2 1) plane of γ phase [19]. Characteristics peaks of amorphous PVC $2\theta = 13$ and 16° are completely absent in all the samples. It may be due to the blending of PVC with PVdF, which induces a change in the crystallographic organization in PVdF,

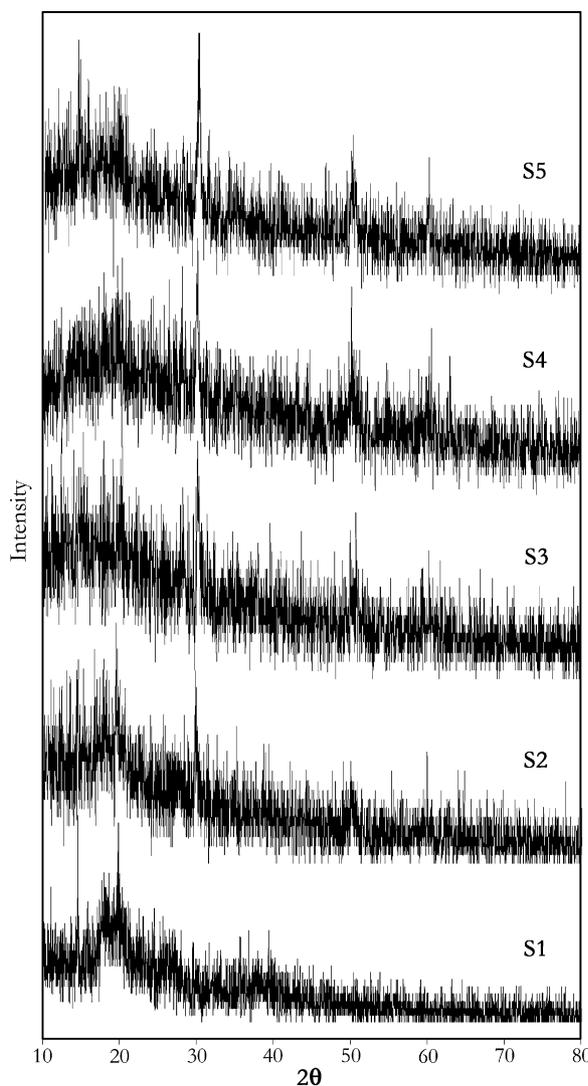


Fig. 4. X-ray diffraction patterns of CPE with different filler concentrations.

which establishes a correlation between the height of the peak and the degree of crystallinity. As the ZrO_2 content increases, the characteristic peaks 2θ around 30, 50 and 60 are corresponding to the monoclinic structure [20]. Intensities of these characteristic peaks are increased if increase the filler content beyond 2.5 wt% shows increase in the crystallinity in accordance with our impedance results and activation energy values.

3.4. Scanning electron microscope

Fig. 5 shows the scanning electron microscope (SEM) images with different magnifications of CPE, which could be seen as

interconnected networks of pores. The pores filled with plasticizers (EC: DEC) are necessary for the transport of Li^+ ions during the charging and discharging. Fig. 5(a) and (b) respectively refer to the porous structures of filler free and filler (2.5 wt%) containing CPE. It could be seen that 0 wt% CPE contains lot of pores when compared to 2.5 wt% CPE. It is important to note that when the weight ratio of filler increases from 0 to 2.5 wt% ionic conductivity increases to one order of magnitude (from 3.27×10^{-5} to $4.38 \times 10^{-4} \text{ S cm}^{-1}$) with variations in porosity suggesting that the porosity is not the only factor that affects ionic conductivity of the composite polymer electrolytes. But there is another factor may be due to the obviously improved

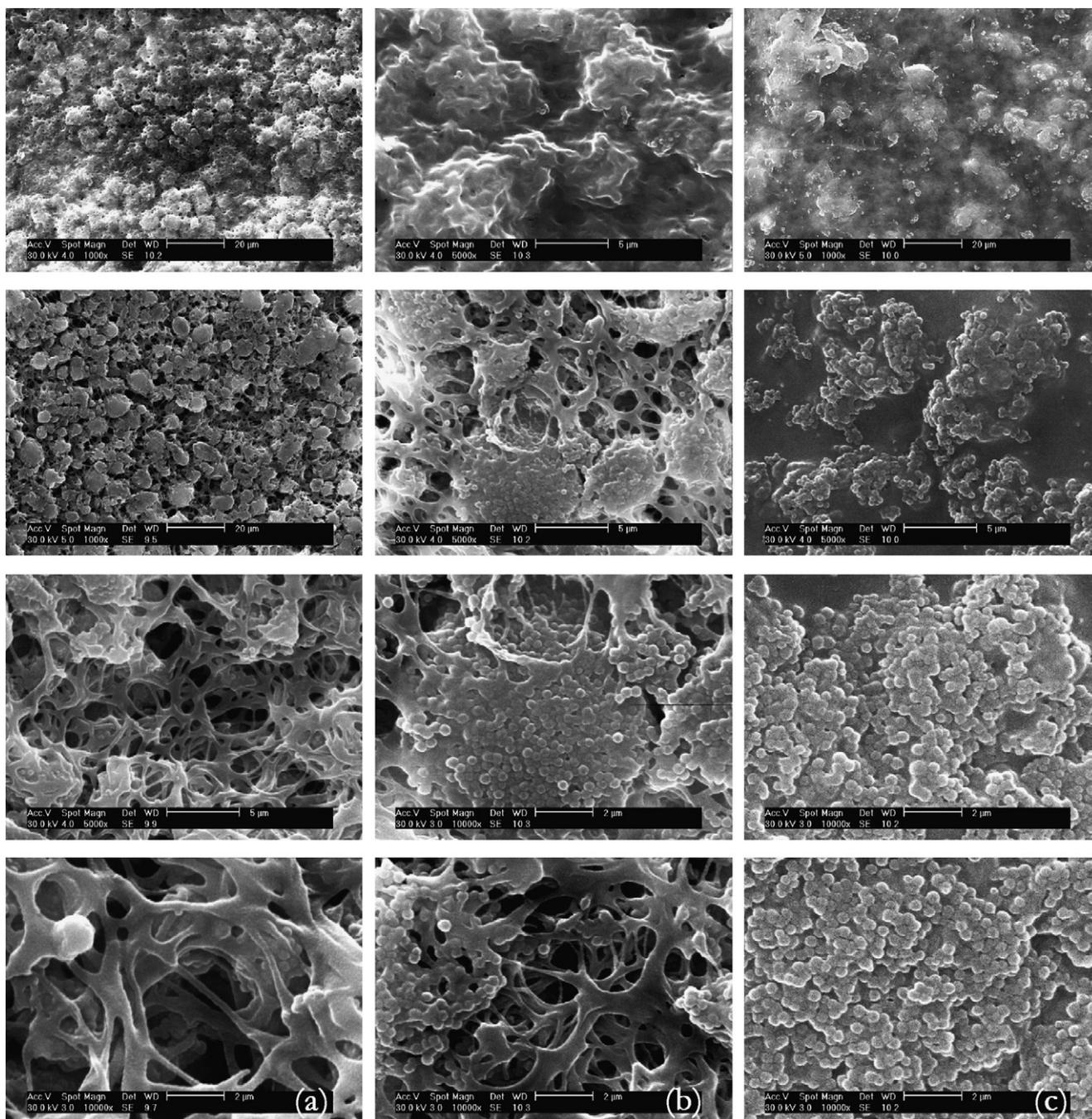


Fig. 5. Scanning electron images of CPEs containing different filler ratios: (a) 0 wt%; (b) 2.5 wt%; (c) 5.0 wt%.

pore connectivity, for Fig. 5(b) compared to Fig. 5(a), which is very important for the transporting of charge carriers in CPE [21] wherein formation of a amorphous interface area surrounding the fillers there by enhancing the ionic conductivity. Thus, it is inferred that the role of the ceramic filler (ZrO_2) is effective in terms of its pore connectivity rather than pore size/number of pores. Beyond an optimum concentration such as around 2.5 wt% ZrO_2 for the CPE, the inert fillers directly contact each other to form continuum percolation clusters which tends to impede lithium movement by acting as mere insulators [13]. Further addition of fillers shows the aggregation of nanoparticles which is clearly displayed in Fig. 5(c). Such kind of aggregation impedes the Li^+ ion which transport leads to a decrease in conductivity. SEM images prominently reflect the ionic conductivity measurements.

4. Conclusion

An LiBOB-based composite polymer electrolyte membrane with 2.5 wt% ZrO_2 gave an ambient-temperature conductivity of $4.38 \times 10^{-4} \text{ S cm}^{-1}$ and possessed porous network for accommodation of large quantities of liquid electrolyte in it. Thus, this membrane is a potential candidate for lithium ion batteries. The high conductivity of the CPE is attributed to its high amorphicity, which facilitates a high mobility of Li^+ ions by way of large free volumes high defect concentrations along the polymer– ZrO_2 particle interface.

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